

Plate Glass Company, the generosity of Mr. B. K. Beecher of that laboratory in making the petrographic examination, and the fine workmanship of Mr. William Latham, toolmaker of the Columbia plant, on the bombs, which contributed much to their success.

Summary

1. Apparatus has been developed for the direct determination of solubilities and pressures at high temperatures and pressures.
2. The solubility of sodium carbonate in water has been determined from 50 to 350°.
3. The transition of the monohydrated into the anhydrous form in contact with solution under its own vapor pressure has been shown to occur at $112.5 \pm 1^\circ$ and 1.27 atmospheres pressure.
4. Crystals of anhydrous sodium carbonate have been grown at elevated temperatures and optical data on them are presented.
5. The vapor pressure of saturated solutions of sodium carbonate has been determined.

NEW YORK, N. Y.

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

A DOUBLE CAPILLARY METHOD FOR THE MEASUREMENT OF INTERFACIAL TENSION

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RECEIVED OCTOBER 23, 1931

PUBLISHED MARCH 5, 1932

In connection with some of our recent work we were confronted with the necessity of determining the interfacial tension of water against several different liquids which were expensive and which were difficult to obtain in large quantities in the pure state. It became highly desirable to develop a method which would require but a small amount of organic liquid for each measurement. The drop volume method of Harkins and the various capillary rise methods previously used, all required appreciable quantities of liquid. Sugden had solved a similar problem for surface tension determinations through the use of either a maximum bubble pressure method¹ or a double capillary method.² The first method did not, in its present form, appear to be applicable to the measurement of interfacial tensions. A modification of the second did seem promising.

Quite recently a method for the measurement of interfacial tensions of liquid-liquid systems based upon the principle of capillary rise had been developed, and had been quite generally used in this Laboratory.³ With this apparatus from 10 to 20 cc. of organic liquid was required for

¹ Sugden, *J. Chem. Soc.*, **119**, 1483 (1921).

² Sugden, *ibid.*, **121**, 858 (1922); **125**, 27 (1924).

³ Bartell and Miller, *THIS JOURNAL*, **50**, 1961 (1928).

each determination. As work progressed certain modifications were made in the method. It was found that by making use of two capillaries of different diameters an apparatus, similar in operation to the one referred to above, could be constructed which would give very good results and which requires not more than about 2 cc. of organic liquid. The apparatus might then quite properly be referred to as a "*micro apparatus*" for the measurement of interfacial tension.

In order to obtain satisfactory interfacial tension measurements for water against organic liquids it is necessary that the capillary tube be coated by a film of water before the organic liquid is admitted. This necessitates somewhat different procedure for different organic liquids, depending upon whether the density of the organic liquid is greater or less than that of water. It was found that one type of construction was more suitable for the heavier-than-water liquids—and another type for the lighter-than-water liquids. Soft glass capillaries were used in the apparatus as the degree of wetting of soft glass by water is higher than that of certain other glasses such as Pyrex. The soft glass is therefore more readily coated with the necessary initial water film.

Apparatus for Liquids of Density Greater than that of Water.—The apparatus for liquids of density greater than that of water is shown in Fig. 1. It consists of two soft glass cups, A and B, each 4 cm. in diameter and 10 cm. in height. The cups are sealed directly to capillary tubes with diameters of about 0.25 and 1.0 mm., respectively. These are joined with 5-mm. tubing to which is sealed a center tube, the upper portion of which is of 10 to 15 mm. bore. This tube has a flared rim.

In carrying out an interfacial tension determination water is poured into Cup A until both capillaries are filled. No air will be entrapped if the liquid is added through the finer capillary. Ten to fifteen cc. of water is now added to each cup and the three liquid levels allowed to come to equilibrium. Or-

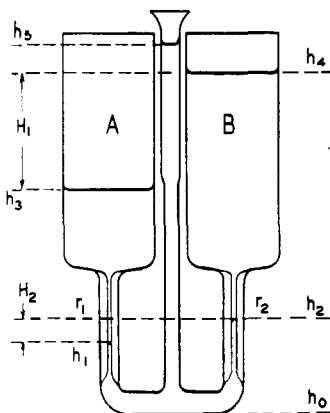


Fig. 1.

ganic liquid is next introduced through the center tube until the two liquid-liquid interfaces reach the lower ends of the capillaries. The organic liquid is then added drop by drop while at the same time water is added to cup B at such a rate as just to prevent the organic liquid from running through the large capillary. When the organic liquid finally enters the lower part of both capillaries the positions of the two menisci are adjusted by suitable addition of liquid so that the smaller meniscus is at a slightly lower level. The organic liquid is now added in small fractions of a drop until the two

menisci rise to the etched reference marks. A total of one or two drops is usually sufficient. Since the head of water over the lower meniscus is the smaller, this meniscus will rise the faster with the result that the final vertical positions of the menisci should be practically identical. The vertical distances, H_1 and H_2 , between the two sets of menisci are now measured with a cathetometer.

As it is practically impossible to get both menisci to coincide exactly with the etch marks the capillaries must be carefully calibrated. Such calibration can be accomplished in the same way as with the original Bartell-Miller apparatus,³ by employing benzene and water as liquids and accepting the value of 34.72 dynes/cm. as the interfacial tension (S_{23}) of this system at 25°. The radius of the capillary at several points at different distances from the reference mark can thus be calculated and a

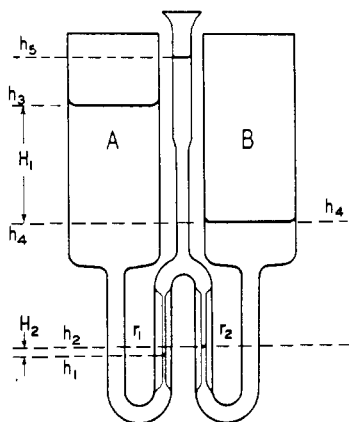


Fig. 2.

curve plotted from which the radius at any given point can be determined accurately.

Apparatus for Liquids of Density Less than that of Water.—The apparatus for the measurement of interfacial tensions of liquids of density less than that of water is shown in Fig. 2. The operation is essentially the same as that described above.

The formulation which can be used for the calculation of interfacial tension by the above methods may be developed as follows.

(a) In case ρ_0 , the density of the organic liquid, is greater than ρ_w , the density of water at the same temperature (Fig. 1), the relation between the weight of liquid

held in the capillaries and the force holding it at heights h_1 or h_2 , in capillaries of radii r_1 and r_2 , respectively, is given by the expressions

$$2\pi r_1 S_{23} = \pi r_1^2 g \{ (h_3 - h_1 + 1/3 r_1) \rho_0 - (h_3 - h_1 + 1/3 r_1) \rho_w \} \quad (1)$$

$$2\pi r_2 S_{23} = \pi r_2^2 g \{ (h_4 - h_2 + 1/3 r_2) \rho_0 - (h_4 - h_2 + 1/3 r_2) \rho_w \} \quad (2)$$

Subtracting and simplifying

$$\frac{2S_{23}}{g} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) = \rho_0 \{ h_2 - h_1 + 1/3 (r_1 - r_2) \} + \rho_w \{ (h_4 - h_3) - (h_2 - h_1) + 1/3 (r_2 - r_1) \} \quad (3)$$

Putting $H_1 = (h_4 - h_3)$, $H_2 = (h_2 - h_1)$ and $R = (r_2 - r_1)$, we have

$$S_{23} = \frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \{ (H_1 - H_2) \rho_w + H_2 \rho_0 - 1/3 R (\rho_0 - \rho_w) \} \quad (4)$$

(b) In case ρ_0 is less than ρ_w (Fig. 2), the formulation is

$$S_{23} = \frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \{ (H_1 - H_2) \rho_w + H_2 \rho_0 + 1/3 R (\rho_0 - \rho_w) \} \quad (5)$$

The final equations differ only in the sign of the meniscus correction, and since the sign of the quantity $(\rho_0 - \rho_w)$ also changes, equations (4) and (5) can be generalized into

$$S_{23} = \frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \{ (H_1 - H_2)\rho_w + H_2\rho_0 - \frac{1}{2}R\Delta \} \quad (6)$$

where Δ is the absolute difference between the densities.

It will be noticed that the Poisson equation for capillary rise has been used throughout this work. Rayleigh⁴ has pointed out that the equation fails when r/h is much greater than 0.4, the maximum radius of the large capillary is limited to 1 mm.

Sugden¹ has developed for surface tension determinations a method in which any size of capillary may be used. In his table he uses four different equations to cover the entire range of radii values. For interfacial tensions similarly obtained, a table would have to be made up for every range of density differences; accordingly calculations would become very laborious. Richards, Speyers and Carver⁵ attempted to use fairly large capillaries. The theoretical basis for their calculations has been attacked by Sugden.⁶

A further advantage of the new type of apparatus, aside from the small amount of liquid used, can be seen from equation (6). If H_2 is made very small, the variations in the magnitude of ρ_0 will have very little effect on the calculated value of S_{23} , and the density of the organic liquid need not be determined more accurately than to two decimal places. This practically disposes of density measurements as a source of error in these interfacial tension determinations.

It is not practical to attempt to make the H_2 value exactly zero. A simple modification of the above apparatus can be made, however, which will cause the H_1 term to vanish entirely. Equation (6) in this case reduces to

$$S_{23} = \frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \{ H_2(\rho_0 - \rho_w) - \frac{1}{2}R\Delta \} \quad (7)$$

For liquids heavier than water the form of apparatus illustrated in Fig. 3 is used, while that shown in Fig. 4 is used for liquids lighter than water.

Tubing of 5 to 6 mm. bore with flared rims is used for the side arms. The capillaries should have about the same radii as those of the apparatus shown in Figs. 1 and 2. The best relative sizes for the capillaries will vary widely with the density differences of the liquids to be used, the interfacial tension value, and the most desirable length of the apparatus. To facilitate cleaning, the fine capillary is made about 3 cm. in length. The wide capillary should then be about 10 to 20 cm. in length.

The operation of the apparatus is simple. Water is poured into the right arm of the apparatus (Fig. 3 or 4) until the capillaries are filled;

⁴ Rayleigh, *Proc. Roy. Soc. (London)*, **A92**, 184 (1915).

⁵ Richards, Speyers and Carver, *THIS JOURNAL*, **46**, 1196 (1924).

⁶ Sugden, *THIS JOURNAL*, **47**, 60 (1925).

then the organic liquid is slowly added to the left arm until the meniscus comes just to the etched mark on the fine capillary tube. The vertical distance between the two menisci is then measured with a cathetometer or by means of a graduated scale placed behind the tube (as is indicated in Fig. 3).

The capillaries are calibrated by inverting the apparatus over a comparatively large open vessel of some reference liquid, such as benzene or water. The radii are then calculated from the surface tension formulation. The radius of the small capillary need be known only at the etched mark, but the other capillary must be carefully calibrated throughout its length.

These double capillary apparatus (*i. e.*, shown in Figs. 3 and 4) will be best suited to interfacial tension measurements in which very careful density determinations can be carried out. They are obviously not well suited to the measurement of the interfacial tensions of systems which have only a slight density difference, but are best suited to those in which an appreciable difference does exist. In the latter case they have some advantages over the first types shown in Figs. 1 and 2. The determination is more easily carried out, as it is necessary to measure but one height. Only the two capillary menisci are involved, and their positions can be determined with a much greater degree of precision than

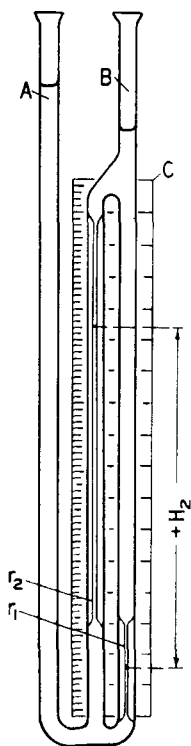


Fig. 3.

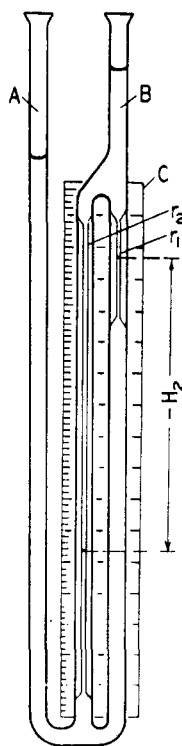


Fig. 4.

is possible with a wide meniscus. Indeed, the uncertainty in reading the height of the wide meniscus is one of the objections to the capillary rise methods in general.

It should be noted that the apparatus shown in Fig. 3 is especially adapted to the measurement of the interfacial tensions of mercury against other liquids. Here the density difference would always be large so that an error in determining the density of the lighter liquid would have no magnified effect upon the value, S_{23} . The usual methods of measuring the interfacial tension at a water surface cannot be extended with equal success to a mercury surface. The drop weight method has been used with success for this measurement, but it appears to involve serious difficul-

ties in operative technique. The capillary apparatus of Bartell and Miller can be used, but the various capillary rise methods used by Von Lerch,⁷ Clark,⁸ Harkins and Humphrey⁹ and Reynolds¹⁰ cannot be used at all, because the capillary meniscus is below the mercury surface and cannot be seen. Preliminary experiments in this Laboratory indicate that measurements comparing favorably in accuracy with the very care-

TABLE I
INTERFACIAL TENSION DATA

Organic liquid	Temp., °C.	Density	H_1 , mm.	H_2 , mm.	$\frac{1}{r_1} - \frac{1}{r_2}$	S_{23} dynes/cm.
Apparatus No. 1 $r_1 = 0.2275 - 0.2300$ mm. ^a $r_2 = 0.5550 - 0.5580$ mm.						
Nitrobenzene	15.13	1.1981	13.73	+1.39	2.574	26.65 ^b
Chlorobenzene	25.13	1.1008	20.02	-0.32	2.575	37.93
Carbon bisulfide	25.13	1.2555	26.30	-3.50	2.572	48.14
Apparatus No. 2a $r_1 = 0.1957 - 0.1961$ mm. $r_2 = 0.5209 - 0.5236$ mm.						
Benzene	25.13	0.8734	22.34	-2.68	3.194	34.71
Toluene	30.12	.8563	23.34	-1.63	3.188	35.90
Ethylbenzene	25.13	.8625	25.09	+0.59	3.189	38.33
Propylbenzene	25.13	.8675	26.21	+0.82	3.192	39.98
Apparatus No. 2b $r_1 = 0.2310 - 0.2320$ mm. $r_2 = 0.5715 - 0.5731$ mm.						
Benzene	25.13	0.8734	18.26	-0.40	2.574	34.74
Butylbenzene	25.13	.8561	21.89	+0.34	2.566	41.58

^a The data given for r_1 and r_2 in these tables represent the limiting values of the radii of the capillaries. ^b The value given for each determination represents the mean of three or more determinations.

TABLE II
INTERFACIAL TENSION DATA

Organic liquid	Temp., °C.	Dens. diff.	H_2 , mm.	$\frac{1}{r_1} - \frac{1}{r_2}$	S_{23} dynes/cm.
Apparatus No. 3 $r_1 = 0.2490 - 0.2510$ $r_2 = 0.5600 - 0.5680$					
Benzene	25.13	0.1237	127.8	2.235	34.68
Toluene	25.13	.1360	120.8	2.234	36.06
Ethylbenzene	25.13	.1345	129.7	2.236	38.26
Apparatus No. 4 $r_1 = 0.1927 - 0.1932$ $r_2 = 0.5033 - 0.5072$					
Nitrobenzene	25.13	0.2011	82.90	3.205	25.51
Carbon bisulfide	25.23	.2584	121.00	3.197	47.95
Carbon tetrachloride	25.07	.5872	48.37	3.206	43.44

⁷ Von Lerch, *Ann. Physik*, **9**, 434 (1902).

⁸ Clark, *Proc. Am. Acad.*, **41**, 361 (1906).

⁹ Harkins and Humphrey, *This Journal*, **38**, 236 (1916).

¹⁰ Reynolds, *J. Chem. Soc.*, **119**, 460 (1921).

TABLE III
INTERFACIAL TENSIONS AGAINST MERCURY

Organic liquid	Temp., °C.	Dens. diff.	H_2 , mm.	$\frac{1}{r_1} - \frac{1}{r_2}$	S_{25} , dynes/cm.
	Apparatus No. 4	$r_1 = 0.1927$	$- 0.1932$		
		$r_2 = 0.5033$	$- 0.5072$		
Water	25.08	12.537	19.47	3.199	374.2
Benzene	25.13	12.660	18.34	3.199	355.5
Nitrobenzene	25.09	12.336	18.20	3.199	344.1

ful work of Harkins can be made quickly and easily with this double capillary apparatus. The use of the double capillary apparatus presents no special difficulties. It does, in fact, possess some advantages over the single capillary. The position of no flat meniscus need be determined. This allows a greater degree of accuracy in measuring the height of the mercury column, which is a very outstanding source of error with a liquid so dense.

Interfacial tension data obtained with the double capillary method are given in Tables I, II and III.

Summary

Two new types of apparatus have been described for making interfacial tension measurements by the capillary rise method. These are the only methods so far devised for securing accurate values of the interfacial tensions where only small amounts of the liquid are available. The first type of apparatus gives good results without the need of determining carefully the density of the organic liquid. The second type gives very accurate results provided the density is known or is determined with precision. The interfacial tension values of a number of standard reference liquids have been determined with these apparatus and the results show good agreement with the most generally accepted of those reported in the literature.

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