Studies on the Oiliness of Liquids. V. Lubricants Consisting of Two or Three Chemical Compounds.

By Hideo AKAMATU.

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In the preceding papers,(1a) (1b) the measurements of the coefficients of static friction of glass surfaces were described when some pure chemical compounds were used as lubricants. The present paper records the results when the lubricants consist of mixtures of chemical compounds.

In conclusion, we observed the good much evidence that a selective adsorption takes place on the friction surfaces. The idea of adsorption has already been applied to the boundary lubrication by some investigators, especially W. B. Hardy(2) to whom we owe the fundamental conception that a semi-polar molecule attaches to the friction surface anchoring itself by means of polar group and presenting to the liquid interface non-polar chain, forming a monomolecular orientated layer.

In the practical engineering, a well known patent "germ process" by Wells and Southcombe,(3) depends on the fact that the addition to mineral oil of small percentage of such compounds as fatty acids that lower the interfacial tension between water and oil gives exceptionally good lubricating values.

Wilson and Barnard,(4) W. G. Wilharm,(5) P. Woog,(6) and W. Bachmann(7) have observed the same results and agreed that there takes place adsorption of lubricant on the surfaces.

Most of these works, however, for the practical purposes, were dealing with the oil, the composition of which are very complex, so that it is difficult to postulate any mechanism. The present work deals with some binary or ternary solutions of pure chemical compounds, and the results

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(1a) J. Sameshima, M. Kidokoro, and H. Akamatu, this Bulletin, **11** (1936), 659.

(1b) J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127.

(2) W. B. Hardy and I. Doubleday, *Proc. Roy. Soc.* (London), A, **104** (1923), 25; W. B. Hardy, *Phil. Trans.*, A, **230** (1931), 1; W. B. Hardy and M. Nottage, *Proc. Roy. Soc.* (London), A, **138** (1932), 259.

(3) Wells and Southcombe, *J. Soc. Chem. Ind.*, **39** (1920), 51.

(4) Wilson and Barnard, *Ind. Eng. Chem.*, **14** (1922), 683.

(5) W. G. Wilharm, *ibid.*, **18** (1926), 463.

(6) P. Woog, "Contribution a l'étude du graissage", Paris (1926).

(7) W. Bachmann and Brieger, *Kolloid-Z.*, **36** (1925), 142; **39** (1926), 334.

support the theories described above, suggesting a new point of view on the mechanism.

The method of measuring the static friction and the conditions were the same as described in the preceding paper.(1a) The friction surfaces consisted of a flat glass and a glass with a spherical surface.

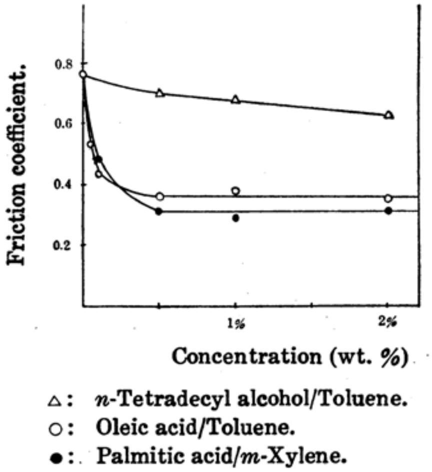

Fig. 1.

In carrying out the experiments with several binary solutions, it came to light that there was much evidence for tendency of selective character. This selectivity depends chiefly upon the polarity of the substance, and this appears most clearly when the mixture consists of polar and non-polar compounds. For example, when the lubricant is made by dissolving oleic acid ($\mu = 0.29$) in toluence ($\mu = 0.76$), the friction coefficient is nearly identical with that of pure oleic acid, being independent upon the concentration of oleic acid. Table 1 and Fig. 1 show how small amounts of a polar substance in a non-polar solvent is effective for the reduction of the friction of the solvent.

In the preceding paper,(1a) we have reported that the friction coefficient of hexane and nonane are 0.68 and 0.64 respectively. These data have been revised, since the samples formerly used may contain some unsaturated hydrocarbons as impurities. This time, hexane and nonane were shaken with fuming sulphuric acid for several days, dried over sodium metal and then distilled. With such samples, the friction coefficients are somewhat greater, that is 0.85 for hexane and 0.76 for nonane. It is supposed that heptane and octane have also values of this order. So it seems that the small amount of unsaturated hydrocarbons are still much effective. It is true also that the measurement of friction of a hydrocarbon is rather difficult, for it is readily contaminated while the measurements and the friction steps down gradually. Such a difficulty is little for polar compounds.

It is well known that, the molecules have to take orientation in such a manner as to prevent the abruptness of potential difference between the two neighbouring phases. In other words, the interfacial energy between polar compound and underlying solid surface, such as glass or metal, is smaller than that between a non-polar compound and solid sur-

Table 1. Polar solute and non-polar solvent.

Solute	Solvent	Conc. of solute (wt. %)	Friction coefficient
—	Toluene	—	0.76
—	*m*-Xylene	—	0.76
—	liq. Paraffin	—	0.55
—	*n*-Nonane	—	0.76
Oleic acid	Toluene	2	0.35
,,	,,	1	0.38
,,	,,	0.5	0.36
,,	,,	0.1	0.43
,,	,,	0.05	0.53
Palmitic acid	*m*-Xylene	4	0.32
,,	,,	2	0.31
,,	,,	1	0.29
,,	,,	0.5	0.31
,,	,,	0.1	0.48
Palmitic acid	*n*-Nonane	2	0.31
n-Tetradecyl alcohol	Toluene	2	0.63
,,	,,	1	0.68
,,	,,	0.5	0.70
,,	*n*-Nonane	2	0.54
Tripalmitin	*m*-Xylene	2	0.35
,,	,,	1	0.33
Stearic acid	liq. Paraffin	1 *	0.28
,,	,,	0.2 *	0.25
,,	,,	0.05	0.45
Benzoic acid	*m*-Xylene	2	0.59
Benzophenone	,,	3	0.77

(* This is not a true solution, but a mixture.)

face, so that if such a solution, polar solute and non-polar solvent, be placed on the glass surface (polar) the polar molecules will attach to the surface preferentially with their polar groups facing to the surface, the phenomena will be like that on the water surface. Many investigations(8)

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(8) H. N. Holmes and J. B. Thor, "Colloid Symposium Monograph VII," (1930), 213; W. Harkins and Gans, *J. Phys. Chem.*, **36** (1932), 86; J. J. Trillat and R. Vaille, *Compt. rend.*, **202** (1936), 2134.

have been carried out on polar and non-polar adsorption. On the other hand, the experiment on the spreading of liquid on solid surfaces,⁽⁹⁾ or the electron diffraction analysis⁽¹⁰⁾ supports this view directly.

It may be said that, in boundary lubrication, the oiliness depends only upon the adsorbed layer and the other part of solution does not impart the friction or oiliness, the non-polar solvent merely furnishing a medium. It seems that oiliness is merely depends on the friction between the surface with such adsorbed layers. Such a adsorption will be a dynamical equilibrium between the solid surface and the liquid in mass, so the orientation of the molecules will not be so complete as that deposited by Blodgett's⁽¹¹⁾ methods. It is natural, therefore, that the friction of the former is much greater than the latter.⁽¹²⁾

The same idea may be extended to the case when the solvent is also polar, but the phenomena become more complicate. The addition of a small quantity of a fatty substance is not effective generally. The results are shown in Table 2 and Fig. 2.

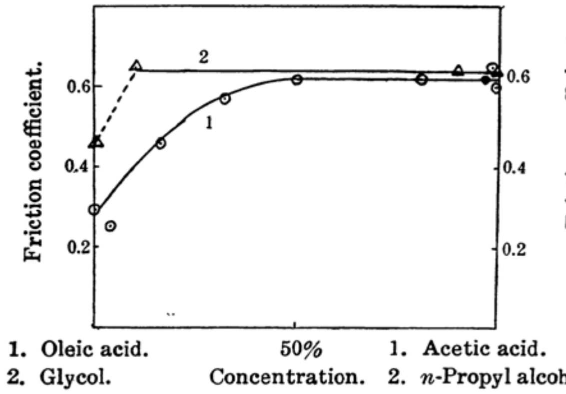

Fig. 2 (a).

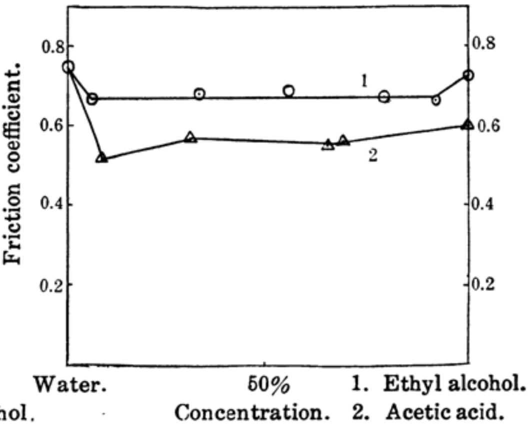

Fig. 2 (b).

There are some differences in the adsorbabilities or adhesion forces of molecules with active groups. If the adsorbabilities of the molecules composing the lubricant are alike each other, they will be adsorbed similarly and the value of the friction coefficient will be averaged. If, however, there is any disparity, one of them will be adsorbed preferentially

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(9) R. Bulkley and Snyder, *J. Am. Chem. Soc.*, **55** (1933), 194.

(10) L. T. Andrew, *Trans. Faraday Soc.*, **32** (1936), 607.

(11) C. Blodgett, *J. Am. Chem. Soc.*, **57** (1935), 1007.

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

Table 2.

Component 1	(wt. %)	Component 2	(wt. %)	Friction coefficient
—	—	Acetic acid	100	0.60
Oleic acid	1	,,	99	0.65
,,	2	,,	98	0.63
,,	3	,,	97	0.62
,,	19	,,	81	0.62
,,	50	,,	50	0.62
,,	68	,,	32	0.57
,,	84	,,	16	0.46
,,	96	,,	4	0.25
,,	100	—	—	0.29
Palmitic acid	4	Acetic acid	96	0.6—0.7
,,	2	,,	98	,,
Glycol	10	*n*-Propyl alcohol	90	0.64
,,	90	,,	10	0.65
—	—	*n*-Propyl alcohol	100	0.64
n-Tetradecyl alcohol	1	*n*-Propyl alcohol	99	0.64
,,	2	,,	98	0.66
Benzophenone	1	Glycol	99	.50
Hydroquinone	2	,,	98	0.46
—	—	Glycol	100	0.46
—	—	Dioxane	100	0.61
Palmitic acid	2	,,	98	0.5—0.6
Sebacic acid	2	,,	98	0.62
Ethyl alcohol	100	—	—	0.72
,,	91.6	Water	8.4	0.66
,,	78.8	,,	21.2	0.67
,,	54.7	,,	45.3	0.69
,,	32.4	,,	67.6	0.68
,,	6	,,	94	0.67
Acetic acid	68.4	Water	31.6	0.56
,,	64.6	,,	35.4	0.55
,,	30	,,	70	0.57
,,	8	,,	92	0.52
—	—	Water	100	0.75

and the friction depends on it only. Such a conception may be too simple, since there are many unknown factors affecting the friction. Hardy found, for example, that the temperature coefficient of a mixed lubricant is very complicated, although a single chemical substance has no temperature coefficient of friction. The present experiments were carried out at room temperature, 18–23°C., so the results may be considered as that of the constant temperature.

It has been observed, by some investigators, that the friction would be reduced with the interfacial energy between the lubricant and the friction surfaces, since the film would be stable. Of course, it seems the first essential condition to cover the active surface of the solid by adsorbed molecules. There is found no parallelism, however, between the interfacial energy and the oiliness. Molecules, which have the lower interfacial energy for the friction surface, are adsorbed preferentially by the surface. The friction, therefore, is determined by those surfaces with adsorbed layers, but the order of reducing the friction depends upon the properties of the individual molecules, molecular structure or other unknown properties. If the reducing power of friction is parallel with the stability of the film, the molecules which are adsorbed preferentially, must also be the better lubricant. But the fact is not so. With such a lubricant, as palmitic acid and acetic acid dissolved in *m*-xylene, the friction coefficient is nearly identical with that of acetic acid itself. It seems that acetic acid is adsorbed preferentially, but the molecular structure of acetic acid is not favourable to reduce the friction, in other words, in such a

Table 3. (Solvent: *m*-Xylene)

Solute	(%)	Friction coefficient	Solute	(%)	Friction coefficient
Acetic acid Palmitic acid	4 4	0.49	Benzophenone Palmitic acid	2 2	0.33
Acetic acid Palmitic acid	8 8	0.57	Benzoic acid Palmitic acid	2 2	0.42
Acetic acid Palmitic acid	6 2	0.64	Oleic acid Acetic acid	2 2	0.64
n-Butyric acid Palmitic acid	2 2	0.35	Tripalmitin Acetic acid	4 4	0.56
n-Butyric acid Palmitic acid	5 5	0.31	Tripalmitin *n*-Butyric acid	1 1	0.58

case acetic acid behaves as an inhibitor. When the lubricant is a solution of palmitic acid and butyric acid in *m*-xylene, the friction coefficient is that of palmitic acid itself. When the lubricant consists of tripalmitin and butyric acid dissolved in *m*-xylene, the friction is identical with butyric acid. In those examples, the order of the adsorbability seems as follows; acetic acid, palmitic acid, butyric acid, tripalmitin. Several examples are shown in Table 3.

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Summary.

The static boundary frictions were measured when some binary or ternary mixtures were placed on the glass surfaces. The results suggest that: (i) the friction is governed by the surfaces with adsorbed layer of lubricant, and (ii) the reducing power of friction depends upon the individual molecular constitution of the molecules which are adsorbed preferentially by the friction surface, rather than the stability of the film.

Selective adsorption by the glass surface has been investigated, and some examples has been reported.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.