340. *The Measurement of Surface and Interfacial Tensions.*

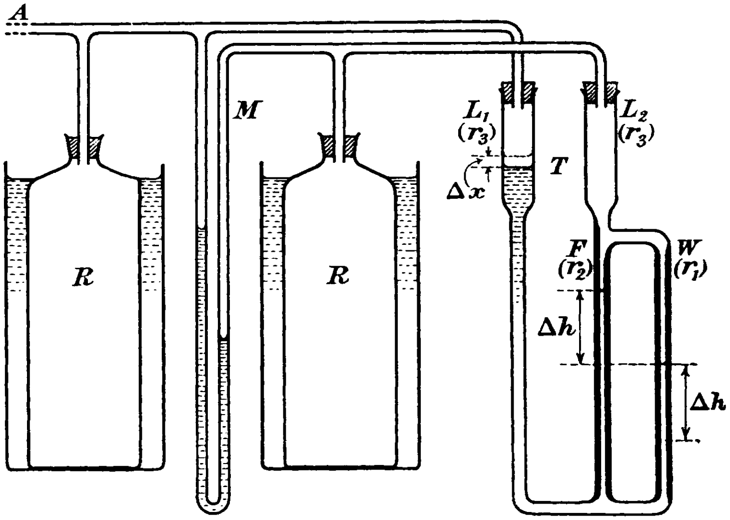
By J. Clare Speakman.

Ferguson and Dowson (*Trans. Faraday Soc.*, 1922, **17**, 384) introduced an important modification of the capillary-rise method for measuring surface tensions, which consisted in determining the *pressure* needed to depress the meniscus down the capillary tube to a selected level. The method was further used by Edwards (J., 1925, **127**, 744), by Ferguson and Hakes (*Proc. Physical Soc.*, 1929, **41**, 214), and independently by Ali (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 155) who made rather bold claims for the accuracy attainable. The manner of measuring interfacial tensions described by Bartell and Miller (*J. Amer. Chem. Soc.*, 1928, **54**, 1961), though not obviously similar, is essentially closely related.

The present paper shows how certain advantages additional to those listed by Ferguson and Dowson (*loc. cit.*) can be realised by using *two* capillary tubes of different bores and observing the *difference* between the pressures required to depress the meniscus to the same level in each successively; and it is further shown that interfacial tensions can be measured in the same way in the same apparatus.

EXPERIMENTAL.

Measurements were made in the apparatus T (see fig.), which could be immersed in a glass trough of water for purposes of temperature control. F and W are the capillary tubes, and in the particular instruments used these were about 22 cm. long and had internal radii of about 0·02 and 0·06 cm. respectively. Some 5 c.c. of liquid were placed in the apparatus before it was connected as shown in the diagram. Suction was applied at A by means of a water aspirator designed so as to allow either rapid or slow action. The pressure, P_1, needed to force the meniscus in the wider capillary (W) down to some arbitrary level was measured on the manometer (M), the meniscus being adjusted so that its convex edge coincided with the eye-piece marking of a low-powered travelling microscope and being illuminated from behind. The microscope, which had been levelled by use of a spirit level, was then turned on the other capillary (F) and the pressure, P_2, needed to bring the second meniscus to the eye-piece marking also observed. The difference, $P_2 - P_1 = \Delta P$, was a measure of the tension as will be shown.



It was imperative to connect both sides of the apparatus T to the manometer as shown; if this were not done the menisci were very unsteady, in particular being disturbed by any sharp sound (presumably on account of the compression in the sound wave). It was also desirable to increase the capacity of the system by adding the reservoirs R, and these were water-jacketed.

Absolute alcohol was originally used as manometric liquid, following the practice of many previous workers. It was, however, found to be highly unsuitable; it is hygroscopic and the absorption of water is accompanied by a serious increase of density (1 or 2% during a month, for instance). *cyclo*Hexane was substituted for alcohol and found to be satisfactory, the choice being made because this liquid is stable in this respect and has as low a density as alcohol.

Calculation of Results.—The derivation of surface or interfacial tensions from the values of ΔP permits of a high degree of precision. The contact angle must be zero (or be exactly known), a limitation which, however, necessarily applies to all similar methods of measuring surface tensions. It being assumed for the moment that the menisci in the capillaries are hemispherical, then if p_1 and p_2 are the pressure differences existing there on account of the curvature of the surfaces, and if r_1 and r_2 are the internal radii, in W and F respectively, it follows that

$$p_1 = 2\gamma/r_1 \text{ and } p_2 = 2\gamma/r_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Between the determinations of P_1 and P_2, as consideration of the fig. will show, the liquid as a whole moves downwards in the capillaries by an amount Δh and upwards in L_1 by an amount Δx. These quantities are determined by the following equations :

$$\Delta h = (p_2 - p_1)/\rho g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

from considerations of hydrostatic pressure, ρ being the density of the liquid, and

$$\Delta x \,.\, \pi r_3^2 = \Delta h \,.\, \pi(r_1^2 + r_2^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

provided the tubes may be assumed to have uniform bores. Finally, we have

$$P_1 = p_1 + K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{and } P_2 = p_2 + K + \Delta x \,.\, \rho g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

K being a constant for any single pair of observations. Subtracting (4) from (5), substituting from (1), (2), and (3), and simplifying, we have

$$P_2 - P_1 = \Delta P = (p_2 - p_1)\left\{1 + \frac{r_1^2 + r_2^2}{r_3^2}\right\}$$

whence

$$\gamma = \Delta P \Big/ 2\left\{1 + \frac{r_1^2 + r_2^2}{r_3^2}\right\}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

i.e.,

$$\gamma = C \,.\, \Delta P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The constant C may be calculated from measurements of r_1, r_2, and r_3. This was done in the present work in order to check the results; r_1 and r_2 were found by observations on threads of mercury, the uncertain "end correction" being eliminated by the procedure described by Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 503), and r_3 by use of calipers; more simply, C can be found by calibration with a liquid of known surface tension.

It will be noticed that the r_1 and r_2 occurring in the term $1/r_2 - 1/r_1$ of equation (6) are not strictly the same quantities as those in the other term in the denominator; the former refer to a particular level of the apparatus, whilst the latter are average values. Since, however, the term in which the latter occur differs only slightly from unity, no appreciable error is introduced by assuming them to be the same [*i.e.*, by assuming for the purpose of equation (3) that the tubes are uniform].

The above treatment refers to surface tensions. When it was desired to measure interfacial tensions, the experimental procedure was similar. The interface was formed either above or below the capillaries, as the system demanded, so that the menisci could be drawn in the direction of their convexity. Sufficient of the two phases needed to be present for their free surfaces to lie in the limbs L_1 and L_2. If ρ_1 and ρ_2 are the densities (bulk) of the upper and the lower phasc, a similar treatment to that given previously leads to the corresponding formula

$$\gamma_i = \Delta P \Big/ 2\left\{1 + \frac{(r_1^2 + r_2^2)}{r_3^2}\,\frac{(\rho_2 + \rho_1)}{(\rho_2 - \rho_1)}\right\}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

When the densities approach equality the term $(\rho_2 + \rho_1)/(\rho_2 - \rho_1)$ becomes large and the method inaccurate or even inapplicable; but the same is true of all known methods of measuring interfacial tensions.

So far no account has been taken of the fact that the meniscus will depart somewhat from the truly hemispherical form; allowance must be made for this in all but the most approximate work. Ferguson and Dowson (*loc. cit.*) make use of Rayleigh's formula (*Proc. Roy. Soc.*, *A*, 1916, **92**, 184), but their treatment subsequently contains so many approximations as to lose much in precision. The results of Bashforth and Adams, which have been made generally available in the form of tables by Sugden (J., 1921, **119**, 1483), enable a very exact computation to be made. If, in equations (1), and in the terms of (6) and (8) derived from (1), r_1 and r_2 are replaced by b_1 and b_2, which are defined as the radii of curvature of the surfaces at the poles of the menisci, then these equations become rigidly true. Sugden's table gives the value of r/b when r/a * is known. So, for example, an approximate value of γ may be obtained from equation (6) and thence one of a^2. From this are calculated in turn r/a, r/b (from the table), and a more exact value of γ, the process being repeated if need be until a constant value emerges though in practice one such approximation is usually enough.

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* In accordance with common practice the capillary constant is defined by the equation, $a^2 = 2\gamma/(\rho_2 - \rho_1)g$, ρ_2 and ρ_1 being the densities of the phases at equilibrium. Some authors, however, including Rayleigh and Ferguson and Dowson, use an a^2 which has half this value.

Sufficient accuracy for most purposes is maintained by using a simple empirical formula based on Sugden's table, *viz.*,

$$\gamma = C\phi \, . \, \Delta P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

where ϕ is a correction factor having the value $(1 - 0{\cdot}3r_1r_2/a^2)$ for radii of the order of those used, and where C is a constant as in (7). This correction factor may also be introduced into (8) for an interface.

Results.—The method was tested by absolute determinations of the surface tensions of water and benzene and of the interfacial tensions of benzene–water, ether–water, and water–chloroform. The water was distilled, the benzene was of " A.R. " quality, and the ether and chloroform were purified by distillation. Before each set of observations, the apparatus (T) was steamed out and dried by drawing a current of filtered air through it. The manometer was read by means of an engraved mirror scale, on which it was found that pressure readings could be reproduced to within 0·02 cm. In each experiment a series of observations was taken at different levels, and the results were worked out with equation (9) or with a corresponding one for interfacial tensions. The slight variations in the term $1/r_2 - 1/r_1$ correspond to different levels of the apparatus and are due to the lack of *exact* uniformity in the capillary tubes, such exact uniformity not being required by this method. Densities when required were taken from the " International Critical Tables," as also were the surface and interfacial tensions given below for comparison (in parentheses). The " gauge factor " is the quantity by which manometer readings must be multiplied in order to convert them to dynes per sq. cm. The following tables give representative results.

I. *Surface tension of benzene.*

Approximate radii : r_1 0·019, r_2 0·059, r_3 0·50 cm. Temp. 16°. Gauge factor 767·0. ϕ 0·995.

	Pressure differences.			
Manometer (cm.).	ΔP (dynes/cm.²).	$\dfrac{\Delta P}{1 + \dfrac{r_1^2 + r_2^2}{r_3^2}}$.	$\dfrac{1}{r_2} - \dfrac{1}{r_1}$.	Surface tension, γ.
2·82	2163	2123	35·84	29·5
2·80	2148	2108	35·74	29·3
2·79	2140	2100	35·59	29·3
2·80	2148	2108	35·51	29·5
2·76	2116	2078	35·11	29·4
				Mean 29·4 (29·40)

II. *Surface tension of water.*

Approximate radii : r_1 0·025, r_2 0·061, r_3 0·50 cm. Temp. 19°. Gauge factor 764·3. ϕ 0·997.

4·60	3517	3457	23·63	73·0
4·58	3501	3442	23·61	72·7
4·62	3533	3473	23·65	73·2
4·61	3525	3465	23·65	73·1
				Mean 73·0 (72·90)

III. *Interfacial tension of benzene–water.*

Approximate radii : as in II. Temp. 23°. Gauge factor 760·9. ϕ 0·999. ρ_1 0·878, ρ_2 0·998.

	Pressure differences.			
Manometer (cm.).	ΔP (dynes/cm.²).	$\dfrac{\Delta P}{1 + \dfrac{(r_1^2 + r_2^2)(\rho_2 + \rho_1)}{r_3^2(\rho_2 - \rho_1)}}$.	$\dfrac{1}{r_2} - \dfrac{1}{r_1}$.	Interfacial tension, γ_i.
2·67	2028	1599	23·63	33·9
2·70	2052	1615	23·65	34·2
				Mean 34·(1) (34·23)

IV. *Interfacial tension of ether–water.*

Approximate radii : as in I. Temp. 19°. Gauge factor 764·3. ϕ 0·993. ρ_1 0·717. ρ_2 0·997.

1·18	902	807	35·74	11·2
1·15	878	787	35·65	10·9
1·14	871	780	35·59	10·9
				Mean 11·(0) (10·7 at 20°)

V. *Interfacial tension of water–chloroform.*

Approximate radii : as in II. Temp. 23°. Gauge factor 760·9. ϕ 0·996. ρ_1 1·000. ρ_2 1·483.

2·19	1665	1530	23·65	32·4
2·11	1605	1473	23·63	31·2
2·22	1688	1550	23·63	32·8
2·08	1552	1425	23·63	30·8
				Mean 32 (32·8 at 20°)

With the surface tensions the agreement between the values found and the accepted ones is very close; for the interfacial tensions it is also satisfactory though not so close; this is to be expected in view of the greater difficulties attending the measurement of interfacial tensions, the susceptibility of the results to any error in the densities of the conjugate solutions, and a possible unreliability in the accepted data (*e.g.*, cf. Bartell, Case, and Brown, *J. Amer. Chem. Soc.*, **1933**, **55**, **2769**). It should be pointed out that the accuracy of this test was limited by the means used for reading the manometer, and if a more accurate means were adopted it seems certain that a corresponding increase in the accuracy of the results would follow.

The advantages of the method over others of the " capillary rise " type may be summarised : (1) It is unnecessary to search for capillary tubing of exactly uniform bore. (2) The uncertainty regarding the position of the free surface of the liquid in an outer vessel is eliminated, as is also the question of its departure from the planar. The method is therefore open to precise mathematical treatment. (3) Surface and interfacial tensions can be measured and compared in the same apparatus.

It is concluded, not only that the method as described is a reliable one, but also that it can be adapted with advantage over others to work of the very highest accuracy.

SUMMARY.

A modification of existing methods for measuring surface and interfacial tensions is described, consisting in observing the *difference* between the pressures required to force the menisci in two capillary tubes of different bores to the same arbitrarily selected level. The method is shown to have certain advantages over others.

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