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Fundamental Studies on Interfacial Tensions in Flotations. III

Tilting-Plate Method of Determining Contact Angle and the Wetting Tension of Aqueous Solutions of Frothers for Paraffin-Wax*

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Synopsis

For the study of the theory of flotation process as well as the flotation agents, the wettablility of paraffin-wax in aqueous solutions of pure frothers as iso-amyl alcohol, meta-cresol, α-terpineol, d-camphor and of a few commercial frothers were measured.

By considering critically the reciprocal action of interfacial energies among solid, liquid and gas, the product of the surface tension of the liquid and the cosine of the angle of contact was selected as the wettability of solid against liquid.

For the measurement of angle of contact, the tilting-plate method was selected and the modified form of the apparatus was developed, in which all parts in contact with liquid under test were made of glass only and the advancing and receding angles were measured more or less readily and precisely by agitating, circulating, and regulating the liquid at any temperature. For the surface tension of solutions, the values obtained by Du Noüy's tensiometer were utilized.

A new wetting isotherm was derived, which held good for the wetting of paraffin-wax in solutions of pure as well as commercial frothers. The wetting isotherm was entirely similar in form to Szyszkovski's equation for water-air interface. By analogy, the wetting activity and the orientation of frothers at paraffin-water interface were considered and it was shown that wetting activity and the orientation of frothers at paraffin-water interface was similar to those at water-air interface.

I. Introduction

The wettability is one of the fundamental properties of minerals in flotation process. There is a number of researches $^{(1-5)}$ on contant angle of minerals against liquids because of the importance of the idea of the contact angle on the study of wetting phenomena

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* The 10th report of the Research Institute of Mineral Dressing and Metallurgy. Published already in Japanese in J. Mining Inst. Japan, **59** (1943), 681-98.

(1) Renpei Goto, Rev. Phys. Chem. Japan, **7** (1934), 138-52; Lectures Inst. Chemical Research, **6** (1936), 1-8.

(2) Jogoro Okada, J. Mining Inst. Japan, **57** (1944), 260-8; **59** (1943), 95-129.

(3) W. Petersen, Schwimmaufbereitung. (1936); (a) 46.

(4) Rensaku Suzuki, Jap. Assoc. Mineralogists, Petrologists and Economic Geologists, **2** (1929), 63-70.

(5) I. W. Wark, Principles of flotation. (1938); (a) 52-4, 78-80; (b) 314; (c) 54.

in flotation. Though there are various methods to measure the angle of contact of solid against liquid, (5a,6,7) in the following experiment the tilting-plate method (8-19) was selected for the simplicity of its principle and the ease of repetition of measurements, the primary requisites for precise measurements, and the apparatus was worked out by referring to those of Nietz and of Wenzel.

From the studies on the collecting action in flotation, it is supposed that the surface of the mineral adsorbing collector is similar to that of paraffin-wax as the collector is oriented at the mineral surface with its non-polar part pointing outside.(5b) Though it is not easy to measure accurately the contact angle of the surface of minerals, being apt to change with various conditions, it is comparatively easy to measure the contact angle of paraffin-wax, which, therefore, may be used as the standard substance for the contact-angle measurements. It is considered that the wettability of paraffin-wax in the solutions of various flotation agents will contribute to the studies on the mechanism of flotation or on the character of flotation agents.

There is a number of investigations regarding the measurement of the contact angle of paraffin-wax in aqueous solutions of surface-active substances. Taubman(20) measured the contact angle of paraffin-wax for saponin, Rehbinder, Lipetz and Rimskaja(21) for various fatty acids, alcohols, phenols, amines, xanthates, soaps, saponin, etc., Veselovskiĭ and Pertsov(22) for lactic and valeric acids, Kneen and Benton(23) for various fatty acids of less than 14 carbon atoms, Powney and Frost(24) for soaps in solutions of various hydrogen ion concentrations, and Harkins and Fowkes(8) for butyl alcohol. These investigations, however, are generally fragmentary and unconnected. Though the investi-

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(6) Hideo Akamatsu, Chemistry of thin films (Chemical experiments. Pt. 1, 4 (1940), 99-107); (a) 100.

(7) N. K. Adam, The physics and chemistry of surfaces. 2nd ed. (1938), 180-84; (a) 180.

(8) Wm. D. Harkins and F. M. Fowkes, J. Am. Chem. Soc., **60** (1938), 1511-2.

(9) C. H. Bosanquet and Harold Hartley, Phil. Mag., **42** (1921), 459.

(10) R. Ablett, Phil. Mag., **46** (1923), 244-56.

(11) N. K. Adam and Gilbert Jessop, J. Chem. Soc., **127** (1925), 1863-8.

(12) A. H. Nietz, J. Phys. Chem., **32** (1928), 255-69.

(13) G. L. Mack, J. Phys. Chem., **40** (1936), 195-67.

(14) R. N. Wenzel, Ind. Eng. Chem., **28** (1936), 988-994.

(15) L. L. English, Illinois State Nat. Hist. Survey, Bull., No. 17, Art. 5 (1928).

(16) E. L. Green, J. Phys. Chem., **33** (1929), 921-35.

(17) A. K. Huntington, Trans. Faraday Soc., **1** (1905), 345-61.

(18) F. Stellwaag, Z. angew. Entomol., **10** (1924), 163-76.

(19) H. L. Sulman, Bull. Inst. Mining Met., No. 182 (1919), 21-95; No. 183 (1919), 1-19.

(20) A. B. Taubman, J. Phys. Chem. (U.S.S.R.), **1** (1930), 563-71.

(21) P. Rehbinder, M. Lipetz and M. Rimskaja, Kolloid-Z., **66** (1934), 212-19.

(22) V. S. Veselovskiĭ and V. N. Pertsov, J. Phys. Chem. (U.S.S.R.), **8** (1936) 245-59.

(23) Eric Kneen and W. W. Benton, J. Phys. Chem., **41** (1937), 1195-203.

(24) J. Powney and H. F. Frost, J. Textile Inst., **28** (1937), T237-54.

gation of Rehbinder and his coworkers is extensive, there are no measurements on terpenes which are the principal constituents of frothers used in flotation, and moreover considerations on the adsorption of surface-active substances on paraffin surface, are insufficient.

In this investigation the contact angles of paraffin-wax in aqueous solutions of representative constituents of frothers as terpineol, camphor, amyl alcohol and cresol, and of several commercial frothers, were measured by the tilting-plate method improved by the author.

II. Definition of wettability of solids

There are various ways to define the degree of wetting, that is the wettability of solids against liquids. The simplest of them is probably to use x, the angle of contact of solid against liquid.((25-27)*

Rehbinder and his coworkers(28) defined the wettability by $\cos x$, the cosine of the angle of contact and the activity of wetting or of flotation by $d \cos x/dc$, the differential coefficient of the wettability by the concentration of surface-active substances.

Freundlich,(29) Bartell and Osterhof, (30,31) and Haller(32) insist that the wettability must be defined by $H \cos x$, the cosine of the angle multiplied by the surface tension of liquid. It is called adhesion tension by Freundlich and wetting tension by Haller. Valentiner(33) expressed the wetting power of collectors by the work of adhesion of solids against liquids,

$$W=H(1+\cos x) \qquad (1)$$

and named it collector index.

Bulkley and Snyder(34) and Harkins and Feldman(35) defined the degree of spreading or the spreading coefficient by the difference obtained by subtracting H', the tension of the liquid-solid interface, and H, that of the gas-liquid interface, from H'', that of the gas-solid interface,

$$S=H''-H'-H=H(\cos x-1) \qquad (2)$$

and expressed the wettability with it.

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* It is usual to adopt the angle between the gas-liquid interface and the solid surface measured across the liquid phase.

(25) W. Luyken and E. Bierbrauer, Mitt. Kaiser-Wilh.-Inst. Eisenforsch. Düsseldorf, 11 (1929), 37-52.

(26) H. Schranz, Metall u. Erz, 11 (1914), 462-70.

(27) S. Valentiner, Metall u. Erz, 11 (1914), 455-62; Physik. Z., 15 (1914), 425.

(28) P. Rehbinder, M. Lipetz, M. Rimskaja and A. Taubmann, Kolloid-Z., 65 (1933), 268-83.

(29) H. Freundlich, Kapillarchemie. 3 Aufl. (1923), 211.

(30) F. E. Bartell and H. J. Osterhof, Ind. Eng. Chem., 19 (1927), 1277-80.

(31) H. J. Osterhof and F. E. Bartell, J. Phys. Chem., 34 (1930), 1399-411.

(32) W. Haller, Kolloid-Z., 53 (1930), 247-55.

(33) S. Valentiner, Metall u. Erz, 33 (1936), 221-6; Kolloid-Z., 83 (1938), 1-9.

(34) R. Bulkley and G. H. S. Synder, J. Am. Chem. Soc., 55 (1933), 194-208.

(35) W. D. Harkins and A. Feldman, J. Am. Chem. Soc., 44 (1922), 2665-85.

Taggart, Taylor and Ince(36) defined the collecting index of collectors, taking into consideration the angle of contact formed by attaching a bubble on the horizontal surface of the ore immersed in liquid and the degree of deformation of the bubble about to detach from the surface of the ore, as follows:

$$\text{Collecting index}=1/2\cdot(x-x_0+100[(d/h)-(d/h)_0]) \qquad (3)$$

where x is the angle of contact formed by a bubble attached to the surface of an ore immersed in the solution of a surface-active substance and x_0 is that in pure water. h is the height of the bubble not deformed, d is the height of the bubble deformed until the bubble just detaches from the surface of the ore by slowly pulling up the bubble holder after attaching the bubble on the surface of the ore, and it is measured by the distance between the lower surface of the bubble just detached from the surface of the ore and the latter. The height h of the bubble not deformed is obtained by subtracting d from the distance between the lower surface of the holder and the surface of the ore. The ratio (d/h) is the ratio of deformation of the bubble in the solution of the surface-active substance and $(d/h)_0$ is that in pure water.

In considering the relation of energies on the interface, solid-liquid, solid-gas and liquid-gas in a solid-liquid-gas system, the liquid-gas interface on the solid surface will move in the direction so that the potential energy of the system will be the minimum according to the fact that whether the energy H'' of the solid-gas is larger or smaller than that H' of the solid-liquid interface.

It is proper to define the wettability of solids by $H''-H'$, the difference of the surface energies of solid-gas and of the solid-liquid interface. According to Young(32,34,37,38)

$$H''=H'+H\cos x \qquad (4)$$

in the equilibrium condition.

Hence,

$$H''-H'=H\cos x \qquad (5)$$

This definition of the wettability of solids coincides with that adopted by Freundlich and others. The work of adhesion or the degree of spreading is similar to the above definition.

According to the above equation both surface tension of liquids and angle of contact affect the wettability of solids. The adoption of the angle of contact or of its cosine as the definition of wettability results in the fault of neglecting the effect of the surface tension of liquids.(3a,32) As for Taggart's collecting index, little theoretical foundations are to be found.

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(36) A. F. Taggart, T. C. Taylor and C. R. Ince, Am. Inst. Mining Met. Engrs., Tech. Pub., No. 204 (1929), 1-75.

(37) Kotaro Honda, Elements of Physics. 17th ed. (1937), 417.

(38) Thomas Young, Phil. Trans.. **95**, I (1805), 65.

In the following consideration, therefore, the wetting tension

$$B=H\cos x\,. \tag{6}$$

is adopted from the standpoint of theory and simplicity as the definition of the wettability of solids.

III. Apparatus for tilting-plate method

Fig. 1 is the diagrammatic sketch of the apparatus. The apparatus consists of three parts, the graduated disk, the measuring dish and the circulating pump. The last two are the same as were used in the determination of surface tension. The details of these parts were already described in the first report.(39)

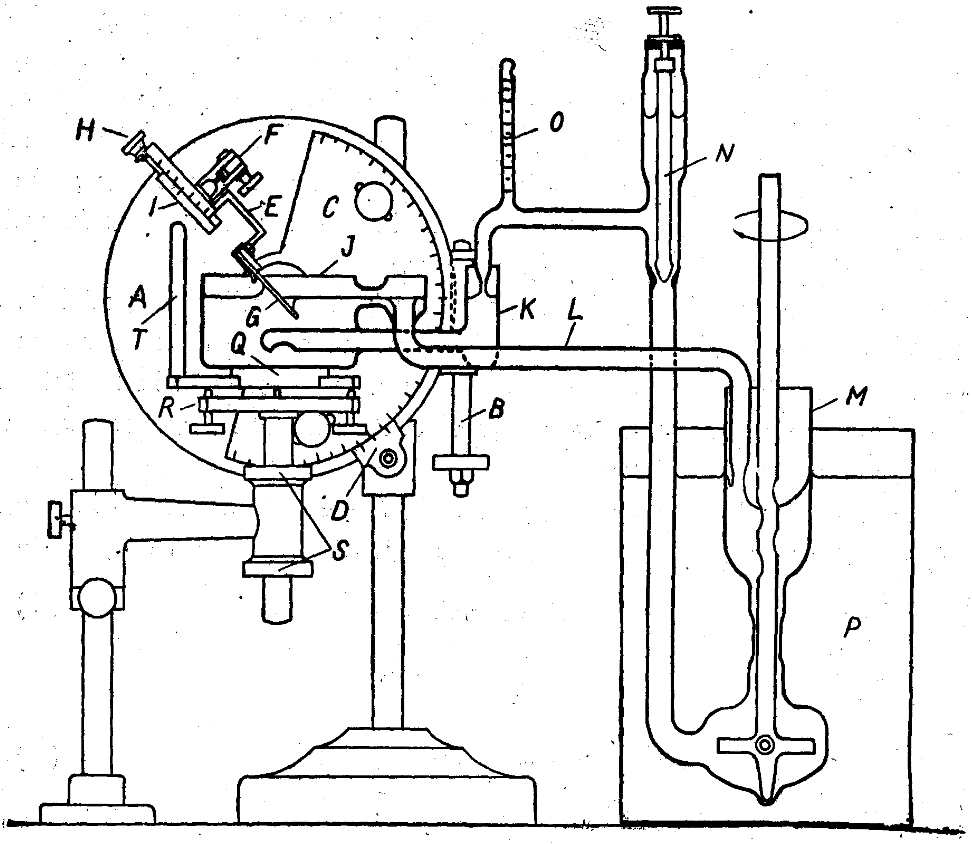

Fig. 1. Apparatus for tilting-plate method.

In Fig. 1, A is the brass disk and there is the shaft, at its center, extending backward and at right angle to it. The shaft is supported horizontally by the bearing attached to a stand. The disk, 156mm in diameter and 4mm in thickness, is toothed around its periphery. B is the worm gear to drive the disk. Its one revolution corresponds to about one degree of graduation on the disk.

C is the semi-circular disk graduated into one degree from 0 to 180 degrees and

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(39) Masayoshi Wada, Sci. Rep. **RITU**, (A) **I** (1949), 121-131.

attached to the surface of the disk A. D is the vernier scale for the graduation of the disk C and the revolution of the disk A can be read off by 0.1 degree with them.

E is the clamp attached to the disk A by the arm F. The clamp has two springs in front of it to hold slide G in position. At the rear end of the clamp there is the screw H. By the revolution of the latter the clamp E is made to slide smoothly on the slide I attached to the arm F. The clamp is graduated and its displacement is read in mm. One revolution of the screw H corresponds to 0.6 mm displacement of the clamp E. By displacing the clamp E forward or backward by means of the revolution of the screw H, the advancing or receding angle can easily be measured. The arm F can be bent at the screw joint in a plane at right angle to the disk and the slide I can be revolved at the point inserted to the arm F in a plane parallel to the disk.

J is the dish containing liquid. From the standpoint of measurement, the rectangular glass box, with the front and back sides perfectly plane and parallel, is preferred. It is difficult, however, to make such glass box by means of the present glass blowing technic without using cement or metal. Therefore the short cylindrical vessel as shown in the figure is used.

Q is the upper platform for the dish J and is supported by three leveling screws attached to the lower platform R. The vertical shaft of the platform R is inserted into the socket of the arm attached to a stand. The platforms with the dish can be adjusted in height by revolving the screw-rings S inserted to the vertical shaft of the lower platform. There is a key insertd in the socket to prevent the shaft from revolving when the screw rings are revolved.

IV. Measurement of contact angles

The slide glass made for microscopes by Matsunami's, 76 mm in length, 26 mm in width and 1.5 mm in thickness, is halved laterally and the half, 38 mm in length and 26 mm in width, is used for experiments.

The slide glass is covered by paraffin-wax as follows. The paraffin to be covered is melted on a piece of slide glass held nearly horizontal and another piece of slide glass, warmed previously, is put on the surface of the former and is made to slide slowly over it until the two glasses separate. Then the two glasses are quickly put with their paraffined surface upwards on a small brass leveling stage kept exactly horizontal. The paraffin on the surface of the glass solidifies in few seconds or so. Thus two slide glasses with the perfect covering of paraffin are obtained by one operation with some skill.

To melt paraffin on a piece of slide glass, a small gas burner consisting of the inner gas outlet of an ordinary burner, the combustion tube being removed and the lower larger part of the stand being cut off, as shown in Fig. 2 is used. The flame is regu-

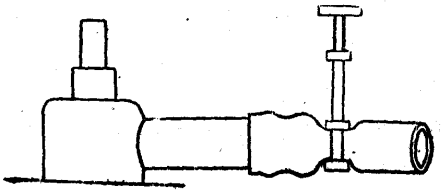

Fig. 2. Small-sized gas burner for melting paraffin-wax.

lated by a pinch cock attached to the rubber tube and a stopcock of the gas supply tube.

The paraffined slide glass is held by the clamp E, which has been exactly adjusted and fixed in position by screws so as to make the upper surface of the slide glass lie at right angle to the plane of the disk A and pass through the center of the latter.

By rotating the disk A by means of the worm gear B, the slide glass is made nearly level; a small light spirit level is put on its surface; then it is made exactly level in respect to the spirit level· The disk A is fixed in position by clamping its shaft by the screw attached to its bearing; after loosening the screws the graduated disk C is adjusted so that its zero reading coincides exactly with that of the vernier D and then it is clamped by the screws.

The cylindrical wall of the measuring vessel is made exactly vertical by means of the leveling screws attached to the platform R. The liquid level in the vessel is adjusted and fixed exactly to the center of the disk A by regulating the height of the platform by means of the screws S.

Closely behind the measuring vesesl, there is a cylindrical reflector concentric to the vessel and attached to the platform so that its height can be regulated.

The concave surface of the reflector is pasted with a sheet of high-quality paper, the upper half of which is smeared black. The reflector is adjusted in height and clamped in position so that the dividing line between the white and the black parts lies slightly below* the liquid level in the vessel.

A beam of light from an adequate electric lamp is reflected by the mirror attached in front of the vessel so as to make it reach the reflector through the liquid in the vessel. The light reflected by the lower white part of the reflector illuminates the surface of the liquid from the under side. In this way the under side of the liquid surface can be clearly seen in the field of a microscope set in front of the vessel and adjusted so that its line of sight lies horizontally and passes through the center of the disk A.

For the microscope, the petrographic one, detached of the object stage and with the tube set horizontal and with the magnification of 13, is used. The cross-hair in the eyepiece is adjusted so that its center exactly coincides with that of the disk A and the one hair with the image of the liquid surface.

In order to see with ease the curvature of the surface when the paraffined plate is immersed in the liquid, Bosanquet and Hartley(9) measured the angle of contact of the slide glass immersed so that its front edge might lie within about 0.5 mm distance from the vessel wall, where the liquid surface was elevated by capillary forces above its free level.

In this experiment, the vessel wall being cylindrical, it is difficult to measure the angle of contact of the slide glass immersed close to the wall. Therefore, the following means are devised. A small clamp is attached to the stand T at the end of the paltform Q. A semicircular glass plate, the curvature of which is coincident with that of the

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* Bosanquet and Hartley(9) pasted the white paper to the rear side of the vessel so that its end might lie about 1 mm lower than the water level.

vessel wall, is suspended close to the front wall of the vessel by the clamp. The surface of the liquid portion under the glass plate is raised slightly above the free surface by its adhesion to the glass plate. In this way, the curvature of the liquid surface where the paraffined plate is immersed is freely observed under the plate as shown in Fig. 3.

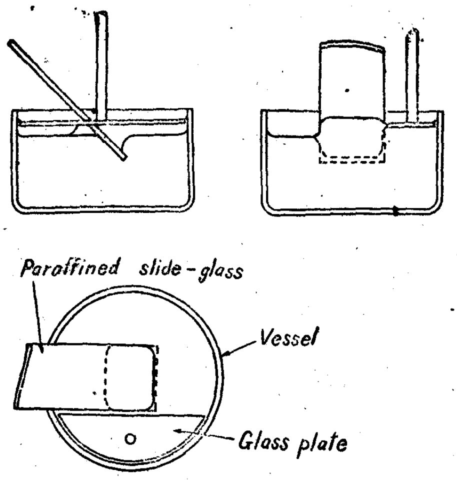

Fig. 3. Observation of angles of contact.

To measure the angle of contact, the paraffined slide glass is immersed in liquid by turning the screw H and the curvature of the surface is observed; the disk A is turned slowly until the surface becomes perfectly horizontal; the angle of revolution of the plate is read at the graduated disk and the displacement of the slide glass by the graduation at the clamp E. The angle x_a thus obtained is the advancing angle. Then the slide glass is raised by 1 mm by turning back the screw H and the curvature of the surface is again observed; the disk is turned in the opposite direction to the above case and the angle x_r is read when the liquid surface becomes horizontal. This is the receding angle. But the angle x_r thus measured corresponds to the point of the paraffined plate 1 mm lower than that where the angle x_a is measured. Thus the angles x_a and x_r for any position of the plate can be measured. In the following experiment, ten measurements are made for the advancing and receding angles respectively and their respective average values are calculated.

The slide glass, the measuring vessel, the centrifugal pump and other glass parts are cleaned with a chromic and sulphuric acid mixture and washed thoroughly with distilled water.

The primary requisites for obtaining the accurate angles of contact are to keep the liquid level constant and the liquid surface quiet. For this purpose the rate of flow of liquid must be kept constant and free from the vibrations due to various origins.

V. Paraffin-wax

For the experiment, the paraffin-wax of Takayama, Tokyo, and that of E. Merck, Darmstadt, was used. The melting point of the former is mentioned to be 56-58°C, and that of the latter, about 67°C.

A small piece of sample is cut from the paraffin-wax by a nichrome wire heated by electric current and it is prepared after the German standard testing procedures for the industry of fats and oils.(40) That is, a piece of paraffin-wax is melted on water, dried

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(40) Gen-itsu Kita, Chemistry and testing methods of fats and fatty oils. 3rd ed. (1940), 796.

at 100-105°C and kept in a desiccator. The water used for boiling was prepared by distillation.

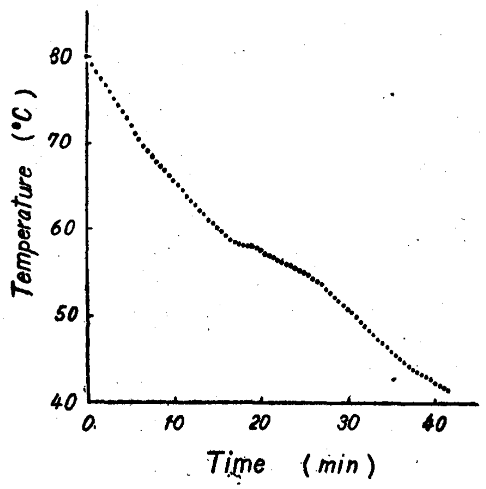

Fig. 4. Cooling curve of Merck's paraffin-wax.

The melting point of the sample of paraffin-wax measured by the melting-point apparatus consisting of the double-walled test tube with a stirring rod and a thermometer.(41-43) The melting point of Takayama's paraffin-wax was measured to be 57.5 58.0°C and that of Merck's 58.0°C. Fig. 4 is the cooling curve of Merck's paraffin-wax. Though it is stated that the transparency of paraffin-wax is not necessarily related to the content of oil in it,(44) it may be added here that Takayama's one is a little more transparent than Merck's.

VI. Angle of contact between paraffin-wax and water

The values of the angle of contact of paraffin-wax and water given in literatures are summarized in Table 1. Among various methods the drop and the tilting-plate methods

Table 1. Literatures on the contact angle between paraffin-wax and water.

Investigator	Contact angle	Remarks
Bigelow and Hunter (1911)(50)	49.2*	Capillary-height method, 20.5-21°C.
Coghill and Anderson (1918)(51)	105	Capillary-height method.
Langmuir (1920)(52)	110	Drop method.
Bosanquet and Hartley (1921)(9)	106.95 106.47	Capillary-height method, 14°C. Tilting-plate method, 14°C.
Ablett (1923)(10)	104.57	Still-cylinder method, paraffin of m. p. 56.7°C, 10°C.
	113.15**	Rotating-cylinder method, paraffin of m. p. 56.7°C, 10°C.
	96.33†	Ditto.
	104.22††	Ditto.
Adam and Jessop (1925)(11)	105	Tilting-plate method, paraffin solidified in air.
	85-100	Tilting-plate method, paraffin solidified in contact with water.

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(41) C. Drucker, Ostwald-Luther Hand-und Hilfsbuch zur Ausführung physikochemischer Messungen. 5. Aufl. (1931), 294.

(42) Jitsusaburo Sameshima, Methods of physico-chemical measurements. (1939), 133.

(43) Yoshiyuki Urushiwara, Melting point, boiling point, solubility and specific gravity (Chemical experiments. Pt. 2, 3 (1941), 165-224).

(44) Yoshio Tanaka, Petroleum, natural gas and shale oil industry (Outline of the newest chemical industry. rev. ed., 7 (1939), 1-237).

Table 1. Literatures on the contact angle between paraffin-wax and water.—*Continued.*

Investigator	Contact angle	Remarks
Adam, Morrel and Norrish (1925)(53)	105	Tilting-plate method.
Nietz (1928)(12)	109	Rotating-cylinder method, paraffin b. p. 218-225°/4mm.
	109	Tilting-plate method, paraffin b.p.218-225°/4mm.
Talmud and Lubman (1930)(54)	105	Drop method.
Wark and Cox (1932)(55)	106	Bubble method, paraffin m. p. 56-58°C, 16°C.
	104	Ditto.
Rehbinder, Lipetz and Rimskaya (1934)(21)	106	Drop method.
	106	Bubble method.
Mack and Lee (1936)(56)	108.9	Drop method, paraffin solidified in dry air.
	107.6	Drop method, paraffin solidified in air of 60% humidity.
Wenzel (1936)(14)	112.8**	Tilting-plate method.
	112.8**	Tilting-plate method, 19°C.
	113.2**	Tilting-plate method, 30°C.
	109.5**	Ditto.
	110.2**	Tilting-plate method, 30.5°C.
Powney and Frost (1937)(24)	102	Bubble method.
Kneen and Benton (1937)(23)	105.1	Drop method, paraffin block.
	110.4	Drop method, paraffin solidified on slide glass.
	115	Ditto.
Wark (1938)(5c)	109	Paraffin extremely purified.
Thiessen and Schoon (1940)(57)	104.15±1.5	Drop method, $C_{30}H_{62}$, on (001) plane, 20°C.
	104.14±0.65	Drop method, $C_{31}H_{64}$, on (001) plane, 20°C.

* Calculated from the measured value of $rh=9.69$ mm^2 by the author using the surface tension $H=72.63$ dynes/cm at 20.5-21°c, (59) where cos $x=rhgd/2H$, g being the acceleration of gravity and d, the density of water.

** Advancing angle.

† Receding angle.

†† Mean of advancing and receding angles.

have been most widely used. The smallest value is 49.2° measured by Bigelow and Hunter by the capillary-height method at 20.5-21°C and the maximum one is 115° by Kneen and Benton by the drop method. The most values are in the range of the angles between 104° and 106°. The most accurate values of all seem to be those of Ablett and of Thiessen and Schoon. The values given by the former are 104.57° for the stationary cylinder and 104.40° for rotating cylinder and those given by the latter are 104.14±0.65° for $C_{31}H_{64}$ and 104.15±1.5° for $C_{30}H_{62}$.

Wark⁽⁵ᶜ⁾ states that the angle of contact of paraffin-wax may be raised from 105° to 109° according to the degree of purification. Wenzel⁽¹⁴⁾ showed that a considerable variation in room temperature, that is, from 19° to 30.5°C, had no great effect on the angles of contact.

Table 2 shows the results of the measurement of contact angles of Merck's paraffin-

Table 2. Contact angles of paraffin-wax against water.*
Paraffin-wax: Merck's make, m.p. 58.0°C.

Measurement A. t:26.6°C, V: 5.5cc/sec.

L in mm	x_a	R_1	$\cos x_a$	R_1'	x_r	R_2	$\cos x_r$	R_2'
5	113.5	−0.4	−0.399	0.006	104.3	1.3	−0.247	−0.023
6	113.0	−0.9	−0.391	0.014	103.7	0.8	−0.237	−0.013
7	112.8	−1.1	−0.383	0.017	104.3	1.4	−0.247	−0.023
8	114.9	1.0	−0.421	−0.016	103.3	0.4	−0.230	−0.006
9	115.0	1.1	−0.423	−0.018	102.4	−0.5	−0.215	0.009
10	115.3	1.4	−0.427	−0.022	102.5	−0.4	−0.216	0.008
11	114.2	0.3	−0.410	−0.005	102.1	−0.8	−0.210	0.014
12	114.6	0.7	−0.416	−0.011	103.0	0.1	−0.225	−0.001
13	112.5	−1.4	−0.383	0.022	101.9	−1.0	−0.206	0.018
14	113.3	−0.6	−0.396	0.009	101.9	−1.0	−0.206	0.018
Average :	113.9	0.9	−0.405	0.014	102.9	0.8	−0.224	0.013

$x=108.4$, $\cos x=-0.315$, $x_a-x_r=11.0$, $\cos x_a-\cos x_r=-0.181$

Measurement B. t: 27.2°C, V: 5.1cc/sec.

L in mm	x_a	R_1	$\cos x_a$	R_1'	x_r	R_2	$\cos x_r$	R_2'
19	116.4	1.6	−0.445	−0.026	101.7	0.6	−0.203	−0.011
18	116.0	1.2	−0.438	−0.019	102.3	1.2	−0.213	−0.021
17	115.0	0.2	−0.423	−0.004	101.8	0.7	−0.205	−0.013
16	114.8	0.0	−0.420	−0.001	100.9	−0.2	−0.190	0.003
15	114.1	−0.7	−0.408	0.011	101.7	0.6	−0.203	−0.011
14	115.1	0.3	−0.424	−0.005	100.2	−0.9	−0.177	0.015
13	114.4	−0.4	−0.413	0.006	99.5	−1.6	−0.165	0.027
12	114.4	−0.4	−0.413	0.006	101.1	0.0	−0.193	−0.001
11	114.4	−0.4	−0.413	0.006	101.7	0.6	−0.203	−0.011
10	113.2	−1.6	−0.394	0.025	99.8	−1.3	−0.170	0.022
Average :	114.8	0.7	−0.419	0.011	101.1	0.8	−0.192	0.014

$x=107.8$, $\cos x=-0.306$, $x_a-x_r=13.7$, $\cos x_a-\cos x_r=-0.227$

* t: temperature of water, V: flow of water, L: graduation on clamp, x: mean contact angle, x_a: advancing contact angle, x_r: receding contact angle, R_1, R'_1, R_2, R'_2: **Residuals.**

wax for pure water. Measurement A is for the results obtained by immersing the paraffined plate, set above the surface of water at first, successively into water by 1 mm and reading the angle of contact each time. Measurement B is for those obtained by drawing the plate, immersed in water at first, successively out of water by 1 mm and reading the angle each time. The position of the measurement is read by the graduation on the clamp L in mm.

Though there are some differences in the flow and the temperature of water, there is not much difference in the mean values of the angle of contact. In measurement A, the average value of the advancing angles x_a is 114±0.9° and that of the receding angles x_r is 103±0.8°. In measurement B, the former is 115±0.7° and the latter, 101±0.8°. The mean value of the cosines of advancing and receding angles, cos x, is —0.315 in A and —0.306 in B. The corresponding angles x are 108.4° and 107.8° respectively. The values of hysteresis expressed in terms of $\cos x_a - \cos x_r$ are —0.181 and —0.227 respectively.

The average accuracy of ±0.75° in the contact-angle measurements obtained in the author's experiments is slightly higher than that of ±1.1° in Thiessen and Schoon's. The mean value of contact angles of 108.1° belongs to the slightly higher class in the results of previous workers.

For Takayama's paraffin-wax, the advancing angles range 116.6°—117.7°, the receding angles, 95.0°—97.6°, and the mean angles, 106.4°—107.1°. These values of mean angle are slightly lower than those of Merck's and the values of hysteresis are slightly larger. Later on it was found that Takayama's paraffin showed slightly different angles of contact with the place of sampling in the batch of paraffin-wax used. Hence the following investigation has been done exclusively on Merck's paraffin.

In this experiment, the following values of contact angle have been adopted as the standard:

$$x_a = 114.3^0, \qquad \cos x_a = -0.412.$$
$$x_r = 102.0^0, \qquad \cos x_r = -0.208.$$
$$x = 108.1^0, \qquad \cos x = -0.310.$$

The work of adhesion W_0 calculated by equation (1) and the wetting tension B_0 calculated by equation (6) are as follows:

$$W_0 = 71.8 \times (1 - 0.310) = 49.5 \text{ ergs/cm}^2,$$
$$B_0 = 71.8 \times (-0.310) = -22.2 \text{ dynes/cm}.$$

As the average temperature difference has little effect on contact angles, the values of W_0 ad B_0 may be regarded as those at the temperature of 25°C where the surface tension has been measured.

VII. Angle of contact between paraffin-wax and aqueous solutions of frothers

The results of measurement of the contact angles of paraffin-wax in aqueous solutions of iso-amyl alcohol, meta-cresol, α-terpineol, and d-camphor, and Takasago's No. 5

flotation oil, Shiono's No. 1 flotation oil and Yarmor "F" S. D. pine oil are shown in Tables 3—9.

Table 3. Contact angles of paraffin-wax in aqueous solutions of iso-amyl alcohol.*
t: 26.4°C, V: 3.35cc/sec.

c in g/kg H_2O	c in mol/kg H_2O	x_a	R_1	x_r	R_2	x	$\cos x$	$x_a - x_r$	$\cos x_a - \cos x_r$
0.0000	0.000000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0.204
0.0330	0.000375	113.2	0.5	102.9	0.4	108.0	−0.309	10.3	−0.171
0.0660	0.000750	112.5	0.7	103.5	0.2	108.0	−0.308	9.0	−0.149
0.132	0.00150	113.3	0.8	103.5	0.9	108.3	−0.315	9.8	−0.162
0.264	0.00300	113.2	0.6	103.6	1.0	108.3	−0.315	9.6	−0.159
0.528	0.00600	111.6	0.7	102.9	0.7	107.2	−0.296	8.7	−0.145
1.06	0.0120	109.3	0.3	100.2	1.0	104.7	−0.254	9.1	−0.153
2.11	0.0240	105.1	0.7	96.7	0.4	100.9	−0.189	8.4	−0.144
4.23	0.0480	96.8	0.4	89.9	0.4	93.3	−0.0583	6.9	−0.120
8.45	0.0960	87.7	1.2	70.4	1.4	79.2	0.188	17.3	−0.295

* c: concentration

Table 4. Contact angles of paraffin-wax in aqueous solutions of meta-cresol.
t: 27.0°C, V: 3.24 cc/sec.

c in g/kg H_2O	c in mol/kg H_2O	x_a	R_1	x_r	R_2	x	$\cos x$	$x_a - x_r$	$\cos x_a - \cos x_r$
0.00000	0.0000000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0.204
0.05032	0.0004657	112.8	0.2	99.7	0.8	106.1	−0.278	13.1	−0.219
0.1505	0 001393	111.5	0.6	98.0	0.5	104.6	−0.253	13.5	−0.227
0.3574	0.003307	110.1	0.6	96.9	0.5	103.4	−0.232	13.2	−0.224
0.7774	0.007194	108.9	0.4	95.7	0.3	102.2	−0.212	13.2	−0.225
1.646	0.01523	106.3	0.5	94.0	0.5	99.8	−0.170	12.3	−0.211
3.352	0.03102	101.5	0.5	89.2	0.6	95.3	−0.0927	12.3	−0.213
6.835	0.06325	94.1	0.3	84.2	0.6	89.2	0.0148	9.9	−0.173
13.03	0.1206	82.5	0.5	70.2	1.0	88.7	0.235	12.3	−0.208

Table 5. Contact angle of paraffin-wax in aqueous solutions of α-terpineol.
t: 27.4°C, V: 3.22 cc/sec.

c in g/kg H_2O	c in mol/kg H_2O	x_a	R_1	x_r	R_2	x	$\cos x$	$x_a - x_r$	$\cos x_a - \cos x_r$
0.0000	0.000000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0.204
0.0596	0.000387	108.8	0.6	100.8	0.3	104.8	−0.255	8.0	−0.135
0.1192	0.000773	106.0	0.7	99.0	0.5	102.5	−0.216	7.0	−0.119
0.2384	0.00155	102.0	0.3	93.3	0.2	97.6	−0.133	8.7	−0.150
0.4768	0.00309	97.9	0.4	88.6	0.5	93.2	−0.0565	9.3	−0.162
0.9536	0.00619	90.6	0.7	80.4	0.8	85.5	0.0782	10.2	−0.177
1.907	0.0124	81.2	1.0	65.6	1.3	73.6	0.283	15.6	−0.260

Table 6. Contact angles of paraffin-wax in aqueous solutions of d-camphor.

t: 26.6°C, V: 3.30cc/sec.

c in g/kg H_2O.	c in mol/kg H_2O	x_a	R_1	x_r	R_2	x	cos x	$x_a - x_r$	cos x_a − cos x_r
0.00000	0.0000000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0.204
0.04479	0.0002444	116.9	0.3	97.4	1.1	106.9	−0.291	19.5	−0.324
0.1411	0.0009275	114.7	0.4	95.7	1.6	105.0	−0.259	19.0	−0.319
0.3203	0.002105	110.4	0.3	94.5	0.8	102.3	−0.214	15.9	−0.270
0.6812	0.004478	105.3	0.3	90.6	0.9	97.9	−0.137	14.7	−0.253
1.360	0.008940	99.0	0.6	85.2	0.6	92.1	−0.0364	13.8	−0.240

Table 7. Contact angles of paraffin-wax in aqueous solutions of Takasago's No. 5 flotation oil.

t: 27.7°C, V: 3.28cc/sec.

c in g/kg H_2O	x_a	R_1	x_r	R_2	x	cos x	$x_a - x_r$	cos x_a − cos x_r
0.00000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0.204
0.05005	110.8	0.4	100.1	0.8	105.4	−0.265	10.7	−0.180
0.09916	108.4	0.4	98.6	0.4	103.5	−0.233	9.8	−0.166
0.1997	105.1	0.8	94.1	1.7	99.6	−0.166	11.0	−0.189
0.3943	99.5	0.8	86.7	0.4	93.1	−0.0537	12.8	−0.223
0.7891	93.3	0.8	80.7	0.4	87.0	−0.0520	12.6	−0.219

Table 8. Contact angles of paraffin-wax in aqueous solutions of Shiono's No. 1 flotation oil.

t: 26.6°C, V: 3.30 cc/sec.

c in g/kg H_2O	x_a	R_1	x_r	R_2	x	cos x	$x_a - x_r$	cos x_a − cos x_r
0.00000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0.204
0.04491	112.8	0.4	99.0	0.7	105.8	−0.272	13.8	−0.231
0.09026	111.3	1.3	99.8	0.3	105.5	−0.267	11.5	−0.193
0.1886	110.3	1.5	98.4	0.5	104.3	−0.247	11.9	−0.201
0.3822	106.7	1.0	88.8	1.3	97.7	−0.133	17.9	−0.308

Table 9. Contact angles of paraffin-wax in aqueous solutions of Hercules' Yarmor "F" S.D. pine oil.

t: 26.6°C, V: 3.26 cc/sec.

c in g/kg H_2O	x_a	R_1	x_r	R_2	x	$\cos x$	$x_a - x_r$	$\cos x_a - \cos x_r$
0.00000	114.3	0.8	102.0	0.8	108.1	−0.310	12.3	−0·204
0.05249	113.9	0.7	98.4	0.3	106.0	−0.276	15.5	−0·259
0.1069	111.7	0.3	96.3	0.5	103.9	−0.240	15.4	−0·260
0.2205	108.1	0.6	93.5	0.4	100.7	−0.186	14.6	−0·250
0.4490	102.1	0.8	88.5	0.7	95.3	−0.0917	13.6	−0·236
0.9301	94.4	0.8	81.3	0.5	87.9	−0.0373	13.1	−0·228
1.907	84.4	1.0	68.4	0.7	76.5	0.233	16.0	−0·271

The accuracy of the measurements is nearly equal to that in case of pure water. The average residuals for both advancing and receding angles, R_1 and R_2 are less than 1.0° except in a few cases. The hysteresis is about 20° in terms of $x_a - x_r$, and less than 0.3 in absolute values in terms of $\cos x_a - \cos x_r$, being comparable with that in case of pure water.

VIII. Discussion of hysteresis in contact angle

Rehbinder, Lipetz and Rimskaja(21) state that the hysteresis in contact angle of paraffin-wax is nearly zero in pure water and it gradually increases and approaches to the limiting value in case of pure water and does not so much vary its value with the increase in the concentration, and moreover, its sign is negative.

Rehbinder and his coworkers denote the cosine of the contact angle measured with the liquid drop attached on the paraffined platinum plate as B_{12} and that measured with the bubble attached to the under side of the paraffined platinum plate immersed in the liquid as B_{21} and defined the hysteresis by the difference between the two.

$$\text{Hysteresis} = B_{12} - B_{21}, \qquad (7)$$

where

$$B_{21}(c) < B_{12}(c),$$

that is, the wettability obtained in case of the liquid drop attached on the paraffined plate is larger than that in case of the bubble attached to the under side of the plate immersed in the liquid.

The value $B_{12} - B_{21}$ defined by Rehbinder and others seems not to express the true hysteresis for the following reasons.

In the nature of contact-angle measurements, the hysteresis is due to the difference resulting from the fact that whether the line of air-liquid-solid contact moves in the advancing or receding direction with respect to the liquid when the contact angle reaches the equilibrium value.

It is not always the case that the contact angle of the liquid drop attached on the paraffined plate is advancing and that of the bubble attached to the under side of the plate is receding. Moreover, there are differences in the condition of measurement in two cases. For example, in the case where the bubble is attached to the paraffined plate in the solution of a certain concentration, a fairly larger quantity of the solution is required, but in the case where the liquid drop is attached on the plate a very little quantity of the solution is needed. Even supposing that both the liquids are taken from the same solution, it is questionable that the composition of the liquid drop of small quantity is equal to that of the original solution.

Finally the air in the bubble is perfectly saturated with the vapor of the liquid, but the air surrounding the liquid drop can not be considered to be in the same condition.

On the other hand, Ablett⁽¹⁰⁾ obtained for pure water the average value of the difference between the advancing and receding angles

$$x_a - x_r = 16°49',$$

or the difference between the consines of the advancing and receding angles

$$\cos x_a - \cos x_r = -0.393 + 0.110 = -0.283$$

These values are comparable with those obtained by the author, the latter being a little smaller in absolute values.

As to the meaning of the hysteresis in contact-angle measurements, there are a number of opinions and it is not yet perfectly solved.(6a, 7a, 45)

Somehow, it seems to leave no room for question that the condition of the surface has certain bearings on the hysteresis.

In this investigation, after Ablett,(10) Adam and Jessop,(11) and Wark,(5a) the mean value of the cosines of advancing and receding angles has been adopted for the sake of convenience for use in further considerations.

$$\cos x = (\cos x_a + \cos x_r)/2, \tag{8}$$

and the corresponding angle x has been computed from $\cos x$ thus obtained.

IX. Wetting isotherm

The change of the wettability of solids in the solutions of surface-active substances is closely related to the adsorption of collectors or of frothers on the surface of minerals in flotation process.

It is of primary importance to investigate the relation between the wettability of solids and the concentration of surface-active solutes at a constant temperature to clear up the action of flotation agents on the surface of minerals.

The equation expressing the above relation may be called the wetting isotherm. Rehbinder, Lipetz, Rimskaja and Taubmann (28) proposed a wetting isotherm for the same purpose:

$$B = B_0 - (B_0 - B_1) \cdot c/(c + a), \tag{9}$$

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(45) F. E. Bartell and A. D. Wooley, J. Am. Chem. Soc., 55 (1933), 3518-27.

where

$B_0=\cos x_0$, the wettability of a solid surface in pure water,

$B_1=\cos x_1$, the wettability of the solid surface where the molecules of a solute are perfectly adsorbed,

$B=\cos x$, the wettability corresponding to any degree of adsorption of the molecules,

a=a constant.

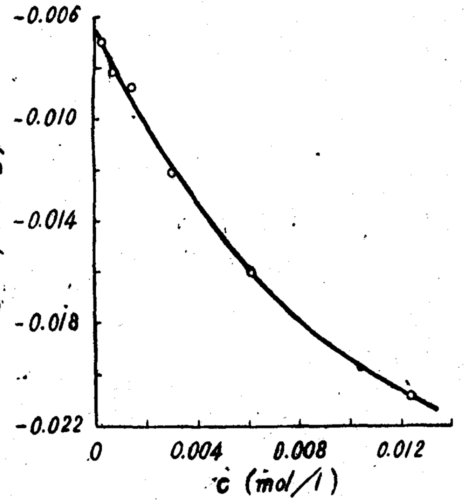

Fig. 5. c-Z curve for aqueous solutions of α-terpineol.

The above equation is theoretically imperfect, for the surface tension of a solution is not taken into account in the definition of wettability of solids as already discussed in Par. II.

As a trial, the author's results of experiment on aqueous solutions of α-terpineol were tested to see if they coincided with equation (9).

As shown in Fig. 5, the relation between c and Z in equation (10) obtained by the transformation of the original one, can not be expressed by a straight line.

$$Z=c/(B_0-B)=a/(B_0-B_1)+c/(B_0-B_1). \tag{10}$$

Therefore a new wetting isotherm was derived under the following considerations.

After Gibbs[46] the quantity u of a solute adsorbed on a unit surface of a solution is expresesd as follows:

$$u=-c/RT\cdot dH/dc, \tag{11}$$

where R is the gas constant and T is the absolute temperature.

Suppose that a similar relation exists between the concentration c of the solute in the body of the solution and the tension H' at the liquid-solid interface when the solute is adsorbed by u' at the interface,

then,

$$u'=-c/RT\cdot dH'/dc. \tag{12}$$

On the other hand, Harkins and Fowkes[8] point out that the adsorption layer of butyl alcohol at paraffin-water interface shows nearly the same state as that of a perfect gas in case of the low surface pressure and approaches that of a highly compressed gas in case of the higher surface pressure. Therefore, the molecules of the adsorbed layer in question may be regarded to be in a gaseous state.

It may be supposed that Langmuir's adsorption isotherm holds true in the relation between the quantity adsorbed at the solid surface and the concentration in the body of the solution.

Then,

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(46) J. W. Gibbs, Collected works. I (1928).

$$n/N_0=q=kp/(j+kp),^{(47)} \tag{13}$$

where n is the number of molecules adsorbed, N_0 is that in case of perfect adsorption, q is the fraction of the area occupied by the adsorbed molecules, j and k are constants, and p is the gas pressure.

If we assume for the sake of convenience that the concentration c may be used instead of the pressure p,

$$q'=kc/(j+kc) \tag{14}$$

Equating the two quantities adsorbed, expressed by equations (12) and (14),

$$-c/RT\cdot dH'/dc=b'c/(a'+c), \tag{15}$$

where a' and b' are constants.

Integrating equation (15) and substituting the boundary conditions, $c=O$, $H'=H_0'$, we get

$$H_0'-H'=b'RT\ \ln(c/a'+1) \tag{16}$$

The equation is similar to that of Szyszkovski⁽⁴⁸⁾ for the lowering of surface tension of solutions. But it is difficult to measure directly the value H_0'—H' in the equation.

From Young's equation (4), the relation of the interfacial tensions for pure water is

$$H_0''=H_0'+H_0\cos x_0, \tag{17}$$

and that for solution is

$$H''=H'+H\cos x. \tag{18}$$

If we can neglect the effect of the molecules of the solute upon the interfacial tension between the solid and the gas or the vapor of the solution⁽⁸⁾,

$$H_0''=H''$$

Hence,

$$H_0'-H'=H\cos x-H_0\cos x_0. \tag{19}$$

From equations (16) and (19),

$$H\cos x-H_0\cos x_0=b'RT\ln(c/a'+1), \tag{20}$$

where the left-hand term is expressed by the difference in the values of the wetting tension, defined by the author, in pure water and in solution. The wetting tensions can be calculated by measuring the surface tension of the solution and the contact angle between the solid and the solution..

As the value of H_0'—H' corresponds to the two-dimensional pressure, that is the surface pressur F' exerted by the adsorbed molecules, at the solid-liquid interface, it may be called the surface pressure of wetting, which quantities the wetting power of a surface-active substance.

In order to test whether equation (20) holds true or not, it is transformed into the form

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(47) I. Langmuir, J. Am. Chem. Soc., **38** (1916), 2221-95; **40** (1918), 1361-1403; Phys. Rev., 8 (1916), 149.

(48) B. von Szyszkovski, Z. physik. Chem., **64** (1908), 385-414.

$$\log(c+a') = \log a' + F'(\log e/b'RT). \tag{21}$$

Hence $\log(c+a')$ and F' are in a linear relation. The value of a' in equation (21) is determined from the relation between F' and c as follows.(49)

Let us take two points, (F'_1, c_1) and (F'_2, c_2), on the curve and take the third point (F'_3, c_3) on the same curve so that $F'_3 = (F'_1 + F'_2)/2$, and obtain graphically the corresponding value of c_3.

Then,

$$-a' = (c_1c_2 - c_3^2)/(c_1 + c_2 - 2c_3). \tag{22}$$

Since $F' = 0$ when $c = 0$, if we take $F'_1 = 0$ and $c_1 = 0$, equation (22) simplifies itself to

$$a' = c_3^2/(c_2 - 2c_3). \tag{23}$$

X. Wetting tension of frothers at paraffin-water-air interfaces

The experimental results on aqueous solutions of iso-amyl alcohol, meta-cresol, α-terpineol, d-camphor, Takasago's No. 5 flotation oil, Shiono's No. 1 flotation oil and Yarmor "F" S. D. pine oil are tabulated in Tables 10—16.

Table 10. Wettability of paraffin-wax in aqueous solutions of iso-amyl alcohol.*
t: 26.4°C, a': 0.0410, b': $9.54 \cdot 10^{-10}$.

c in mol/kg H_2O	$\cos x$	H in dyne/cm	$H\cos x$ in dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.000000	−0.310	71.0	−22.0	0.0	—	—
0.000375	−0.309	70.6	−21.8	0.2	0.2	0.0
0.000750	−0.308	70.2	−21.6	0.4	0.4	0.0
0.00150	−0.315	69.4	−21.8	0.2	0.8	−0.6
0.0030	−0.315	68.1	−21.5	0.5	1.6	−1.1
0.0060	−0.296	65.7	−19.5	2.5	3.2	−0.7
0.0120	−0.254	61.9	−15.7	6.3	6.1	0.2
0.0240	−0.189	56.6	−10.7	11.3	10.9	0.4
0.0480	−0.0583	49.7	− 2.89	19.1	18.4	0.7
0.0960	0.188	42.0	7.90	29.9	28.6	1.3
					Average :	0.58

*. a', b': constants, H: surface tension, F': surface pressure. F'_c: surface pressure calculated.

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(49) Takeo Nagasawa, Methods of calculating in experiments and observation. 2nd ed. (1932), 150.

(50) S. L. Bigelow and F. W. Hunter, J. Phys. Chem., **15** (1911), 367-80.

(51) W. H. Coghill and C. O. Anderson, J. Phys. Chem., **22** (1918), 237-55.

(52) I. Langmuir, Trans. Faraday Soc., **15** (1920), Pt. 3, 62-74.

(53) N. K. Adam, R. S. Morrell and R. G. W. Norrish, J. Chem. Soc., **127** (1925), 2793-5.

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(55) I. W. Wark and A. B. Cox, Am. Inst. Mining Met. Engrs., Tech. Pub., No. 461 (1932), 1-48.

(56) G. L. Mack and D. A. Lee, J. Phys. Chem., **40** (1936), 169-76.

(57) P. A. Thiessen and E. Schoon, Z. Elektrochem., **46** (1940), 170-81.

Table 11. Wettability of paraffin-wax in aqueous solutions of meta-cresol.
t: 27.0°C, a': 0.0108, b': $5.47 \cdot 10^{-10}$.

C in mol/kg H_2O	$\cos x$	H in dyne/cm	$H \cos x$ dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.0000000	−0.310	71.8	−22.3	0.0	—	—
0.0004657	−0.278	71.3	−19.8	2.5	0.6	1.9
0.001393	−0.253	71.0	−18.0	3.3	1.7	1.6
0.003307	−0.232	69.9	−16.2	6.1	3.7	2.4
0.007194	−0.212	67.8	−14.4	7.9	7.0	0.9
0.01523	−0.170	64.4	−11.0	11.3	12.0	−0.7
0.03102	−0.0927	59.2	− 5.49	16.8	18.5	−1.7
0.06325	0.0148	52.3	0.773	23.1	26.3	−3.2
0.1206	0.235	44.6	10.5	82.8	34.1	−1.3
					Average :	1.7

Table 12. Wettability of paraffin-wax in aqueous solutions of α-terpineol.
t: 27.4°C, a': 0.000641, b': $4.45 \cdot 10^{-10}$.

c in mol/kg H_2O	$\cos x$	H in dyne/cm	$H \cos x$ in dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.000000	−0.310	71.8	−22.3	0.0	—	—
0.000387	−0.255	67.0	−17.1	5.2	5.3	−0.1
0.000773	−0.216	63.7	−13.8	8.5	8.8	−0.3
0.00155	−0.133	59.1	− 7.86	14.4	13.7	0.7
0.00309	−0.0565	53.4	− 3.02	19.3	19.6	−0.3
0.00619	0.0782	46.8	3.66	26.0	26.3	−0.3
0.0124	0.283	39.9	11.3	33.6	33.5	0.1
					Average :	0.30

Table 13. Wettability of paraffin-wax in aqueous solutions of d-camphor.
t: 26.3°C, a': 0.00181, b': $4.60 \cdot 10^{-10}$.

c in mol/kg H_2O	$\cos x$	H in dyne/cm	$H \cos x$ in dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.0000000	−0.310	71.9	−22.3	0.0	—	—
0.0002944	−0.291	70.3	−20.4	1.9	1.7	0.2
0.0009275	−0.259	67.5	−17.5	4.8	4.8	0.0
0.002105	−0.214	63.7	−13.6	8.7	8.9	−0.2
0.004478	−0.0137	58.6	− 8.04	14.3	14.3	0.0
0.008940	−0.0364	53.0	− 1.93	20.4	20.4	0.0
					Average :	0.08

Table 14. Wettability of paraffin-wax in aqueous solutions of Takasago's No. 5 flotation oil.

t: 27.7°C, a': 0.101, b': $4.50 \cdot 10^{-10}$.

c in g/kg H_2O	$\cos x$	H in dyne/cm	$H \cos x$ in dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.00000	−0.310	71.9	−22.3	0.0	—	—
0.05005	−0.265	68.9	−18.3	4.0	4.5	−0.5
0.09916	−0.233	66.6	−15.5	6.8	7.7	−0.9
0.1997	−0.166	63.1	−10.5	11.8	12.3	−0.5
0.3943	−0.0537	58.6	− 3.15	19.1	17.9	1.2
0.7891	0.0520	53.0	2.76	25.1	24.5	0.6
					Average :	0.74

Table 15. Wettability of paraffin-wax in aqueous solutions of Shiono's No. 1 flotation oil.

t: 27.6°C, a': 0.347, b': $8.73 \cdot 10^{-10}$.

c in g/kg H_2O	$\cos x$	H in dyne/cm	$H \cos x$ in dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.00000	−0.310	71.6	−22.2	0.0	—	—
0.04491	−0.272	69.1	−18.8	3.4	2.7	0.7
0.09028	−0.267	66.7	−17.8	4.4	5.1	−0.7
0.1886	−0.247	61.5	−15.2	7.0	9.5	−2.5
0.3822	−0.133	51.6	− 6.88	15.3	16.2	−0.9
					Average :	1.2

Table 16. Wettability of paraffin-wax in aqueous solutions of Hercules' Yarmor "F" S.D. pine oil.

t: 26.6°C, a': 0.153, b': $4.84 \cdot 10^{-10}$.

c in g/kg H_2O	$\cos x$	H in dyne/cm	$H \cos x$ in dyne/cm	F' in dyne/cm	F'_c dyne/cm	R
0.00000	−0.310	71.6	−22.2	0.0	—	—
0.05249	−0.276	69.0	−19.0	3.2	3.6	−0.4
0.1069	−0.240	66.7	−16.0	6.2	6.4	−0.2
0.2205	−0.186	62.9	−11.7	10.5	10.8	−0.3
0.4490	−0.0917	57.4	− 5.27	16.9	16.5	0.4
0.9301	0.0373	50.3	1.88	24.1	23.6	0.5
					Average :	0.36

In Fig. 6 and 7, F' and log $(c+a')$ are plotted for the pure and the commercial frothers to see whether the theoretical equation is applicable to the experimental results or not. Though for meta-cresol the points scatter more or less, for each of other frothers they lie in a fairly straight line.

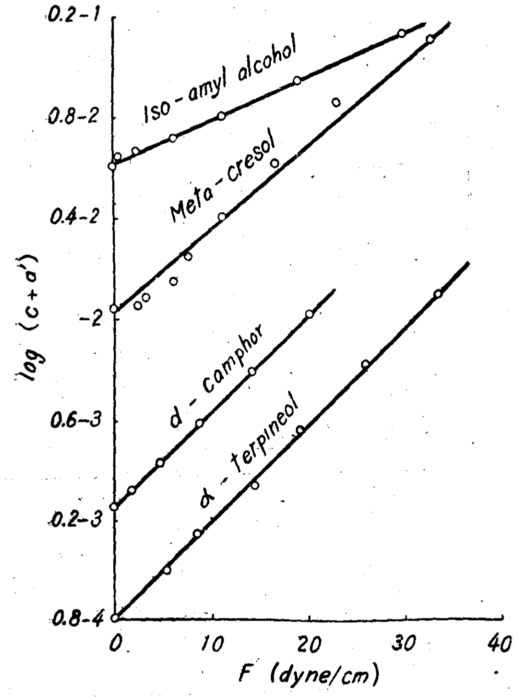

Fig. 6. Wetting isotherms for pure frothers at air-water-paraffin interfaces.

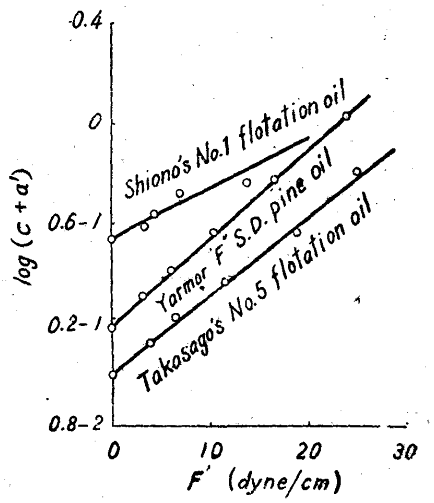

Fig. 7. Wetting isotherms for commercial frothers at air-water-paraffin interfaces.

From the figures it is clear that the experimental results are expressed well by the above equation. As to the concentration of surface-active substances, the value approaching saturation may be taken. In such concentrations, however, the experimental values deviate more or less from the calculated ones. In Tables 10-16, the residuals between measured and calculated values of F' given range from 0.08 for d-camphor to 1.7 for meta-cresol.

XI. Wetting activity and Orientation of frothers at paraffin-water-air interfaces

The wetting isotherm (20) obtained above is entirely similar in form to Szyszkovski's equation. Hence, by analogy, the wetting activity and the orientation of frothers at paraffin-water interface may be considered to be as in the second report.⁽⁵⁸⁾

By differentiating equation (20) with respect to the concentration of surface-active substance, we get

$$A' = dF'/dc = b'RT/(a'+c), \qquad (24)$$

which may be called wetting activity. It varies in nearly parabolic relation as the con-

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(58) Masayoshi Wada, Sci. Rep. RITU, (A), 1 (1949), 425-34.

(59) National Research Council of the U. S. A., Intern. critical tables of numerical data, physics, chemistry and technology. 4 (1928), 447.

centration varies.

If we denote the value of A' when c is zero by A_0',

$$A_0' = (dF'/dc)_{c=0} = b'RT/a'. \tag{25}$$

Since the value of A_0' depends upon the value of b'/a', the latter may be called wetting activity coefficient of surface-active substances. The larger the value b'/a', the larger the wetting power.

In Table 17 the wetting activities of frothers at paraffin-air interfaces are tabulated.

Table 17. Wetting activities of frothers at paraffin-water-air interfaces.*
Paraffin-wax: m.p. 58°C, t: 25°C.

Frothers	a' in g/kg H_2O	$b' \cdot 10^{10}$	$b'/a' \cdot 10^{10}$	A_0' in dyne/cm	A_0'/A_0
α-terpineol	0.0988	4.45	45.0	111.6	1.1
d-camphor	0.275	4.60	16.7	41.5	1.1
Meta-cresol	1.17	5.47	4.69	11.6	2.0
Iso-amyl alcohol	3.61	9.54	2.64	6.55	0.52
Takasago's No. 5 flotation oil	0.101	4.50	44.5	110.4	1.6
Hercules' Yarmor "F" S.D. pine oil	0.153	4.84	31.6	78.4	1.4
Shiono's No. 1 flotation oil	0.347	8.73	25.1	62.3	1.1

* b'/a': coefficient of wetting activity, A_0': wetting activity, A_0: surface activity.

According to the table, α-terpineol is the most wetting active and followed by Takasago's No. 5 flotation oil, Hercules' Yarmor "F" S. D. pine oil, Shiono's No. 1 flotation oil, d-camphor, meta-cresol and iso-amyl alcohol in the order.

The ratio of the wetting activity A_0' to the surface activity A_0 varies but little with the kind of frothers. The extreme values are 0.52 for iso-amyl alcohol and 2.0 for meta-cresol and the average of all is 1.26. Hence it may be considered that the activities of frothers tested are nearly same at the water-air and the paraffin-water interfaces within experimental errors.

Table 18. Least area occupied by a gram molecule and reciprocal of lateral molecular cohesion of frothers at paraffin-water interface.*

Frothers	$B' \cdot 10^9$ in cm^2 per mole	B'/N in $Å^2$ per molecule	x'	B'/B	x'/x
α-terpineol	1.74	28.7	0.48	0.96	1.1
d-camphor	1.59	26.2	0.84	0.96	0.93
Meta-cresol	1.47	24.2	0.71	1.3	0.77
Iso-amyl alcohol	0.685	11.3	0.93	0.53	1.1
Takasago's No. 5 flotation oil	1.67	27.5	0.81	0.94	0.96
Hercules' Yarmor "F" S. D. pine oil	1.50	24.8	0.85	1.1	1.1
Siono's No. 1 flotation oil	0.645	10.6	0.99	5.6	1.0

* B': least area occupied by a gram molecule at paraffin-water interface, B: ditto at air-water interface, N: Avogadro-Loschmidt's number, x': reciprocal of lateral molecular cohesion at paraffin-water interface, x: ditto at air-water interface.

Table 18 shows the results of calculation of the least area B' occupied by a gram molecule and reciprocal of lateral molecular cohesion x' of frothers at the paraffin-water interface.

The value of B'/N ranges from 10.6Å^2 to $28.7\ \text{Å}^2$ and the value of x' ranges from 0.71 to 0.99.

The ratio of B'/B, that is the ratio of the least area occupied by a molecule at paraffin-water interface to that at water-air interface, is 0.53-1.3 except 5.6 for Shiono's No. 1 flotation oil and the corresponding ratio x'/x is 0.77-1.1.

Summary

(1) By considering critically the reciprocal action of interfacial energies among solid, liquid and gas, the product of the surface tension of the liquid and the cosine of the angle of contact, the wetting tension, was selected as the irreproachable definition of the wettability of solid against liquid.

(2) The titling-plate method was selected for the simplicity of its principle and the ease of the repetition of measurements, the primary requisites for the precise measurements.

(3) The modified form of the apparatus for tilting-plate method was developed, in which all parts in contact with the liquid under test were made of glass only and the advancing and receding angles were measured more or less readily and precisely by agitating, circulating, and regulating the liquid at any temperature.

(4) The contact angles of Merck's paraffin-wax, melting at 58°C, against water were: the advancing angle, 114.5±0.8°, the receding angle, 102.0±0.8°, and the average angle, 108.1±0.8°. The average wetting tension was calculated to be -22.2 dynes/cm at 25°C.

(5) The hysteresis in contact angle of the paraffin in aqueous solutions of frothers was about 20° being comparable with that in case of pure water. The nature of hysteresis was discussed and the mean value of the cosines of the advancing and receding angles was adopted for use in further considerations.

(6) A new wetting isotherm was derived, which held good for the wetting of paraffin in solutions of pure as well as commercial frothers.

$$H\cos x - H_0\cos x_0 = F' = b'RT\ln(c/a' + 1),$$

where F' is the surface pressure in wetting, a' is the concentration coefficient and b' is the coefficient of wetting tension. The residuals between measured and calculated values of F' ranged from 0.08 to 1.7.

(7) The wetting isotherm was entirely similar in form to Szyszkovski's equation for water-air interface. By analogy, the wetting activity and the orientation of frothers at paraffin-water interface were considered. It was shown that the wetting activity and the orientation of frothers at paraffin-water interface was similar to those at water-air interface.

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