Investigation on vapor–liquid equilibrium for 2-propanol + 1-butanol + 1-pentanol at 101.3 kPa

Juan Wang, Zonghong Bao*
College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China

Abstract
Isobaric vapor–liquid equilibrium (VLE) data for 2-propanol + 1-butanol, 2-propanol + 1-pentanol, 1-butanol + 1-pentanol and 2-propanol + 1-butanol + 1-pentanol were measured at 101.3 kPa by using an improved Rose still. All the binary VLE data have passed the traditional area test proposed by Herington. The interaction parameters for the Wilson, NRTL and UNIQUAC equations were determined by regressing the binary VLE data. The prediction for ternary system was given by using the three pairs of binary parameters correlated. And the ternary data predicted agreed well with the experiment data.

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1. Introduction

Currently the international oil price has been rising, and the domestic oil resources are increasingly scarce. All these lead to a trend about producing mixed alcohols by using coal. The C1–C8 mixed alcohols were produced at the same time by a new coal chemical synthesis technology in a set of device. This production has already begun to accelerate the domestic industrial process [1]. Mixed alcohols can continue to conduct multi-fractionations and result in a series of single alcohol include methanol, ethanol, propanol, etc. But the vapor–liquid equilibrium (VLE) data play an important role in the design and optimized operations of distillation processes. So far many useful VLE data among the mixed alcohols have been presented. However, for 2-propanol + 1-pentanol system, there is only one report about VLE data in 313.15 K [2], and no report is in isobaric condition. To 1-butanol + 1-pentanol system, data in low pressure are available [3], but they may not meet the requirement of design calculations. As for 2-propanol + 1-butanol system, Wang et al. [4] determined temperature and liquid phase mole fraction in 101.3 kPa without giving vapor-phase mole fraction. Therefore, it is necessary to measure the VLE data for 2-propanol + 1-butanol, 2-propanol + 1-pentanol, and 1-butanol + 1-pentanol at atmospheric pressure condition.

In this paper, isobaric VLE results for binary mixture of 2-propanol + 1-butanol, 2-propanol + 1-pentanol and 1-butanol + 1-pentanol and ternary mixture of 2-propanol + 1-butanol + 1-pentanol were obtained at 101.3 kPa. The experimental values were correlated by the Wilson, NRTL and UNIQUAC equations, in which the binary parameters were obtained through the maximum likelihood. The quality of the experimental binary values was verified by the Herington method [5].

2. Experimental

2.1. Chemicals

The physical properties of chemical reagents used are given in Table 1. Methanol and 1-pentanol were supplied by Shanghai Lingfeng Chemical Co. Ltd. 2-Propanol and 1-butanol were supplied by Shanghai Shenbo Chemical Co. Ltd. Methanol and 2-propanol were used without further purification. 1-Butanol and 1-pentanol were further purified by distillation in a column. All the reagents were dried on 0.4 nm molecular sieves and degassed by ultrasound before use. The purity of chemicals used was checked by the gas chromatography equipped with a thermal conductivity detector and a stainless steel column. The refractive indices and normal boiling points were measured by the WYA Abbe refractometer and the improved Rose still, respectively.

2.2. Apparatus and procedures

In this study, the VLE data were obtained with a glass recirculation apparatus called improved Rose still described by Zhang et al. [7]. A mercury thermometer was used to measure the equilibrium...
temperature with an accuracy of temperature of 0.1 K, and conducted exposed neck correction to obtain the true temperature. The experiment pressure was controlled by a constant pressure system (a vacuum pump, a U-tube, and a buffer tank), and the precision was within ±133 Pa.

In the experiments, all the analytical work was carried out by a gas chromatograph (GC6890, supplied by Shandong Lunan Ruihong instruments company), which was equipped with a flame ionization detector (FID). The composition of vapor phase and liquid phase was calculated by the area normalization method, which can accurate to 0.001. The GC column was 30 m long and 0.32 mm in diameter silica capillary column packed with OV-1701. The carrier gas was high purity nitrogen, and head pressure was 400 kPa. The injector and detector temperature of column were 473.15 K and 493.15 K, respectively.

Methanol + 2-propanol system as a checking system was measured first. The VLE at 101.3 kPa and comparisons to literature are shown in Fig. 1. The results matched very well with previous literature and this result gives us a confidence of our instruments and analysis method.

3. Results and discussion

3.1. VLE model and experiment data

The VLE results of binary system (2-propanol + 1-butanol, 2-propanol + 1-pentanol, and 1-butanol + 1-pentanol) and ternary system (2-propanol + 1-butanol + 1-pentanol) are shown in Tables 2 and 3. The activity coefficient of pure component was calculated by:

\[ p y_i^{\text{sat}} = x_i p_i^{\text{sat}} \exp \left( \sum_i \frac{V_i}{R_T} dp \right) \]

Note: u(T) = ±0.01 K, u(x) = ±0.001, u(y) = ±0.001.

Fig. 1. Comparisons of T-x-y diagram for methanol + 2-propanol between experiment and literature at 101.3 kPa. ∆, Ref. [8]; ⊳, Ref. [9]; ●, this work.
Table 4  
The physical properties of pure component.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>2-Propanol</th>
<th>1-Butanol</th>
<th>1-Pentanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_i$ / cm$^3$ mol$^{-1}$</td>
<td>222</td>
<td>274</td>
<td>326</td>
</tr>
<tr>
<td>$z_i$</td>
<td>0.25</td>
<td>0.258</td>
<td>0.26</td>
</tr>
<tr>
<td>$R_0$ / Å</td>
<td>2.726</td>
<td>3.225</td>
<td>3.679</td>
</tr>
<tr>
<td>$\mu_i$ / D</td>
<td>1.679</td>
<td>1.679</td>
<td>1.799</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>2.51</td>
<td>3.052</td>
<td>3.592</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>2.78</td>
<td>3.45</td>
<td>4.1287</td>
</tr>
</tbody>
</table>

The Antoine coefficients$
\begin{align*}
A & = 6.40823 \\
B & = 1107.303 \\
C & = -103.944 \\
\Delta T/K & = 358–461
\end{align*}

where $\chi_i$ is the liquid-phase mole fraction of component $i$, $\gamma_i$ is the vapor-phase mole fraction of component $i$, $p$ is the total pressure, $\gamma_i^v$ is the activity coefficient of component $i$, $\gamma_i^2$ and $\gamma_i^3$ are the fugacity coefficient and the fugacity coefficient at saturation of component $i$. The saturated vapor pressure $p_i^{\text{sat}}$ was calculated by the Antoine equation:

$$\log p_i^{\text{sat}}(\text{kPa}) = A - \frac{B}{T(K) + C} \quad (2)$$

where $\exp \int_{p_i}^p (\frac{V_i^L}{RT}) dp$ is called Poynting coefficient. It can be considered to be 1 at the moderate or low pressure conditions. So Eq (1) can be written:

$$\gamma_i^v p_i^{\text{sat}} = \gamma_i^v p_i^{\text{sat}} \varphi_i^2$$

where $\varphi_i^2$ is:

$$\ln \varphi_i^2 = \frac{p_i^{\text{sat}}}{RT} \left\{ B_i + \frac{1}{2} \sum_j \sum_k [y_j y_k (2 \delta_{ji} - \delta_{jk})] \right\}$$

$\delta_{ji}$ and $\delta_{jk}$ can be given by:

$$\delta_{ji} = \delta_{ij} = 2B_{ji} - B_{jj} - B_{ii}$$

$$\delta_{jk} = \delta_{kj} = 2B_{jk} - B_{jj} - B_{kk}$$

where $B_{ii}, B_{jj}$ and $B_{kk}$ are the second term of the virial state equation; $B_{jj}$ and $B_{kk}$ are the cross second term of the virial state equation, which are calculated by the Hayden and O’Connell method [10]. All the physical properties required in this calculation are shown in Table 4. The relationship between liquid-phase mole fractions and activity coefficients is also displayed in Fig. 2.

We carried out Herington method which is based on Gibbs-Duhem equation to check the thermodynamic consistency of binary system. The method includes two parameters ($D$ and $J$), an area function and a temperature function, respectively. If the value of ($D - J$) is less than 10, the isobaric VLE data pass the thermodynamic consistency test. In this research, the results ($D - J$) for 2-propanol + 1-butanol, 2-propanol + 1-pentanol and 1-butanol + 1-pentanol system are 3.37, 0.72 and 2.25, respectively. Obviously, all the binary isobaric data passed the thermodynamic consistency test.

3.2. Correlation for binary VLE data

In this research, the VLE data was correlated with the Wilson, NRTL, and UNIQUAC equations, respectively. The interaction parameters of binary system were obtained by iterative solution, and they were based on the maximum likelihood of objective function:

$$F = \sum_{n} \left[ (\gamma_i^{\text{cal}} - \gamma_i^{\text{exp}})^2 + (\gamma_j^{\text{cal}} - \gamma_j^{\text{exp}})^2 \right]$$

(7)
where $y_i^{cal}$, $y_i^{exp}$ are the activity coefficients calculated by correlation and the activity coefficients calculated by Eq. (3). $N$ refers to the number of experiment data.

The average deviations ($\Delta y$ and $\Delta T$) were expressed as:

$$\Delta y = \frac{\sum_{i=1}^{N} |y_i^{cal} - y_i^{exp}|}{N}$$

$$\Delta T = \frac{\sum_{i=1}^{N} |T_i^{cal} - T_i^{exp}|}{N}$$

(8)

(9)

The regression parameters and average deviations ($\Delta y$ and $\Delta T$) are listed in Table 5. In Table 5, the deviation whether in vapor-phase mole fraction or in temperature is very close among three models, so we only showed the comparisons between experiment data and the Wilson model regression results in Figs. 3–5.

3.3. Ternary system

The experimental VLE data of 2-propanol + 1-butanol + 1-pentanol have been given in Table 3. The predictions of ternary system with binary interaction parameters of Wilson, NRTL and UNIQUAC equations were made. The correlation average deviations in 2-propanol vapor-phase mole fraction were 0.0057, 0.0043, and 0.0049, and in temperature were 0.52, 0.50, and 0.49, respectively, for Wilson, NRTL and UNIQUAC models. The quality of results for ternary system was tested by the McDermott-Ellis method [14], which compares maximum deviation $D_{max}$ and local deference $D$ of the adjacent point c and d. The data passed the thermodynamic consistent test if it satisfies:

$$|D| < D_{max}$$

(10)

Table 5
Regression parameters in equations for activity coefficients.

<table>
<thead>
<tr>
<th>Equation</th>
<th>$A_{12}$/([J mol$^{-1}$])</th>
<th>$A_{21}$/([J mol$^{-1}$])</th>
<th>$\Delta y$</th>
<th>$\Delta T/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Propanol(1) + 1-butanol(2) Wilson</td>
<td>-35.22</td>
<td>56.87</td>
<td>0.0031</td>
<td>0.20</td>
</tr>
<tr>
<td>NRTL ($\omega = 0.3$)</td>
<td>415.27</td>
<td>-3027.73</td>
<td>0.0029</td>
<td>0.21</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>2512.93</td>
<td>-1793.08</td>
<td>0.0032</td>
<td>0.20</td>
</tr>
<tr>
<td>2-Propanol(1) + 1-pentanol(2) Wilson</td>
<td>26.90</td>
<td>-25.49</td>
<td>0.0037</td>
<td>0.26</td>
</tr>
<tr>
<td>NRTL ($\omega = 0.3$)</td>
<td>-1966.54</td>
<td>1905.90</td>
<td>0.0040</td>
<td>0.40</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>-568.78</td>
<td>542.39</td>
<td>0.0049</td>
<td>0.49</td>
</tr>
<tr>
<td>1-Butanol(1) + 1-pentanol(2) Wilson</td>
<td>-133.80</td>
<td>648.30</td>
<td>0.0054</td>
<td>0.25</td>
</tr>
<tr>
<td>NRTL ($\omega = 0.3$)</td>
<td>3697.42</td>
<td>-2967.98</td>
<td>0.0047</td>
<td>0.21</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>2305.76</td>
<td>-1754.10</td>
<td>0.0048</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Note: Wilson, $A_{12} = (\lambda_{12} - \lambda_{11})$; NRTL, $A_{12} = (g_{12} - g_{22})$; UNIQUAC, $A_{12} = (u_{12} - u_{22})$.

Fig. 4. $T$–$x_1$–$y_1$ diagram for 2-propanol (1) + 1-pentanol (2) at 101.3 kPa. ●, experimental data; ▼, Wilson regression $p(x_1 = 0) = 101.39$ kPa, $p(x_1 = 1) = 101.20$ kPa.

The $D$ and $D_{max}$ can be calculated by (11) and (12).

$$D = \sum_{i=1}^{N} (x_{ic} + x_{id}) (\ln y_{id} - \ln y_{ic})$$

(11)

$$D_{max} = \sum_{i=1}^{N} (x_{ic} - x_{id}) \left( \frac{1}{x_{ic}} + \frac{1}{x_{ic}} + \frac{1}{x_{id}} \right) \Delta x + 2 \sum_{i=1}^{N} |\ln y_{id} - \ln y_{ic}| \Delta x$$

(12)

where $x_{ic}$, $x_{id}$, $y_{ic}$ and $y_{id}$ refer to liquid-phase mole fraction and vapor-phase mole fraction of adjacent point c and d, respectively; $T_c$, $T_d$, $y_{ic}$ and $y_{id}$ are temperature and activity coefficient of adjacent points c and d; B and C are the Antoine constants; $\Delta x$, $\Delta p$ and $\Delta T$ are the experiment errors of liquid-phase mole fraction, pressure and temperature, respectively. In this research, $\Delta x = 0.001$, $\Delta p = 0.065$, $\Delta T = 0.1$.
4. Conclusions

The VLE data for 2-propanol + 1-butanol, 2-propanol + 1-pentanol, 1-butanol + 1-pentanol and 2-propanol + 1-butanol + 1-pentanol were obtained with an improved Rose still at 101.3 kPa. We got the binary interaction parameters by regressing model equations, and also made a prediction for every system, with a good agreement between experiment data and correlation data. What is more important is that the data both for binary and for ternary systems have passed the thermodynamic consistent test. At last, the VLE data in our experiment conditions have few reports, so this paper filled a blank in literature.

List of symbols

\( A_{12}, A_{21} \) interaction parameters
\( A, B, C \) Antoine coefficients
\( B_{ii}, B_{ij}, B_{kk} \) second virial coefficients
\( B_{ij}, B_{ji}, B_{kj}, B_{jk} \) cross second virial coefficients
\( F \) objective function
\( N \) number of components
\( n_D \) refractive index
\( P \) pressure
\( q, r \) structure parameters of UNIQUAC model
\( R \) universal gas constant
\( R_D \) mean radius of gyration
\( T \) absolute temperature
\( T_b \) boiling point
\( V \) liquid mole volume
\( x \) liquid phase mole fraction
\( y \) vapor phase mole fraction
\( Z_c \) compressibility factor
\( \gamma \) activity coefficient
\( \mu \) dipole moment
\( \varphi \) fugacity coefficient
\( \omega \) eccentric factor

Superscripts and subscripts

\( \text{cal} \) calculated value
\( \text{exp} \) experimental value
\( \text{sat}, s \) saturation property
\( V \) vapor phase property
\( i \) component \( i \)
\( j \) component \( j \)

Greek letters

\( \alpha \) adjustable parameter of NRTL model

References