Measurement and Correlation of Vapor−Liquid Equilibria for the Ethanol + *n*-Heptane System near the Critical Region

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Isothermal VLE data for ethanol + *n*-heptane have been obtained at near-critical temperatures. The critical pressures determined from the critical opalescence of the mixtures were compared with published work for ethanol + *n*-butane, ethanol + *n*-pentane, and ethanol + *n*-hexane systems. A circulating type apparatus with a view cell has been used. These mixtures are highly nonideal because of the association of ethanol, and the data could be correlated with sufficient accuracy by using the Peng−Robinson-Stryjek−Vera (PRSV) equation of state with Wong−Sandler mixing rules.

Introduction

Near the critical region, vapor−liquid equilibrium measurements for polar and nonpolar mixtures are necessary because the properties of such mixtures cannot be predicted from corresponding pure-component values. Therefore, vapor−liquid equilibrium data for these mixtures are essential to develop new thermodynamic models and to design and operate new processes. Seo et al.[1,2] measured VLE data for the systems ethanol + *n*-pentane and ethanol + *n*-hexane by the circulating method, and Deak et al.[3] measured the VLE for the system ethanol + *n*-butane by the static nonanalytic method. In this work, we have measured the equilibrium pressure (P), temperature (T), liquid-phase composition (x), and vapor-phase composition (y) for the ethanol + *n*-heptane system.

Experimental Section

Materials. Ethanol was supplied by J. T. Baker with a minimum purity of 99.9%, and *n*-heptane was supplied by Fisher Scientific with a purity of 99.6% (HPLC grade). To degas the dissolved air out of the chemicals, the chemicals were kept at a slightly higher pressure than the vapor pressure of each chemical.

Apparatus and Procedures. Details of this apparatus are described in our previous works.[1,2] Briefly, the equilibrium cell has quartz sight glass on two faces, and the apparatus uses two circulation magnetic pumps to promote equilibrium. A forced-convection oven keeps the temperature of the cell and pumps uniform. 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 is ±0.1%, according to the manufacturer's specifications and was established to be ±0.05% after calibration of the Korea Testing Laboratory.

The liquid and vapor samples were simultaneously analyzed by on line gas chromtography (GC). Two sets of thermal conductivity detectors and Porapak Q packing column were used. Manifold valves with two needle type stems were used as sampling valves. The inner volume of each valve was large, about 0.05 mL. Thus, the GC columns were specially manufactured with 0.95 cm o.d. by 85 cm length of Type 316 stainless steel tube for application to large amounts of sample. A total of 13.5 g of packing material was used for each column.

Results and Discussion

Thermodynamic Model. For correlation of the experimental data, we used the Peng−Robinson equation of state,[4]

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

where

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

$$\alpha(T) = [1 + \kappa(1 - {T_r}^{0.5})]^2 \tag{3}$$

For κ, the form proposed by Stryjek and Vera[5] was used

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

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{5}$$

The parameter κ_1 was fitted to produce the correct vapor pressures of the pure components. For ethanol, vapor pressures were taken from Reid et al.[6] at $T_r > 0.7$, and for *n*-heptane, the correlation by Stryjek and Vera[5] was used. Table 1 shows the parameter values.

The reformulated Wong−Sandler mixing rules[7] for evaluating the parameters a and b were used, where the combining rule is written as follows:

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \tag{6}$$

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Table 1. Critical Temperature, Critical Pressure, and PRSV Parameters for the Pure Components

			PRSV parameters		
substance	T_c/K	P_c/bar	w	κ_1	reduced temp range
ethanol[a]	513.9	61.48	0.644 39	0.080 55	$T_r > 0.7$
n-heptane[b]	540.1	27.36	0.350 22	0.046 48	$0.470 < T_r < 0.987$

[a] For ethanol, we correlated the parameter κ_1 at $T_r > 0.7$ on the basis of the data given by Reid et al.[6] [b] Stryjek and Vera.[5]

Table 2. Experimental VLE Data for the n-Heptane (1) + Ethanol (2) System

T/K	P_{exp}/bar	P_{cal}/bar	$x_{1,exp}$	$y_{1,exp}$	$y_{1,cal}$
483.15	35.83	35.84	0.000	0.000	0.000
	36.55	36.59	0.051	0.059	0.059
	36.77	36.85	0.092	0.097	0.097
	36.77	36.88	0.133	0.133	0.129
	36.47	36.72	0.178	0.175	0.159
	35.72	35.97	0.265	0.227	0.208
	34.21	34.2	0.382	0.314	0.267
	30.80	30.68	0.533	0.411	0.352
	25.99	25.9	0.685	0.546	0.458
	22.39	22.17	0.785	0.644	0.552
	17.20	17.33	0.896	0.793	0.708
	11.63	11.76	1.000	1.000	1.000
508.15	55.76	55.73	0.000	0.000	0.000
	56.10	56.07	0.027	0.030	0.029
	56.49	56.46	0.073	0.076	0.074
	56.55	56.52	0.081	0.084	0.081
	56.58[a]	56.55	0.085	0.085	0.085
	44.80[a]		0.471	0.471	
	44.64		0.475	0.462	
	43.84		0.500	0.465	
	40.83	40.8	0.578	0.492	0.492
	38.71	38.68	0.621	0.524	0.521
	34.21	34.18	0.713	0.591	0.582
	26.17	26.32	0.859	0.753	0.728
	17.22	17.39	1.000	1.000	1.000
523.15	37.72[a]		0.721	0.721	
	37.54		0.740	0.707	
	37.05		0.752	0.707	
	34.90		0.798	0.730	
	27.95	27.95	0.910	0.852	0.849
	21.50	21.63	1.000	1.000	1.000

[a] Critical pressure.

A^E_∞ was chosen from the NRTL model,[8]

$$A^E_\infty = \sum_{i=1}^{n} x_i \frac{RT\sum_{j=1}^{n} x_j G_{ji}\tau_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} \quad \text{with} \quad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{7}$$

where

$$\tau_{ji} = \frac{c_{ji}}{RT} \tag{8}$$

Vapor–Liquid Equilibrium Measurements. Isothermal vapor–liquid measurements were determined at 483.15, 508.15, and 523.15 K for n-heptane and ethanol. The experimental data are listed in Table 2. When the Wong–Sandler mixing rule was applied, the nonrandomness parameter α was fixed at 0.1, and the three parameters k_{12}, c_{12}/R, and c_{21}/R were fitted. The objective function for evaluating the parameters was

$$\mathrm{SQP} = \sum_{N=1}^{N_T}\left(\frac{P_{cal} - P_{exp}}{P_{exp}}\right)^2 \tag{9}$$

Table 3. Results of VLE Correlation by the PRSV Equation of State and WS Mixing Rule

T/K	k_{12}	c_{12}/R	c_{21}/R	$100\sqrt{\mathrm{SQP}/N_T}$
523.15	0.2623	728.7	−16.94	0.42
508.15	0.2765	707.9	−16.46	0.37
483.15	0.2921	779.6	−82.96	0.58

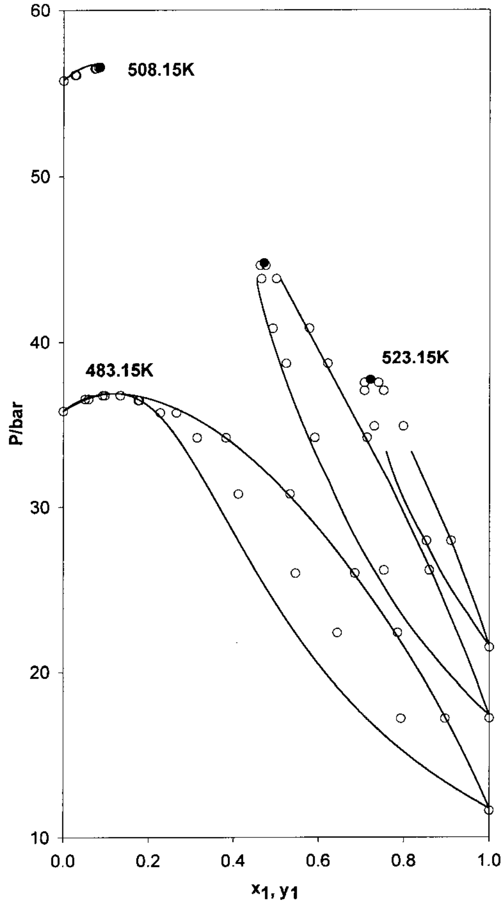

Figure 1. Correlation of n-heptane (1) and ethanol (2) system: ●, critical points. Two critical pressures are shown at 508.15 K. One critical pressure is shown at 523.15 K.

The percentages of the root-mean-squared relative deviations between the measured and calculated pressures, $100\sqrt{\mathrm{SQP}/N_T}$ and the values of k_{12}, c_{12}/R, and c_{21}/R are listed in Table 3. The maximum deviation of pressure does not exceed 0.58%. The comparison between the calculated and the experimental $P-x_1-y_1$ values is presented in Figure 1. In case of the temperature 483.15 K, the data correlation cannot predict reliable vapor compositions, y.

Critical points were also determined from the critical opalescence of the mixture. The critical mole fractions of n-heptane were found to be 0.085, 0.471 (at 508.15 K), and 0.721 (at 523.15 K), respectively. Previously, Seo et al.[1,2] reported VLE data for the systems ethanol + n-pentane and ethanol + n-hexane and Deak et al.[3] reported VLE data for the system ethanol + n-butane. In Figure 2, a $P-T$ diagram of critical loci for the systems ethanol + n-butane, ethanol + n-pentane, ethanol + n-hexane, and ethanol + n-heptane is given for comparison. The loci of the ethanol + n-alkane systems show a systematic critical behavior similar to that of the methanol + n-alkane systems reported by de Loos et al.[9]

To the critical point calculation we applied the method reported by Castier and Sandler.[10] $P-T-x$ data at a subcritical temperature, 483.15 K, were used to estimate

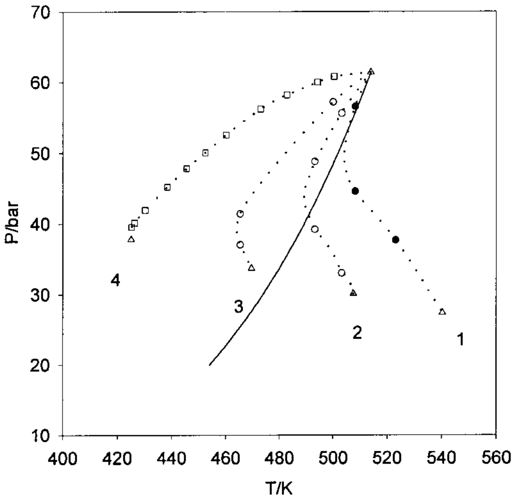

Figure 2. Critical locus and pure vapor pressure curve for ethanol + n-heptane (1), n-hexane (2), n-pentane (3), and n-butane (4): ○, Seo et al.;[1,2] ●, this work; □, Deak et al.;[3] —, vapor pressure of ethanol from the data bank by Reid et al.;[6] △, critical points of pure components from the data bank by Reid et al.;[6] ···, interpolation curve.

Table 4. VLE Parameters for the System Studied

T/K	α	c_{12}/R	c_{21}/R	k_{12}	$100\sqrt{\mathrm{SQP}/N_\mathrm{T}}$
483.15	0.05	802.7	−87.02	0.2722	0.63
	0.1	779.6	−82.96	0.2921	0.58
	0.1391	937.7	−249.5	0.3240	0.54

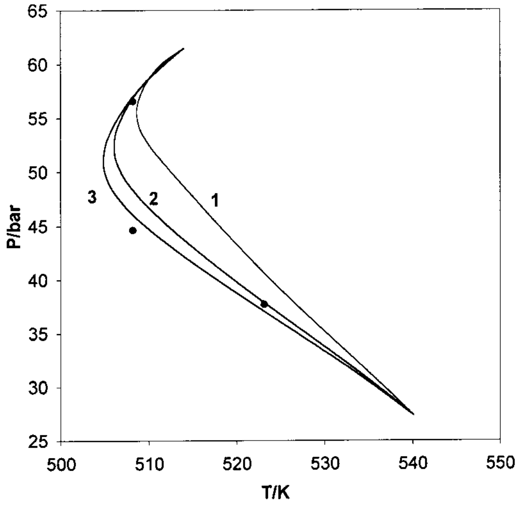

Figure 3. Critical curve of the system n-heptane + ethanol, pressure−temperature projection: 1, predicted with α correlated as 0.1391; 2, predicted with α fixed as 0.1; 3, predicted with α fixed as 0.05.

four model parameters (the binary parameter k_{12} in eq 6, and the three parameters in the NRTL model α, c_{12}/R, and c_{21}/R). Table 4 presents the parameters used for critical point calculations. For this system, three sets of parameters yielded a similar correlation of the VLE data but resulted in noticeably different behavior when used to predict the critical loci shown in Figure 3. Thus, the model parameters derived from only vapor−liquid equilibrium data at subcritical temperatures could not calculate the critical locus consistently. However, critical points are useful for guidance to select a proper correlation of the experimental data. In this system, a fixed $\alpha = 0.1$ and $\alpha = 0.05$ predicted the more reliable critical locus than a correlated $\alpha = 0.1391$ at 483.15 K.

Conclusions

Isothermal vapor−liquid equilibria for n-heptane and ethanol were obtained at near-critical temperatures. The PRSV EOS and Wong−Sandler mixing rules produced good correlation parameters of the data in the subcritical region. $P-T-x-y$ data are more essential than $P-T-x$ data to explain the reliable vapor compositions because the data correlation cannot predict vapor composition, y. Critical points are useful for guidance to select a proper correlation of the experimental data.

List of Symbols

A^E_∞ = molar excess free energy at the high density
a = parameter in the equation of state
b = parameter in the equation of state
k_{ij} = binary interaction parameter
N_T = number of data points
P = pressure
R = perfect gas constant
SQP = mean-squared relative deviation of pressure
T = temperature
v = molar volume
x = mole fraction of liquid phase
y = mole fraction of vapor phase

Greek Letters

α = nonrandomness parameter
τ = parameter in the mixing rule

Subscripts

c = critical
cal = calculated
exp = experimetal
r = reduced

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Literature Cited

(1) Seo, J.; Lee, J.; Kim, H. Isothermal vapor-liquid equilibria for ethanol and n-pentane system at the near critical region. *Fluid Phase Equilib.* **2000**, *172*, 211−219.

(2) Seo, J.; Lee, J.; Kim, H. Isothermal vapor-liquid equilibria for the system ethanol and n-hexane in the near critical region. *Fluid Phase Equilib.* **2001**, *182*, 199−207.

(3) Deák, A.; Victorov, A. I.; de Loos, Th. W. High-pressure VLE in alkanol + alkane mixtures. Experimental results for n-butane + ethanol, + 1-propanol, + 1-butanol systems and calculations with three EOS methods. *Fluid Phase Equilib.* **1995**, *107*, 277−301.

(4) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(5) Stryjek, R.; Vera, J. H. PRSV: An improved Peng−Robinson equation of state for pure compounds and mixtures. *Can. J. Chem. Eng.* **1986**, *64*, 323−333.

(6) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*, 4th ed.; McGraw-Hill: Singapore, 1988; pp 656−732.

(7) Orbey, H.; Sandler, S. I. Reformulation of Wong-Sandler mixing rule for cubic equation of state. *AIChE J.* **1995**, *41*, 683−690.

(8) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

(9) De Loos, Th. W.; Poot, W.; de Swaan Arons, J. Vapour-liquid equilibria and critical phenomena in methanol + *n*-alkane systems. *Fluid Phase Equilib.* **1988**, *42*, 209−227.

(10) Castier, M.; Sandler, S. I. Critical points with the Wong-Sandler mixing rule − II. Calculations with a modified Peng−Robinson equation of state. *Chem. Eng. Sci.* **1997**, *52*, 3579−3588.

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