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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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

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.

2. Method, Apparatus, and Procedure

For the measurement of the surface tension of aqueous solutions of *p*-toluidine and similar substances, the drop weight method has certain advantages. For while such solutions wet with ease the ground-glass tip used in the drop weight method, it has been observed that solutions of even very pure *p*-toluidine wet polished glass with some difficulty. The capillary height method is therefore not suitable.

The apparatus which was employed is shown in Fig. 1, and is a modified form of the standard apparatus described by Harkins and Brown.[4] The metal box B, which contains the glass tip, adequately cleaned, and the solution, is immersed in a thermostat kept accurately at 20.0°. The ground surface of the glass tip is maintained in the horizontal plane indicated by the L-shaped level shown. Each drop is pulled over to almost full size by very gentle suction at a rubber tube attached to the metal tip-holder A. The first drop is allowed to hang for some minutes in the weighing bottle V, in order to saturate the enclosed air with the vapors from the solution. The drop is then drawn over and made as large as is possible without causing it to fall, and the level between the bottles S and V is so adjusted that the drop falls as slowly as is possible. The supply bottle S is raised or lowered for this purpose by means of the microscope stand T. This adjustment is accomplished through the pinion head P which is attached to the microscope stand by means of a small universal joint and a long metal rod that extends to the chair of the operator, who watches the formation of the drops through a small telescope, the cross hairs of which mark the maximum size of the stable drop and thus help in its control. When the required number of drops has been drawn over, the metal box is at once removed from the thermostat and opened, the weighing bottle V is chilled for exactly one minute in an ice-water mixture in order to condense most of the vapors within, and the bottle is removed, quickly stoppered and weighed.

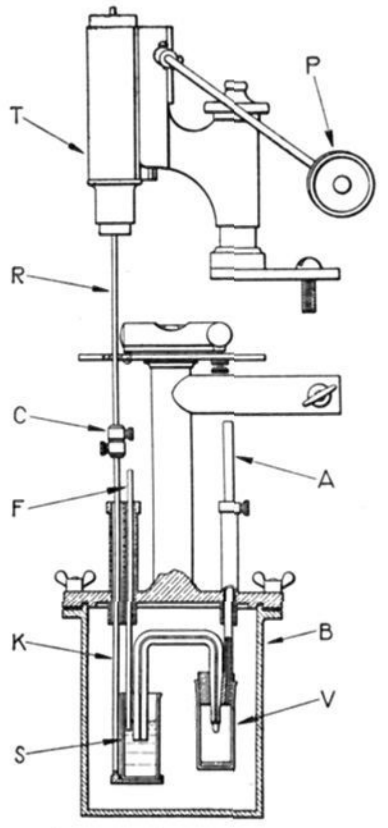

Fig. 1.—Apparatus for the accurate determination of surface tension by the drop weight method.

3. Results

In the work here reported, each determination consisted of one run of twenty drops, and another, immediately following, of five drops. The

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

difference represented the weight, in their own saturated vapor, of fifteen drops. In this difference the errors caused by the weight of the moisture condensed on the interior of the bottle by chilling are mostly eliminated. Three such determinations were made with each solution, and the average per drop was taken as the drop weight for that solution. Of the three results, none differed from the average by as much as 0.15%, while in only two of the twenty-seven single determinations was this difference greater than 0.10%.

The drops were usually allowed to hang for twenty to thirty seconds before they were permitted to fall. That this length of time was sufficient to enable the surface of the drop to attain equilibrium with the interior of the drop was demonstrated by work with a solution, containing 0.00606 mole of *p*-toluidine per kilogram of water, which, since this was the most dilute solution studied, gave the slowest diffusion into the surface. The drop weight was determined for drops which maintained approximately their full size, before falling, for four minutes, and also for about twenty seconds each. The two results differed from their mean by only 0.08%. Apparently an age of one-half minute for the full-sized drop gives equilibrium of the surface with the liquid and the vapor phase.

With the solution containing 0.03376 mole of *p*-toluidine per kilogram of water, the drop weight of drops held at almost full size for four minutes differed from that of drops held at full size for twenty-five seconds each by only 0.06%. This demonstrates that, even for this relatively concentrated solution, oxidation of the *p*-toluidine in the surface of the drop did not take place to a sufficient extent to alter the surface tension of the solution.

The density of each solution at 20.0° was determined in duplicate with a pycnometer of approximately 20-cc. capacity, the volume of which was accurately determined with conductivity water as the standard.

Experiments were carried out over practically the entire concentration range. The results are given in Table I. In Col. 5 is listed the weight of a single drop in air saturated with the vapor from the respective solution.

TABLE I

SURFACE TENSION OF AQUEOUS SOLUTIONS OF *p*-TOLUIDINE

Soln.	Mole per kg. of water, m	Mole per kg. of soln.	$\text{Log}_e\, m$	Density, g. per cc. at 20.0°	Drop weight, g.	Volume per drop, v, in cc.	r^3/v	Φ	γ in dynes per cm. at 20.0°
1	0.00000	0.00000	$-\infty$	0.99820	0.085367	0.08562	0.3119	1.6327	72.75
2	.00606	.00606	−5.1069	.99830	.083970	.08421	.3172	1.6343	71.63
3	.00716	.00715	−4.9402	.99832	.083658	.08390	.3184	1.6347	71.38
4	.01174	.01172	−4.4455	.99832	.081734	.08197	.3258	1.6367	69.82
5	.01985	.01981	−3.9202	.99837	.075256	.07547	.3539	1.6440	64.57
6	.02753	.02745	−3.5931	.99834	.070120	.07032	.3798	1.6499	60.38
7	.03376	.03364	−3.3891	.99828	.066889	.06708	.3982	1.6537	57.73
8	.04935	.04909	−3.0093	.99838	.060395	.06057	.4410	1.6606	52.35
9	.06218	.06177	−2.7781	.99843	.056533	.05669	.4712	1.6641	49.10

Each value is the average of three determinations, as outlined above. In Col. 7 is given the calculated value of r^3/v where r, the radius of the tip used, is 0.2989$_2$ cm., the average of measurements made with a calibrated traveling microscope over six different diameters, and v is the volume of the drop in question. The experimentally determined correction factor Φ tabulated in Col. 8 is a function of r^3/v and was taken from a graph which plots the values of Harkins and Brown.

The equation by means of which the surface tension was calculated is

$$\gamma = \frac{Mg}{2r}\Phi$$

in which γ is the surface tension in dynes per centimeter, M is the weight in grams of the drop in air saturated with the vapors from the solution, g is the acceleration due to gravity, which is 980.28 cm. per sec. per sec. in this Laboratory, and r and Φ have the significance pointed out above.

4. Purification of Materials

The *p*-toluidine used was obtained from the Eastman Kodak Company and was purified from it isomers and other impurities as recommended, in general, by Berliner and May.[5] The *p*-toluidine was twice distilled, the end fraction being discarded each time. It was dissolved in five times its volume of ether, and the oxalate precipitated by addition of an ethereal solution of oxalic acid. The salt was washed with ether and recrystallized four times from hot water. A little oxalic acid was added to the water each time to hinder hydrolysis. The *p*-toluidine was liberated with sodium carbonate solution, recrystallized from hot water, steam distilled and again recrystallized from hot water. The snow-white crystals were dried *in vacuo* over stick potassium hydroxide for twelve days. The elaborate purification reduced the yield to 15%. The crystals melted at 43.6°, while the value given by the "International Critical Tables" is 43.7°.

Conductivity water was used for all of the solutions, which were made up by weight.

5. Comparison with Other Data

The measurements of Edwards were obtained at temperatures between 15 and 17.5°. The values which he found for the surface tension of water are higher than the corresponding value given by the "International Critical Tables."[6] His values were, therefore, multiplied by 0.9780, which brings his average value for pure water to 73.34 dynes per centimeter, the accepted value. The densities at 20° of *p*-toluidine solutions are very nearly that of water, and so the densities at 16°, required for the conversion to the concentration units used in this paper, were obtained by adding to

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[5] Berliner and May, THIS JOURNAL, 49, 1007 (1927).

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

the density of water at 16° the difference between the densities of the corresponding solution and of water at 20°.

The data of Frumkin, Donde and Kulvarskaya were corrected in the same way, by use of the factor 1.0022.

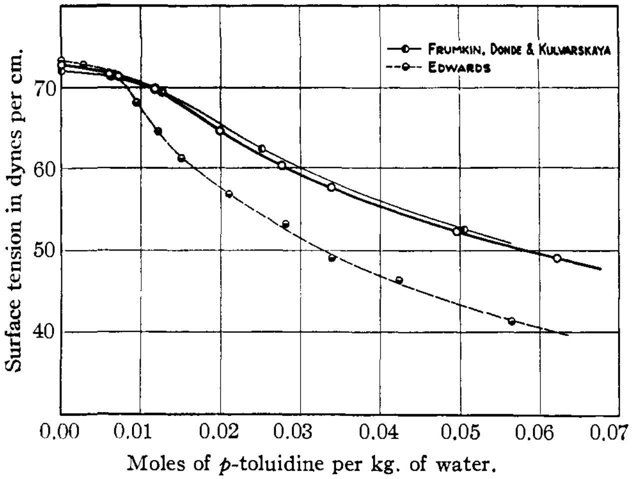

Fig. 2.—Surface tension of aqueous solutions of *p*-toluidine as given by different observers.

These data, together with those obtained in the present work, are given in Fig. 2. It is obvious that the results of Edwards are much too low. This difference is strikingly brought out in the logarithmic plot in Fig. 3;

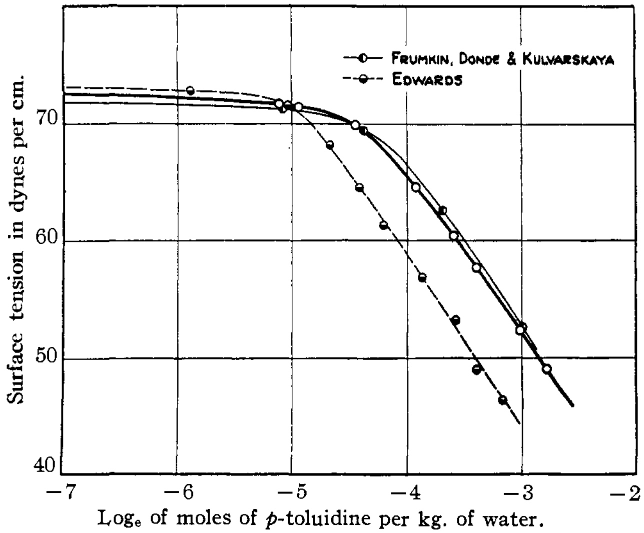

Fig. 3.—Surface tension of aqueous solutions of *p*-toluidine as given by different observers.

curiously enough, however, all of the three curves have almost the same slope in the straight portions of this graph.

6. Calculation of the Adsorption

The adsorption of *p*-toluidine at the air–solution interface may be calculated by means of the Gibbs adsorption equation

$$u = \frac{-1}{RT}\frac{d\gamma}{\mathrm{d}\log_e a}$$

where γ is the surface tension in dynes per centimeter, a is the activity of the solute, R is the gas constant, 8.315×10^7 ergs per mole degree, T is the absolute temperature and u is the number of moles of solute which must be added to the solution after the surface has been increased by one square centimeter, in order to bring the solution back to its initial concentration.

McBain and his co-workers[7] have found the activity of aqueous solutions of *p*-toluidine to be proportional to the concentration. While this result is probably not exact and is unexpected for a substance of the type of *p*-toluidine, the adsorption may, for the present, be calculated on this basis. In this case

$$\mathrm{d}\log_e a = \mathrm{d}\log_e m$$

in which m is the number of moles of solute per kilogram of water. The slope of the curve representing our data in Fig. 3 is, therefore, directly $\mathrm{d}\,\gamma/\mathrm{d}\log_e a$.

The calculations are tabulated in Table II for the more concentrated solutions included in Table I. The adsorption is listed in Col. 3 as the number of moles per square centimeter of surface, in Col. 4 as the number of molecules per square centimeter of surface and in Col. 5 as the apparent surface area in sq. Å. occupied by each molecule.

TABLE II

ADSORPTION OF *p*-TOLUIDINE IN AQUEOUS SOLUTION CALCULATED BY THE GIBBS ADSORPTION EQUATION

Soln.	Mole per kg. of water, m	$\frac{-d\gamma}{d\log_e m}$	$u \times 10^{10}$	$u' \times 10^{-14}$	Area per molecule in sq. Å.	Mole per cc. of soln.	Mole per cc. of soln. $\times 10^{-21}$	Molecules, per sq. cm. of soln. $\times 10^{-14}$	Total no. of molecules, per sq. cm. $\times 10^{-14}$	Effective area per molecule, Sq. Å.
5	0.01985	12.14	4.981	3.02	33.1	0.04198	0.0120	0.05	3.07	32.6
6	.02753	13.25	5.436	3.30	30.3	.04274	.0166	.07	3.36	29.8
7	.03376	13.77	5.649	3.43	29.2	.04336	.0204	.07	3.50	28.6
8	.04935	14.10	5.785	3.51	28.5	.04490	.0297	.09	3.60	27.8
9	.06218	14.10	5.785	3.51	28.5	.04617	.0374	.11	3.62	27.6

If one square centimeter of new surface were to be instantaneously formed, a certain amount of solute would already be present in the fresh surface.

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[7] McBain, Wynne-Jones and Pollard, "Colloid Symposium Monograph," The Chemical Catalog Company, New York, **1928**, Vol. VI, p. 57.

This amount is further increased by the quantity *u* which is then adsorbed. The total number of molecules in each square centimeter of surface is thus the sum of these two amounts. The number already in the surface is unknown, but may be taken as approximately the two-thirds power of the number of molecules in each cubic centimeter of solution, a value given in Col. 8. This correction is not great for solutions as dilute as these, but is considerable for more soluble substances. In Col. 10 is listed the corrected apparent area in sq. Å. occupied by each molecule in the surface region.

The apparent surface area per molecule of *p*-toluidine appears to be 28 sq. Å. The work of Adam[8] with insoluble films gives the value 23.8 sq. Å. for the benzene ring perpendicular to the surface. In view of the fact that the activity of solutions of *p*-toluidine is not known accurately, this agreement is satisfactory and serves as an indication that the adsorbed solute forms a monomolecular film on the surface of the solution.

7. Summary

1. The drop weight method for the measurement of surface tension has the advantage over the capillary height method in that the former is independent of the angle of contact, and can thus be used with substances like *p*-toluidine, whose aqueous solutions do not wet glass easily.

2. A slightly improved procedure for the determination of surface tension by the drop weight method is presented.

3. Measurements of the surface tension of aqueous solutions of *p*-toluidine by means of the drop weight method are given and compared with earlier results. *p*-Toluidine is a very surface-active substance, for at 20.0° it lowers the surface tension by 8.18 dynes when dissolved in water to the extent of 0.0199 mole per kilogram of solvent, and by 23.65 dynes with 0.0622 mole.

4. By use of the Gibbs adsorption equation, the area occupied by each molecule of *p*-toluidine in the surface region is found to be 28 sq. Å. for the nearly saturated solution, which is in agreement with the area expected from other sources for a monomolecular film.

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[8] Adam, *Proc. Roy. Soc.* (London), **103**, 676 (1923).