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Vapor−Liquid Equilibria for the *n*-Pentane + 1-Propanol and *n*-Pentane + 2-Methyl-1-propanol Systems near the Critical Region

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Vapor−liquid equilibria (VLE) and critical point for the (*n*-pentane + 1-propanol) and (*n*-pentane + 2-methyl-1-propanol) at temperature of (468.15, 483.15, 498.15, and 513.15) K were measured with a circulation-type apparatus with a visual method. Critical points were identified by critical opalescence and compared with the published results for (*n*-pentane + alkanols). The results were correlated with the Peng−Robinson−Stryjek−Vera (PRSV) equation of state with Wong−Sandler mixing rule. This model correlates the experimental data with a good accuracy.

Introduction

Vapor−liquid equilibria (VLE) and critical point data are important to industry for the design, simulation, and optimization of chemical processes. The estimation of phase behavior near the critical region has been one of the most difficult tasks in thermodynamic theory owing to the diverse and complex behavior. In addition, when the mixture contained a polar component, it was not possible to predict the VLE precisely, particularly near the critical region from the properties of the pure components.

De Loos et al.[1] have reported bubble pressures and critical points for (n-C$_m$H$_{2m+2}$ + methanol) with $m = 6, 7, 8, 9, 10, 12,$ and 14. Others have reported VLE measurements for methanol mixed with alkanes with $m < 6$.[2−5] Seo et al. have measured the VLE of (*n*-pentane + ethanol)[6] with a circulating method while Kim et al. reported measurements with (*n*-pentane + 1-butanol) and (*n*-pentane + 2-butanol).[7]

In this work, we have measured the VLE for (*n*-pentane + 1-propanol) and (*n*-pentane + 2-methyl-1-propanol). The results were correlated with the PRSV[8,9] with Wong−Sandler mixing rule.

Experimental Section

Chemicals. The *n*-pentane was supplied by Fluka (Switzerland) with a minimum purity of 99.5 % (weight fraction) determined by gas chromatography and stored over a molecular sieve. 1-Propanol and 2-methyl-1-propanol were supplied by Aldrich (Milwaukee, WI) with a minimum purity of 99.5 % (weight fraction) determined with high-pressure liquid chromatography. The chemicals were degassed prior to use.

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

	T_c	P_c	PRSV parameters		reduced temperature range
substance	K	MPa	w	κ_1	
n-pentane[a]	469.7	3.37	0.251	0.03946	
1-propanol[b]	536.8	5.17	0.623	0.21419	$T_r > 0.7$
2-methyl-1-propanol[b]	547.8	4.30	0.585	0.38784	$T_r > 0.7$

[a] Stryjek and Vera.[9] [b] For 1-propanol and 2-methyl-1-propanol, we correlated the parameter κ_1 at $T_r > 0.7$ on the basis of the data given by KDB.[12]

Table 2. Experimental Data for the *n*-Pentane (1) + 1-Propanol (2) System

T	P_{exp}			T	P_{exp}		
K	MPa	$x_{1,exp}$	$y_{1,exp}$	K	MPa	$x_{1,exp}$	$y_{1,exp}$
468.15	1.558	0.000	0.000	483.15	3.484	0.341	0.455
	1.679	0.020	0.064		3.639	0.390	0.494
	1.833	0.050	0.128		3.823	0.472	0.540
	2.021	0.091	0.209		3.914	0.514	0.565
	2.198	0.134	0.264		3.964	0.541	0.576
	2.425	0.200	0.351		4.029[a]	0.592	0.592
	2.631	0.270	0.426	498.15	2.733	0.000	0.000
	2.824	0.351	0.487		2.864	0.020	0.042
	3.017	0.448	0.559		2.999	0.044	0.085
	3.208	0.577	0.643		3.204	0.075	0.140
	3.306	0.650	0.684		3.457	0.118	0.211
	3.408	0.772	0.780		3.713	0.169	0.272
	3.416	0.787	0.789		3.966	0.240	0.330
	3.425	0.836	0.833		4.183	0.303	0.368
	3.408	0.868	0.863		4.362	0.376	0.401
	3.352	0.948	0.946		4.423	0.404	0.413
	3.286	1.000	1.000		4.445[a]	0.415	0.415
483.15	2.081	0.000	0.000	513.15	3.546	0.000	0.000
	2.239	0.026	0.072		3.726	0.025	0.047
	2.357	0.046	0.119		3.883	0.049	0.089
	2.477	0.067	0.161		4.088	0.083	0.134
	2.664	0.105	0.227		4.326	0.117	0.181
	2.880	0.155	0.285		4.561	0.162	0.217
	3.090	0.210	0.339		4.729	0.201	0.240
	3.277	0.270	0.400		4.824[a]	0.245	0.245

[a] Critical pressure.

Apparatus and Procedures. The modified version of the apparatus reported by Kim et al. was used for these measurements.[7] In this apparatus (shown in Figure 1), a sampling box was attached in the rear of the convection oven. The sampling box was maintained at the same temperature as convection oven. The accuracy of the temperature measurement was as cited by the supplier ± 0.03 K at temperatures in the range (373 to 673) K. The accuracy of the pressure transducer was cited by the supplier as ± 0.1 % and when calibrated by the Korea Testing Laboratory found to have an uncertainty of ± 0.05 %. The visual cell had quartz sight glasses. The volume of the equilibrium cell was 100 mL, and the total volume of circulating system was about 130 mL. Two circulation pumps were used to mix

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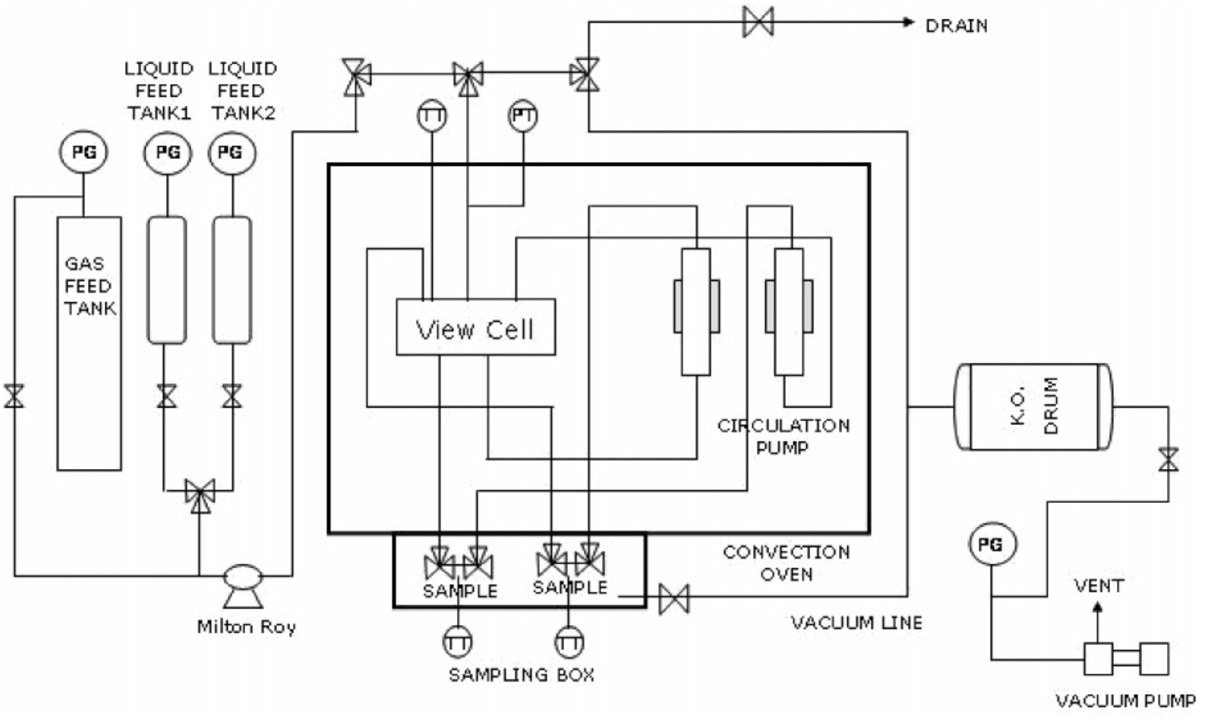

Figure 1. Schematic diagram of the experimental apparatus.

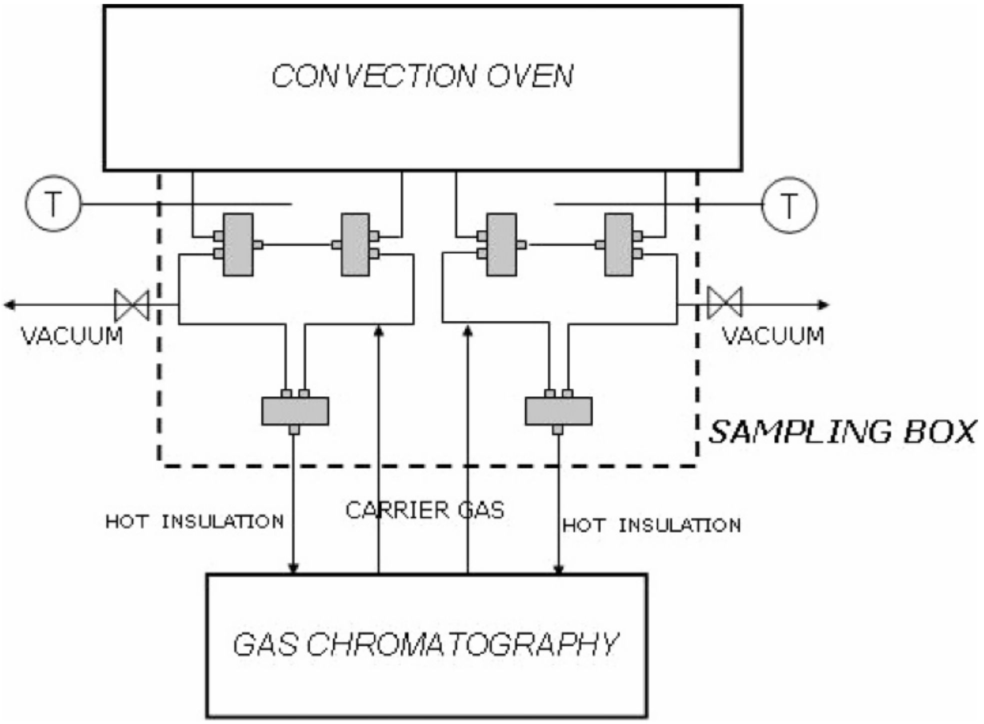

Figure 2. Schematic diagram of the sampling loop.

the fluid, one passed the liquid through the vapor (via the liquid sampling valves in the sampling box) while the other passed the vapor through the liquid (via the vapor sampling valves in the sampling box). When the contents of the cell reached equilibrium, samples were taken from the circulation lines as shown in Figure 2 and sent to a gas chromatography. Three-way needle valves with graphite yarn packing (Autoclave Engineers, 10V2075) were used as the sampling valves. The transfer circuit between the sampling box and GC was heated to prevent condensation. The loop was evacuated after sampling in order to eliminate the resident carrier gas that would give rise to an error in the pressure measurement.

The critical pressures were determined from observation of critical opalescence. When the phenomenon was observed, measured pressure was the critical pressure. In the case of pressure near the critical points of the mixture, we had observed phase behavior while feeding a small quantity of samples using a hand pump.

The liquid and vapor samples were analyzed simultaneously with gas chromatography (GC). For the measurements with (*n*-pentane + 1-propanol), the GC was fitted with thermal conductivity detectors, and the column was packed with Porapak Q while for the measurements with (*n*-pentane + 2-methyl-1-propanol) Porapak S column packing was used. The tempera-

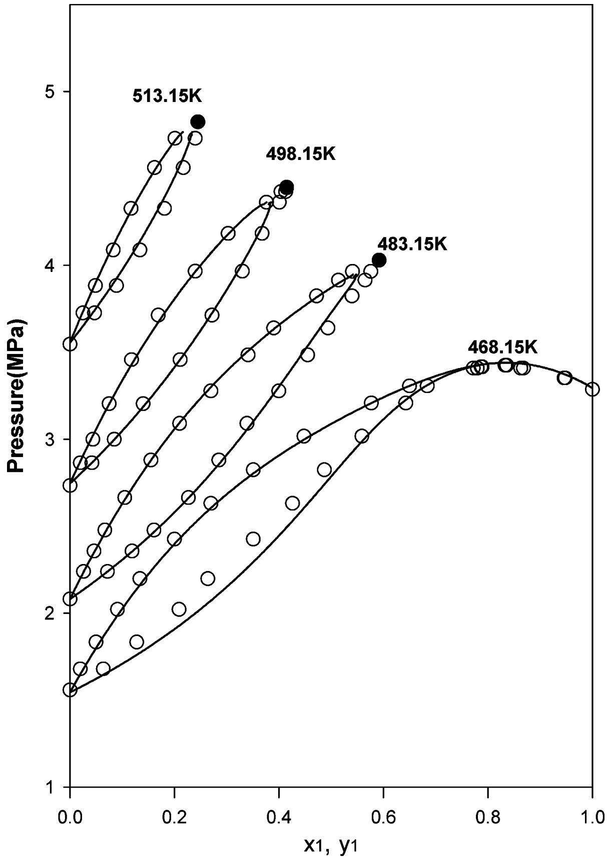

Figure 3. Correlation of *n*-pentane (1) and 1-propanol (2) system; ○, experimental; ●, critical points; - -, calculated results of PRSV EOS.

tures of the injector and the detector were maintained at 523.15 K. The column temperature was 453.15 K. Helium was used as the carrier gas at the rate of 30 $cm^3 \cdot min^{-1}$. Single-phase samples of known composition were used to calibrate the gas chromatograph in the composition range of interest. The samples of each phase at the same temperature were analyzed at least three times, and the average values were used. The accuracy of compositions was on the average 0.003 as weight fraction after calibrations.

Table 3. Experimental VLE Data for the *n*-Pentane (1) + 2-Methyl-1-propanol (2) System

T / K	P_{exp} / MPa	$x_{1,exp}$	$y_{1,exp}$	T / K	P_{exp} / MPa	$x_{1,exp}$	$y_{1,exp}$
468.15	1.113	0.000	0.000	483.15	3.079	0.477	0.580
	1.244	0.037	0.080		3.275	0.558	0.627
	1.443	0.092	0.163		3.407	0.614	0.668
	1.599	0.137	0.229		3.515	0.668	0.697
	1.724	0.174	0.280		3.659[a]	0.726	0.726
	1.942	0.250	0.385	498.15	1.933	0.000	0.000
	2.126	0.311	0.447		2.157	0.037	0.085
	2.314	0.390	0.526		2.450	0.107	0.190
	2.537	0.506	0.622		2.642	0.156	0.247
	2.774	0.621	0.694		2.944	0.213	0.351
	2.953	0.722	0.757		3.181	0.271	0.409
	3.122	0.827	0.852		3.413	0.341	0.442
	3.188	0.889	0.897		3.581	0.389	0.471
	3.241	0.945	0.950		3.716	0.443	0.501
	3.253	0.959	0.960		3.951[a]	0.550	0.550
	3.264	1.000	1.000	513.15	2.505	0.000	0.000
483.15	1.506	0.000	0.000		2.723	0.039	0.079
	1.715	0.055	0.113		2.904	0.074	0.141
	1.892	0.096	0.177		3.122	0.119	0.196
	2.003	0.131	0.227		3.309	0.170	0.249
	2.133	0.165	0.268		3.523	0.211	0.295
	2.338	0.223	0.344		3.810	0.277	0.351
	2.553	0.287	0.419		4.080	0.343	0.376
	2.751	0.361	0.480		4.155[a]	0.375	0.375
	2.942	0.434	0.549				

[a] Critical pressure.

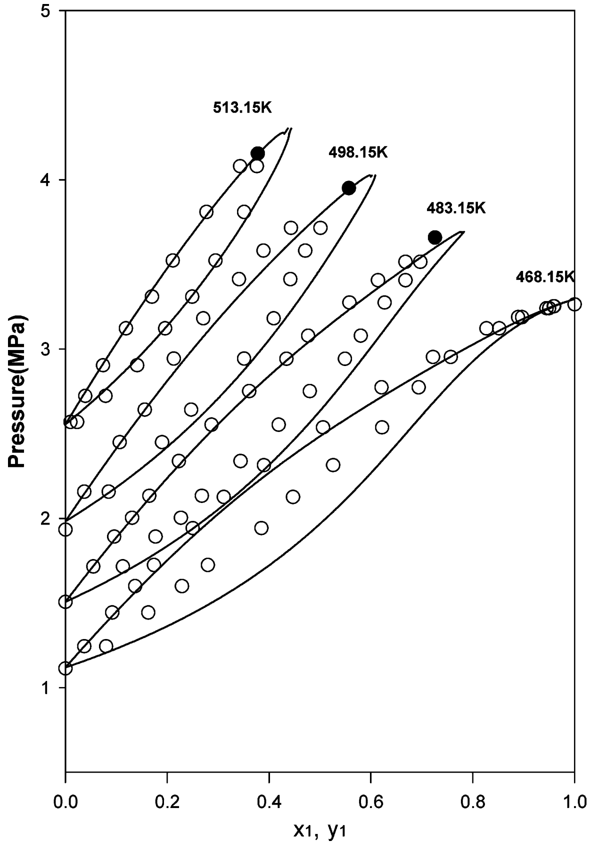

Figure 4. Correlation of *n*-pentane (1) and 2-methyl-1-propanol (2) system; ○, experimental; ●, critical points; - -, calculated results of PRSV EOS.

Table 4. Correlation Results by the PRSV EOS

system	k_{12}	$100\sqrt{SQP/N_T}$	$\sqrt{SQY/N_T}$
n-pentane + 1-propanol	0.0624	0.1750	0.0072
n-pentane + 2-methyl-1-propanol	0.1618	0.2390	0.0184

Thermodynamic Model

The experimental results were correlated with the Peng−Robinson−Stryjek−Vera (PRSV) equation of state (EOS).[8,9]

In the PRSV EOS, we used the Wong−Sandler mixing rule[10] with the NRTL model.[11] The parameter κ_1 of PRSV EOS is an characteristic parameter that is adjusted for each pure compound. For *n*-pentane, the value of κ_1 reported by Stryjek and Vera.[9] was used while for 1-propanol and 2-methyl-1-propanol, we used the vapor pressure measurements reported by KDB (Korea Thermophysical Properties Databank)[12] at $T_r > 0.7$ to obtain the parameters. These are listed in Table 1.

Results and Discussion

The isothermal VLE data were measured at temperature of (468.15, 483.15, 498.15, and 513.15) K and are listed in Tables 2 and 3.

The binary interaction parameters k_{12} in the Wong−Sandler mixing rule were obtained by regression. The non-randomness parameter α in the NRTL model was set equal to 0.3. The object function to fit these parameters was as follows:

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

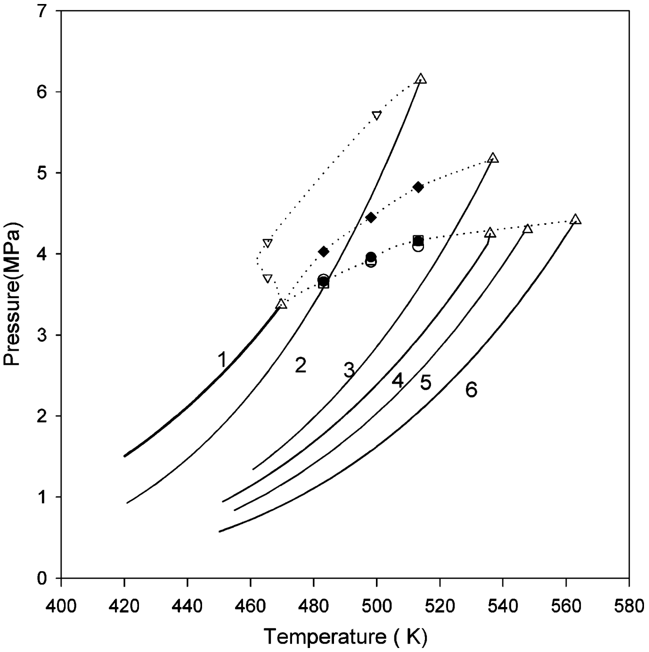

Figure 5. Critical locus and pure vapor pressure curve of the system *n*-pentane (1), ethanol (2), 1-propanol (3), 2-butanol (4), 2-methyl-1-propanol (5), and 1-butanol (6): ◇, Seo et al.;[6] ○, □, Kim et al.;[7] ◆, ● this work; △, critical points of pure components from the databank by KDB[12]; —, vapor pressures by KDB; ···, interpolation curves of experimental data.

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

We fitted g_{12}/R and g_{21}/R at a temperature of 468.15 K in the NRTL model and obtained $g_{12}/R = 895.2\ \text{K}^{-1}$ and $g_{21}/R = 110.4\ \text{K}^{-1}$ for (*n*-pentane + 1-propanol) and $g_{12}/R = 736.7\ \text{K}^{-1}$ and $g_{21}/R = -306.2\ \text{K}^{-1}$ for (*n*-pentane + 2-methyl-1-propanol). The fitted values of g_{12}/R and g_{21}/R were used to calculate all the other isothermal data. The percentage of the root mean-squared relative deviations between the measured and calculated pressure, $100\sqrt{\text{SQP}/N_\text{T}}$, the root mean-squared relative deviations of vapor composition of *n*-pentane, $\sqrt{\text{SQY}/N_\text{T}}$, and the values of the fitted parameters are listed in Table 4. The comparison of phase diagrams between the experimental data and the calculated values are shown in Figures 3 and Figure 4.

We also determined the critical points for these systems at temperature of (483.15, 498.15, and 513.15) K. For (*n*-pentane + 1-propanol), the critical mole fractions of *n*-pentane were 0.592 at $T = 483.15$ K, 0.415 at $T = 498.15$ K, and 0.245 at $T = 513.15$ K. For (*n*-pentane + 2-methyl-1-propanol) the critical mole fractions of *n*-pentane were 0.726 at $T = 483.15$ K, 0.55 at $T = 498.15$ K, and 0.375 at $T = 513.15$ K. These systems show type I fluid phase behavior according to the classification of von Konynenburg and Scott.[13,14] The (p, T) projection and the critical locus for these systems together with those of (*n*-pentane + alkanol) are shown in Figure 5.

Conclusions

The isothermal VLE data for (*n*-pentane + 1-propanol) and (*n*-pentane + 2-methyl-1-propanol) were obtained at temperature of (468.15, 483.15, 498.15, and 513.15) K. The results were represented by the PRSV EOS, and the estimations were found in very good agreement with the experimental data in the subcritical region. However, this EOS did not correlate perfectly the experimental data in the vicinity of critical points and suggests that, as expected, improvements are required in these models to give more accurate correlation for near the critical fluids.

List of Symbols

g_{ij}	NRTL model parameter
k_{ij}	binary interaction parameter
N_T	total number of data
SQP	mean-squared relative deviation of pressure
SQY	mean-squared relative deviation of vapor
T_r	residual temperature
R	gas constant

Greek Letters

α	non-randomness parameter of the NRTL model
κ_1	PRSV parameter

Superscripts

cal	calculated value
exp	experimental value

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