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Total Vapor Pressure Measurements for 2-Ethoxyethanol with Methanol, Ethanol, 1-Propanol, and 2-Propanol at 313.15 K

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Total vapor pressure measurements at 313.15 K are reported for binary systems of 2-ethoxyethanol with methanol, ethanol, 1-propanol, and 2-propanol. The results were obtained using a Van Ness type apparatus and were fitted with a three-suffix Margules equation using Barker's method. The Margules equation represents the data to within an average absolute deviation of approximately 0.03 kPa. Methanol + 2-ethoxyethanol shows very small negative deviations from Raoult's law while the other three systems show very small positive deviations.

Introduction

As part of a continuing study of vapor−liquid equilibrium in binary systems containing an alkoxyethanol, we will report total pressure data for 2-ethoxyethanol with methanol, ethanol, 1-propanol, and 2-propanol at 313.15 K. Earlier, we investigated the vapor−liquid equilibria of 1-hexane, 1-heptane, and cyclohexane with 2-methoxyethanol [1] and with 2-ethoxyethanol.[2]

Several sets of vapor−liquid equilibrium data have been reported previously for systems consisting of 2-ethoxyethanol and methanol or ethanol. Isothermal results for methanol + 2-ethoxyethanol are available at 298.15[3] and at 313.15, 323.15, and 333.15 K.[4] Isobaric data at 1 bar[5,6] have been reported for ethanol + 2-ethoxyethanol. We have been unable to locate data for systems of 2-ethoxyethanol with a C3 alcohol.

Experimental Section

Apparatus and Procedures. The apparatus is essentially the same as that described in detail by Bhethanabotla and Campbell.[7] It is of the Van Ness type,[8] in which total pressure is measured as a function of overall composition in the equilibrium cell. Two modifications to the apparatus described by Bhethanabotla and Campbell have been made. The pressure gauge has been replaced with one of 0.001 kPa resolution as described by Pradhan et al.[9] and the piston-injectors have been replaced with Ruska pumps (model 2200) having a resolution of 0.001 cm^3.

The overall composition in the equilibrium cell was changed by charging metered amounts of the pure components from their respective piston-injectors. The pressure in the cell was read after equilibration. The small correction (usually less than 0.001 in mole fraction) to convert the overall mole fraction in the equilibrium cell to the liquid-phase mole fraction was made as part of the data reduction procedure as described by Bhethanbotla and Campbell.

Experimental uncertainties are 0.1% in pressure, 0.02 K in temperature, and between 0.0005 and 0.001 in mole fraction, the smaller value applying at the extremes in composition.

Table 1. Comparison of Pure Component Vapor Pressures P_i^{sat}/kPa at 313.15 K to Values Obtained from the Literature

substance	P_i^{sat}/kPa, this study	P_i^{sat}/kPa, literature
methanol	35.341	35.091,[10] 35.431 [11]
ethanol	17.819	17.992,[10] 17.877 [11]
1-propanol	6.939	6.988,[10] 6.924 [11]
2-propanol	13.806	14.226,[10] 13.853 [11]
2-ethoxyethanol	1.842 ± 0.012[a]	1.766,[4] 1.863 [11]

[a] Average of four measurements.

Table 2. Saturated Liquid Volumes V_i^L and Second Virial Coefficients[a] for Single Components B_{ii} and Mixtures B_{ij} Used for Alcohol (1) + 2-Ethoxyethanol (2) Systems at 313.15 K

substance	B_{11}/cm^3·mol^{-1}	B_{12}/cm^3·mol^{-1}	V_1^L/cm^3·mol^{-1}
methanol	−1975	−2170	41.5
ethanol	−1649	−2349	59.7
1-propanol	−2010	−2606	76.3
2-propanol	−1878	−2612	78.2

[a] For 2-ethoxyethanol, B_{22}/cm^3·mol^{-1} = −2993 and V_2^L/cm^3·mol^{-1} = 98.6.

Materials. Methanol, 1-propanol, and 2-propanol were obtained from Aldrich and had percent purities (by chromatographic analysis, as given by the manufacturer) of 99.99, 99.99, and 99.94, respectively. 2-Ethoxyethanol was obtained from Fluka, and ethanol, from Aaper Alcohol and Chemical with percent purities of 99.9 and 99.9, respectively. All chemicals were degassed by vacuum distillation and were used without additional purification. The pure component vapor pressures measured in this study are reported in Table 1, where they are compared to the values reported by Antosik et al.[4] and with the compilations of the Thermodynamic Research Center[10] and of Riddick et al.[11] Generally, good agreement is found between the reported results and those of the present study.

For internal consistency, the pure component vapor pressures should be determined as part of the isotherm measurements. Thus, the vapor pressure of 2-ethoxyethanol, a component of all four isotherms, was measured on four separate occasions. The average value, along with the uncertainty (0.012 kPa), is given in Table 1. Half of this value is due to apparatus uncertainties (temperature bath,

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Table 3. Total Pressure P/kPa as a Function of Liquid-Phase Mole Fraction x_1 for Alcohol (1) + 2-Ethoxyethanol (2) at 313.15 K

Methanol (1) + 2-Ethoxyethanol (2)		Ethanol (1) + 2-Ethoxyethanol (2)		1-Propanol (1) + 2-Ethoxyethanol (2)		2-Propanol (1) + 2-Ethoxyethanol (2)	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	1.832	0.0000	1.840	0.0000	1.865	0.0000	1.829
0.0382	3.112	0.0298	2.392	0.0298	2.046	0.0291	2.230
0.0922	4.826	0.0595	2.909	0.0606	2.224	0.0604	2.662
0.1986	8.323	0.1008	3.622	0.1001	2.452	0.1005	3.193
0.2811	11.028	0.1500	4.456	0.1500	2.732	0.1497	3.837
0.3221	12.360	0.1995	5.282	0.1997	3.005	0.1996	4.480
0.3588	13.575	0.2497	6.114	0.2503	3.282	0.2500	5.114
0.3989	14.909	0.2995	6.927	0.2997	3.550	0.2996	5.728
0.4493	16.559	0.3492	7.735	0.3497	3.813	0.3496	6.335
0.4987	18.209	0.3994	8.534	0.3997	4.070	0.3996	6.937
0.5493	19.896	0.4494	9.326	0.4498	4.326	0.4497	7.530
0.5992	21.576	0.4995	10.111	0.4498	4.578	0.4997	8.115
0.6494	23.283	0.5496	10.894	0.5498	4.825	0.5497	8.695
0.6997	24.989	0.5997	11.668	0.5499	4.829	0.5497	8.711
0.6997	25.061	0.5997	11.684	0.5999	5.072	0.5997	9.279
0.7496	26.752	0.6498	12.454	0.6499	5.309	0.6497	9.850
0.7996	28.475	0.6996	13.214	0.7000	5.554	0.6997	10.415
0.8496	30.199	0.7496	13.980	0.7498	5.785	0.7498	10.984
0.8996	31.932	0.7995	14.744	0.7998	6.022	0.7996	11.543
0.9396	33.325	0.8498	15.503	0.8496	6.249	0.8496	12.104
0.9697	34.371	0.8998	16.272	0.8998	6.477	0.8997	12.690
1.0000	35.341	0.9398	16.891	0.9401	6.662	0.9400	13.159
		0.9702	17.371	0.9701	6.785	0.9701	13.492
		1.0000	17.819	1.0000	6.939	1.0000	13.806

pressure reading, and zero of pressure gauge). The remainder is probably due to the uncertainty in completion of the degassing procedure.

Data Reduction. Data were reduced using Barker's method,[12] in which the parameters in an expression for the excess Gibbs free energy of the liquid phase are obtained by minimizing the sum of the squares between the measured and calculated pressures. Calculated pressures are obtained from

$$P_{\text{calc}} = \frac{\gamma_1 x_1 f_1^{\text{L}}}{\phi_1^{\text{V}}} + \frac{\gamma_2 x_2 f_2^{\text{L}}}{\phi_2^{\text{V}}} \tag{1}$$

where γ_i is the activity coefficient of species i in the liquid phase and ϕ_i is the fugacity coefficient of species i in the vapor phase. The fugacity f_i^{L} of pure liquid i is obtained from

$$f_i^{\text{L}} = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp\left[\frac{V_i^{\text{L}}}{RT}(P - P_i^{\text{sat}})\right] \tag{2}$$

where φ_i^{sat} is the fugacity coefficient of pure species i at its vapor pressure. Liquid-phase activity coefficients were modeled by the three-suffix Margules equation:

$$\frac{G^{\text{E}}}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \tag{3}$$

and vapor-phase fugacity coefficients were calculated using the two-term virial equation (explicit in pressure).

The values of second virial coefficients and saturated liquid volumes used in these calculations are given in Table 2. Second virial coefficients were calculated using the Hayden−O'Connell correlation.[13] Required constants for the alcohols were obtained from Fredenslund et al.,[14] and those for 2-ethoxyethanol were obtained as described by Carmona et al.[2] In the calculation of all second virial cross coefficients, the solvation parameters were taken to be 1.55, as recommended[14] for alcohol + alcohol systems. Saturated liquid volumes were obtained from the *TRC Thermodynamic Tables*[10] for the alcohols and from smoothing densities reported by Riddick et al.[11] and Venkatesulu et al.[15] for 2-ethoxyethanol.

Results

The results of the data reduction procedure are a set of corrected liquid-phase mole fractions for each pressure and values for the parameters appearing in the G^{E} model. $P-x$ data are given for each system in Table 3 and are plotted in Figures 1−4. In each figure, the solid line represents the fit of the G^{E} model to the $P-x$ data and the dashed line represents the predicted vapor-phase mole fractions. Parameter values and resulting average and maximum deviations between calculated and experimental pressures are given in Table 4. The data are represented by the G^{E} model generally to within an average of 0.03 kPa with a maximum deviation of 0.08 kPa.

Table 4. Values of Parameters Appearing in Eq 3 and Resulting Average Deviations ΔP_{avg} and Maximum Deviations ΔP_{max} for Alcohol (1) + 2-Ethoxyethanol (2) Systems at 313.15 K

2-ethoxyethanol (2) with	A_{12}	A_{21}	ΔP_{avg}/kPa	ΔP_{max}/kPa
methanol	0.0011	−0.0236	0.028	0.075
ethanol	0.1000	0.1406	0.015	0.027
1-propanol	0.1053	0.1806	0.005	0.015
2-propanol	0.1206	0.1763	0.015	0.048

Figures 1−4, as well as values for the Margules parameters given in Table 4, indicate that methanol + 2-ethoxyethanol exhibits small negative deviations from ideality while the other three systems show small positive deviations.

Direct comparison between literature data and the data reported here can be made only for methanol + 2-ethoxyethanol. As shown in Figure 1, the pressures reported here are generally higher than those reported by Antosik et al.[4] The dashed line in Figure 1 represents vapor-phase mole fraction calculated from the correlation of our $P-x$ data, and the diamond symbols represent vapor-phase mole

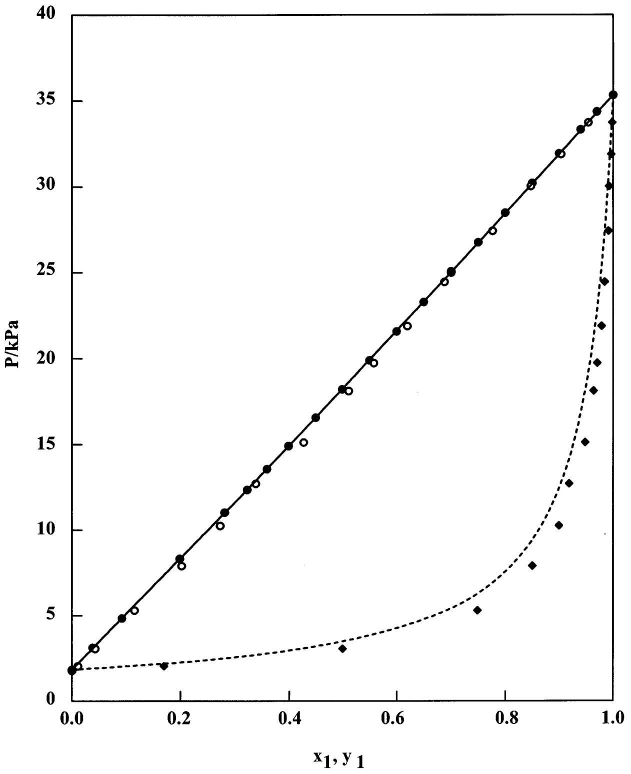

Figure 1. Pressure P versus liquid-phase mole fraction x_1 and vapor-phase mole fraction y_1 for methanol (1) + 2-ethoxyethanol (2) at 313.15 K: (●) experimental $P-x_1$ result, this study; (○) experimental $P-x_1$ result, Antosik et al.;[4] (◆) experimental $P-y_1$ result, Antosik et al., 1999; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

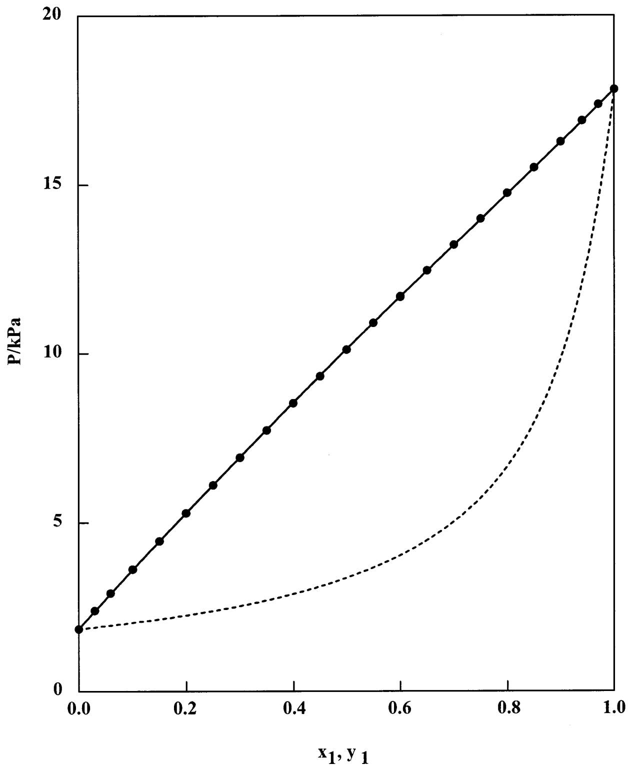

Figure 2. Pressure P versus liquid-phase mole fraction x_1 and vapor-phase mole fraction y_1 for ethanol (1) + 2-ethoxyethanol (2) at 313.15 K: (●) experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

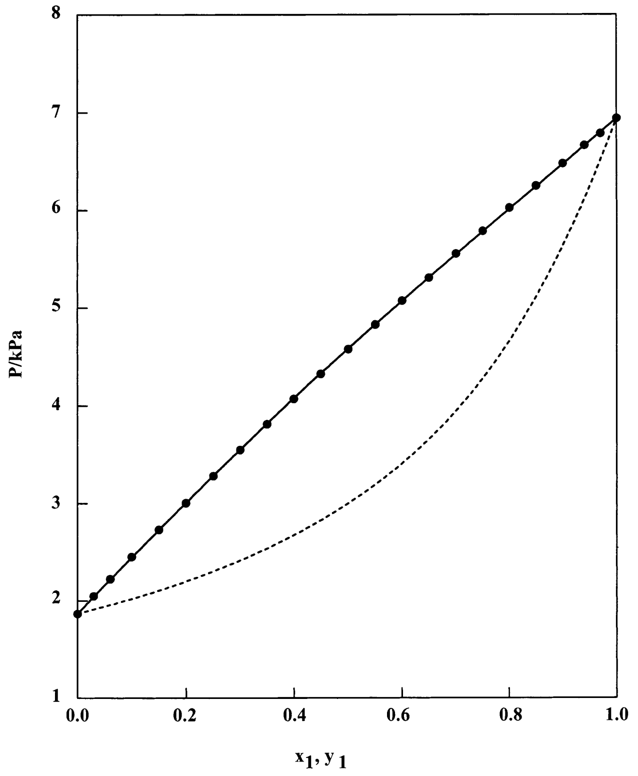

Figure 3. Pressure P versus liquid-phase mole fraction x_1 and vapor-phase mole fraction y_1 for 1-propanol (1) + 2-ethoxyethanol (2) at 313.15 K: (●) experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

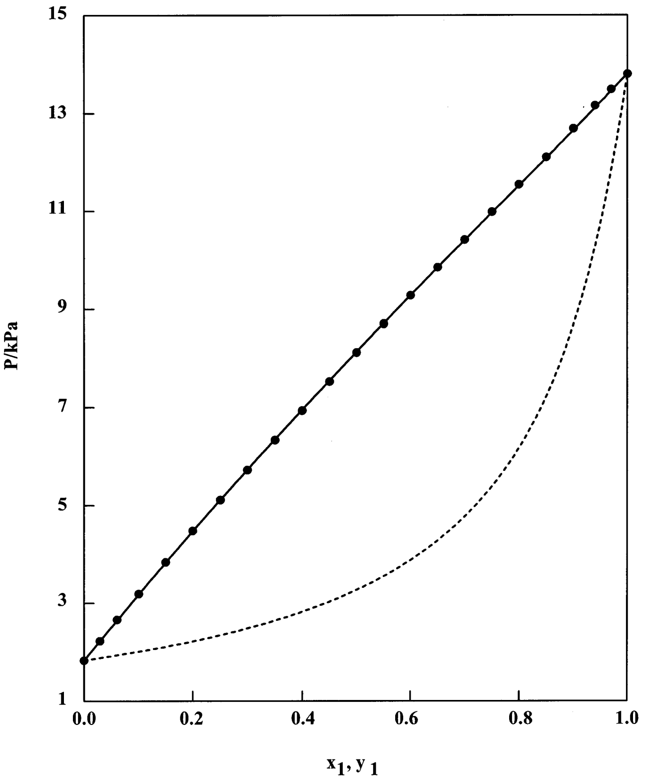

Figure 4. Pressure P versus liquid-phase mole fraction x_1 and vapor-phase mole fraction y_1 for 2-propanol (1) + 2-ethoxyethanol (2) at 313.15 K: (●) experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

Table 5. Average Percent Deviation between Measured Pressures and Those Predicted by UNIFAC for Alcohol (1) + 2-Ethoxyethanol (2) Systems at 313.15 K

alcohol (1)	avg % devn in P
methanol	4.5
ethanol	2.6
1-propanol	1.9
2-propanol	2.3

fractions reported by Antosik et al. To compare the two sets of data quantitatively, we have calculated pressures at the liquid compositions reported by Antosik et al. using the parameters obtained from fits to our data set. Pure component vapor pressures reported by Antosik et al. were used in these calculations. The pressures calculated in this manner were higher than the experimental pressures of Antosik et al. by an average of 0.3 kPa. Calculated vapor-phase compositions differed from those reported by Antosik et al. by an average of 0.012 in mole fraction. It is interesting to note that a direct Barker fit to the data of Antosik et al. results in a lower average deviation in pressure (0.08 kPa) but a larger deviation (0.016) in vapor-phase mole fraction.

Since the systems examined here contain two different oxygen-containing functional groups and, yet, exhibit nearly ideal solution behavior, it is of interest to determine whether predictive, group contribution methods can describe their properties. In this context, we applied the UNIFAC[16] method, as applied by Sandler,[17] to the four systems studied here. Poynting factors and corrections for gas-phase nonideality were made as described above. Average percent deviations between measured pressures and those calculated from UNIFAC are given in Table 5. The results indicate that UNIFAC provides a reasonable prediction, although it should be noted that, in all cases, deviations were lowest near the pure alcohol extreme of the isotherm and highest at the other extreme. It is also interesting to note that UNIFAC predicted that methanol + 2-ethoxyethanol shows slight negative deviations from ideal solution behavior while all other isotherms show slight positive deviations. This result is in accord with the measured values.

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