Isothermal Vapor−Liquid Equilibria for the *n*-Pentane + 1-Butanol and *n*-Pentane + 2-Butanol Systems near the Critical Region of the Mixtures

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Isothermal vapor−liquid equilibria (VLE) data and mixture critical points data were measured for the *n*-pentane + 1-butanol and *n*-pentane + 2-butanol systems at 468.15 K, 483.15 K, 498.15 K, and 513.15 K. A circulation-type apparatus with a view cell was used, and critical pressures were determined from the critical opalescence of the mixtures. These mixtures show non-ideal behavior because of the hydrogen bonding of the alkanol. The measured data were correlated with the Peng−Robinson−Stryjek−Vera equation of state (EOS) with the Wong−Sandler mixing rule and the statistical associated fluid theory. Both the EOS failed to correlate the experimental data near the critical region.

Introduction

The estimation of phase behavior near the critical region has been one of the most difficult tasks of thermodynamic theory for a long time due to the diverse and complex behavior. Hicks and Young[1] introduced computer solution techniques about critical locus for non-polar mixtures. Heidemann and Khalil[2] formulated the conditions at critical points using the Helmholtz free energy. Castier and Sandler[3,4] suggested the calculation method of critical points with the Wong−Sandler mixing rule. But most thermodynamic models still have frailty in calculating the variable non-ideal fluid phase behavior near the critical region. So measuring more experimental data near the critical region is necessary to develop and create thermodynamic models.

Only a few data are available near the critical region of the mixtures because of difficulties in measuring phase behavior data in high-pressure and high-temperature conditions. VLE data near the critical region of the mixture have been measured by a few researchers for alkane + alkanol systems. de Loos et al.[5] reported the bubble point pressures and critical points for methanol + n-C_mH_{2m+2} ($m = 6, 7, 8, 9, 10, 12, 14$) systems by the synthetic method. More data[6−9] were measured for methanol with lighter alkanes. High-pressure VLE data for ethane + ethanol were reported by Brunner and Hültenschmidt.[10] VLE data and critical points of propane + ethanol were reported by Gomez-Nieto and Thodos.[11] Deak et al.[12] measured *n*-butane + ethanol, *n*-butane + 1-propanol, and *n*-butane + 1-butanol systems. Zawisza and Vejrosta[13] measured critical points of *n*-heptane + 1-propanol. Seo et al. measured the VLE data for the ethanol + n-C_mH_{2m+2} ($m = 5, 6, 7$) systems[14−16] and the 2-propanol + *n*-hexane system[17] by a circulating method. van Nhu and Liu[18] and Sauermann et al.[19] also reported the ethanol + *n*-hexane system at high pressure. Oh et al. reported the *n*-hexane + 1-propanol system[20] and the *n*-heptane + 2-propanol system.[21] In this work, we measured the vapor−liquid equilibrium data for the *n*-pentane + 1-butanol and *n*-pentane + 2-butanol systems.

Experimental Section

Chemicals. *n*-Pentane was supplied by Fluka (Switzerland) with a minimum purity of 99.5 % (GC) and stored over a molecular sieve. 1-Butanol and 2-butanol were supplied by Aldrich (U.S.A.) with a minimum purity of 99.5 % (HPLC). We stored the chemicals at a slightly higher pressure than the vapor pressure of each chemical to degas the resident air.

***Apparatus and Procedure*.** We used the experimental apparatus of previous works.[20] As shown in Figure 1, a sampling box was closely attached on a convection oven. The sampling box and the convection oven were maintained at the same temperature. The cell was installed with the especially designed quartz sight glasses. Two circulation magnetic pumps mixed the chemicals of both phases to promote equilibrium. The accuracy of the temperature measuring system is ± 0.03 K in the range 373 K to 673 K, as specified by the manufacturer, and the accuracy of the pressure transducer is ± 0.1 % on the specification and ± 0.05 % after the calibration of Korea Testing Laboratory. The circulation pumps mixed the chemicals of both phases sufficiently because the liquid was circulated from the liquid phase to the vapor phase, and the vapor phase was circulated reversely. When the cell reached the equilibrium, the samples are transported to the gas chromatography (GC) online, so no samples were discarded.

Figure 2 shows the sampling loop diagram. Three-way needle valves with graphite yarn packing (Autoclave Engineers, 10V2075) were used instead of one six-port sampling valve. The transfer circuit between the sampling box and GC was heated to prevent condensation. We determined the critical pressures from critical opalescence of the mixtures.

To analyze the samples, we used an online GC. TCD and Porapak Q packing column were used. The sample volume was quite large (0.05 mL), so it was inevitable to manufacture GC columns (0.95 cm o.d. and 185 cm long). Carrier

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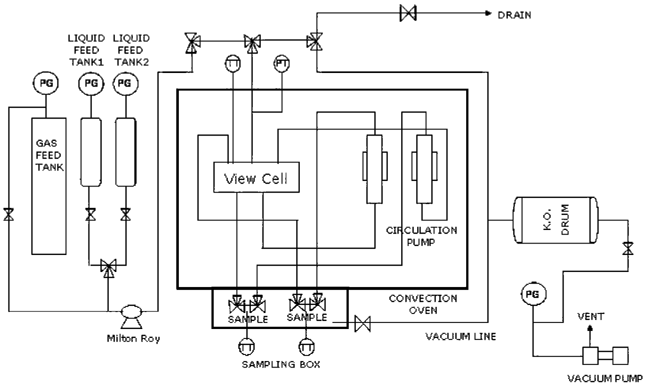

Figure 1. Schematic diagram of the experimental apparatus.

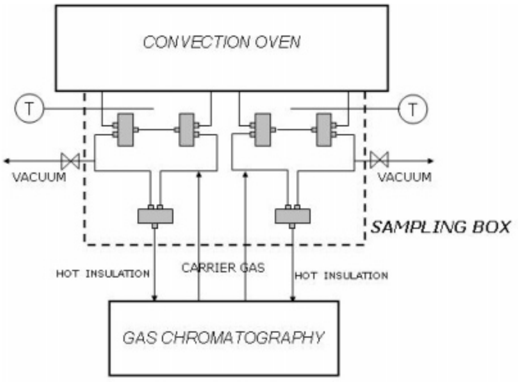

Figure 2. Schematic diagram of the sampling loop.

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

substance	T_c K	P_c bar	PRSV parameters w	PRSV parameters κ_1	reduced temperature range
n-pentane[a]	469.7	33.7	0.251	0.03946	
1-butanol[b]	563.1	44.2	0.593	0.31939	$T_r > 0.7$
2-butanol[b]	536.1	41.8	0.577	0.32750	$T_r > 0.7$

[a] Stryjek and Vera.[23] [b] For 1-butanol and 2-butanol, we correlated the parameter k_1 at $T_r > 0.7$ on the basis of the data given by Reid et al.[27]

gas was helium, and the GC oven was maintained at 443.15 K during analysis.

Thermodynamic Model

To correlate the experimental data, we chose the Peng–Robinson–Stryjek–Vera (PRSV)[22,23] equation of state (EOS) and the statistical associated fluid theory (SAFT).[24]

In the PRSV EOS, We chose the Wong–Sandler mixing rule[25] with the NRTL model.[26] The parameter κ_1 of PRSV EOS is an adjustable characteristic parameter of each pure compound. For n-pentane, the correlated value κ_1 by Stryjek and Vera[23] was used. But for 1-butanol and 2-butanol, we correlated the data collection by Reid et al.[27] at $T_r > 0.7$ to produce correct vapor pressure. The parameter values are listed in Table 1.

We chose the original version of SAFT.[28,29] The SAFT EOS requires three pure component parameters for non-associating fluids and five pure component parameters for associating fluids. These parameters are the potential well depth (u^0/k), the segment volume (v^{00}), the number of segments of the molecule (m), the interaction volume (κ^{AB}), and the association energy (ϵ^{AB}) between sites A and B. These parameters can be estimated from the regression of saturated vapor pressure and liquid density data. For n-pentane, v^{00}, m and u^0 were fitted. For 1-butanol, 2-butanol, m, u^0, κ^{AB}, and ϵ^{AB} were fitted. The segment volumes v^{00} were set equal to 12.0 mL/mol. We correlated the data collected by Reid et al.[27] to obtain all segment parameters. The SAFT pure component parameters are listed in Table 2.

Table 2. SAFT EOS Pure Component Segment Parameters

	v^{00} mL·mol^{-1}	m	u^0/k K	ϵ^{AB} K	$10^2\,\kappa^{AB}$
n-pentane	10.1	4.782	184.69		
1-butanol	12.0	3.904	227.70	2617	1.637
2-butanol	12.0	3.895	217.27	2459	1.644

Table 3. Experimental and Calculated VLE Data for the n-Pentane (1) + 1-Butanol (2) System

T/K	P_{exp}/bar	$x_{1,exp}$	$y_{1,exp}$	P_{exp}/bar	$x_{1,exp}$	$y_{1,exp}$
468.15	8.33	0.000	0.000	28.68	0.721	0.809
	12.02	0.052	0.149	30.91	0.861	0.885
	15.23	0.140	0.350	32.06	0.938	0.943
	18.52	0.258	0.478	32.57	0.979	0.979
	21.88	0.402	0.608	32.86	1.000	1.000
	25.32	0.535	0.711			
483.15	11.82	0.000	0.000	33.04	0.588	0.719
	14.84	0.067	0.158	34.91	0.686	0.766
	20.47	0.165	0.373	35.91	0.732	0.786
	26.51	0.321	0.544	36.39[a]	0.789	0.789
	30.75	0.482	0.677			
498.15	15.58	0.000	0.000	34.38	0.439	0.578
	17.40	0.033	0.064	36.51	0.515	0.617
	20.50	0.098	0.181	38.22	0.588	0.656
	24.09	0.160	0.304	39.24[a]	0.661	0.661
	29.39	0.288	0.450			
513.15	20.27	0.000	0.000	35.78	0.283	0.390
	23.40	0.051	0.106	40.05	0.403	0.460
	26.54	0.104	0.200	41.65[a]	0.476	0.476
	30.84	0.173	0.304			

[a] Critical pressure.

Table 4. Experimental and Calculated VLE Data for the n-Pentane (1) + 2-Butanol (2) System

T/K	P_{exp}/bar	$x_{1,exp}$	$y_{1,exp}$	P_{exp}/bar	$x_{1,exp}$	$y_{1,exp}$
468.15	13.51	0.000	0.000	27.75	0.569	0.639
	15.88	0.064	0.147	29.46	0.672	0.732
	16.49	0.086	0.183	30.66	0.753	0.792
	18.79	0.167	0.281	31.68	0.842	0.861
	21.62	0.279	0.407	32.32	0.913	0.921
	23.57	0.362	0.487	32.72	0.977	0.978
	25.84	0.461	0.573	32.86	1.000	1.000
483.15	17.91	0.000	0.000	29.72	0.370	0.475
	19.39	0.042	0.097	31.61	0.447	0.533
	20.69	0.075	0.163	33.54	0.536	0.594
	22.76	0.139	0.225	34.37	0.584	0.621
	24.88	0.200	0.305	35.96	0.654	0.674
	27.08	0.266	0.375	36.80[a]	0.706	0.706
498.15	23.29	0.000	0.000	33.08	0.250	0.316
	25.01	0.033	0.060	35.34	0.325	0.385
	26.49	0.070	0.111	36.91	0.389	0.442
	28.51	0.121	0.177	38.29	0.440	0.480
	30.62	0.179	0.250	39.06[a]	0.495	0.495
513.15	29.46	0.000	0.000	38.07	0.195	0.252
	31.62	0.049	0.079	39.75	0.243	0.284
	33.28	0.084	0.129	40.94[a]	0.301	0.301
	35.76	0.141	0.197			

[a] Critical pressure.

Results and Discussion

The isothermal VLE data were measured at 468.15, 483.15, 498.15, and 513.15 K because the critical temperature of n-pentane is 469.7 K. These data are listed in Tables 3 and 4.

The binary interaction parameters k_{12} in the Wong–Sandler mixing rule and the SAFT EOS were fitted. Non-

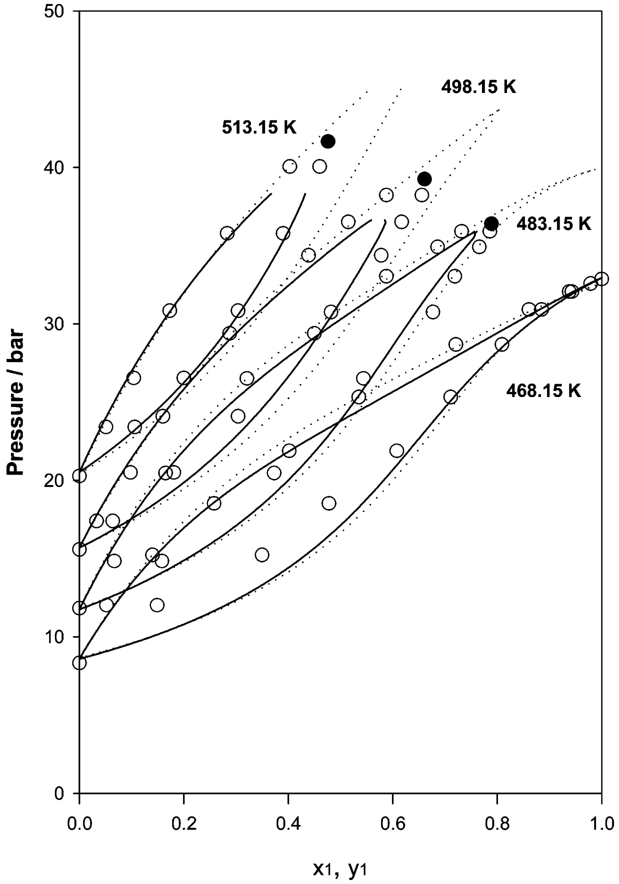

Figure 3. Correlation of *n*-pentane (1) and 1-butanol (2) system; ●, critical points; —, calculated results of PRSV EOS; ···, calculated results of SAFT EOS.

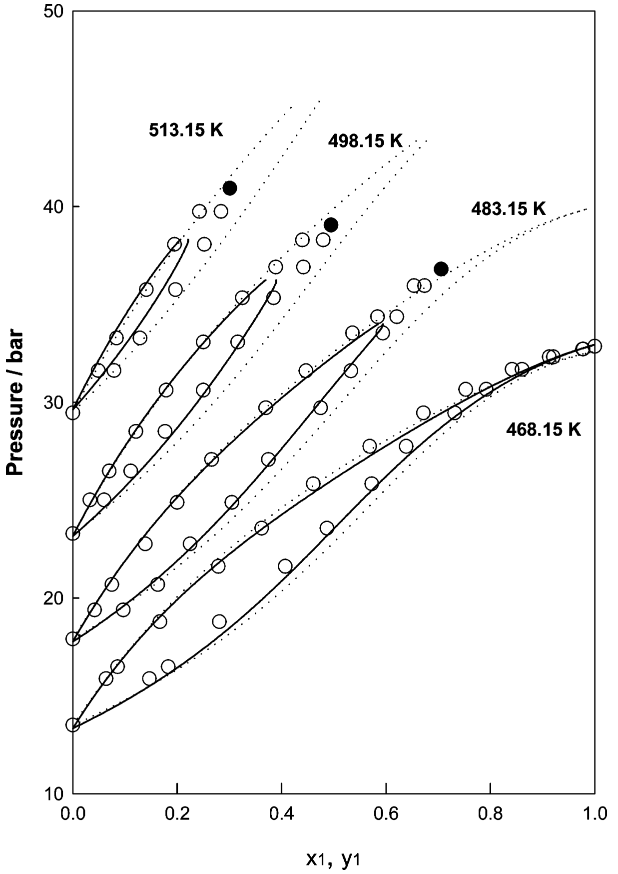

Figure 4. Correlation of *n*-pentane (1) and 2-butanol (2) system; ●, critical points; —, calculated results of PRSV EOS; ···, calculated results of SAFT EOS.

Table 5. Correlation Results by the PRSV EOS and SAFT EOS

T/K	model	k_{12}	$100\sqrt{\mathrm{SQP}/N_\mathrm{T}}$	$\sqrt{\mathrm{SQY}/N_\mathrm{T}}$
		n-Pentane + 1-Butanol		
468.15	PRSV	0.0822	2.54	0.045
	SAFT	0.0251	2.55	0.060
483.15	PRSV	0.1293	3.21	0.049
	SAFT	0.0360	3.00	0.049
498.15	PRSV	0.0475	2.48	0.044
	SAFT	0.0190	1.34	0.050
513.15	PRSV	0.0305	1.75	0.017
	SAFT	0.0242	0.89	0.049
		n-Pentane + 2-Butanol		
468.15	PRSV	0.0202	1.14	0.019
	SAFT	0.0161	1.19	0.036
483.15	PRSV	0.0156	1.23	0.018
	SAFT	0.0160	0.94	0.034
498.15	PRSV	0.0235	0.46	0.022
	SAFT	0.0189	0.60	0.043
513.15	PRSV	0.0082	1.15	0.020
	SAFT	0.0142	0.30	0.038

randomness parameter α in the NRTL model was fixed as 0.3. The object function to fit these parameters was used as follows:

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

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

Especially, we fitted values of g_{12} and g_{21} at 468.15 K for the NRTL model. These values are $g_{12} = 509.9$ cal/mol and $g_{21} = 719.1$ cal/mol for the *n*-pentane + 1-butanol system and $g_{12} = 483.1$ cal/mol and $g_{21} = 650.4$ cal/mol for the *n*-pentane + 2-butanol system. The percentage of the root mean squared relative deviations between the measured and calculated pressures, $100\sqrt{\mathrm{SQP}/N_\mathrm{T}}$; the root mean squared relative deviations of vapor composition of *n*-pentane, $\sqrt{\mathrm{SQY}/N_\mathrm{T}}$; and the values of the fitted parameters are listed in Table 5. The comparison of phase diagrams between the experimental data and the calculated values are shown in Figures 3 and 4.

We could also find critical points of the mixture for these systems at 483.15 K, 498.15 K, and 513.15 K. In the *n*-pentane + 1-butanol system, the critical mole fractions of *n*-pentane were 0.789 at 483.15 K, 0.661 at 498.15 K, and 0.476 at 513.15 K. In the *n*-pentane + 2-butanol system, the critical mole fractions of *n*-pentane were 0.706 at 483.15 K, 0.495 at 498.15 K, and 0.301 at 513.15 K. These systems show type I fluid phase behavior according to the classification of von Konynenburg and Scott.[30,31]

The P−T projection and the critical locus for these systems together with that of *n*-pentane + ethanol system are presented in Figure 5.

Conclusions

The isothermal VLE data for *n*-pentane + 1-butanol and *n*-pentane + 2-butanol systems were obtained at 468.15 K, 483.15 K, 498.15 K, and 513.15 K. The PRSV EOS and SAFT EOS for correlating parameters resulted in a good agreement with experimental data in the subcritical region. However, calculated results of PRSV EOS could not correlate the experimental data in the vicinity of critical points. The SAFT EOS also could not correlate in the vicinity of critical points. There are quite large deviations

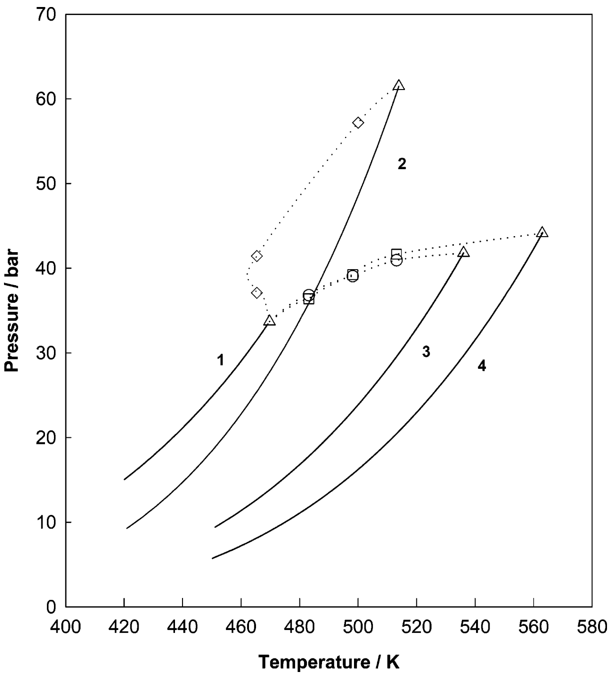

Figure 5. Critical locus and pure vapor pressure curve of the system *n*-pentane (1), ethanol (2), 2-butanol (3), and 1-butanol (4); ◇, Seo et al.;[14] ○, □, this work; △, critical points of pure components from the data bank by Reid et al.[27]; —, property data bank by Reid et al.; ···, interpolation curves of experimental data.

of vapor composition near the critical points. Near the critical region, PRSV EOS and SAFT EOS could not correlate the experimental data. Many thermodynamic models have been developed for a long time, but they still fail in calculating the critical point of mixture because of the diverse and complex behavior. These experimental data near the critical region of mixtures will be a good guidance to develop thermodynamic models.

Symbols

g_{ij}	NRTL model parameter
k	Boltzmann's constant
k_{ij}	binary interaction parameter
N_T	total number of data
m	number of segments within the molecule
SQP	mean squared relative deviation of pressure
SQY	mean squared relative deviation of vapor
T_r	regidual temperature
u^0/k	temperature-independent dispersion energy of interaction between segment
v^{00}	temperature-independent segment volume

Greek Letters

α	non-randomness parameter of the NRTL model
κ_1	PRSV parameter
κ^{AB}	volume of interaction between sites A and B
ϵ^{AB}	association energy of interaction between sites A and B

Superscripts

cal	calculated value
exp	experimental value

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