[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE DROP WEIGHT METHOD FOR THE DETERMINATION OF SURFACE TENSION. THE EFFECT OF AN INCLINATION OF THE TIP UPON THE DROP WEIGHT

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Introduction

The drop weight method has been developed as an accurate method for the determination of surface tension. If the greatest accuracy is not required, a simple form of apparatus gives reliable measurements with ease and rapidity. For any type of work, the variation of the drop weight with the angle of inclination of the tip should be known, and so the requisite values were determined.

Results

With the apparatus and procedure described in detail elsewhere,[1] the drop weights for conductivity water were determined at 25.0°, with the tip at various angles of inclination. The angle α which the tip made with the horizontal plane was set at from 0.0 to 20.0°, and was measured to within 0.1° by the use of a level. At an angle of 3.0°, the inclination of the tip was very apparent to the eye.

Table I gives the average weights in air of one drop of water. The apparent surface tension, for an observer unaware of the tilt of the tip, may be calculated by means of the equation

$$\gamma = \frac{Mg}{2\pi r}\phi\left(\frac{r^3}{v}\right) \tag{1}$$

in which M is the weight of the drop in air, g is the acceleration due to gravity, r is the radius of the tip (0.2989 cm. in the present case) and ϕ, a function of r^3/v where v is the volume of the drop, is the empirical correction factor of Harkins and Brown,[1] taken from a graph of their results. These calculated surface tensions were plotted against the corresponding angle α, and from the smoothed curve, which passed exactly through four of the points and came within 0.07 dyne of the other two, the apparent surface tention γ_α was read for each value of α employed. Since γ_α is the apparent surface tension when the dropping surface makes the angle α with the horizontal, γ_0 will be the surface tension when the dropping surface of the tip is accurately horizontal, that is, the true surface tension of water at this temperature. In Col. 3 of Table I are given the differences $\gamma_0 - \gamma_\alpha$. The apparent surface tension is obviously not very different from the true value, when α is less than 5.0°. When α is 20.0°, which is a very large

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

angle under the conditions, this difference is only 2.3% of γ_0 for the tip used.

TABLE I

AVERAGE WEIGHTS IN AIR OF ONE DROP OF WATER

α	M	$\gamma_0 - \gamma_\alpha$	$\gamma_0 - \gamma'$	$2.025 \times 10^{-4}\ \alpha^3$
0.0°	0.08424	0.00	0.00	0.00
5.0°	.08420	.03	− .08	.03
7.5°	.08420	.10	− .20	.09
10.0°	.08391	.23	− .18	.20
15.0°	.08333	.73	− .26	.68
20.0°	.08224	1.62	− .16	1.62

It is desirable to know, first, whether the true surface tension of water may be calculated from a measurement of the drop weight at a large angle α, and, second, how large α may be without affecting the results appreciably.

When the tip is inclined, its projection upon a horizontal plane is no longer a circle of radius r, but an ellipse of semi-major axis r and semi-minor axis $r \cos \alpha$. Therefore, the drop weight should not be that for a circular tip of radius r, but would more nearly correspond to that for a circular tip of radius r', where r' would be an average semi-axis of the ellipse. The surface tension should be given more accurately by

$$\gamma' = \frac{Mg}{2\pi r'}\, \phi\left(\frac{r'^3}{v}\right) \tag{2}$$

provided the proper value of r' is known.

If the radius of the circle whose circumference is that of the ellipse is taken for r', then $r' = r\sqrt{(1 + \cos^2\alpha)/2}$ very nearly. The calculated values of $\gamma_0 - \gamma'$ are given in Col. 4 of Table I. For all values of α, Equation 2 gives results that are within 0.4% of the true surface tension. For small values of α, however, the results obtained with Equation 1 are better. If r' is taken to be the radius of the circle whose area is that of the ellipse, then $r' = r\sqrt{\cos \alpha}$. The results in this case are practically identical with those already listed in Col. 4 of Table I. Other methods for obtaining the average r' may lead to smaller values of $\gamma_0 - \gamma'$. Equation 2 thus gives a good approximation for the true surface tension.

To determine what the values of γ_α are for small angles α, equations of various forms were fitted to the data in Col. 3 of Table I. The equation

$$\gamma_0 - \gamma_\alpha = 2.025 \times 10^{-4}\, \alpha^3 \tag{3}$$

for α in degrees was found to fit well, as is shown in Col. 5 of Table I. By means of this equation, the values of $\gamma_0 - \gamma_\alpha$ for the small angles in Table II are secured. The values of γ_α are also included, for 71.97 dynes per cm. as the accepted surface tension[2] of water at 25.0°. For angles of inclina-

[2] "International Critical Tables," McGraw-Hill Book Co., New York, Vol. IV, p. 447.

Table II

Values for Small Angles

α	$2.025 \times 10^{-4}\ \alpha^3$	γ_α	α	$2.025 \times 10^{-4}\ \alpha^3$	γ_α
0.00°	0.000	71.97_0	4.00°	0.013	71.95_7
0.25°	.000	71.97_0	5.00°	.025	71.94_5
0.50°	.000	71.97_0	6.00°	.044	71.92_6
1.00°	.000	71.97_0	8.00°	.104	71.86_6
2.00°	.002	71.96_8	10.00°	.203	71.76_7
3.00°	.005	71.96_5			

tion less than 3°, the effect of the tilt on the calculated surface tension is not appreciable. Unlike other methods for the determination of surface tension, the drop weight method is thus particularly insensitive to any inclination of the measuring apparatus. The utmost precautions need not therefore be taken to insure a horizontal dropping surface, and a setting of within 2° of the horizontal, an angle quite apparent to a trained eye, will probably suffice in all cases.

Summary

Results obtained with the drop weight method for the determination of surface tension are found to be unaffected by a slight inclination of the apparatus. The effect upon the weight of a drop of a tilt of the tip of less than 3° is not appreciable. Precautions need not, therefore, be taken to set the dropping surface at an angle of less than 2° with the horizontal.

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THE SURFACE TENSION OF AQUEOUS SOLUTIONS OF PARA-TOLUIDINE

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1. Introduction

During the progress of work in this Laboratory on surface phenomena, there arose a need for reliable data on the surface tension of aqueous solutions of *p*-toluidine. Such measurements had already been made by Edwards,[1] who used a modification devised by Ferguson of the capillary height method, and by Frumkin, Donde and Kulvarskaya,[2] who employed the capillary height method. The two sets of results are in very poor agreement. While Frumkin did not lay claim to great accuracy in his own determinations,[3] these showed the work of Edwards to be seriously in error.

[1] Edwards, *J. Chem. Soc.*, **127**, 744 (1925).

[2] Frumkin, Donde and Kulvarskaya, *Z. physik. Chem.*, **123**, 321 (1926).

[3] Private communication.