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Isothermal Vapor−Liquid Equilibria for the 2-Propanol + *n*-Heptane System near the Critical Region

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$P-T-x-y$ data for the binary system *n*-heptane + 2-propanol were measured near the critical temperatures (483.15, 498.15, 508.15, and 523.15) K using a two-phase recirculating apparutus. We observed critical points at 508.15 and 523.15 K. The experimental data were correlated by the Peng−Robinson−Stryjek−Vera (PRSV) equation of state combined with the NRTL model and the Wong−Sandler mixing rules. We also calculated the critical points and presented the critical locus.

Introduction

Vapor−liquid equilibria have been intensely studied for years. Alkane + alkanol phase equilibrium data have been extensively investigated at low pressures, but only a few data are available for elevated temperature and pressure. Furthermore, near the critical region, VLE measurements for polar and nonpolar mixtures are especially important because the properties of such mixtures cannot be predicted from the pure component values.

Seo et al.[1] measured the VLE data for the systems 2-propanol + *n*-hexane and ethanol + *n*-heptane by a circulating method, and De Loos et al.[2] measured the VLE data for the system methanol + *n*-heptane by the static nonanalytic method. In this work, we have measured the vapor−liquid equilibrium data for the 2-propanol + *n*-heptane system and compared the critical locus with related experimental data.

Experimental Section

Materials. 2-Propanol was supplied by Aldrich with a minimum purity of 99.5% (GC grade). *n*-Heptane was supplied by Fisher Scientific with a 99.6% purity (GC grade). Before use, we kept the chemicals at a slightly higher temperature than the boiling temperature of each chemical for degassing.

Apparatus and Procedure. We have carried out the experiments using the apparatus shown in a previous work.[3] The essential features of this apparatus are the two-phase recirculation method,[4] the online sampling method, and the view cell. Equilibrium between the vapor and liquid phases could be achieved rapidly by recirculating the two phases countercurrently using magnetic pumps. We could minimize composition gradients by diverting temporarily the circulating lines into the sampling lines. Additionally, we observed critical points through the view cell.

The accuracy of the temperature measuring system is ±0.03 K in the range (373 to 673) K, as specified by the manufacturer, and the accuracy of the pressure transducer was ±0.1% according to the specifications and was ±0.05% after the calibration of Korea Testing Laboratory.

The liquid and vapor samples were simultaneously analyzed by online gas chromatography (GC). In GC, two sets of TCD and Porapak Q packing columns were used. The manifold valves with two needle type stems were used as sampling valves. The sampling volume of each valve was large, about 0.05 mL. The GC columns were specially manufactured from 316 stainless steel tubing of 0.95 cm o.d. and 85 cm long. A total of 13.5 g of packing material was used for each column.

Results and Discussion

Thermodynamic Model. For the correlation of the experimental data, a modified Peng−Robinson equation of state was used, as suggested by Stryjek and Vera[5,6]

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2} \qquad (1)$$

where

$$a(T) = \frac{0.457235\alpha(T)R^2{T_c}^2}{p_c}; \quad b = \frac{0.077796RT_c}{p_c} \qquad (2)$$

$$\alpha = [1 + \kappa(1 - {T_R}^{0.5})]^2 \qquad (3)$$

$$\kappa = \kappa_0 + \kappa_1(1 + {T_R}^{0.5})(0.7 - T_R) \qquad (4)$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196544\omega^3 \qquad (5)$$

The parameter κ_1 is an adjustable parameter characteristic of each pure compound. The correlation values, κ_1, by Stryjek and Vera were used for *n*-heptane and 2-propanol.

The Wong−Sandler mixing rule[7] for the evaluation of the parameters *a* and *b* was used. In the case of the PRSV equation of state:

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$$b_{\mathrm{m}} = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - \sum_i x_i (a_i/b_i RT) - (A^{\mathrm{E}}_{\infty}/CRT)} \qquad (6)$$

$$a_{\mathrm{m}} = b_{\mathrm{m}}\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A^{\mathrm{E}}_{\infty}}{C}\right) \quad \text{with} \quad C = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1)$$

We chose the reformulated[8] Wong–Sandler mixing rules for evaluating the parameters a and b, where the combining rule is given by

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \qquad (7)$$

The expression for A^{E}_{∞} is the molar excess Helmholtz energy at the high density for the NRTL model:[9]

$$\frac{A^{\mathrm{E}}_{\infty}}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} x_j G_{ji} \tau_{ji}}{\sum_{k=1}^{n} x_k G_{kj}} \quad \text{with} \quad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (8)$$

where

$$\tau_{ji} = \frac{g_{ji}}{RT} \qquad (9)$$

Vapor–Liquid Equilibrium Measurement. The isothermal vapor–liquid equilibrium data for n-heptane + 2-propanol were measured at (483.15, 498.15, 508.15, and 523.15) K. These data are listed in Table 1. The binary interaction parameters, k_{12} in the Wong–Sandler mixing rule and τ_{12} and τ_{21} in the NRTL model, were obtained by fitting, and α was fixed as 0.1. The object function to fit these parameters is given by

$$\mathrm{SQ} = \mathrm{SQP} + \mathrm{SQY} = \sum_{N=1}^{N_{\mathrm{T}}} \left(\frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}}\right)^2 + \sum_{N=1}^{N_{\mathrm{T}}} (y_{\mathrm{cal}} - y_{\mathrm{exp}})^2 \qquad (10)$$

where SQP is the mean squared relative deviation of pressure and SQY is the mean squared relative deviation of vapor composition.

Especially, we have chosen values of τ_{12} and τ_{21} that showed minimum deviation when we fitted them independently on temperature. The percentage of the root-mean-squared relative deviations between the measured and calculated pressure, $100(\mathrm{SQP}/N_{\mathrm{T}})^{1/2}$, the root-mean-squared relative deviations of vapor composition of n-heptane, $(\mathrm{SQY}/N_{\mathrm{T}})^{1/2}$, and the values of the fitted parameters are listed in Table 2. The comparison of the phase diagram between the experimental data and the calculated values is shown in Figure 1. In the case of the temperature 483.15 K, we found that the data correlation could not predict the vapor composition properly.

We could also find the critical points for this system at (508.15 and 523.15) K. The critical mole fractions of n-heptane were 0.410 at 508.15 K and 0.725 at 523.15 K.

To predict the critical points, we applied the method reported by Castier and Sandler.[10,11] The adjustable parameters in the thermodynamic models used in this work are the binary parameter k_{12} in eq 6 and the parameters in the NRTL model, τ_{12}, τ_{21}, and α in eqs 8 and 9. Table 3 presents the parameters used for critical point calculations. The P–T projection for the system n-heptane + 2-propanol is presented in Figure 2, where the critical locus is calculated using parameters fitted from isothermal VLE data at 483.15 K (fixed $\alpha = 0.1$). The predictions using the fitted parameter from VLE data at 483.15 K have shown a little better agreement with experimental data than those at other temperatures. We also presented and compared the critical loci for the systems n-heptane + methanol,[2] n-heptane + ethanol,[12] and n-heptane + 2-propanol in Figure 3.

Table 1. Experimental and Calculated VLE Data for the *n*-Heptane (1) + 2-Propanol (2) System

T/K	P_{exp}/bar	P_{cal}/bar	$x_{1,\mathrm{exp}}$	$y_{1,\mathrm{exp}}$	$y_{1,\mathrm{cal}}$
483.15	31.01	30.90	0.000	0.000	0.000
	31.21	30.93	0.039	0.039	0.039
	31.16	30.90	0.059	0.054	0.057
	30.89	30.68	0.114	0.109	0.104
	30.41	30.35	0.162	0.151	0.141
	29.79	29.71	0.229	0.208	0.189
	28.89	28.69	0.310	0.266	0.244
	27.26	26.84	0.427	0.350	0.321
	24.59	24.05	0.570	0.487	0.420
	21.68	21.24	0.692	0.588	0.517
	17.90	17.68	0.824	0.730	0.655
	15.14	15.05	0.908	0.853	0.782
	11.60	11.76	1.000	1.000	1.000
498.15	40.09	40.20	0.000	0.000	0.000
	40.21	40.20	0.039	0.039	0.038
	40.18	40.17	0.051	0.046	0.050
	39.80	39.89	0.101	0.094	0.096
	39.41	39.32	0.158	0.148	0.145
	38.11	38.13	0.237	0.219	0.212
	36.61	36.34	0.327	0.295	0.283
	34.37	34.12	0.421	0.365	0.354
	31.92	31.61	0.517	0.433	0.423
	28.44	28.20	0.636	0.537	0.511
	24.27	24.11	0.765	0.665	0.625
	19.70	19.89	0.882	0.806	0.765
	14.79	14.95	1.000	1.000	1.000
508.15	47.55[a]		0.000	0.000	
	39.67[a]	39.56	0.410	0.410	0.410
	39.38	38.27	0.421	0.406	0.420
	36.30	36.19	0.520	0.475	0.520
	33.29	33.18	0.610	0.530	0.536
	29.63	29.58	0.713	0.632	0.612
	25.20	25.73	0.814	0.732	0.705
	22.45	22.47	0.892	0.837	0.801
	17.25	17.42	1.000	1.000	1.000
523.15	34.17[a]		0.725	0.725	
	34.13		0.731	0.724	
	33.81	33.89	0.743	0.714	0.723
	32.68	32.76	0.772	0.723	0.745
	30.05	30.17	0.824	0.763	0.773
	26.79	26.91	0.898	0.848	0.849
	21.51	21.63	1.000	1.000	1.000

[a] Critical pressure.

Table 2. Results of the VLE Correlation by the PRSV Equation of State and the WS Mixing Rule

T/K	k_{12}	τ_{12}	τ_{21}	$100(\mathrm{SQP}/N_{\mathrm{T}})^{1/2}$	$(\mathrm{SQP}/N_{\mathrm{T}})^{1/2}$
483.15	0.1618	0.4949	0.5696	1.15	0.041
498.15	0.1617	0.4949	0.5696	0.60	0.020
508.15	0.1687	0.4949	0.5696	0.81	0.023
523.15	0.1521	0.4949	0.5696	0.40	0.012

Conclusion

The isothermal VLE data for the system n-heptane + 2-propanol were obtained at (483.15, 498.15, 508.15, and 523.15) K. The PRSV EOS combined with the NRTL model and Wong–Sandler mixing rules for correlating parameters

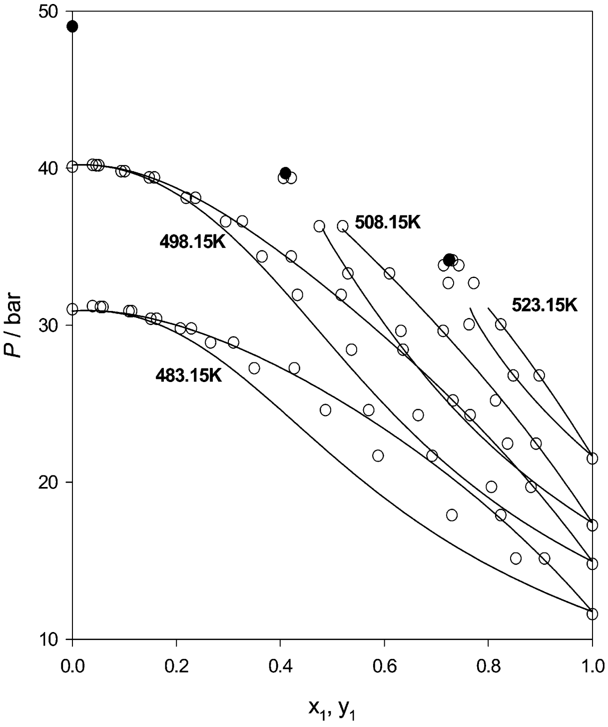

Figure 1. Correlation of the *n*-heptane (1) and 2-propanol (2) system: ●, critical points. Two critical pressures are shown at 508.15 K. One critical pressure is shown at 523.15 K.

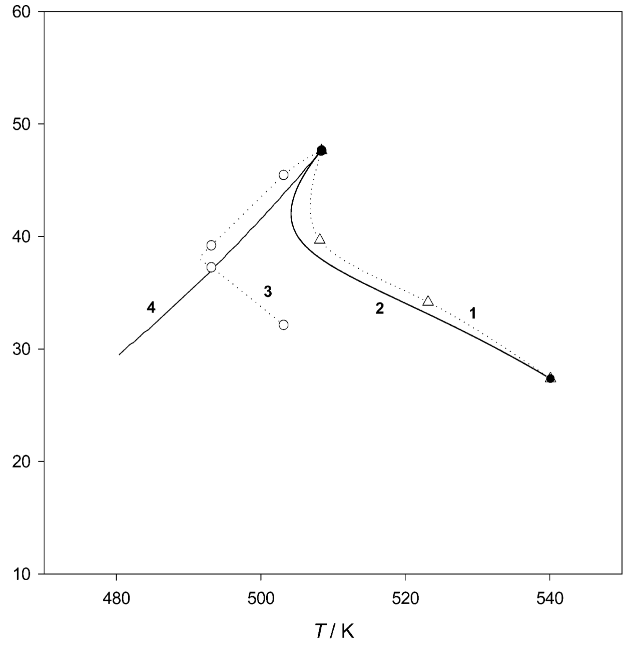

Figure 2. *P*−*T* projection of the critical loci of the system 2-propanol + *n*-heptane (1,2) and *n*-hexane (3): △, this work; ○, Seo et al.;[1] ●, critical points of pure components from the data bank by Reid et al.;[13] · · ·, interpolation curve of experimental data; — (2), prediction of critical locus from this work; — (4), vapor pressure of 2-propanol from the data bank by Reid et al.[13]

Table 3. Parameters for the Prediction of the Critical Locus of the 2-Propanol + *n*-Heptane System at 483.15 K

α	k_{12}	τ_{12}	τ_{21}
0.3	0.0588	0.5882	1.7978
0.1	−0.0680	−0.3471	2.8801
0.05	−0.0547	−0.5457	3.1395

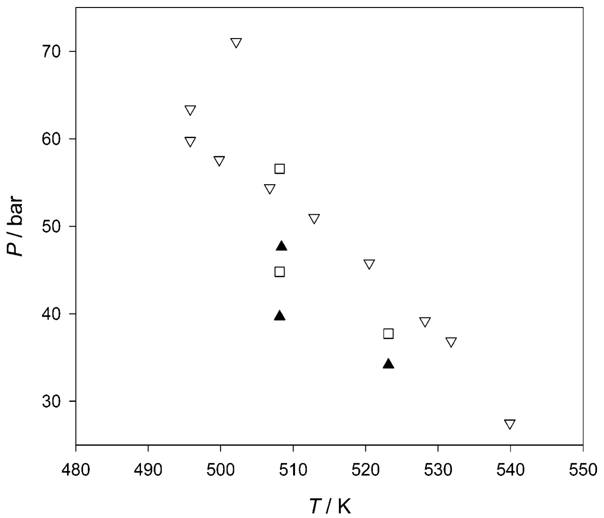

Figure 3. Comparison of critical loci for *n*-heptane + methanol (□), + ethanol (▽), and + 2-propanol (▲).

resulted in a good agreement with experimental data. However, the prediction of vapor composition at 483.15 K has shown a small deviation from experimental data. This system exhibited a continuous critical line between the two pure components such as *n*-heptane + methanol and *n*-heptane + ethanol. The fitted parameter obtained from the VLE data near the critical region gave guidance to calculate and predict critical loci.

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