Interfacial Tension at the Boiling Point and Vapor Viscosity near the Dew Point of Binary Mixtures

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Interfacial tension (or surface tension) of compounds and mixtures of compounds is a basic property, the knowledge of which is valuable to the scientist and engineer. Emulsion and foam characteristics, mass transfer and fluid flow phenomena, film characteristics, liquid-liquid and vapor-liquid reaction behavior, and other process operations are affected by this property to a greater or lesser extent. In the absence of data for a particular system or mixture it is desirable to have methods of predicting this property with a reasonable degree of accuracy. Before this can be achieved it is necessary to obtain accurate data on a large number of systems having widely differing characteristics.

Data have been reported in the literature on the surface tension of pure compounds at temperatures ranging from 15° to 30°C.; other data relate the variation of surface tension of pure compounds with temperature, and some relate the surface tension of mixtures at constant temperature with composition. There are few, if any, data on surface tension or interfacial tension of homogeneous binary liquid mixtures in contact with their equilibrium vapors at their boiling points. To develop equipment for the determination of data of this type was one of the purposes of the present investigation.

EXPERIMENTAL EQUIPMENT

It was necessary to develop a unique apparatus and experimental procedure for the evaluation of interfacial tension at the boiling points of the mixtures in contact with their equilibrium vapors.

THEORY

The pressure differential across a curved liquid surface may be expressed as

$$p_1 - p_2 = \sigma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \qquad (1)$$

where

p_1, p_2 = pressures on the concave and convex sides of the liquid surface
σ = interfacial tension
R_1, R_2 = principal radii of curvature of the liquid surface

Equation 1 shows that the pressure is greater on the concave side of the curved liquid surface than on the convex, by an amount which is equal to the product of the interfacial tension and the sum of the reciprocals of the principal radii of curvature. The above relationship is known as Laplace's equation, of which Adam (*1*) has presented a simplified mathematical derivation.

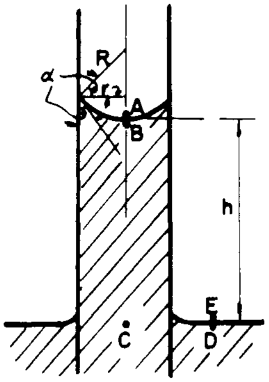

Figure 1. Capillary rise

If the surface is part of a sphere

$$R_1 = R_2 = R \qquad (2)$$

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{R} \qquad (3)$$

$$p_1 - p_2 = \frac{2\sigma}{R} \qquad (4)$$

For the particular case where the surface is plane $R_1 = R_2 = \infty$, and the pressure differential is zero.

If a glass capillary tube is standing vertically with one end immersed in a bath of liquid (Figure 1), the liquid will rise to a height *h*. *A* and *B* are the points on the two sides of the liquid surface in the capillary, and *D* and *E* are two points in the liquid surface in the bath outside the capillary. Distances *AB* and *DE* are allowed to approach the thickness of the surface film as a limit, or the distances are zero for the purpose of measurement of the pressure differential. *C* and *D* are on the same level. In case the system is static, the pressures at *A*, *E*, *D*, and *C* are equal to atmospheric pressure. The pressure differential between *A* and *B* can then be expressed as hydrostatic head *BC* or *h*. If the density of the liquid is ρ, $\Delta p = h\rho g$, where g is the gravitational acceleration.

$$\Delta p = h\rho g = \frac{2\sigma}{R} = \frac{2\,\sigma\cos\alpha}{r} \qquad (5)$$

$$\sigma = \frac{rh\rho g}{2\cos\alpha} \qquad (6)$$

where r is the inside radius of the capillary and α is the contact angle.

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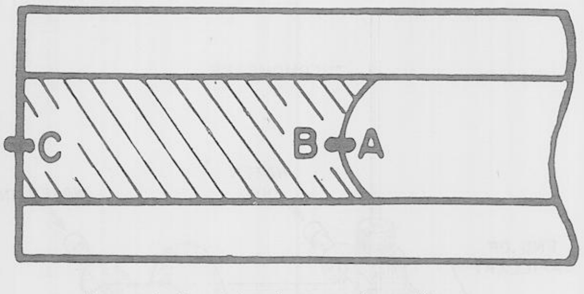

Figure 2. Liquid in horizontal capillary tube

If the liquid wets the tube, $\alpha = 0$ and the equation resolves to

$$\sigma = \frac{rh\rho g}{2}$$

For the case of a drop of liquid in a horizontal tube (Figure 2), the liquid surface between *C* and *D* is plane or the pressures at *B*, *C*, and *D* are equal. The pressure differential across the surface in the capillary may be determined by measuring the pressure difference between *A* and *D*. The interfacial tension may be calculated if the radius of the capillary is known.

A horizontal capillary tube may then be used to measure surface tension of a very small liquid sample. This method was first employed by Ferguson and Kennedy (*3*).

Thus far, the contact angle between the glass and the liquid is assumed to be zero. If the glass is clean, the contact angle is almost always zero with water and organic liquids (*1*).

The measurement of the interfacial tension of a binary system at its boiling point may be accomplished by placing a drop of liquid in the capillary, introducing the vapor in equilibrium with the liquid at its boiling point into the capillary, controlling the temperature in the capillary at the boiling point of the liquid, and measuring the pressure differential between the vapor and the liquid.

EQUIPMENT FOR MEASURING INTERFACIAL TENSION AT BOILING POINT

The equipment shown in Figure 3 was for measurement of interfacial tension of liquids at their boiling points. It is composed mainly of borosilicate glass parts connected by standard-taper ground joints or ball and socket joints. No stopcock lubricants were used, so that contamination of the systems by foreign materials from this source was avoided.

A horizontal capillary tube having a radius of 1.783 × 10^{-2} cm. and an approximate length of 17 cm. was sealed to a male 30/10 standard-taper joint, which in turn was sealed to a 12/5 ball ground joint. The distance between the two joints was 16 cm. to furnish space for mounting a spirit level. The open end of the capillary was ground with No. 1000 Carborundum to a flat surface perpendicular to the long axis of the capillary.

This capillary assembly, which is the essential part of the apparatus, has a male 30/10 standard-taper joint inserted into the female 30/10 standard-taper joint that was sealed or welded to the outer jacket at one end. Two parallel baffles perpendicular to the capillary were sealed into the other end. A small hole was located at the center of each baffle to allow the capillary tube to pass through with slight clearance. The baffles acted as a support for the capillary and as a barrier to passage of the vapor and liquid mixture pumped up from the boiling flask. A large opening on the lower part of the jacket allowed the inner mantle to be inserted. This mantle provided a means of heating the capillary to the equilibrium temperature by bathing the tube with equilibrium boiling mixture. Holes in the side of the jacket enabled the vapors to escape. A pressure tap in the outer jacket was provided to detect

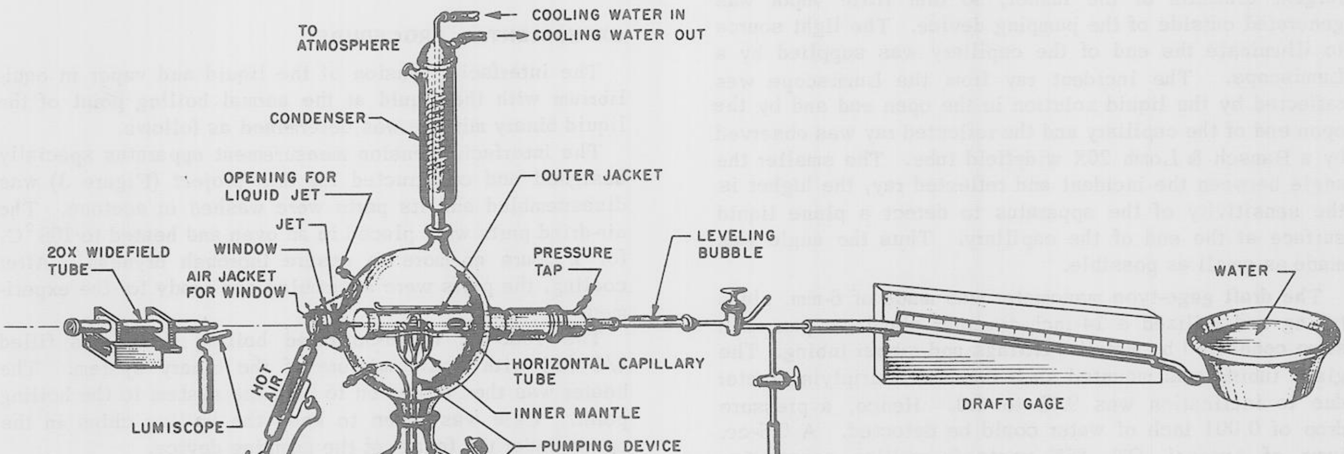

Figure 3. Interfacial tension measurement apparatus

any measurable pressure drop through the condenser. A 45/50 standard-taper joint was used to mount the outer jacket horizontally in the chamber which houses the jacket.

The chamber was constructed of a flattened 1000-ml. round-bottomed flask. It was connected to the Friedrichs condenser by means of a 24/40 standard-taper ground joint, to the boiling flask below by a 55/50 joint, and to the outer jacket by a 45/50 joint. A liquid line and a liquid jet tube were sealed in the chamber with openings at the outside of the chamber closed by 12-mm. ground-glass balls. The pressure tap was also closed by means of a 12-mm. ground-glass ball which was made by sealing the opening in a 12/2 ball ground joint. Pinch clamps were used to hold the balls into the socket joints provided at the openings.

The optically flat window of the chamber was placed perpendicular to the axis of the capillary tube. A parallel plate providing an air jacket was positioned outside the window by steel springs. The jacket consisted of a 1/4-inch glass disk sealed to a short glass cylindrical ring. The contact rim between the jacket and window was ground. Two openings were provided in the jacket for passage of hot air to prevent condensation of vapor on the window.

The liquid jet was adjusted to occupy such a position that the tip was not on the same line as the longitudinal axis of the capillary but placed such that a liquid jet would hit directly the opening of the capillary. The openings were fitted with 12/5 socket ground joints. A 50-cc. borosilicate glass medical syringe sealed to a 12/5 ball joint was used as the outside pumping device for the liquid line.

The boiling flask is a two-necked 1000-ml. round-bottomed flask. The larger neck was provided with a female 55/50 standard-taper joint and the smaller with a female 24/40 joint. The smaller neck was closed with a ground-glass plug.

The pumping device (2) consisted of a small funnel resting on three 1/8-inch legs and sealed to the inner mantle. The height of the pumping device was adjusted so that the two sets of shorted jets of vapor and liquid mixture hit the capillary directly.

The 500-watt heater has an opening equivalent to the largest diameter of the funnel, so that little vapor was generated outside of the pumping device. The light source to illuminate the end of the capillary was supplied by a Lumiscope. The incident ray from the Lumiscope was reflected by the liquid solution in the open end and by the open end of the capillary and the reflected ray was observed by a Bausch & Lomb 20X widefield tube. The smaller the angle between the incident and reflected ray, the higher is the sensitivity of the apparatus to detect a plane liquid surface at the end of the capillary. Thus the angle was made as small as possible.

The draft gage-type manometer was made of 6-mm. glass tubing and utilized a 14-inch-diameter aluminum pan as a sump connected by metallic fittings and rubber tubing. The glass tubing was mounted such that the multiplying factor due to inclination was 9.75 to 1.0. Hence, a pressure drop of 0.001 inch of water could be detected. A 0.5-cc. lump of Aerosol OT, 85% paste (a wetting agent) was placed in the water in the pan to facilitate movement of water in the glass tubing. The large diameter of the pan relative to that of the glass tubing maintained the base water level constant.

The pressure in the capillary was regulated by a small change in the mercury level in the mercury leveling bowl. A stationary leveling bottle was connected between the leveling bowl and the gage to absorb sudden change in pressure.

A three-way stopcock was sealed between a 12/5 socket ground joint and the pressure-regulating system. The other outlet of the stopcock was open to the atmosphere. When the apparatus was not in use, the pressure-regulating system was open to the atmosphere to avoid surge of water from the gage. When a slight vacuum was needed, the open outlet of the three-way cock was connected to a suction bulb.

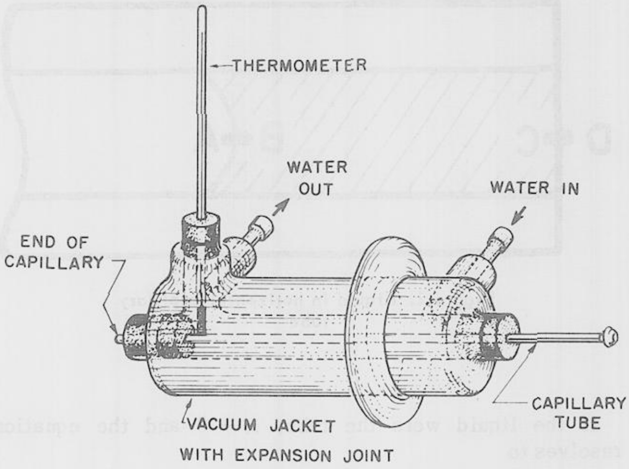

Figure 4. Constant temperature jacket for capillary tube

The ball and socket joints and stopcocks in the pressure-regulating system were lubricated with Dow-Corning stopcock grease.

The boiling flask was insulated with glass fiber cloth to prevent excessive heat loss.

Apparatus for 30 °C. The equipment shown in Figure 4 was used to determine interfacial tension at 30 °C. The capillary was surrounded by a concentric liquid jacket through which water at a closely controlled temperature was circulated. The radius of the capillary tube was 2.239×10^{-2} cm.

EXPERIMENTAL PROCEDURE

The interfacial tension of the liquid and vapor in equilibrium with the liquid at the normal boiling point of the liquid binary mixture was determined as follows.

The interfacial tension measurement apparatus specially designed and constructed for this project (Figure 3) was disassembled and its parts were washed in acetone. The air-dried parts were placed in an oven and heated to 105 °C. for 2 hours or more to ensure thorough dryness. After cooling, the parts were assembled and ready for the experiment.

The 1000-ml. round-bottomed boiling flask was filled 4/5 full with liquid mixture of the binary system. The heater was then turned on to heat the system to the boiling point. Care was taken to keep the boiling chips in the space under the funnel of the pumping device.

At least 15 minutes were allowed after the mixture started boiling for the liquid and its vapor to reach equilibrium. The length of time needed to reach equilibrium was determined by analyzing successive vapor samples from the system.

The vapor was drawn through the capillary by means of an aspirator bulb in order to fill the capillary tube with the vapor which was in equilibrium with the liquid in the boiling flask. A drop of the boiling liquid was injected into the opening of the capillary. The 50-cc. syringe was used to draw the liquid out of the flask through the liquid line and to inject the liquid into the liquid jet. A 5-ml.

sample of the liquid was taken from the syringe. The inner mantle bathed the outside of the capillary with boiling mixture to keep the capillary at the boiling point temperature. The excess liquid in the capillary was bled off by the increase of pressure inside the capillary, such that the final position of the meniscus was in the heated portion of the capillary.

The capillary was originally placed in a horizontal position with the aid of a spirit level during assembly. The external surface of the window was heated by hot air in order to remove any condensed vapor from the inside surface of the window. The Lumiscope was used to supply the light to illuminate the open end of the capillary. The reflected light from the liquid surface in the capillary opening and the open end of the capillary tube were viewed through the Bausch & Lomb widefield tube. The angle between the incident ray and the reflected ray was kept as small as possible to furnish high sensitivity in the observation of the plane surface at the capillary opening which was obtained by the regulation of the pressure inside the capillary tube.

The pressure inside the capillary tube was regulated by means of a mercury leveling bulb. The pressure necessary to maintain a plane liquid surface at the opening of the capillary was measured by the use of the inclined draft gage. No pressure drops higher than 0.0005 inch of water between the chamber housing the capillary and the atmosphere were detected through the pressure tap during the measurement.

A small drop of the liquid in the capillary was bled off, and the procedure was repeated to obtain a new pressure. The arithmetic average value of several gage pressures was used as the pressure drop across the meniscus inside the capillary at the boiling point. The gage pressure in inches of water, the water temperature, and the radius of the capillary were used to calculate the interfacial tension of the system at the boiling point.

The liquid composition was determined by the method of refractive index, and the sample taken from the syringe was used for the determination.

The surface tension at 30 °C. was determined in a similar manner, except that the arrangement of the apparatus was as shown in Figure 4. Liquid samples of known composition were introduced to the capillary by means of a 0.2-ml. pipet. The temperature of water circulating in the water jacket was regulated by means of a Precision thermal bath.

ANALYTICAL PROCEDURE

Interfacial Tension. The interfacial tension of a binary system at the boiling point of the liquid mixture was obtained by determination of the pressure drop across the interface in the horizontal capillary. The calibration of the capillary and the conversion of the pressure drop to interfacial tension are described as follows.

Conversion to Interfacial Tension. For the boiling point apparatus

$$\sigma = \frac{r \rho g}{2} (\Delta h) = \frac{r g}{2} \rho (\Delta h) \qquad (7)$$

$$\sigma = \frac{(1.7833 \times 10^{-2})(980.7)}{2} (\rho)(2.5400)(\Delta h)$$

or

$$\sigma = 22.21 \rho \Delta h \text{ dynes per cm.} \qquad (8)$$

where

σ = interfacial tension, dynes per cm.
ρ = water density, grams per cc.
Δh = pressure drop, inches of water

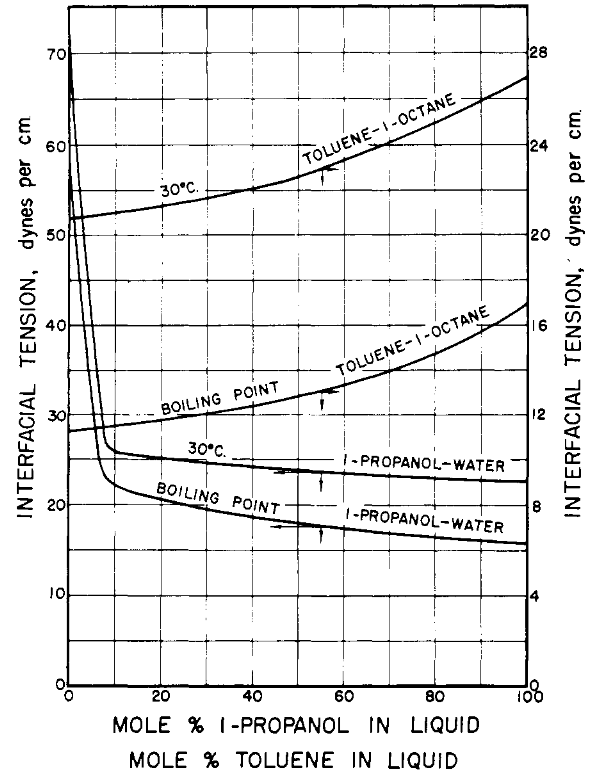

Figure 5. Interfacial tension, 1-propanol-water system and toluene-n-octane system

Table I. Interfacial Tension at Normal Bailing Point and at 30 °C.

1-Propanol–Water			Toluene-*n*-Octane		
Mole % 1-propanol	Dynes/cm.	t °C.	Mole % toluene	Dynes/cm.	t °C.
0.00	58.9	100.00	0.00	11.3	125.2
2.81	43.4	91.3	10.38	11.5	121.0
6.01	26.5	89.3	19.75	11.8	119.0
8.19	22.8	88.7	27.68	12.0	117.3
16.90	20.9	88.2	44.01	12.6	114.5
22.15	20.3	88.1	56.15	13.1	113.2
31.47	19.4	87.9	67.42	13.8	112.3
40.34	18.7	87.8	77.68	14.6	111.5
53.24	17.9	88.0	90.60	15.8	110.6
66.10	17.2	88.6	100.00	16.8	110.1
84.61	16.5	91.4			
100.00	15.9	97.3			
At 30 °C.			At 30 °C.		
0.00	71.2		0.00	20.7	
10.19	26.2		10.46	21.1	
23.21	25.4		31.91	21.8	
57.73	24.1		49.38	22.7	
79.70	23.7		66.32	24.0	
100.00	22.9		86.00	25.7	
			100.00	27.4	

For the arrangement to measure surface tension at 30 °C.

$$\sigma = 27.89 \rho \Delta h \text{ dynes per cm.} \qquad (9)$$

Equations 8 and 9 are valid when the contact angle is zero. This was assumed to be true within the precision of the measurements.

EXPERIMENTAL RESULTS

The results of interfacial tension measurements at the boiling point and at 30 °C. on two of the eight binary systems studied are shown in Figure 5 and Table I. These systems are 1-propanol-water and toluene-*n*-octane.

The precision for the measurements of interfacial tension is a function of the nature of the system, the cleanliness of the apparatus, and the accuracy of the pressure determination. Dirty apparatus may have a nonzero contact angle between the liquid and glass and the clean liquid may not have a zero contact angle with the glass. Contact angles between zero and 5° are extremely difficult to detect. Precision in the determination of the interfacial tension due to errors introduced by neglecting a nonzero contact angle is estimated as follows.

Precision in Interfacial Tension, Dynes/Cm.

Interfacial Tension, Dynes/Cm.	Error (Dynes/Cm.) Resulting from Neglecting Contact Angle of		
	0°	5°	10°
0.00	0.00	0.00	0.00
15.00	0.00	0.06	0.23
30.00	0.00	0.12	0.46
45.00	0.00	0.18	0.69
60.00	0.00	0.24	0.92

Contact angles larger than 5° can be detected; therefore, the smallest precision for the determination would correspond to the values given in the column under 5°.

The zero point of the draft gage was determined by means of an induced oscillation of the water meniscus in the 6-mm. glass tube of the gage. The rest point of the meniscus was recorded, and the arithmetic average value was used as the zero point of the gage. The zero point was evaluated twice during each series of runs. The precision of obtaining the zero point, which controls the precision of the pressure-drop determination, is estimated to be 0.003 inch of water for the draft gage, or 0.07 dyne per cm. expressed in terms of interfacial tension.

Therefore, the over-all precision for the interfacial tension measurement apparatus was estimated to be approximately 0.6%, which amounts to 0.1 dyne per cm. for 15 dynes per cm. or 0.3 dyne per cm. for 60 dynes per cm.

From the plots of data on a large scale the precision obtained for the 1-propanol-water and toluene-*n*-octane systems was 0.2 dyne per cm.

VISCOSITY OF VAPOR MIXTURES AT TEMPERATURES NEAR THEIR DEW POINT

Another property of interest to scientists and engineers is vapor viscosity of compounds and mixtures of compounds. Wherever gas or vapor mixtures are encountered in mass transfer, heat transfer, and fluid flow, their viscosity is one of the variables to be considered. One particular region of interest is that at temperatures at or near the dew points of mixtures. Some data have been reported on light hydrocarbon mixtures, but few on organic compound mixtures normally liquid at atmospheric pressure and at temperatures in the neighborhood of 100°C. One phase of the investigation was concerned with devising a means of evaluating the viscosity of vapors of binary mixtures at temperatures near their dew points.

Experimentally it is extremely difficult to obtain viscosities of vapors near their dew point temperatures because of the possibility of encountering phase change resulting in both liquid and vapor phases occurring in the viscometer. Because of this and other difficulties, it was considered necessary to devise a special type of viscometer to measure vapor viscosities of mixtures of known composition at temperatures above their dew points. Thus, with experimental determinations made at a number of temperatures such that the mixture was entirely in the vapor state, extrapolation could give viscosity at the dew point temperature.

The apparatus devised was one from which the data could be utilized in Poiseuille's equation (7)

$$\eta = \frac{\pi (p_1 - p_2) r^4 t}{8 LV} \qquad (10)$$

where

η = viscosity, poises
p = pressure, dynes per sq. cm.
L = length of capillary, cm.
V = volume of vapor passing through the capillary, cc.
π = 3.1416
t = time of efflux of volume of vapor V through the capillary, seconds

If the system downstream from the capillary is considered ideal

$$p_{2i}V_2 = n_{2i}RT \qquad (11)$$

and

$$p_{2f}V_2 = n_{2f}RT \qquad (12)$$

Subtracting

$$(p_{2f} - p_{2i})V_2 = (n_{2f} - n_{2i})RT \qquad (13)$$

or

$$(\Delta p_2)V_2 = (\Delta n_2)RT$$

Under the average capillary conditions assuming ideal gas

$$p_{av}V = (\Delta n_2)RT \qquad (14)$$

because the volume V of the vapor is the only source of vapor entering the space V_2

$$V = \frac{\Delta n_2 RT}{p_{av}} = \frac{(\Delta p_2)V_2}{p_{av}} \qquad (15)$$

where

V = volume of vapor passing through the capillary during time t
Δp_2 = increase in pressure in the system downstream from the capillary during time t
V_2 = volume of the system downstream from the capillary

Subscripts i, f indicate initial and final conditions, respectively.
Subscripts 1, 2 indicate upstream and downstream conditions, respectively.

$$\Delta p_2 = p_{2f} - p_{2i} \qquad (16)$$

$$p_{av} = \frac{p_1 + p_2}{2} = \frac{(p_{1i} + p_{1f}) + (p_{2i} + p_{2f})}{4} \qquad (17)$$

Then

$$\eta = \pi \frac{[(p_{1i} + p_{1f})^2 - (p_{2i} + p_{2f})^2]\, r^4 t}{64L(\Delta p_2)V_2} \qquad (18)$$

The relative viscosity of the vapor with respect to air may be expressed as

$$\frac{\eta_g}{\eta_a} = \frac{[(p_{1i} + p_{1f})^2 - (p_{2i} + p_{2f})^2]_g\, t_g\, (\Delta p_2)_a}{[(p_{1i} + p_{1f})^2 - (p_{2i} + p_{2f})^2]_a\, t_a\, (\Delta p_2)_g} \qquad (19)$$

where g indicates vapor and a indicates air.

VAPOR VISCOMETER

The vapor viscometer shown in Figure 6 consisted of two stainless steel cylindrical chambers of 4-inch diameter and 6.5-inch height, and 3-inch diameter and 4-inch height connected by a 0.015-inch inside diameter stainless steel tube, 6.5 feet long, coiled into two loops to fit into the

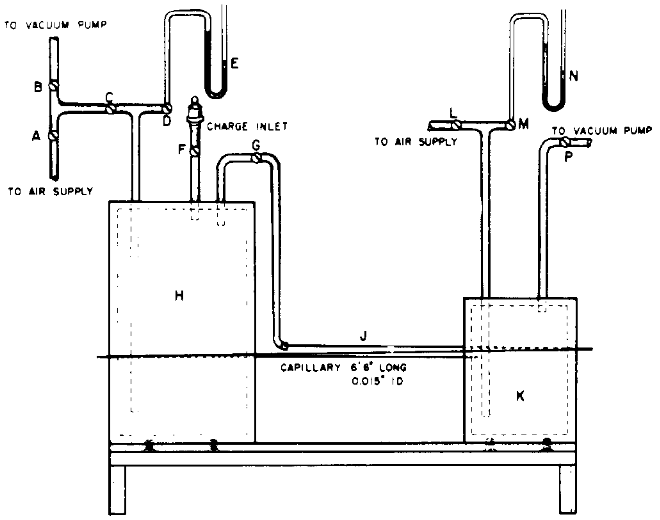

Figure 6. Vapor viscometer assembly

Table II. Comparison of Average Values of Air Viscosity

Temp., °C.	Average Air Viscosity, Poise x 10^5 (*6*)	(*4*)	This work
0.00	17.165	17.16	17.165
23.00	18.273	18.28	18.273
100.00	22.038	21.74	21.780
191.00	25.563	25.38	25.403

Table III. Vapor Viscosity as a Function of Temperature and Compostion

Vapor Composition, y_1, Mole % 1-Propanol	Vapor Viscosity, Poise × 10^5 110 °C.	130 °C.	150 °C.
1-Propanol–Water System			
0	12.81	13.53	14.25
10.19	12.45	13.15	13.80
22.31	12.08	12.73	13.36
57.73	11.20	11.72	12.24
79.70	10.79	11.22	11.70
100.0	10.42	10.83	11.24
Toluene—*n*-Octane System			
Mole % Toluene			
0.00		8.22	8.62
26.34		8.76	9.15
41.84		9.11	9.50
82.82		10.20	10.58
94.17		10.57	10.94
100.0		10.76	11.11

temperature control bath. The valves were series 411 straight, high vacuum, Hoke, packless valves with silver-soldered diaphragm seals. All joints were silver soldered.

The temperature control bath was a 16 x 12 inch borosilicate glass jar insulated by aluminum foil-covered asbestos. An electric stirrer, fixed heater, intermittent heater, electronic relay, a Precision Magna-set thermoregulator, and two mercury manometers were used as accessory equipment.

EXPERIMENTAL PROCEDURE

The vapor viscometer was brought to temperature with all the diaphragm valves open (to avoid expansion damage). With the valves *B, C, D, G, M,* and *P* open (Figure 6) and the rest of the valves closed, the system was evacuated. Then with the valves *B, D, F,* and *M* closed, and the rest open, chambers *H* and *K*, maintained at the same temperature within the bath, were purged with dry air.

The system was again evacuated and after evacuation valves *C, F, G, L,* and *P* were kept closed. A liquid sample of known composition was introduced into chamber *H* through the charge inlet by means of valve *F* and was then evaporated. The charging was terminated when manometer *E* indicated a pressure of 100 to 200 mm. of mercury. The system was then allowed to reach thermal equilibrium prior to the viscosity measurement.

Valves *D* and *M* were opened so that the pressures could be read from manometers *E* and *N* by a vertical cathetometer. Valve *G* was opened and an electric timer was started. After 5 minutes valve *G* was closed and the timer was stopped simultaneously. The pressures in chambers *H* and *K* were again measured and the corrected barometric pressure was recorded. The time, barometric pressure, initial and final pressures in the chambers, bath temperature, and liquid charge composition (composition of the vapor since the charge was totally evaporated) comprised the data necessary for calculation of the vapor viscosity.

For fluid flow in metal capillary, the critical Reynolds number, above which turbulent flow can be expected, is of the order of 10 (*5, 8*). The largest Reynolds number for vapor viscosity determinations in this investigation is 5.0; therefore the flow of vapor in the capillary was in the viscous region, where Poiseuille's equation may be applied with confidence. No error, therefore, was considered to be introduced because of inapplicability of Poiseuille's equation. Possible sources of errors which could affect the accuracy of the vapor viscosity determination are listed as follows:

A. Air viscosity at lower than atmospheric pressure may differ from that at atmospheric. This error is considered small.

B. The true average pressure in the capillary may not be the arithmetic average of the upstream and downstream pressures in the capillary.

C. The assumption of ideality of the vapor phase may not be valid even at the subatmospheric pressures employed.

D. Errors may be introduced in making pressure readings, in that the manometers did not respond simultaneously and could not be read simultaneously.

E. Condensation of the vapor in the line connecting chamber *K* (Figure 6) with manometer *N* might possibly occur. This might introduce a relatively large error.

F. The temperature in the capillary could possibly vary as much as 0.5 °C. from the indicated bath temperature.

It is believed that the combined errors resulting from A and B could only be a fraction of 1%. It is possible for factor C to cause an error in the neighborhood of 2%. The slow manometer response under D could cause an estimated error of around 5%. Condensation E could introduce an error of large magnitude, although it was doubtful that any condensation was encountered in the work. The temperature factor under F could amount to around 0.3% maximum.

It is believed that vapor mixture viscosity could be determined with a maximum deviation of 4%.

VISCOSITY OF AIR

A collection of air viscosity data in the range from 0° to 200 °C. and the weighted average values for 0°, 23°, 100°, and 191 °C. were reported by Myerson and Eicher (*6*). Their average values for 0° and 23 °C. were used by the authors. With the same original data an arithmetical average for 191 °C. was computed. This value was lower than that reported (*6*). Four of the latest reported values of air viscosity at 100 °C. were selected to determine the average at this temperature. Table II gives a comparison of the average data.

Viscosity values for air for intermediate temperatures were calculated by Sutherland's equation (*9*).

The relative viscosities of the vapors with respect to air were calculated by means of Equation 19. The absolute viscosities of the vapors were then calculated using the viscosity values of air determined by means of the Sutherland equation.

EXPERIMENTAL DATA

Experimental vapor viscosity data for the 1-propanol–water system were determined at 110°, 130°, and 150°C. and for the *n*-octane–toluene system at 130° and 150°C. (Table III).

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Properties of Binary Mixtures as a Function of Composition

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Data on physical properties of mixtures as a function of composition and temperature are valuable in correlating other properties and in analytical studies. In this and subsequent investigations an attempt was made to develop experimental data for a number of systems on which generalized correlations could be developed relating composition and the property evaluated based on the properties of the pure components. Thus, eight binary systems having a rather wide range of properties (particularly interfacial tension) and in most cases, representing nonideal liquid mixtures were studied. The systems were: 1-propanol–water; toluene–*n*-octane; water–1-butanol; acetone–1-butanol; benzene-2-chloroethanol; carbon tetrachloride–1-propanol; ethyl alcohol–1,4-dioxane; and methanol–1,4-dioxane. The properties determined were: refractive index *vs.* composition, liquid density *vs.* composition and temperature, interfacial tension at the boiling point and at 30°C. as a function of composition, liquid viscosity as a function of temperature and composition, and vapor viscosity as a function of temperature and composition. Because of the peculiar variation of interfacial tension and viscosity with composition at the boiling point, no general correlations have been developed. More data on both binary and ternary systems are necessary.

MATERIALS

All the chemicals used for this project except toluene and water were reagent grade chemicals. Nitration grade toluene was used. Water was purified by distillation in this laboratory to a maximum conductivity of 1.4×10^{-6} mho or less. The refractive index of the materials was measured and compared with the reported values in the literature. They are listed in Table I.

REFRACTIVE INDEX

Refractive index *vs.* composition data for each binary system were obtained in the following manner.

Table I. Refractive Index of Material Used

Material	Temp., °C.	Literature	Exptl.
Acetone	20.0	1.35911 (*18*)	1.35860
	25.0	1.35662 (*18*)	1.35625
Benzene	20.0	1.5011 (*9*)	1.50116
	25.0	1.49790 (*18*)	1.49733
	30.0	1.49486 (*18*)	1.49459
1-Butanol	20.0		1.39919
	25.0	1.3970 (*18*)	
		1.3974 (*18*)	1.39739
	30.0		1.39538
Carbon tetrachloride	20.0	1.4602 (*18*)	1.46014
		1.46026 (*18*)	
		1.46036 (*18*)	
		1.46023 (*18*)	
	25.0	1.45732 (*18*)	1.45740
		1.4576 (*18*)	
2-Chloroethanol	20.0	1.44208 (*18*)	1.44198
	25.0		1.43977
1,4-Dioxane	20.0	1.4224 (*9*)	1.42223
	25.0	1.42025 (*18*)	
		1.4202 (*18*)	1.41973
		1.4202 (*18*)	
Ethyl alcohol	20.0	1.36139 (*18*)	1.36132
	25.0	1.3596 (*18*)	
		1.3595 (*18*)	
		1.359408 (*18*)	1.35937
Methanol	15.0	1.33057 (*18*)	1.33065
	20.0		1.32895
	25.0		1.32707
n-Octane	20.0		1.39775
	25.0	1.39534 (*18*)	
		1.39530 (*18*)	
		1.39509 (*18*)	
		1.39505 (*18*)	1.39564
	30.0		1.39303
1-Propanol	20.0	1.3854 (*9*)	1.38572
	23.6	1.3840 (*18*)	1.38452
	25.0		1.38391
	30.0		1.38183
Toluene	20.0	1.49682 (*18*)	1.49680
	25.0	1.49405 (*18*)	1.49407
	30.0		1.49134
Water	20.0	1.33300 (*10*)	1.33316
	25.0	1.33255 (*14*)	1.33277
	30.0	1.3320 (*10*)	1.33213

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