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Experimental Determination and Correlation of Phase Equilibria for the Ethane + 1-Propanol and Propane + 1-Propanol Systems

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In this work, isothermal vapor−liquid equilibrium (VLE) for the ethane + 1-propanol and propane + 1-propanol systems were measured in an apparatus based on the static-analytic method. VLE data and the critical point for the ethane + 1-propanol system were measured at (317.59, 324.51, and 348.68) K. Upper critical end point, lower critical end point, and liquid−liquid−vapor locus were also obtained. For the propane + 1-propanol system, equilibrium measurements were performed at (318.30, 324.31, and 348.93) K. Experimental VLE data were correlated with the Peng−Robinson equation of state using the classical and the Wong−Sandler mixing rules. A better representation of the phase behavior was obtained using the Wong−Sandler mixing rule.

Introduction

Phase equilibrium data provide thermodynamic knowledge about solvents and solutes in the process that help to design the best arrangement of equipment and vessels. Important information obtained from experimental data can be the solubility of a desired solute in a supercritical solvent, the selectivity of solvent, the dependence of solvent properties on conditions of state, and the enhancement factor due to addition of a cosolvent.[1]

As well as carbon dioxide, ethane and propane are also used as supercritical solvents. Their critical temperature and pressure are easy to reach; they are nontoxic, noncorrosive, and extremely stable. Ethane has been used in some polymerization processes: fractionation of polysiloxanes, polymer−organic solvent phase separation, and extracting natural products.[2,3] For the case of propane, it has been used for de-asphalting of lube oils and concentrating polyunsaturated triglycerides.[2,3] The addition of a cosolvent such as 1-propanol improves the solubility of a solid in the supercritical solvent.[4,5]

Brunner[6] measured the critical curve from the ethane to 1-propanol critical points. He also determined the upper critical end point (UCEP), lower critical end point (LCEP), and the liquid−liquid−vapor equilibrium (LLVE) line. Lam et al.[7] obtained the LLVE, UCEP, and LCEP from (313 to 315) K for the ethane + 1-propanol system. Suzuki et al.[8] reported the VLE at (313.4 and 333.4) K. The most recent work for this system was reported by Kodama et al.,[9] who reported phase equilibrium and saturation densities at 314.15 K. VLE data for the propane + 1-propanol system was reported by Mühlbauer and Raal[10] at (354.75, 378.37, and 393.25) K.

In this work, we report the VLE data and the critical points for the ethane + 1-propanol at (317, 324, and 348) K as well as the UCEP, LCEP, and LLVE line. This system exhibits type V phase behavior according to the classification of van Konynenburg and Scott.[11] These data were compared with the critical line reported by Brunner.[6] For the propane + 1-propanol system, the VLE data are reported at (318.30, 324.31, and 348.93) K. Both systems were correlated with the Peng−Robinson equation of state (PR EoS)[12] using the classical and the Wong−Sandler[13] mixing rules.

Experimental Section

Materials. 1-Propanol ($x = 0.997$) was supplied by Sigma-Aldrich, USA. Ethane ($x = 0.99999$), propane ($x = 0.9999$), and helium with a minimum purity of $x = 0.99998$ were obtained by Air Products-Infra, México. These compounds were used without any further purification. 1-Propanol was degassed and stirred under vacuum before the measurements.

Apparatus. The apparatus is based on the static-analytic method and consists of a stainless steel cell where the VLE conditions are achieved and of a gas chromatograph (GC) used for the phase compositions determination. The equilibrium cell is connected on-line to the GC (Hewlett-Packard, 6890) through a thermoregulated transfer circuit. This apparatus has been previously described by Galicia-Luna et al.[14] The cell has an internal volume of about 40 cm^3 and is equipped with two sapphire windows to observe the phase behavior. A magnetic rod located inside the cell is used to reduce the time needed to reach equilibrium. The cell is placed in an air bath in order to control the temperature. Pressure is achieved by using a syringe pump to feed the light component into the cell.

Temperature conditions were monitored using two platinum probes (Specitec, Pt100) positioned at the top and bottom of the cell; they were connected to a digital indicator (Automatic System Laboratories, F250). The platinum probes were calibrated with a 25-Ω reference probe (Rosemount, 162CE ± 0.005 K) connected to a calibration system (Automatic System Laboratories, F300S). The estimated uncertainty was found to be within ± 0.03 K. A thermoregulated pressure transducer (Druck, PDCR 910-1756) coupled to a pressure indicator (Druck, DPI 145) records the pressure conditions. The transducer was calibrated against a dead weight balance (Desgranges & Huot, 5304 Class S2, ± 0.005 %). The total uncertainty for pressure was estimated to be within ± 0.04 %.

A desired sample was withdrawn from the equilibrium cell with a ROLSI[15] sampler-injector and was injected on-line into

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Table 1. Experimental Vapor−Liquid Equilibria for the Ethane (1) + 1-Propanol (2) System

$T = 317.59$ K			$T = 324.51$ K			$T = 348.68$ K		
x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa
0.221	0.993	2.817	0.232	0.991	3.243	0.041	0.946	0.841
0.316	0.994	3.844	0.298	0.992	3.899	0.092	0.968	1.817
0.378	0.994	4.349	0.363	0.992	4.624	0.142	0.977	2.809
0.435	0.993	4.836	0.420	0.991	5.241	0.188	0.979	3.603
0.525	0.992	5.336	0.507	0.988	5.880	0.229	0.980	4.344
0.587	0.977	5.595	0.551	0.985	6.111	0.268	0.979	5.057
0.650	0.968	5.727	0.590	0.965	6.362	0.307	0.978	5.711
0.657	0.960	5.773	0.644	0.944	6.546	0.345	0.976	6.324
0.688	0.923	5.868	0.675	0.925	6.676	0.397	0.971	7.076
0.708	0.872	5.957	0.704	0.880	6.782	0.455	0.965	7.682
0.789	0.789	5.978[a]	0.734	0.845	6.824	0.548	0.948	8.529
			0.774	0.774	6.932[a]	0.600	0.919	8.929
						0.657	0.887	9.170
						0.706	0.866	9.396
						0.772	0.772	9.488[a]

[a] Critical point.

the GC equipped with a thermal conductivity detector TCD. The alkane and the 1-propanol were separated in a packed column (Alltech, 80/100 Porapak Q) that used helium as the carrier gas at a rate of 30 mL·min^{-1}. The oven temperature was set up at 463 K, and the detector temperature was at 473 K for the ethane + 1-propanol system. The temperature conditions for propane + 1-propanol were (443 and 503) K for the oven and the TCD detector, respectively. The TCD detector was previously calibrated by injecting pure compounds at the temperatures cited above using gastight syringes (Hamilton).

Experimental Procedure. Initially, the equilibrium cell was loaded with about 20 mL of 1-propanol and placed into the air bath to set the desired temperature. The entire system was degassed under vacuum and stirred by a magnetic rod for 20 min. Then, the alkane was carefully loaded into the cell from a supply tank using the syringe pump. When the equilibrium conditions were reached, the VLE measurements were carried out. The sampler-injector was positioned in the desired phase. A small sample of about 1 μL was sent to the GC. Then, the composition of each compound into the sample is determined in a GC workstation. To obtain a reliable average composition values, at least five successive samples were taken. Uncertainties for the liquid and vapor compositions were estimated to be about 1 % for both systems.

After the vapor and liquid compositions were determined at the desired pressure, ethane or propane was gradually added into the cell to achieve another pressure. The isothermal envelopes were measured by obtaining the equilibrium compositions up to near the critical pressure of the mixture.

Measurements for the LLV locus were performed by observation of the meniscus disappearance. It started from the UCEP by decreasing temperature in the VLL region until the second liquid disappeared and therefore the LCEP formation. Pressure and temperature was monitored along the measurements.

Results and Discussion

VLE data and the critical points for the binary mixture ethane + 1-propanol were measured at (317.59, 324.51, and 348.68) K. These data are presented in Table 1. The critical points of the mixture are in good agreement with those reported by Brunner[6] as shown Figure 1. Raw data for the LLV locus, the UCEP, and the LCEP of this system are reported in Table 2. Isothermal VLE data for the propane + 1-propanol system were obtained at (318.30, 324.31, and 348.93) K and are listed in Table 3.

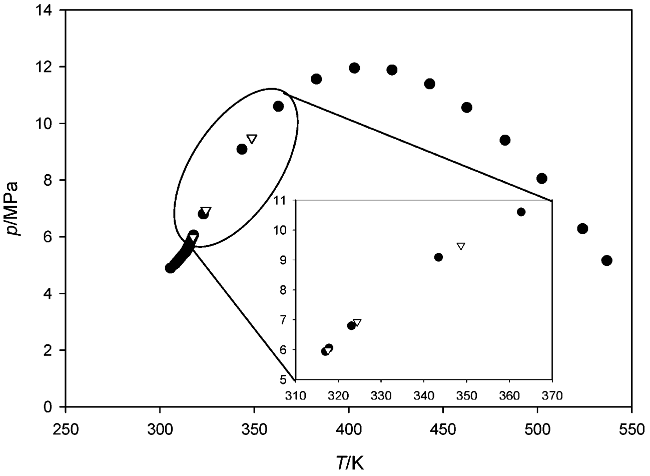

Figure 1. Critical points for the ethane (1) + 1-propanol (2) system: ●, ref 6; ▽, this work.

Table 2. UCEP, LCEP, and LLV Locus for the Ethane (1) + 1-Propanol (2) System

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
315.261	5.597[a]	314.386	5.496	313.992	5.450	313.661	5.415
314.888	5.556	314.300	5.486	313.928	5.445	313.604	5.408
314.658	5.527	314.225	5.478	313.883	5.441	313.523	5.399
314.512	5.510	314.149	5.469	313.836	5.434	313.432	5.391
314.487	5.508	314.101	5.464	313.774	5.427	313.324	5.379
314.458	5.504	314.062	5.459	313.711	5.421	313.033	5.348[b]

[a] UCEP. [b] LCEP.

Table 3. Experimental Vapor−Liquid Equilibrium for the Propane (1) + 1-Propanol (2) System

$T = 318.30$ K			$T = 324.31$ K			$T = 348.93$ K		
x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa
0.139	0.988	0.575	0.111	0.983	0.528	0.097	0.948	0.540
0.176	0.990	0.671	0.167	0.988	0.765	0.213	0.972	1.166
0.203	0.991	0.782	0.247	0.990	0.980	0.284	0.977	1.521
0.255	0.992	0.883	0.332	0.992	1.175	0.412	0.982	2.030
0.296	0.992	0.977	0.461	0.993	1.391	0.527	0.984	2.255
0.367	0.994	1.097	0.549	0.993	1.448	0.664	0.986	2.435
0.443	0.994	1.184	0.732	0.994	1.520	0.864	0.987	2.549
0.596	0.995	1.287	0.871	0.994	1.571	0.940	0.989	2.641
0.665	0.995	1.314						

The experimental data were correlated with the PR EoS:[12]

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{1}$$

where p, T, and R are pressure, temperature, and gas constant, respectively; v is the molar volume; a and b, parameters for mixtures, were calculated by using the classical and the Wong−Sandler[13] mixing rules.

The classical mixing rule can be expressed as follows:

$$a_{\mathrm{m}} = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \tag{2}$$

$$b_{\mathrm{m}} = \sum_i x_i b_i \tag{3}$$

where k_{ij} is the binary interaction parameter.

The Wong−Sandler mixing rule[13] is defined as:

$$b_{\mathrm{m}} = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A^{\mathrm{E}}_{\infty}}{CRT}} \tag{4}$$

with

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{5}$$

$$a_{\mathrm{m}} = b_{\mathrm{m}}\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A^{\mathrm{E}}_{\infty}}{C}\right) \tag{6}$$

for the PR EoS:

$$C = \frac{\ln(\sqrt{2} - 1)}{\sqrt{2}} \tag{7}$$

In this work, the NRTL model[16] was only used to obtain the Helmholtz free energy that is needed in eq 4 and eq 6. The excess Helmholtz free energy (A^{E}_{∞}) at infinite pressure can be expressed with the excess Gibbs free energy G^{E} at low pressure as deduced by Wong and Sandler:[13]

$$\frac{A^{\mathrm{E}}_{\infty}}{RT} = \sum_i x_i \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \tag{8}$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{9}$$

$$\tau_{ij} = \frac{A_{ij}}{RT} \tag{10}$$

G_{ij} is the local composition factor, τ_{ij} is the binary interaction parameters, and A_{ij} is the interaction energy between the components i and j. For the NRTL model, the nonrandomness parameter (α_{ij}) was fixed at 0.3 in both binary systems.

The binary parameters for each system were determined using the Marquardt−Levenberg method[17] based on the following objective function:

$$F = \sum_{j=1}^{N_{\mathrm{d}}} \left[\sum_{i=1}^{N_{\mathrm{c}}} \left(\frac{y_{ij}^{\mathrm{calcd}} - y_{ij}^{\mathrm{exptl}}}{y_{ij}^{\mathrm{exptl}}}\right)^2 + \left(\frac{P_j^{\mathrm{calcd}} - P_j^{\mathrm{exptl}}}{P_j^{\mathrm{exptl}}}\right)^2\right] \tag{11}$$

where N_{d} is the number of data points; N_{c} is the number of components; y is the vapor mole fraction; and the superscripts calcd and exptl denote the calculated and experimental data, respectively.

The measured VLE results were compared with those calculated from the PR EoS using the classical and the Wong−Sandler mixing rules. Better results were found in the representation of the phase behavior for the studied systems using the Wong−Sandler mixing rule as shown in Figure 2 for the ethane + 1-propanol system and in Figure 3 for the propane + 1-propanol system than using the classical mixing rule.

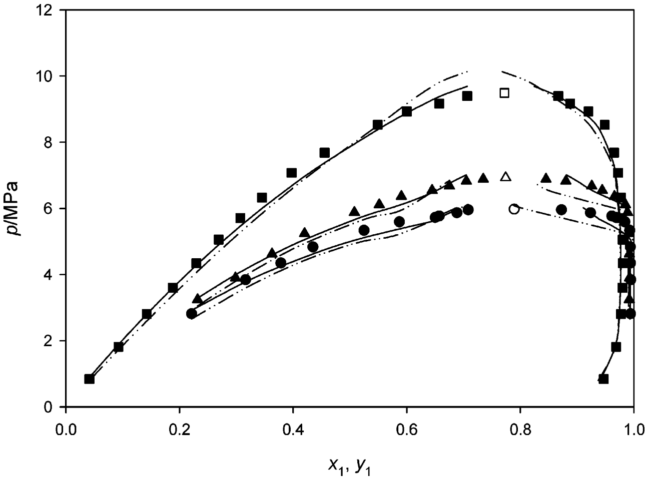

Figure 2. Experimental VLE data for the ethane + 1-propanol system at ●, 317.59 K; ▲, 324.51 K; ■, 348.68 K; - - -, correlated results using the PR EoS and classical mixing rule; —, correlated results using the PR EoS and Wong−Sandler mixing rule; open symbols denote critical point.

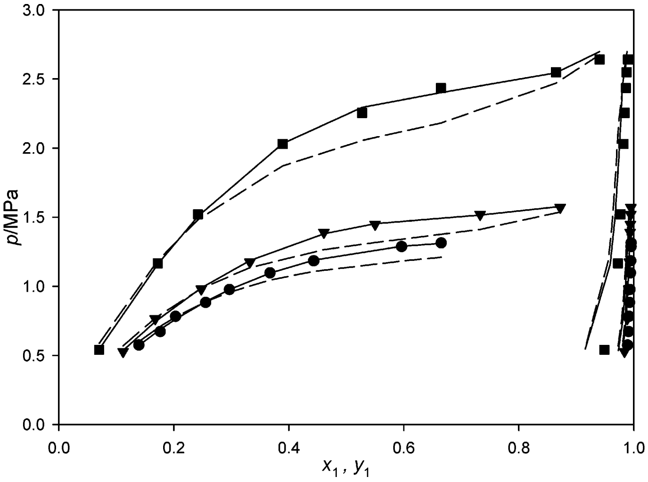

Figure 3. Experimental VLE data for the propane + 1-propanol system at ●, 318.30 K; ▼, 324.31 K; ■, 348.93 K; - - -, correlated results using the PR EoS and classical mixing rule; —, correlated results using the PR EoS and Wong−Sandler mixing rule.

The deviations between experimental and calculated data sets for p and y of each system are presented in Figures 4, 5, 6, and 7. As shown in these figures, the PR EoS using the Wong−Sandler mixing rule provides lower deviations than those obtained with PR EoS using the classical mixing rule. For the VLE correlation, the absolute average deviation (AAD) using the PR EoS and the Wong−Sandler mixing rule for the ethane (1) + 1-propanol (2) system was less than 2.9 % and 0.0082 mole fraction for p and y_1, respectively. Meanwhile using the same model, the AAD for the propane (1) + 1-propanol (2) system was estimated to be less than 1.70 % and 0.0071 for p and y_1, respectively. The AAD was calculated as follows:

$$\%\ \mathrm{AAD}(p) = \left(\frac{1}{N_{\mathrm{d}}}\right) \sum_{i=1}^{N_{\mathrm{d}}} \frac{|p^{\mathrm{exptl}} - p^{\mathrm{calcd}}|}{p^{\mathrm{exptl}}} \times 100 \tag{12}$$

and

$$\mathrm{AAD}(y_i) = \left(\frac{1}{N_{\mathrm{d}}}\right) \sum_{i=1}^{N_{\mathrm{d}}} |y_i^{\mathrm{exptl}} - y_i^{\mathrm{calcd}}| \tag{13}$$

Table 4. Binary Interaction Parameters and Deviations for the PR EoS Using Different Mixing Rules

	classical mixing rule			Wong−Sandler mixing rule				
T/K	k_{12}	% AAD(p)	AAD(y_1)	k_{12}	A_{12}/kJ·mol^{-1}	A_{21}/kJ·mol^{-1}	% AAD(p)	AAD(y_1)
				Ethane (1) + 1-Propanol (2)				
317.59	0.0476	5.113	0.026	0.3861	0.7100	2.1231	2.698	0.008
324.51	0.0518	4.296	0.024	0.3750	1.3898	1.4983	2.392	0.005
348.68	0.0673	5.839	0.011	0.3586	2.6449	0.7826	2.916	0.007
				Propane (1) + 1-Propanol (2)				
318.30	0.0548	4.526	0.005	0.3811	0.2808	1.8495	0.791	0.004
324.31	0.0584	4.943	0.006	0.3855	0.5475	1.5712	0.972	0.005
348.93	0.0472	5.984	0.011	0.4028	4.0154	−2.0557	1.704	0.007

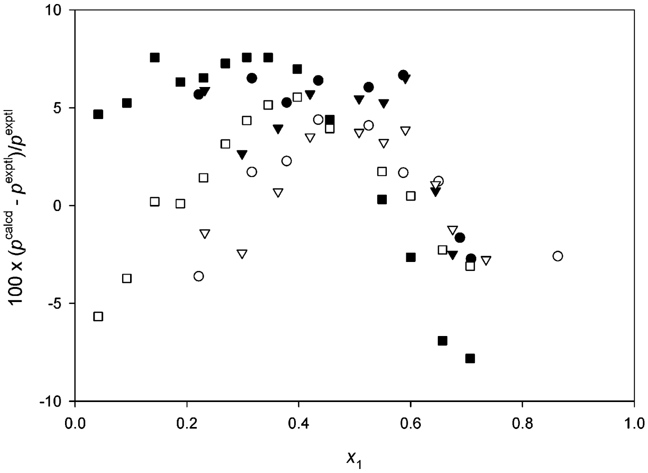

Figure 4. Pressure deviations for the ethane (1) + 1-propanol (2) system using the classical (closed symbols) and the Wong−Sandler (open symbols) mixing rules at ●, 317.59 K; ▼, 324.51 K; ■, 348.68 K.

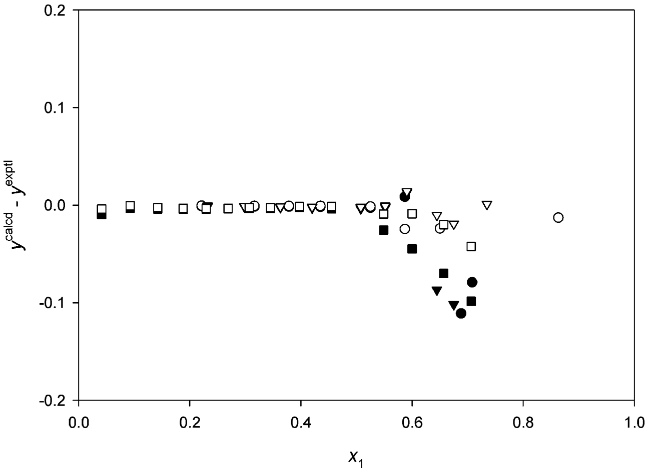

Figure 5. Composition deviations for the ethane (1) + 1-propanol (2) system using the classical (closed symbols) and the Wong−Sandler (open symbols) mixing rules at ●, 317.59 K; ▼, 324.51 K; ■, 348.68 K.

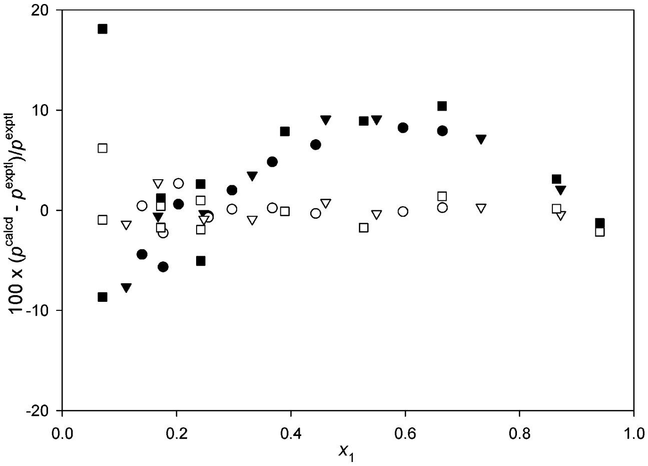

Figure 6. Pressure deviations of the experimental VLE data for the propane (1) + 1-propanol (2) system using the classical (closed symbols) and the Wong−Sandler (open symbols) mixing rules at ●, 318.30 K; ▼, 324.31 K; ■, 348.93 K.

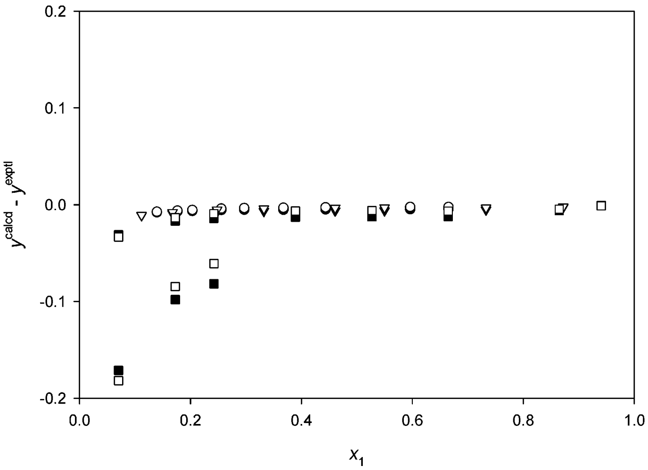

Figure 7. Composition deviations for the propane (1) + 1-propanol (2) system using the classical (closed symbols) and the Wong−Sandler (open symbols) mixing rules at ●, 318.15 K; ▼, 324.31 K; ■, 348.93 K.

where N_d is the number of data points, and the superscripts calcd and exptl denote the calculated and experimental data, respectively. These values are given in Table 4 for each temperature. The optimized binary interaction parameters for the PR EoS using the classical and Wong−Sandler mixing rules are also reported.

VLE for the ethane (1) + 1-propanol (2) system reported by Suzuki et al.[8] and Kodama et al.[9] were predicted with the PR EoS using the Wong−Sandler mixing rule. The used parameters were taken from Table 4 at 317.59 K. Absolute average deviations for this system were estimated to be 3.4 % and 0.0033 for p and y_1, respectively. The VLE for the propane (1) + 1-propanol (2) system reported by Mühlbauer and Raal[10] at ∼354 K was also predicted. The calculated AAD were 5.25 % and 0.015 for p and y_1, respectively. Higher deviations were found for the other temperatures reported by the same authors. It was expected because of the used parameters have been assumed to have a temperature dependency as shown in Table 4.

Conclusions

VLE measurements for the binary mixtures ethane + 1-propanol and propane + 1-propanol were carried out using an apparatus based on the static-analytic method. Equilibrium data obtained in this work were correlated with the PR EoS. VLE representation using the Wong−Sandler mixing was better than the classical mixing rule. However, in the calculated isotherms, some deviations can be observed in the vapor phase composition. For the ethane + 1-propanol system, a good agreement was observed when the critical points and the LLV locus obtained here were compared with those reported by Brunner[6] and Lam et al.,[7] respectively.

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