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Vapor Pressure Data for Toluene, 1-Pentanol, 1-Butanol, Water, and 1-Propanol and for the Water and 1-Propanol System from 273.15 to 323.15 K

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Vapor pressures were measured by using the static method for toluene, 1-pentanol, 1-butanol, water, and 1-propanol and for five mixtures of water and 1-propanol over the temperature range of 273.15–323.15 K. The compositions of the water–propanol mixtures expressed as liquid mole fractions of water were 0.160, 0.330, 0.503, 0.660, and 0.830. Vapor pressure equations are given in addition to the experimental values. The excess Gibbs energy of the water–propanol system is expressed by the Renon equation, and constants are given at seven different temperatures. A newly constructed vapor pressure apparatus which uses an electronic capacitance pressure gauge is described.

To the chemical engineer and scientist, vapor pressure and vapor–liquid equilibrium data have a broad range of applications from theoretical studies of molecular interactions to design analysis of separation processes such as distillation. Yet vapor pressure data for many compounds and mixtures commonly used in industry are sparse. In this paper, we report vapor pressure data for toluene, 1-pentanol, 1-butanol, water, and 1-propanol and for the water–propanol system from 273.15 to 323.15 K. The vapor pressures of toluene and water have been accurately measured by a number of experimentalists within the temperature range of this work. For example, Besley and Bottomley (*2*) and Pitzer and Scott (*9*) recorded measurements for toluene and Besley and Bottomley (*1*) and Douslin (*6*) recorded measurements for water. The available data for toluene and water provide a convenient basis of comparison for the present work.

Experimental Section

Apparatus. A newly constructed apparatus of the "static" type was used in this work and is shown schematically in Figure 1. The apparatus consists primarily of a sample bulb, 1, a differential electronic capacitance gauge, 2, a mercury manometer, 3, a constant-temperature bath, 4, a platinum resistance thermometer, 5, and vacuum system. The capacitance gauge, manufactured by Datametrics Co., is capable of measuring a range of pressure differences from 1×10^{-5} to 10 torr. The maximum rated error of this particular gauge and readout device is 0.3% of reading. The capacitance gauge was kept at a constant temperature of about 355 K and all lines leading from the sample bulb were maintained at temperatures above the sample temperature. For pressures greater than 10 torr, a certain amount of inert gas must be leaked into the space above the capacitance gauge to make the pressure difference across the gauge less than 10 torr. The pressure of the inert gas is measured by using a precision mercury manometer. Temperatures (IPTS 68) are measured by using a platinum resistance thermometer calibrated by the National Bureau of Standards.

Reagents. The 1-butanol, 1-pentanol, 1-propanol, and toluene were certified reagents obtained from Fisher Scientific Co. A chromatographic study detected less than 0.01% benzene and a negligible amount of xylene in the toluene. A similar study detected no impurities in 1-butanol, 1-pentanol, and 1-propanol although no specific tests were made for water. These compounds were used without further purification. The water was distilled tap water.

Degassing. The procedure used to degas the liquid samples consisted of freezing the sample with liquid nitrogen, evacuating the space above its surface, closing the valve to the vacuum system, and allowing the sample to melt. In the case of the pure compounds, it was helpful to pump on the surface of the melted sample for short periods of time. This could not be done with the mixtures since it would change the composition.

The water–propanol mixtures, pentanol, butanol, and water were relatively easy to degas, requiring only 6–8 h. The propanol was more difficult to degas, and we subjected it to about 24 freeze–thaw cycles over a period of $1^1/_2$ days. Toluene was by far the most difficult to degas and required 6 days to completely degas.

A normal procedure used to degas the samples consisted of (1) subjecting the sample to freeze–thaw cycles until no more bubbles are seen evolving from the surface of the melting sample, (2) taking a vapor pressure reading at the ice point, (3) subjecting the sample to three or four additional freeze–thaw cycles, and (4) repeating the vapor pressure reading at the ice point. A constant pressure supposedly indicated that the sample had been degassed. This procedure was found to be inadequate for toluene because of the tendency to reach what appeared to be a stable, minimum vapor pressure reading only for the pressure to increase sharply if the sample was disturbed by heating or stirring. For this reason, we did not consider a sample adequately degassed until it gave a constant vapor pressure reading at the ice point after having been heated to over 323.15 K for about 30 min. The sample was also stirred between freeze–thaw cycles.

Procedure. To determine the vapor pressure for the pure compounds, we placed about 20 mL of the compound in the sample bulb, and after degassing of the compounds, the vapor pressure was measured at the first temperature of interest by using the capacitance gauge. The reference side of the gauge was evacuated. The sample was then heated to higher temperatures of interest, and the pressure readings were repeated. For pressures exceeding 10 torr enough dry air was admitted to the reference side of the capacitance gauge to bring the differential pressure to less than 10 torr. The vapor pressure of the sample was taken as the sum of the mercury manometer and capacitance gauge reading.

Vapor pressure readings for the water–propanol mixtures were taken in a similar manner except that the mixtures were carefully prepared to the desired composition. The mass of the sample was determined before and after the measurements to ensure that not enough of the sample was lost during degassing and measuring to affect the liquid composition.

Results and Discussion

Pure Compounds. Table I contains the results of the vapor pressure measurements for the pure compounds. The maximum

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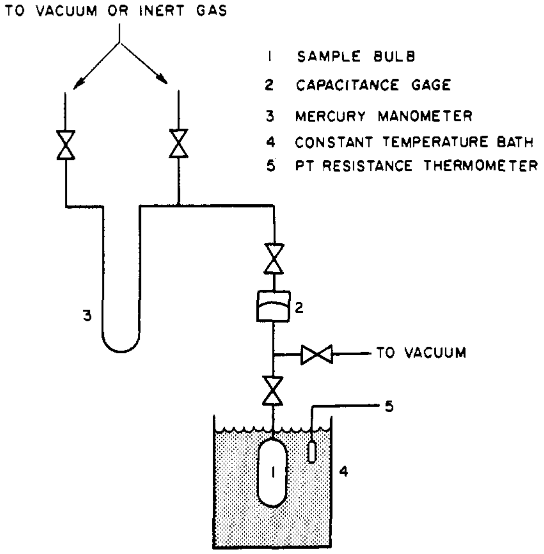

Figure 1. Schematic diagram of the vapor pressure apparatus.

Table I. Unsmoothed Vapor Pressure Data for Pure Compounds

T, K	P, torr	T, K	P, torr
Toluene		Water	
273.15	6.76	273.15	4.58
279.21	9.82	278.12	6.51
284.17	13.22	284.41	9.96
293.14	21.78	293.47	17.94
303.04	36.48	301.58	29.06
312.75	58.08	312.24	52.77
322.41	89.03	322.11	87.78
1-Pentanol		1-Propanol	
273.15	0.29	273.15	3.58
283.13	0.72	278.45	5.38
293.16	1.63	286.95	9.93
303.16	3.43	298.10	21.18
313.11	6.88	308.28	39.71
323.42	13.49	323.10	91.56
1-Butanol			
273.15	1.03		
283.16	2.34		
293.14	5.02		
303.16	10.06		
313.14	19.33		
323.31	35.39		

estimated error in the pressure reading is the lesser of ±0.44% or ±0.15 torr. Table II gives the form of the vapor pressure fitting equation and the constants for each compound. The maximum percent deviation of the fitting equation from the experimental values for the compounds is −0.57%. We believe that the fitting equation more accurately represents the true vapor pressure of the compounds than do the experimental values since the fitting equation tends to smooth the data.

Literature data for the vapor pressure of 1-butanol and 1-pentanol are scarce. Two vapor pressure values for 1-pentanol reported by Thomas and Meatyard (*12*) at 37.3 and 44.6 °C were higher by 10.1 and 7.0% than the results reported here. Three measurements of the vapor pressure of 1-butanol between 25 and 35 °C by Butler et al. (*3*) were lower by 3.90 to 5.0% than the values reported here. For 1-propanol, our reported vapor pressures compare favorably with values reported by Schmidt (*11*) and Paraskevopoulos and Missen (*8*). All of the six data points of Schmidt were lower than those reported here but with a maximum deviation of 2.8%. The single point of Paraskevopoulos and Missen at 35 °C was less than 1% lower than the value reported here. The vapor pressure of water has been precisely determined by numerous experimentalists and is in excellent agreement with values reported here. For example, the measurements by Besley and Bottomley (*1*) and Douslin (*6*) are less than 0.35% higher than our smoothed values. Besley and Bottomley (*2*) and Pitzer and Scott (*9*) have measured the vapor pressure of toluene. Figure 2 illustrates the comparison of our results with the measurements of Pitzer and Scott and arbitrarily selected values of Besley and Bottomley. The values reported by Pitzer and Scott are in complete agreement with our smoothed values and the values reported by Besley and Bottomley deviate less than 1%.

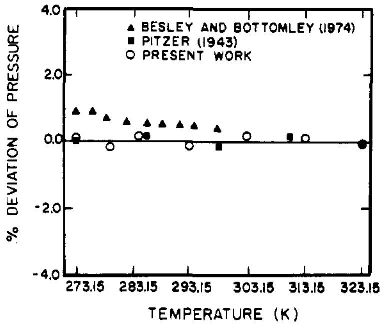

Figure 2. Deviation of vapor pressures calculated by the fitting equation from experimental values for toluene.

Reduction of Water-Propanol Data. We correlated the measured P–x data for the water-propanol system by using Barker's method as described by Prausnitz (*10*) in conjunction with a Hooke-Jeeves optimization program described by Carnahan and Wilkes (*5*). For the low-pressure system of this work, the following equations were used:

$$P = \gamma_1 x_1 P_1^{s'} + \gamma_2 x_2 P_2^{s'} \tag{1}$$

$$P_1^{s'} = P_1^{s} \exp \frac{(V_1^L - B_{11})(P - P_1^{s}) - P\delta_{12} y_2^2}{RT} \tag{2}$$

$$P_2^{s'} = P_2^{s} \exp \frac{(V_2^L - B_{22})(P - P_2^{s}) - P\delta_{12} y_1^2}{RT} \tag{3}$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{4}$$

where $P_i^{s'}$ = "corrected" vapor pressure of component i, V_i^L = liquid molar volume of component i, B_{ii} = second virial coefficient of component i, B_{ij} = second virial interaction coefficient, γ_i = activity coefficient of component i. The B_{ii} and B_{ij} were calculated by using the correlation method by Tsonopoulos (*13*). In addition, one must assume a form for the molar

Table II. Vapor Pressure Equation for the Pure Compounds

$$\log_e P(\text{torr}) = C_1/T + C_2 + C_3T + C_4T^2 \ (T = \text{K})$$

compd	C_1	C_2	C_3	C_4	av abs % dev	max % dev
toluene	−5541.623	25.080 47	−0.010 553 21		0.12	−0.19
1-pentanol	−18309.21	136.776 9	−0.368 510 8	0.000 397 903 6	0.10	+0.19
1-butanol	−7257.969	29.782 39	−0.011 644 88		0.32	−0.52
1-propanol	−6567.294	27.908 24	−0.009 485 247		0.17	−0.44
water	−6081.629	26.174 48	−0.008 749 507		0.17	−0.41

Table III. Unsmoothed Vapor Pressure Data for Five Liquid Mole Fractions of Water in 1-Propanol

T, K	P, torr	T, K	P, torr
0.160 mole fraction		0.503 mole fraction	
273.15	5.58	273.15	6.55
279.77	8.97	278.84	9.86
290.10	18.12	287.90	18.44
298.25	30.47	298.11	35.34
311.85	67.54	310.20	71.65
323.02	121.41	323.25	142.80
323.67	125.66	0.660 mole fraction	
0.330 mole fraction		273.15	6.63
273.15	6.40	278.30	9.61
273.15	6.37	298.20	35.77
278.76	9.52	310.12	71.70
288.23	18.30	323.23	143.72
298.19	34.32	0.830 mole fraction	
310.21	69.41	273.15	6.55
323.17	137.62	279.05	9.98
		288.51	19.13
		298.11	35.19
		310.29	71.66
		323.09	140.83

excess Gibbs energy, g^E. We found that the Renon (9) equation adequately represented the data.

$$\frac{g^E}{RT} = x_1x_2\left[\frac{\tau_{21}g_{21}}{x_1 + x_2g_{21}} + \frac{\tau_{12}g_{12}}{x_2 + x_1g_{12}}\right] \qquad (5)$$

where

$$\tau_{12} = (g_{12} - g_{22})/RT \qquad \tau_{21} = (g_{12} - g_{11})/RT \qquad (6)$$

$$g_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad g_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad (7)$$

The expressions for the activity coefficients which correspond to eq 5 are

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left[\frac{g_{21}}{x_1 + x_2g_{21}}\right]^2 + \frac{\tau_{12}g_{12}}{(x_2 + x_1g_{12})^2}\right] \qquad (8)$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left[\frac{g_{12}}{x_2 + x_1g_{12}}\right]^2 + \frac{\tau_{21}g_{21}}{(x_1 + x_2g_{21})^2}\right] \qquad (9)$$

The values of the parameters τ_{12}, τ_{21}, and α_{12} of eq 8 and 9 were found which minimize the sum of the squares of the deviations in pressure calculated from eq 1 and the smoothed experimental values calculated at each of the experimental compositions from the fitting equation.

Table V. Correlation of Mixtures of Water and 1-Propanol Using the Three-Parameter Renon Equation

temp, K	τ_{12}	τ_{21}	α_{12}	av abs % dev[a]	max % dev[a]
273.15	2.001	0.635	0.369	0.244	−0.61
283.15	2.026	0.611	0.389	0.167	−0.43
293.15	2.093	0.556	0.389	0.115	−0.29
298.15	2.129	0.535	0.389	0.094	−0.23
303.15	2.159	0.516	0.389	0.074	−0.19
313.15	2.225	0.493	0.399	0.081	+0.19
323.15	2.288	0.471	0.419	0.161	+0.35

[a] These deviations in pressure are based on values of pressure calculated from the Renon constants in Table V and the smoothed values of the experimental pressures from the constants given in Table IV.

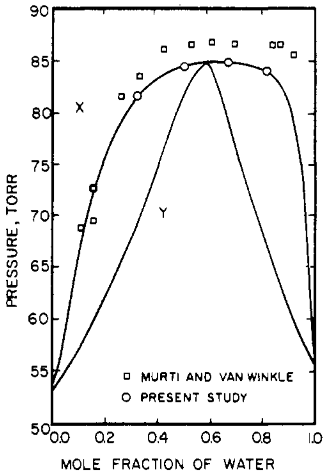

Figure 3. P-x-y diagram for the water-propanol system at 313.15 K.

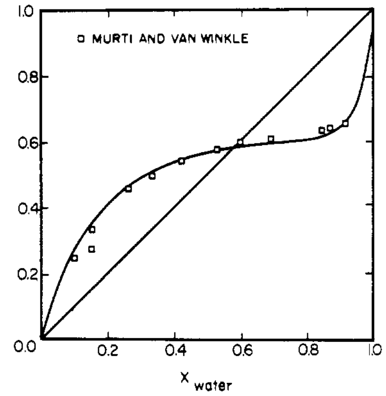

Figure 4. x-y diagram for the water-propanol system at 313.15 K.

Results. Table III contains the results of the vapor pressure measurements for the water-propanol measurements. The maximum estimated error in the pressure reading is the lesser of ±0.44% or ±0.40 torr. Table IV gives the form of the vapor pressure fitting equation and the constants for each compound. The maximum percent deviation of the fitting equation from the experimental values for the compounds is ±0.42%. Table V contains the constants for the Renon equation, for seven temperatures from 273.15 to 323.15 K. The maximum percent deviation of the pressures calculated from the Renon constants using eq 1 from the smoothed experimental pressures is also given in Table V.

Murti and Van Winkle (7) have reported values for P-x-y at 313.15 K for the water-propanol system. We show in Figure 3 their P-x data compared with our own measurements. The

Table IV. Vapor Pressure Equation for Mixtures of Water and 1-Propanol

$$\log_e P\,(\text{torr}) = C_1T^2 + C_2T + C_3\ (T = \text{K})$$

mole fraction of water in 1-propanol	C_1	C_2	C_3	av abs % dev	max % dev
0.160	−0.000 235 912 3	0.202 446 3	−35.978 27	0.081	−0.12
0.330	−0.000 234 966 7	0.201 504 0	−35.656 54	0.217	+0.42
0.503	−0.000 240 007 0	0.204 636 8	−36.109 89	0.127	+0.28
0.660	−0.000 231 933 1	0.199 723 8	−35.357 77	0.096	−0.20
0.830	−0.000 238 007 5	0.203 346 8	−35.907 51	0.138	+0.25

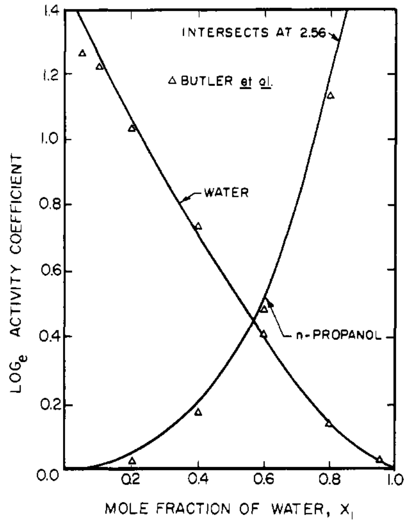

Figure 5. Activity coefficients for the water–propanol system at 298.15 K vs. the liquid mole fraction of water.

agreement is poor. However, in Figure 4 their x–y data are seen to be generally in good agreement with the results reported here. Thus, we conclude that their P–x–y data are inconsistent and that their pressure measurements are probably in error. Butler et al. (*4*) report activity coefficients for this system at 298.15 K. Their values are shown in Figure 5 compared with the activity coefficients calculated by using the Renon constants from Table V. The agreement is excellent.

Although corrections were made to P_1^s and P_2^s as given by eq 2 and 3, the corrections are very small and need not be made for any practical use of these data. At the maximum temperature of 325 K the use of P_1^s and P_2^s without correction resulted in a total pressure difference in eq 1 of about 0.3 torr or 0.2% and a resultant effect on y_1 of less than 0.001 mole fraction. Thus for practical use of the data, smoothed values of P–x–y at any desired temperature can easily be found and therefore are not included here.

Conclusions

The current trend of determining vapor liquid equilibria by measuring only P–x data has been used here to slightly lower pressures than normally reported. This has been accomplished by using a differential pressure gauge with the reference side evacuated at low pressures. We have found that adequate degassing is essential at these low pressures and suggest that large errors encountered in reported vapor pressure measurements are attributed primarily to inadequate degassing.

Glossary

B_{ii}	second virial coefficient of component i
B_{ij}	second virial interaction coefficient of components i and j
g_{12}	Gibbs energy parameter defined by eq 7
g^E	molar excess Gibbs energy
P	total pressure of the system
$P_i^{s'}$	"corrected" vapor pressure of component i
R	universal gas constant
T	temperature of system
V_i^L	liquid molar volume of component i
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i
γ_i	activity coefficient of component i
δ_{12}	interaction coefficient defined by eq 4
τ_{ij}	parameter related to the nonrandomness of a mixture in the Renon equation

Literature Cited

(1) Besley, L., Bottomley, G., *J. Chem. Thermodyn.*, **5**, 397 (1973).
(2) Besley, L., Bottomley, G., *J. Chem. Thermodyn.*, **6**, 577 (1974).
(3) Butler, J., Ramchandani, C., Thomson, D., *J. Chem. Soc.*, **138**, 280 (1935).
(4) Butler, J., Thomson, D., Machennan, W., *J. Chem. Soc.*, **136**, 674 (1933).
(5) Carnahan, B., Wilkes, J., "Digital Computing and Numerical Methods", Wiley, New York, 1973.
(6) Douslin, D., *J. Chem. Thermodyn.*, **3**, 187 (1971).
(7) Murti, P., Van Winkle, M., *Ind. Eng. Chem.*, **3**, 72 (1957).
(8) Paraskevopoulos, G., Missen, R., *Trans. Faraday Soc.*, **58**, 869 (1962).
(9) Pitzer, K., Scott, D., *J. Am. Chem. Soc.*, **65**, 803 (1943).
(10) Prausnitz, J., "Molecular Thermodynamics of Fluid Phase Equilibria", Prentice-Hall, Englewood Cliffs, NJ, 1969.
(11) Schmidt, G., *Z. Phys. Chem.* (*Leipzig*), **8**, 628 (1891).
(12) Thomas, L., Meatyard, R., *J. Chem. Soc.*, 1986 (1963).
(13) Tsonopoulos, C., *AIChE J.*, **20**, 263 (1974).

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Interfacial Tension Measurements for $HClO_4$ Solutions at the Mercury Electrode

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The interfacial tension at the mercury/perchloric acid interface was determined by the polarographic drop-time method for $HClO_4$ concentrations from 10^{-3} to 1.0 M. The experimental data are presented in the form of fourth-order polynomial expressions and E^{pzc}, the potential, and γ^{pzc}, the interfacial tension at the point of zero charge, are tabulated. Appropriate mathematical treatment of these data allows calculations of double-layer parameters including the cationic and ionic surface excesses presented here.

Experimental Section

All solutions were prepared by dilution from bidistilled water and 70% Matheson Coleman Grade ACS perchloric acid, and their concentrations were verified by acid–base titrations. The solutions were deoxygenated by bubbling nitrogen, which had been previously passed through ammonium metavanadate and water traps, through them. Mallinckrodt "Triple distilled" mercury was vacuum distilled three times before use. All data were obtained at 25 ± 1 °C according to previously published techniques.

Interfacial tension measurements using the procedure described by Mênard and Kimmerle (*1*) based on the polarographic drop-time technique used a 0.1 M KCl reference solution $\gamma^{pzc} = 426.2$ mJ m^{-1} (*2*). The potentials applied to the dropping mercury electrode were measured against a saturated calomel reference SCE electrode. $E_{ClO_4^-}{}^{SCE}$ (the potential between the SCE and an anion-sensitive electrode, ORION Model 92-81) and $E_{H^+}{}^{SCE}$ (the potential between the SCE and a reversible hydrogen

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