

# THE MEASUREMENT OF SURFACE TENSION BY MEANS OF SESSILE DROPS

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## 1. Introduction

THE main object of this paper is to describe a technique for the production and measurement of sessile drops, which offers a convenient and accurate method of measuring surface tension. Although the method has been known in principle for many years, its possibilities have not hitherto been fully exploited, for the following reasons:

(1) Drops have usually been formed on a flat plate, which limits the application of the method to cases where an angle of contact greater than  $90^\circ$  can be realized.

(2) It is difficult to form drops on a plate of reproducible size, and still more difficult to ensure freedom from contamination. The method has thus compared unfavourably with, *e.g.*, the maximum bubble-pressure method, where a fresh surface is formed immediately before each observation.

(3) The elementary text-book theory applies only to a drop of infinite, or at least very large radius, and until recently there have been very few attempts to develop the theory of small drops. The theory available to the earlier workers was wholly inadequate.

For these reasons the sessile drop method, though familiar as a laboratory exercise, has seldom been used in exact work. Sieg, in 1887, obtained the value  $74.3$  dyn./cm. for the surface tension of pure water at  $20^\circ$  C., from the measurement of sessile drops. This value is now known to be in error by about  $1\frac{1}{2}$  units, which gives an idea of the magnitude of the uncertainties involved. In the present modification of the method we consider that the difficulties have been largely overcome.

## 2. Theory

The form of a liquid surface depends on the fundamental capillary equation

$$p_1 - p_2 = a(1/R_1 + 1/R_2), \quad (1)$$

where  $p_1 - p_2$  is the pressure difference across the surface,  $\alpha$  the surface tension, and  $R_1, R_2$ , are the principal radii of curvature. For a sessile drop, formed in air saturated with the vapour of the liquid, this becomes

$$\alpha (1/R_1 + 1/R_2) = gz(d_1 - d_2) + A, \quad (2)$$

where  $z$  is the depth below the uppermost point,  $d_1$  the density of the liquid and  $d_2$  that of the saturated air, and  $A$  is a constant depending on the size of the drop and having the value zero for an infinitely large drop. Introducing  $x$  as a horizontal co-ordinate and taking the uppermost point as origin, the equation may be put in the form (*vide* Adam, 1941, p. 365):

$$\frac{1}{\rho/b} + \frac{\sin \phi}{x/b} = 2 + \beta \frac{z}{b}, \quad (3)$$

where  $\phi$  is the inclination of the surface at any point to the horizontal,  $\rho$  the radius of curvature in the vertical section at that point,  $b$  the radius of curvature at the origin, and  $\beta$  is the ratio  $2b^2/a^2$ ,  $a^2$  being the capillary constant defined by

$$a^2 = 2\alpha/g(d_1 - d_2). \quad (4)$$

Equation (3) cannot be integrated in finite terms, but a numerical solution was given by Bashforth and Adams (1883) for surfaces of revolution. Their tables give the values of  $x/b$ ,  $z/b$ , and  $V/b^3$  for given values of  $\phi$  and  $\beta$ ,  $V$  being the volume between the origin and a horizontal plane at the level  $z$ . Nearly all studies of the theory of surface tension measurements have been based on Bashforth and Adams' tables. Unfortunately the tables are out of print and very rare, and no copy has been available to us for the present work.

In experiments with sessile drops, the quantities which it is practicable to measure are  $h$ , the height of the drop measured from its equatorial plane, and  $r$ , its radius in that plane. For a very large drop we have the simple relation

$$a^2/r^2 = h^2/r^2 \quad (5)$$

from which  $a^2$  is at once found. A formula equivalent to this is used in the well-known experiment with mercury ("Quincke's method") usually to be found in laboratory courses. Even to secure 1% accuracy with this simple formula, it can be shown that  $h/r$  must not exceed 1/60, which means an impossibly large drop of at least 24 cm. radius for water, and 16 cm. for mercury. For smaller, but still approximately 'flat' drops, formulæ have been given by Worthington (1885), Fergusson (1913), and Rayleigh (1915). These formulæ enable  $a^2$  to be obtained with fair accuracy for values of  $h/r$  less than about 0.18. This means, for water, a radius greater than 2.2 cm. and for mercury, 1.5 cm.

Smaller drops have been considered by Porter (1933). He gives a table of corresponding values of  $\sigma^2/r^2$  and  $h^2/r^2$  for values of  $h/r$  from 0.457 upwards. These are obtained directly from Bashforth and Adams' tables, and are therefore exact, at least to the fifth figure. The gap between Rayleigh's formula and the B. and A. values is then filled by an empirical equation, adjusted to fit the known points as closely as possible. His proposed equation (expressed in the notation of the present paper) is

$$\sigma^2/r^2 - h^2/r^2 = -0.6094(1 - 4h^2/r^2)h^3/r^3. \quad (6)$$

Unfortunately this does not fit accurately the B. and A. values which Porter himself quotes. In a later paper (1938) while not admitting this explicitly, he gives a modified curve, which is equivalent to a formula with slightly changed values of the constants.

According to Porter's equation, the simple relation (5) holds exactly for  $h/r = 0.50$ . In the later paper, this is corrected to 0.498. Porter recommends that all measurements should be made on drops which have a value of  $h/r$  close to this. The correction to equation (5) is then small, and may be obtained from his table. The corresponding radii of the drop would be about 7.7 mm. for water, and 5.4 mm. for mercury.

In the present work we have thought it advisable to work with drops of a slightly larger radius, falling entirely within the range of the B. and A. values quoted by Porter. If this is to take its place as one of the standard methods, an accuracy approaching 1 in 1000 must be aimed at. There is no means of knowing whether Porter's curve is of this accuracy over the whole range.

We have therefore fitted an empirical equation, of the same form as Porter's, to the standard B. and A. values which he gives. The new equation is

$$\sigma^2/r^2 = h^2/r^2 - 0.67338(h/r)^3 + 2.71434(h/r)^5. \quad (7)$$

The five standard values between  $h/r = 0.46$  and  $h/r = 0.56$  fit the new equation with residuals which in no case exceed 1 in 1,250. We believe, therefore, that the equation has the required accuracy over this range. It reduces to the simple equation (5) for the value  $h/r = 0.498$ , in agreement with Porter's revised value. Since the equation agrees in form with Porter's equation, which was designed for lower values of  $h/r$ , we consider that the new equation may be extrapolated to slightly smaller values with safety. On this basis we have calculated  $\sigma^2/r^2$  for values of  $h/r$  from 0.446 to 0.558, at intervals of 0.002. Intermediate values may be read off by direct interpolation. The results are given in Table I, and all our observations have been reduced by the use of this table.

TABLE I

$h/r$	$a^2/r^2$	$h/r$	$a^2/r^2$	$h/r$	$a^2/r^2$
0.446	0.18708	0.484	0.23000	0.522	0.28190
0.448	0.18914	0.486	0.23249	0.524	0.28492
0.450	0.19123	0.488	0.23501	0.526	0.28797
0.452	0.19333	0.490	0.23755	0.528	0.29105
0.454	0.19546	0.492	0.24012	0.530	0.29416
0.456	0.19760	0.494	0.24271	0.532	0.29730
0.458	0.19977	0.496	0.24533	0.534	0.30048
0.460	0.20196	0.498	0.24798	0.536	0.30369
0.462	0.20417	0.500	0.25065	0.538	0.30693
0.464	0.20642	0.502	0.25335	0.540	0.31020
0.466	0.20866	0.504	0.25608	0.542	0.31351
0.468	0.21094	0.506	0.25883	0.544	0.31685
0.470	0.21324	0.508	0.26162	0.546	0.32022
0.472	0.21557	0.510	0.26443	0.548	0.32363
0.474	0.21792	0.512	0.26727	0.550	0.32707
0.476	0.22028	0.514	0.27014	0.552	0.33055
0.478	0.22268	0.516	0.27303	0.554	0.33407
0.480	0.22510	0.518	0.27596	0.556	0.33762
0.482	0.22754	0.520	0.27892	0.558	0.34121

### 3. Experimental Arrangements

Drops are formed conveniently by means of the apparatus shown in Fig. 1. The liquid is contained in a wide tube  $T$ , connected by a capillary  $A$  to a vertical tube  $V$ .  $B$  is a cylindrical brass ring cemented to the upper end of the tube  $V$ . When the clip  $C$  is opened liquid flows through the system under gravity, and a drop is formed on the ring  $B$ . The capillary serves to reduce the rate of flow, so that the drops form slowly. With water, the complete process takes 25 sec. or more, depending on the pressure, and it may be stopped at any stage by closing the clip.

The various stages of formation are shown in Fig. 2. A very remarkable 'overhang' can be attained before the drop runs over. During the early stages the contact angle is variable up to about  $90^\circ$ , but this has no special significance. When the drop reaches the edge of the ring it begins to bulge out, and the apparent contact angle increases to  $180^\circ$  before the drop collapses. This is due to the reluctance of the line of contact between the liquid and the brass to pass the sharp edge of the ring. This property of sharp edges has been discussed by Coghill and Anderson (1918) in connection with the stability of flotation of solid particles.

The tube is mounted on a substantial wooden holder fitted with levelling screws. The surface through which the tube  $V$  projects is plane, and on it rests the removable cylinder  $D$  enclosing the ring  $B$  in a small chamber. This maintains thermal equilibrium. The temperature is read by a thermometer graduated in tenths of a degree, with its bulb a few mm. above the

drop. The drops which overflow from *B* accumulate on the floor of the chamber, where filter-paper is placed. This ensures that the air in the chamber is saturated with vapour. The excess liquid can escape slowly through a small aperture, and drips into a beaker placed below the apparatus. The drop is illuminated and observed through windows  $W_1$  and  $W_2$ .

Recording is done photographically. An objective of 4" focus, provided with a sensitive focussing adjustment, throws an image of the drop on a photographic plate, with a magnification of about 2.7. An ordinary 40 W electric lamp, with a condenser, provides the illumination. A large glass tank filled with water is interposed in order to reduce the danger of temperature fluctuations when the lamp is switched on. These arrangements are not shown in the figure. A weighted thread hangs as a plumb line immediately in front of the plate, and its image defines the vertical. Ilford R plates are used, as the laboratory happens to have a considerable stock of these. They are slow, and require an exposure of some 12 seconds at  $f/6.5$ , but they are of fine grain and yield excellent images. We generally use a smaller aperture, but not smaller than  $f/11$ . It is evident from the geometry of the arrangement that a very small aperture could not form a sharp image of the profile of the drop in a plane passing exactly through its centre.

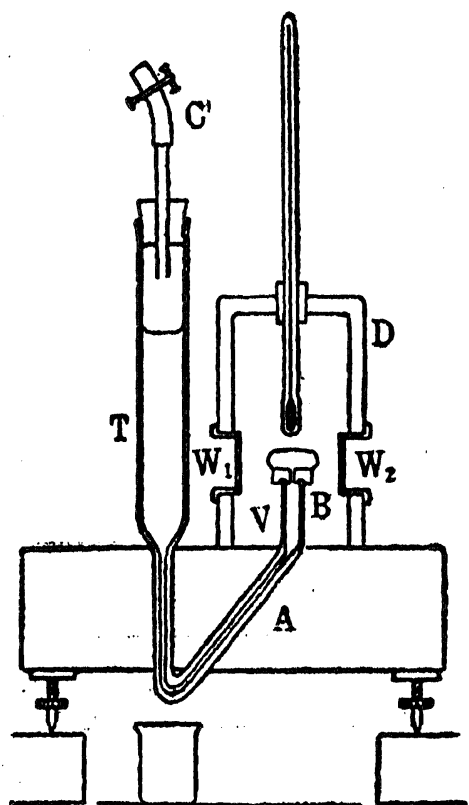


FIG. 1

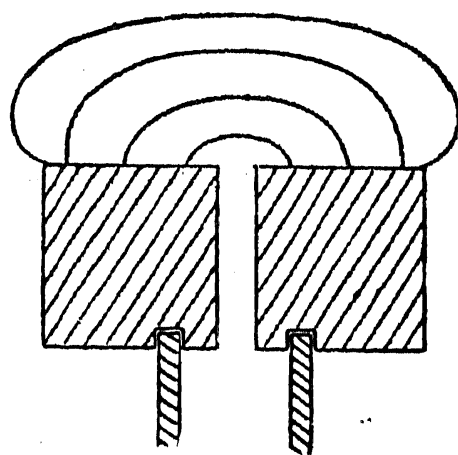


FIG. 2

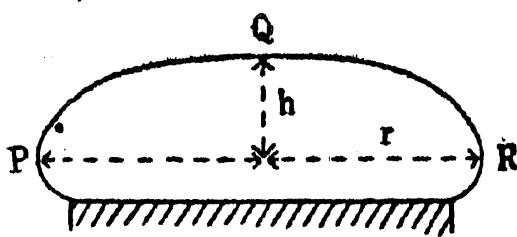


FIG. 3

After development the plates are measured on a Gaertner comparator reading to 1/1000 mm. The plate is placed on a holder mounted on a rack

and pinion, so that it may be displaced perpendicularly to the direction of traverse of the comparator. The vertical height  $h$  is measured (Fig. 3) by setting the vertical along the direction of traverse. By using the auxiliary motion at right angles, the cross hairs are set successively on  $P$ ,  $Q$ , and  $R$ . The mean reading at  $P$  and  $R$  is used, to eliminate any small error in the perpendicularity of the two motions. We find in practice that the estimate of the point of contact of the vertical tangent at  $P$  and  $R$  can be made with considerable precision, and the accuracy is much greater than can be attained by observing the original drop directly with a travelling microscope. A reproduction of one of the photographs is shown in Fig. 4.

In an actual experiment the procedure is as follows. After cleaning and mounting the tube on the holder, the levelling screws are adjusted until the upper surface of the ring  $B$  is horizontal. This is done by placing on it a small mirror, and observing the image of a plumb-line. When the surface is horizontal the plumb-line and its image are in one straight line. This gives quite a sensitive test. The cover is then placed in position, and the liquid introduced. A preliminary drop is formed, which is focussed accurately on the screen. A number of drops are then allowed to form and run over, in order to remove any residual trace of contamination. The final drop is then formed, and a photograph taken immediately. The plate is measured as already described. Since the diameter of the ring  $B$  is known accurately, the actual dimensions of the drop can be deduced immediately from the measurements.

#### 4. The Surface Tension of Distilled Water

To test the possibilities of the method, we have applied it to measure the surface tension of distilled water. Due precautions have been taken to secure purity and cleanliness. The following results are based on photographs of six different drops, and ten independent sets of measurements have been made on each plate. The measurements are very concordant, and are summarized in Table II.

TABLE II  
(Dimensions are given in mm.)

Plate	$H$	$R$	$H/R = h/r$	$r$	$a^2/r^2$	$\alpha$	Temp.
1	10.424 $\pm$ 0.008	22.180	0.46997	8.3097	0.21321	71.687 $\pm$ 0.19	27.6
2	10.634 $\pm$ 0.007	22.490	0.47283	8.2344	0.21655	71.497 $\pm$ 0.19	27.7
3	10.492 $\pm$ 0.005	21.650	0.48462	7.9860	0.23077	71.665 $\pm$ 0.16	27.7
4	10.538 $\pm$ 0.005	22.025	0.47846	8.1062	0.22324	71.429 $\pm$ 0.16	27.7
5	10.596 $\pm$ 0.004	22.475	0.47146	8.2759	0.21493	71.680 $\pm$ 0.15	27.7
6	10.652 $\pm$ 0.004	22.905	0.46505	8.4071	0.20760	71.448 $\pm$ 0.15	27.7

In this table,  $H$  and  $R$  refer to the photographs,  $h$  and  $r$  to the original drops. Equation (7) shows that  $a^2$  is relatively insensitive to small errors in  $r$ . The probable error of  $a^2$  thus depends chiefly on the uncertainty in the value of  $H$  and in the magnification. The result is also affected by uncertainties in the temperature. The latter has not been very rigorously controlled, but we are satisfied that the probable error in  $a$ , from this cause alone, would not exceed 0.01. The density of water and of saturated air have been taken from standard tables, and are not subject to any appreciable uncertainty.

We have analysed the influence of these various factors on the accuracy of the result, and have deduced the following weighted mean as a final value:

$$a = 71.56 \pm 0.07 \text{ dyn./cm. at } 27.7^\circ \text{ C.}$$

In order to compare this result with others, it is convenient to reduce it to  $20^\circ \text{ C}$ . This can be done without appreciably increasing the probable error, since the temperature variation is known far more accurately than the absolute values. We use the formula of Richards, Speyers, and Carver (1924)

$$a_t = a_0 - 0.1585 t + 0.00023 t^2$$

which gives the result

$$a_{20^\circ} = 72.70 \pm 0.07 \text{ dyn./cm.}$$

In Table III we have collected a number of other published values for comparison. The list is representative, but by no means exhaustive. It is evident that the extreme uncertainty in this constant is still of the order of one-tenth of a unit. The present result agrees very well with other modern determinations.

TABLE III

*Surface Tension of Water at  $20^\circ \text{ C}$ .*

1885	Volkman	..	..	..	Capillary rise	72.53
1919	Harkins and Brown	..	..	..	do.	72.80
1921	Sugden	..	..	..	do.	72.70
1921	Richards and Carver	..	..	..	do.	72.73
1922	Sugden	..	..	..	Bubble pressure	72.91
1927	Moser	..	..	..	Ring detachment	72.58
1928	<i>International Critical Tables</i>	..	..	..	Adopted mean	72.75
1931	Schwenker	..	..	..	Ring detachment	72.55
1934	Achmatov	..	..	..	Differential Capillary	72.70
1939	Cockett and Ferguson	..	..	..	Plane meniscus method	72.80

### 5. Discussion

We believe this to be the first attempt to put the sessile drop method on a footing with the other standard methods. It bears some resemblance to the method of Andreas, Hauser and Tucker (1938), who photographed hanging drops and measured the dimensions. The hanging drop, however, has a very different shape, since its curvature is a maximum at the apex, while that of a sessile drop is a minimum. Further their reduction table is based on observations made with distilled water, of which the surface tension was taken as known. Our method has many of the advantages of theirs, and also yields absolute values. It may be useful to indicate the chief advantages as follows:

- (1) The observations, made on a free liquid surface, are entirely independent of contact angles.
- (2) The apparatus is simple to construct and operate, and the procedure involves no special technical skill.
- (3) It is a static method, and there are no viscosity effects.
- (4) The method, unlike those involving jets and capillary tubes, is relatively insensitive to small departures from perfection in the apparatus.
- (5) A fresh surface is formed for each observation, so that with reasonable care the risk of contamination is practically nil.
- (6) Successive observations can be made on the same surface, if it is desired to study the variation with time.
- (7) Permanent records are obtained.

The chief disadvantages are:

- (1) Relatively large quantities of liquid are required, since each filling of the tube takes some 25 c.cm.
- (2) In its present form the method is applicable to water and aqueous solutions only. (It is probable, however, that slight modifications would permit its extension to other liquids.)

The possible sources of systematic error in this method are not numerous. Imperfections in the optical system would be one possible source. In the present arrangement the rays forming the marginal parts of the image make an angle of less than  $2\frac{1}{2}^\circ$  with the axis. The lens is a standard photographic objective of excellent quality, and the effect of any residual astigmatism or other aberration in such a small angular field is almost certainly inappreciable. The window  $W_2$  is actually a piece of a microscope slide, selected for its optical quality from many pieces tested. It is placed as close as



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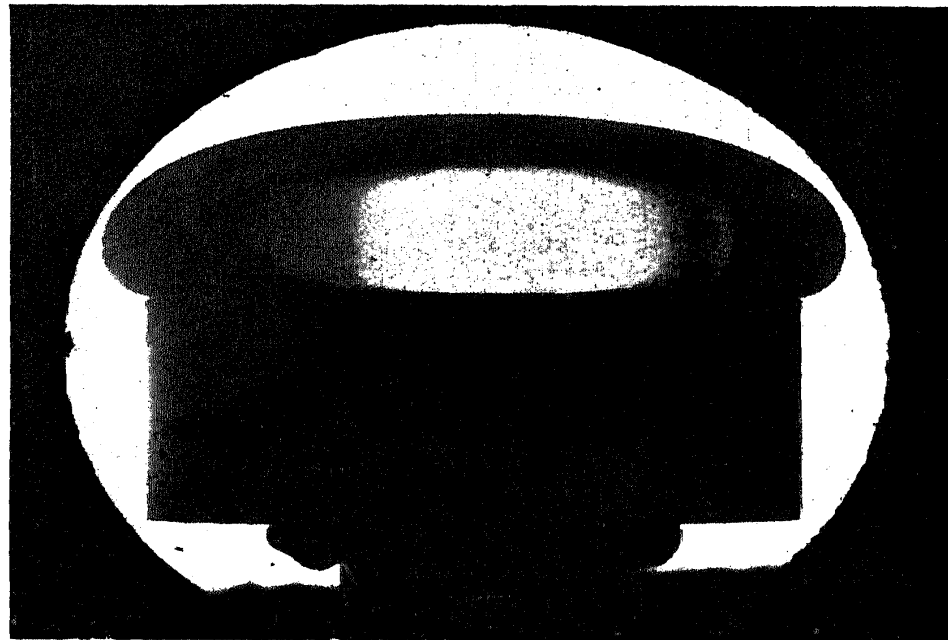


FIG. 4



possible to the drop. Systematic errors might also conceivably arise in the temperature readings, and in the measurement of the plates. On examining these possibilities we conclude that any such errors, if present, are very small.

We are of the opinion that the fluctuations in the results are almost entirely due to the random errors of observation. In further work it seems probable that an appreciably higher accuracy can be attained. To secure this, more rigorous temperature control will be needed, and closer attention to the details of photography and measurement. It will be necessary, moreover, to give further attention to the theory. We believe Table I, within its range, to be the most reliable reduction table for sessile drops yet available, but the probable errors of the measurements are already small enough to be comparable with the uncertainties in the tabulated values.

### *Summary*

Apparatus is described by means of which sessile drops can be formed on the upper end of a vertical tube. The drops can be renewed as frequently as desired. Photographs of the drops are measured and from the dimensions the surface tension is calculated with the help of a new reduction table given in the paper. The method in this form is considered to be as reliable as any of the other standard methods. It has been applied to measure the surface tension of pure water against saturated air. The value at 20° C. is found to be  $72.70 \pm 0.07$  dyn./cm., in good agreement with other determinations.

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