[CONTRIBUTION FROM THE PEDIATRIC RESEARCH LABORATORY OF BROOKLYN JEWISH HOSPITAL]

A Device for the Determination of the Surface Tension of Small Amounts of Liquid

BY SAMUEL NATELSON AND AARON H. PEARL

The use of surface tension measurements as an aid in studying biological processes has been hindered partly by the lack of a practical device for the convenient, accurate and rapid determination of the surface tension of small amounts of liquid.

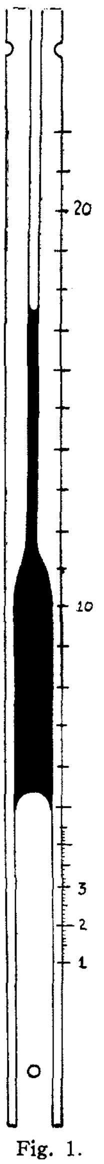

Fig. 1.

This paper deals with a method, practical for the determination of the surface tension of less than 0.1 cc. of liquid. The instrument used consists of a fine capillary tube joined to a tube of wider bore. The entire tube is engine divided to read to millimeters.

The theory underlying the applicability of this tube depends upon the observations of Mouquin and Natelson[1] during the study of equilibria existing in conical capillaries. At equilibrium, the effective force upward is the tension of the liquid in the narrow tube. This is balanced by the hydrostatic pressure of the column of liquid and the tension of the liquid downward in the wider tube. The forces acting in this tube are independent of the shape of the joint. The formula suggested for tubes of conical bore (1) applies here.

$$S = \frac{hdgRr}{2(R - r)} \qquad \text{(I)}$$

in which S = surface tension, R = radius of large bore, r = radius of small bore, h = height, d = density and g = acceleration of gravity.

A direct method for the derivation of Equation I is to equate the force per unit area upward to the force per unit area downward, *viz.*

$$\frac{2rS\cos\Theta_r}{\pi r^2} = \frac{2RS\cos\Theta_R}{\pi R^2} + hdg$$

Solving for S

$$S = \frac{hdgRr}{2(R\cos\Theta_r - r\cos\Theta_R)} \qquad \text{(II)}$$

Equation II is a general equation for the rise of a liquid into a capillary when the counterbalancing pull of the liquid in the container is considered. Equation II may be reduced to the usual equation for capillary rise when R becomes infinitely large as compared with r. Equation II then becomes:

$$S = \frac{hdgRr}{2R\cos\Theta_r} = {}^1/_2\,\frac{hdgr}{\cos\Theta_r}$$

In practice, Equation I is used for the calculation of the surface tension. Measurements may be made as follows, using the same tube but varying the means by which the pressure is applied to keep the liquid stationary.

Method I.—The tube is suspended perpendicularly and the height is read directly.

$$S = hd\frac{gRr}{2(R - r)} = hdK_1 \qquad \text{(III)}$$

Method II.—The tube is held at some fixed angle and the length of the column is read. This has the effect of magnifying the reading and decreasing the error in the measurement of the length. This change in length with the angle follows the usual sine curve. It is apparent that slight deviation from the 90° angle has no serious effect on the height for at this point the flat part of the sine curve allows for slight deviation from the 90° angle without appreciable change in height. Substituting for h in Equation III, $h = l \sin a$, Equation III becomes

$$S = l \sin adK_1 \qquad \text{(IV)}$$

The volume of the liquid in the narrow capillary is small in comparison with the volume of the liquid in the large capillary. As the tube is turned, therefore, the lower meniscus remains almost motionless. If the liquid is drawn up to a decided marking in the wider tube and then inverted, the angle may be varied to bring the meniscus in the narrow tube to a previously decided marking. The length is always constant and the angle varies for different liquids. The tube needs in this case only two markings. Since (l) is constant, Equation V may be reduced to

$$S = \sin adK_2$$

Method III.—To avoid the necessity for the measurement of density, the tube may be placed horizontally. The surface tension then becomes a direct function of the pressure necessary to keep the liquid stationary in both tubes, when the pressure is applied at the narrow end. The direct relationship between pressure and surface tension

---

(1) H. Mouquin and S. Natelson, *Mikrochemie*, **13**, 293 (1932–1933).

is illustrated in the Mouquin–Natelson straight line curve[2] for pressure against surface tension in a tube of similar nature. This has been recently confirmed[3]

$$S = p\frac{Rr}{2(R - r)} = pK_3$$

The lag which is observed in establishing equilibrium varies with the viscosity of the liquid studied. The pressure readings may be increased by driving the liquid to the end of the wider tube and measuring the pressure necessary to flatten the meniscus at the end of the tube. The difficulties in reading the end-point and the small additional pressure obtained make this method less valuable.[4]

For absolute determinations the constant in all cases may be easily determined by measuring the radii and substituting in the formulas in each case. For relative determinations, a liquid of known surface tension may be used to determine each of the above constants for the tube.

Technique

Choice of Tubes.—The wider tube should be chosen so that its bore is not wide enough to allow for slippage down the sides, but sufficiently wide so as to allow for a reasonable length of column. In order to determine the effect its radius (R) would have on the value of the constant $Rr/R - r$ for a particular tube, R was plotted against the value of this expression for a series of values of r.

It is apparent that where r is small R can be varied widely, the value of the expression remaining practically constant. From the curve it can be seen that if the value for R is outside the rapidly changing range of the curve, slight variation in the diameter of the wider tube has no serious effect on the rise for a given narrow tube. The length is determined, mainly, by the diameter of the narrow tube and the latter should be chosen to give a height, for the particular liquids to be studied, where the error in reading would be less than 1%. If too narrow a tube be chosen, a longer time is needed for equilibrium to be established. For liquids of high viscosity, a tube of at least 0.3 mm. diameter ($2r$) should be employed. For the usual pure liquids, a diameter ($2r$) of 0.2 to 0.3 mm. will give a good height with rapidity in coming to equilibrium. A wider tube may be chosen, and the tube held at 30° to double the length. For biological fluids where the surface tension is high, relative to organic liquids, but where the viscosity is increased, a diameter ($2r$) of 0.3 to 0.4 mm. is used to best advantage.

The radii of the tubes were determined accurately by drawing up a column of mercury into each tube, measuring the length of the columns by means of the scale on the tube or with the aid of calipers and weighing the mercury. No error in the uniformity of the radii over the relatively short lengths needed was observed in the tubes obtainable (Table IV). The volume of the joint was determined by weighing mercury, extended into both tubes and subtracting the weights in each tube to within a half centimeter on each side of the joint. This volume was useful in determining the density of liquids when small amounts were obtainable. The tube was tared empty and then weighed with the liquid suspended in it as for a surface tension determination.

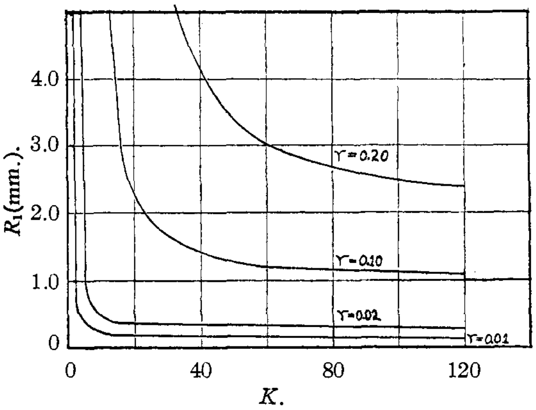

Fig. 2.—$K = Rr/R - r$.

Procedure and Results.—The fine capillary was touched to the liquid to be determined, and drawn up to a length slightly longer than desired, by means of an attached rubber tube. The liquid was allowed to run out freely, inverting the tube when a sufficient length was reached. On inverting, the upper meniscus should be well in the fine capillary tube and the lower meniscus, a few centimeters below the seal to ensure its being in the uniform part of the tube. The amount of liquid used should not produce a column which is longer, in the wider tube, than can be supported by the difference in radii of the tube. The column automatically adjusts itself to read the same length for the same liquid (Table III). The

---

(2) H. Mouquin and S. Natelson, *J. Phys. Chem.*, **35**, 1931 (1931).

(3) A. Achmatov, *Kolloid-Z.*, **66**, 266–270 (1934).

(4) Kiplinger, THIS JOURNAL, **42**, 472 (1920); Ferguson, *Proc. Phys. Soc. London*, **36**, 37–44 (1923).

liquid is made to run back and forth past the point of equilibrium and then allowed to come to equilibrium from above and from below. The rate of rise or fall of the liquid in the narrow capillary is a function of surface tension, density and viscosity. Since h is constantly changing as equilibrium is approached, the driving force is constantly diminishing. Close to the point of equilibrium the rate of fall or rise becomes extremely slow, especially for viscous liquids. The readings from above and below, therefore, usually differ by a small amount. This difference can be as great as 0.5 cm. after five minutes in the case of viscous liquids. For most liquids encountered, one to three minutes is sufficient time for the height to come to equilibrium, within the accuracy of reading. For biological fluids about six to ten minutes was allowed for equilibrium to be established. The tube is suspended to ensure perpendicularity and the length is read by means of the scale on the tube. When the tube is to be held perpendicularly the over-all length need not be more than about 15 cm.

For determinations at constant temperatures, the wider tube is bent around so that the whole can be immersed in a thermostat.

Table I lists results obtained on several liquids. This table includes results obtained by keeping the tube perpendicular, measuring the pressure necessary to keep the liquid motionless in the tube when held horizontally, using the same pressure gage as described in an earlier paper[2] and comparing these results with the Du Nouy tensimeter.

TABLE I

Room temp., 26°, $R = 0.097$, $r = 0.015$, $K_1 = 8.69$, $K_3 = 0.00887$.

	Tube perpendicular (K_1)			Tube horizontal (K_3)		Du Nouy ring
Liquid	d	h, cm.	S, dynes/cm.	Pressure dynes/sq. cm.	S, dynes/cm.	S, dynes/cm.
Water	0.997	8.31	72.1	8149	72.9	72.2
Ethyl alcohol	.785	3.15	21.5	2406	21.6	21.8
Acetone	.790	3.22	22.2	2608	23.2	23.6
Benzene	.872	3.65	27.7	3114	27.9	28.3
Toluene	.861	3.60	27.0	3053	27.3	27.3
Methyl alcohol	.792	3.20	22.0	2421	21.9	22.1
Chloroform	1.498	2.05[a]	26.8	2973	26.6	27.0
Carbon tetrachloride	1.583	1.92[b]	26.2	2932	26.2	26.8
Ether	0.714	2.68	16.6	1772	15.9	16.7
Amyl alcohol (n)	.815	3.45	24.4	2629	23.7	24.4

[a] Held at 30° angle, $l = 4.10$. [b] Held at 30° angle, $l = 3.83$.

The surface tension was determined for methyl alcohol at various angles noting the height and the angle.

TABLE II

Absolute methyl alcohol, 26°, $R = 0.097$ cm., $r = 0.015$ cm.

Angle °	Length of column	h, cm.	Surface tension dynes/cm.
10	18.93	3.22	22.2
15	12.54	3.26	22.4
20	9.51	3.23	22.2
30	6.49	3.25	22.3
35	5.66	3.23	22.1
45	4.55	3.23	22.2
55	3.95	3.23	22.2
75	3.33	3.23	22.2
85	3.28	3.25	22.3
90	3.22	3.22	22.2

To observe what effect position of the liquid in the tube has on the reading or whether the volume of the liquid used will affect the results, readings were taken for several liquids using different amounts of liquid. It was observed that no serious variation is obtained due to the amount of liquid used. The following table (III) for water is representative of the readings obtained.

TABLE III

Water, 26°, $R = 0.097$ cm., $r = 0.015$ cm., $K_1 = 8.69$.

Reading in wider tubes	h, cm.	Surface tension, dynes/cm.
9.40	8.30	71.9
9.91	8.33	72.2
10.01	8.32	72.2
10.20	8.32	72.2
11.05	8.29	71.7
12.11	8.32	72.2
13.60	8.30	71.9
13.79	8.31	72.1

To test the applicability of the instrument for the determination of the surface tension of biological fluids, the following table (IV) lists a few representative results on such liquids. The tube was held perpendicularly. No interpretation is made of the results obtained.

TABLE IV

Room temp. 26°, $R = 0.097$, $r = 0.015$, $K_1 = 8.69$.

Biological fluid	Diagnosis	Density	h, cm.	S, dynes/cm.[a]
Cerebro-spinal	Normal	1.006	7.91	69.2
Cerebro-spinal	Normal	1.007	7.52	65.9
Cerebro-spinal	Normal	1.007	7.59	66.4
Cerebro-spinal	Normal	1.006	7.65	67.0
Blood serum[b]	Acute hepatitis	1.027	6.45	57.7
Blood serum[c]	Cancer of stomach	1.024	6.65	59.2
Blood serum	Normal	1.029	6.54	58.5
Urine	Normal	1.028	6.55	58.6
Urine	Normal	1.026	6.65	59.3
Urine	Normal	1.026	6.54	58.4

[a] Because of the viscosity of these liquids, the point of equilibrium is uncertain and the error is as great as 5% in some cases. [b] Blood chemistry normal but Icterus index high. [c] Blood chemistry normal.

Acknowledgment.—The authors are indebted to Dr. B. Kramer and A. E. Sobel for their valuable suggestions and criticism in preparing this manuscript, and to Dr. H. Gruber for supplying some of the biological fluids tested.

Summary

The surface tension of small amounts of liquid is determined by the height attained in a calibrated tube consisting of a narrow capillary fused to a wider one. This method is as accurate as, and subject to most of the limitations of, the usual capillary rise method.

BROOKLYN, N. Y. RECEIVED APRIL 22, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Cryoscopic Investigation of Anomalies in the Behavior of Ethylene Chloride

BY HUGO HUETTIG, JR., AND CHARLES P. SMYTH

The abnormally high value found for the dipole moment of ethylene chloride in benzene as compared to its value in other solvents has been attributed to the presence of a very strong field of force immediately surrounding the benzene molecule or to the actual linking of the solute and solvent molecules to form a complex.[1,2,3,4,5,6] Anomalous dispersion found in solutions of ethylene chloride in ether at low temperatures was regarded as indicating the formation of an intermolecular compound of ethylene chloride and ether, which received support from the high apparent moment calculated for ethylene chloride with an equimolecular quantity of ether in solution in carbon tetrachloride.[5] In view of the importance of ethylene chloride as providing a means of studying intramolecular potential energy, it has seemed of interest to investigate these solutions by freezing point determinations.

Purification of Materials

Ethylene Chloride.—Material from the Eastman Kodak Company was washed with very dilute sodium hydroxide, dried over calcium chloride and fractionally distilled; b. p. 83.5°.

Benzene.—Thiophene-free material was washed with concentrated sulfuric acid, dried over sodium and fractionally distilled; b. p. 80.2°.

Ethyl Ether.—U. S. P. grade material was treated with acid permanganate solution, washed with sodium hydroxide in a saturated sodium chloride solution, dried over calcium chloride and fractionally distilled; b. p. 35.1°.

Experimental Procedure

The freezing points of the solutions were measured in a Pyrex tube 30 cm. long and 2.2 cm. in diameter fitted with a stirrer and surrounded by an air jacket formed by a second tube 3.2 cm. in diameter, which dipped into a Dewar tube containing, in the case of the benzene solutions, an acetone–carbon dioxide slush and, for the ether solu-

TABLE I

FREEZING POINT DATA

Mol. % ethylene chloride	Freezing point, °K.	Eutectic arrest, °K.
	Ethylene Chloride–Benzene	
0.0	278.5	
10.3	271.2	
17.2	266.2	
27.4	258.3	218.9
39.8	247.6	
50.8	236.5	
61.7	223.9	
67.3	218.9	218.9
77.6	224.5	
89.5	232.0	218.9
100.0	237.3	
	Ethylene Chloride–Ethyl Ether	
0.0	149.9	
	156.9	
2.0	149.3	149.1
3.0	149.1	149.1
4.7	149.9	149.1
	151.7	149.1
6.1	151.6	149.0
	155.6	149.0
9.7	154.7	
	161.0	
11.4	157.9	149.1
	162.8	149.1
13.4	164.2	
16.4	166.9	149.2
21.5	168.5	149.0
25.0	169.4	169.4
29.3	173.3	169.3
31.8	178.2	169.5
32.8	180.9	
47.2	200.2	
65.4	217.9	
76.6	224.4	
90.6	232.2	
100.0	237.3	

---

(1) Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).

(2) Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

(3) Van Arkel and Snoek, *Z. physik. Chem.*, **B18**, 159 (1932).

(4) Müller, *Physik. Z.*, **34**, 689 (1933).

(5) Stearn and Smyth, THIS JOURNAL, **56**, 1667 (1934).

(6) Mizushima and Higasi, *Proc. Imp. Acad.* (Japan), **8**, 482 (1932).