# Vapor Pressure and Evaporation Coefficient of Glycerol

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**Measurements of the vapor pressure in the range 291 to 341 K and of the evaporation coefficient of liquid glycerol are reported. In contrast to the results of other authors a unit evaporation coefficient is found. The higher vapor pressures given by several other authors are shown to be due to minute traces of water. Using our low temperature data and the data of reliable investigations at higher temperatures the following vapor pressure equation for liquid glycerol was obtained by a least-squares treatment: $\log p/\mathrm{Torr} = 41.98405 - 6024.479/T/\mathrm{K} - 10.3272 \log T/\mathrm{K}$.**

Whereas higher vapor pressures of a certain substance measured by different authors usually agree reasonably well, the scatter of data in the range below 1 Torr increases considerably. In this region the dynamic methods of measurement that are usually used are more sensitive to sources of errors (probe contamination, poor vacuum, self-cooling of sample, restrictions to vapor flow, etc.).

As can be seen from Figure 1, vapor pressure data of glycerol in the micron range published by different authors are not in good accord. Stedman (*21*) obtained his values by measuring the vapor pressure over glycerol/water mixtures of different concentration and extrapolating to zero water content. Zil'berman-Granovskaya (*25*) gives only four measurements, the temperature dependence of which seems much too low. The same is true to a lesser extent for the three data sets of Filosofo, Merlin, and Rostagni (*9*). Wyllie's vapor pressure measurements made during his determination of the evaporation coefficient (*24*) are in good accord with a vapor pressure equation given by Bondi (*2*)

$$\log p/\mathrm{Torr} = 32.706726 - \frac{5335.088}{T/\mathrm{K}} - 7.401 \log T/\mathrm{K} \qquad (1)$$

though this gives values about twice as high as the results of Ross and Heideger's (*20*) careful investigation in the micron range.

As to the evaporation coefficient, a similar disagreement exists. With the exception of Hickman and Trevoy (*12, 23*), who obtained a value of unity on using the jet tensimeter, several authors have reported an evaporation coefficient of about 0.05 (*1, 10, 24*). In view of these discrepancies we decided to redetermine the vapor pressure of glycerol in the micron region as well as its evaporation coefficient.

## Purification of Glycerol

Since glycerol is very hygroscopic all operations including filling the effusion cells etc. were performed in a glove box equipped with a large amount of phosphorus pentoxide on an inert carrier material providing a large active area. Analytical grade glycerol (DAB 7, double distilled) from Merck, which contained about 1% water according to the manufacturer, was purified further by (1) a twofold fractional vacuum distillation (at 140 °C, 4 Torr), then (2) passing the vapor at low pressures through 3 Å molecular sieve, and (3) collecting and storing the distillate over freshly activated molecular sieve. The glycerol used had a refractive index $n^{20}_{\mathrm{D}}$ 1.475 38 ± 0.000 02 (1.4750) and a density $\rho_{20} = 1.2633 \pm 0.0001$ (1.2613) g cm$^{-3}$. Literature values are given in parentheses. These are slightly lower and, together with the possibility of undercooling the liquid glycerol to the glassy state without crystallization, indicate the purity of the sample and the complete absence of traces of water.

## Effusion Measurements

***Apparatus.*** The integral weight loss type of effusion method was used in vapor pressure determination. A more detailed description of the apparatus and procedure may be found in ref 6 and 7. Cylindrical effusion cells of cross sectional area *S* made from Pyrex glass were used. At an inner height $h = 2.13r_{\mathrm{c}}$ ($r_{\mathrm{c}}$ inner radius) above sample surface the cells were closed by a molybdenum foil of thickness 0.001 30 ± 0.000 02 cm in the center of which was the circular effusion orifice of area *A*. The vapor effused was trapped on a silvered condenser cooled by liquid nitrogen. High vacuum of less than $10^{-6}$ Torr residual gas pressure was established by a one-stage and a three-stage mercury diffusion pump in series backed by a mechanical pump. Temperature was controlled to ±0.01 °C and measured to an absolute accuracy of ±0.03 °C with a mercury thermometer and a NiCr/Ni thermocouple, both calibrated against the IPTS-68. The Clausing factors *W* of the orifices ranged from 0.9605 to 0.9947, *S* could be varied between 0.923 and 5.027 cm$^2$ and *A* between $0.8342 \times 10^{-3}$ and $49.81 \times 10^{-3}$ cm$^2$. The orifice area *A* was determined by planimetry of orifice microphotographs and from direct measurements of the diameter by a traveling microscope giving identical results to within ±0.1%. Weight loss was determined to 0.003 mg on a microbalance using calibrated weights and corrected for buoyancy. As previously reported the overall absolute accuracy of vapor pressure determination with the apparatus used was ± 0.6% in the case of mercury (*6, 8*) and is probably somewhat less in the case of glycerol.

***Measurements and Results.*** From the measured quantities the saturated vapor pressure *p* was calculated using the equations (*6, 7*)

$$p = \left(1 + \frac{WA}{\alpha S}\right)p' \qquad (2)$$

with

$$p' = -\frac{\left(\frac{\mathrm{d}m_{\mathrm{e}}}{\mathrm{d}t}\right)_T}{WA}\left(\frac{2\pi RT}{M}\right)^{1/2} \qquad (3)$$

where $\alpha$ was the evaporation coefficient, $p'$ the apparent vapor pressure, $-\mathrm{d}m_{\mathrm{e}}/\mathrm{d}t$ the rate of weight loss by effusion, *R* the universal gas constant, *T* the absolute temperature ($T_{68}$), and *M* the molecular weight of glycerol. The other symbols have already been defined.

Two different series of measurements were performed. On varying the ratio *WA/S* from experiment to experiment at a constant temperature of 40.38 °C a plot of the apparent vapor pressures $p'$ vs. $WAp'/S$ should yield $-1/\alpha$ as the slope and *p* as the intercept (*6, 7*). Figure 1 shows the experimental points (rhombi) together with a line calculated for $\alpha = 1$, which fits the results quite well. We thus conclude that pure anhydrous glycerol exhibits a unit evaporation coefficient. The dotted lines are calculated for $\alpha = 0.05$ and $\alpha = 0.025$, respectively. Experimental points (dotted circles) and a straight line calculated for

**Table I. Results of Different Authors on Glycerol**

| Author | Year | Exptl method | No. of meas | $\overline{\Delta H_v}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| Stedman | 1928 | Vapor composition | 8 | >88.7 |
| Zil'berman-Granovskaya | 1940 | Effusion (total weight loss) | 4 | 20.4 |
| Wyllie | 1949 | Effusion (total weight loss) | 1 | — |
| Filosofo et al. | 1950 | Fiber manometer | 3 | 76.7 |
| Bondi | 1962 | Unstated | ? | 83.79 |
| Ross and Heideger | 1962 | Effusion (cont. weighing) | 17 | 85.78 |
| This work | 1975 | Effusion (total weight loss) | 16 | 86.76 ± 0.70 |

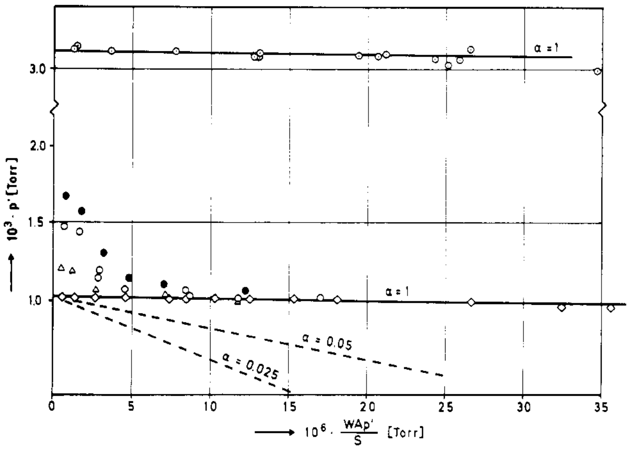

**Figure 1.** Apparent vapor pressure $p'$ of glycerol as a function of $WAp'/S$. Experimental points for mercury at 30.40 °C ⊙. Straight line was calculated for $\alpha = 1$. Anhydrous glycerol at 40.38 °C ◇. The straight lines were calculated for $\alpha = 1$, 0.05, and 0.025. Points △ O ● refer to glycerol of increasing water content (see text).

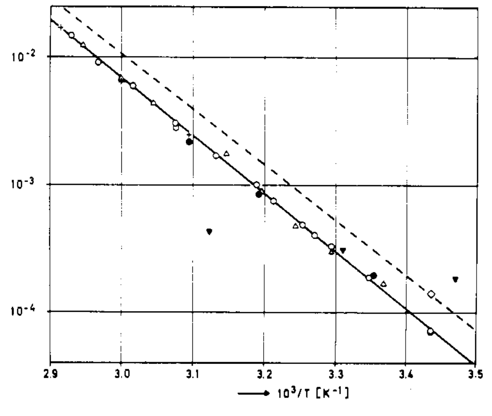

**Figure 2.** Low vapor pressure data of glycerol: +, Stedman (*21*); ▼, Zil'berman-Granovskaya (*25*); ◇, Wyllie (*24*); ● Filosofo et al. (*9*); - - -, Bondi (*2*); △, Ross and Heideger (uncorrected data series) (*20*); O, this work.

**Table II. Glycerol Vapor Pressures Determined in This Work**

| $T$ [K] | $10^3p$ [Torr] | $T$ [K] | $10^3p$ [Torr] |
|---|---|---|---|
| 291.13 | 0.0697 | 313.48 | 1.02 |
| 291.18 | 0.0716 | 313.53 | 1.02 |
| 298.75 | 0.187 | 319.19 | 1.71 |
| 303.46 | 0.336 | 325.07 | 2.86 |
| 305.65 | 0.407 | 325.11 | 3.09 |
| 307.23 | 0.493 | 331.44 | 6.13 |
| 307.24 | 0.500 | 337.12 | 9.10 |
| 311.16 | 0.757 | 341.35 | 14.8 |

$\alpha = 1$ for mercury, which is well known to exhibit a unit evaporation coefficient, is given for comparison in the upper part of Figure 1 (*6*). The extrapolated $p$ agrees to within ±0.3% with the mercury vapor pressure at this temperature. (*8*).

It was observed that minute traces of water in glycerol can give rise to erratic results for $p'$, and thus $\alpha$ and $p$, depending on the water content of glycerol and on the undersaturation present in the effusion cells. At low undersaturation (low hole area/surface area ratios) water molecules diffusing from inside the glycerol to the surface evaporate together with glycerol molecules, leading to an apparently higher vapor pressure. At greater deviations from equilibrium within the cell this effect becomes less important, because the water concentration in the vicinity of the surface rapidly decreases. Diffusion is slow and convective motion absent in the highly viscous glycerol. Figure 1 shows this behavior for three samples of glycerol with water contents ranging approximately from 0.01 to 0.03% by weight.

To determine the saturated vapor pressure of glycerol and its temperature dependence 16 measurements in the temperature range 18 to 68 °C were made using an effusion cell with an effective orifice/surface area ratio of $WA/S = 1.554 \times 10^{-2}$. Using this value (and $\alpha = 1$) $p$ was calculated from $p'$ according to eq 2 and the results are given in Table I. By a least-squares treatment we obtained the following correlating equation for the indicated temperature range

$$\log p/\text{Torr} = -\frac{4532 + 37}{T/\text{K}} + (11.44 \pm 0.12) \qquad (4)$$

The mean enthalpy of vaporization is $\overline{\Delta H_v} = 86.76 \pm 0.70$ kJ mol$^{-1}$.

Equation 4 and our results are shown in Figure 2 together with the data of the other authors, which are also summarized in Table II. The low temperature experimental values of Stedman are in good agreement with our results. The same applies to the data of Ross and Heideger although these data show greater scatter, probably due to varying back-pressure of glycerol vapor and self-cooling of their sample, which was freely suspended in vacuo on a quartz spring balance. If Ross and Heideger's data are recalculated using our value $\alpha = 1$ instead of 0.05 used by them, the agreement in vapor pressure and enthalpy of vaporization becomes even better. The few values given by Zil'berman-Granovskaya and by Filosofo, Merlin, and Rostagni show a wrong temperature dependence. The vapor pressure data of Wyllie and of Bondi are high by a factor of approximately 2 in the range considered here, probably because the glycerol used in these measurements was not anhydrous.

Since glycerol is an important substance in chemical industry (e.g., in the food, explosives, and detergents industry) a more accurate vapor pressure equation than eq 1 seemed desirable. Using the data presented in this paper and the data of reliable investigations at higher temperatues (*15, 16, 19, 21*) the following vapor pressure equation for liquid glycerol was obtained by a least-squares treatment

$$\log p/\text{Torr} = 41.98405 - \frac{6024.479}{T/\text{K}} - 10.3272 \log T/\text{K} \qquad (5)$$

For the reasons outlined above, the data given in the papers (*2, 9, 24, 25*) have not been considered.

## Evaporation Rate Measurements

In contrast to nonpolar liquids, which are believed to exhibit unit evaporation coefficients, for most polar and associated

**Table III. Results of Different Authors on the Evaporation Coefficient of Glycerol**

| Author | Year | Exptl method | $t$, °C | $\alpha$ |
|---|---|---|---|---|
| Wyllie | 1949 | Free evaporation | 18 | 0.052 |
| Hickman and Trevoy | 1952 | Evaporation from large stagnant surface | 70 | 0.001 |
| Trevoy | 1953 | Evaporation from falling liquid jet | 18 . . 70 | 1 |
| Heideger and Boudart | 1962 | Pressure rise in constant volume | 13 . . 25 | 0.05 |
| Baranova et al. | 1966 | Condensation on cooled surface | 64 . . 70 | 0.051 |
| This work | | Evaporation at low undersaturation | 40.4 | 1 |
| | | Free evaporation | 18.0 | 1 |

liquids such as water, the alcohols, glycerol, and nitrobenzene evaporation coefficients far from unity are reported in the literature (cf. the compilations (*13, 14, 17, 18, 22*)). In recent years this difference in evaporation behavior has been doubted by several authors (*3–5, 11*). As mentioned above, $\alpha = 0.05$ for liquid glycerol has been reported in three papers (cf. Table III), whereas Hickman and Trevoy obtained a unit evaporation coefficient from measurements with a freely falling liquid jet. To confirm our value of $\alpha = 1$ obtained by effusion measurements at constant temperature and low vapor undersaturation ($(p - p')/p < 0.03$) we also determined the free evaporation rate of glycerol into vacuum.

***Apparatus and Procedure.*** The essential part of the apparatus is shown in Figure 3. The cells from which evaporation took place closely fitted into the recess R of a metal block B which also contained bores for a calibrated "Anschütz"-thermometer A and thermocouple TH. By "Torr-Seal" (Varian Ass.) the metal block was cemented to the other part of the apparatus made from Pyrex glass which by the flange F was connected to the high vacuum system described above. The evaporated molecules were trapped on the condenser K, which was silvered both on the inside and the outside and was surrounded by the silvered radiation shield S. To reduce radiative heat transfer further the condenser carried a glossy aluminum cap and the metal block was polished.

The cells for free evaporation (Z2) were filled with glycerol to the rim in the glove box and then closed by the lid containing a Teflon seal TE. After weighing on the microbalance Z2 was placed, by means of a manipulating rod M1, in the recession R of the metal block. The lid was then removed by another manipulating rod M2, the cell with the exposed surface was covered by the sliding shutter TP, and the apparatus closed by the condenser. After a residual gas pressure of less than $10^{-6}$ Torr had been reached the condenser was filled with liquid nitrogen. By turning the condenser around its ground glass joint the shutter TP was opened by the pin M and evaporation commenced. After several hours TP was closed again. Dry air was admitted and the cell closed within the apparatus, removed, and weighed again.

***Calculation and Results.*** The rate of free evaporation into vacuum is given by the Hertz–Knudsen–Langmuir equation (*13*)

$$-\frac{1}{S}\left(\frac{dm_v}{dt}\right)_T = \alpha p\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{6}$$

where $-dm_v/dt$ was the rate of weight loss by free evaporation. If we introduce a Clausing factor for the apparatus $W_a$ and take into account eq 2 and 3 we obtain

$$-\frac{1}{S}\left(\frac{dm_v}{dt}\right)_T = \alpha\left(-\frac{dm_e}{dt}\right)_T\frac{W_a}{WA}\left(1+\frac{WA}{\alpha S}\right) \tag{7}$$

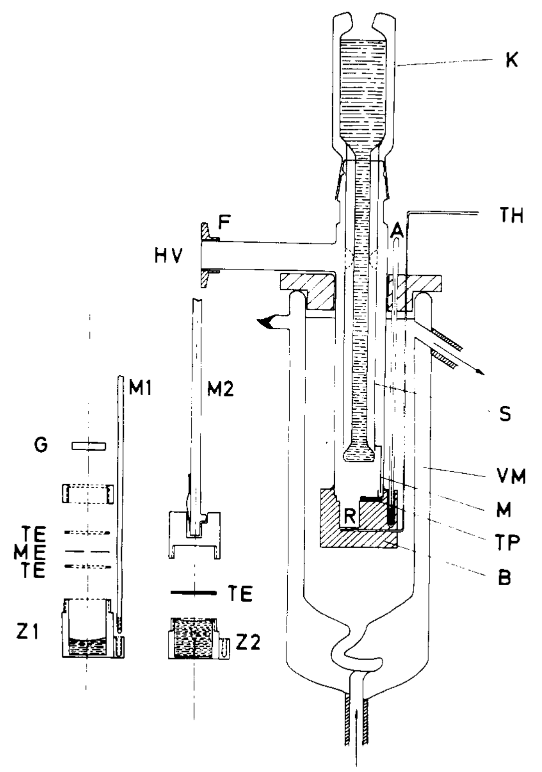

**Figure 3.** Apparatus for measurement of free evaporation rate: A, "Anschütz"-thermometer; B, metal block; F, flange NW 20 to high vacuum line; G, glass plate; K, silvered condenser; M, driving pin for shutter; M1, threaded rod; M2, rod to remove the lid from Z2; ME, metal foil with effusion orifice; R recession in metal block to hold Z1 or Z2; S, radiation shield; TE, Teflon gasket; TH, thermocouple; TP, shutter; VM, vacuum jacket of thermostating bath; Z1, effusion cell; and Z2, cell for free evaporation (shown in enlarged scale), both fitting into recession R.

and finally

$$\alpha = \frac{WA}{S}\,\frac{\dfrac{1}{W_a}\left(\dfrac{dm_v}{dt}\right)_T - \left(\dfrac{dm_e}{dt}\right)_T}{\left(\dfrac{dm_e}{dt}\right)_T} \tag{8}$$

$-dm_e/dt$ was determined by measuring the integral effusive weight loss from cells Z1 (cf. Figure 3) at the same temperature as the free evaporation experiments were done. The effusion cells (Z1) had the same cross sectional area, $S$, as the cells for free evaporation (Z2) but were closed by a molybdenum foil carrying the effusion hole of Clausing factor $W$ and area $A$. This foil was pressed between two Teflon gaskets TE. The procedure followed in these effusion measurements was analogous to the experiments described above and in the section on the effusion measurements with the other apparatus.

Five measurements with glycerol at 18.00 ± 0.05 °C yield $\alpha = 1.0 \pm 0.2$, in agreement with the other determination described above. The molecular distillation of a polar liquid as glycerol may thus proceed with the maximum rate of evaporation as given by the Hertz–Knudsen–Langmuir equation with a unit evaporation coefficient.

## Literature Cited

(1) Baranova, A. I., Amelin, A. G., Antonova, N. M., *Kolloidn. Zh.*, **28**, 14 (1966).
(2) Bondi, A. A., personal communication cited in Heideger, W. J., Boudart, M., *Chem. Eng. Sci.*, **17**, 1 (1962).
(3) Burrows, G., *Vacuum*, **15**, 389 (1965).
(4) Cammenga, H. K., Klinge, H., Rudolph, B.-E., Schulze, F. W., *Tenside Deterg.*, **12**, 19 (1975).
(5) Cammenga, H. K., Klinge, H., Rudolph, B.-E., *Fortschr. Kolloide Polym.*, **55**, 118 (1971).

(6) Cammenga, H. K., Proc. First Int. Conf. Cal. Therm., Warsaw, Pol. Sci. Publ., 429 ff (1971).
(7) Cordes, H., Cammenga, H., *Z. Phys. Chem. (Frankfurt am Main)*, **63**, 280 (1969).
(8) Cordes, H., Dost, L., Cammenga, H. K., *Z. Metallkd.*, **62**, 915 (1971).
(9) Filosofo, I., Merlin, M., Rostagni, A., *Nuovo Cimento*, **7**, (9), 69 (1950).
(10) Heideger, W. J., Boudart, M., *Chem. Eng. Sci.*, **17**, 1 (1962).
(11) Hickman, K., *Desalination*, **1**, 13 (1966).
(12) Hickman, K., Trevoy, D. J., *Vacuum*, **2**, 3 (1952).
(13) Hirth, J. P., Pound, G. M., *Prog. Mater. Sci.*, **11** (1963).
(14) Hölzel, I. Knacke, I., Parthey, H., "Verdampfungskoeffizienten", Landolt-Börnstein, Zahlenwerte und Funktionen, 6. Aufl., Band II, 5b, 1968, p 238.
(15) Kailan, A., *Z. Anal. Chem.*, **51**, 81 (1912).
(16) Mayer-Bugström, H., *Z. Dtsch. Oel- Fett-Ind.*, **44**, 418 (1924).
(17) Paul, B., *ARS J.*, **32**, 1321 (1962).
(18) Pound, G. M., *J. Phys. Chem. Ref. Data*, **1**, 135 (1972).
(19) Richardson, A., *J. Chem. Soc.*, **49**, 761 (1886).
(20) Ross, G. R., Heideger, W. J., *J. Chem. Eng. Data*, **7**, 505 (1962).
(21) Stedman, D. F., *Trans. Faraday Soc.*, **24**, 289 (1928).
(22) Strickland-Constable, R. F., "Kinetics and Mechanism of Crystallization from the Fluid Phase and of the Condensation and Evaporation of Liquids", Academic Press, London, 1968.
(23) Trevoy, D. J., *Ind. Eng. Chem.*, **45**, 2366 (1953).
(24) Wyllie, G., *Proc. R. Soc. London, Ser. A*, **197**, 383 (1949).
(25) Zil'berman-Granovskaya, A. A., *Zh. Fiz. Khim.*, **14**, 759 (1940).

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# Vapor–Liquid Equilibrium Data for the Systems 2-Methoxyethanol–Ethylbenzene, 2-Methoxyethanol–*p*-Xylene, and 2-Ethoxyethanol–*p*-Xylene

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**Experimental vapor–liquid equilibrium data were obtained for the binary systems 2-methoxyethanol–ethylbenzene, 2-methoxyethanol–*p*-xylene, and 2-ethoxyethanol–*p*-xylene at 760 mmHg. The activity coefficients were calculated taking into account the nonideality of the vapor phase. The data satisfied the thermodynamic consistency tests of Herington, Norrish-Twigg, and Black. The correlations of van Laar, Redlich-Kister, Wilson, NRTL, and Wiehe-Bagley, with the constants evaluated by the method of nonlinear least squares, represented the data well.**

Isobaric vapor–liquid equilibrium data for the binary systems 2-methoxyethanol–ethylbenzene, 2-methoxyethanol–*p*-xylene, and 2-ethoxyethanol–*p*-xylene were obtained at 760 ± 2 mmHg pressure using a vapor recirculating type of equilibrium still. All these systems formed minimum boiling azeotropes. The azeotropic conditions for 2-methoxyethanol–ethylbenzene and 2-ethoxyethanol–*p*-xylene systems are 118.8 °C, 61.5 mole % 2-methoxyethanol, and 128.5 °C, 51.5 mole % 2-ethoxyethanol, respectively, whereas the corresponding literature values (11) are 117 °C, 59.3 mole % 2-methoxyethanol, and 128.6 °C, 54.1 mole % 2-ethoxyethanol, respectively. The system 2-methoxyethanol–*p*-xylene has an azeotropic temperature of 119.3 °C at 64.0 mole % 2-methoxyethanol. Garber and Bovkun (7) determined the azeotropic temperature for this system as 119.5 °C at 63 mole % 2-methoxyethanol at 750 mmHg, using a distillation column. Vapor–liquid equilibrium data for the system 2-methoxyethanol–ethylbenzene at 62 mmHg were reported by Jakubiček et al. (12). Garber and Bovkun (8) have reported vapor–liquid equilibrium data for the systems 2-methoxyethanol–*p*-xylene and 2-ethoxyethanol–*p*-xylene at 60 mmHg pressure.

## Experimental Section

***Materials.*** Ethylbenzene obtained from British Drug Houses and *p*-xylene from Riedel were dried by contacting them overnight with pure anhydrous calcium chloride whereas 2-methoxyethanol and 2-ethoxyethanol obtained from Riedel were dried by refluxing for about 4 h with anhydrous potassium carbonate. These were further purified by distillation in a well-insulated 30-mm glass column packed to a height of 1 m with 4 mm helices made from nichrome wire. The heart cuts were collected by maintaining an approximate reflux ratio of 9:1 using a reflux head described by Miller (16).

***Apparatus.*** The vapor recirculating type equilibrium still used, incorporates the salient features of the stills reported by Jones (13) and Raju et al. (24). Figure 1 gives details of the apparatus which essentially consists of the boiler (B), condensate receiver (C), and vaporizer (V). The vapors from the boiler pass through the entrainment trap (E) and then bubble through the condensate in (C) providing thorough mixing of the condensate before they are totally condensed by the condenser (W). The condensate overflows through the capillary tubing (T) into the total vaporizer (V) from where the vapors bubble through the boiling liquid in (B) providing thorough mixing of the liquid in boiler. Double-walled thermometer pockets ($P_1$ and $P_2$) were introduced to avoid surface heating of mercury from the neighboring heater elements. The heaters ($H_1$, $H_2$, and $H_3$) having wattages of 125, 125, and 250, respectively, are controlled separately by using a combination of "Sunvic" energy regulators and autotransformers. The still has a capacity of about 100 mL of liquid. The system pressure was kept constant at 760 ± 2 mmHg with the help of an air blower. The fluctuations in the manometer readings were minimized by using two empty vessels with a total capacity of 40 L in the circuit between the blower and the manometer. The air used for maintaining the pressure was dried by passing first through sulfuric acid bubblers and then through U-tubes containing anhydrous calcium chloride. Temperatures were measured with the help of short range "Anschutz" thermometers having an accuracy of 0.1 °C. Stem corrections were applied to the observed thermometer readings. Care was taken to avoid any refluxing in the vapor space above the boiler (B) by keeping the temperature of the vapors slightly higher than the boiler temperatures by means of the heater ($H_2$). Also superheating of vapors in the vaporizer (V) was minimized by observing, at frequent intervals, wetting of the vaporizer outlet tube with the help of a magnifying lens. The circulation was continued for 3 h so as to ensure complete equilibrium between the vapor and liquid phases. About 7 mL each of the samples of the liquid in the boiler and the condensate receiver was collected through stopcocks $K_1$ and $K_2$, respectively, after flushing the stagnant liquid collected just above the stopcocks. Narrow-necked chilled sampling bottles, provided with standard ground joint stoppers,