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Surface Tension of Mercury on Glass, Molybdenum and Tungsten Substrates

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The surface tension of mercury on a glass substrate has been determined by the sessile drop technique. It was found that the uncorrected value of surface tension varied with changes in the drop diameter in the range from 0.60 to 4.10 cm. From the Worthington equation for curvature a corrected surface tension of 456 dyn/cm was obtained for the 4.1 cm diameter drop, a value which is in reasonable agreement with previous investigations. However, application of a curve fitting procedure to the results from the smaller drops gave a corrected surface tension which was approximately independent of diameter but at a smaller average value of 413 dyn/cm. The surface tension of a 1.20 cm diameter drop was also measured on tungsten and molybdenum substrates and, in general, corrected values larger than on glass were derived. It is suggested that the small corrected values obtained for drops $\leqslant 2.06$ cm in diameter are due to adsorption of impurity from the glass substrate.

1. Introduction

For an infinitely large sessile mercury drop, it can be assumed that there is no curvature at the summit of the drop and that any portion of the circumference is straight. Hence for these conditions the surface tension of an element of unit width at the centre of the drop supports the total horizontal thrust at the maximum diameter. From these concepts the relation:

$$\gamma = \rho g h^2/2 \qquad (1)$$

where γ is the surface tension, ρ is the density and h the distance from the plane of the maximum diameter to the vertex of the drop (fig. 1a) has been obtained [1]. Clearly the use of equation 1 for "small" rather than infinitely large mercury drops will give an appreciable error in the derived value of surface tension. A further complication arises from the qualitative observation [1] that the height of a mercury drop (as measured by h) varies with the diameter, d, of the drop, which will give a range of values of surface tension. This variation was noted and measured by Gibson [2] for water drops, whose results show that equation 1 is appreciably in error for drops less than 12 cm in diameter. However, he found that by using a correction for curvature derived by Worthington [3] a constant value of surface tension was obtained for drops with diameter $\geqslant 4$ cm. Worthington's equation is:

$$\gamma = \frac{\rho g h^2}{2}\left(\frac{1.641(d/2)}{1.641(d/2) + h}\right) \qquad (2)$$

As a result of this work, subsequent determinations of the surface tension of mercury by the sessile drop technique [4, 5], have concentrated exclusively on the measurement of a mercury drop of diameter $\geqslant 4$ cm, with the subsequent use of Worthington's equation to obtain a corrected "absolute" value of surface tension.

An alternative approach to obtaining an "absolute" value of surface tension for a drop with diameter < 4 cm is to characterise more accurately the shape of the drop. Bashforth and Adams [6] proposed a second order differential equation for the drop shape from which they developed a number of numerical solutions. A useful approximation of this approach was developed by Dorsey [7], in which the surface tension can be obtained (involving an error $< 1\%$) from:

$$\gamma = \rho g (0.5d)^2\,[(0.052/f) - 0.12268 + 0.0481f] \qquad \ldots\ldots (3)$$

with

$$f = \frac{2y}{d} - 0.41421$$

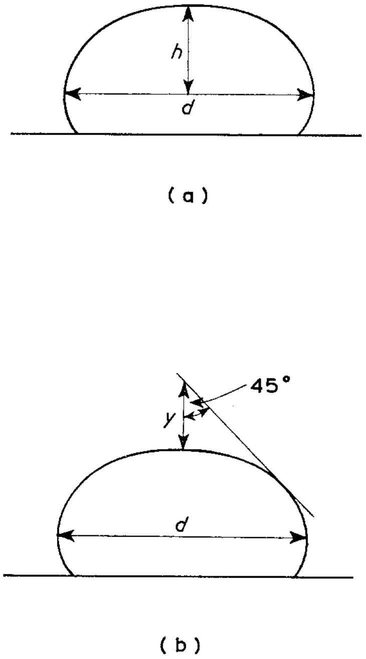

Figure 1 Schematic diagram of mercury drop showing measured dimensions.

where y is the distance from the intersection of two 45° tangents to the top of the drop (fig. 1b). This equation was utilised by Kingery and Humerik [8] in their experiments on water drops and good agreement was obtained with surface tension measurements by other techniques.

Alternative, more complex, curve-fitting procedures have been suggested by Smolders and Duyvis [9], Butler and Bloom [10] and Robertson and Lehman [11], which reduce the fitting error to $\pm$ 0.2% [10].

The objective of the present investigation was not simply to obtain another measure of the surface tension of mercury for one particular condition, but, for the first time, to determine quantitatively the influence of drop size on the derived value of surface tension. Consequently the effect of an increase in drop diameter from 0.60 to 4.10 cm, i.e. encompassing both the "small" and "large" drop situation, on the surface tension was evaluated, utilising both Worthington's and Dorsey's corrections. The Dorsey correction was selected as the curve-fitting procedure because it gives adequate accuracy, in view of the intrinsic experimental error, and requires a relatively small number of measurements. As the previous investigations were made entirely on glass substrates, which were assumed to be inert, these measurements were made on molybdenum and tungsten substrates, as well as on glass.

2. Experimental Procedure

The mercury was contained in a stainless steel chamber with an optically ground quartz window through which the drop could be illuminated and photographed. The chamber was evacuated with an oil free vacuum system consisting of a cryosorbent roughing pump and a "VacIon" diffusion pump. A vacuum of approximately 10^{-8} torr was achieved readily before introduction of the mercury, falling to 1×10^{-6} torr in the presence of the drop. Stainless steel tubing was used, except for a brass liquid nitrogen trap and the connections were mainly metal to metal seals. No grease or oil was employed in any part of the system, as it has been shown that they can have a large effect on the surface tension measurement [4]. The assembly was mounted on a granite block supported on an air cushion to minimise vibration.

Horizontal alignment was sensitively achieved by rotating the specimen chamber first in one direction, and then in the reverse, until the mercury drop just started to move. These limits were measured on a goniometer and the chamber was then adjusted to the mid point of the angle traversed.

There are two principal errors involved in a photographic measurement of drop shape. First, as discussed by Kemball [4] unless the faces of the optical window are parallel to within 15 sec of arc, the wedge angle of the glass introduces an appreciable error in the measurement of the height of the drop. Such an error was avoided by using a window with faces parallel to 5 sec (with a $\frac{1}{4}$ wave transmission figure). Second, unless the distance from the drop to the film is infinitely large the absolute maximum height will not be observed. The error has been analysed by Smolders and Duyvis [9]. From their discussion the following experimental conditions, namely a lens to drop distance of 7 cm, an aperture of 0.8 cm and a drop height of 0.3 cm, were chosen to give an error appreciably less than 1%.

The photographs of the mercury drops which were taken on glass plates to minimise dimensional changes, were measured with a micro-comparator, which could be reproducibly read to 2.5×10^{-4} cm. Hence a typical drop height, h, of 0.3 cm could be measured with an error of

~ 0.1 %. The dimensions measured for each drop were *h*, *d* and *y* (see figs. 1a and b) as required for equations 1, 2, and 3.

The mercury used was "high purity" grade, although precise details of the trace impurity present were not given, and all the drops were taken from one particular batch under identical conditions. Most of the experiments were performed on glass substrates, which were cleaned with nitric acid and rinsed with deionised water. In addition, some measurements were made on molybdenum and tungsten substrates. The metals were of commercial purity and were used both in the degreased and polished conditions (Mo – chemically polished with chromic/sulphuric acid, W – electropolished in sodium hydroxide).

3. Results

For each mercury drop the values of *h*, *d* and *y*, as shown in figs. 1a and b were measured and then substituted into equations 1, 2, and 3, together with values for ρ (13.534 g/cc) [4] and g (981.2 cm/sec^2). The calculated values of surface tension (to the nearest dyn/cm) for a series of mercury drops on a cleaned glass substrate are shown together in table I and are plotted in fig. 2. Successive measurements on the same drop indicated a reproducibility of $\pm$ 1 dyn/cm and there was no significant variation in the measured surface tension with time (for contact times from 30 min (the minimum required for a measurement) to 3 h). Repeating the measurements on different drops of the same size gave variations of $\pm$ 2 and $\pm$ 6 dyn/cm for the surface tension calculated respectively from equations 1 and 2 (i.e. depending on *h* and *d*) and equation 3 (i.e. depending on *y*).

It can be seen that the "uncorrected" surface tension increased with drop diameter to d = 1.72 cm and then decreased slightly for larger drops. In contrast the surface tension derived from Worthington's equation increased progressively with drop diameter, while Dorsey's equation gave an approximately constant value of surface tension for drop diameters $\leqslant$ 2.06 cm.

For one particular diameter (d = 1.20 cm) the mercury drop dimensions were also determined on tungsten and molybdenum substrates (both in the degreased and chemically polished conditions) and the surface tension calculated using Dorsey's correction equation. As it was found that the surface tension of mercury on a molybdenum substrate varied with time of contact, two values were obtained, namely an "initial" value (after 30 min) and an "equilibrium" value (after a time (~ 100 min) when no further change in shape was detectable). Similar values were measured on the tungsten substrate, but the changes in surface tension observed were within the experimental error. The results are summarised in table II.

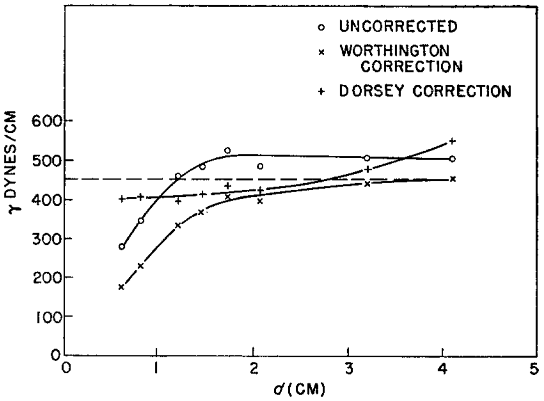

Figure 2 The variation of surface tension of mercury on glass with drop diameter at 25° C.

TABLE I Surface tension of mercury drops on a glass substrate at 25° C

Drop diameter (cm)	Surface tension (dyn/cm)		
	Uncorrected (equation 1)	Worthington's correction (equation 2)	Dorsey's correction (equation 3)
0.60	280	175	402
0.80	346	228	408
1.20	462	333	398
1.45	486	372	414
1.72	526	408	434
2.06	490	400	424
3.20	510	444	480
4.10	508	456	552

TABLE II Surface tension obtained from Dorsey's correction (equation 3) for mercury drops (d=1.20 cm) on glass, Mo and W at 25°C

Substrate	Surface tension (dyn/cm)	
	(a) Initial	(b) Equilibrium
Glass	—	398
Mo (degreased)	456	414
Mo (chem. polished)	465	432
W (degreased)	450	442
W (elect. polished)	445	442

From the table it can be seen that the equilibrium values of surface tension were significantly larger for mercury on the metal substrates (except for Mo (degreased)) than on the glass substrate.

4. Discussion

The uncorrected surface tension obtained from equation 1, which depends entirely on the value of h, has confirmed the assertion [1] that the value obtained is related to the diameter of the drop. The variation of uncorrected surface tension with diameter follows the general form noted for water drops [2], except that the maximum occurs at a smaller diameter. One effect of this finding is that Worthington's correction for curvature should produce a constant surface tension value for mercury at a diameter somewhat less than the 4 cm minimum found for water, and the results provide evidence for a "levelling off" between diameters of 3.20 and 4.10 cm. However, following the procedure of previous investigators [4, 5] the "absolute" value of surface tension would be taken as that derived from the 4.10 cm diameter drop by the Worthington equation, i.e. 456 ± 2 dyn/cm. This value is to be compared with a value of 484 dyn/cm [4, 5] derived for mercury which had been refined to a "high" level of purity. Hence the general agreement between the values is reasonable and the difference between the results can probably be attributed to trace impurities in the mercury used in the present experiments. This result is also comparable with the mercury surface tension derived from other techniques, with for example values of 472, 475 and 484 dyn/cm measured respectively by the drop weight [12], flowing sheet [13] and bubble pressure [14] methods.

Worthington's correction for curvature is not applicable for drop diameters < 3.20 cm as the corrected surface tension was not constant. In contrast, Dorsey's equation gave a corrected surface tension which was approximately constant for drop diameters from 0.6 to 2.06 cm. The Dorsey corrected surface tension was variable for larger drops, which was probably due to the difficulty in accurately locating y by a tangent method, as the drop shape tends to a flat summit.

The "absolute" surface tension of mercury on glass from Dorsey's equation, which is 413 ± 6 dyn/cm, is appreciably different from the value given for the 4.10 cm drop by Worthington's equation. Consequently, it is significant that the initial average value of corrected surface tension determined for a 1.20 cm diameter drop on molybdenum and tungsten substrates was 454 ± 6 dyn/cm, which is in good agreement with the 4.10 cm drop results. The value obtained for mercury on tungsten was approximately independent of the nature of the surface and time of contact indicating that there was no transfer of impurity from the tungsten to the mercury. However, the surface tension of mercury on molybdenum decreased appreciably with time, particularly for the substrate which was degreased, but not chemically polished. This effect can be attributed to adsorption of some impurity from the substrate into the mercury, producing slight wetting of the surface and a small reduction in surface tension. As the equilibrium value for mercury on molybdenum was similar to that of mercury on glass it is reasonable to suggest that some adsorption of trace impurity from the glass substrate also occurred. Such adsorption must have occurred during the 30 min period which elapsed before the first reading was completed. It is suggested that the adsorption of a small amount of impurity from the substrate contributed to the difference between the corrected surface tension values obtained on 4.1 cm diameter and 1.20 cm diameter drops, as the large drop, which was about ten times the volume of the small drop, probably contained a smaller *concentration* of impurity and hence had a larger surface tension. As the corrected surface tension derived for the 4.10 cm diameter drop on glass (456 dyn/cm) is in agreement with that measured for the 1.20 cm drop on molybdenum or tungsten, it appears that at this size the effect of adsorbed impurity from the glass substrate is negligible.

5. Conclusions

(1) The uncorrected surface tension of mercury on glass depends on the diameter of the drop.

(2) For a 4.10 cm diameter mercury drop, the Worthington equation gives a corrected surface tension of 456 ± 2 dyn/cm.

(3) For mercury drops in the diameter range 0.60 to 2.06 cm, the average Dorsey corrected surface tension is 413 ± 6 dyn/cm.

(4) The initial corrected surface tension of a 1.20 cm diameter mercury drop on a molybdenum or tungsten substrate is larger than a similar size drop on glass and in good agreement with the 4.10 cm diameter drop result. The value for mercury on molybdenum decreases to an equilibrium value (due to impurity adsorption) which is about the same as the mercury on glass

value.

(5) It is concluded that impurity is adsorbed from the glass substrate into the mercury. The difference between the corrected values for "large" and "small' mercury drops on glass is attributed to different concentrations of adsorbed impurity.

(6) It is concluded that tungsten is a more suitable substrate than glass for the determination of surface tension by the sessile drop technique.

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References

1. R. S. BURDON, "Surface tension" (Cambridge University Press, 1949).
2. H. GIBSON, *Proc. Roy. Soc. S. Aust*, **56** (1932) 51.
3. A. M. WORTHINGTON, *Phil. Mag.* **20** (1885) 51.
4. C. KEMBALL, *Trans. Faraday Soc.* **42** (1946) 526.
5. M. E. NICHOLAS, P. A. JOYNER, B. M. TESSEM, and M. D. OLSON, *J. Phys. Chem.* **65** (1961) 1373.
6. F. BASHFORTH and J. C. ADAMS, "An attempt to test the theories of capillary action" (Cambridge University Press, 1883).
7. N. E. DORSEY, *J. Washington Acad. Sci.* **18** (1928) 505.
8. W. D. KINGERY and M. HUMERICK, *J. Phys. Chem.* **57** (1953) 359.
9. C. A. SMOLDERS and E. M. DUYVIS, *Rec. Trav. chim.* **80** (1961) 635.
10. J. H. BUTLER and B. H. BLOOM, *Surface Sci.* **4** (1960) 1.
11. W. M. ROBERTSON and G. W. LEHMAN, *J. Appl. Phys.* **39** (1968) 1994.
12. T. IREDALE, *Phil. Mag.* **45** (1923) 1088.
13. H. O. PULS, *ibid* **22** (1936) 970.
14. R. C. L. BOSWORTH, *Trans. Faraday Soc.* **34** (1938) 1501.

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