[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Surface and Interfacial Tension of Mercury by the Sessile Drop and Drop Weight Methods

BY H. BROWN

A reappraisal of the value of the surface tension of mercury is desirable considering the variation of over one hundred dynes/cm. in even the recently published values (from about 400 to over 500 dynes/cm. for the value at ordinary temperatures.[1]) Nor does the interfacial tension value of mercury in contact with the liquid most commonly measured, water, show much better agreement (370–427 dynes/cm.). This wide divergence in results is still largely unexplained. The greatest disagreement exists in the surface tension values as obtained by the use of the sessile drop method. It was thought that some light would be thrown on the true value of the surface tension of mercury by making determinations with the sessile drop method and the drop weight method of the following quantities: (1) the surface tension of mercury in air and *in vacuo,* (2) the surface tension of mercury in air saturated with water vapor and in saturated water vapor alone and (3) the interfacial tension of mercury in contact with water. It was found from the relation of these quantities that certain of the published values for the surface tension of mercury in air or *in vacuo* cannot be correct.

In this work a new modification of sessile drop apparatus was used which permitted the convenient use of drops of mercury of different diameters, and allowed thorough cleaning of the apparatus before each set of determinations. The optical system used in making the measurements of the drop was set up with strict attention to accurate leveling of the microscope for each of the different vertical and horizontal settings. This accurate leveling is of the same order of importance as the means used in defining the summit and the plane of greatest section of the drop. In view of the varied results which have been obtained with the extensively used sessile drop method, it is perhaps superfluous to add that without strict attention to the many sources of systematic error the method is unreliable.

Discussion of the Methods

Sessile Drop Method.—The surface tension is most commonly determined from a sessile drop by measurements of the height h of the drop from the summit to the plane of greatest cross-section, and the radius r of this section. The theory of the calculation of surface tension from such measurements has been the subject of many mathematical investigations since the time of Laplace.[2] Recently an important critical analysis of the theory of the sessile drop method has been made by Porter.[3]

For an infinitely large drop ($r/h \doteq 0$) the formula is

$$\sigma = {}^1/_2 h^2(d_1 - d_2)g \qquad (1)$$

where σ is the surface or interfacial tension, d_1 the density of the drop, d_2 the density of the fluid in which the drop is measured, and g the gravitational constant. Surface tension of drops for which the curvature at the top is still negligible (for mercury, drops of $r > 2$ cm.) may be calculated from the formulas given by Worthington[4] or Ferguson.[5] Worthington's formula is:

$$\sigma = \frac{1}{2}h^2(d_1 - d_2)g\,\frac{1}{1 + 0.609\,(h/r)} \qquad (2)$$

For mercury drops of less than 2 cm. radius the curvature of the top of the drop is not negligible and the correction terms are more complex and uncertain.[3] But for drops of mercury at ordinary temperatures of less than 0.6 cm. radius, the tables of Bashforth and Adams apply, and then very exact calculations of the surface tension can be made, provided of course that the experimental data are exact. Porter has put the necessary transformations from the Bashforth and Adams tables in a form that emphasizes the important properties of these corrections. It was found that the corrections for the curvature of the top cancel those for the sides when $h^2/r^2 = 0.25$,[6] and the simple formulation (1) again holds. The curvature, however, changes rapidly with

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(1) For a review of earlier work see Quincke, *Ann. Physik.* (*Wiedemann*), **61**, 267 (1897), and Sauerwald and Drath, *Z. anorg. allgem. Chem.*, **154**, 79 (1926); and for recent work see Burdon, *Trans. Faraday Soc.*, **28**, 866 (1932).

(2) Bakker, "Kapillarität und Oberflächenspannung," 1928, p. 99.

(3) Porter, *Phil. Mag.*, [7] **15**, 163 (1933).

(4) Worthington, *ibid.*, **20**, 51 (1885).

(5) Ferguson, *ibid.*, **25**, 507 (1913).

(6) According to the values given in Table 11 of Porter's paper $h^2/r^2 = 0.2485$ would appear to be more accurate.

drops of these dimensions, and accurate measurements of the radius of the plane of greatest section of the drop must be made.

The apparatus used in this work made possible the use of mercury drops with negligible curvature at the top, and those which come under the scope of the tables of Bashforth and Adams.

Drop Weight Method.—The method as standardized by Harkins and Brown[7] was employed. The correction terms (the $f(r/a)$ values obtained experimentally by Harkins and Brown) which apply for the tips used in dropping mercury are derived from the left-hand branch of the correction curve, and it is for this part of the curve that the theoretical correction values of Lohnstein agree with those experimentally determined.

Description of Apparatus

Sessile Drop Apparatus.—Two forms (Figs. 1 and 2), constructed entirely of Pyrex glass, were used, though the principal part WTRW of each was essentially the same. The auxiliary parts, consisting of mercury reservoir and connections, differed, making apparatus 1, Fig. 1, convenient for interfacial tension measurements, and apparatus 2, Fig. 2, for work in a high vacuum. It should be noted that for work at varying pressures all ground glass joints leading to the mercury drop should be eliminated, because of the possible variation of the size of the drop due to loosening of the joints with change of pressure. Each apparatus possessed two plane windows W, 50 mm. in diameter, which were optically available almost right up to the seal. This was accomplished by melting (shrinking) the tube down over the edge of the circular windows, thus sealing in the disks without blowing on the glass. The two windows permitted the measurement of the height of the drop through one and the width through the other. This was of distinct advantage in the carrying out of the measurements.

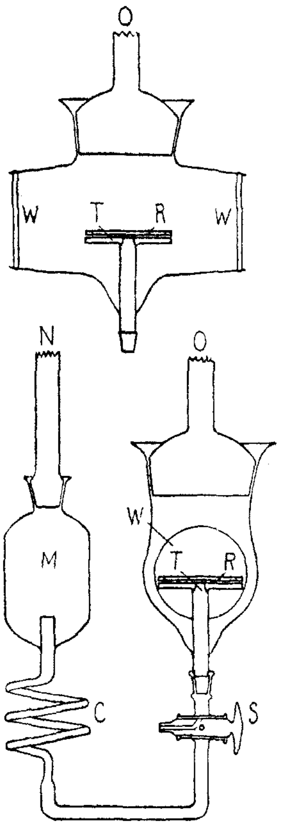

Fig. 1.—Sessile drop apparatus for interfacial tension of mercury.

The drops were allowed to form in circular glass rings R about 3 mm. thick. These rings were cut from ordinary Pyrex window glass by using slotted brass cylinders of different diameter (wall about 1 mm. thick) as drills, with 200 mesh carborundum as the grinding powder and water as lubricant, the brass cylinders being rotated in a drill press. These rings were then ground plane with fine carborundum powder, leaving a sharp-edged inner bore. Rings of inside bore of about 9 mm. and 44 mm. were used. The desired ring was placed on the plane top of the table T by means of clean forceps.

Apparatus 1 was mounted on a heavy iron stand provided with leveling screws, and table top T was leveled by observation of a mercury drop on it, the glass coils C giving much flexibility to the apparatus. When everything was in readiness, the mercury was allowed to flow from the reservoir M into the ring R and bulge slightly over the edge, and by means of the stopcock S further flow was stopped. After measurements on a particular drop, the mercury surface could be renewed by overflowing or by moving the ring to one side by means of a long clean glass rod, pushing the drop completely off—the latter method assuring a completely fresh surface for the next drop.

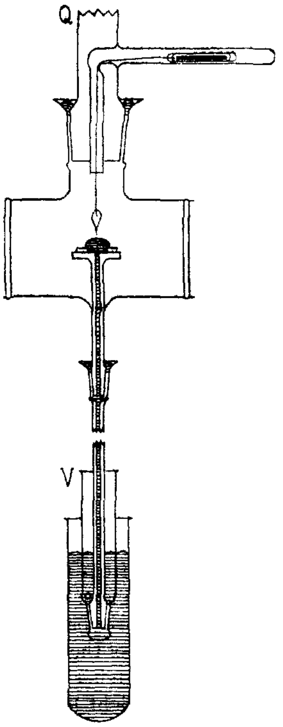

Fig. 2.—Sessile drop apparatus for surface tension of mercury *in vacuo*.

In vacuum apparatus 2 the mercury in the capillary rose to a height equivalent to the atmospheric pressure less the capillary depression. The height of the mercury in the reservoir was adjusted by means of a ratchet and pinion until the mercury began to flow into the glass ring, and then by means of the submerged valve V on the end of the siphon, the final adjustment of the size of the drop to a slight bulging over the inner bore was made. The evacuation of the apparatus through Q was done by means of a Langmuir pump with liquid air surrounding the trap.

Before each set of determinations the principal part of each apparatus was placed in a warm chromic acid bath, later thoroughly washed with water, and finally steamed and dried in an oven at 150°.

Drop Weight Method.—The apparatus was the one previously described in work on interfacial tension measurements with mercury.[8] The same dropping tip, diameter 0.1242 cm., was again used.

Purification of Liquids

Mercury.—Redistilled mercury was shaken repeatedly with dilute nitric acid to a gray mercury emulsion and

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[7] Harkins and Brown, THIS JOURNAL, **41**, 499 (1919).

[8] Bartell, Case and Brown, *ibid.*, **55**, 2419 (1933); **55**, 2769 (1933).

then washed thoroughly with water; next it was dried and filtered through a hard filter with a pin-point opening. It was then redistilled twice in a current of air at low pressure according to the method of Hulett.[9] In each apparatus the mercury drop was siphoned from the interior of the mercury in the reservoir.

Water.—Ordinary distilled water was distilled from alkaline permanganate through a block tin condenser. It was then redistilled in an all-quartz still, a portion of the distillate being allowed to escape as steam throughout the distillation.

Method of Measurement

The height and diameter of the sessile drop were measured separately through the two windows by means of two microscopes of 150 mm. working distance and 15-fold magnification. The height was measured in the following manner. The top of the drop was defined in apparatus 1 by approaching the surface with a pointed glass rod which passed through O and was connected outside to a fine adjusting screw. In apparatus 2 a magnetically controlled pointer was used; an iron nail was sealed in a glass capsule and the latter connected by a fine platinum wire to a bob made from glass rod and which was lighter in weight than the nail (Fig. 2). The plane of greatest section was obtained by placing a galvanometer lamp at more than a meter distant from the drop. The single wire filament was put in the plane of maximum diameter of the drop by the use of a telescope, focusing first on the drop and then on the filament of the lamp, adjusting the latter, which was mounted on a ratchet and pinion, until all were in the same plane. The height h from the fine line image of the filament at the equator of the drop to the summit was then measured with the microscope. This microscope was mounted on a cathetometer stand, the base of which was provided with two levels. A level with scale divisions equivalent to three seconds of arc was used on the microscope *tube* itself. The diameter was measured with a microscope mounted in a comparator frame.

Discussion of Results

It was found for the interfacial tension of mercury in contact with water that each method gave easily duplicable results, and the values obtained with the two methods were in agreement within about 0.3% which is also about the extent of the deviations between some of the individual measurements in each method. The average value at 25° of 374.2 by the sessile drop method and 374.5 by the drop weight method are in good agreement with the value 374.8 obtained by Harkins and Grafton[10] at 20°.

The value 473, obtained for the surface tension of mercury in a vacuum in which the pressure was lower than could be detected with a McLeod gage of 150-cc. capacity, was also duplicable easily within less than 0.3%. This value is in good agreement with the 475.1 at 25° obtained by Harkins and Ewing[11] with the drop weight method in a similar high vacuum.

The results obtained for the surface tension of mercury in contact with air and with water vapor on the other hand were rather complicated. In air that is dry and free from organic vapors, the observation of a sessile drop showed that the surface tension of the mercury remains fairly constant, dropping only slowly over several hours (4 or 5 dynes overnight).[12] If the air is not dried, the surface tension starts dropping almost immediately and much more rapidly than in dry air. The initial values in both cases are, however, the same as obtained in a high vacuum, that is, within experimental error. By the drop weight method the surface tension in ordinary air free from organic vapors was consistently 471.5, the dropping time being about five minutes for each drop. After these results were obtained the sessile drop method was used for measurements in the presence of water vapor, but in the absence of air. This was accomplished by sealing in a trap containing water into the vacuum line, surrounding the trap with carbon dioxide snow, and then pumping the system out. It was found that the water vapor alone did not lower the surface tension of mercury until vapor pressures approaching saturation were attained. When the drops were formed in the saturated water vapor the value 447 was obtained, but the observation of the same drop showed that it continued to fall slowly, and in the course of a day would fall nearly to 430. The surface tension was also measured in air saturated with water vapor, and it was found from the observation of a sessile drop that the surface tension fell rapidly from the initial value of about 447 to 430 and lower in the course of half an hour, and continued to fall on longer standing. Using the drop weight method in air saturated with water vapor, the average value obtained in eight determinations was about 447, with a dropping time of about five minutes. The consistency of the results with this system was less than with any other system previously used with the drop weight method, the results being more often slightly higher than 447 than lower.

The interesting phenomena occurring in air and water vapor deserve a separate quantitative study, but the results available at present seem to

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[9] Hulett, *Phys. Rev.*, **33**, 307 (1911).

[10] Harkins and Grafton, This Journal, **42**, 2534 (1920).

[11] Harkins and Ewing, *ibid.*, **42**, 2539 (1920).

[12] Observed first by Burdon, *Trans. Faraday Soc.*, **28**, 866 (1932).

be well enough defined to admit of at least a qualitative explanation on the basis that mercury undergoes surface oxidation very slowly, if at all, in dry air; but that in moist air surface oxidation does occur, or takes place at a much more rapid rate than in dry air. Furthermore, the oxidation of the surface evidently can lower the surface tension of mercury more than can a continuous film of water, and this is probably the reason that water does not spread on a mercury surface that has been exposed to ordinary clean air (free from organic vapors which readily lower the surface tension of mercury). The surface oxidation occurring in the presence of water vapor would also explain the irreversible adsorption effects often noticed in studies of the adsorption on the surface of mercury,[13] when using methods like the sessile drop, in which the mercury surface remains in contact with the gas atmosphere for a much longer time than in the drop weight method. The latter time difference is also probably often the cause of the apparent difference in results sometimes obtained between a static and a dynamic method with mercury.

These observations are in accord with the observations made some time ago by Macaluso,[14] who showed that in the absence of moisture, the well-known gray pellicle of lower oxide does not form on mercury in contact with air, and also that water vapor alone does not give a gray pellicle, but that with a mixture of the two, oxidation takes place, forming a pellicle of oxide. Macaluso compared this action to the difference in action on mercury of an aqueous solution of hydrogen chloride when in the presence of air, and when in the complete absence of air. In the first case a white film of mercurous chloride is formed, and in the second case no visible film is detected. These phenomena could perhaps be followed delicately by a surface tension study, though great difficulties would probably be met in the complete drying and degassing of the apparatus.

It is a fact, observed first by Quincke, that water spreads on a fresh clean mercury surface, and this is an excellent criterion of the cleanliness of a mercury surface. From this observation, and from the fact that no value less than about 375 has been reported for the interfacial tension of mercury against water by any method, it follows thermodynamically that the surface tension of a fresh clean mercury surface cannot be less than about 447 at ordinary temperatures (the sum of 375, the interfacial tension and 72, the surface tension of water); that is, it cannot be less than the value obtained for the surface tension of mercury in saturated water vapor.[15] This, it seems, definitely eliminates the values below 447 that have been obtained by some workers for the surface tension of mercury *in vacuo*.

SUMMARY OF THE INTERFACIAL AND SURFACE TENSION VALUES OBTAINED FOR MERCURY AT 25°

(A) By the Sessile Drop Method[a]

Fluid against the mercury	r, cm.	h, cm.	σ dynes/cm.
Water (liq.)	0.4950	0.2466	373.6
	2.26	.2554	374.8
Satd. water vapor alone	0.5185	.2595	447
Air	.5340	.2668	472.1
	2.26	.2769	473.2
Vacuum	0.5350	.2670	472.9

(B) By the Drop Weight Method[b]

	M uncorr. drop wt., g.	$f(r/a)$	
Water (liq.)	0.1162	0.7225	374.5
Satd. water vapor in air	.1293	.7270	447
Air	.1368	.7291	471.5

[a] The values were calculated for the large sessile drops, $r = 2.26$ cm., with Worthington's formulation. The small drops were, in the cases cited above, adjusted by the ring R and by the aid of stopcock S (Fig. 1) or the valve V (Fig. 2) to conform accurately to the condition $h^2/r^2 = 0.249$, so that the simple formulation (1) applied. Other sizes of small drops were more conveniently used.

[b] The $f(r/a)$ values were obtained from values given by Harkins and Brown in Tables I, II and the recommended Table VIII, and not from Table IX. In their Table IX, the value for $f(r/a)$ of 0.7256 for $r/V^{1/3} = 0.30$ does not agree with the value shown in their Fig. 5, the value in the latter being somewhat less than 0.725. In our previous paper[8] values from Table IX were used, but the difference is not appreciable in any cases other than possibly with water vapor, because the corrections were so nearly the same for all the liquids and vapors used.

Finally it is well to compare the results obtained *in vacuo* and in air with some of the recent results obtained by other investigators. Harkins and Ewing[11] obtained 475 *in vacuo* at 25°, and Iredale[16] obtained practically the same result, also using the drop weight method. Burdon[12] has obtained values between 475 and 480 in air and *in vacuo*, using an all-quartz sessile drop apparatus, though he accepts the value 488 that he also obtained. Values of 436[17] at 20°, 515[18] at

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(13) Iredale, *Phil. Mag.*, **49**, 603 (1925).

(14) Macaluso, *Gazz. chim. ital.*, **13**, 485 (1883).

(15) Brown, This Journal, **55**, 4521 (1933).

(16) Iredale, *Phil. Mag.*, **48**, 177 (1924).

(17) Kernaghan, *Phys. Rev.*, **37**, 990 (1931).

(18) Cook, *ibid.*, **34**, 513 (1929).

31°, and 500[19] at 16.5° for the surface tension of mercury *in vacuo*, however, have also been obtained recently with the sessile drop method. It would seem, however, that Burdon has taken the most precautions, testing his experimental set-up by measurements of the surface tension of water in paraffin dishes. Nevertheless, the recent results that have been reported with the maximum bubble pressure method, a method which, unlike the sessile drop method, has given consistent results in the hands of different investigators as well as the same investigator, indicate values between 470 and 480 for the surface tension of mercury in dry gases. R. C. Brown[20] obtained 472 at 18° using glass jets and 477 using platinum jets, with nitrogen; Sauerwald and Drath[21] obtained 473 at 19° using silica jets with carbon dioxide; and Bircumshaw[22] obtained 480 as his highest value at 20°, using hydrogen.

I wish to express my thanks to Professor F. E. Bartell and Professor L. O. Case for encouragement and advice.

Summary

A new modification of sessile drop apparatus has been used for the determination of the surface and interfacial tension values of mercury. The results obtained with large flat drops and with small ones were found to be in good agreement with those also obtained by the drop weight method. The following are the main results: (1) for the interfacial tension against water, 374.3 dynes/cm. at 25°; (2) for the surface tension of mercury in dry air and *in vacuo*, the same value within experimental error of about 0.3%, 473 at 25°. (3) It was shown thermodynamically that the surface tension of mercury *in vacuo* has to be at least as high as 447 at 25°. This eliminates some of the values obtained by previous workers. (4) On the basis that the surface oxidation of mercury in air takes place only in the presence of water vapor, some of the perplexing phenomena often observed with mercury can be explained, such as irreversible adsorption effects, and the difference in results sometimes obtained with a static and a dynamic method.

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[19] Bradley, *J. Phys. Chem.*, **38**, 231 (1934).

[20] Brown, *Phil. Mag.*, [7] **6**, 1044 (1928).

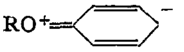
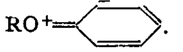
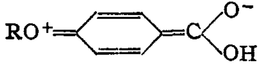
[21] Sauerwald and Drath, *Z. anorg. allgem. Chem.*, **154**, 79 (1926).

[22] Bircumshaw, *Phil. Mag.*, [7] **12**, 596 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Anomalous Strength of Salicylic Acid

BY G. E. K. BRANCH AND DAVID L. YABROFF

The hydroxyl and alkoxyl groups are negative since they increase the strength of a saturated aliphatic acid when substituted on the α-carbon atom. The negativity factor thus tends to make the hydroxy- and alkoxybenzoic acids stronger than benzoic acid, and to have the ortho, meta, para order of decreasing strengths. Because of the unshared electron pairs on the oxygen atom, there is a resonance that tends to decrease the strengths of the hydroxy and alkoxy aromatic acids, especially the ortho and para compounds. The resonating forms that decrease the strength are  and . This acid-weakening resonance is still further enhanced when an ortho or para acidic group can combine with the negatively charged atoms of a quinoidal form. This theory has been used by Ingold[1] to explain the weakness of *p*-methoxybenzoic acid, and by Branch, Yabroff and Bettman[2] to explain the weakness of *o*- and *p*-phenetylboric acids. In the benzoic acid derivative the quinoidal form involving the carboxyl group is , and a similar form is possible in an ortho compound.

That *p*-hydroxybenzoic and *p*-methoxybenzoic acids are definitely weaker than benzoic acid shows that the resonance is an important factor. Since the negativity of the hydroxyl group is not great, this theory would lead one to suppose that *o*-hydroxybenzoic (salicylic) and *o*-methoxybenzoic acids should be weaker or, at most, only slightly stronger than their meta isomers. This deduction is entirely erroneous, however, in the case of salicylic acid and other *o*-hydroxybenzoic acid derivatives. In water salicylic acid (*Ka* =

[1] Ingold, *J. Chem. Soc.*, 1120 (1933).

[2] Branch, Yabroff and Bettman, THIS JOURNAL, **56**, 937 (1934).