Vapor-Liquid Equilibria for n-Pentane + Alkanol Systems near the Critical Region

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**ABSTRACT**

Isothermal vapor-liquid equilibria data and mixture critical points data for the n-pentane + 1-propanol, 1-butanol, 2-butanol systems were measured. A circulation type equipment with the view cell was used and the critical pressures were determined from the critical opalescence of the mixtures. These mixtures show non-ideal behavior because of the hydrogen bond of alkanol. The measured data were correlated with the Peng-Robinson-Stryjek-Vera (PRSV) equation of state with Wong-Sandler mixing rule and Multi-Fluid Nonrandom Lattice Fluid with Hydrogen Bonding(MF-NLF-HB) equation of state.

**KEY WORD**

Vapor liquid equilibria, pentane, alkanol, critical point

**INTRODUCTION**

Vapor-liquid equilibrium data are very important in the various chemical industrial fields. Alkane + alkanol phase equilibrium data have been generally measured at low pressure, only a few data are available near the mixture’s critical region. Especially near the critical region, VLE measurements for polar and non-polar mixtures are important because the properties of such mixtures cannot be predicted from the pure component values. More data near the critical region would be useful to develop and create thermodynamic models. Seo et al. (2000) measured the VLE data for the system n-pentane + ethanol by circulating method and de Loos et al. (1988) reported VLE data for methanol + n-alkane systems by the synthetic method. In this work, we measured the vapor-liquid equilibrium data for the n-pentane + 1-propanol, 1-butanol and 2-butanol systems.
EXPERIMENTAL

Materials

n-Pentane was supplied by Fluka with a minimum purity of min 99.5%(GC) and stored over a molecular sieve. 1-propanol, 1-butanol and 2-butanol were supplied by Aldrich with a minimum purity of min 99.5%(HPLC).

Apparatus

Figure 1. shows the schematic diagram of the experimental apparatus. A convection oven and a sampling box attached on it 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 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 samples are transported to the gas chromatography (GC) on-line, so no samples were discarded. 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. In order to analyze the samples, we used an online gas chromatography (GC). TCD and Porapak Q packing column were used.

Figure 1. Experimental apparatus
Procedures
After the cell’s inner temperature increased, we evacuated cell and sampling loop. Then we input the chemicals to the cell and started two magnetic pumps to mix chemical’s both phases. When the equilibrium was reached, samples were taken to the gas chromatograph and analyzed composition of each phase.

RESULTS AND DISCUSSION

PRSV-WS EOS
Experimental data were correlated with modified Peng-Robinson (1976) equation of state suggested by Stryjek and Vera (1986).

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

where

\[
a(T) = \frac{0.457235\alpha(T)R^2T_e^2}{p_c}; \quad b = \frac{0.077796RT_e}{p_c}
\]  
(2)

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

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

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

We chose the Wong-Sandler mixing rule (Orbey, et al., 1995) to evaluate the parameters a and b, where the combining rule is written as following:

\[
\left( b - \frac{a}{RT} \right)_i = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] \left( 1 - k_{ij} \right)
\]  
(6)

The expression for \( A_o^E \) is molar excess free energy at the high density for the NRTL model (Renon, et al., 1968):
\[
\frac{A^ε_{\kappa}}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} x_j G_{ji} \tau_{ji}}{\sum_{k=1}^{n} x_k G_{kj}} \quad \text{with} \quad G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{7}
\]

where
\[
\tau_{ji} = \frac{g_{ji}}{RT} \tag{8}
\]

The parameter \( \kappa_i \) is an adjustable characteristic parameter of each pure compound. The \( \kappa_i \) was fitted to produce correct vapor pressure of pure components. The correlation values, \( \kappa_i \), by Stryjek and Vera (1986) were used for n-pentane. For 1-propanol, 1-butanol and 2-butanol, we correlated the data collection by Reid et al. (1988) at \( T_r > 0.7 \). Physical properties of each component are listed Table 1.

**Table 1. Critical temperature, critical pressure, acentric factor and PRSV parameters for the pure components**

<table>
<thead>
<tr>
<th>substance</th>
<th>( T_c (K) )</th>
<th>( P_c (\text{bar}) )</th>
<th>( w )</th>
<th>( \kappa_i )</th>
<th>Reduced temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>469.7</td>
<td>33.7</td>
<td>0.251</td>
<td>0.03946</td>
<td></td>
</tr>
<tr>
<td>1-Propanol</td>
<td>536.8</td>
<td>51.7</td>
<td>0.623</td>
<td>0.21419</td>
<td>( T_r &gt; 0.7 )</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>563.1</td>
<td>44.2</td>
<td>0.593</td>
<td>0.31939</td>
<td>( T_r &gt; 0.7 )</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>536.1</td>
<td>41.8</td>
<td>0.577</td>
<td>0.32750</td>
<td>( T_r &gt; 0.7 )</td>
</tr>
</tbody>
</table>

**MF-NLF-HB EOS**

The MF-NLF-HB EOS proposed by the present authors based on the two-liquid approximation of the Guggenheim’s (1984) combinatory of the lattice-hole theory (Yoo, et al., 1997) was extended for the phase equilibria of hydrogen-bonding systems. Under a fundamental assumption that the intermolecular forces are divided into physical and chemical forces, generalized Veytsman’s statistics (Veytsman, et al., 1990 and Park, et al. 2002) for hydrogen bonding theory was combined with the nonrandom lattice-fluid theory. The pressure explicit form of the EOS written by :

\[
P = \frac{1}{\beta V_H} \left\{ \frac{z}{2} \ln \left[ 1 - \left( \frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1 - \rho) - (\nu_{HB} - \nu_{HBO}) \rho + \frac{z}{2} \sum_{i=1}^{c} \left( \frac{\tau_{0i}}{\sum_{k=0}^{\theta_i} \theta_{ik} \tau_{ik}} - 1 \right) \right\} \tag{9}
\]

where \( \beta = 1/kT \), \( q_M = \sum x_i q_i \) and \( r_M = \sum x_i r_i \). \( r_i \) and \( q_i \) are the segment number and the surface
area parameters and they related by \( zq_i = r_i(z-2)+2 \). \( \rho \) is the system density defined by \( \rho = \sum \rho_i \), where \( \rho_i = N_i r_i / N_i \) and \( N_r = N_0 + \sum N_i r_i \). The overall surface area fraction is defined by \( \theta = \sum \theta_i \), where \( \theta_i = N_i q_i / N_q \) and \( N_q = N_0 + \sum N_i q_i \). \( N_0 \) and \( N_i \) are the number of vacant sites and molecules of species \( i \). The fraction of hydrogen bonds, \( \nu_{HB} \), and the fraction of zero hydrogen bonds, \( \nu_{HB0} \), in system was reported by Park et al. (2002) as follows:

\[
\nu_{HB} - \nu_{HB0} = \frac{\sum_i \sum_j (N_{ij}^{HB} - N_{ij}^{HB0})}{\sum_i r_i N_i}
\]

(10)

The nonrandomness factor \( \tau_{ji} \) is defined as:

\[
\tau_{ji} = \exp \left\{ \beta \left( \epsilon_{ji} - \epsilon_{ii} \right) \right\}
\]

(11)

where \( \epsilon_{ji} \) is the absolute value of the interaction energy between species \( j \) and \( i \). We set the coordination number, \( z \), at 10 and the unit lattice cell volume, \( V_\mu \), at 9.75 cm\(^3\)mol\(^{-1}\). Other expressions such as chemical potential necessary for phase equilibria calculation are omitted here. They are also available elsewhere (Oh, et al., 2003). Two molecular energy and size parameters were fitted to the saturated liquid density and vapor pressure data. They were correlated by the following equation of states as functions of temperature.

\[
e_{11} / k = E_a + E_b (T - T_0) + E_c [T \ln(T_0 / T) + T - T_0]
\]

(12)

\[
r_i = R_a + R_b (T - T_0) + R_c [T \ln(T_0 / T) + T - T_0]
\]

(13)

where \( T_0 = 298.15 \text{ K} \) is a reference temperature. The EOS has one binary interaction parameter \( k_{12} \) for a binary system which is defined by:

\[
e_{12} = (e_{11} e_{22})^{1/2} (1 - k_{12})
\]

(14)

where \( k_{12} \) is determined by experimental data fitting and may be temperature dependent.
Table 2. Coefficient of molecular parameters for MF-NLF-HB EOS

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>$E_a$</th>
<th>$E_b$</th>
<th>$E_c$</th>
<th>$R_a$</th>
<th>$R_b$</th>
<th>$R_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-Pentane</td>
<td>64.5927</td>
<td>0.4962</td>
<td>1.3096</td>
<td>14.9330</td>
<td>-0.8508</td>
<td>-2.3118</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>84.5705</td>
<td>0.2690</td>
<td>0.4957</td>
<td>6.0588</td>
<td>-0.0455</td>
<td>-0.2308</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>90.4512</td>
<td>0.2196</td>
<td>0.3655</td>
<td>7.3486</td>
<td>-0.0233</td>
<td>-0.1546</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>76.4709</td>
<td>0.2867</td>
<td>0.5009</td>
<td>7.6963</td>
<td>-0.0896</td>
<td>-0.3451</td>
</tr>
</tbody>
</table>

Result correlation

Figure 2. Vapor-liquid equilibria of $n$-Pentane + 1-Propanol system: (○) this work; (●) experimental critical point: (—) PRSV EOS: (——) MF-NLF-HB

Figure 3. Vapor-liquid equilibria of $n$-Pentane + 1-Butanol system: (○) this work; (●) experimental critical point: (—) PRSV EOS: (——) MF-NLF-HB
The isothermal vapor-liquid equilibria data were measured at 468.15, 483.15, 498.15 and 513.15 K. These data are shown in Figure 2, Figure 3 and Figure 4. We found the mixture critical points for these systems at 483.15K, 498.15 K and 513.15K. In n-pentane + 1-propanol system, the critical mole fractions of n-pentane were 0.592 at 483.15K, 0.415 at 498.15K and 0.245 at 513.15 K. In n-pentane + 1-butanol system, the critical mole fractions of n-pentane were 0.789 at 483.15K, 0.661 at 498.15K and 0.476 at 513.15 K. In n-pentane + 2-butanol system, the critical mole fractions of n-pentane were 0.706 at 483.15K, 0.495 at 498.15K and 0.301 at 513.15 K. These systems show type I fluid phase behavior according to the classification of van Konynenburg et al.(1980) and Rowlinson et al.(1982).

The binary interaction parameter, $k_{12}$ in the Wong-Sandler mixing rule was fitted at each temperature and nonrandomness parameter $\alpha$ was fixed as 0.3. In each system, NRTL model parameters $g_{ij}/R$ was fixed at 468.15K. Table 3 shows NRTL model parameters. Binary interaction parameter in the MF-NLF-HB was also fitted at each temperature.

**Table 3. NRTL model parameters in each system**

<table>
<thead>
<tr>
<th>System</th>
<th>$g_{12}/R$ (1/K)</th>
<th>$g_{21}/R$ (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane + 1-Propanol</td>
<td>1547.6</td>
<td>113.4</td>
</tr>
<tr>
<td>n-Pentane + 1-Butanol</td>
<td>256.6</td>
<td>361.9</td>
</tr>
<tr>
<td>n-Pentane + 2-Butanol</td>
<td>243.1</td>
<td>327.3</td>
</tr>
</tbody>
</table>

The object function to fit these parameters was used as following:
\[ SQ = SQP + SQY = \sum_{i=1}^{N} \left( \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2 + \sum_{i=1}^{N} \left( y_{i,\text{cal}} - y_{i,\text{exp}} \right)^2 \]  

(15)

where SQP is mean squared relative deviation of pressure and SQY is mean squared relative deviation of vapor composition. The percentage of the root mean squared relative deviations between the measured and calculated pressure, \(100\sqrt{\text{SQP}/N_T}\), the root mean squared relative deviations of vapor composition of n-heptane, \(\sqrt{\text{SQY}/N_T}\), and values of the fitted parameters are listed in Table 2.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>EOS</th>
<th>k_{12}</th>
<th>100\sqrt{\text{SQP}/N_T} (%)</th>
<th>\sqrt{\text{SQY}/N_T}</th>
</tr>
</thead>
<tbody>
<tr>
<td>468.15</td>
<td>PRSV</td>
<td>0.1219</td>
<td>1.00</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>/1-Propanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>483.15</td>
<td>MF-NLF-HB</td>
<td>0.0034</td>
<td>0.48</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>PRSV</td>
<td>0.1284</td>
<td>0.49</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0022</td>
<td>0.68</td>
<td>0.024</td>
</tr>
<tr>
<td>498.15</td>
<td>PRSV</td>
<td>0.1193</td>
<td>0.89</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0113</td>
<td>0.84</td>
<td>0.023</td>
</tr>
<tr>
<td>513.15</td>
<td>PRSV</td>
<td>0.1432</td>
<td>0.59</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0181</td>
<td>0.45</td>
<td>0.023</td>
</tr>
<tr>
<td>468.15</td>
<td>PRSV</td>
<td>0.0822</td>
<td>2.54</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>/1-Butanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>483.15</td>
<td>MF-NLF-HB</td>
<td>-0.0062</td>
<td>3.14</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>PRSV</td>
<td>0.1293</td>
<td>3.21</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0078</td>
<td>2.15</td>
<td>0.044</td>
</tr>
<tr>
<td>498.15</td>
<td>PRSV</td>
<td>0.0475</td>
<td>2.48</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0267</td>
<td>1.23</td>
<td>0.056</td>
</tr>
<tr>
<td>513.15</td>
<td>PRSV</td>
<td>0.0305</td>
<td>1.75</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0313</td>
<td>0.78</td>
<td>0.051</td>
</tr>
<tr>
<td>468.15</td>
<td>PRSV</td>
<td>0.0202</td>
<td>1.14</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>/2-Butanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>483.15</td>
<td>MF-NLF-HB</td>
<td>-0.0180</td>
<td>0.96</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>PRSV</td>
<td>0.0156</td>
<td>1.23</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0226</td>
<td>0.75</td>
<td>0.045</td>
</tr>
<tr>
<td>498.15</td>
<td>PRSV</td>
<td>0.0235</td>
<td>0.46</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0236</td>
<td>1.19</td>
<td>0.044</td>
</tr>
<tr>
<td>513.15</td>
<td>PRSV</td>
<td>0.0082</td>
<td>1.15</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>MF-NLF-HB</td>
<td>-0.0371</td>
<td>0.33</td>
<td>0.026</td>
</tr>
</tbody>
</table>
The P-T projection for these systems is presented in Figure 5. We also presented and compared the critical loci for the systems n-pentane + ethanol (Seo, et al., 2000).

![Figure 5](image)

**Figure 5.** Critical loci and pure vapor pressure curves of the system (1) n-Pentane, (2) Ethanol, (3) 1-Propanol, (4) 2-Butanol, (5) 1-Butanol : (▽) Seo et al. (2000) : (●, ◊, ○,) this work : (△)critical points of pure components from the data bank by Reid et al. (1998) : (……) interpolation curves of experimental data

**CONCLUSIONS**

The isothermal VLE data for n-pentane + ethanol, n-pentane + 1-butanol and n-pentane + 2-butanol systems were obtained at 468.15K, 483.15K, 498.15K and 513.15 K. The PRSV EOS combined with NRTL model and Wong-Sandler mixing rule and Multi-Fluid Nonrandom Lattice Fluid with Hydrogen Bonding (NF-NLF-HB) equation of state for correlating parameters resulted in a good agreement with an experimental data in the sub-critical region. However, calculated results couldn’t correlate the critical points. In near the critical region more improvements are demanded to obtain accurate correlation results.
ACKNOWLEDGEMENT

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REFERENCES