CCXXXVIII.—*Some Observations on the Determination of Surface Tension by Means of Capillary Rise. The Surface Tension of Water, Ethyl Alcohol, Boron Trichloride, and Silicon Tetrachloride.*

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THE availability of sufficient quantities of boron trichloride and silicon tetrachloride of high purity, together with the absence from the literature of a determination of the surface tension of the former, and the doubtful nature of the value ascribed to the latter, prompted this investigation. To establish the necessary technique, work was begun on water, the value for which has been determined with sufficient frequency to warrant its use for this purpose. Ethyl alcohol was included because of the present uncertainty in the accepted surface tension of this liquid, and also in order to extend certain observations made in the course of the measurements with water.

The capillary-rise method for the determination of surface tension has received considerable attention in recent years, particularly by Richards and Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1656, where brief mention is made of previous work), Harkins and Brown (*ibid.*, 1919, **41**, 499), Richards and Carver (*ibid.*, 1921, **43**, 827), and Sugden (J., 1921, **119**, 1483). Study of the literature led at once to a decision to use the important suggestion of Sugden (*loc. cit.*) and Michaelis (" Praktik. d. physikal. Chemie," 1921, 61), *viz.*, that the difference in the capillary rise in two tubes should be used to measure surface tension. This constituted the most convenient method in that it removed at once the difficulty of ascertaining the exact height of the surface of the liquid in the containing vessel, which the elaborate experiments of Richards and Harkins (*loc. cit.*) and their co-workers were designed to overcome. In the present work, however, three instead of two capillary tubes were used, and a vacuum apparatus was devised capable of giving a good fall of liquid surface and of being completely submerged in a thermostat. All measurements were made in an atmosphere consisting solely of the vapour of the liquid in question.

Preliminary work showed that the level of the water in the capillaries fluctuated to an easily measurable extent over a very long period, and furthermore that the movements were not necessarily in the same direction in the three tubes at the same time. All the liquids examined behaved in this way.

Calculation of Surface Tension.

From the general formula relating surface tension to capillary rise, the equation

$$\gamma = r_1 r_2 g(3h + r_2 - r_1)(D - d)/6(r_1 - r_2)$$

may be derived, where r_1 and r_2 are the radii of two capillaries, h is the observed difference in height of two meniscuses in these tubes, D and d are, respectively, the densities of the liquid and the atmosphere over it, and g is the acceleration due to gravity. The value of g used was 981·45, and the surface tension, γ, is expressed in dynes per cm. In this investigation the capillaries were narrow enough to avoid any serious departure of the meniscuses from a hemispherical form, thus rendering unnecessary the corrections suggested by Sugden (*loc. cit.*). The diameters of tubes available were such that the rises in two were to nearly the same height, while that in the third was much lower, and as the proportional error in the measurements of h tends to increase as h diminishes, the smallest difference was not used in the calculation of surface tension.

EXPERIMENTAL.

The Preparation and Calibration of the Capillary Tubes.—The importance of a very rigorous cleaning of the capillary tubes cannot be overestimated : Harkins and Brown (*loc. cit.*), who gave this matter particular consideration, used prolonged passage of the vapour of the liquid concerned in the determination as the final cleaning process before use. The tubes here employed were steeped for several days in a solution of chromic acid in concentrated nitric acid, washed well by drawing water through them, almost submerged for 3 hours in boiling alcohol in such a manner that there was a continuous regular flow of liquid up through them, and finally steamed for 3 hours in the apparatus shown in Fig. 1—A is the capillary under treatment, B the jacket surrounding it, and C a tube of special form delivering steam under pressure from the purest distilled water. For the determinations with water the tubes were put into the apparatus wet from the steaming, but for the other determinations they were drained by holding them in a vertical position and touching the lower end with clean filter paper, and then dried at 110° in an electrically heated oven. After their introduction into boiling alcohol the capillaries were handled only with several layers of clean filter paper between the fingers and the glass, in order entirely to prevent the possibility of the formation of a grease film.

The calibration of the capillary tubes was effected by three different methods in the case of A, B, and C, using (1) an ordinary physical travelling microscope, (2) a cathetometer, and (3) a travelling microscope, made by the Cambridge Instrument Company, and reading directly to 0·01 mm. and by estimation to 0·002 mm. The last instrument only was used in the case of D, E, and F. The mercury threads employed were weighed, after being removed from the tubes by means of dry air to a small glass weighing-bottle lid, on a special balance with calibrated weights, with the precautions usually taken in precise work. The weighings were to 0·01 mg. The uniformity of the bore was first examined by the introduction of a short thread of pure mercury, the length of which was accurately measured, in overlapping positions, along the whole length to be used. The results obtained by using the Cambridge instrument are in Table I, where the lengths of the threads are given in mm., and the figures marked with an asterisk denote the distance of the middle of the threads from the lower ends of the tubes.

FIG. 1.

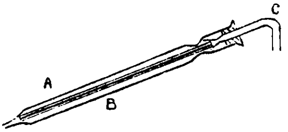

FIG. 2.

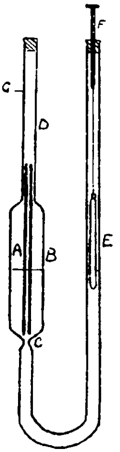

FIG. 3.

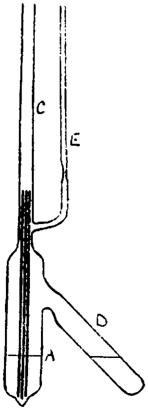

TABLE I.

A.		B.		C.	
8 cm.*	8·235	7 cm.*	10·980	8 cm.*	11·397
	8·246		10·991		11·391
	8·233	2 cm.*	10·991		11·395
	8·238				11·394
2 cm.*	8·247				11·399
				2 cm.*	11·396

D.		E.		F.	
8 cm.*	13·498	5 cm.*	14·757	4 cm.*	13·173
	13·478		14·767		13·174
	13·477		14·760	2 cm.*	13·164
2·5 cm.*	13·489	1 cm.*	14·757		

The uniformity of the tubes may be expressed as a maximum percentage difference in the length of the threads; the following results are obtained : A, 0·17% ; B, 0·09% ; C, 0·07% ; D, 0·09% ; E, 0·08% ; F, 0·08%. These tubes compare unfavourably with those of Richards and Coombs (*loc. cit.*), for which uniformity was claimed, and also with those of Harkins and Brown (*loc. cit.*), where the difference was 0·03% on a thread of about 16·8 mm. in length, but they were the best from 50 lb. of capillary tubing, much of it specially drawn for this research, and their selection involved 4 weeks of constant work. The radii were obtained by measuring and weighing three threads about 4 cm. long and one or more shorter threads of pure mercury about 1 cm. long in each tube, the temperature at the time of measurement being noted and the density of the metal being computed (Smithsonian Physical Tables, 7th Edtn.). The observation of Harkins and Brown (*loc. cit.*) that there is a definite sag in the mercury meniscus with the tubes in a horizontal position even when the radius is as small as 0·2 mm. was confirmed; it was corrected for, as suggested by them, by subtracting the length and weights respectively of a shorter thread. The radii of the tubes were determined with the Cambridge measuring microscope, the calibrations being restricted to the lengths actually used, and are believed to have an accuracy of 0·1% and 0·05% for the narrower and the wider tubes respectively.

TABLE II.

Tube	A.	B.	C.	D.	E.	F.
r (in mm.)	0·07325	0·20168	0·25287	0·27165	0·41354	0·49920

The ends of all tubes were examined for ellipticity with a microscope and found to be satisfactory in this respect.

The Surface Tension of Water.—Preliminary work with three capillary tubes of approximately the bore indicated above showed that definite vertical movement of the meniscuses took place with the tubes either arranged in a triangular formation 4 cm. apart or bound together in a bundle. The results indicated that concordant surface tensions would be obtained from either arrangement provided that sufficient time was allowed to elapse after lowering the level of the liquid. This led to the construction of a vessel of the form indicated in Fig. 2, in which A represents the prepared capillaries, held in position in the wider tube, B, by the taper at C and the extension, D. The fall in level of the liquid was secured by raising the glass plunger, E, which was suspended from the long screw, F. This apparatus, charged with first-quality water, was submerged to the point G in a thermostat at 25° ± 0·01°, and the height of the water in the capillaries was observed by means of a cathetometer reading to 0·01 mm. at intervals of about 10 minutes for 2·5 hours from the time at which the level of the liquid was lowered. During this period the heights of the meniscuses in the three tubes fell irregularly, giving, when plotted against time, a sinuous downward-sloping curve, recording maximum falls of 0·72 mm., 0·64 mm., and 0·74 mm., respectively. As the upper part of the apparatus, which was closed with a loosely fitting cork, had protruded from the bath, the fall was ascribed, correctly as it was subsequently proved, to evaporation. This explanation was tested by maintaining the bath at 17·4°, *i.e.*, about 0·5° below laboratory temperature, and repeating the observations without changing the water or re-treating the tubes; 24 observations, spread uniformly over 5 hours, were taken, with the result that sinuous, slightly rising curves were now obtained, showing minimum points 0·12, 0·17, and 0·17 mm., respectively, below the initial heights after about 2·5 hours, and a maximum rise at the end of the period of 0·39, 0·22, and 0·04 mm. above. Such changes could not be explained by either evaporation or irregular drainage, and further investigation was undertaken in an apparatus (Fig. 3) which consisted of a barrel, A, 2·5 cm. wide, terminated below in a cone-shaped point and above in the centrally disposed tube, C, suitable in width for holding steadily the three capillary tubes. The side limb, D, was provided for lowering the level of the liquid, and E with its capillary served for filling and evacuation. This vessel was cleaned with chromic–nitric acid mixture, well washed with distilled water, maintained full of boiling alcohol for 4 hours, and finally well rewashed with best-quality water. When thus prepared, the freshly steamed capillary tubes were slid down C into such a position that the three could be observed from the selected direction, and C was drawn off just above the tops of the capillaries. Water (prepared by treating first-quality distilled water with a trace of alkaline permanganate, redistilling with considerable rejection of head and tail fractions, and again twice distilling the main fraction with rejections) was used for the three final washes in the apparatus. These distillations were carried out successively without delay, and the final material, which was distilled directly into E, served as the sample to be examined. E was at once attached to the pump and the whole of the air was removed, the water being warmed to facilitate this, after which the apparatus was sealed off under the pressure of water vapour only. The surface-tension vessel was completely submerged in a thermostat maintained within ± 0·01° of the required temperature and, a fall in level of the liquid having been obtained by tilting the apparatus and allowing a portion to run into D, the heights of the meniscuses were observed with a cathetometer reading to 0·01 mm. The tubes were arranged so that the threads of all could be observed without swinging the telescope of the instrument in a horizontal plane, both they and the cathetometer having been brought to a vertical position. The glass forming the barrel, A, had been carefully selected for uniformity and lack of distortion, and careful measurements, made at different places over the range actually used, indicated that the images of the meniscuses were not appreciably changed in apparent relative position. The regularity of the results derived from different sets of observations bears out this conclusion. Table III gives one complete set (Set K) of observations for water at 25° and indicates the general nature of the fluctuations in height observed throughout this work, namely, that the most rapid and extreme variations are found within the first hour, that these variations grow less with time, and that after a period of about 10 hours they have almost entirely vanished. Table IV gives the surface tension calculated from the data in Table III, and shows that the two values come closer together with the passage of time, the difference falling from 0·26 to 0·07 unit.

TABLE III.

Time from zero (min.) ...	6	18	34	50	86	123	158	219	271	340
Tube F (mm.)	0·62	0·77	0·71	0·69	0·72	0·75	0·75	0·78	0·78	0·78
Tube D (mm.)	25·56	25·41	25·49	25·46	25·48	25·49	25·52	25·53	25·56	25·55
Tube C (mm.)	29·59	29·60	29·63	29·65	29·60	29·62	29·67	29·66	29·66	29·71

Time from zero (min.) ...	389	458	520	575	636	696	754	787	813
Tube F (mm.)	0·85	0·77	0·84	0·83	0·83	0·83	0·83	0·83	0·83
Tube D (mm.)	25·55	25·56	25·58	25·60	25·63	25·64	25·64	25·64	25·64
Tube C (mm.)	29·70	29·70	29·72	29·69	29·70	29·71	29·70	29·71	29·70

TABLE IV.

	First hour.		Middle hour.		Last hour.	
Tubes.	Mean h (mm.).	γ.	Mean h (mm.).	γ.	Mean h (mm.).	γ.
C and F	28·920	72·31	28·900	72·26	28·875	72·20
D and F	24·783	72·05	24·770	72·01	24·810	72·13

TABLE V.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
I.	25°	11·5	C, F	28·86	72·16	72·16
J.	21	7	C, F	29·07	72·75	72·75
K.	25	14	C, F	28·88	72·20	72·17
			D, F	24·81	72·13	

Table V summarises the data for water using $(D - d)_{25^\circ} = 0·99705$ and $(D - d)_{21^\circ} = 0·99800$. In Sets I and J only one result is recorded because of the behaviour of tube E, which, although free from irregularity of bore or defect obvious under the microscope, persisted in preventing water from rising beyond a certain point. Presumably this was due to some condition of the surface of the glass at this point which tended to inhibit wetting.

The Surface Tension of Alcohol.—A vessel similar to that described in the case of water was successively cleaned with chromic–nitric acid mixture, alkali, water, alcohol, and ether, and finally dried along with the capillary tubes, which had been treated as described previously, in an electrically heated oven. The alcohol used in Sets D and E was only roughly dried, that used in Set F was dried rather more thoroughly but still probably contained traces of moisture. Special precautions were, however, taken in the preparation of the alcohol for Set H, which was absolute alcohol redistilled with considerable rejections, refluxed over lime warm from burning for 3·5 days, the lime being changed at the end of the first day and a head and a tail fraction being rejected in the process. In distilling the liquid into the dried-out vessel, special precautions were taken to avoid contact with the air as far as possible; the whole operation lasted less than 0·25 hour and the apparatus was at once evacuated and sealed off. Table VI summarises the results for alcohol, all but Set H being considered as preliminary work with material containing water. The values $(D - d)_{25^\circ} = 0{\cdot}78491$ and $(D - d)_{15^\circ} = 0{\cdot}79352$ were used throughout.

TABLE VI.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.	Remarks.
C.	25°	4·0	A, B	49·81	22·04	22·06	Alcohol containing moisture.
			A, D	57·12	22·09		
E.	15	7·0	A, B	51·33	22·96	22·96	
			A, D	58·86	22·96		
F.	25	12	A, B	49·01	21·70	21·69	Drier alcohol.
			A, D	56·19	21·68		
H.	25	24	A, B	48·77	21·58	21·59	Dry alcohol.
			A, D	55·97	21·60		

The Surface Tension of Boron Trichloride.—Boron trichloride of high purity (for history of material and manipulation see subsequent paper by Parker and Robinson) was distilled into a similar surface-tension apparatus which had been thoroughly cleaned, dried, and evacuated. Two sets of observations were taken—at 25° with 15 readings, and at 21° with 10 readings. The data are given in Table VII, the values $(D - d)_{25^\circ} = 1{\cdot}3144$ and $(D - d)_{21^\circ} = 1{\cdot}3207$ being used.

The Surface Tension of Silicon Tetrachloride.—The procedure was exactly as with boron trichloride (for history of material and manipulation see Parker and Robinson, *loc. cit.*), but, unfortunately,

TABLE VII.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
M.	25°	10	A, B	21·71	16·07	16·07
			A, D	24·91	16·07	
N.	21	9·5	A, B	22·22	16·52	16·52
			A, D	25·49	16·52	

at the end of the distillations the sudden boiling of a drop or two of liquid in the plunger arm of the special joint caused a fracture, and air entered the apparatus. The broken portion was at once drawn off and the apparatus attached to the pump and evacuated so that exposure to air was not longer than 1·5 minutes. There was no evidence of hydrolysis in the apparatus, nor did the behaviour of the liquids in the capillaries suggest that the admission of air had had any detrimental effect; nevertheless, these results are given provisionally and it is proposed to repeat this portion of the work with other material of similar purity which is available. Table VIII gives these provisional results, 15 observations being taken in each set; $(D - d)_{25^\circ} = 1{\cdot}4685$ and $(D - d)_{21^\circ} = 1{\cdot}4771$ were used.

TABLE VIII.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
O.	25°	12	A, B	23·11	19·11	19·11
			A, D	26·51	19·11	
P.	21	12	A, B	23·54	19·58	19·59
			A, D	27·01	19·59	

Discussion.

It has been shown that tubes of a much smaller bore than have usually been employed can be used in the determination of surface tension to a high degree of accuracy by the method suggested by Sugden (*loc. cit.*), but concordant results with two or more such tubes are obtained only several hours after the lowering of the liquid level. The thorough cleaning of the capillaries emphasised by other workers is found to be necessary. Distinct advantage attends the use of three in place of two tubes, and the results are the same whether they be separated from one another by several cm. or bound together in a bundle, the latter arrangement being more convenient. During the first hour or so, the meniscuses in the capillary tubes show slow oscillations, sometimes opposite in direction in two tubes at the same time, or coinciding with no movement in another tube, while the mean heights tend to decrease throughout the same period, and surface tensions calculated from differences in the heights obtained at any moment do not show good agreement amongst themselves. These movements gradually decrease and are followed by a series of more or less spasmodic rises which continue, although they may be separated by intervals as long as one or two hours, until the maximum rise for each tube is reached. That these rises are to be ascribed to surface forces, and not to any change in level of the main liquid surface from drainage or other causes, is proved by the fact that they are invariably preceded by a greatly increased curvature of the meniscus, as though the centre were being drawn down, whilst, furthermore, the movements take place at times and to extents which are not the same in the different tubes.

If the forces producing the rises were being applied at the base of the columns, a flattening of the meniscuses and concurrent rises in the three tubes would be anticipated. The whole subject is being investigated, but a careful examination of the available data leads to the conclusion that for the same liquids the changes in the heights of the meniscuses decrease with increasing size of capillary, while the period required to reach the maximum rise and the equilibrium is slightly less in the wider tubes, and that with the same bore the magnitude of these changes in the liquids considered grows less in the order alcohol, water, silicon tetrachloride, boron trichloride. The inference made here is that, after the oscillations of the initial period have damped down, the change in level of the meniscus due to spasmodic rises is probably related to viscosity, for the viscosities of alcohol and water are known to decrease in the order noted, while those of the chlorides, although apparently not determined, are certainly less than that of water. It is suggested that the maximum rise attained when the meniscuses are at rest corresponds to the true static equilibrium between surface energy and gravity, and that the figure calculated from h in these conditions corresponds to the true surface tension. It should be pointed out that, once equilibrium is reached, the meniscuses are not observed to move either of their own accord or when the vessel has been made to tremble by tapping, thus suggesting the stability above implied.

Surface tensions are usually given at 20°, and Table IX records the values now found (in contact with only the vapour of the substance) corrected to this temperature, together with the change per degree.

TABLE IX.

Substance.	γ.	Change in γ per degree.
Water	72·90 ± 0·04	0·15
Alcohol	22·05 ± 0·01	0·09
Boron trichloride	16·70 ± 0·01	0·11
Silicon tetrachloride	19·71 ± 0·01	0·12

The value for water agrees most closely with the 72·80 of Harkins and Brown (*loc. cit.*), but is much higher than the 72·74 of Richards and Coombs (*loc. cit.*), the 72·70 of Sugden (*loc. cit.*), the 72·61 of Worley (J., 1914, **105**, 266), or the 72·8 given as the most probable value by Freundlich ("Colloid and Capillary Chemistry," 1927, 24). In the case of alcohol there have been numerous previous determinations yielding results varying from 21·2 to 22·4. The value given above agrees closely with the 22·0 of Ramsay and Shields (*Phil. Trans.*, 1893, **184**, 647), and the precautions taken in this work render it the most probable value at the present time. The surface tension of boron trichloride has not hitherto been recorded. Silicon tetrachloride has received attention from Ramsay and Shields (*loc. cit.*), who found $\gamma = 16{\cdot}31$ at 18·9°, *i.e.*, 16·20 at 20°; from Walden (*Z. anorg. Chem.*, 1900, **25**, 218), who found $\gamma = 18{\cdot}20\ (1 - 0{\cdot}00548t)$, *i.e.*, 16·23 at 20°; and from Mendeléev (*Pogg. Ann.*, 1870, **141**, 618), who found 15·13 at the b. p. (57°), which is approximately equivalent to 19·20 at 20°.

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