[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Properties of Liquids in Fine Capillaries. I. Surface Tension and Density

BY LEONARD H. COHAN* AND GLEN E. MEYER

Some years ago Shereshefsky[1] in this Laboratory measured ΔP, the lowering in the normal vapor pressure of liquid in capillaries 2 to 6 microns in radius. Shereshefsky found that ΔP for water in a quartz capillary 2.07 μ in radius was eight times the lowering, ΔP_K, calculated from Lord Kelvin's equation.[2] Kelvin's equation states

$$\ln \frac{P}{P_0} = \frac{-2\sigma V}{rRT} \qquad (1)$$

where

σ = surface tension of the liquid
V = molar volume of the liquid
r = radius of the capillary
R = gas constant in ergs/deg. if σ is in dynes and V in cc. per mole
T = absolute temperature
P_0 = normal vapor pressure of the liquid
P = vapor pressure of the liquid in the capillary
$\Delta P_K = P_0 - P$

In the same work the measured value of ΔP for toluene was more than nine times ΔP_K in a capillary 5.3 μ in radius. Shereshefsky attributed these considerable effects chiefly to an increase in σ in the small capillaries. The results of Woodland and Mack[3] with water vapor in Pyrex capillaries approximately 6 μ in radius show that σ and V are equal to the normal values. These results agree essentially with Shereshefsky, who found that in quartz tubes of radius 5 μ or greater the vapor pressure lowering for water was normal within limits of accuracy (about 0.002 mm.) of his experiments. However, in a capillary 2.07 μ in radius he found ΔP to be abnormally large.

In the following experiments an attempt was made to determine whether the surface tension does change in small capillaries. In the first part of the work the product σV was obtained by measuring the capillary rise of water and toluene in small capillaries. In the second part σ was obtained directly by measuring the pressure, π, which was required to just prevent any capillary rise.

Apparatus and Procedure

Measurement of h.—Capillaries were made by drawing out tubes of Pyrex glass. Long sections of the capillaries which were found to be circular and of uniform diameter were suspended from the ceiling with their lower ends dipping into a tube of the desired liquid. A reading was taken when the liquid reached its maximum height in the capillary. By manipulation of the capillary the meniscus was raised past its equilibrium height and allowed to fall until equilibrium was again attained, whereupon a second reading was taken. The mean of these two readings was considered to be the true equilibrium height and is listed in column 2, Table I, as h. It should be noted that h changes by less than 0.5% per degree centigrade. Since we were unable to obtain r to better than 3%, accurate temperature control was unnecessary. The temperature in all the experiments was approximately 23°.

Measurement of r.—The equilibrium position of the meniscus in the capillary was marked. Then, after measurements of h were completed, the diameter of the capillary in the region of the mark was measured with a microscope to ± 0.2 μ. The true radius was calculated by using the approximate formula $r = D/n$ where D is the apparent radius and n the refractive index of Pyrex glass (1.47). The most probable value of r appears in column 3 of Tables I and II.

TABLE I

Liquid	h, cm.	r, microns	σV, dynes/sq. cm.	$(\sigma V)_0$, dynes/sq. cm.	σ_m, dynes/cm.
H_2O	106	14.4	1350	1310	74.4
Toluene	68	10.0	3060	3020	29.8
Toluene	77.5	8.25	2880	3020	27.1
Toluene	235	2.8	2970	3020	28.0
Toluene	255	2.8	3210	3020	31.0

TABLE II

Liquid	π, dynes/sq. cm.	r, microns	σ_0, dynes/cm.	σ_m, dynes/cm.
H_2O	55.5×10^4	2.6	72.3	72.2
Toluene	30.8×10^4	1.9	28.7	29.2

Measurement of σ.—Figure 1 is a sketch of the apparatus used to determine σ directly.[4] The pressure over the liquid in tube "A" was reduced until the meniscus in the capillary came to rest in the neighborhood of the surface of the bulk liquid. The difference between this reduced pressure and atmospheric pressure is equal to π which was read directly on the open end manometer. The apparent equilibrium values of π for both a rising and falling meniscus differed by less than 2 mm. of mercury. The average of the two values is recorded in column 2 of Table II.

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* Present address: Continental Carbon Company, 6130 West 51st St., Chicago, Ill.

[1] J. L. Shereshefsky, THIS JOURNAL, **50**, 2966 (1928).

[2] Several typographical errors appear in Shereshefsky's article (1). To avoid confusing the reader the correct values are as follows: on p. 2979 "...a straight line is obtained which cuts the ΔP axis at 0.05 mm. of mercury" should read, "...0.005 mm. of mercury." Further down the same page, "...is equal to 0.004 mm. of mercury" should be, "0.003 mm." On page 2980, "The value...for this capillary is 0.08 mm." should read "...0.008 mm."

[3] Woodland and Mack, THIS JOURNAL, **55**, 3149–3161 (1933).

[4] *Cf.* Ferguson and Dowson, *Trans. Faraday Soc.*, **17**, 384 (1921).

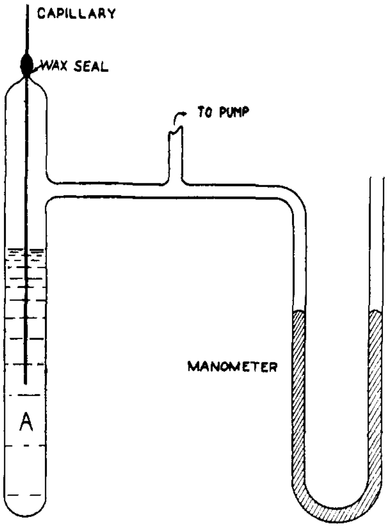

Fig. 1.

Discussion of Results

The product σV, Table I, column 4, was calculated from the equation for capillary rise

$$\sigma V = \frac{rMgh}{2\cos\theta} = \frac{rMgh}{2} \qquad (2)$$

where M is the molecular weight of the vapor and g the acceleration of gravity. The angle of contact, θ, of the liquid against the wall is zero for clean glass surfaces according to Richards and Carver.[5] In column 5, Table I, $(\sigma V)_0$ the value of the product σV for normal liquid is given. The agreement between σV and $(\sigma V)_0$ is well within the limits of experimental error, which are approximately ±5%. The surface tension, σ_m, of the liquid in the capillaries can be determined by assuming that V is the same as the normal molal volume. Column 5, Table I, gives these values of σ_m. In column 5, Table II, appear the values of σ_m calculated from the equilibrium pressure by means of the relation

$$\pi = 2\sigma_m/r \qquad (3)$$

where π is in dynes/sq. cm., r in cm. and σ_m in dynes/cm. The normal surface tension, σ_0, is listed in column 4. It is seen that in both Tables I and II, $\sigma_m = \sigma_0$ within the limits of experimental error (±5%). Furthermore, from the experimental value of σV in Table I, this product is seen to have its normal value. Since in Table II, σ is shown to be normal, V as well as σ must have its normal value in capillaries of the size listed in Table I.

The above results are at variance with Shereshefsky's explanation of the abnormal lowering of the vapor pressure of water and toluene which he obtained from his measurements of rates of evaporation. Moreover, the results of R. Bulkley,[6] who found that the viscosity of various oils and fatty acids was entirely normal even in tubes as small as 5 μ also appear incompatible with Shereshefsky's assumption of markedly increased surface tension. Certainly Bulkley's work would preclude the explanation of Shereshefsky's experiments advanced by McBain,[7] who suggested that the abnormal decrease in vapor pressure might be due to the formation of oriented chains of molecules across the narrow capillaries. If such oriented chains were to form across a capillary the flow of liquid through the capillary would be impeded; hence, the viscosity as measured by the capillary method would be increased. As pointed out by Bulkley the absence of any increase in viscosity precludes the formation of these chains. If long chain polar molecules such as fatty acids do not orient themselves under the above conditions, toluene and water would not be expected to do so.

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Summary

The surface tensions of water and toluene were measured in capillaries of radii as small as 2 μ. The results indicate that the surface tensions and densities of these liquids do not vary from their normal values within the limit of accuracy of the experiments (±5%).

According to this evidence increase in surface tension cannot be accepted as the explanation for the abnormal vapor pressure lowerings found by Shereshefsky.

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[5] Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

[6] R. Bulkley, Res. Paper 264, *Bur. Standards, J. of Research*, **6**, (Jan., 1931).

[7] J. W. McBain, "Sorption of Gases by Solids," G. Routledge and Sons Ltd., London, 1932, p. 445.