Liquid—Liquid Equilibrium of Ternary Systems of Cyclohexane + (Benzene, + Toluene, + Ethylbenzene, or + o-Xylene) + 4-Methyl-N-butyl Pyridinium Tetrafluoroborate Ionic Liquid at 303.15 K

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Liquid—liquid equilibrium data are critical for designing the extraction equipment or calculating the thermodynamic limit of a given separation. In this work, the LLE data were measured for the cyclohexane + (benzene, + toluene, + ethylbenzene, or + o-xylene) + 4-methyl-N-butyl pyridinium tetrafluoroborate ([bmpy]BF₄) systems at 303.15 K under atmospheric pressure. The consistency of the measured LLE data was tested using the Othmer—Tobias correlation and the root-mean-square deviation (rmsd) in the mass fraction of [bmpy]BF₄ in the lower phase and the average value of the absolute difference (AAD) between experimental mass fraction of cyclohexane in the upper phase and that calculated using the Othmer—Tobias correlation.

Introduction

Ionic liquids find a wide range of applications in the chemical separation industry, water and wastewater treatment, and environmental protection. Ionic liquids are organic salts, with negligible vapor pressure, have high thermal stability, with a wide temperature range for the liquid phase, and properties adapted by changing cations and/or anions.

Extraction of aromatics from refinery products such as naphtha, kerosene, and fuel jets has a potential of commercial importance in the oil refining industry. There are several solvents used for the extraction of aromatics including sulfolanes, glycols, ionic liquids, and/or combinations of solvents to balance selectivity and solvency. A list of references on these methods is found elsewhere.¹

Because of their nonvolatile nature, the application of ionic liquids for separation processes is promising. This facilitates solvent (i.e., ionic liquid) recovery using techniques as simple as flash distillation or stripping of the organic phase. They also have other interesting properties, such as high thermal and chemical stability or nonflammability, which enhances their utility.²⁻⁴ However, the use of ionic liquids also has some disadvantages: the physical properties are not always known, their viscosity is usually higher than common solvents, and their chemical stability or nonflammability, which enhances their utility.²⁻⁴ However, the use of ionic liquids also has some disadvantages: the physical properties are not always known, their viscosity is usually higher than common solvents, and their toxicity is unknown. For a successful application of ionic liquids in industrial processes, these aspects must be taken into consideration.⁵ The initial cost of ionic liquids may be relatively high, but since they are nonvolatile compounds and can be easily recovered, only the processing costs are the most important costs to think about. For example, Meindersma et al.⁶ found that preliminary calculations show that both the investment costs and the energy costs will be considerably lower with ionic liquids than with sulfolane as the solvent.

Accurate liquid—liquid equilibrium data are one of the main prerequisites for the design and evaluation of industrial extraction processes. Liquid—liquid equilibrium data are also needed to evaluate the accuracies of prediction of thermodynamic models or to develop new ones. Most of the papers published about ionic liquids and their use as solvents for extraction purposes investigate the solubility or the distribution coefficient of different chemicals [see citations in ref 2]. The reported phase behavior or liquid—liquid equilibrium (LLE) data for ternary mixtures are very limited.⁷⁻¹⁴

The γᵢᵣ are important to predict the possibility of using a solvent in the extractive distillation processes. Diedenhofen et al.¹⁵ used a general and fast method (COSMO-RS) for the prediction of the activity coefficients at infinite dilution (ln γᵢᵣ) for 38 organic solutes in several ionic liquids (including 4-methyl-N-butylpyridinium tetrafluoroborate, [bmpy]BF₄) at (314 and 344) K. The experimental values used there were taken from the literature.¹⁶,¹⁷ Eike¹⁸ used statistical analysis and molecular simulation (QSPR method) to estimate γᵢᵣ values for organic solutes in three ionic liquids (including the [bmpy][BF₄] used in this work) at 298 K. Other methods for the estimation of the activity coefficients at infinite dilution can also be used such as NRTL, Wilson equations, etc.

In this work, the LLE data will be measured for the cyclohexane + (benzene, + toluene, + ethylbenzene, or + o-xylene) + 4-methyl-N-butyl pyridinium tetrafluoroborate ([bmpy][BF₄]) systems at 303.15 K under atmospheric pressure. The consistency of the measured LLE data will be tested, and the affinity of these solutes to the [bmpy][BF₄] solvent will be examined.

Experimental Section

The ionic liquid, 4-methyl-N-butyl pyridinium tetrafluoroborate, [bmpy]BF₄, was supplied by IoLiTec (Germany) with a quoted mass fraction purity of > 0.995, bromide mass fraction < 1·10⁻⁴, and water mass fraction < 1·10⁻⁴. No further purification was applied on the ionic liquid. Benzene, toluene, ethylbenzene, and o-xylene were supplied by BDH with stated mass fractions of > 0.99 (< 0.001 H₂O), > 0.995 (< 0.0003 H₂O), > 0.99, and > 0.981 (no H₂O), respectively, and cyclohexane by Riedel-DeHaen with a stated mass fraction of > 0.995 (< 0.0001 H₂O). All materials were used as received without any further purification. All chemicals used for this
The oven temperature was programmed as follows: the initial pressure of the carrier nitrogen gas was set to 40 kPa for benzene- and toluene-, ethylbenzene-, and (383.15, 393.15, and 405.15) K was attained for benzene-, cyclohexane-rich layer [bmpy]BF₄-rich layer density values than refractive indices. Also, because of the negligible thumbwheel of the pipet pump can be rotated up and down to 0.1 K. The temperature in the jacket was measured with a mercury-in-glass thermometer that was set to 10 K. The equilibrium temperature was measured with a tightly closed, jacketed equilibrium cell with 100 mL volume. The temperature was measured with a mercury-in-glass thermometer with an uncertainty of ± 0.1 K. The temperature in the jacket of the cell was kept constant by circulating water from a water bath (Julabo Labortechnik GmbH Germany) equipped with a temperature controller (Julabo PC) capable of maintaining the temperature at a fixed value (within ± 0.1 K). The equilibrium cell was cleaned and dried. A mixture with known compositions of the above-mentioned compounds was fed to the cell, followed by mixing for 2 h, and then left for 6 h without mixing to equilibrate and settle down into a lower layer ([bmpy]BF₄-rich phase) and an upper layer (cyclohexane-rich phase). Samples from both layers were taken and analyzed using a gas chromatograph (Chrompack CP 9001) with a flame ionization detector (FID).

Chromatographic separation of the mixture constituents was achieved using a 50 m long × 0.32 mm I.D. WCOT (wall-coated-open-tube) fused silica capillary column coated with a 1.2 µm stationary phase (CP-Sil 5CB). The inlet gauge pressure of the carrier nitrogen gas was set to 40 kPa for benzene- and toluene-containing systems and to 45 kPa for ethylbenzene- and o-xylene-containing systems. The temperatures of the detector and the injector were set to (573.15 and 548.15) K, respectively. The oven temperature was programmed as follows: the initial temperature was set to 343.15 K for 2 min followed by a constant heating rate of 5 K min⁻¹ until a final temperature of (383.15, 393.15, and 405.15) K was attained for benzene-, toluene-, ethylbenzene-, and o-xylene-containing systems, respectively. The final temperature was kept for 8 min, and then the cycle was repeated. Mixtures of known concentrations of reagents were used to calibrate the gas chromatograph.

Another essential measurement for theionic liquid system was carried out for all samples using a calibrated portable density meter (Kem, model DA-130 N, Japan) with an uncertainty of 1.0 high precision of measuring densities than refractive indices. Also, because of the negligible volatility of ionic liquids, gas—liquid chromatography cannot be used for their detection. The reproducibility of the density measurements is clear when one compares the reported density data for the first tie line in Tables 1 to 4 when the aromatic mass fraction was 0.0 (relative error was less than 0.4 %). The uncertainty in all density measurements was within ± 0.5 %. After the completion of each equilibrium test, a 15 mL sample was taken from the top of the equilibrium cell for each liquid layer (phase) using a safe and accurate dry clean pipet fitted with a Pipette Pump (from Sigma-Aldrich Labware). The thimbewheel of the pipet pump can be rotated up and down to get precise control of filling or dispensing. All the samples were stored in cap-sealed vials till further analysis. The caps of these vials are made of special polymers that ensure an absolute seal.

An amount of 2 mL was used for the GC analysis and the rest
for the density measurement. Air flow through the pipet tip was used to prevent the contamination of the lower layer sample by the upper layer. When no more bubbles were present, the sample was carefully taken from the bottom layer and the pipet slowly pulled up. The pipet was then carefully wiped with a dry clean cloth.

For the GC analysis, the 2 mL sample was poured into a 25 mL flask. The pipet used was washed with acetone in the flask. An amount of 3 mL of the internal standard, dissolved in acetone, was added to the flask, and the volume of the solution in the flask was completed to 25 mL by adding more acetone. This means a dilution factor of 12.5 was used for each sample. The acetone was used here to keep a homogeneous one-layer solution in the flask. The GC measurements were carried out in triplicates or more. The averages of these measurements were used in the reported data. The uncertainty in the GC measurements was estimated at ± 1.5 %.

The concentration of the ionic liquid (g per 100 mL) was taken as the difference between the measured liquid density of the phase (g per 100 mL) and the sum of the GC measured mass concentrations of the hydrocarbon species (g per 100 mL). If the calculated difference was negative, the concentration of the [bmpy]BF₄ for that sample was set equal to zero. Mass fraction measurements were reproducible to within ± 0.1 %. The average of the absolute relative deviation in mass concentration measurements was less than 1.0 % for the hydrocarbon components. The material balance was checked from the sum of the product of the measured volume and density of each phase in the cell and compared with the sum of the initial masses of the three components used to constitute the LLE data. The greatest error in the material balance in the above experiments was found to be less than 1.0 % in most cases.

Again, since the ionic liquid was nonvolatile, some deposition of the ionic liquid was noticed on the injector of the GC, but the column suffered less deposition. To ensure more accurate
analysis, frequently the injector was cleaned and the possibly contaminated part of the column was cut (by up to 1 m length). It should also be mentioned that in all density measurements the excess volume of mixing was assumed negligible.

Results and Discussion

The experimental liquid—liquid equilibrium data for the ternary systems cyclohexane + (benzene, + toluene, + ethylbenzene, or + -xylene) + [bmpy]BF₄ systems at 303.15 K under atmospheric pressure are shown in Tables 1 to 4, and their corresponding LLE molar compositions are presented in Figures 1 to 4. The reliability of the experimental data can be ascertained by applying the well-known Othmer—Tobias correlation¹⁹ at the test temperature.

\[
\ln \left( \frac{1 - w_3}{w_3} \right) = \ln a + b \ln \left( \frac{1 - w_1^\infty}{w_1^\infty} \right) \tag{1}
\]

where \(w_1^\infty\) is the mass fraction of cyclohexane in the upper (cyclohexane-rich) phase; \(w_3^1\) is the mass fraction of the ionic liquid [bmpy]BF₄ in the lower ([bmpy]BF₄-rich) phase; and \(a\) and \(b\) are constants of eq 1. The linearity of the plot indicates the degree of consistency of data. The constants of Othmer—Tobias correlation are shown in Table 5. Table 5 also shows the root-mean-square deviation (rmsd) between experimental data and the corresponding ln \(\gamma_i^\infty\) values at 303.15 K.

It is obviously impossible to measure all possible equilibrium compositions because there are infinitely many of them. Therefore, only a finite set of these compositions can be measured, and thermodynamic models such as UNIFAC and NRTL can be used to provide estimates for the full range of concentrations that can be used to generate the binodal curve and, eventually, the plait point at the inflection point of the curve.

For binary systems, the infinite dilution limiting behavior is important because it represents the case where the solute (the infinitely dilute species) interacts only with solvent molecules, so \(\gamma_i^\infty\) directly reflects the strength of interaction between the two species. Stronger interactions between the solute and the solvent give activity coefficients less than one, and vice versa. Using available activity coefficients at infinite dilution, \(\gamma_i^\infty\), at (298, 314, and 344) K,¹⁵,¹⁸ the best fit of ln \(\gamma_i^\infty\) vs temperature for the studied organic solutes in [bmpy]BF₄ was found to be a second-order polynomial of the form ln \(\gamma_i^\infty\) = \(a(T/K)^2 + bT/K + c\). The fitting parameters for these systems are given in Table 6 along with the estimated values of ln \(\gamma_i^\infty\) at 303.15 K. The data presented in Table 6 show that the interaction between the solutes and the [bmpy]BF₄ ionic liquid decreases in the following order: benzene (highest), toluene, ethylbenzene, -xylene, then cyclohexane (lowest).

The % removal of the studied aromatics (benzene, toluene, and ethylbenzene) using sulfolane²⁰ (M.W. = 120) in comparison with [bmpy]BF₄ ionic liquid (M.W. = 237) presented in this work is shown in Table 7. The % removal was expressed as 100(amount of aromatic extracted by the liquid divided by the total amount of the aromatic in the two phases). The % removals presented in Table 7 also indicate that the affinity of the solvent toward the solutes is highest for benzene and lowest for -xylene followed by ethylbenzene. That is, as the number of the side chain increases, the extraction tendency of the studied aromatics by the [bmpy]BF₄ ionic liquid decreases.

Table 7 also shows the sulfolane/[bmpy]BF₄ molar removal ratios, 0.92, 0.92, and 1.11, for benzene, toluene, and ethylbenzene, respectively, while the corresponding sulfolane/[bmpy]BF₄ molar removal ratio was 1.35, 1.41, and 1.83. This means that the separation of these aromatics using sulfolane is better than that using the [bmpy]BF₄ ionic liquid at the studied conditions. Based on molar selectivity and molar distribution coefficients (see ref 21 for definitions), Meidensma et al.² and Meidensma²¹ concluded that the ionic liquid [bmpy]BF₄ is a suitable solvent to replace sulfolane for industrial extraction processes for the separation of aromatic and aliphatic hydrocarbons. The authors believe that this is only true if the comparison is made on a molar basis but not on a mass basis.

Conclusion

In this work, the liquid—liquid equilibrium data for the four ternary systems comprising cyclohexane (+ benzene, + toluene, + ethylbenzene, or + -xylene) + 4-methyl-N-butyl pyridinium tetrafluoroborate ([bmpy]BF₄) were measured at 303.15 K under

### Table 5. Correlated Othmer—Tobias Coefficients, rmsd, and AAD for the Studied Systems (See Equation 1)

<table>
<thead>
<tr>
<th>system</th>
<th>a</th>
<th>b</th>
<th>rmsd</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane + benzene + [bmpy]BF₄</td>
<td>0.6843</td>
<td>1.5931</td>
<td>0.0295</td>
<td>0.0176</td>
</tr>
<tr>
<td>cyclohexane + toluene + [bmpy]BF₄</td>
<td>5.4064</td>
<td>2.2074</td>
<td>0.0108</td>
<td>0.0073</td>
</tr>
<tr>
<td>cyclohexane + ethylbenzene + [bmpy]BF₄</td>
<td>0.4326</td>
<td>2.7534</td>
<td>0.0053</td>
<td>0.0046</td>
</tr>
<tr>
<td>cyclohexane + o-xylene + [bmpy]BF₄</td>
<td>0.5556</td>
<td>2.4878</td>
<td>0.0173</td>
<td>0.0104</td>
</tr>
</tbody>
</table>

### Table 6. Coefficients of the Second-Order Polynomial Used to Fit ln \(\gamma_i^\infty\) of Individual Solutes in [bmpy]BF₄ and the Corresponding ln \(\gamma_i^\infty\) Values at 303.15 K

<table>
<thead>
<tr>
<th>solute</th>
<th>(10^4) a</th>
<th>(10^4) b</th>
<th>(10^{-4}) c</th>
<th>(\ln \gamma_i^\infty) at 303 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>3.8193</td>
<td>-0.2588</td>
<td>46.977</td>
<td>3.6211</td>
</tr>
<tr>
<td>benzene</td>
<td>-0.7817</td>
<td>0.0517</td>
<td>-8.033</td>
<td>0.4560</td>
</tr>
<tr>
<td>toluene</td>
<td>1.2690</td>
<td>-0.0828</td>
<td>14.456</td>
<td>1.0173</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>-1.3836</td>
<td>0.0905</td>
<td>-13.218</td>
<td>1.5018</td>
</tr>
<tr>
<td>o-xylene</td>
<td>5.4389</td>
<td>-0.3572</td>
<td>59.833</td>
<td>1.5313</td>
</tr>
</tbody>
</table>

### Table 7. Average % Removal of Aromatics by Sulfolane and [bmpy]BF₄ at 303.15 K

<table>
<thead>
<tr>
<th>solute/solvent</th>
<th>benzene</th>
<th>toluene</th>
<th>ethylbenzene</th>
<th>o-xylene</th>
<th>benzene</th>
<th>toluene</th>
<th>ethylbenzene</th>
<th>o-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>mole basis</td>
<td>39.49</td>
<td>30.16</td>
<td>22.95</td>
<td>-</td>
<td>34.45</td>
<td>24.49</td>
<td>18.56</td>
<td>-</td>
</tr>
<tr>
<td>mass basis</td>
<td>43.05</td>
<td>32.61</td>
<td>20.61</td>
<td>25.89</td>
<td>25.58</td>
<td>17.44</td>
<td>10.14</td>
<td>13.42</td>
</tr>
<tr>
<td>[bmpy]BF₄</td>
<td>39.49</td>
<td>30.16</td>
<td>22.95</td>
<td>-</td>
<td>34.45</td>
<td>24.49</td>
<td>18.56</td>
<td>-</td>
</tr>
<tr>
<td>sulfolane/[bmpy]BF₄ removal ratio</td>
<td>0.92</td>
<td>0.92</td>
<td>1.11</td>
<td>-</td>
<td>1.35</td>
<td>1.41</td>
<td>1.83</td>
<td>-</td>
</tr>
</tbody>
</table>
atmospheric pressure. The consistency of the LLE data was proved by the linearity of the Othmer—Tobias plots and the small values of the rmsd in the mass fraction of [bmipy]BF$_4$ in the lower phase (0.0053 to 0.0295) and the corresponding average value of the absolute difference (AAD) between experimental mass fraction of cyclohexane, w$_1$, in the upper phase and that calculated using the Othmer—Tobias correlation (0.0046 to 0.0176) for the four ternary systems studied. On the basis of the mass percent removal of the studied aromatics, using sulfolane as the extracting solvent is better than using the [bmipy]BF$_4$ ionic liquid at the studied conditions.

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**Literature Cited**


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