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Fundamental Studies on Interfacial Tensions in Flotation. I

Determination of Surface Tension with Data on Aqueous Solutions of Frothers*

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I. Introduction

The author has undertaken the following studies to supplement the fundamental flotation researches. The subject, studies on the interfacial tensions, has been selected because of the utmost importance of interfacial tensions as the fundamental quantities concerned with flotation process. As already pointed out, the accurate calculation or measurement of the absolute values of these tensions remains unsolved and the mechanism of flotation reactions is rather ambiguous.

For such complex problem as flotation mechanism, it is customary to simplify the problem by floating small amount of pure mineral with pure chemicals as flotation agents in a small flotation cell as Gaudin and others have done in their floatability studies. Thus we may evaluate more exactly the effect of variables than in commercial flotation operations in respect to the purity of mineral and flotation agents and may simplify operations by the reduction in amount of mineral and flotation agents and in size of the cell. However, the reduction in the area of interfaces and other unfavourable effects may result consequently. It seems that these important points have generally been overlooked and no efforts for provision have been made.

There may be at least three ways to overcome these difficulties, that is, (a) to raise the accuracy of the measurement, (b) to in-

crease the number of measurement and (c) to modify the system to be investigated to suit the nature of experiment. These points have been taken into account as fully as possible in the following studies. Thus, for example, the pure substances as paraffin, or glass as solid phase, conductivity water as liquid phase and the pure compounds as agents have been selected and used. The apparatus to be used have been newly developed or extensively improved to suit the purpose of the experiment.

II. Tensiometer

The tensiometer is a torsion balance of Du Nouey's type. The scale indicating the amount of torsion is divided into 1 degree.

The ring must be perfectly circular and in a perfect plane. As the ring is made of thin platinum wire, its shaping is not an easy matter. In this experiment the shaping tool of brass as shown in Fig. 1 is used with fair success.

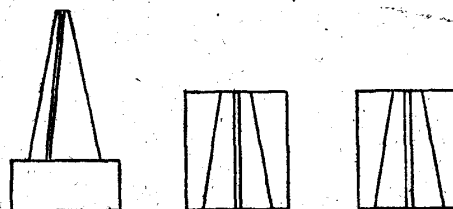


Fig. 1. Shaping tool for platinum ring.

To measure the diameter of the ring and of the wire, the measuring stage as used by Harkins and Jordan⁽¹⁾ and a micrometer

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microscope are used. The reading scale of the microscope is 20 mm in length and the distance down to 1/1,000 mm can be read by the vernier scale.

The micrometer microscope is calibrated by a stage micrometer of E. Leitz, Wetzlar, which is a photographed scale of 2 mm graduated into 200 parts, and used as a standard for petrographic microscope, as shown in Table 1.

Table 1. Calibration of the micrometer microscope.

Scale of the micrometer: $l = 2.00\text{mm}$.

No.	Graduation in mm		Length measured in mm $L_2 - E_1$	Correction factor $1/(L_2 - L_1)$
	L_1	L_2		
1	0.040	2.030	1.990	1.005
2	8.803	10.787	1.984	1.008
3	17.641	19.620	1.979	1.011
Average:				1.008

The celluloid disk of the measuring stage is graduated in 30 degrees in its periphery. Twelve measurements are made by turning the ring by 30 degrees with the celluloid disk. In every position of the ring four readings corresponding to L_1 , L_2 , L_3 and L_4 in Fig. 2 are taken and the diameter of the platinum wire $2r$ and that of the platinum ring $2R$ are calculated and average values are obtained as shown in Table 2.

$$2r = L_2 - L_1 \text{ and } L_4 - L_3.$$

$$2R = L_3 - L_1 \text{ and } L_4 - L_2.$$

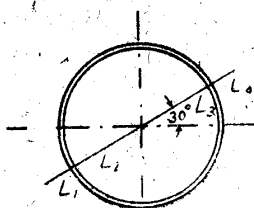


Fig. 2. Measurement of dimension of platinum ring.

The average values obtained are as follows:
The radius of the wire

$$r = 0.0157 \text{ cm},$$

the radius of the ring

$$R = 0.6351 \text{ cm},$$

and the circumference of the ring

$$2\pi r = 3.990 \text{ cm}.$$

Table 2. Measurement of the dimension of the platinum ring.

No.	Diam. of wire in mm		Diam. of ring in mm	
	$L_2 - L_1$	$L_4 - L_3$	$L_3 - L_1$	$L_4 - L_2$
1	0.3330	0.3365	12.6950	12.6985
2	0.3100	0.2850	12.6900	12.6650
3	0.3290	0.3015	12.7040	12.6765
4	0.3285	0.2950	12.7790	12.7455
5	0.3185	0.3035	12.7200	12.7050
6	0.3210	0.3135	12.6635	12.6560
7	0.3225	0.3195	12.6935	12.6905
8	0.3010	0.3150	12.6830	12.6970
9	0.3070	0.3180	12.6905	12.7015
10	0.2935	0.3220	12.7495	12.7780
11	0.3060	0.3195	12.7165	12.7300
12	0.3055	0.3205	12.6535	12.6685
Average:	0.3135		12.702	

The scale of the torsion balance is calibrated by the ordinary weights used for chemical balances. As there is no mark to indicate exactly the normal position of the beam, it is customary to make the beam lie just clear of the supporting arm. In this experiment the metal fitting as shown in Fig. 3 is attached to the support and the mark indicating the normal position of the beam are cut on the fitting and on the corresponding point of the beam.

Table 3. Calibration of the Du Nouey tensiometer.

$$M = 0.007235 a.$$

Angle of twist α°	Weight in g		Residual R
	M	M_c	
0.6	0.005	0.004	0.001
1.2	0.010	0.009	0.001
2.8	0.020	0.020	0.000
6.9	0.050	0.050	0.000
13.9	0.100	0.101	-0.001
27.7	0.200	0.200	0.000
41.5	0.300	0.300	0.000
55.1	0.400	0.399	0.001
69.2	0.500	0.501	-0.001
96.8	0.700	0.700	0.000
124.1	0.900	0.898	0.002
138.3	1.000	1.001	-0.001
166.2	12.00	1.202	-0.002
Average:			0.0008

The results of calibration are shown in

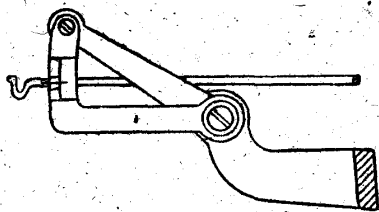


Fig. 3. Metal fitting for indicating zero point of Du Nouey's tensiometer.

Table 3. The relation between the weight M in g and the angle of twist a is expressed by the following equation:

$$M = 0.007235 a, \quad (1)$$

where the average residual is 0.0008 g.

III. Measuring Dish

Fig. 4 is the diagram of the measuring dish and circulating pump arranged in position. The dish is held in place on the platform of the tensiometer by four thin brass blades attached to the platform, the height of which can be adjusted within some distance by the screw attached to it. Both dish and pump are made of ordinary hard glass or "Terex" glass, made by the Tokyo Electric Co., as metal or other material may contaminate the liquid under test. In the following experiments those of "Terex" glass are exclusively used.

The dish is equipped with the inflow and overflow tube and the liquid level in it may be kept constant by feeding it with liquid through the circulating pump. It is stated that regulation of the temperature of liquid is difficult with the Du Nouey's tensiometer,

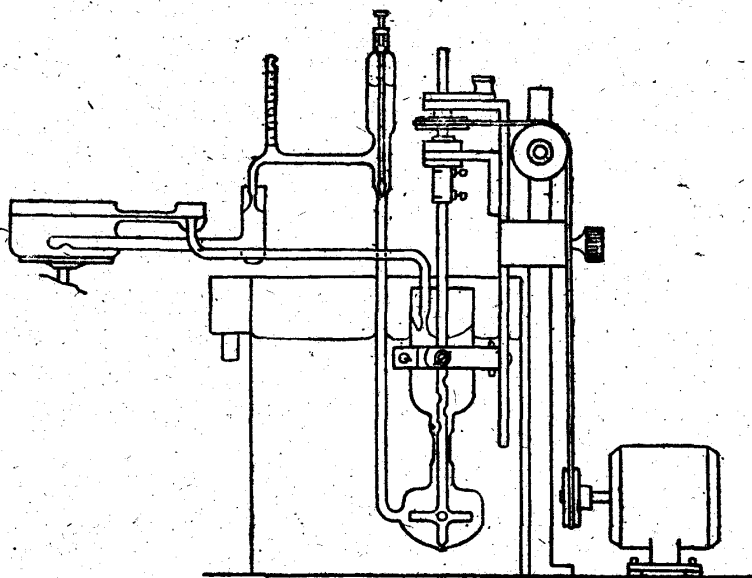


Fig. 4. Measuring dish and circulating pump.

but in the following experiments this is easily done by immersing the pump in a constant-temperature water bath. By feeding the dish with fresh liquid the measurement may always be done on fresh surface. It is of great advantage as compared with the method of cleaning liquid surface with a paraffined barrier as used by Langmuir and others⁽²⁾⁻⁽⁴⁾. For ordinary purposes it is sufficient not to make liquid flow out continuously but to circulate adequate quantity of it. There is still another advantage that solutions such as those of flotation agents may effectively be agitated by the pump.

The inside diameter 7 cm of the dish is selected after the recommendation of Harkins and Jordan⁽¹⁾, and its inside depth is designed to be 4 cm. The inside diameter of its inflow tube is 6 mm and that of its overflow tube is 8 mm.

IV. Circulating Pump

For feeding or circulating liquid the centrifugal glass pump of Luther's type⁽⁵⁾, modified by the author, is used. The shaft, 9 mm in diameter, is made of hollow tube and has the impeller, 45 mm in diameter, at its lower end. The impeller is composed of four horizontal hollow tubes, 4 mm in inside diameter, extending radially and communicating with the shaft. There are four elliptical holes, the major axis of which is about 10 mm, at about the middle height of the shaft.

The upper end of the shaft is covered by a short hollow brass cylinder and they are cemented together by Khotinsky cement. This is inserted in the socket at the lower end of the pulley shaft and is fixed in position by six screws attached to the socket so that its center line coincides with that of the pulley shaft. The upper part of the pulley shaft is inserted in a brass bearing and its lower part is supported by a ball bearing. Both bearings are attached to the pump stand.

The body of the pump is composed of three parts. The upper cylindrical part, about 4 cm in inside diameter and about 8 cm in depth, is for receiving liquid. The lower part, about 5 cm in both inside diameter and height, is the impeller chamber and at the

center of its bottom there is a depression, in which the tip of the end of shaft fits. The middle narrow part connects the receiving and impellar chambers and its inner surface has but little clearance between it and the surface of the shaft. The liquid in the receiving chamber can hardly flow into the impellar chamber through that clearance.

The impellar chamber has a side tube extending upwards. At the upper part of the latter there is the constriction for a needle valve, above which the tube becomes wide and constitutes the liquid reservoir, about 2 cm in diameter and about 9 cm in height. The screw cap of the needle valve fits in the upper narrower part of the reservoir. From the lower narrower part the branch tube extends horizontally and its end is bent vertically downwards and its mouth is narrowed to 3 mm in inside diameter. At above its bent there stands a simple flow meter graduated for 50 mm.

The body of the pump is fixed in position so that its center line coincides with that of the shaft by tightening its receiving chamber by the wide brass ring, the inner surface of which being covered with woolen cloth, attached to the pump stand by two screws lying at right angles with each other and adjustable in position.

The pulley attached to the shaft and that of an electric motor, of 50 watts and of revolutions from 1,400 to 1,700 per min, is connected by a thin rubber belt through two loose pulleys. The revolutions of the pump is

Table 4. Calibration of the flow meter of the centrifugal pump.

$$H = 12.5 V^2 - 41.8 V + 30.0.$$

Revolutions of the pump: 1,190/min.

Water flow in cc/sec V	Height of water column in mm		Residual R
	H	H_c	
2.29	0	0	0.0
2.52	5	4.2	0.8
2.79	10	10.9	-0.9
2.89	13	13.9	-0.9
3.24	26	26.1	-0.1
3.32	30	29.3	0.7
3.49	36	36.7	-0.7
3.64	44	43.9	0.1
Average:			0.5

about 1,190 per min.

On causing the impellar to rotate rapidly, liquid is sucked in at the inflow holes of the shaft and forced out through the ends of the impellar tubes and is made rise through the side tube. The needle valve regulates the rate of flow of liquid and the liquid reservoir acts to smooth down the fluctuation of the flow. Table 4 shows the relation between the quantity of flow and the height of the column of water read by the graduation in the flow meter. The relationship may be expressed by the following empirical formula:

$$H = 12.5V^2 - 41.8V + 30.0, \quad (2)$$

where H is the height of the water column in mm and V is the rate of the water flow in cc/sec. The average residual is 0.5 mm.

V. Constant-Temperature Water Bath

The inside dimension of the bath is 19 cm in length, 18 cm in width and 20.5 cm in depth. The larger sides and the bottom are made of brass sheet and the smaller sides are of glass plates. At the upper end of a brass side there is an overflow box which keeps the water level constant.

As heating element an insulated immersion heater, 30.5 ohm resistance at room temperature, is used and the current is controlled by means of an electro-magnetic relay, in conjunction with a thermo-regulator. The core of the magnet is 18×18 mm² in cross-section. The coil is wound by the enameled copper wire of 0.25 mm diameter and of 70.3 ohm resistance. The thermo-regulator is the ordinary toluene-mercury regulator of 5 cm diameter at the spiral part and of 18 cm length. It is of the temperature range of 0–80°C and of the sensitivity of $\pm 0.02^\circ\text{C}$.

The sparkings at the platinum-mercury contact of the regulator and at the platinum contact of the relay are prevented to some extent by inserting a paper block condenser of 1 microfarad capacity across each spark gap. To prevent the fouling of the platinum-mercury contact in the regulator the mercury is covered by a layer of glycerin⁽⁶⁾.

In the circuit of the regulator and the electromagnet a 16 candle-power tungsten lamp, of 42.5 ohm resistance at room temperature, is inserted in series. In the heater circuit two 120-watt gas-filled lamps, of 6.5

ohm resistance at room temperature, and a knife-switch, used for shortcircuiting the lamps if necessary, are inserted in parallel.

For the agitation of water a brass impellar, having four blades of 0.9 cm width and of 3 cm length, is rotated by the 1/32 h.p. motor capable of regulating its revolution from 80 to 6,000 per min by means of the friction disks.

The whole arrangement is satisfactorily operated by the alternating current supplied from the 100 volt main. The temperature of liquid in the measuring vessel is maintained constant within $26 \pm 1^\circ\text{C}$ except for special cases, as the control of temperature becomes difficult in summer owing to the rise of temperature, up to about 25°C , of the city water used for cooling.

VI. Method of Measurement

The measurement is done referring to some literature^{(7),(8)}. The points to which special attention has been paid have already been discussed in detail.

Prior to the measurement the platinum ring is first thoroughly cleaned with a hot sulphuric acid and dichromate mixture, washed with distilled water and heated for a moment in non-luminous Bunsen flame. It is stated that the ring may preferably be heated to red heat several seconds in gas flame. It is to be noted, however, that sometimes the ring happens to separate at welded joints at red heat. The contact angle of the platinum ring thus cleaned may be regarded as zero or nearly zero against pure water or aqueous solutions of frothers. This condition is requisite for the precise measurement of surface tension⁽¹⁾.

In the ordinary method of measurement the pointer of the scale is set at zero, the beam is adjusted to lie in its normal position, the platform with dish containing the liquid under test is raised until the liquid surface just touches the ring, and then the knob which twists the wire is turned slowly until the ring is suddenly torn from the surface of the liquid. In this way, however, the error corresponding to the angle by which the liquid surface is raised by the ring, may be introduced. In the following experiment the platform is lowered so as to keep the beam always in its normal position while the knob

is being turned^{(9),(10)}.

Both measuring dish and circulating pump are cleaned by a sulphuric acid and dichromate mixture, thoroughly washed with distilled water and used for experiments.

VII. Preparation of Pure Water

The water used for the experiment is prepared by distillation of ordinary distilled water once from alkaline permanganate and then from very dilute sulphuric acid⁽¹¹⁾.

As silver or tin has been difficult to obtain, the "Terex" tube is used as the condenser tube of the distillation apparatus.

The pure water thus prepared is used as soon as possible. If necessary it is kept in the Erlenmeyer's flask, made of Jena "Duran" glass, equipped with a zigzag outflow tube and a soda-lime tube⁽¹²⁾.

VIII. Effect of the Rise of the Beam from the Zero Point During Measurement

As a preliminary test it is examined to what degree the zero point affects the surface tension of pure water. Table 5 shows the data obtained by two methods of measurement, the one is the ordinary method and the other is the method in which the beam is adjusted to the zero point during measurement as already explained. The error introduced by the ordinary method for pure water amounts to 4.5° in angle or 0.033 g in weight. It is indeed of a considerable value and can not be neglected.

Table 5. Effect of zero point on the surface tension of pure water.

Method of measurement	Angle of twist α°	Weight in g M	Temp. $t^\circ\text{C}$
Ordinary method...	87.2	0.631	17.3
Method of adjusting zero point.....	82.7	0.598	17.3
Difference:	4.5	0.033	

IX. Surface Tension of Pure Water

Table 6 shows the results of measurement of the surface tension of pure water. The average angle is 81.9° when the average water flow is 3.21 cc/sec and the average temperature of water is 26.2°C . There is not much difference in the angles obtained

within the limits of change of the flow and temperature of water. Hence any appreciable error may not be introduced in the value of surface tension calculated from the average values thus obtained.

Table 6. Measurement of the surface tension of pure water.

Date	Angle of twist α°	Water flow in cc/sec V	Temp. $t^\circ\text{C}$
17 Mar., 1943	82.0	3.25	26.6
	81.9	3.25	26.6
29 Mar., 1943	82.1	3.17	26.2
	81.8	3.25	26.3
30 Mar., 1943	82.0	3.17	26.3
	81.8	3.11	26.4
31 Mar., 1943	81.8	3.14	25.4
	81.9	3.20	25.6
1 Apr., 1943	81.8	3.28	26.4
	81.5	3.25	26.5
Average:	81.9	3.21	26.2

According to Harkins and Jordan⁽¹⁾ the surface tension may be calculated by the following formula:

$$H = Mg/4\pi R \cdot F, \quad (3)$$

where H = surface tension in dynes per cm.

M = maximum weight of liquid raised above the free surface of the liquid in g.

g = acceleration due to gravity in cm. per sec.² *.

R = radius of the ring measured from the center of the ring to the center of the wire in cm.

F = correction factor.

By substituting the measured values in the above formula we obtain:

$$H = \frac{0.007235 \times 81.9 \times 980.1}{4\pi \times 0.6351} \times F = 72.77 F.$$

The value of F is obtained from the table given by Harkins and Jordan⁽¹⁾.

$V = M/(D-d)$ = the maximum volume of liquid raised above the free surface of the liquid in cm³.

D = density of the liquid in g/cm³ ⁽¹⁴⁾.

d = density of the air saturated with vapour of the liquid in g/cm³ ⁽¹⁴⁾.

* The value of g in Sendai was measured to be 980.1 cm/sec² ⁽¹⁵⁾.

By utilizing the measured values of these quantities, the ratio of the cube of the radius of the ring to the volume of the liquid

$$R^3/V = \frac{(0.6351)^3 \times (0.997 - 0.001)}{0.007235 \times 81.9} = 0.431$$

and the ratio of the radius of the ring to the radius of the wire

$$R/r = \frac{0.6351}{0.0157} = 40.5$$

are obtained. From the table the value of F is found to be

$$F = 0.987.$$

Hence the measured surface tension of water at 26.2° C.

$$H = 72.77 \times 0.987 = 71.82.$$

The value of the surface tension of water at 26.2° C obtained by interpolation from the International Critical Tables, is 71.79 dynes/cm ⁽¹⁶⁾. The difference between the value of the surface tension measured and that obtained from the Critical Tables is but 0.03 dyne/cm.

It is to be satisfied with the fact that the absolute value of surface tension can be accurately measured by a simple Du Nouey's tensiometer modified by the author with adequate precautions.

X. Frothers

As frothers amyl alcohol, cresol and terpineol, most widely used in laboratories⁽¹⁹⁾, solid camphor as a substitute of camphor oil⁽¹⁷⁾, samples of citronella oil treated with sulphuric acid or with oxidation⁽¹⁸⁾, and two commercial frothers of Japanese made and two of American made are used.

The boiling point of pure agents measured by Pawlewski's method⁽¹⁹⁾ are 129.4–131.9° C (760 mm.) for amyl alcohol, 199.3–202.3° C (760 mm.) for cresol and 218.2–220.2° C (760 mm.) for terpineol. The melting point of camphor is measured to be 178–179° C. The solubility of camphor in water at the ordinary temperature is 1 in 598^{(20)*}.

The sample of citronella oil treated with

* According to literatures the boiling point of isoamyl alcohol is 132.05° C⁽¹⁵⁾, that of meta cresol 202.2° C⁽¹⁵⁾, and that of α -terpineol 219° C⁽²¹⁾, 217–218° C⁽²²⁾ or 218.8–219.4° C (752 mm.)⁽²³⁾ and the melting point of d -camphor is 178–179° C⁽²²⁾.

sulphuric acid was prepared by the Takasago Chemical Industrial Works, Tokyo, and that treated with oxidation was prepared by the Japan Perfumery and Chemicals Co., Kobe.

As commercial frothers No. 5 flotation oil of the Takasago Chemical Industrial Works, No. 1 flotation oil of the Shiono Chemical Industrial Works, Osaka, Yarmor "F" S. D. pine oil of the Hercules Powder Co., Wilmington, Delaware, and Frother B-22 of E. I. du Pont de Nemours & Co., Wilmington, Delaware, are used.

XI. Preparation of Aqueous Solutions of Frothers

About 220 cc of water is poured into a 250 cc measuring flask and its weight is indirectly weighed by a balance of 1 kg capacity and 50 mg sensitivity. Then the measured amount of frother is added into the flask and mixed thoroughly with water.

Frothers are in most cases added by a 1 cc syringe, to which a glass capillary is fused in place of a steel needle to avoid any contamination. On few occasions when the weight of a drop from the capillary is too large the syringe with a steel needle is used.

As the weight of a drop of frother, it is usual to adopt the average weight of 10 or more drops of frother accurately measured previously. This method seems to be somewhat inaccurate for the present purpose. In this experiment the weight of the syringe inserted in a glass cap as shown in Fig. 5 is accurately weighed by a chemical balance before and after dropping the liquid.

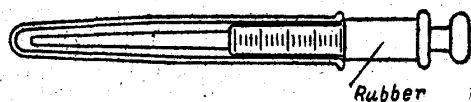


Fig. 5. Glass cap for weighing syringe.

For example the accuracy of the ordinary method is shown in Table 7. In the test the syringe is clamped firmly and vertically by a stand. Special attention is paid so that the drop of liquid is not pushed out by the piston but it drops down freely by its own weight. Drops of liquid are received in a watch-glass and covered by another and weighed. The results show that there is about 1% error in weight in summer and about 2% in winter.

The large error in winter seems to be due to the increase of the viscosity of liquid by the depression of temperature.

Table 7. Weight of a drop of terpineol delivered by a syringe.

	4 Aug., 1942	7 Mar., 1943
Room temperature in °C ...	31.2	6.9
Weight of 10 drops in g:		
Measurement No. 1.....	0.0938	0.1228
Measurement No. 2.....	0.0921	0.1188
Average	0.0930	0.1208
Error:		
in g	0.0009	0.002
in %	0.97	1.7

XII. Surface Tension of Aqueous Solutions of Frothers

As the surface tension of aqueous solutions of isoamyl alcohol, α -terpineol and *d*-camphor are already given in literature, only that of meta cresol and of commercial frothers are measured by Du Nouey's tensiometer described previously.

Tables 8-17 show the values of the surface tension of solutions of isoamyl alcohol*, of meta cresol, of α -terpineol**, of *d*-camphor***, of sulphuric acid treated and oxidized citronella oils and of commercial frothers.

* As to aqueous solutions of isoamyl alcohol there are works of B. von Szyszkowski⁽²⁴⁾, W. Seith⁽²⁵⁾, P. R. Edwards⁽²⁶⁾, and H. Freundlich and A. Schnell⁽²⁷⁾. Here the data given by Freundlich and Schnell are used as they are newer and seems to be more accurate than others.

** As regards aqueous solutions of α -terpineol there are works of C. C. DeWitt and R. F. Makens⁽²⁸⁾, and A. M. Gaudin, H. Glover, M. S. Hansen and C. W. Orr⁽²⁹⁾. As the latter workers' paper can not be referred to, DeWitt and Makens' data are made use of. However, instead of the value of $H_{av.}$, 31.82 dynes/cm, at the concentration of 0.011095 mol/1,000 g H₂O, the value 41.82 is used, as the former seems to be misprinted.

*** Of the works of DeWitt and Makens⁽²⁸⁾, and Edwards⁽²⁶⁾ regarding aqueous solutions of *d*-camphor, the data given by the former are used.

Table 8. Surface tension of aqueous solutions of isoamyl alcohol. (After the data of Freundlich and Schnell)

$t: 18^{\circ}\text{C}$, $a: 0.0120$, $b: 0.186$.

Concn. in mol/kg H ₂ O c	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
		F	F_c	
0.00000	72.26	0.0	—	—
0.01281	63.2	9.1	9.7	-0.6
0.02562	57.1	15.2	15.3	-0.1
0.05125	49.6	22.7	22.3	0.4
Average:				0.4

Table 9. Surface tension of aqueous solutions of α -terpineol. (After the data of De Witt and Makens)

$t: 25^{\circ}\text{C}$, $a: 0.0007043$, $b: 0.1513$.

Concn. in mol/kg H ₂ O c	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
		F	F_c	
0.0000000	72.13	0.0	—	—
0.0002245	67.63	4.5	3.02	1.48
0.001500	60.15	11.98	12.44	-0.46
0.002218	57.08	15.05	15.52	-0.47
0.003995	51.86	20.27	20.70	-0.43
0.006704	47.02	25.11	25.67	-0.56
0.011095	41.82*	30.31	30.75	-0.44
0.0136	38.38	33.75	32.84	0.91
Average:				0.68

* The value 31.82 given in the original paper may be misprinted.

Table 10. Surface tension of aqueous solutions of d -camphor. (After the data of De Witt and Makens)

$t: 25^{\circ}\text{C}$, $a: 0.001751$, $b: 0.1456$.

Concn. in mol/kg H ₂ O c	Surface tension in dynes/cm H	Surface Pressure in dynes/cm		Residual R
		F	F_c	
0.000000	72.13	0.00	—	—
0.001009	67.43	4.70	4.78	-0.08
0.001540	65.34	6.79	6.62	0.17
0.005083	57.21	14.92	14.29	0.63
0.007250	54.07	18.06	17.18	0.88
0.012	52.10	20.03	21.63	-1.60
Average:				0.67

Table 11. Surface tension of aqueous solutions of meta cresol.

$t: 27.1^{\circ}\text{C}$, $V: 3.22$ cc/sec,
 $a: 0.02401$, $b: 0.2112$.

Concn. in mol/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
			F	F_c	
0.0000000	82.0	71.82	0.00	—	—
0.0004987	81.3	71.21	0.61	0.31	0.30
0.002494	80.3	70.55	1.27	1.50	-0.23
0.01121	77.9	67.89	3.93	5.81	-1.88
0.04776	64.3	54.78	17.04	16.61	0.43
0.09740	55.3	46.37	25.45	24.58	0.87
0.1493	49.8	41.32	30.50	29.98	0.52
Average:					0.70

Table 12. Surface tension of aqueous solutions of citronella oil treated with sulphuric acid.

$t: 28.8^{\circ}\text{C}$, $V: 3.22$ cc/sec,
 $a: 0.02085$, $b: 0.1334$.

Concn. in g/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
			F	F_c	
0.00000	83.2	71.2	0.0	—	—
0.04654	75.6	63.7	7.5	7.6	-0.1
0.09309	66.1	55.1	16.1	14.2	1.9
0.1862	60.9	50.2	21.0	20.8	0.2
0.3750	56.0	45.7	25.5	27.5	-2.0
Average:					1.1

Table 13. Surface tension of aqueous solutions of oxidized citronella oil.

$t: 28.4^{\circ}\text{C}$, $V: 3.26$ cc/sec,
 $a: 0.06284$, $b: 0.1013$.

Concn. in g/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
			F	F_c	
0.00000	83.2	71.2	0.0	—	—
0.04827	79.4	67.6	3.6	4.1	-0.5
0.09975	77.1	65.3	5.9	6.9	-1.0
0.2046	70.7	59.3	11.9	10.4	1.5
Average:					1.0

Table 14. Surface tension of aqueous solutions of No. 5 Flotation Oil of the Takasago Chemical Industrial Works.

t : 27.5°C, V : 3.25 cc/sec,
 a : 0.147, b : 0.142.

Concn. in g/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
			F	F_c	
0.00000	82.0	71.9	0.0	—	—
0.04842	80.0	69.9	2.0	2.9	-0.9
0.09921	78.8	68.8	3.1	5.2	-2.1
0.2003	74.3	64.4	7.5	8.7	-1.2
0.4059	65.4	55.8	16.1	13.5	2.6
0.8208	60.4	51.1	20.8	19.2	1.6
Average:					1.7

Table 15. Surface tension of aqueous solutions of No. 1 Flotation Oil of the Shiono Chemical Industrial Works.

t : 26.5°C, V : 3.25 cc/sec,
 a : 4.10, b : 3.12.

Concn. in g/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
			F	F_c	
0.00000	81.9	71.7	0.0	—	—
0.04756	79.9	69.8	1.9	2.6	-0.7
0.09326	79.1	68.9	2.8	5.0	-2.2
0.1921	70.0	60.3	11.4	10.8	0.6
0.3888	58.5	49.4	22.3	20.3	2.0
Average:					1.4

Table 16. Surface tension of aqueous solutions of Yarmor "F" S. D. Pine Oil of the Hercules Powder Co.

t : 25.7°C, V : 3.23 cc/sec,
 a : 0.2460, b : 0.1898.

Concn. in g/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface tension in dynes/cm		Residual R
			F	F_c	
0.00000	81.9	71.69	0	—	—
0.05091	80.1	69.94	1.75	2.56	-0.81
0.1037	77.8	67.80	3.89	4.79	-0.90
0.2074	73.2	63.26	8.43	8.32	0.11
0.4092	67.0	57.32	14.37	13.33	1.04
0.8617	59.9	50.66	21.03	20.47	0.56
Average:					0.68

Table 17. Surface tension of aqueous solutions of B-22 Frother of the E. I. du Pont de Nemours & Co.

t : 26.4°C, V : 3.25 cc/sec,
 a : 0.5464, b : 0.1616.

Concn. in g/kg H ₂ O c	Angle of twist A°_{av}	Surface tension in dynes/cm H	Surface pressure in dynes/cm		Residual R
			F	F_c	
0.00000	81.65	71.51	0.0	—	—
0.01432	81.5	71.39	0.12	0.30	-0.18
0.02863	81.4	71.30	0.21	0.59	-0.38
0.05680	81.0	70.73	0.78	1.14	-0.36
0.1011	80.6	70.38	1.13	1.96	-0.83
0.1833	79.0	68.85	2.66	3.51	-0.85
0.3436	76.2	66.20	5.31	5.64	-0.33
0.6599	72.1	62.19	9.32	9.15	0.17
1.311	65.8	56.11	15.40	14.14	1.26
2.601	59.6	50.40	21.11	20.23	0.88
4.959	52.9	44.17	27.34	26.70	0.64
Average:					0.59

XIII. Surface Tension-Concentration Curves

Duclaux⁽³⁰⁾ carried out a series of experiments on the surface tension of mixtures of the homologous series of alcohols and fatty acids with water in varying proportions and proposed the following formula to express the surface tension-concentration curves:

$$H = k(e^c - 1), \quad (4)$$

where H being the surface tension and c the percentage composition of the mixture by weight.

For the surface tension-concentration curve for acetic acid in water Milner⁽³¹⁾ used the following formula:

$$(H_0 - H)/H_0 = a + b \ln c, \quad (5)$$

where H_0 being the surface tension of pure water.

For isobutylic acid Szyszkowski⁽²⁴⁾ found that through a wide range of concentration, the ratio y of the capillary elevation h of the solution to that h_0 of water could be expressed by the equation

$$y = 1 - b \ln(c/a + 1), \quad (6)$$

where c in mol/l and a being the capillary constant. For valeric or caproic acid the agreement between observed and calculated values is not quite so satisfactory.

Freundlich⁽³²⁾ proposed the following parabolic formula:

$$(H_0 - H)/H_0 = s \cdot c^{1/n}, \quad (7)$$

by which the calculation was done with certain approximation.

Butler and Ockrent⁽³³⁾ presented a modified form of Szyszkowski's equation for highly active solutes.

Bennett⁽³⁴⁾ found that the Freundlich equation held over a sufficiently wide range of concentrations of methyl, ethyl and propyl alcohols and of acetic acid and acetone in water.

Korzheniovskii⁽³⁵⁾ derived the following equation:

$$(H_0 - H)/(H - H_b) = K(c_b/c_0)^n, \quad (8)$$

in which H_0 is the surface tension for saturated solution, c_b is the concentration of solute and c_0 is that of solvent.

Dole⁽³⁶⁾ introduced a general equation for surface tension versus concentration applicable for strong electrolytes, non-electrolytes and fatty acids equally well. For sucrose solution it reduces to

$$H - H_0 = RTkc. \quad (9)$$

For the lower molecular weight fatty acids, it reduces to Szyszkowski's equation.

After critical study of the above works, it is concluded that the Szyszkowski equation is the most adequate one among these equations for the present investigation.

The surface tension-concentration relations in the measurements given in Tables 8-17 are calculated by Szyszkowski's equation. The calculated values of the surface pressure are given in the tables. It is shown in the tables that the measured and calculated values of surface tension coincide generally well.

The average residuals of surface pressures, arranged in increasing order, are 0.4 for isoamyl alcohol, 0.6 for Du Pont's B-22 frother, 0.7 for *d*-camphor, α -terpineol, Yarmor "F" S. D. pine oil and meta cresol, 1.0 for oxidized citronella oil, 1.1 for sulphuric acid-treated citronella oil, 1.4 for Shiono's No. 1 flotation oil and 1.7 for Takasago's No. 5 flotation oil.

Summary

(1) The determination of surface tension by the ring method is studied in detail.

(2) A metal fitting for indicating the normal position of the beam of the tensio-

meter is devised and the scale is calibrated.

(3) The measuring dish and the circulating pump, made of glass and capable of agitating and feeding fresh liquid at any constant temperature, are developed. The constant-temperature water bath for the circulating pump is described.

(4) The error due to the rise of the beam from the zero point during measurement of the surface tension of pure water prepared by distillation from alkaline permanganate and from sulphuric acid amounts to 4.5° in angle or 0.033 g in weight.

(5) It is shown that the accurate value of the surface tension of pure water of 71.82 dynes/cm at 26.2°C, differing by only 0.03 dyne/cm from the standard value given in the International Critical Tables, can be obtained by the Du Nouey's tensiometer modified by the author with adequate precautions.

(6) The syringe fused with a glass capillary is used for the preparation of aqueous solutions of frothers and it is accurately weighed by inserting it in a glass cap. The error of the ordinary method using the average weight of 10 or more drops as the weight of one drop of frother, is found to be about 1% in summer and 2% in winter for terpineol.

(7) Various existing equations expressing the relation between the surface tension and concentration of solutions are critically studied.

(8) The measured values of the surface tension of aqueous solutions of pure as well as commercial frothers are in good agreement with the values calculated by Szyszkowski's equation.

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