Total Vapor Pressure Measurements for 2-Ethoxyethanol with Methyl Acetate, Ethyl Acetate, Propyl Acetate, and Ethyl Propionate at 313.15 K and for 2-Ethoxyethanol with Methyl Formate at 308.15 K

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Total pressure measurements are reported for the binary mixtures of 2-ethoxyethanol with methyl acetate, ethyl acetate, propyl acetate, and ethyl propionate at 313.15 K and for 2-ethoxyethanol with methyl formate at 308.15 K. The data were obtained using a Van Ness type apparatus and were fitted to the modified Margules equation (or one of its simplified cases) using Barker's method. All mixtures show positive deviations from ideality and are represented by the model to within an average absolute deviation of approximately 0.06 kPa.

Introduction

In an effort to gain a better understanding of the inter-actions between molecules in binary mixtures containing 2-ethoxyethanol, vapor–liquid equilibrium data are reported for systems of 2-ethoxyethanol with methyl formate, methyl acetate, ethyl acetate, propyl acetate, and ethyl propionate. Previously, Carmona et al.[1] and DeBord et al.[2] studied paraffin and alcohol interactions with 2-ethoxy-ethanol.

Limited sets of vapor–liquid equilibrium data have been reported for binary mixtures of esters with 2-ethoxyethanol. Isothermal data at 298.15 K have been reported by Martin et al.[3] for methyl acetate + 2-ethoxyethanol, and isobaric data at 1 bar for mixtures of 2-ethoxyethanol with butyl acetate[4] and with ethyl acetate and propyl acetate[5] have been reported by Miller.

Experimental Section

Apparatus and Procedure. The apparatus is essentially the same as described in detail by Bhethanabotla and Campbell.[6] It is of the Van Ness type[7] 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.[8] and the original pumps have been replaced with Ruska pumps (model 2200) having a resolution of 0.001 cm^3. The operating ranges in temperature and pressure for the apparatus are (298 to 328) K and (0 to 133) kPa, respectively.

The overall composition in the equilibrium cell was changed by charging metered amounts of the pure components from their respective pumps. 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 is made as part of the data reduction procedure as described by Bhethanbotla and Campbell.[6]

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

substance	T	P_i^{sat}	P_i^{sat}
	K	kPa, this study	kPa, literature
methyl formate	308.15	114.881	114.3[9]
2-ethoxyethanol	308.15	1.303	1.322[9,10]
methyl acetate	313.15	53.808	54.11[11]
ethyl acetate	313.15	25.078	25.04[11]
propyl acetate	313.15	9.586	9.61[11]
ethyl propionate	313.15	10.602	10.58[9]
2-ethoxyethanol	313.15	1.823 ± 0.030[a]	1.779[9,10]

[a] Average of four measurements.

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

substance	T	B_{11}	B_{12}	V_1^L
	K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
methyl formate	308.15	−853	−2087	63.1
methyl acetate	313.15	−1385	−2170	81.7
ethyl acetate	313.15	−1657	−2473	101.2
propyl acetate	313.15	−2288	−2760	118.0
ethyl propionate	313.15	−2344	−2706	117.8

[a] For 2-ethoxyethanol, $B_{22}/(cm^3 \cdot mol^{-1}) = -3268$ and $V_2^L/(cm^3 \cdot mol^{-1}) = 98.5$ at 308.15 K and $B_{22}/(cm^3 \cdot mol^{-1}) = -2993$ and $V_2^L/(cm^3 \cdot mol^{-1}) = 99.2$ at 313.15 K.

Experimental uncertainties are 0.1 percent 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.

Materials. Methyl acetate, ethyl acetate, propyl acetate, methyl formate, and 2-ethoxyethanol were obtained from Aldrich Chemical and had purities (by chromatographic analysis, as given by the manufacturer in area percent) of 99.9%, 99.8%, 99.6%, 99.8%, and 99.9%, respectively. Ethyl propionate was obtained from Fluka with a purity of 99.7%. All chemicals were degassed by vacuum distillation and were used without any additional purification.

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

methyl acetate(1)+ 2-ethoxyethanol(2)		ethyl acetate(1)+ 2-ethoxyethanol(2)		propyl acetate(1)+ 2-ethoxyethanol(2)		ethyl propionate(1)+ 2-ethoxyethanol(2)	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	1.864	0.0000	1.796	0.0000	1.803	0.0000	1.829
0.0381	5.226	0.0374	3.421	0.0602	2.785	0.0300	2.437
0.0893	9.375	0.0972	5.690	0.0998	3.340	0.0693	3.129
0.1594	14.487	0.1316	6.866	0.1501	3.976	0.0998	3.618
0.2318	19.361	0.1993	9.010	0.2001	4.536	0.1488	4.320
0.2736	21.713	0.2679	10.910	0.2499	5.033	0.1989	4.982
0.3814	27.547	0.3202	12.219	0.3001	5.488	0.2491	5.557
0.4200	29.418	0.3701	13.402	0.3504	5.897	0.2994	6.074
0.4678	31.708	0.4277	14.613	0.4004	6.265	0.3496	6.535
0.4982	33.024	0.4833	15.736	0.4504	6.614	0.3998	6.962
0.5480	35.154	0.4987	16.029	0.4505	6.564	0.4498	7.361
0.5481	35.160	0.5486	16.969	0.5005	6.885	0.4497	7.370
0.5979	37.204	0.5991	17.867	0.5505	7.182	0.4996	7.683
0.6479	39.199	0.6486	18.728	0.6004	7.470	0.5497	8.009
0.7179	41.942	0.6989	19.593	0.6505	7.733	0.5997	8.334
0.7682	43.935	0.7486	20.410	0.7006	7.997	0.6498	8.603
0.8183	45.930	0.7993	21.312	0.7505	8.249	0.6997	8.891
0.8690	47.996	0.8520	22.182	0.8005	8.503	0.7497	9.177
0.9128	49.883	0.9010	23.130	0.8504	8.749	0.8000	9.463
0.9698	52.440	0.9423	23.913	0.9003	9.007	0.8499	9.694
1.0000	53.808	0.9751	24.566	0.9404	9.209	0.8917	9.935
		1.0000	25.078	0.9728	9.397	0.9213	10.105
				1.0000	9.586	0.9517	10.267
						1.0000	10.602

Table 4. Total Pressure P/kPa as a Function of Liquid-Phase Mole Fraction x_1 for Methyl Formate(1) + 2-Ethoxyethanol(2) at 308.15 K
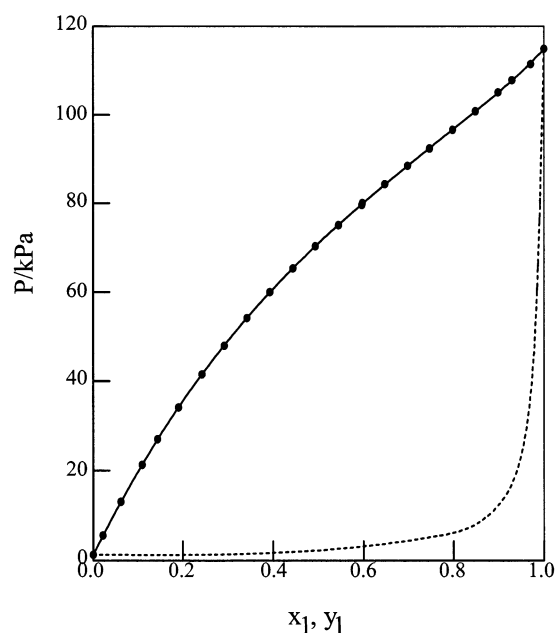
methyl formate(1) + 2-ethoxyethanol(2)					
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	1.303	0.3425	54.157	0.6977	88.471
0.0217	5.596	0.3933	59.954	0.7467	92.402
0.0616	13.030	0.4442	65.353	0.7978	96.572
0.1093	21.265	0.4944	70.358	0.8485	100.770
0.1440	26.967	0.5451	75.106	0.8985	105.057
0.1906	34.091	0.5961	79.641	0.9290	107.790
0.2430	41.513	0.5975	80.085	0.9706	111.442
0.2921	47.941	0.6475	84.336	1.0000	114.881

With the exception of 2-ethoxyethanol, the pure component vapor pressures reported here are within 0.5% of values smoothed from the literature data[9-11] as shown in Table 1. Vapor pressures of 2-ethoxyethanol at 308.15 and 313.15 K were 1.5% lower and 2.4% higher, respectively, than literature values. The vapor pressure of 2-ethoxyethanol, a component of every isotherm, was measured at 313.15 K on four separate occasions. The average value, along with the uncertainty (0.030 kPa), is given in Table 1. This value exceeds the measurement uncertainty of 0.006 kPa (based on uncertainties in the bath temperature, pressure reading, and zero of pressure gauge) and must therefore be assigned to uncertainty in completion of the degassing procedure.

The uncertainties in the vapor pressure of 2-ethoxyethanol at 313.15 K (1.6% for the present study and estimated by us as 0.7% for the work of Antosik et al.[10]) sum to 2.3%, which is comparable to the 2.4% difference between the values given in Table 1.

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

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

Figure 1. Pressure P versus liquid-phase mole fraction, x_1, and vapor phase mole fraction, y_1, for methyl formate(1) + 2-ethoxyethanol(2) at 308.15 K: (●) experimental P–x_1 result; solid line is fitted P–x_1 result; dashed line is predicted P–y_1 result.

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

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

where ϕ_i^{sat} is the fugacity coefficient of pure species i at its vapor pressure.

Liquid-phase activity coefficients were represented by the four-parameter modified Margules equation (or a
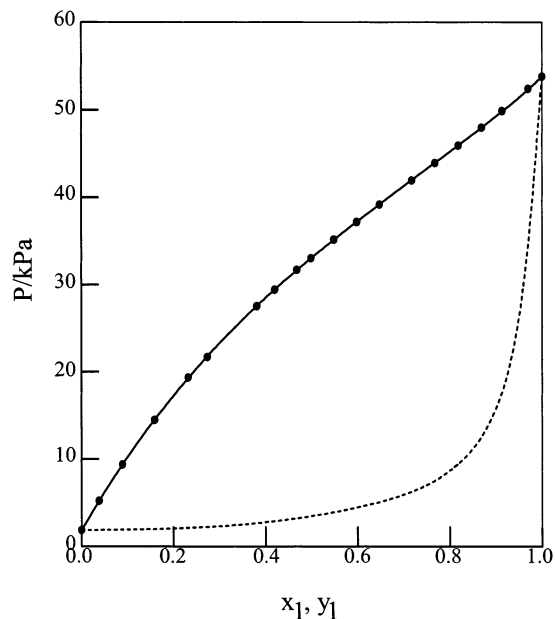
Figure 2. Pressure P versus liquid-phase mole fraction, x_1, and vapor phase mole fraction, y_1, for methyl acetate(1) + 2-ethoxyethanol(2) at 313.15 K: (●) experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.
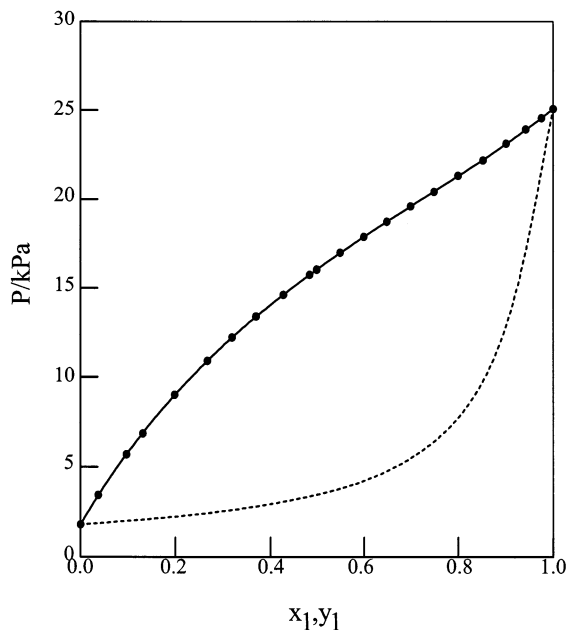

Figure 4. Pressure P versus liquid-phase mole fraction, x_1, and vapor phase mole fraction, y_1, for propyl acetate(1) + 2-ethoxyethanol(2) at 313.15 K: (●) experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

Figure 3. Pressure P versus liquid-phase mole fraction, x_1, and vapor phase mole fraction, y_1, for ethyl acetate(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 5. Pressure P versus liquid-phase mole fraction, x_1, and vapor phase mole fraction, y_1, for ethyl propionate(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.

simplification of it) proposed by Abbott and Van Ness:[13]

$$\frac{G^{E}}{RT} = x_1 x_2 \left[A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1 x_2}{\alpha_{12}x_1 + \alpha_{21}x_2} \right] \quad (3)$$

Vapor phase fugacity coefficients were calculated using the two-term virial equation (explicit in pressure). 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.[14] Required constants for methyl formate and
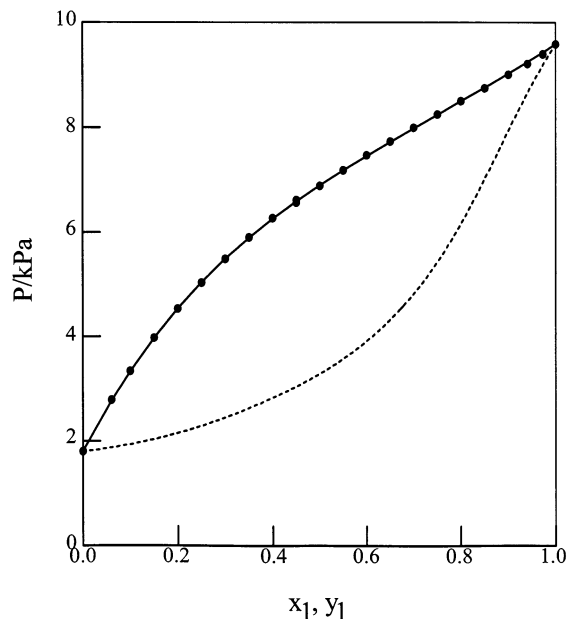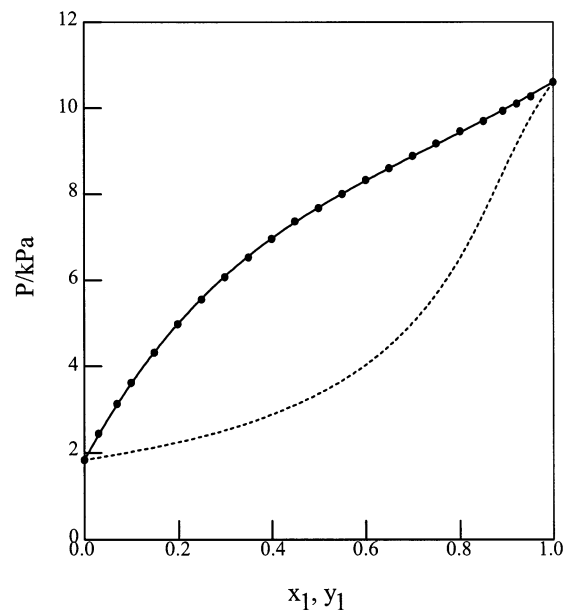
ethyl acetate were obtained from Fredenslund et al.,[15] and those for 2-ethoxyethanol were obtained as described by Carmona et al.[1] Critical constants, radii of gyration, and dipole moments for propyl acetate and ethyl propionate were taken from Reid et al.[16] The association parameters for ethyl propionate and propyl acetate were assumed to be the same as for methyl propionate[15] and ethyl acetate,[15] respectively. In the calculation of all second virial cross coefficients, the solvation parameters were taken to be 1.3 as recommended[17] for 2-ethoxyethanol with both methyl acetate and ethyl acetate.

Saturated liquid volumes for 2-ethoxyethanol were obtained from smoothing values from Riddick et al.[9] and

Table 5. Values of Parameters Appearing in Equation 3 and Resulting Average Deviations ΔP_{avg} and Maximum Deviations ΔP_{max} for Ester(1) + 2-Ethoxyethanol(2) Systems

ester(1)	T/K	A_{12}	A_{21}	α_{12}	α_{21}	ΔP_{avg}/kPa	ΔP_{max}/kPa
methyl formate	308.15	0.5958	1.0268	0.2622	1.0406	0.059	0.257
methyl acetate	313.15	0.5684	0.8370	0.1429	0.7041	0.032	0.100
ethyl acetate	313.15	0.6317	0.7678	0.1112	0.1112	0.011	0.030
propyl acetate	313.15	0.7065	0.7787	0	0	0.013	0.044
ethyl propionate	313.15	0.7253	0.8826	0	0	0.017	0.040
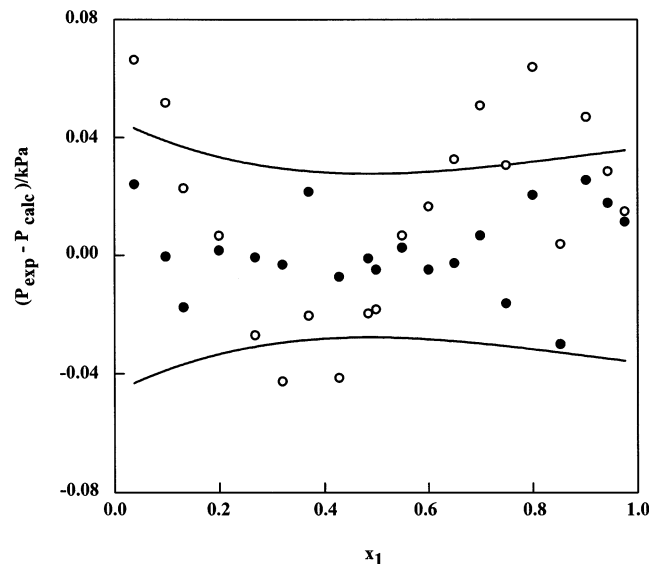
Figure 6. Pressure residual, $P_{exp} - P_{calc}$, versus liquid-phase mole fraction, x_1, for ethyl acetate(1) + 2-ethoxyethanol(2) at 313.15 K: (○) 3-suffix Margules model; (●) 4-suffix Margules model; solid curves indicate measurement uncertainty.

Venkatesulu et al.,[18] whereas those for methyl acetate, ethyl acetate, propyl acetate, and ethyl propionate were taken from Liu et al.[19] Values for methyl formate were taken from Riddick et al. and covered the range of temperature needed to convert volume pumped into mass. An extrapolation of these data was required for obtaining the value at 308.15 K, but this was needed only for the Poynting correction.

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 Tables 3 and 4 and are plotted in Figures 1–5. Parameter values and resulting average and maximum deviations between calculated and experimental pressures are given in Table 5. The data are represented by the G^E model to within an average of 0.06 kPa. Figures 1–5 indicate that all of the binary systems of 2-ethoxyethanol with an ester exhibit positive deviations from ideality.

In the data reduction procedure, the full form of eq 3 was required only for 2-ethoxyethanol with methyl acetate and with methyl formate. For 2-ethoxyethanol + ethyl acetate, it was found that the 4-suffix Margules equation, obtained by setting α_{12} equal to α_{21}, was sufficient to fit the data to within experimental uncertainty. For systems of 2-ethoxyethanol with propyl acetate and with ethyl propionate, the 3-suffix Margules equation, for which $\alpha_{12} = \alpha_{21} = 0$, was adequate.

The proper model for each system was selected using the procedure outlined by Campbell and Bhethanabotla.[20] Briefly, all three models (3-suffix, 4-suffix, and modified Margules equations) were applied to each data set. The pressure residuals ($P_{exp} - P_{calc}$) for each model and the combined measurement uncertainty (reflecting uncertainties in the composition, pressure reading and bath temperature) were then plotted as a function of composition. The simplest model for which the pressure residuals showed more or less random scatter within the uncertainty bounds was then considered appropriate for the system under consideration. The example shown in Figure 6 for ethyl acetate (1) + 2-ethoxyethanol(2) demonstrates that, for this system, the 4-suffix Margules equation is suitable.

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