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Liquid-liquid equilibrium measurements and interaction explorations for separation of azeotrope \( n \)-butyl acetate and \( n \)-butanol using three ionic liquids

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Abstract

To separate the azeotropic mixture \( n \)-butyl acetate and \( n \)-butanol by liquid-liquid extraction, three ionic liquids (ILs) 1-ethyl-3-methylimidazolium dihydrogen phosphate ([Emim]H\(_2\)PO\(_4\)), 1-butyl-3-methylimidazolium dihydrogen phosphate ([Bmim]H\(_2\)PO\(_4\)) and 1-hexyl-3-methylimidazolium dihydrogen phosphate ([Hmim]H\(_2\)PO\(_4\)) were adopted as extractants. The liquid-liquid equilibrium data for the ternary mixtures (\( n \)-butyl acetate + \( n \)-butanol + [Emim]H\(_2\)PO\(_4\) / [Bmim]H\(_2\)PO\(_4\) / [Hmim]H\(_2\)PO\(_4\)) was measured at 298.15 K and 101.3 kPa. The extraction capacity of the ionic liquids was evaluated by partition coefficient and selectivity. The NRTL model was applied to fit the measured data with the root mean square deviation less than 0.009. The hydrogen bond length and interaction energy between the ionic liquids and \( n \)-butyl acetate / \( n \)-butanol was calculated and the effect of the ionic liquid cations with different carbon chain length was explored.

Keywords: Liquid-liquid equilibrium; Extraction; \( n \)-butanol; \( n \)-butyl acetate; Ionic liquids
1. Introduction

\( n \)-Butyl acetate (NBAC) is an essential chemical and has been used as an important solvent in food, pharmaceutical, and cosmetics industries [1, 2]. Generally, NBAC is produced by esterification with \( n \)-butanol (NBA) and acetic acid [3-5]. Because NBAC and NBA can form the azeotropic mixture composed of (NBA/NBAC, 47/53, mass fraction) at 390.35 K and 101.3 kPa, conventional distillation cannot be applied to separate the aze trope. Usually, in order to separate the azeotrope, some special distillation methods have been adopted, such as azeotropic distillation [6-8], extractive distillation [9-12] and pressure-swing distillation [13, 14]. In addition, liquid-liquid extraction [15-18] was applied because of its less energy consumption.

For separating the azeotrope NBA and NBAC by liquid-liquid extraction, Wang et al. [5] selected ethanolamine, 1,3-propanediol and ethylene glycol as the extractants and explored the LLE behavior. Artemiy et al. [19] and Bevia et al. [20] determined the equilibrium data for the quaternary mixture (\( n \)-butanol + \( n \)-butyl acetate + acetic acid + water) at 298.15 K and 308.15 K. Recently, ionic liquids (ILs) as green solvents have been extensively applied in many fields, including catalysis [21], electrochemistry [22], polymer synthesis [23] and separation [24-26] owing to their good properties of chemical stability, low toxicity and low vapor pressure [27-29]. Xu et al. [4] chose 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim]PF\(_6\)) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF\(_6\)) as the extracting agents and measured the liquid-liquid equilibrium (LLE) data for the two ternary mixtures (\([\text{Bmim}]\text{PF}_6 + n\text{-butyl acetate} + n\text{-butanol}\)). Cai et al. [30] adopted 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim]PF\(_6\)) as the extractant for separation of \( n \)-butanol and \( n \)-butyl acetate, and measured the LLE data for the mixture (\( n \)-butanol + \( n \)-butyl acetate + [Omim]PF\(_6\)). Meng et al. [31] used 1-butyl-3-methylimidazolium methyl sulfate [Bmim]MeSO\(_4\), 1-butyl-3-methylimidazolium dihydrogen phosphate [Bmim]H\(_2\)PO\(_4\) and 1-butyl-3-methylimidazolium hydrogen sulfate [Bmim]HSO\(_4\) as the extractive solvents to separate the azeotropic mixture (isobutyl alcohol and isobutyl acetate) and measured the LLE data. The IL [Bmim]H\(_2\)PO\(_4\) showed the better extraction performance than the other two ILs. Zhang
et al. [32] selected five imidazolium-based ILs in separation of the azeotrope (ethyl acetate and ethanol) and performed the liquid-liquid extraction experiment. The results showed that the ILs extraction capability decreased with the increase of cationic carbon chain length in separating the azeotrope (ethyl acetate and ethanol).

In this paper, three ionic liquids ([Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$) were adopted in separation of the azeotropic mixture (NBA / NBAC). The LLE data for the three mixtures (NBAC + NBA + [Emim]H$_2$PO$_4$/ [Bmim]H$_2$PO$_4$/ [Hmim]H$_2$PO$_4$) was measured at 298.15 K. The experimental data were fitted by the NRTL thermodynamic model and the coherence of the fitted NRTL parameters was checked using the method proposed by Reyes Labarta [33, 34]. In addition, the influence of the ILs with different cations in separating the azeotropic mixture NBA and NBAC was analyzed and the interactions between the ILs and NBA/NBAC were explored.

2. Experimental

2.1 Chemical reagents

The chemicals NBA and NBAC were analytical grade and purchased commercially. The chemicals were applied directly without purification. The ILs [Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$ were purchased from Lanzhou Zhongke Ketko Industry & Trade Co. Ltd. The ILs [Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$ were dried in a vacuum rotary evaporator with the temperature of 423.2 K before using. The detailed information of the chemicals and the structures of [Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$ is listed in Table 1 and are shown in Fig. 1.
Table 1
The details of the chemical reagents

<table>
<thead>
<tr>
<th>Component</th>
<th>CAS number</th>
<th>Mass fraction</th>
<th>Water content /10^6</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butanol</td>
<td>71-36-3</td>
<td>0.998^a</td>
<td>20.7^b</td>
<td>Chengdu Kelong Chemical Reagent Co., Ltd</td>
</tr>
<tr>
<td>n-butyl acetate</td>
<td>123-86-4</td>
<td>0.998^a</td>
<td>-</td>
<td>Shandong West Asia Chemical Industry Co., Ltd</td>
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<tr>
<td>[Emim]H₂PO₄</td>
<td>262297-14-3</td>
<td>0.990^a</td>
<td>92.4^b</td>
<td>Lanzhou Zhongke Ketko Industry &amp; Trade Co. Ltd</td>
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<tr>
<td>[Bmim]H₂PO₄</td>
<td>478935-31-8</td>
<td>0.990^a</td>
<td>86.0^b</td>
<td>Lanzhou Zhongke Ketko Industry &amp; Trade Co. Ltd</td>
</tr>
<tr>
<td>[Hmim]H₂PO₄</td>
<td>262297-16-5</td>
<td>0.990^a</td>
<td>74.6^b</td>
<td>Lanzhou Zhongke Ketko Industry &amp; Trade Co. Ltd</td>
</tr>
</tbody>
</table>

^a Analyzed by the suppliers.
^b Determined by KLS701 Micro-moisture Meter.

Fig. 1. The structures of ILs: a. [Emim]H₂PO₄; b. [Bmim]H₂PO₄; c. [Hmim]H₂PO₄.

2.2 Apparatus and procedure

The LLE measurement for the three ternary systems (NBAC + NBA + [Emim]H₂PO₄ / [Bmim]H₂PO₄ / [Hmim]H₂PO₄) was carried out at 101.3 kPa and 298.15 K. Detailed apparatus and procedure were exhibited in the past work [35, 36]. For ensuring the two-phase region as large as possible, the IL mass was fixed, the NBA mass decreased and that of NBAC increased to keep the total quality of the ternary system constant. The prepared mixture was discharged into a particular equilibrium device [37] in a water bath with a magnetic stirrer (DF-101S). After that, the mixture was stirred strongly for 4 h and then was settled down for 14 h. After reaching the phase equilibrium state, the samples were withdrawn from the organic layer and IL layer by syringes carefully for analyzing.

2.3 Sample analysis
To analyze the composition of the samples from extraction phase and raffinate phase, GC (Lunan, SP6890) was adopted and the conditions of analysis were listed in Table 2. For analyzing content of the ILs ([Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$), the gravimetric method [38] was adopted. The samples were dried for 14 h in a vacuum drying oven and weighted using an electronic balance (AR124CN).

### Table 2

<table>
<thead>
<tr>
<th>Name</th>
<th>Characteristic</th>
<th>Description</th>
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</thead>
<tbody>
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<td>Specification</td>
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<tr>
<td>Pre-column</td>
<td>Specification</td>
<td>GDX-403(10cm×0.53mm×1.00μm), Zibo Gannuo Instrument Co., Ltd.</td>
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<td>Hydrogen</td>
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<tr>
<td>Carrier gas</td>
<td>Purity</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>Flow rate</td>
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</tr>
<tr>
<td>Injector</td>
<td>Temperature</td>
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</tr>
<tr>
<td>Oven</td>
<td>Temperature</td>
<td>423.15 K</td>
</tr>
<tr>
<td>Detector</td>
<td>Type</td>
<td>Thermal conductivity detector (TCD)</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>443.15 K</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

#### 3.1 LLE experimental data

The determined LLE data for the three mixtures (NBAC + NBA + [Emim]H$_2$PO$_4$), (NBAC + NBA + [Bmim]H$_2$PO$_4$) and (NBAC + NBA + [Hmim]H$_2$PO$_4$) are listed in Table 3, where $x$ denotes mole fraction, II and I represent the down and upper phases. The ternary phase diagrams for the three mixtures are given in Figs. 2-4. As shown in Figs 2-4, the ILs ([Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$) are soluble in NBAC partially and soluble in NBA completely. In the meantime, with decreasing the cationic carbon chain length, the two-phase region increases, which means that the ILs extraction capability decreases with the increase of cationic carbon chain length.
Table 3

LLE Experimental data (x, mole fraction) for the ternary system NBAC (1) + NBA (2) + ILs (3) with partition coefficient (D) and selectivity (S) at \( T = 298.15 \) K and \( p = 101.3 \) kPa.\(^a\)

<table>
<thead>
<tr>
<th>Upper phase</th>
<th>Lower phase</th>
<th>( D )</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
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<td>( x^1 )</td>
<td>( x^2 )</td>
<td>( x^1 )</td>
<td>( x^2 )</td>
</tr>
<tr>
<td>( x^1 )</td>
<td>( x^2 )</td>
<td>( x^1 )</td>
<td>( x^2 )</td>
</tr>
</tbody>
</table>

NBAC (1) + NBA (2) + [Emim]H\(_2\)PO\(_4\) (3)

\[
\begin{align*}
0.4606 & \quad 0.5153 & \quad 0.1483 & \quad 0.6227 & \quad 1.208 & \quad 3.754 \\
0.5183 & \quad 0.4663 & \quad 0.1346 & \quad 0.5963 & \quad 1.278 & \quad 4.924 \\
0.5676 & \quad 0.4235 & \quad 0.1089 & \quad 0.5734 & \quad 1.354 & \quad 7.058 \\
0.6240 & \quad 0.3704 & \quad 0.0996 & \quad 0.5390 & \quad 1.455 & \quad 9.113 \\
0.6606 & \quad 0.3348 & \quad 0.0936 & \quad 0.5130 & \quad 1.532 & \quad 10.81 \\
0.7231 & \quad 0.2750 & \quad 0.0757 & \quad 0.4560 & \quad 1.658 & \quad 15.85 \\
0.7724 & \quad 0.2267 & \quad 0.0662 & \quad 0.4064 & \quad 1.792 & \quad 20.90 \\
0.8344 & \quad 0.1653 & \quad 0.0552 & \quad 0.3278 & \quad 1.983 & \quad 29.96 \\
\end{align*}
\]

NBAC (1) + NBA (2) + [Bmim]H\(_2\)PO\(_4\) (3)

\[
\begin{align*}
0.5818 & \quad 0.3916 & \quad 0.2836 & \quad 0.4798 & \quad 1.225 & \quad 2.513 \\
0.6354 & \quad 0.3502 & \quad 0.2355 & \quad 0.4651 & \quad 1.328 & \quad 3.584 \\
0.6703 & \quad 0.3214 & \quad 0.1896 & \quad 0.4557 & \quad 1.418 & \quad 5.014 \\
0.7148 & \quad 0.2805 & \quad 0.1584 & \quad 0.4251 & \quad 1.515 & \quad 6.838 \\
0.7637 & \quad 0.2328 & \quad 0.1391 & \quad 0.3762 & \quad 1.616 & \quad 8.873 \\
0.7871 & \quad 0.2105 & \quad 0.1216 & \quad 0.3545 & \quad 1.684 & \quad 10.90 \\
0.8251 & \quad 0.1735 & \quad 0.1070 & \quad 0.3127 & \quad 1.802 & \quad 13.89 \\
0.8484 & \quad 0.1509 & \quad 0.1025 & \quad 0.2853 & \quad 1.891 & \quad 15.65 \\
\end{align*}
\]

NBAC (1) + NBA (2) + [Hmim]H\(_2\)PO\(_4\) (3)

\[
\begin{align*}
0.6499 & \quad 0.3170 & \quad 0.3966 & \quad 0.3527 & \quad 1.113 & \quad 1.823 \\
0.6917 & \quad 0.2842 & \quad 0.3615 & \quad 0.3403 & \quad 1.197 & \quad 2.291 \\
0.7276 & \quad 0.2583 & \quad 0.3122 & \quad 0.3352 & \quad 1.298 & \quad 3.024 \\
0.7663 & \quad 0.2249 & \quad 0.2794 & \quad 0.3157 & \quad 1.404 & \quad 3.851 \\
0.7992 & \quad 0.1955 & \quad 0.2456 & \quad 0.2968 & \quad 1.518 & \quad 4.941 \\
0.8342 & \quad 0.1631 & \quad 0.2169 & \quad 0.2669 & \quad 1.636 & \quad 6.290 \\
0.8607 & \quad 0.1384 & \quad 0.1902 & \quad 0.2433 & \quad 1.758 & \quad 7.953 \\
0.8946 & \quad 0.1047 & \quad 0.1699 & \quad 0.2037 & \quad 1.946 & \quad 10.25 \\
\end{align*}
\]

\(^a\) Standard uncertainties \( u \) are \( u(T) = 0.05 \) K, \( u(p) = 0.35 \) kPa, \( u(x) = 0.0056 \)
Fig. 2. Measured LLE data and correlated values by the NRTL model for the ternary mixture NBAC (1) + NBA (2) + [Emim]H$_2$PO$_4$ (3) at 298.15 K: (—■—), experimental data; (—Δ—), correlated value by NRTL model.

Fig. 3. Measured LLE data and correlated values by the NRTL model for the ternary mixture NBAC (1) + NBA (2) + [Bmim]H$_2$PO$_4$ (3) at 298.15 K: (—■—), experimental data; (—Δ—), correlated value by NRTL model.
Fig. 4. Measured LLE data and correlated values by the NRTL model for the ternary mixture NBAC (1) + NBA (2) + [Hmim]H$_2$PO$_4$ (3) at 298.15 K: (— ■ —), experimental data; (—△—), correlated value by NRTL model.

3.2 Partition coefficient ($D$) and selectivity ($S$)

For exploring the extraction ability of the extractants [Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$, partition coefficient ($D$) and selectivity ($S$) were applied. The corresponding formulas are as follows [39]:

$$D = \frac{x_2^p}{x_1^p}$$

(1)

$$S = \frac{(x_2^p/x_2^i)}{(x_1^p/x_1^i)}$$

(2)

where $x$ indicates mole fraction; the superscripts land ll refer to the NBAC-rich phase (upper phase) and the IL-rich phase (lower phase); the subscripts 1 and 2 stand for NBA and NBAC. The values of partition coefficient of NBA and selectivity for the three mixtures are listed in Table 3 and presented in Figs. 5-6, respectively.

As seen from Figs. 5 and 6, the three ILs ([Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$) have the ability in separating the azeotrope NBA and NBAC because the calculated values of selectivity and partition coefficient are all larger than unity. [Emim]H$_2$PO$_4$ has the biggest values of selectivity and partition coefficient, which means that the extraction ability of [Emim]H$_2$PO$_4$ is better than [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$. The ability in separating the azeotrope NBAC and NBA of the three ILs follows the order: [Emim]H$_2$PO$_4$ > [Bmim]H$_2$PO$_4$ > [Hmim]H$_2$PO$_4$, which shows
that the extraction capability of the ILs decreases when the cationic carbon chain length
increases in the separation of the azeotrope NBAC and NBA.

Fig. 5. Partition coefficient ($D$) versus $x_2^j$ for the ternary systems (NBAC + NBA + ILs) at 298.15 K. (■), NBAC + NBA + [Emim]H$_2$PO$_4$; (●), NBAC + NBA + [Bmim]H$_2$PO$_4$ and (▲), NBAC + NBA + [Hmim]H$_2$PO$_4$.

Fig. 6. Selectivity ($S$) versus $x_2^j$ for the ternary systems NBAC + NBA + ILs at 298.15 K. (■), NBAC + NBA + [Emim]H$_2$PO$_4$; (●), NBAC + NBA + [Bmim]H$_2$PO$_4$ and (▲), NBAC + NBA + [Hmim]H$_2$PO$_4$.

3.3 Correlation of LLE data
For correlating and predicting LLE data, the activity coefficient thermodynamic models such as NRTL [40], UNIQUAC [41], UNIFAC [42] and UNIFAC-Lei [43-45] are usually adopted. In this study, the NRTL thermodynamic model [40, 46] was adopted to correlate the LLE experimental values, which is expressed as follows:

\[
\ln \gamma_i = \frac{\sum x_j \Delta g_{ij}}{\Sigma x_i \delta_{ji}} + \sum \frac{x_j \delta_{ij}}{\Sigma x_i \delta_{ji}} \left( \tau_{ij} - \frac{\sum x_k \delta_{kj}}{\Sigma x_i \delta_{ji}} \right) \tag{3}
\]

\[
\tau_{ij} = \frac{\Delta g_{ij}}{RT},
\]

\[
G_{ij} = \exp \left( -\alpha \cdot \tau_{ij} \right)
\]

where subscripts \(i\) and \(j\) represent the component; \(\gamma_i\) refers to the activity coefficient; \(\Delta g_{ij}\) stands for the binary interaction parameter; \(T\) represents the experimental temperature; \(\alpha\) refers to the non-randomness factor.

The objective function was adopted to optimize the NRTL model parameters, which is given as follow:

\[
\text{OF} = \sum_{k}^{M} \sum_{j}^{2} \sum_{i}^{3} \left( x^{\exp}_{ij,k} - x^{\text{cal}}_{ij,k} \right)^2
\]

where \(i\) and \(M\) refer to the component and experimental point; \(x^{\text{cal}}\) and \(x^{\exp}\) are the correlated values and experimental data in mole fraction; \(j\) represents phase, \(k\) stands for tie-line.

Meanwhile, the root mean square deviation (RMSD) [47] was adopted to assess the correlated and is expressed as follow:

\[
\text{RMSD} = \left( \frac{\sum_{k}^{M} \sum_{j}^{2} \sum_{i}^{3} \left( x^{\exp}_{ij,k} - x^{\text{cal}}_{ij,k} \right)^2}{6M} \right)^{1/2}
\]

The RMSD values, the non-randomness factor and the regressed parameters of the NRTL model are listed in Table 4. The measured data were compared with the correlated values and are shown in Figs. 2-4. As given in Table 4, the calculated values of RMSD are no more than 0.009, which means that the NRTL thermodynamic model can be used to fit the LLE data for the three mixtures.

The coherence of the NRTL parameters was examined by the analysis tool GUI-MATLAB provided by Reyes-Labarta [33, 34]. The checked results are presented in
Figs. S1-S18 in the Supplementary Materials. As seen from the figures, the coherent consistency of the regressed NRTL parameters was confirmed.

**Table 4**
The binary interaction parameters of the NRTL model and the calculated values of RMSD for the ternary systems (NBAC + NBA + ILs) at 298.15 K and 101.3 kPa.

<table>
<thead>
<tr>
<th>Interaction parameter</th>
<th>$\Delta g_{ij}$(kJ·mol$^{-1}$)</th>
<th>$\Delta g_{ji}$(kJ·mol$^{-1}$)</th>
<th>$\alpha$</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBAC (1) + NBA (2) + [Emim]$\text{H}_2\text{PO}_4$ (3)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>108.203</td>
<td>-54.228</td>
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<td></td>
</tr>
<tr>
<td>1-3</td>
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<td>755.142</td>
<td>0.2</td>
<td>0.0023</td>
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<tr>
<td>2-3</td>
<td>1110.606</td>
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<td></td>
</tr>
<tr>
<td>NBAC (1) + NBA (2) + [Bmim]$\text{H}_2\text{PO}_4$ (3)</td>
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<tr>
<td>1-2</td>
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3.4 Calculation of hydrogen bond length and interaction energy

The intermolecular interaction between NBAC, NBA and ILs was explored by use the Dmol$^3$ in Material Studio. The detailed information for the calculation was presented in the previous work [48, 49]. Firstly, the structures of NBAC, NBA and ILs were plotted. Then, the “Geometry Optimization” calculation was performed and the optimized structures of NBAC, NBA and ILs were obtained. Then, NBAC and NBA were put together with the ILs ([Emim]$\text{H}_2\text{PO}_4$, [Bmim]$\text{H}_2\text{PO}_4$ and [Hmim]$\text{H}_2\text{PO}_4$) to calculate the hydrogen bond lengths, respectively. In the meantime, the value of “Cutoff Global” was set as “5.5000 angstrom”. To get the interaction energies between NBAC/NBA and the ILs ([Emim]$\text{H}_2\text{PO}_4$, [Bmim]$\text{H}_2\text{PO}_4$ and [Hmim]$\text{H}_2\text{PO}_4$), the calculation of “Energy” was carried out and the “Calculate Basis Set Superposition Error (BSSE) correction” was selected. To avoid the BSSE and ensure the calculation accuracy of interaction energy, the counterpoise correction method [50] was adopted, which was expressed as follows:

$$\Delta E_{interaction} = E_{AB} - E_A - E_B + E_{BSSE}$$ (6)
\[ E_{BSSE} = E_A - E_{(AAB)} + E_B - E_{(B,AB)} \]  
(7)

where \( E_A \) is the energy of A (A basis set), \( E_B \) stands for the energy of B (B basis set), \( E_{AB} \) denotes the energy of the complex of AB (A, B basis set), \( E_{(AAB)} \), refer to the energy of A and B (A basis set), and \( E_{(B,AB)} \), represents the energy of A and B (B basis set), respectively.

The calculated values of the hydrogen bond lengths between the ILs and NBA and the interaction energies are plotted in Fig. 7 and are given in Table 5.

\[
\begin{array}{c|c|c}
\text{System} & E/(kJ\cdot mol) & \Delta E/(kJ\cdot mol) \\
\hline
\text{NBA} & -613735.679 & - \\
\text{NBAC} & -1014721.877 & - \\
\text{[Emim]H}_2\text{PO}_4 & -2595838.436 & - \\
\text{[Bmim]H}_2\text{PO}_4 & -2802346.692 & - \\
\text{[Hmim]H}_2\text{PO}_4 & -3008838.589 & - \\
\text{[Emim]H}_2\text{PO}_4 + \text{NBA} & -3209625.297 & -48.681 \\
\text{[Emim]H}_2\text{PO}_4 + \text{NBAC} & -3610512.761 & -25.115 \\
\text{[Bmim]H}_2\text{PO}_4 + \text{NBA} & -3416136.758 & -47.453 \\
\text{[Bmim]H}_2\text{PO}_4 + \text{NBAC} & -3817004.639 & -44.212 \\
\text{[Hmim]H}_2\text{PO}_4 + \text{NBA} & -3622625.341 & -40.956 \\
\text{[Hmim]H}_2\text{PO}_4 + \text{NBAC} & -3761144.160 & -38.877 \\
\end{array}
\]

As seen from Fig. 7, the bond length between [Emim]H\(_2\)PO\(_4\) and NBA is 1.737 Å, the bond length between [Bmim]H\(_2\)PO\(_4\) and NBA is 1.762 Å, and the bond length between [Hmim]H\(_2\)PO\(_4\) and NBA is 1.768 Å. Compared to the calculated results, the hydrogen bond length between [Emim]H\(_2\)PO\(_4\) and NBA is the shortest, which indicates
that [Emim]H$_2$PO$_4$ has the best extract ability in separating NBA and NBAC. With the increase of cationic carbon chain length, the hydrogen bond length between NBA and ILs increases. As listed in Table 5, the interaction energy between [Emim]H$_2$PO$_4$ and NBA is -48.681 kJ·mol$^{-1}$, the interaction energy between [Bmim]H$_2$PO$_4$ and NBA is -47.453 kJ·mol$^{-1}$ and that between [Hmim]H$_2$PO$_4$ and NBA is -40.956 kJ·mol$^{-1}$. The interaction energy between NBA and ILs reduces when the cationic carbon chain length increases. Thus, [Emim]H$_2$PO$_4$ can be considered as the most suitable extractant compared to the other two ILs [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$.

4. Conclusion

In this work, liquid-liquid extraction was adopted to separate the azeotropic mixture NBA and NBAC using the ILs [Emim]H$_2$PO$_4$, [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$. The LLE data for the three mixtures (NBAC + NBA + [Emim]H$_2$PO$_4$ / [Bmim]H$_2$PO$_4$ / [Hmim]H$_2$PO$_4$) were determined at 298.15 K. The partition coefficient and selectivity were calculated for the three ILs, which increased with decreasing the cationic carbon chain length. The NRTL model was used to fit the measured data with the RMSD less than 0.009 and the coherent consistency of the regressed parameters of the NRTL model was checked. The results showed that [Emim]H$_2$PO$_4$ had the largest interaction energy and the least hydrogen bond length with NBA among the three ILs, which demonstrates that [Emim]H$_2$PO$_4$ is a more suitable extractant for separating the mixture NBA and NBAC than [Bmim]H$_2$PO$_4$ and [Hmim]H$_2$PO$_4$.

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Note

The authors declare no competing financial interest.
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Author Contribution Statement

Liquid-liquid Equilibrium Measurements and Interaction Explorations for
Separation of Azeotrope n-Butyl acetate and n-Butanol Using Three Ionic Liquids

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Highlights

1. Three ionic liquids were adopted to separate the azeotrope NBAC and NBA.
2. The LLE data for NBAC + NBA + ILs were measured and correlated by the NRTL model.
3. The interaction was explored by hydrogen bond length and interaction energy.
4. The influence of the carbon chain length of cations on phase behavior was explored.