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Total Vapor Pressure Measurements for 2-Ethoxyethanol with Carbon Tetrachloride, Chloroform, and Dichloromethane at 303.15 K

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Total pressure measurements are reported for the binary mixtures of 2-ethoxyethanol with carbon tetrachloride, chloroform, and dichloromethane at 303.15 K. The data were obtained using a Van Ness type apparatus and were fitted with a modified Margules equation using Barker's method. The total pressure data are represented by the model to within an average absolute deviation of approximately 0.06 kPa. Solutions of 2-ethoxyethanol with carbon tetrachloride show positive deviations from ideality, while those of 2-ethoxyethanol with chloroform and with dichloromethane show negative deviations at low chloroalkane mole fraction and positive deviations at high chloroalkane concentration.

Introduction

As part of a continuing study in this laboratory of vapor−liquid equilibrium for binary mixtures containing 2-ethoxyethanol, total pressure data are reported for systems of 2-ethoxyethanol with carbon tetrachloride, chloroform, and dichloromethane. Previously, Carmona et al.,[1] DeBord et al.,[2] and Alderson et al.[3] reported total pressure data for binary mixtures of 2-ethoxyethanol with paraffins, alcohols, and esters, respectively. We have not located any vapor−liquid equilibrium data in the literature for mixtures of 2-ethoxyethanol with the chloroalkanes considered here.

Experimental Section

Apparatus and Procedure. The apparatus is essentially the same as described in detail by Bhethanabotla and Campbell.[4] It is of the Van Ness type,[5] 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.,[6] 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 298−328 K and 0−133 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 measured after equilibration. A 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.[4]

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 applied at the extremes in composition.

Materials. All chemicals were obtained from Aldrich Chemical and had purities (by chromatographic analysis, as given by the manufacturer in area percent) of 99.97%, 99.98%, 99.96%, and 99.98% for carbon tetrachloride, chloroform, dichloromethane, and 2-ethoxyethanol, respectively. All chemicals were degassed by vacuum distillation and were used without any additional purification.

Table 1. Comparison of Pure-Component Vapor Pressures $P_i^{\rm sat}$/kPa to Values Obtained from the Literature at 303.15 K

substance	$P_i^{\rm sat}$/kPa, this study	$P_i^{\rm sat}$/kPa, literature
carbon tetrachloride	18.826	18.90[7]
chloroform	32.408	32.31[7]
dichloromethane	70.486	70.91[7]
2-ethoxyethanol	0.978 ± 0.009[a]	0.971[7,8]

[a] Average of three measurements.

The pure-component vapor pressures reported here are within 0.7% (and scatter both high and low) of values smoothed from the literature data[7,8] as shown in Table 1. The vapor pressure of 2-ethoxyethanol, a component of every isotherm, was measured at 303.15 K on three separate occasions. The fact that the uncertainty (0.009 kPa) is slightly outside the measurement uncertainty of the apparatus (0.006 kPa, based on uncertainties in the bath temperature, pressure reading, and zero of pressure gauge) is probably due incomplete degassing.

Data Reduction. Data were reduced using Barker's method,[9] 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

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

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

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

where $\phi_i^{\rm sat}$ is the fugacity coefficient of pure species i at its vapor pressure.

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Table 2. Saturated Liquid Volumes V_i^L and Second Virial Coefficients (in cm^3·mol^{-1}) for Single Components B_{ii} and Mixtures B_{ij} Used for Chloroalkane (1) + 2-Ethoxyethanol (2) Systems[a]

chloroalkane (1)	B_{11}	B_{12}	V_1^L
carbon tetrachloride	−1622	−1442	97.7
chloroform	−1143	−1342	81.0
dichloromethane	−824	−1146	64.9

[a] For 2-ethoxyethanol, $B_{22} = -3584$ cm^3·mol^{-1} and $V_2^L = 97.8$ cm^3·mol^{-1} at 303.15 K.

Liquid-phase activity coefficients were represented by the modified Margules equation proposed by Abbott and Van Ness[10]

$$\frac{G^E}{RT} = x_1x_2\left[A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2}\right] \qquad (3)$$

Corresponding expressions for the activity coefficients[10] are

$$\ln \gamma_1 = {x_2}^2\left[A_{12} + 2(A_{21} - A_{12})x_1 - \frac{2\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2} + \frac{{\alpha_{12}}^2\alpha_{21}{x_1}^2}{(\alpha_{12}x_1 + \alpha_{21}x_2)^2}\right] \qquad (4)$$

and

$$\ln \gamma_2 = {x_1}^2\left[A_{21} + 2(A_{12} - A_{21})x_2 - \frac{2\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2} + \frac{{\alpha_{21}}^2\alpha_{12}{x_2}^2}{(\alpha_{12}x_1 + \alpha_{21}x_2)^2}\right] \qquad (5)$$

Vapor-phase nonidealities were accounted for by using the two-term virial equation

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \qquad (6)$$

which yields the following expressions for the fugacity coefficients

$$\ln \phi_1 = \frac{P}{RT}\,[B_{11} + {y_2}^2\delta_{12}] \qquad (7)$$

$$\ln \phi_2 = \frac{P}{RT}\,[B_{22} + {y_1}^2\delta_{12}] \qquad (8)$$

where $\delta_{12} = 2B_{12} - B_{11} - B_{22}$. Expressions for ϕ_1^{sat} and ϕ_2^{sat} are obtained from eqs 7 and 8 by applying them at their pure-component states.

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 method,[11] which explicitly accounts for effects due to polarity, solvation, and association. Required constants for the chloroalkanes were obtained from Fredenslund et al.,[12] and those for 2-ethoxyethanol were obtained as described by Carmona et al.[1] Solvation parameters for interactions between 2-ethoxyethanol and the chloroalkanes were obtained from Prausnitz et al.;[13] they are 0, 0.1, and 0 for carbon tetrachloride, chloroform, and dichloromethane, respectively.

Saturated liquid volumes for 2-ethoxyethanol were obtained from smoothing values from Riddick et al.[7] and Venkatesulu et al.,[14] while those for carbon tetrachloride and chloroform were taken from the DIPPR database.[15] Saturated liquid volumes for dichloromethane were taken from Riddick et al.[7]

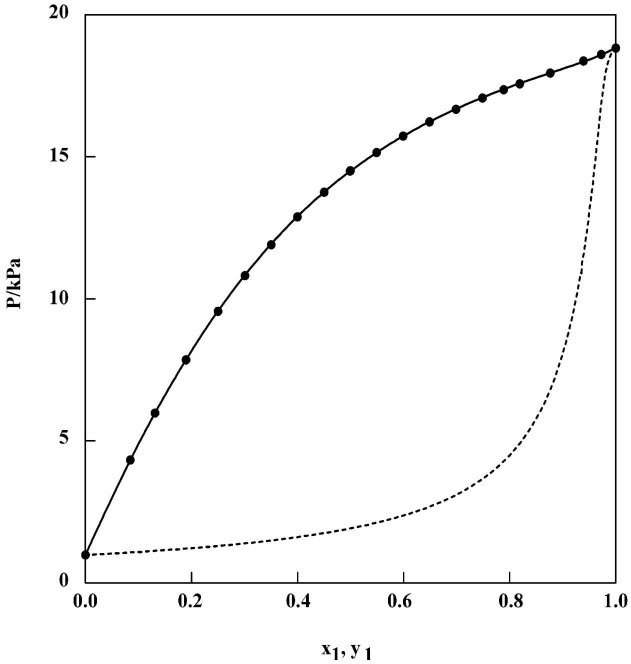

Figure 1. Pressure P vs liquid-phase mole fraction, x_1, and vapor-phase mole fraction, y_1, for carbon tetrachloride (1) + 2-ethoxyethanol (2) at 303.15 K: ●, experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

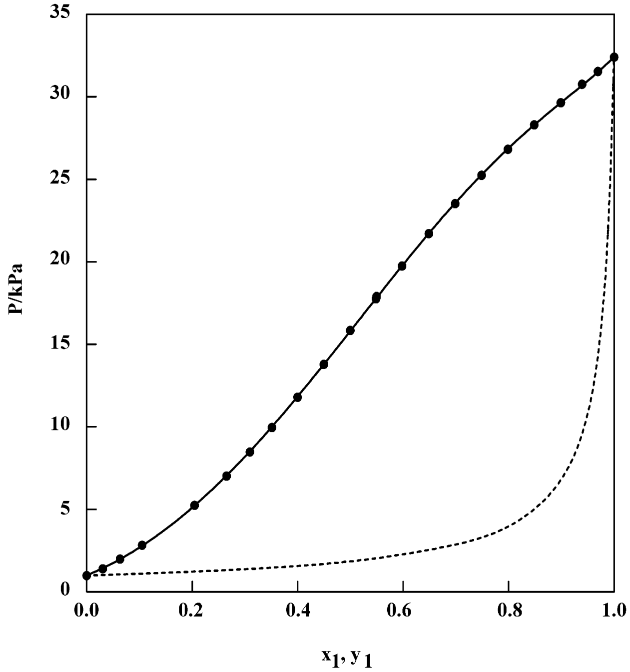

Figure 2. Pressure P vs liquid-phase mole fraction, x_1, and vapor-phase mole fraction, y_1, for chloroform (1) + 2-ethoxyethanol (2) at 303.15 K: ●, experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

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 1−3. Parameter values and resulting average

Table 3. Total Pressure P/kPa as a Function of Liquid-Phase Mole Fraction x_1 for Chloroalkane (1) + 2-Ethoxyethanol (2) at 303.15 K

carbon tetrachloride (1) + 2-ethoxyethanol (2)		chloroform (1) + 2-ethoxyethanol (2)		dichloromethane (1)+ 2-ethoxyethanol (2)	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	0.981	0.0000	0.984	0.0000	0.968
0.0846	4.322	0.0302	1.396	0.0355	2.403
0.1313	5.979	0.0630	1.988	0.0651	4.110
0.1896	7.848	0.1050	2.834	0.1068	6.696
0.2499	9.552	0.2042	5.235	0.1555	9.939
0.3007	10.809	0.2651	7.021	0.1953	12.819
0.3501	11.897	0.3094	8.474	0.2727	18.863
0.3998	12.875	0.3511	9.954	0.3182	22.676
0.4501	13.742	0.3995	11.792	0.3502	25.388
0.4996	14.494	0.4497	13.787	0.4033	29.987
0.4989	14.488	0.4997	15.833	0.4498	34.034
0.5488	15.144	0.5496	17.892	0.4981	38.165
0.5987	15.719	0.5487	17.761	0.5486	42.332
0.6487	16.218	0.5980	19.740	0.5995	46.346
0.6986	16.663	0.6486	21.708	0.5976	46.230
0.7487	17.059	0.6985	23.530	0.6474	49.894
0.7886	17.351	0.7484	25.238	0.6975	53.364
0.8190	17.557	0.7985	26.809	0.7476	56.547
0.8762	17.934	0.8486	28.284	0.7976	59.450
0.9391	18.355	0.8987	29.645	0.8481	62.212
0.9724	18.583	0.9390	30.749	0.8985	64.876
1.0000	18.826	0.9691	31.520	0.9388	67.000
		1.0000	32.408	0.9695	68.720
				1.0000	70.486

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

chloroalkane (1)	A_{12}	A_{21}	α_{12}	α_{21}	ΔP_{avg}/kPa	ΔP_{max}/kPa
carbon tetrachloride	0.8344	2.2979	0.9606	6.3147	0.009	0.028
chloroform	−0.7876	0.1354	0.5353	1.6334	0.028	0.079
dichloromethane	−0.4398	0.7033	0.5205	2.7365	0.055	0.223

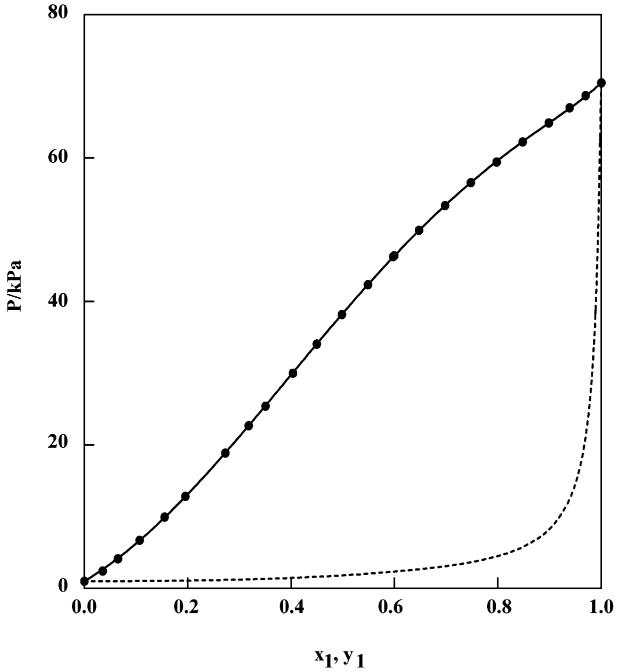

Figure 3. Pressure P vs liquid-phase mole fraction, x_1, and vapor-phase mole fraction, y_1, for dichloromethane (1) + 2-ethoxyethanol (2) at 303.15 K: ●, experimental $P-x_1$ result; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

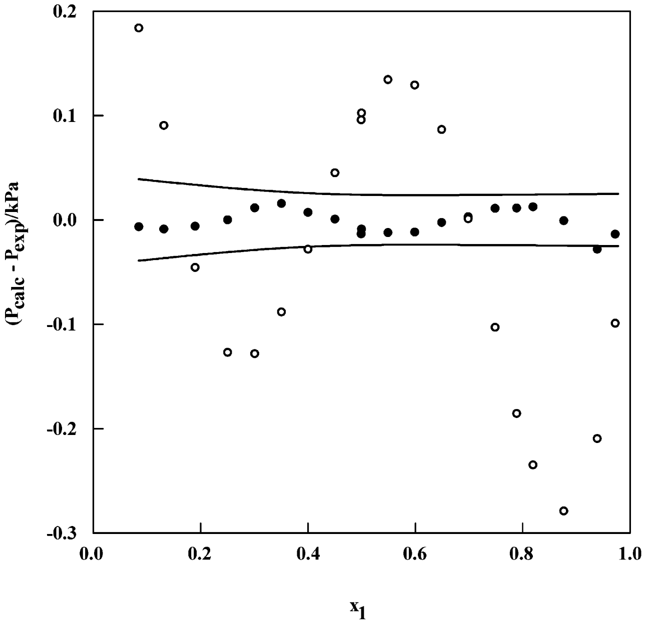

Figure 4. Pressure residual, $P_{calc} - P_{exp}$, vs liquid-phase mole fraction, x_1, for carbon tetrachloride (1) + 2-ethoxyethanol (2) at 303.15 K: ○, 4-suffix Margules model; ●, modified Margules model; solid curves indicate measurement uncertainty.

and maximum deviations between calculated and experimental pressures are given in Table 4. The data are represented by the G^E model to within an average of 0.06 kPa. Figure 1 indicates that the binary system of 2-ethoxyethanol with carbon tetrachloride exhibits positive deviations from ideality over the entire composition range, while Figures 2 and 3 show that the systems containing chloroform and dichloromethane exhibit negative deviations at low chloroalkane mole fractions and positive deviations at high chloroalkane mole fractions.

It was attempted to use models simpler than eq 3 to fit the data. In particular, the three-suffix Margules equation is a special case of eq 3 obtained by setting α_{12} and α_{21} equal to zero, and the four-suffix Margules model may be obtained by setting α_{12} equal to α_{21}. The proper model for each system was selected using the procedure outlined by Campbell and Bhethanabotla.[16] In this approach, all three models (3-suffix, 4-suffix, and modified Margules equations) were applied to each data set. The pressure residuals ($P_{\text{calc}} - P_{\text{exp}}$) for each model and the combined measurement uncertainty were then plotted as a function of composition. The combined measurement uncertainty ΔP reflects uncertainties in the composition, pressure reading, and bath and is given by

$$\Delta P = \left(\left(\frac{\partial P}{\partial T}\,\Delta T\right)^2 + \left(\frac{\partial P}{\partial x_1}\,\Delta x_1\right)^2 + \left(\frac{\partial P}{\partial P_{\text{read}}}\,\Delta P_{\text{read}}\right)^2\right)^{1/2} \tag{9}$$

where ΔT, Δx_1, and ΔP_{read} are the experimental uncertainties in temperature, mole fraction, and pressure, respectively.

The simplest model for which the pressure residuals fall within the uncertainty bounds was considered appropriate for the system under consideration. The plot in Figure 4 for carbon tetrachloride (1) + 2-ethoxyethanol (2) compares results for the four-suffix and modified Magules equations. The residuals for the three-suffix equation were larger than those of the four-suffix equation and are not shown. This example demonstrates that the modified Margules equation is suitable for this system. The same trend was observed for the systems containing chloroform and dichloromethane.

Conclusions

Negative deviations from ideal solution behavior often are associated with solvation effects, as in the classic case of acetone + chloroform. The negative deviations observed for chloroform and dichloromethane at low chloroalkane composition may be due to solvation driven by nonuniform charge distributions on the chloroalkane molecules. Such behavior is not exhibited by the system containing carbon tetrachoride, for which all four bonds are equivalent.

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