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Isopropanol dehydration via extractive distillation using low transition temperature mixtures as entrainers

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Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Separation Technology Group, Den Dolech 2, 5612 AZ Eindhoven, Netherlands

Abstract

Low transition temperature mixtures (LTTMs), also known as deep eutectic solvents, show properties that make them suitable as entrainers for extractive distillation. Two different low transition temperature mixtures were considered as potential entrainers for the extractive distillation of the azeotropic mixture (isopropanol + water). (Lactic acid + choline chloride) (2:1) and (glycolic acid + choline chloride) (3:1) were selected for this work. (Vapor + liquid) equilibrium measurements of the pseudo-ternary systems (isopropanol + LTTM) and (water + LTTM) were measured at different concentrations of LTTM in a pressure range of 10 to 100 kPa. (Vapor + liquid) equilibrium data of the pseudo-ternary system (isopropanol + water + LTTM) were also measured at constant pressure (100 kPa) and constant LTTM molar fraction of 0.05 and 0.1. It was found that these LTTMs cannot break the azeotrope at those concentrations. However, the azeotrope was displaced to a much higher isopropanol concentration. The NRTL model was successfully applied to fit the experimental data.

Keywords: Low transition temperature mixtures, Deep eutectic solvents, (Vapor + liquid) equilibrium, Extractive distillation, Azeotrope

1. Introduction

Isopropanol (IPA) is a bulk chemical mainly used as solvent or as a chemical intermediate for the production of mono-isopropyl amine or isopropyl acetate. Mixtures of IPA and water that need to be dehydrated can be found in the production of IPA by indirect hydrogenation or by fermentation of cellulosic materials as well as byproducts in many other processes where IPA is involved. The (IPA + water) mixture presents an azeotrope at 87.5 wt%; therefore, the IPA dehydration by ordinary distillation is basically impossible [1]. Several alternative dehydration processes have been reported: azeotropic distillation [2–5], pervaporation [6–17], (liquid + liquid) extraction [18–20], reactive distillation [21,22], adsorption [23,24], and extractive distillation [25–37].

Extractive distillation is distillation in the presence of a separation agent, also called an entrainer, which interacts differently with the components of the original mixture and, therefore, alters their relative volatilities [38]. The main characteristics of a separation agent are: higher boiling point than the components of the original mixture, miscibility with the mixture, recycability, low toxicity, and biodegradability [39]. Different salts [26,33,36,37] and ionic liquids (ILs) [40] were reported to be feasible separation agents in the extractive distillation of the (IPA + water) mixture.

The usage of salts as separation agents displays several advantages, such as selective association properties, as well as less energy consumption and small amounts of separation agent needed. The main disadvantages of salts are solid handling, corrosion, and pollution [33]. ILs were also reported to show good selective association properties, and because they are liquid, the handling problem is overcome. However, their main drawbacks for large-scale applications are their price, the complexity of the synthesis, and the amount of separation agent required [40]. Low transition temperature mixtures (LTTMs), discovered in 2003 [41], seem to be a promising alternative to ILs because they share many of their properties, but they can be prepared more easily and cheaply. Originally, LTTMs were called deep eutectic solvents (DESs), but this name does not cover the complete class of solvents, because many mixtures do not show an (eutectic) melting point, but a glass transition instead.

LTTMs were recently found to be a feasible alternative to organic solvents in different applications such as electrochemistry, material preparation, catalytic reactions, biomass deconstruction, biodiesel processing, and separation processes such as (liquid + liquid) extraction [42,43]. LTTMs are a mixture of one or more hydrogen bond donors (HBDs) and one or more hydrogen bond acceptors (HBAs) that together, in the proper ratio, have much lower melting point than the individual components. LTTMs generally present properties such as low vapor pressure, wide liquid range, water compatibility, biodegradability, non-flammability, and most

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importantly, easy and cheap preparation by mixing natural and readily starting materials [43]. All of these are desired properties for an entrainer in extractive distillation.

The target of this work is to determine if LTTMs can be used as entrainers in the separation of the azeotropic mixture (IPA + water) via extractive distillation. In order to demonstrate that, (vapor + liquid) equilibrium (VLE) data of the corresponding pseudo-binary and pseudo-ternary systems were measured, where the LTTM was treated as single component. Two LTTMs were selected with this purpose: (1) (glycolic acid + choline chloride) (molar ratio = 3:1) (GC 3:1) and (2) (lactic acid + choline chloride) (molar ratio = 2:1) (LC 2:1). Both LTTMs were used as entrainers in the IPA dehydration at different concentrations. The molecular structures of the LTTMs are illustrated in table 1. The NRTL model was used to fit the experimental data. Also during the NRTL fitting, the LTTMs were treated as a single compounds (HBD + HBA pair).

2. Experimental

2.1. Materials

The chemicals used were of the high purity and purchased from trustful sources. They are shown in table 2. Deionized MilliQ water was used in all the studied mixtures ( \( \geq 18.2 \) MΩ · cm). The water content was measured by using Karl Fischer moisture analysis, type Metrohm795. The water content was between 0.4 and 0.7 wt% in all cases.

2.2. LTTMs preparation

LTTMs were prepared by following procedure already reported [44]. Mixtures were prepared using a Mettler AX205 balance with a precision of ±0.02 mg. Both HBD and HBA were added to a flask and heated while stirring. The uncertainty in the molar mixing ratio is (±2%). This is based on the uncertainty of the molar reading and the purity of the constituents used. The temperature was controlled using a thermostatic bath with temperature controller (IKA ETS-D5). GC 3:1 was prepared at 343.15 (±0.1) K, while LC 2:1 was produced at 333.15 (±0.1) K.

2.3. VLE determination

Experimental VLE data were obtained using an all-glass ebulliometer (i-Fisher LABODEST® VLE 602D). Pressure and equilibrium temperature were determined with an accuracy of ±0.1 kPa and ±0.5 K. All solutions were prepared gravimetrically by an electronic balance (Mettler Toledo AX 205) with a readability of ±10^{-4} g. For the VLE measurements of the pseudo-ternary systems, after the equilibrium was reached, a sample of the vapor phase and a sample of the liquid phase were taken. Then, a certain amount of the system was removed and a new mixture of (IPA + LTTM) or (water + LTTM) was added, keeping the LTTM concentration constant.

The composition of the condensed vapor phase (IPA + water) was analyzed using a Varian CP-3800 gas chromatograph (GC) equipped with a flame ionization detector and a Varian CP-SIL 5CB column. The GC method is described in table 3. No presence of entrainer was detected in the vapor phase.

In the liquid phase, the IPA mole fraction was determined using the same GC method (where the low-volatile LTTM was captured in a liner placed before the column), while the water content was analyzed using Karl Fischer moisture analysis, type Metrohm795, the LTTM concentration was determined via a mass balance calculation.

3. Results and discussion

3.1. Binary VLE data

The VLE data of the pseudo-binary systems (IPA + LTM) and (water + LTTM) were measured in a pressure range of 10 to 100 kPa at LTTM molar fractions of 0.05 and 0.1. Experimental data for (IPA + LC 2:1), (IPA + GC 3:1), (water + LC 2:1) and (water + GC 3:1) are displayed in table 4. A representation of these data is shown in figure 1. In order to calculate the activity coefficient, modified Raoult’s law (equation (1)) was used.

\[
\gamma_i \approx \frac{y_i p_i}{x_i p_{i0}},
\]

where \( \gamma_i \) is the activity coefficient, \( y_i \) and \( x_i \) are the vapor and liquid mole fractions of component \( i \), \( p \) is the total pressure and \( p_{i0} \) is the pure component vapor pressure. The vapor mole fraction of water and IPA in the binary system with LTTM is \( y = 1 \), because no presence of LTTM was detected in the vapor phase due to its low volatility. The pure component vapor pressure was calculated using the Antoine equation. Antoine parameters for IPA and water were taken from literature [45].

The activity coefficient shows the deviation from the ideal solution. Positive deviations commonly involve repulsive forces between the molecules. Subsequently, negative deviations mean attractive forces between the molecules. Greater deviations from

<table>
<thead>
<tr>
<th>Name</th>
<th>Source</th>
<th>Purity (w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol</td>
<td>VWR</td>
<td>≥98</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>Sigma Aldrich</td>
<td>≥99</td>
</tr>
<tr>
<td>L-lactic acid</td>
<td>Purac</td>
<td>≥99</td>
</tr>
<tr>
<td>Choline chloride</td>
<td>Sigma Aldrich</td>
<td>≥98</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>Chemicals used in this work.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Source</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>VWR</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>L-lactic acid</td>
<td>Purac</td>
</tr>
<tr>
<td>Choline chloride</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE 3</th>
<th>GC conditions employed for analysis of the condensed vapor phase.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column type</td>
<td>CP-SIL CB (30 m;0.25 mm;0.25 μm)</td>
</tr>
<tr>
<td>Detector type</td>
<td>FID</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>523 K</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>423 K</td>
</tr>
<tr>
<td>Injection volume</td>
<td>1 μL</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Flow rate (constant)</td>
<td>2.0 cm³ min⁻¹</td>
</tr>
<tr>
<td>Split ratio</td>
<td>200</td>
</tr>
</tbody>
</table>
TABLE 4
Experimental VLE data (temperature, $T$; pressure, $P$; liquid mole fraction, $x$; activity coefficients, $\gamma$) of the pseudo-binary systems (IPA (1) + LC 2:1 (2)), (IPA (1) + GC 3:1 (2)), (water (1) + LC 2:1(2)) and (water (1) + GC 3:1(2)) at constant LTTM molar fraction in a pressure range of 10 to 100 kPa.$^a$

<table>
<thead>
<tr>
<th>$P$/kPa</th>
<th>$T$/K</th>
<th>$\gamma_1$</th>
<th>$P$/kPa</th>
<th>$T$/K</th>
<th>$\gamma_1$</th>
<th>$P$/kPa</th>
<th>$T$/K</th>
<th>$\gamma_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>319.5</td>
<td>1.02</td>
<td>10.0</td>
<td>320.5</td>
<td>1.02</td>
<td>10.0</td>
<td>320.0</td>
<td>0.99</td>
</tr>
<tr>
<td>15.0</td>
<td>327.3</td>
<td>1.03</td>
<td>15.0</td>
<td>328.2</td>
<td>1.04</td>
<td>15.0</td>
<td>328.1</td>
<td>1.00</td>
</tr>
<tr>
<td>20.0</td>
<td>333.8</td>
<td>1.02</td>
<td>20.0</td>
<td>334.2</td>
<td>1.06</td>
<td>20.0</td>
<td>333.8</td>
<td>1.02</td>
</tr>
<tr>
<td>25.0</td>
<td>338.3</td>
<td>1.04</td>
<td>30.0</td>
<td>342.4</td>
<td>1.10</td>
<td>25.0</td>
<td>338.7</td>
<td>1.02</td>
</tr>
<tr>
<td>30.0</td>
<td>342.3</td>
<td>1.05</td>
<td>30.0</td>
<td>349.1</td>
<td>1.10</td>
<td>30.0</td>
<td>342.2</td>
<td>1.05</td>
</tr>
<tr>
<td>40.0</td>
<td>349.1</td>
<td>1.05</td>
<td>40.0</td>
<td>354.6</td>
<td>1.11</td>
<td>40.0</td>
<td>349.3</td>
<td>1.04</td>
</tr>
<tr>
<td>60.0</td>
<td>359.1</td>
<td>1.05</td>
<td>60.0</td>
<td>359.2</td>
<td>1.11</td>
<td>50.0</td>
<td>354.8</td>
<td>1.04</td>
</tr>
<tr>
<td>70.0</td>
<td>362.4</td>
<td>1.08</td>
<td>70.0</td>
<td>363.2</td>
<td>1.11</td>
<td>50.0</td>
<td>354.8</td>
<td>1.04</td>
</tr>
<tr>
<td>80.0</td>
<td>365.7</td>
<td>1.09</td>
<td>80.0</td>
<td>369.9</td>
<td>1.12</td>
<td>80.0</td>
<td>366.7</td>
<td>1.10</td>
</tr>
<tr>
<td>100.0</td>
<td>371.1</td>
<td>1.12</td>
<td>100.0</td>
<td>371.6</td>
<td>1.16</td>
<td>100.0</td>
<td>371.8</td>
<td>1.15</td>
</tr>
</tbody>
</table>

$^a$ Standard uncertainties $u$ are $u(T) = 0.5$ K, $u(P) = 0.1$ kPa, $u(x) = 0.001$.

FIGURE 1. (a) Experimental activity coefficients for the binary system (IPA + GC 3:1) at constant entrainer molar fraction of 0.05 (○) and 0.1 (■). (b) Experimental activity coefficients for the binary system (water + GC 3:1) at constant entrainer molar fraction of 0.05 (○) and 0.1 (■). (c) Experimental activity coefficients for the binary system (IPA + LC 2:1) at constant entrainer molar fraction of 0.05 (○) and 0.1 (■). (d) Experimental activity coefficients for the binary system (water + LC 2:1) at constant entrainer molar fraction of 0.02 (○) and 0.1 (■).
ideality make it easier to find significant changes in the relative volatilities and, therefore, break the azeotrope.

In figure 1 it is observed that the activity coefficient increases with the concentration of LTTM in all the pseudo-binary systems. Therefore, the boiling point of the most volatile compound was decreased upon LTTM addition. Reason is that the hydrogen bonding nature of the LTTMs creates weak interactions between the solvent and the solute. These weak interactions interfere with the hydrogen bonds already present in the most volatile component (IPA or water). Therefore, both the water and the IPA become relatively more volatile.

If the pressure is considered, it is observed that the higher the pressure, the larger the activity coefficient. Taking into account that the larger the activity coefficient, the better the performance of the LTTMs in the separation, a pressure of 100 kPa was selected as working condition in the pseudo-ternary experiments.

Furthermore, in figure 1(a) and (c) it is shown that GC 3:1 increases the activity coefficient of IPA more than LC 2:1 under the same conditions. Therefore, it is possible to say that the interactions between the IPA and the GC 3:1 are stronger (more repulsion) than the interactions between the IPA and the LC 3:1. In figure 1(b) and (d) it is shown that both LTTMs produce similar increments in the activity coefficient of the water; thus, both LTTMs produce similar repulsive forces.

Moreover, higher activity coefficients for the system containing (IPA + LTTM) than for the system containing (water + LTTM) (water volatility is less increased compared to IPA volatility) are desired in order to break the azeotrope. Therefore, figure 1(a) and (b) must be considered simultaneously, as well as figure 1(c) and (d). In all cases the activity coefficient of IPA and water are higher than one; consequently, a displacement of the azeotrope is expected. Only for GC 3:1 at molar fraction of 0.1 the activity coefficient of IPA is over the entire pressure range higher than the activity coefficient of water. Consequently, azeotrope breaking is only expected for this system.

The pseudo-binary systems were correlated using the non-random two liquid (NRRTL) model. The parameters obtained with this model can later be used to predict the behavior of the pseudo-ternary systems. In the model, the LTTMs were treated as a single compound. The NRRTL model is defined as follows:

\[ \ln y_i = \sum x_i \tau_{ij} G_{ij} \frac{\sum x_i G_{ij}}{\sum x_i G_{ij} (\tau_{ij} - \sum x_i G_{ij} \tau_{mj} G_{mj} \sum x_i G_{ij})} \]  

where:

\[ G_{ij} = e^{-\varepsilon x_{ij} T} \]  

\[ \tau_{ij} = a_j + b_j T \]  

\[ x_{ij} = c_j \]  

In equation (5) it is shown that the \( c_j \) parameter is symmetrical. In this work it was fixed to 0.3 (this is the recommended value for nonpolar substances and nonpolar with polar non-associated liquids). The correlation was made with an Aspen Plus® regression, using the Maximum-Likelihood objective function and solved with the New Britt–Luecke algorithm. The estimated values of the binary parameters including the weighted sum of squares (WSS) between the experimental and calculated data points are shown in Table 5.
The VLE data of the pseudo-ternary systems (IPA + water + LTTM) were measured at constant pressure of 100 kPa and constant LTTM molar fraction of 0.05 and 0.1. Experimental results for the system (IPA + water + GC 3:1) and for the system (IPA + water + LC 2:1) can be found in Table 6.

A graphical representation of the experimental data is shown in Figure 2. Figure 2 is an x'y' diagram, where x' represents the IPA molar fraction in the liquid phase on a LTTM-free basis, and y represents the IPA molar fraction in the vapor phase (which is also LTTM-free, because of the low-volatility nature of the LTTM). The relative volatility can be defined as:

\[
x = \frac{y_i / x_i}{y_j / x_j} = \frac{y_i p_i^0}{y_j p_j^0},
\]

where \(x\) is the liquid mole fraction, \(y\) is the vapor mole fraction, \(y_i\) is the activity coefficient, \(p_i^0\) corresponds to the pure component vapor pressure and the subscript \(i\) and \(j\) refer to components \(i\) and \(j\).

The relative volatility is a comparison between the vapor pressure of the components of a mixture. It indicates the difficulty in the separation of the components via distillation. If the relative volatility of the more volatile component is always larger than one, then the azeotrope is broken. Besides, the larger the relative volatility, the easier the separation. Moreover, if the relative volatility is at any point smaller than one, then the azeotrope is not broken.

As shown in Figure 2, both LTTMs produce a positive displacement of the azeotropic point (to the pure IPA-side of the x'y'-diagram), although the azeotrope is not broken in any case. In addition, when the effect of both LTTMs is compared, greater displacements are detected for GC 3:1 than for LC 2:1. Figure 2 shows that GC 3:1 at a molar fraction of 0.1 almost breaks the azeotrope. For the systems GC 3:1 and LC 2:1 at molar fraction of 0.05 a

![FIGURE 2](image-url)

**Figure 2.** (a) Experimental x'y' diagram for (IPA + water + GC 3:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.05. (b) Experimental x'y' diagram for (IPA + water + GC 3:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.1. (c) Experimental x'y' diagram for (IPA + water + LC 2:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.05. (d) Experimental x'y' diagram for (IPA + water + LC 2:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.1. In all the graphs the solid circles (■) represent the experimental data, the solid line represent the VLE data of the azeotropic mixture (IPA + water), the grey dashed lines represent the prediction using the NRTL model and the black dotted line represent the fitting using the NRLT model.

**Table 7**

Values of the binary interaction parameters for the NRTL model obtained from the correlation of the experimental VLE data for the pseudo-ternary mixtures at constant LTTM molar fraction of 0.05 and 0.1 and the weighted sum of squares (WSS (P)) for the fits.

<table>
<thead>
<tr>
<th>Comp. i</th>
<th>Comp. j</th>
<th>(a_i)</th>
<th>(a_j)</th>
<th>(b_{ij})</th>
<th>(b_{ji})</th>
<th>(c_{ij})</th>
<th>WSS (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.05)</td>
<td>Water</td>
<td>202.75</td>
<td>68.71</td>
<td>1000.7</td>
<td>–24989</td>
<td>0.3</td>
<td>0.006</td>
</tr>
<tr>
<td>IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.1)</td>
<td>IPA</td>
<td>195.48</td>
<td>–15.86</td>
<td>–3498.1</td>
<td>6257.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)</td>
<td>Water</td>
<td>–277.61</td>
<td>–2.72</td>
<td>103,793</td>
<td>1835.1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)</td>
<td>IPA</td>
<td>2.31</td>
<td>68.51</td>
<td>–66.06</td>
<td>–204.81</td>
<td>0.3</td>
<td>0.001</td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)</td>
<td>Water</td>
<td>4.69</td>
<td>3.97</td>
<td>133.81</td>
<td>–113.81</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)</td>
<td>IPA</td>
<td>1.85</td>
<td>3.25</td>
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<td>0.3</td>
<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)</td>
<td>Water</td>
<td>138.33</td>
<td>121.58</td>
<td>4029.8</td>
<td>4536.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)</td>
<td>IPA</td>
<td>215.46</td>
<td>28.26</td>
<td>202.75</td>
<td>68.51</td>
<td>0.3</td>
<td>10.91</td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)</td>
<td>Water</td>
<td>136.00</td>
<td>–28.26</td>
<td>–42,174</td>
<td>9129.8</td>
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<td>0.003</td>
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<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)</td>
<td>IPA</td>
<td>133.33</td>
<td>121.58</td>
<td>4029.8</td>
<td>22,119</td>
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<td>0.004</td>
</tr>
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<td>Water</td>
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<td>42.61</td>
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<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)</td>
<td>IPA</td>
<td>–35.94</td>
<td>119.95</td>
<td>13,666</td>
<td>–42,694</td>
<td>0.3</td>
<td>8.6 × 10^{-5}</td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)</td>
<td>Water</td>
<td>–215.46</td>
<td>–1.14</td>
<td>81,083</td>
<td>171.49</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)</td>
<td>IPA</td>
<td>10.91</td>
<td>50.03</td>
<td>–3837.6</td>
<td>–16,318</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

**Table 8**

The values of weighted sum of squares (WSS (P)) obtained in prediction of the pseudo-binary systems VLE data using the binary interaction parameters from the correlation of the pseudo-binary systems VLE data.

<table>
<thead>
<tr>
<th>System</th>
<th>WSS (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.05)</td>
<td>0.030</td>
</tr>
<tr>
<td>IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.1)</td>
<td>0.004</td>
</tr>
<tr>
<td>IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.05)</td>
<td>0.003</td>
</tr>
<tr>
<td>IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.1)</td>
<td>0.005</td>
</tr>
</tbody>
</table>
displacement of the azo trope have been noticed from 0.68 to 0.78 and 0.73 molar fraction, respectively. Finally, in the system LC 2:1 at molar fraction of 0.1 almost no effect of the entrainer is observed.

These results were also expected on basis of the binary measurements, where only the LT TM GC 3:1 at 0.1 molar fraction increased the IPA volatility more than the water volatility. This is the only system where the azo trope is almost broken, although at concentrations higher than \( x = 0.89 \) the compositions of vapor and liquid phase are nearly identical (\( \alpha = 1 \)).

The pseudo-ternary systems were predicted using the NRTL model, with the binary parameters obtained from the pseudo-binary VLE experiments. The binary parameters for the (IPA + water) were taken from Aspen\textsuperscript{\textregistered} database. It is observed that the prediction is accurate for LT TM molar fractions 0.05. However, when the LT TM molar fraction is increased, the accuracy of the predictions using the NRTL model for the systems containing LT TMs is lower. One of the main reasons why the prediction is not so accurate in these systems may be the consideration of the LT TM as a single component (neglecting any interactions between the LT TM constituents).

Therefore, the NRTL model was also used to fit the pseudo-ternary systems directly (without the use of the previously obtained binary parameters). Both the predicted (on basis of binary data) and the regressed (on basis of ternary data) VLE data using the NRTL model are graphically depicted in figure 2. In table 7, the parameters for the fitting are shown, together with the WSS of the difference between the regressed and the experimental data. In table 8, the WSS of the pseudo-ternary systems prediction are shown.

4. Conclusions

Two different LT TMs were tested as entrainers for the extractive distillation of the azo trope mixture (IPA + water). Firstly, the VLE of the pseudo-binary mixtures was measured. It was found that both LT TMs increase the activity coefficient of IPA and water, but only the LT TM GC 3:1 at 0.1 molar fraction increased the IPA volatility more than the water volatility.

Secondly, the VLE of the pseudo-ternary systems (IPA + water + LT TM) were measured at a constant pressure of 100 kPa and a constant LT TM molar fraction of 0.05 and 0.1. It was found that the azo trope compositions were displaced to much higher IPA concentrations, although the azo trope was not broken in any case. The LT TM GC 3:1 at 0.1 molar fraction showed the highest displacement of the azo trope (from 0.68 to 0.89), which was also expected on basis of the binary results.

Finally, the pseudo-binary systems were successfully correlated using the NRTL model. The obtained binary parameters were used to predict the behavior of the pseudo-ternary systems, but the prediction was not adequate in all cases. The ternary systems were also correlated using the NRTL model, where the fitting was found to be adequate.

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References