

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Direct Measurement of the Spreading Pressures of Volatile Organic Liquids on Water

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The spreading pressures of organic liquids on water can be measured directly with the use of a hydrophil balance.^{2,3} The method is convenient and practical but until recently it was limited to measurements with non-volatile liquids. Extension of the method to include volatile liquids was accomplished by Washburn and Keim,⁴ who employed a monomolecular film to confine the volatile liquids to a small area of water surface, and to transmit the spreading pressures of the liquids to the balance. These investigators compared their results with the values of the spreading coefficient which Harkins⁵ has calculated from surface tension and interfacial tension data. For five of the six liquids investigated, they found that their measured spreading pressures agreed with Harkins' coefficients to within 2 dynes. But for the remaining liquid, isoamyl chloride, they found a difference which was so great (19 dynes) that questions were raised as to whether the principle they used was sound, and whether the quantities they measured were actually spreading pressures.

To answer the above questions and to lend confirmation to the method in general, it was decided to make a careful study of a few volatile liquids, and to redetermine not only spreading pressures, but spreading coefficients as well. Accordingly, the spreading pressures of carefully purified samples of four liquids were measured by the principle used by Washburn and Keim. Surface and interfacial tension measurements were then made with the same samples, to provide data for the calculation of spreading coefficients by Harkins' method. Isoamyl chloride was chosen for this work because of the questions its use had raised. Benzene and toluene were chosen since they are liquids with well established constants and, as such, serve to confirm the correctness of the surface and interfacial tension measurements of the other liquids. The fourth liquid, acetophenone, has not been used previously in spreading pressure studies, and is interesting because it has a

much higher spreading pressure and a greater solubility in water than the other liquids.

Materials.—Stearic Acid: the best grade obtainable from Eastman Kodak Company was used for film material.

Isoamyl chloride: the best grade from Eastman Kodak Company was carefully refractionated through a twenty-one stage Snyder column.⁶ Only the middle third of the distillate was taken for use. The specific gravity d^{25}_4 was 0.8700.

Benzene: Coleman and Bell c. p. grade was dried over sodium, distilled from an all glass apparatus, and recrystallized twice, f. p. 5.44°, d^{25}_4 , 0.8734.

Toluene: the best grade of synthetic product from Eastman Kodak Company was used as purchased. However, the reproducibility of interfacial tension measurements was improved by a preliminary extraction with water. This treatment apparently removed minute amounts of surface active impurity. The specific gravity d^{25}_4 was 0.8623.

Acetophenone: the best grade from Eastman Kodak Company was recrystallized slowly seven times, f. p. 19.02°, d^{25}_4 , 1.0239.

Water: distilled water was redistilled from alkaline permanganate through a block tin condenser and collected while hot. It was stored in soft glass bottles which had been used for years for the storage of redistilled water, and was used within a few days after distillation.

Apparatus.—For spreading pressure measurements a hydrophil balance was used which was very similar to that previously described,³ except that the tray was constructed of bronze instead of aluminum. The tray and aluminum barriers were covered with many coats of Bakelite lacquer as described by McBain and Perry,⁷ and additional, fresh coats were applied from time to time throughout the investigation to maintain a clean, nonwetttable surface. The instrument was housed in a dust-proof cabinet having glass sides and top. The temperature in the cabinet was regulated so that the temperature of the water in the tray remained at $25 \pm 0.4^\circ$.

For surface tension measurements a Pyrex glass capillary of the closed type described by Bigelow and Washburn⁸ was used. The large arm was made of tubing having a diameter of 50 mm. The capillary tube was selected for uniformity. At ten different positions distributed over a 3-cm. length of the capillary tube, the radius was determined by measuring the capillary rise of pure water in the tube. (The surface tension of water was taken as 72.08 dynes/cm. at 25°.)⁹ From this calibration the radius was found to be 0.01920 cm., and at any one position it was known to within ± 0.00001 cm. The calibration was con-

(1) Samuel Avery Research Fellow, 1940-1941.

(2) Marcella, *Compt. rend.*, **173**, 38 (1921).

(3) Langmuir and Schaeffer, *Chem. Rev.*, **24**, 181 (1939).

(4) E. R. Washburn and C. P. Keim, *This Journal*, **62**, 1737 (1940).

(5) Harkins, Clark and Roberts, *ibid.*, **42**, 700 (1920).

(6) The Snyder column is described by Hill and Ferris, *Ind. Eng. Chem.*, **19**, 379 (1927).

(7) McBain and Perry, *ibid.*, **31**, 35 (1939).

(8) S. L. Bigelow and E. R. Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

(9) Bartell, Case and Brown, *This Journal*, **55**, 2760 (1933).

firmed by the well-known mercury thread method, which gave a radius of 0.01920 ± 0.00004 cm.

Interfacial tension measurements were made with a soft glass capillary instrument which was similar to the double-cylinder type designed by Bartell and Miller¹⁰ except that it could be closed. A reference mark was etched on the capillary tube, and within a 3-mm. range above this mark, eight measurements of the capillary rise of water gave a radius of 0.03114 ± 0.00002 cm. The calibration was confirmed by the mercury thread method, which gave a radius of 0.03114 ± 0.00003 cm. In order to measure the capillary rise of water in the interfacial capillarimeter it was necessary to modify the design of the instrument temporarily. An outlet tube was sealed to the bottom, and the top openings were tightly stoppered. Then the instrument could be inverted and used as an ordinary surface tension capillarimeter.

Measurements of capillary rise were made with a Gaertner cathetometer designed to read to 0.0001 cm. A careful study was made of the problem of accurate measurement of the location of the large meniscus, and of the proper illumination for this measurement. Very satisfactory results were obtained with the use of metal shields which aligned the axis of the cathetometer telescope with the exact center of the meniscus and excluded all light which came from points below a plane tangent to the bottom of the meniscus. Accurate focusing was obtained by first bringing into sharp focus the nearest wall of the large glass tube containing the meniscus, and then moving the telescope nearer the meniscus by a distance of r/n mm., where r is the radius of the tube and n is the index of refraction of the liquid in the tube. In actual practice, sharpness of focus was improved, without apparent change in meniscus position, when the distance through which the telescope was moved was shortened to $[(r/n) - 4]$ mm. This improvement in focus is to be expected when one remembers that the center portion of a large meniscus is almost exactly flat.¹¹

Temperature control for all capillary rise measurements was obtained by immersing the capillarimeters in a water-bath regulated to $25 \pm 0.01^\circ$. The front and back sides of the bath were equipped with parallel plate glass windows.

Procedure and Results

For spreading pressure measurements the procedure of Washburn and Keim was used with some modifications, as follows. A film of stearic acid on water was slowly compressed as in the usual determination of pressure-area curves. At intervals the compression was stopped, the film pressure (hereafter called "initial" film pressure) was recorded, and a few drops of volatile liquid were allowed to fall on the film. The liquid spread on the water and pushed back the film, thus increasing the film pressure. Greater pressure increases resulted when larger amounts of liquid were used, but the maximum pressure which could

be obtained in this manner was a very definite, reproducible value, and was taken to be the spreading pressure of the liquid. The spreading pressure thus measured was constant over a wide range of initial pressures, as can be seen in column 2 in Table I. It was reproducible to within ± 0.1 dyne.

During the time that elapses while a direct measurement of spreading pressure is being made, organic liquid and water are in direct contact, and some of each must dissolve in the other. The effect is a lowering of surface tensions. Recently, Harkins¹² made a thorough analysis of this effect, and as a result distinguished three possible types of spreading coefficients: (1) the "initial" coefficient—obtained with pure water and pure organic liquid, (2) the "semi-initial"—obtained with pure water and water-saturated organic liquid, and (3) the "final" coefficient—obtained with mutually saturated water and organic liquid. The spreading pressures we report in this paper are those which are realized experimentally within a few seconds of the time that a drop of organic liquid is placed on the surface of water. They should be expected to correspond to spreading coefficients which fall between the "initial" and "semi-initial" coefficients. These two coefficients are nearly identical for isoamyl chloride,

TABLE I
SPREADING PRESSURES AT 25° (DYNES/CM.)

(1) Initial pressure	(2) Pressure as added drop spreads	(1) Initial pressure	(2) Pressure as added drop spreads
Isoamyl chloride		Toluene	
2.8	11.8	0.2	2.5
5.8	11.7	0.6	8.7
7.4	11.7	1.8	8.8
9.0	11.6	4.7	8.8
10.5	11.7	6.3	8.8
11.5	11.7	7.9	8.8
		8.8	9.1
Benzene		Acetophenone	
0.6	2.9	2.8	9.8 ^a
0.6	10.0	2.8	21.6 ^a
4.5	10.1	8.7	21.7 ^a
6.7	10.1	9.4	20.6
7.4	10.0	13.4	21.1
8.5	10.0	14.9	21.6 ^a
9.2	10.0	16.5	21.0
9.8	10.1	16.5	21.6 ^a
10.1	10.3	19.5	21.6 ^a
11.1	11.3	21.5	21.6 ^a

^a Measured with fresh water in tray of balance.

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

(11) Richards and Coombs, *ibid.*, **37**, 1636 (1915).

(12) W. D. Harkins, *J. Chem. Phys.*, **9**, 552 (1941).

benzene, and toluene on account of the very slight solubility of water in these liquids. The spreading coefficients which we report in this paper are "initial" coefficients.

In Table I those pressure values which fell above or below the spreading pressure can be explained readily. When the initial pressure was as great or greater than the spreading pressure, no spreading could occur, and liquid added to the film took the form of a lens. Unstable lenses were formed even at pressures slightly below the spreading pressure. Whenever a lens formed, the pressure was abnormally high, for the film had to maintain the shape of the lens against the action of gravity.¹³ Pressures which appear too low were obtained when insufficient volatile liquid was used or enough volatile liquid dissolved in the water to lower its surface tension. This last effect was noticeable only in the case of acetophenone. With this liquid, maximum spreading pressure values could be reproduced only two or three times before increasing concentration of acetophenone necessitated a change of water.

For surface tension and interfacial tension measurements the procedures used were those which are standard for the instruments employed. Corrections were made for the shape of the small meniscus and for the weight of vapor above the large meniscus. The values obtained were used to calculate spreading coefficients, and the results are summarized in Table II.

The agreement between spreading pressures and spreading coefficients in Table II is evidence that the method used to measure spreading pressure is sound. The disagreement with Harkins' values in the case of isoamyl chloride is due chiefly to a disagreement in interfacial tension values (Harkins reports 15.44 dynes/cm. at 20°). In this

(13) Hardy, *Proc. Roy. Soc. (London)*, **86A**, 510 (1912)

TABLE II
SURFACE TENSIONS, INTERFACIAL TENSIONS, SPREADING PRESSURES AND SPREADING COEFFICIENTS AT 25° (DYNES/CM.)

	Surface tension of water = 72.08 ⁹			
	Isoamyl chloride	Benzene	Toluene	Acetophenone
Surface tension	22.90	28.24	27.94	38.80
Interfacial tension	37.71	33.9	35.7	12.32
Spreading coefficient	11.5	9.9	8.5	21.0
Spreading pressure	11.7	10.0	8.8	21.6
Harkins' values ⁸ for spreading coefficient (20°)	33.88	8.91	6.84	..

investigation it was found that the best isoamyl chloride sold by Eastman Kodak Company gave interfacial tension values which fell very rapidly with time. Only after careful refractionation were reproducible and constant values obtained.

In the determination of spreading coefficients, the errors in all three of the necessary measurements contribute to the error in the result. An examination of accepted surface and interfacial tension data^{5,9,14} shows that calculated spreading coefficients may vary over a range of 0.5–0.9 dyne even for liquids such as benzene and toluene, which have comparatively well established properties.

Summary

1. The method of direct measurement of the spreading pressures of volatile liquids involving the use of monomolecular films has been shown to give good results for isoamyl chloride, benzene, toluene, and acetophenone.
2. The surface tensions and the interfacial tensions of the organic liquid–water interface for the above four liquids have been measured.
3. The spreading coefficients of these four liquids have been redetermined.

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(14) Harkins, Brown and Davies, *THIS JOURNAL*, **39**, 354 (1917).