7-1-1955

Liquid-Vapor Equilibrium in Microscopic Capillaries. II. Non-Aqueous Systems

Leon J. Shereshefsky

Recommended Citation

Shereshefsky, Leon J., "Liquid-Vapor Equilibrium in Microscopic Capillaries. II. Non-Aqueous Systems" (1955). *Faculty Reprints*. 184.
https://dh.howard.edu/reprints/184

LIQUID–VAPOR EQUILIBRIUM IN MICROSCOPIC CAPILLARIES. II. NON-AQUEOUS SYSTEMS

By M. Folman and J. L. Shereshefsky[1]

*Contribution from the Physical Chemistry Laboratory,
Israel Institute of Technology, Haifa, Israel*

The lowering of the vapor pressure of toluene and isopropyl alcohol over concave surfaces was measured in capillaries 0.8 to 3.0 μ in radius. The determination was based on the principle of equilibrium between the liquid contained in a cone-shaped capillary and the vapor of the same liquid over a solution of a non-volatile solute. The results obtained point out the inapplicability of Kelvin's relation to capillaries of the order concerned. Moreover, it seems that the polarity of the liquid influences the extent of the deviation from the equation. These deviations are explained on basis of assumption of long range forces.

The vapor pressure lowering over curved surfaces is given by Kelvin's relation[2]

$$\ln \frac{P}{P_0} = \pm \frac{2\sigma M}{dRTr} \qquad (1)$$

where P_0 is the vapor pressure over a plane surface; P the vapor pressure over a curved surface of radius of curvature r; d the density; M the molecular weight; σ the surface tension; R the gas constant, and T the absolute temperature. The positive and negative signs apply to convex and concave surfaces, respectively.

For convex surfaces (1) has been verified for radii of curvature of several microns, for water droplets by Goodris and Kulikova,[3] for droplets of dibutyl phthalate by Shereshefsky and Steckler,[4] by Lyalikov[5] for mercury droplets and by La Mer and Gruen,[6] for dioctyl phthalate and oleic acid droplets less than a micron in diameter.

For concave surfaces the experimental results are considerably different from the calculated. Shereshefsky[7] found that the lowering of the vapor pressure in capillaries of 4.05 μ radius is twenty-three fold. On the other hand, Thoma[8] working with capillaries of tenths of a millimeter radius obtained results in agreement with Kelvin's relation. Recently Shereshefsky and Carter,[9] in capillaries 3 to 10 μ in radius, obtained lowerings of the vapor pressure of water 30 to 80 times that calculated.

The present work was undertaken with the view of testing the applicability of the Kelvin relation in cases of concave surfaces of organic liquids, and to observe the influence of polarity on the abnormal effects found by Shereshefsky.

Experimental

1. Method.—Similar to the method of Shereshefsky and Carter,[9] the measurements were based on the equilibrium established between the liquid in a cone-shaped capillary and its vapor from a bulk solution of the liquid and a non-volatile solute. The liquid column in a capillary of this shape, when brought in contact with the vapor of the solution, will either increase or decrease in height, depending on the relative vapor pressures of the two parts of the system. In a full capillary, the liquid will evaporate, and the radius of the meniscus will decrease until the vapor pressure over the meniscus will equal the vapor pressure of the solution. After this point is reached, continued contact of the two parts of the system will not affect the position and radius of the meniscus. The latter may be obtained from the relation

$$r \cos \theta = r' \qquad (2)$$

where r and r' are the radii of the meniscus and capillary, respectively, and θ is the contact angle. The vapor pressures of the solutions at the concentrations involved in these experiments were calculated with adequate accuracy from Raoult's law.

2. Apparatus.—The apparatus consisted of a high vacuum system, thermostat, vessel containing the capillaries and the solution, a vessel for weighing the solvent, an arrangement for the purification and storage of the solvent and a microscope-cathetometer with a source of light.

The capillaries were prepared from 0.5 mm. Pyrex capillary tubing. The tubing was cleaned with hot concentrated nitric acid and rinsed with redistilled water for several hours. The drawing of the cone-shaped capillaries was carried out in a cross flame produced by two microburners by a twisting motion in two steps. Suitable portions were then selected for calibration and use. The calibration was made on a microscope with a screw micrometer eyepiece of tenfold magnification and an objective with a 44-fold magnification. The micrometer eyepiece was previously calibrated against a stage micrometer consisting of a glass plate with an engraved line one mm. in length and divided into one hundred equal parts.

The capillary diameter was measured at 0.5-mm. intervals starting from the open end. The light used came from a microscope lamp provided with a blue filter. The precision of the measurements was 0.1 μ for radii of 0.7 μ and larger. In order to eliminate capillaries with an elliptical cross section, three calibrations were made at different positions after the rotation of each capillary around its axis. Owing to the fact that the walls of the capillary act as lenses, it was necessary to introduce a correction in order to obtain the real radius. It can be shown that if the thickness of the capillary wall is at least ten times greater than the inner radius, the real radius may be obtained by dividing the apparent radius by the refractive index of the glass.

Eight suitable capillaries were attached to the inner wall of a Pyrex tube 14 mm. in diameter which served as the capillary chamber. They were arranged in four pairs and placed on different levels 30 mm. apart. The attachment of the capillaries was carried out by heating carefully, with a microburner from the outside, the point of the tube opposite the capillary's closed end, until the glass melted slightly. This prevented any possible damage to the capillary.

A 100-cc. bulb attached to the lower end of the capillary chamber served as the solution vessel.

The thermostat was of 250-liters capacity. It included a toluene–mercury thermoregulator, a 400 watt heating element with a variable resistance in series, an electronic relay, a copper coil connected to a refrigerating unit with a circulating pump, and a powerful electrical stirrer. The

(1) Visiting Professor of Physical Chemistry (1950–1952) under sponsorship of U.S.A. State Department.

(2) W. Thomson, *Phil. Mag.*, [4] **42**, 448 (1871).

(3) N. Goodris and L. Kulikova, *J. Russ. Phys. Chem. Soc., Physical Part*, **56**, 167 (1924).

(4) J. L. Shereshefsky and S. Steckler, *J. Chem. Phys.*, **4**, 108 (1936).

(5) K. S. Lyalikov, *Acta Physicochim., U.R.S.S.*, **12**, 42 (1940).

(6) V. L. La Mer and R. Gruen, *Trans. Faraday Soc.*, **48**, 410 (1952).

(7) J. L. Shereshefsky, *J. Am. Chem. Soc.*, **50**, 2966 (1928).

(8) H. Thoma, *Z. Physik*, **64**, 224 (1938).

(9) J. L. Shereshefsky and C. P. Carter, *J. Am. Chem. Soc.*, **72**, 3682 (1950).

TABLE I
TOLUENE DATA AT 20°

Mol. frac.	Kelvin radius, μ	Cap. 7	Cap. 16	Cap. 14	Cap. 5	Cap. 17	Cap. 1	Cap. 18	Cap. 2	Obsd./Calcd.
0.00466[b]	0.51	...	1.55	1.60	1.70	2.35	1.50	1.45	1.50	2.9
.00611[a]	.41	1.80	1.80	1.30	full	2.10	1.20	1.20	1.30	3.5
.00611[b]	.41	...	1.20	1.30	1.30	2.20	1.00	1.35	1.30	3.0
.00763[b]	.34	...	1.15	1.30	1.30	1.65	0.95	1.20	1.25	3.5
.00763[a]	.34	...	1.30	1.35	1.30	2.00	1.00	1.10	1.25	3.6
.00900[b]	.28	...	...	1.30	1.35	2.05	1.10	1.05	1.10	4.2
.01080[b]	.23	...	...	1.25	1.30	2.00	1.00	1.00	1.00	4.8
.01174[b]	.21	...	...	1.10	1.25	1.90	0.90	0.95	0.95	4.9
.01174[a]	.21	...	...	1.20	1.30	1.90	0.95	1.00	0.95	5.1
.01375[b]	.18	...	...	1.05	1.20	1.85	0.90	0.90	0.85	5.4

[a] Evaporation. [b] Condensation.

TABLE II
ISOPROPYL ALCOHOL DATA AT 20°

Mol. frac.	Kelvin radius, μ	Cap. 14	Cap. 5	Cap. 17	Cap. 1	Cap. 18	Cap. 2	Obsd./Calcd.
0.00342[a,c]	0.39	1.90	2.15	...	2.30	2.50	2.60	5.8
.00342[a,c]	.39	2.00	2.25	...	2.35	2.55	2.65	5.7
.00342[b,c]	.39	1.80	2.10	...	2.20	2.50	2.55	6.0
.00342[b,c]	.39	1.80	2.10	...	2.20	2.60	2.60	5.9
00411[a]	.33	1.70	1.70	...	1.50	1.60	1.80	5.1
.00471[a]	.29	1.60	1.30	...	1.30	1.35	1.60	4.9
.00471[a]	.29	1.50	1.40	...	1.40	1.30	1.50	5.0
.00552[a]	.25	1.55	1.20	1.90	1.35	1.20	1.30	5.3
.00552[a]	.25	1.60	1.30	1.90	1.30	1.25	1.40	5.4
.00663[a]	.20	1.40	1.20	1.70	1.20	1.20	1.30	6.3
.00923[a]	.15	1.30	1.00	1.80	1.25	1.20	1.30	8.0
.01226[b]	.11	0.95	0.95	1.55	1.00	1.00	1.10	9.0
.01226[a]	.11	1.00	1.00	1.65	1.05	1.10	1.20	9.6
.01578[a]	.086	0.95	1.10	1.65	1.10	1.10	1.10	12.6
.01578[a]	.086	0.95	1.00	1.75	1.00	1.05	1.00	11.6

[a] Evaporation. [b] Condensation. [c] Measurements at 25°.

temperature was maintained constant within 0.001 to 0.002° for 24 hours.

The weighing vessel was a glass bulb of 60 cc. with a stopcock. It was connected to the vacuum system by means of a ground glass joint and a three-way stopcock. The vessel for storing pure liquid consisted of two conjugated bulbs attached to the system through a stopcock.

The position of the meniscus was measured by a Gaertner cathetometer that permitted adjustment to 0.01 mm. A fluorescent lamp placed outside the thermostat served as a source of diffuse light.

Dibutyl phthalate was used as the non-volatile solute. It was prepared from an analytical grade sample by double vacuum distillation and collection of the middle fractions. The toluene with which the first series of measurements was carried out was purified from an analytical grade sample by shaking with concentrated sulfuric acid until no brown color appeared, washing with dilute NaOH solution and distilled water, drying over metallic sodium by refluxing for 24 hours and distilling. The isopropyl alcohol, of analytical grade, was twice distilled and dried over calcium oxide under reflux for 24 hours and distilled.

3. Procedure.—A weighed quantity of the solute was introduced into the solution vessel which was then pumped for 24 hours and left under high vacuum for several days. The purified solvent was introduced into the storage vessel, and was freed of dissolved air by vacuum distillation from one bulb to the other and subsequent pumping off of the freed air. The solvent was then transferred to the weighing bulb by distillation *in vacuo*. The bulb was removed and weighed, and after its re-attachment to the system the solvent was transferred by evaporation to the solution vessel. Equilibrium was approached from two directions, by evaporation from full capillaries and by condensation into empty or partially filled capillaries. The positions of the meniscus were measured at intervals of 15 to 30 minutes.

The level at which the meniscus remained unchanged for one or two hours was accepted as the equilibrium point.

Results

The contact angles of toluene and isopropyl alcohol as determined macroscopically on glass are zero. To determine the angle in microscopic capillaries a series of microphotographs were taken of capillaries of approximately 10 μ radius and partially filled with the liquid. The menisci were clearly seen and showed that the contact angle was not appreciably different from zero. Figure 1 shows the variation of the radii of the capillaries with the distance from the open end.

The measurements on toluene were carried out at 20°. They were made at seven different concentrations of the solution. Three of the determinations were made both by evaporation and condensation. The results are given in Table I. In column 1 is given the concentration of the solutions in mole fractions, in column 2 the theoretical Kelvin radius, in the remaining columns except the last are given the observed radii of the capillaries at the level of the meniscus at equilibrium, and in the last column is given the ratio of the average observed radius to the calculated one. The results in capillary 17 are not included in the averages.
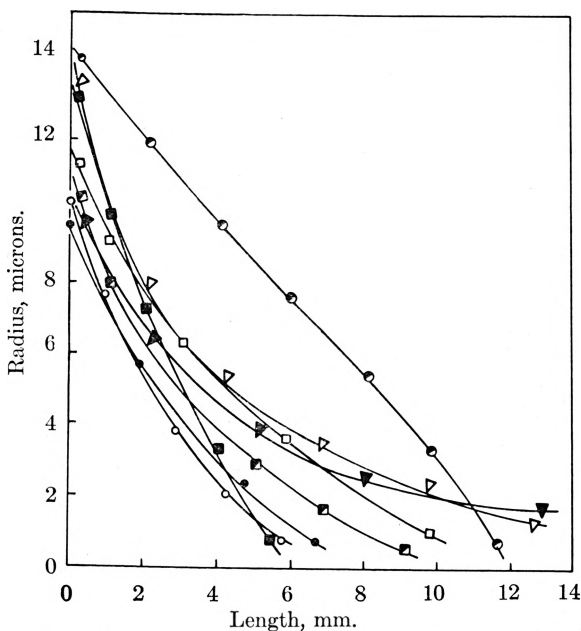
Good agreement can be observed between the

Fig. 1.—Variation of capillary bore: cap. 1, ●; cap. 2 ■; cap. 5, ○; cap. 7, ▲; cap. 14, □; cap. 16, △; cap. 17, ◑; cap. 18, ◪.

Fig. 2.—Relative vapor pressure lowering. Isopropyl alcohol: Kelvin 1, measurements ○; toluene: Kelvin 2, measurements ■.

results in different capillaries with the exception of capillary 17 which for yet unknown reasons always gave higher results, as compared with the others. There is also good agreement between the values obtained by evaporation and condensation procedures, except for capillaries 7 and 16 at the mole fraction 0.00611. At this concentration the capillaries 7 and 16 gave values which were higher than the average, perhaps, because being the largest capillaries they required a long time to reach equilibrium at this low concentration. These two capillaries were calibrated to 1.7 and 1.1 μ, respectively, and therefore show no data for radii below these. It can be seen from the last column that the ratio $r(\text{obs.})/r(\text{calcd.})$ increases from 2.9 for the lower concentration to 5.4 for the highest concentration.

All measurements on isopropyl alcohol were carried out at 20°, except for the mole fraction 0.00342. For technical reasons, the latter had to be made at 25°. Table II contains the results obtained for ten different concentrations. Here also, good agreement exists between the values for the several capillaries. An exception is capillary 17 which again gave higher values. At low concentrations the spread in the results for the different capillaries is rather great, although the agreement between capillaries on the same level in the capillary vessel is remarkably good. The ratio $r(\text{obs.})/r(\text{calcd.})$ for all capillaries, except no. 17, varies from 4.9 to 12.6.

Discussion

The results of these measurements show that the Kelvin equation cannot be applied in estimating vapor pressure lowering over concave surfaces in microscopic capillaries. Nor can it be applied in estimating pore radii at given vapor pressures as it is done in adsorption analysis. The observed lowering is many times greater than the value
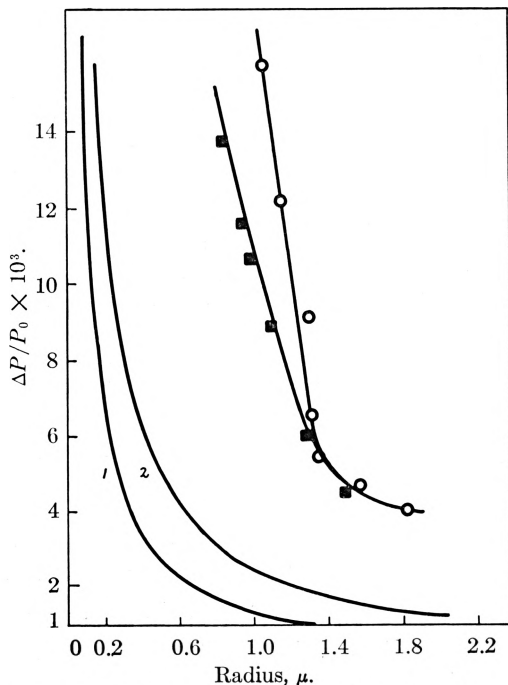
calculated with this equation. Moreover, the effect differs in magnitude with the nature of the liquid. The lowering for isopropyl alcohol was found to be much greater than for toluene, and the results for water reported in the preceding paper[9] show that the effect for the latter is still greater. This effect seems to change with the polarity of the liquid, and increases with increasing dipole moment of the molecule.

It is well known that many physical properties of capillary held liquids are different from those for the bulk liquid. To the literature references given in the preceding paper, describing these anomalies, can be added the observations on the freezing point of capillary condensates,[10-12] the increase in the heat of vaporization,[13] the rise in the critical temperature,[14] and the increase in specific polarization.[15] In so far as density[16,17] and surface tension[18] are concerned, experimental data show values which are very near those of the bulk liquid. Theoretical considerations by Tolman[19] and Hill[20] require that the effect of curvature on surface tension be slight at the curvatures prevailing in these experiments, and become

(10) S. Brunauer, "The Adsorption of Gases and Liquid," Princeton University Press, Princeton, N. J., 1945, p. 444.

(11) J. P. Jones and R. A. Gortner, THIS JOURNAL, **36**, 387 (1932).

(12) M. Shimizu and I. Higuti, *ibid.*, **56**, 198 (1952).

(13) L. F. Gleysteen and V. R. Deitz, *J. Research Natl. Bur. Standards*, **35**, 283 (1935).

(14) W. A. Patrick, W. C. Preston and A. E. Owens, THIS JOURNAL, **29**, 431 (1925).

(15) S. Kurosaki, *ibid.*, **58**, 320 (1954).

(16) E. O. Wiig and A. J. Juhola, *J. Am. Chem. Soc.*, **71**, 561 (1949).

(17) H. L. McDermot and W. G. M. Tuck, *Can. J. Res.*, **28B**, 292 (1950).

(18) L. H. Cohan and G. L. Meyer, *J. Am. Chem. Soc.*, **62**, 2715 (1940).

(19) R. C. Tolman, *J. Chem. Phys.*, **17**, 338 (1949).

(20) T. L. Hill, *J. Am. Chem. Soc.* **72**, 3923 (1950).

appreciable for radii of about ten millimicrons or less. It is of interest to point out that the observation on the specific polarization of the condensed water vapor made by Kurosaki is in good agreement with the observations on the elastic properties of liquid water in microscopic capillaries made by Deryagin.[21] In both instances, the capillary held water behaves as if it were in a solid-like form, resembling ice. These physical properties do not all depend on the curvature of the meniscus, and their abnormal values point to appreciable changes in the state of aggregation of the substances.

No anomalies have been observed in connection with positive curvatures of these magnitudes. Shereshefsky and Steckler,[4] and LaMer and Green[6] have shown that the Kelvin equation is valid for convex surfaces of droplets of various liquids ranging from 1.67 to a fraction of a micron in radius.

Furthermore, the effect observed in the present study is different in nature from that of Kelvin in several respects. Figure 2, in which is illustrated the behavior of the two liquids with respect to the theoretical and to each other, shows that the abnormal relative lowering of the vapor pressure at large capillary radii is approximately the same for both, toluene and isopropyl alcohol, while the Kelvin effect is widely different. As the capillary radius decreases, the curves diverge, with the abnormal relative lowerings of the latter liquid becoming greater. The contrary behavior is observed for the Kelvin curves; they tend to approach each other, and the difference between the relative lowerings tends to decrease with decreasing capillary radius.

These considerations lead us to believe that the

(21) B. Deryagin, *Z. Physik*, **84**, 657 (1933).

abnormal vapor pressure lowering observed in this study and, perhaps, the other abnormal capillary properties, are induced by the capillary walls. Furthermore, the magnitude of the effect and the size of the capillaries in which it is manifested leads us to believe that the forces involved are effective over appreciable distances from the wall. Instances in which forces of long range were observed have been recently gathered and reviewed by Henniker,[22] citing cases where the forces were effective over several thousands ångströms

This explanation is also supported by the observation made in the present study that the magnitude of the effect is proportional to the total molecular moments of the substances measured in the direction of the electric field. These moments were calculated to be approximately 30 D, for isopropyl alcohol, and 19 D, for toluene. The total moment for the water molecule is approximately the same as for isopropyl alcohol, while the effect is very much greater. The greater effect for water is, perhaps, due to the increased specific polarization observed by Kurosaki.[15]

Another factor supporting the explanation of the effect is the observation of the inverse relation between the effect and the capillary radius. As a wall effect, its magnitude should be proportional to the extent of surface exposed to unit volume of liquid. The ratio of lateral surface to volume in a right cone is given by $3(r^2/h^2 + 1)/r$, where r is the radius of the base and h is the height of the cone. The capillaries used in the present study approximated right cones in which r^2/h^2 was negligible with respect to unity, and in which the lateral area per unit volume was equal to $3/r$. The relative lowering of the vapor pressure was found to vary directly with this ratio.

(22) J. L. Henniker, *Rev. Mod. Phys.*, **21**, 322 (1949).