The determination of interfacial tension by differential capillary rise

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Abstract. A method for directly determining interfacial tension without iteration from the difference in height between two capillaries is presented. An experimental technique is described for organic liquids both lighter and heavier than water, in which the menisci recede over surfaces wetted by the aqueous phase, thus providing the most favourable conditions for zero contact angle. The values determined experimentally using tables prepared from the known shapes of sessile interfaces agree well with accepted values of the interfacial tension.

1. Introduction

Capillary rise is accepted as being one of the most exact methods of measuring surface and interfacial tensions and several workers employed this method to determine the surface tension of liquids (Richards and Coombs 1915; Richards and Carver 1921; Harkins and Brown 1919; Sugden 1921; Richards *et al* 1924). However it is difficult to locate the flat external meniscus or the free surface of the bulk liquid because of the curvature of the liquid meniscus adhering to the walls. This difficulty may be overcome by using a pair of capillaries and measuring the differential capillary rise. This technique has been used by Mack and Bartell (1932) to measure the interfacial tension of organic liquids against water. In this paper we suggest a refinement of their method which is both simpler and more accurate.

2. Theoretical

The shape of the meniscus in the capillary tube is that of a sessile interface, the dimensions of which were determined by Bashforth and Adams (1883) and more recently by Hartland and Hartley (1976). Figure 1a shows a sessile interface in a capillary tube of radius r when the contact angle between the liquid and the

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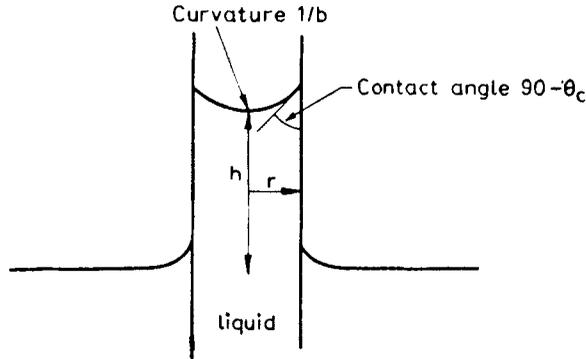* To whom all correspondence should be made.

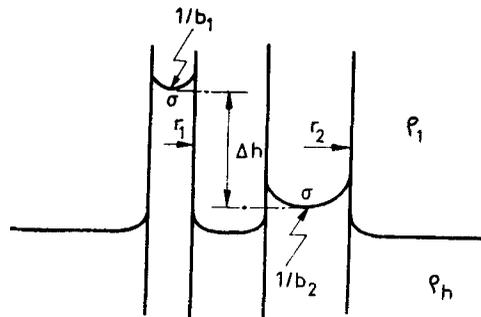**Figure 1a.** Notation for capillary rise in a single tube.

Figure 1b. Notation for differential capillary rise in two tubes of different radii.

wall is $90 - \theta_e$. The difference in pressure across the apex of the interface is $2\sigma/b$ and equating this to the gravitational pressure difference of $\Delta \rho g/h$ gives, in dimensionless form

$$B = 2/H, \tag{1}$$

where $H = h(\Delta \rho g/\sigma)^{1/2}$, $B = b(\Delta \rho g/\sigma)^{1/2}$ and $\Delta \rho = \rho_h - \rho_l$.
If the contact angle and hence θ_e are known, the interfacial tension can be determined. Multiplying both sides of (1) by the radius r of the capillary tube gives

$$BX_e = 2r/h, \tag{2}$$

since $r(\Delta \rho g/\sigma)^{1/2}$ is now equal to X_e. For a sessile interface B is a unique function of θ_e and X_e and so is the product BX_e. From experimental measurements of r and h we can determine BX_e using (2) and hence X_e from the tables to define the shape of sessile drops. The interfacial tension can thus be calculated using :

$$\sigma = \Delta \rho g (r/X_e)^2. \tag{3}$$

If the contact angle is zero, (i.e. $\theta_e = 90°$) as is usually assumed, (2) and (3) become

$$BX_{90} = 2r/h, \tag{4}$$

and $\qquad \sigma = \triangle\rho g\,(r/X_{90})^2.$ (5)

The variation of X_{90} with $(BX_{90})^{1/2}$ is almost linear for the range of B between 0·12 and 1·6 which covers the experimental values and hence linear interpolation between the tabulated values is almost exact. As the value of X_c is not sensitive to θ_c close to 90°, (4) and (5) may be used with confidence when the contact angle is small. For very small tubes, $X_{90} \simeq (BX_{90})^{1/2}$ and $b \simeq r$, so combining (4) and (5) gives

$$\sigma = \triangle\rho g\,hr/2.$$ (6)

Equation (1) also reduces directly to this expression when the contact angle is zero. For non-zero contact angles, b is never equal to r, no matter how small the tube and the interfacial tension cannot be determined unless the contact angle is known.

As the vessel in which the capillary tube is located is finite the bulk interface is curved and therefore has a small but finite pressure difference across it which is not allowed for in the above equations. In addition it is difficult to exactly locate the position of the interface when viewed from the side. These errors can be avoided by using two tubes of different radii r_1 and r_2, as shown in figure 1b, and measuring the difference in capillary rise $\triangle h$ between them. We may then write

$$\frac{2\sigma}{b_1} - \frac{2\sigma}{b_2} = \triangle h\,(\rho_h - \rho_i)\,g,$$ (7)

where b_1 and b_2 are the radii of curvature at the apex of the two menisci. In dimensionless form the equation becomes

$$\frac{2}{B_1} - \frac{2}{B_2} = \triangle H,$$ (8)

where $B_1 = b_1 c^{1/2}$, $B_2 = b_2 c^{1/2}$, $\triangle H = \triangle h c^{1/2}$ and $c = (\rho_h - \rho_i)\,g/\sigma$.
From the tables of Hartland and Hartley (1976) the values of $\triangle H$ are calculated from chosen values of B_1 and B_2 and values of $R_1 = r_1 c^{1/2}$ and $R_2 = r_2 c^{1/2}$ obtained from the corresponding values of X_{90} when the contact angle is zero.

Table 1 presents values of $\log_{10}\triangle H$ corresponding to constant values of R_1/R_2 and $\log_{10}\triangle H/R_1$ obtained by interpolation within the original values. The experimental measurements of $\triangle h$, r_1 and r_2 yield the ratios $\triangle h/r_1$ and r_1/r_2 which are equal to $\triangle H/R_1$ and R_1/R_2 respectively. Values of $\triangle H$ may then be obtained from table 1 and the interfacial tension calculated from

$$\sigma = (\rho_h - \rho_i)\,g\,(\triangle h/\triangle H)^2.$$ (9)

The variation of $\log_{10}\triangle H$ with $\log_{10}\triangle H/R_1$ at constant R_1/R_2 is linear, as shown in figure 2, except for the smallest values of $\log_{10}\triangle H/R_1$ and R_1/R_2; so linear interpolation between the values of $\log_{10}\triangle H$ and $\log_{10}\triangle H/R_1$ in table 1 is almost exact.

3. Experimental

Two quartz capillary tubes of radii 0·3575 and 0·11675 cm were fused into quartz reservoirs and the arrangement placed in a quartz vessel, as shown in figures 3a

Table 1. Values of $\log_{10}\Delta H$ for constant values of R_1/R_2 (between 0·1 and 0·9) and constant values of $\log_{10}\Delta H/R_1$ (between 0 and 3·0) for difference in capillary rise between two tubes when the contact angle is zero.

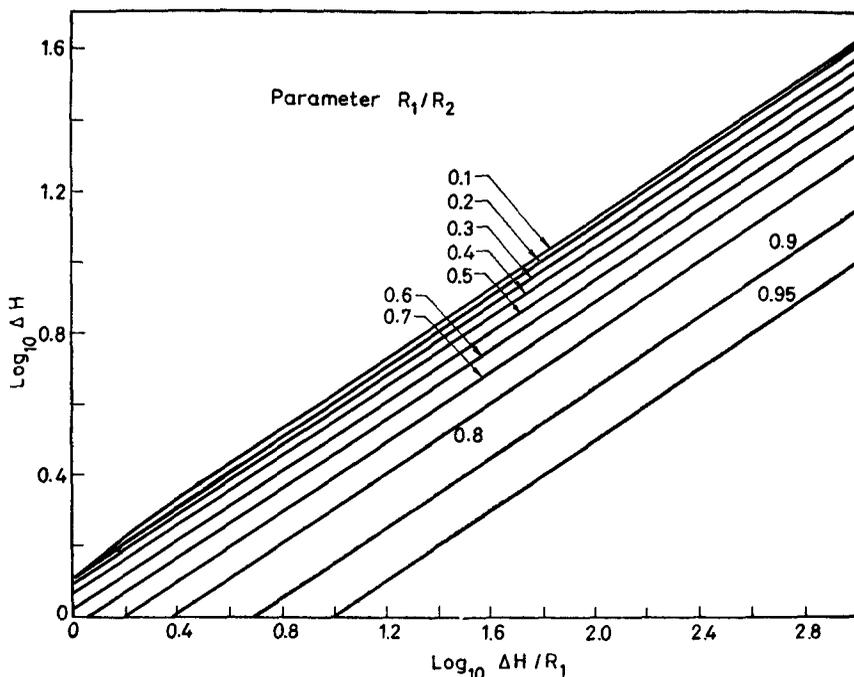| $\log_{10}\Delta H/R_1$	Values of R_1/R_2								
	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0·0	0·099733	0·098083	0·087322	0·063562	0·026785	−0·023482	−0·090583	−0·18482	−0·34228
0·1	0·15793	0·15538	0·14181	0·11488	0·075693	0·024085	−0·043356	−0·13716	−0·29364
0·2	0·21502	0·21123	0·19463	0·16482	0·12379	0·071404	0·0040031	−0·089208	−0·24475
0·3	0·27109	0·26566	0·24596	0·21370	0·17141	0·11870	0·051593	−0·040965	−0·19567
0·4	0·32620	0·31875	0·29605	0·26187	0·21882	0·16613	0·099461	0·0075468	−0·14643
0·5	0·38044	0·37060	0·34518	0·30962	0·26623	0·21378	0·14762	0·056313	−0·097026
0·6	0·43386	0·42136	0·39363	0·35720	0·31379	0·26170	0·19605	0·10530	−0·047517
0·7	0·48652	0·47122	0·44168	0·40479	0·36156	0·30990	0·24474	0·15446	−0·0020780
0·8	0·53847	0·52038	0·48953	0·45251	0·40959	0·35837	0·29366	0·20379	0·051771
0·9	0·58975	0·56906	0·53736	0·50043	0·45790	0·40710	0·34277	0·25324	0·10151
1·0	0·64044	0·61744	0·58529	0·54860	0·50646	0·45603	0·39204	0·30279	0·15131
1·1	0·69060	0·66568	0·63338	0·59701	0·55525	0·50516	0·44146	0·35244	0·20115
1·2	0·74031	0·71392	0·68167	0·64566	0·60425	0·55445	0·49098	0·40215	0·25102
1·3	0·78967	0·76223	0·73019	0·69453	0·65342	0·60388	0·54060	0·45192	0·30092
1·4	0·83878	0·81067	0·77891	0·74359	0·70275	0·65341	0·59029	0·50174	0·35083
1·5	0·88774	0·85927	0·82784	0·79282	0·75221	0·70303	0·64004	0·55160	0·40077
1·6	0·93663	0·90805	0·87694	0·84219	0·80176	0·75273	0·68985	0·60148	0·45072
1·7	0·98551	0·95699	0·92620	0·89167	0·85141	0·80249	0·73969	0·65139	0·50068
1·8	1·0344	1·0061	0·97559	0·94126	0·90113	0·85230	0·78956	0·70132	0·55064
1·9	1·0834	1·0553	1·0251	0·99092	0·95090	0·90215	0·83946	0·75126	0·60062
2·0	1·1325	1·1047	1·0747	1·0407	1·0007	0·95202	0·88939	0·80121	0·65060
2·1	1·1817	1·1542	1·1244	1·0904	1·0506	1·0019	0·93932	0·85117	0·70058
2·2	1·2310	1·2038	1·1741	1·1403	1·1005	1·0518	0·98927	0·90114	0·75057
2·3	1·2804	1·2534	1·2239	1·1901	1·1504	1·1018	1·0392	0·95112	0·80056
2·4	1·3299	1·3032	1·2737	1·2400	1·2003	1·1517	1·0892	1·0011	0·85055
2·5	1·3795	1·3530	1·3236	1·2899	1·2502	1·2017	1·1392	1·0511	0·90054
2·6	1·4291	1·4028	1·3735	1·3399	1·3002	1·2517	1·1892	1·1011	0·95054
2·7	1·4788	1·4526	1·4234	1·3898	1·3501	1·3016	1·2391	1·1511	1·0005
2·8	1·5286	1·5025	1·4733	1·4398	1·4001	1·3516	1·2891	1·2011	1·0505
2·9	1·5784	1·5524	1·5233	1·4897	1·4501	1·4016	1·3391	1·2511	1·1005
3·0	1·6283	1·6023	1·5732	1·5397	1·5001	1·4516	1·3891	1·3010	1·1505

Figure 2. Variation of $\log_{10}\triangle H$ with $\log_{10}\triangle H/R_1$ for different values of R_1/R_2 for differential capillary rise.

and 3b. The capillary tubes could be moved in a vertical direction by vernier screws. The most important part of the experimental programme is the choice of suitable capillaries. The radius of the capillary should be uniform and must be known exactly. A mercury pellet was accurately weighed and its length at different positions in the capillary was measured to check whether the bore was uniform. The ellipticity of the capillaries was checked by measuring the diameter in four different places with a travelling microscope accurate to $0\cdot01$ mm, the capillaries being rejected if any two diameters differed by more than twice the amount.

The capillary tubes and the vessel were initially cleaned with a mixture of nitric acid and ethanol, rinsed with hot detergent solution and then several times with doubled-distilled water (Wilkinson *et al* 1979). The capillaries were not dried as they had to be initially wetted by water. The organic liquids were of Fluka Puriss grade; water was distilled in a quartz still. The differential capillary height was measured using a cathetometer (accurate to $0\cdot01$ mm) which was also used to check the verticality of the capillary tubes in two mutually perpendicular directions. The equipment was surrounded by a water bath controlled to $0\cdot1°$ C. The experimental procedure adopted depended on whether the organic liquid was lighter or heavier than water.

3·1. *Organic liquid lighter than water*

Water was slowly poured into the vessel till the menisci rose through the capillaries, finally filling a small portion of the reservoir to which the capillary tubes
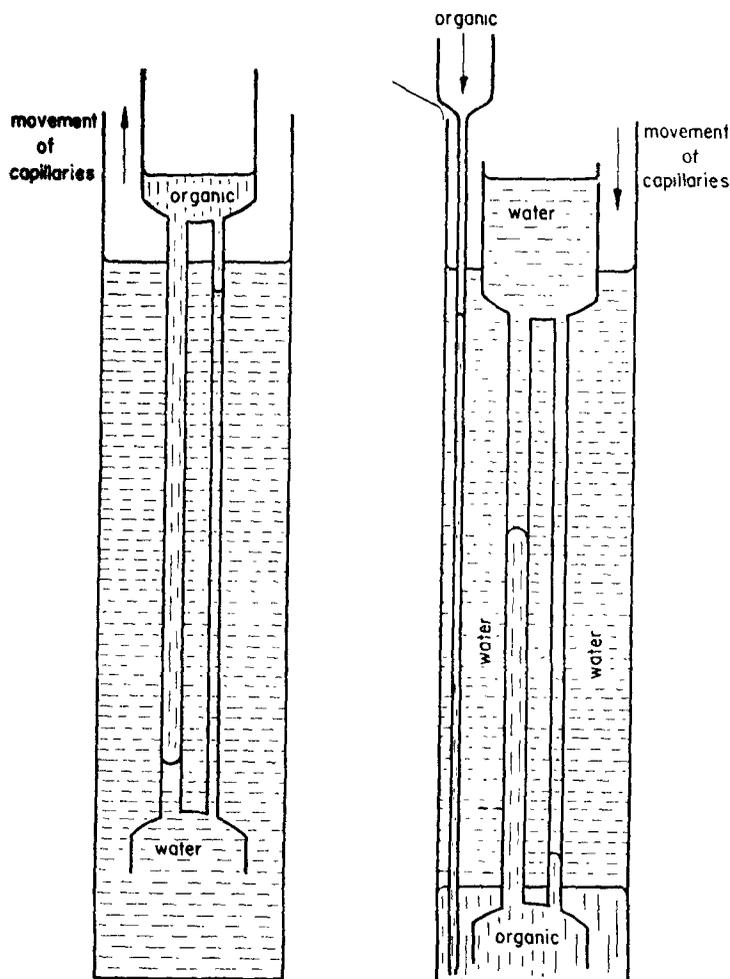
Figure 3. Measurement of interfacial tension using differential capillary rise : (*a*) organic phase lighter than water. (*b*) organic phase heavier than water.

were fused, as shown in figure 3a. This ensured that the capillaries were wet by water before the organic liquid was admitted (Richards and Carver 1921). Reynolds (1921) emphasized that the perfectly cleaned tube must be completely filled with the liquid having the greater surface tension (in general, an aqueous solution) and the other immiscible liquid must travel continuously in one direction only. A small quantity of the lighter organic liquid was then added to the upper reservoir, the interface still remaining inside this reservoir. The reservoirs and capillary tubes were then moved slowly and continuously upwards so the interface moved down, finally forming two menisci in the two capillaries. The differential height was measured. Measurements were repeated at regular time intervals until the steady state was reached (usually after about 30 min.).

3.2. *Organic liquid heavier than water*

The capillary tubes, reservoirs and vessel were filled with water as before. The organic liquid was then introduced slowly near the bottom of the vessel through

a tube inserted between the reservoir and the vessel wall, as shown in figure 3b. The liquid collected at the base of the vessel until an interface was formed in the lower reservoir. The capillary tubes and reservoirs were then moved slowly downwards so the menisci rose into the capillaries. (The menisci formed in the capillaries were curved upwards, as water wets glass better than the organic liquid used). The differential height was measured. Measurements were repeated at regular time intervals until the steady state was reached.

4. Results

The values of interfacial tension for the different liquids used are given in table 2. The values are quoted at 20° C and represent the average of at least five measurements. The densities of the liquids are taken from the Handbook of Chemistry and Physics (1973–74). The literature values of interfacial tension are taken from the International Critical Tables (1928), except for heptane which is taken from Krynitsky and Garrett (1963). Table 3 gives values of interfacial tension published by different authors. The method may also be used without difficulty for measuring surface tensions, providing the liquid used wets the quartz capillaries, which is the usual case in practice. (Contact angles between 0 and 10° have very little effect on the predicted values). We have measured the surface tension of 16 organic liquids (including water). Five pairs of capillaries with values of R_1/R_2 equal to 0·8445, 0·5014, 0·4275, 0·3495 and 0·3062 were used. These measurements showed that the accuracy increased as the ratio R_1/R_2 decreased, being better than 0·1 dyn/cm for the smallest ratio. We therefore chose a ratio of 0·3062 for the measurement of interfacial tension.

4.1. *Errors*

Differentiating (9) shows that the fractional error in σ is given by

$$\frac{d\sigma}{\sigma} = \frac{d\triangle\rho}{\triangle\rho} + \frac{dg}{g} + \frac{2d\triangle h}{\triangle h} - \frac{2d\triangle H}{\triangle H} \, . \tag{10}$$

Since $\triangle H$ is a function of $R_1/R_2 (= r_1/r_2)$ and $\triangle H/R_1 (= \triangle h/r_1)$ we may write

$$\frac{d\triangle H}{\triangle H} = M_1 \frac{d(r_1/r_2)}{r_1/r_2} + M_2 \frac{d(\triangle h/r_1)}{\triangle h/r_1} \tag{11}$$

Table 2. Experimental values of interfacial tensions of organic liquids against water using pair of capillaries, with $r_1/r_2 = 0.30621$.

System	$\triangle\rho$ g/cm^3	$\triangle h$ cm	$\log_{10}\triangle h/r_1$	σ_{exp} dyn/cm	σ_{lit}[17] dyn/cm
Benzene	0·1195	11·596	2·5110	34·94	35·00 ± 0·05
Tert. butylchloride	0·1562	6·011	2·2257	23·62	23·75
Carbon tetrachloride	0·5958	3·033	1·9286	45·27	45·00 ± 1·0
Diethylether	0·2844	1·518	1·6280	10·73	10·70 ± 0·2
Heptane	0·3152	6·447	2·2561	51·14	50·40—51·4[22]

Table 3. Interfacial tension of various liquids in dyn/cm against water at 20° C (some values are given at 25° C as indicated)

Author	Method	Benzene	Tert. butyl-chloride	Carbon tetra-chloride	Diethyl-ether	Heptane
Landolt—Börnstein (1905)	Reported value	33·6				
Harkins and Humphery (1916)	Capillary rise	34·52				
Harkins et al (1920)	Drop weight	35·03	23·75	43·26		
Harkins and Cheing (1921)	Drop weight	34·96		45·05		
Reynolds (1921)	Capillary rise	34·4		43·8		
Bartell and Miller (1928)	Capillary rise	34·85			10·62 (25° C)	
		34·94			10·74 (25° C)	
Harkins (1928)	Drop weight	35·03	23·75	43·26		
Int. Critical Tables (1928)	Reported value	35·0± 0·05	23·75	45·0± 1·0	10·70± 0·2	
Mack and Bartell (1932)	Double Capillary	35·00 35·03 34·97		43·94		
Bartell et al (1933)	Capillary rise	34·21		43·99		
Andreas et al (1938)	Pendent drop	30·39		44·34	11·05 (25° C)	
Donahue and Bartell (1952)	Pendent drop	34·39		44·19	11·00 (25° C)	
Girifalco and Good (1957)	Calculated	35·0	23·75	45·0	10·7	50·2
Krynitsky and Garrett (1963)	Ring					50·4
						50·4
						51·4
Harkins and Alexander (1965)	Reported value	34·96		45·05		52·55
Padday and Uffindell (1968)	Calculated					53·6
Handbook of Chem. Phys. (1973–74)	Reported value	35·00		45·00	10·7	
Tornberg (1977)	Pendent drop	33·35± 0·06			10·81± 0·10	
Aronson and Princen (1978)	Rotating drop	35·4± 1·0				
Present work	Double capillary	34·94	23·62	45·27	10·73	51·14

where $\quad M_1 = \dfrac{R_1/R_2}{\triangle H}\left(\dfrac{\partial \triangle H}{\partial (R_1/R_2)}\right)\Big|_{\triangle H/R_1}$,

and $\quad M_2 = \dfrac{\triangle H/R_1}{\triangle H}\left(\dfrac{\partial \triangle H}{\partial (\triangle H/R_1)}\right)\Big|_{R_1/R_2}$.

Expanding $d(r_1/r_2)$ and $d(\triangle h/r_1)$, assuming the fractional errors in r_1 and r_2 are both equal to dr/r and taking proper regard of the sign of $d\triangle h/\triangle h$ in (10) and (11) shows that the maximum fractional error in σ may be estimated by

$$\frac{|d\sigma|}{\sigma} = \frac{|d\triangle\rho|}{\triangle\rho} + \frac{|dg|}{g} + 2(1 - M_2)\frac{|d\triangle h|}{\triangle h}$$

$$+ 2(2M_1 + M_2)\frac{|dr|}{r}. \tag{12}$$

The fractional error in g ($= 9 \cdot 80686$ m/s^2 at the ETH Zürich) may be neglected. Densities are known to the fourth decimal place so the error in $\triangle\rho$ is less than $0 \cdot 002$ for interfacial tensions. The density differences lie between $0 \cdot 1195 \cdot 10^3$ and $0 \cdot 5958 \cdot 10^3$ kg/m^3, so the fractional error is from $0 \cdot 0017$ to $0 \cdot 00034$. The height difference $\triangle h$ can be measured to $0 \cdot 01$ mm and the values of $\triangle h$ are between $15 \cdot 18$ and $115 \cdot 96$ mm so the values of $d\triangle h/\triangle h$ lie between $0 \cdot 00066$ and $0 \cdot 00009$. The radius of each capillary was found by weighing a mercury pellet and measuring its length l at different positions with a travelling microscope, the resulting fractional error in r being less than $0 \cdot 0012$.

Values of M_1 were found by varying the value of R_1/R_2 about the experimental value of $0 \cdot 3062$ at the constant values of $\log_{10}\triangle H/R_1$ $1 \cdot 6$, $2 \cdot 1$ and $2 \cdot 6$ (which cover the experimental range) and determining the change in $\triangle H$. Values of M_2 were similarly found by varying the value of $\triangle H/R_1$ about the three values of $1 \cdot 6$, $2 \cdot 1$ and $2 \cdot 6$ of $\log_{10}\triangle H/R_1$ for the constant value of R_1/R_2 of $0 \cdot 3062$. The values of M_1 varied between $0 \cdot 233$ and $0 \cdot 222$ and hence were almost independent of $\triangle H/R_1$. The values of M_2 changed from $0 \cdot 489$ to $0 \cdot 496$ being practically independent of $\triangle H/R_1$.

The fractional error in σ was found by adding together the fractional errors in r, $\triangle\rho$ and $\triangle h$, as indicated in (12). The values of $d\sigma/\sigma$ lie between $0 \cdot 0031$ and $0 \cdot 0027$, corresponding to an absolute error in σ of about $0 \cdot 1$ dyn/cm. Note that these limiting values do not usually occur at the maximum and minimum values of $d\triangle\rho/\triangle\rho$ or $d\triangle h/\triangle h$ has the fractional error in σ is dominated by that in r because of the large multiplying factor $2(2M_1 + M_2)$.

List of symbols

b	radius of curvature at apex of sessile interface
$B = bc^{1/2}$	dimensionless b
$c = \triangle\rho g/\sigma$	constant characterizing physical properties
g	acceleration due to gravity
h	capillary rise
$\triangle h$	differential capillary rise
$H = hc^{1/2}$	dimensionless h
$\triangle H = \triangle hc^{1/2}$	dimensionless $\triangle h$
M_1, M_2	constants
r	radius of tube
$R = rc^{1/2}$	dimensionless r
x	radial distance from axis of symmetry of sessile interface

$X = xc^{1/2}$ dimensionless x

θ angle of inclination of sessile interface to horizontal

ρ density

$\triangle\rho$ density difference

σ interfacial tension

Subscripts

1   value referring to first interface or tube

2   value referring to second interface or tube

90   value where $\theta = 90°$

c contact circle

h heavy liquid

l light liquid

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