JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

# Extraction of Benzene from Aliphatic Compounds Using Commercial Ionic Liquids as Solvents: Study of the Liquid−Liquid Equilibrium at $T$ = 298.15 K

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Ⓢ *Supporting Information*

**ABSTRACT:** In this paper, the liquid extraction of benzene from aliphatic compounds (heptane, octane, cyclooctane, and methylcyclohexane) using commercial ionic liquids (ILs; 1-propyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide, [PMim][$NTf_2$], and 1-butyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide, [BMim][$NTf_2$]) as solvents was studied. The liquid−liquid equilibrium (LLE) data for five ternary systems (aliphatic compound + benzene + IL) are reported at $T$ = 298.15 K and atmospheric pressure. The cloud point method was used to determine the solubility curves, and the tie-line compositions were obtained by density measurements. From the experimental LLE data, the selectivity and the solute distribution ratio were calculated. The degree of consistency of the tie-lines was tested using the Othmer−Tobias equation, and the experimental LLE data were correlated using nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) thermodynamic models. Moreover, a systematic study about the influence of the size of the aliphatic and IL on the aromatic extraction was carried out.

## ■ INTRODUCTION

Aromatic compounds are obtained almost exclusively from naphtha, where they are combined with other hydrocarbons, mainly aliphatic and naphthenic compounds. Since these compounds have close boiling points and in some cases they form azeotropic mixtures, conventional distillation is not suitable, and the liquid extraction is the recommended technique to perform these separations.

The extraction of aromatic from aliphatic compounds using organic compounds as solvents, for example, sulfolane[1−3] or glycols,[4,5] is widely studied and offers high yields with a reduced energy cost. However, this separation process presents an important disadvantage because these organic solvents are generally toxic, flammable, and difficult to recover. For this reason, it is advisable to develop new solvents that allow an effective separation and cause less damage to the environment.

Since ionic liquids (ILs) present a negligible vapor pressure at moderate temperature and pressure and their recovery is easier, in the last years these compounds have received great attention among academics and researchers. Among other many applications in the field of the separation processes,[6] these liquid salts were suggested as possible substitutes to the traditional organic solvents for “clean” liquid extraction.[7]

To understand the role of ILs as solvents in this kind of separation, the knowledge of the liquid−liquid equilibrium (LLE) is very necessary. As reflected in a recent review published by Meindersma et al.,[8] several authors are interested in this line of investigation, and they have published LLE data for ternary systems aliphatic compound + aromatic compound + IL,[9−19] obtaining quite satisfactory results.

This work is a continuation of our research on the extraction of benzene from different aliphatic/aromatic mixtures using ILs as solvents. In previous papers,[20−29] the extraction of benzene from aliphatic compounds using ILs containing alkylsulfate anions as solvent were tested, and since the results were satisfactory, now the research is expanded to the separation of benzene and aliphatic compounds using imidazolium-based ILs containing the bis{trifluoromethylsulfonyl}imide anion.

In this work, LLE data for the ternary systems (aliphatic compound (1) + benzene (2) + IL (3)) were determined at 298.15 K and atmospheric pressure. The aliphatic compounds used in this work were heptane, octane, cyclooctane, and methylcyclohexane, and the ILs studied were 1-propyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide, [PMim][$NTf_2$], and 1-butyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide, [BMim][$NTf_2$]. The reliability of the experimentally measured LLE data was tested by the Othmer−Tobias[30] equation. From the tie-line compositions, the selectivity and the solute distribution ratio were calculated. Moreover, comparing the five studied systems, an analysis about the effect of the size and structure of the aliphatic compound and the IL on the extraction was carried out. Finally, the nonrandom two-liquid (NRTL)[31] and universal quasichemical (UNIQUAC)[32] thermodynamic models were employed to correlate the experimental LLE data.

## ■ EXPERIMENTAL SECTION

**Chemicals.** Heptane and octane were supplied by Fluka with a purity higher than 99.5 %, by mass, and benzene, cyclooctane,

**Received:** April 5, 2011
**Accepted:** July 10, 2011
**Published:** July 22, 2011

**Table 1. Density ($\rho$) and Refractive Index ($n_D$) of Pure Components at $T$ = 298.15 K**

| | $\rho/(\text{g}\cdot\text{cm}^{-3})$ | | $n_D$ | |
|---|---|---|---|---|
| component | exp. | lit. | exp. | lit. |
| $[\text{PMim}][\text{NTf}_2]$ | 1.47444 | 1.47570[a] | 1.42525 | n.a. |
| $[\text{BMim}][\text{NTf}_2]$ | 1.43635 | 1.43658[b] | 1.42706 | 1.42692[b] |
| benzene | 0.87357 | 0.87360[c] | 1.49774 | 1.49792[c] |
| heptane | 0.67956 | 0.67946[c] | 1.38515 | 1.38511[c] |
| octane | 0.69860 | 0.69862[c] | 1.39519 | 1.39505[c] |
| methylcyclohexane | 0.76502 | 0.76506[c] | 1.42062 | 1.42058[c] |
| cyclooctane | 0.83147 | 0.83151[d] | 1.45598 | 1.4560[e] |

[a] From ref 33. [b] From ref 34. [c] From ref 35. [d] From ref 36. [e] From ref 37.

and methylcylcohexane were purchased from Sigma-Aldrich with purities higher than 99.9 %, 99.9 %, and 99.0 %, respectively. Alkanes were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere to avoid moisture.

$[\text{PMim}][\text{NTf}_2]$ and $[\text{BMim}][\text{NTf}_2]$ ILs were selected to study the influence of the alkyl chain length of the cation in the LLE, and both compounds were supplied by Iolitec with purity higher than 99.0 %, by mass. The water content, $w_w$, and halide content, $w_{\text{halide}}$, for these ILs were certificated by the company, and their values are $w_w$ = 90 ppm and $w_{\text{halide}}$ < 100 ppm for $[\text{PMim}][\text{NTf}_2]$ and $w_w$ = 10 ppm and $w_{\text{halide}}$ = 90 ppm for $[\text{BMim}][\text{NTf}_2]$, respectively.

To reduce the water content and volatile compounds to negligible values, prior to their use, both ILs were subjected to vacuum ($p$/Pa = 0.2) at moderate temperature ($T$/K = 323.15) until the density value was constant, indicating that all volatile compounds were removed from the sample.

The physical properties (density and refractive index) of the pure components and available literature data[33−37] at 298.15 K are listed in Table 1. The small differences between experimental and literature data may be due to the presence of water or nonvolatile impurities in our samples or their samples.

**Apparatus and Procedure.** For the preparation of samples, a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3\cdot10^{-4}$ g was used. The density of the pure liquids and their mixtures was measured using an Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of $\pm 3\cdot10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$. The refractive indices of pure components were measured using an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm 4\cdot10^{-5}$. The combined expanded uncertainties ($k$ = 2) for density and refractive index are $\pm 5\cdot10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$ and $\pm 8\cdot10^{-5}$, respectively.

The experimental LLE were determined at $T$ = 298.15 K and atmospheric pressure, and the procedure includes obtaining the solubility curves and the tie-lines. The solubility curves were obtained by titrating binary mixtures of known compositions with the third component until a transition in the samples was obtained. Then, the density of each sample was measured, and a polynomial expression for the density as a function of the composition of two components was obtained, since the material balance must be satisfied and the composition of the third component can be written in terms of the other two. Taking into account that each point of the solubility curve shows a different density value, one property is enough to determine the composition of the IL-rich phase. To estimate the error of the technique used for the determination of these curves, several validation points of known composition were prepared by weighing, their densities were measured, and from these values, their compositions were calculated using the above-mentioned polynomial expression. Comparing the experimental and calculated compositions of these validation points, the maximum error was estimated to be ± 0.008 in mole fraction.

For the tie-line determination, mixtures of known compositions inside the immiscible region were introduced into glass cells, closed, stirred for 6 h, and left overnight to settle down. The temperature was maintained constant in a PoliScience thermostatic bath with a precision of ± 0.01 K, and the temperature of the samples was controlled using a digital thermometer ASL model F200 with an uncertainty of ± 0.01 K. Once equilibrium is reached, one sample of each phase was withdrawn with a syringe, and its density was measured to determine the composition of the conjugated phases. The analysis of both phases was carried out by correlating the densities of the two immiscible liquid phases with the polynomial expressions of density versus composition. Regarding to the composition of the alkane-rich phase, it is important to comment that, as the IL is immiscible in the pure studied hydrocarbons (aliphatic compounds and benzene) and also in whole composition range of the binary mixtures (aliphatic + benzene), the presence of IL in the raffinate was assumed zero, and the composition of this phase was determined using the values of density versus molar fraction for the binary systems (aliphatic compound (1) + benzene (2)), previously published.[38,39]

## RESULTS AND DISCUSSION

The compositions of the solubility curves for the five studied systems (aliphatic compound (1) + benzene (2) + IL (3)) at 298.15 K and the corresponding validation points are given in Table S1 and Table S2, available in Supporting Information (SI). From these composition data, the solubility of the studied hydrocarbons in $[\text{BMim}][\text{NTf}_2]$ and $[\text{PMim}][\text{NTf}_2]$ ILs was analyzed. The first value of the composition of aliphatic compound ($x_1$) for each system, shown in Table S1 of the SI, represents the solubility of each hydrocarbon in the studied ILs. Comparing these values for the five studied systems, it can be concluded that the solubility of the studied aliphatic compounds in $[\text{BMim}][\text{NTf}_2]$ decreases in the order methylcyclohexane > cyclooctane > heptane > octane. Comparing the solubility values for the pairs heptane/octane ($x_1 = 0.065/x_1 = 0.043$), methylcyclohexane/cyclooctane ($x_1 = 0.130/x_1 = 0.071$), and cyclooctane/octane ($x_1 = 0.071/x_1 = 0.043$), it is possible to conclude that an increase in the molecular mass of the alkane, linear or cyclic, results in a decrease of the solubility of these compounds in $[\text{BMim}][\text{NTf}_2]$. According to this behavior, the cycloalkane (cyclooctane) is more soluble than the linear alkane with the same number of carbons (octane). Moreover, taking into account the solubility values for methylcyclohexane in $[\text{PMim}][\text{NTf}_2]$ and $[\text{BMim}][\text{NTf}_2]$, whose values are $x_1 = 0.099$ and $x_1 = 0.130$, respectively, the results indicate that this hydrocarbon is slightly more soluble in the IL containing a larger alkyl chain. Similar results were obtained by Arce et al.[10] and García et al.[12] in their study about the effect of the alkyl-substituent length on the extraction of aromatic compounds from its binary mixtures with alkanes using 1-alkyl-3-methylimidazolium bis{trifluoromethylsulfonyl}amide ILs as solvents.

**Table 2. Experimental Liquid–Liquid Equilibrium Data in Mole Fraction for Ternary Systems Aliphatic Compound (1) + Benzene (2) + IL (3) at $T$ = 298.15 K, Solute Distribution Ratio, $\beta$, and Selectivity, $S$, Values**

| upper phase | | lower phase | | | |
|---|---|---|---|---|---|
| $x_1^{\mathrm{I}}$ | $x_2^{\mathrm{I}}$ | $x_1^{\mathrm{II}}$ | $x_2^{\mathrm{II}}$ | $\beta$ | $S$ |
| Heptane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | | |
| 1.000 | 0.000 | 0.065 | 0.000 | - | - |
| 0.957 | 0.043 | 0.059 | 0.074 | 1.72 | 27.91 |
| 0.916 | 0.084 | 0.059 | 0.143 | 1.70 | 26.43 |
| 0.866 | 0.134 | 0.058 | 0.214 | 1.60 | 23.85 |
| 0.825 | 0.175 | 0.056 | 0.263 | 1.50 | 22.14 |
| 0.777 | 0.223 | 0.055 | 0.321 | 1.44 | 20.34 |
| 0.732 | 0.268 | 0.054 | 0.367 | 1.37 | 18.56 |
| 0.633 | 0.367 | 0.052 | 0.453 | 1.23 | 15.03 |
| 0.526 | 0.474 | 0.052 | 0.530 | 1.12 | 11.31 |
| 0.404 | 0.596 | 0.054 | 0.592 | 0.99 | 7.43 |
| 0.270 | 0.730 | 0.047 | 0.665 | 0.91 | 5.23 |
| 0.165 | 0.835 | 0.036 | 0.719 | 0.86 | 3.95 |
| 0.000 | 1.000 | 0.000 | 0.820 | 0.82 | - |
| Octane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | | |
| 1.000 | 0.000 | 0.043 | 0.000 | - | - |
| 0.955 | 0.045 | 0.040 | 0.073 | 1.62 | 38.73 |
| 0.864 | 0.136 | 0.038 | 0.208 | 1.53 | 34.77 |
| 0.822 | 0.178 | 0.039 | 0.267 | 1.50 | 31.62 |
| 0.775 | 0.225 | 0.039 | 0.313 | 1.39 | 27.64 |
| 0.731 | 0.269 | 0.040 | 0.360 | 1.34 | 24.46 |
| 0.585 | 0.415 | 0.041 | 0.485 | 1.17 | 16.67 |
| 0.468 | 0.532 | 0.040 | 0.557 | 1.05 | 12.25 |
| 0.337 | 0.663 | 0.035 | 0.632 | 0.95 | 9.18 |
| 0.203 | 0.797 | 0.022 | 0.720 | 0.90 | 8.34 |
| 0.000 | 1.000 | 0.000 | 0.820 | 0.82 | - |
| Cyclooctane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | | |
| 1.000 | 0.000 | 0.071 | 0.000 | - | - |
| 0.873 | 0.127 | 0.065 | 0.211 | 1.66 | 22.31 |
| 0.832 | 0.168 | 0.065 | 0.262 | 1.56 | 19.96 |
| 0.787 | 0.213 | 0.065 | 0.312 | 1.46 | 17.74 |
| 0.735 | 0.265 | 0.064 | 0.361 | 1.36 | 15.64 |
| 0.659 | 0.341 | 0.062 | 0.430 | 1.26 | 13.40 |
| 0.566 | 0.434 | 0.058 | 0.494 | 1.14 | 11.11 |
| 0.476 | 0.524 | 0.052 | 0.552 | 1.05 | 9.64 |
| 0.378 | 0.622 | 0.045 | 0.613 | 0.99 | 8.28 |
| 0.196 | 0.804 | 0.030 | 0.707 | 0.88 | 5.75 |
| 0.000 | 1.000 | 0.000 | 0.820 | 0.82 | - |
| Methylcyclohexane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | | |
| 1.000 | 0.000 | 0.130 | 0.000 | - | - |
| 0.961 | 0.039 | 0.115 | 0.078 | 2.00 | 16.71 |
| 0.908 | 0.092 | 0.106 | 0.155 | 1.68 | 14.43 |
| 0.866 | 0.134 | 0.107 | 0.210 | 1.57 | 12.68 |
| 0.825 | 0.175 | 0.110 | 0.249 | 1.42 | 10.67 |
| 0.777 | 0.223 | 0.112 | 0.302 | 1.35 | 9.40 |
| 0.728 | 0.272 | 0.112 | 0.348 | 1.28 | 8.32 |
| 0.625 | 0.375 | 0.109 | 0.428 | 1.14 | 6.54 |
| 0.573 | 0.427 | 0.106 | 0.465 | 1.09 | 5.89 |
| 0.457 | 0.543 | 0.094 | 0.546 | 1.01 | 4.89 |
| 0.320 | 0.680 | 0.077 | 0.625 | 0.92 | 3.82 |
| 0.183 | 0.817 | 0.049 | 0.686 | 0.86 | 2.91 |
| 0.000 | 1.000 | 0.000 | 0.820 | 0.82 | - |
| Methylcyclohexane (1) + Benzene (2) + [PMim][NTf$_2$] (3) | | | | | |
| 1.000 | 0.000 | 0.099 | 0.000 | - | - |
| 0.950 | 0.050 | 0.094 | 0.083 | 1.66 | 16.78 |
| 0.899 | 0.101 | 0.091 | 0.152 | 1.50 | 14.87 |
| 0.858 | 0.142 | 0.090 | 0.200 | 1.41 | 13.43 |
| 0.811 | 0.189 | 0.089 | 0.268 | 1.42 | 12.92 |
| 0.766 | 0.234 | 0.086 | 0.301 | 1.29 | 11.46 |
| 0.718 | 0.282 | 0.084 | 0.342 | 1.21 | 10.37 |
| 0.615 | 0.385 | 0.077 | 0.426 | 1.11 | 8.84 |
| 0.506 | 0.494 | 0.070 | 0.494 | 1.00 | 7.23 |
| 0.382 | 0.618 | 0.058 | 0.577 | 0.93 | 6.15 |
| 0.251 | 0.749 | 0.044 | 0.651 | 0.87 | 4.96 |
| 0.178 | 0.822 | 0.036 | 0.687 | 0.84 | 4.13 |
| 0.000 | 1.000 | 0.000 | 0.794 | 0.79 | - |

On the other hand, the last value of the composition of benzene ($x_2$) for each system, also shown in Table S1 of the SI, represents the solubility of benzene in the studied ILs. Since these values for the systems containing [PMim][NTf$_2$] and [BMim][NTf$_2$] are $x_2$ = 0.794 and $x_2$ = 0.820, respectively, it can be concluded that this aromatic compound is more soluble in the IL containing a larger alkyl chain, which is also in accordance with the results published by Arce et al.[10] and García et al.[12] A discussion about this behavior, in terms of different types of interactions between the cation and the aromatic compound was developed out by Lachwa et al.[40]

According with these results, one would expect that the extraction process using [BMim][NTf$_2$] as solvent was slightly more favorable since a higher amount of benzene should be extracted. However, as shown by the $S$ values discussed later, this behavior was not observed.

The experimental LLE data in mole fraction for the ternary systems (aliphatic compound (1) + benzene (2) + IL (3)) at $T$ = 298.15 K and atmospheric pressure are presented in Table 2. As mentioned above, alkane-rich phases were assumed to be totally free of IL; this assumption was confirmed after $^1$H-NMR analysis of some hydrocarbon-rich phases. Therefore, the IL-rich phase (lower phase) is composed by a mixture of IL and hydrocarbons (heptane, octane, methylcyclohexane, cyclooctane, or benzene) in different proportions, while the hydrocarbon-rich phase (upper phase) is only composed by a mixture of aliphatic and aromatic compounds. This fact is also observed by other authors studying the LLE of systems with different ILs.[9−12]

The reliability of the experimental tie-line compositions was ascertained by applying the equation provided by Othmer–Tobias:[30]

$$\ln\left(\frac{1-w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) = a + b\ln\left(\frac{1-w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) \qquad (1)$$

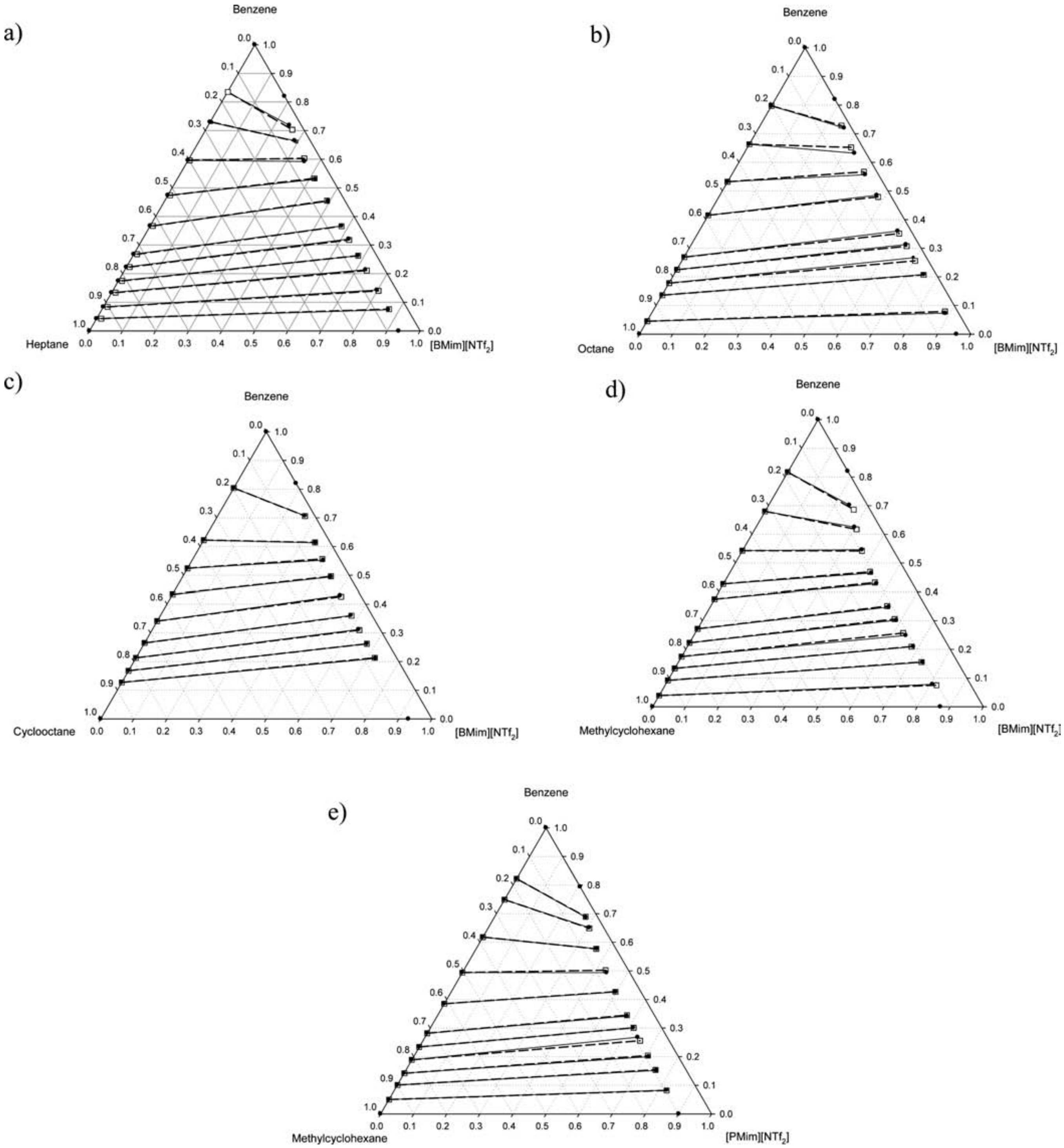

**Figure 1.** LLE of the ternary systems (a) heptane (1) + benzene (2) + [BMim][NTf$_2$] (3); (b) octane (1) + benzene (2) + [BMim][NTf$_2$] (3); (c) cyclooctane (1) + benzene (2) + [BMim][NTf$_2$] (3); (d) methylcyclohexane (1) + benzene (2) + [BMim][NTf$_2$] (3); and (e) methylcyclohexane (1) + benzene (2) + [PMim][NTf$_2$] (3) at $T$ = 298.15 K. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from the NRTL model.

where $w_1^{\mathrm{I}}$ is the mass fraction of aliphatic compound in the upper phase and $w_3^{\mathrm{II}}$ is the mass fraction of the IL in the lower phase; $a$ and $b$ are adjustable parameters. The linearity of this fitting indicates the degree of consistency of the experimental data. The parameters obtained from the Othmer–Tobias equation are presented in Table S3, available in the SI, together with the correlation factor, $R^2$, for all of the studied ternary systems at 298.15 K.

From the experimental LLE, the triangular diagrams of the LLE at $T$ = 298.15 K for the five studied systems are plotted in Figure 1. As it can be seen, all of the studied systems correspond to a Type 2 category, according to the classification proposed by

Sørensen et al.,[41] in which two of the pairs of compounds exhibit partial miscibility, and only one pair is miscible in the whole range of compositions. In this case, the hydrocarbons are completely soluble in all proportions, and these compounds display partial solubility in the two studied ILs. Moreover, by the inspection of Figure 1, it can be observed that benzene is more soluble in both studied ILs than alkanes. Regarding to the tie-lines, their slopes change from positive to negative along the triangular diagram, showing a solutropic behavior. In this way, solute distribution ratio, $\beta$, values are higher than unity for positive slopes and lower than unity when the slopes are negative, indicating that a higher amount of solvent (IL) will be required for feeds with a high aromatic content. The ability of the two studied ILs to separate benzene from aliphatic compounds was evaluated using the solute distribution ratio, $\beta$, and the selectivity, $S$, defined as:

$$\beta = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \tag{2}$$

$$S = \frac{x_2^{\mathrm{II}} x_1^{\mathrm{I}}}{x_2^{\mathrm{I}} x_1^{\mathrm{II}}} \tag{3}$$

where $x_1^{\mathrm{I}}$ and $x_2^{\mathrm{I}}$ are the mole fractions of aliphatic compound and benzene, respectively, in the upper phase; and $x_1^{\mathrm{II}}$ and $x_2^{\mathrm{II}}$ are the mole fractions of aliphatic compound and benzene, respectively, in the lower phase. The $S$ and $\beta$ values are also presented in Table 2, together with experimental LLE data.

The variation of $S$ and $\beta$ versus mole fraction of benzene in the alkane-rich phase for all of the studied systems is plotted in Figure 2. As it can be observed in this figure, these parameters decrease with increasing composition of the aromatic compound in the upper phase.

From a comparative study of the $S$ values for the studied systems, it is possible to conclude that the linear alkanes lead to higher $S$ values than those obtained with the cyclic hydrocarbons. Comparing the results for ternary systems (methylcyclohexane + benzene + IL), it can be seen that $S$ values for the system with [PMim][NTf$_2$] are slightly higher than those obtained for the system containing [BMim][NTf$_2$]. As commented above, although the solubility of benzene is higher in [BMim][NTf$_2$], the solubility of methylcyclohexane in this IL is also higher, and a greater amount of this compound is present in the IL rich-phase, causing a decline of the $S$ values.

Finally, comparing the $S$ values for heptane/octane, methylcyclohexane/cyclooctane, and cyclooctane/octane pairs, it is possible to conclude that an increase in the molecular mass of the alkane, linear or cyclic, results in an increase of the selectivity, showing an opposite behavior to the solubility. In this way, literature data for the ternary system (hexane (1) + benzene (2) + [BMim][NTf$_2$] (3)) published by Arce et al.[10] were also included in Figure 2 for comparison purposes, confirming this conclusion.

Regarding the $\beta$ values, they are very similar for all of the studied systems containing [BMim][NTf$_2$] IL and slightly lower for the ternary system (methylcyclohexane + benzene + [PMim]-[NTf$_2$]). This suggests that the size and structure of the alkane seem to have a small influence on this parameter.

In all cases, $S$ and $\beta$ values for the studied systems are higher than unity at low concentrations of benzene in the upper phase, which confirms that the extraction of benzene from its mixtures with alkanes, linear or cyclic, using [BMim][NTf$_2$] or [PMim]-[NTf$_2$] ILs as solvent could be a possible alternative to traditional organic solvents, especially at those low concentrations of benzene. Nevertheless, it is necessary to remark that if the solute distribution ratio is calculated using mass fraction instead of molar fraction, the obtained $\beta$ values are lower, which means that a higher amount of IL would be necessary for the extraction in comparison with usual organic solvents as sulfolane. In any case, it is important to note that the recovery of sulfolane from the extract and raffinate streams is complex, thus resulting in an additional increase in the installation and operational costs of the processes. On the contrary, as ILs have a negligible vapor pressure at normal conditions and, in this case, no presence of this compound was detected in the alkane-rich phase, their recovery is easier, and their use as solvent can be a possible alternative to traditional solvents. Although the price of the ILs is still high, their cost will be significantly reduced when these compounds can be produced to a larger scale.

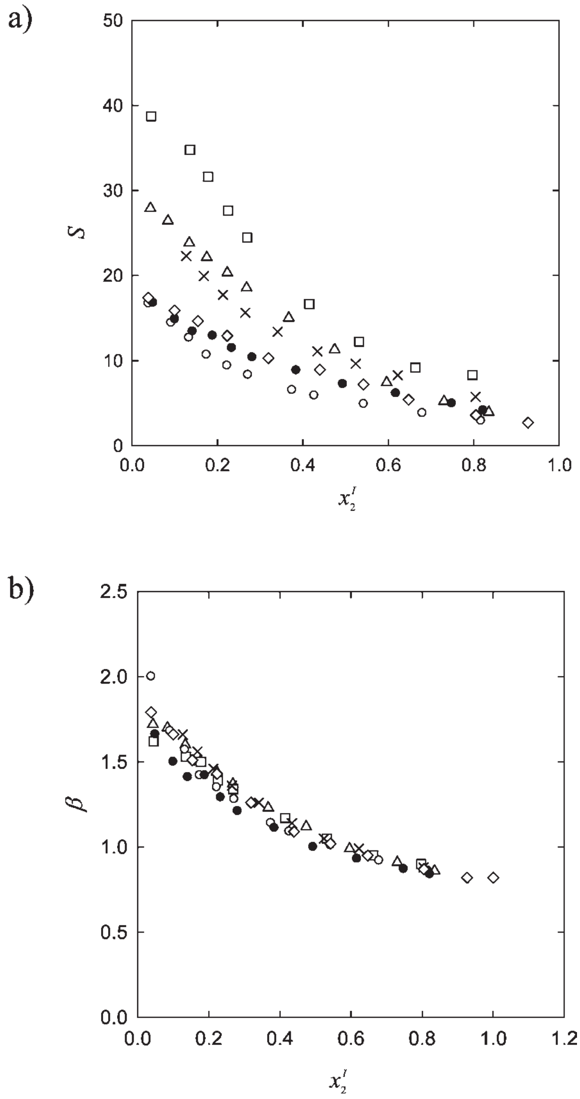

**Figure 2.** (a) Selectivity and (b) solute distribution ratio as a function of the mole fraction of benzene in the upper phase, at $T$ = 298.15 K, for the ternary systems: △, heptane (1) + benzene (2) + [BMim][NTf$_2$] (3); □, octane (1) + benzene (2) + [BMim][NTf$_2$] (3); ×, cyclooctane (1) + benzene (2) + [BMim][NTf$_2$] (3); ○, methylcyclohexane (1) + benzene (2) + [BMim][NTf$_2$] (3); ●, methylcyclohexane (1) + benzene (2) + [PMim][NTf$_2$] (3); ◇, hexane (1) + benzene (2) + [BMim][NTf$_2$] (3) from ref 10.

Table 3. NRTL Binary Interaction Parameters and Standard Deviations for LLE Data of Ternary Systems at $T$ = 298.15 K

| $i{-}j$ | $\Delta g_{ij}$ kJ·mol$^{-1}$ | $\Delta g_{ji}$ kJ·mol$^{-1}$ | $\alpha_{ij}$ | $\sigma x$ | $\Delta\beta$ |
|---|---|---|---|---|---|
| | Heptane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | |
| 1−2 | −1.127 | 4.588 | 0.30 | 0.474 | 1.47 |
| 1−3 | 8.252 | 5.187 | | | |
| 2−3 | 30.273 | −0.790 | | | |
| | Octane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | |
| 1−2 | −3.349 | 5.494 | 0.30 | 0.409 | 3.51 |
| 1−3 | 13.555 | 6.577 | | | |
| 2−3 | 30.854 | −2.872 | | | |
| | Cyclooctane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | |
| 1−2 | −6.580 | 9.532 | 0.10 | 0.100 | 0.58 |
| 1−3 | 91.391 | 5.190 | | | |
| 2−3 | 128.371 | 2.976 | | | |
| | Methylcyclohexane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | | |
| 1−2 | −4.690 | 6.687 | 0.10 | 0.326 | 1.83 |
| 1−3 | 112.289 | 1.681 | | | |
| 2−3 | 126.422 | −2.130 | | | |
| | Methylcyclohexane (1) + Benzene (2) + [PMim][NTf$_2$] (3) | | | | |
| 1−2 | −1.386 | 2.977 | 0.25 | 0.198 | 1.68 |
| 1−3 | 15.667 | 3.582 | | | |
| 2−3 | 39.301 | −1.374 | | | |

**Thermodynamic Correlation.** The NRTL[31] and UNIQUAC[32] models were used to correlate the LLE experimental data, except for the ternary system methylcyclohexane + benzene + [PMim][NTf$_2$], for which the UNIQUAC model was not applied because the required van der Waals parameters for this IL were not found in literature.

In the correlation using the NRTL model, although $\alpha_{ij}$ can be an adjustable parameter, in this case it was considered fixed. For each system, several values for $\alpha_{ij}$ were tested (from $\alpha_{ij}$ = 0 to 0.5), and the best results were achieved for the values presented in Table 3. The used objective function minimizes the differences between the experimental and the calculated mole fraction of the components in both phases. The NRTL binary interaction parameters of the correlated ternary systems are also listed in Table 3, as well as the values of the root-mean-square deviation of the composition, $\sigma x$, and the mean error of the solute distribution ratio, $\Delta\beta$. These deviations were calculated as follows:

$$\sigma x = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N-1}\left(\left(x_{ij}^{\mathrm{I,exp}} - x_{ij}^{\mathrm{I,calc}}\right)^2 + \left(x_{ij}^{\mathrm{II,exp}} - x_{ij}^{\mathrm{II,calc}}\right)^2\right)}{2MN}} \tag{4}$$

$$\Delta\beta = 100\sqrt{\frac{1}{M}\sum_{k}\left(\frac{\beta_k - \beta_k^{\mathrm{calc}}}{\beta_k}\right)^2} \tag{5}$$

Table 4. UNIQUAC Binary Interaction Parameters and Standard Deviations for LLE Data of Ternary Systems at $T$ = 298.15 K

| $i{-}j$ | $\Delta g_{ij}$ kJ·mol$^{-1}$ | $\Delta g_{ji}$ kJ·mol$^{-1}$ | $\sigma x$ | $\Delta\beta$ |
|---|---|---|---|---|
| | Heptane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | |
| 1−2 | 0.641 | −0.014 | 0.145 | 1.44 |
| 1−3 | 1.975 | 0.395 | | |
| 2−3 | 3.557 | −1.599 | | |
| | Octane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | |
| 1−2 | 2.501 | −1.611 | 0.385 | 3.43 |
| 1−3 | 6.329 | −0.583 | | |
| 2−3 | 20.661 | −2.636 | | |
| | Cyclooctane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | |
| 1−2 | 1.771 | −1.025 | 0.104 | 0.31 |
| 1−3 | 7.480 | −0.834 | | |
| 2−3 | 9.944 | −2.463 | | |
| | Methylcyclohexane (1) + Benzene (2) + [BMim][NTf$_2$] (3) | | | |
| 1−2 | 2.734 | −1.597 | 0.169 | 1.20 |
| 1−3 | 4.458 | −0.492 | | |
| 2−3 | 11.922 | −2.459 | | |

where $M$ is the number of tie-lines and $N$ the number of components in the mixture.

The required van der Waals parameters, $r_i$ and $q_i$, for the UNIQUAC model for the studied hydrocarbons and for [BMim][NTf$_2$] IL were taken from literature.[42,43] The binary interaction parameters, the root-mean-square deviation of the composition, $\sigma x$, and the mean error of the solute distribution ratio, $\Delta\beta$, are summarized in Table 4.

Both models are capable to successfully correlate the experimental LLE data, as can be inferred from the $\sigma x$ and $\Delta\beta$ values included in Tables 3 and 4 for NRTL and UNIQUAC models, respectively. As an example of this appropriate correlation, in Figure 1 the experimental tie-lines and those obtained from the correlation with the NRTL model are plotted, observing that NRTL model fits quite satisfactorily the experimental data.

## CONCLUSIONS

In this paper, LLE data for five ternary systems (aliphatic compound (1) + benzene (2) + IL (3)) at $T$ = 298.15 K and atmospheric pressure are presented and analyzed. The studied aliphatic compounds were heptane, octane, cyclooctane, and methylcyclohexane, and the investigated ILs were 1-propyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide, [PMim]-[NTf$_2$], and 1-butyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide, [BMim][NTf$_2$].

The consistency of the tie-lines was ascertained by applying the Othmer−Tobias equation, obtaining good results, and the NRTL and UNIQUAC thermodynamic models were satisfactorily applied to correlate the experimental LLE data.

From the experimental LLE data, the selectivity and solute distribution ratio were calculated. The selectivity values show that linear alkanes lead to higher selectivity values than the cyclic hydrocarbon, that $S$ values for the system with [PMim][NTf$_2$] are slightly higher than those obtained for the system with

$[BMim][NTf_2]$, and an increase in the molecular mass of the alkane, linear or cyclic, results in an increase of the selectivity. With respect to the solute distribution ratio, the size and structure of the alkane seem to have a small influence on this parameter, with similar values for the studied systems containing $[BMim][NTf_2]$ and slightly lower for the system with $[PMim][NTf_2]$. In all cases, the selectivity and solute distribution ratio are higher than unity at low concentrations of benzene, indicating that both ILs could be considered as potential solvents for the extraction of benzene from aliphatic compounds. Moreover, as the presence of IL in upper-phases was not detected, the recovery and reuse of the solvent is easy and cheap because a solvent recovery unit in raffinate stream would be not necessary, decreasing the operational costs.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Solubility curves, validation points, and Othmer−Tobias parameters, at $T = 298.15$ K and atmospheric pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Funding Sources

The authors are grateful to Xunta de Galicia (Spain) for the financial support of this work via the project INCITE09314258PR. I.D. is also grateful to the Ministerio de Ciencia e Innovación (Spain) for awarding a FPI grant (BES-2008-003074).

## ■ REFERENCES

(1) Ashour, I.; Abu-Eishah, S. I. Liquid-liquid equilibria of ternary and six-component systems including cyclohexane, benzene, toluene, ethylbenzene, cumene, and sulfolane at 303.15 K. *J. Chem. Eng. Data* **2006**, *51*, 1717–1722.

(2) Lin, W.; Tsai, T.; Lin, T.; Yang, C. Influence of the temperature on the liquid-liquid equilibria of heptane + toluene + sulfolane and heptane + *m*-xylene + sulfolane. *J. Chem. Eng. Data* **2008**, *53*, 760–764.

(3) Lee, S.; Kim, H. Liquid-liquid equilibria for the ternary systems sulfolane + octane + benzene, sulfolane + octane + toluene and sulfolane + octane + *p*-xylene. *J. Chem. Eng. Data* **2008**, *40*, 499–503.

(4) Al-Sahhaf, T. A.; Kapetanovic, E. Measurement and prediction of phase equilibria in the extraction of aromatics from naphtha reformate by tetraethylene glycol. *Fluid Phase Equilib.* **1996**, *118*, 271–285.

(5) Wang, W.; Gou, Z. M.; Zhu, S. L. Liquid-Liquid equilibria for aromatics extraction systems with tetraethylene glycol. *J. Chem. Eng. Data* **1998**, *43*, 81–83.

(6) Dandan, H.; Kyung, H. R. Recent applications of ionic liquids in separation technology. *Molecules* **2010**, *15*, 2405–2426.

(7) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room temperature ionic liquids as novel media for 'clean' liquid−liquid extraction. *Chem. Commun.* **1998**, 1765–1766.

(8) Meindersma, G. W.; Hansmeier, A. R.; De Haan, A. B. Ionic liquids for aromatics extraction. Present status and future outlook. *Ind. Eng. Chem. Res.* **2010**, *49*, 7530–7540.

(9) Abu-Eishah, S. I.; Dowaidar, A. M. 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. *J. Chem. Eng. Data* **2008**, *53*, 1708–1712.

(10) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R. Separation of benzene and hexane by solvent extraction with 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ionic liquids: Effect of the alkyl-substituents lenth. *J. Phys. Chem. B* **2007**, *111*, 4732–4736.

(11) Domanska, U.; Pobudkowska, A.; Królikowski, M. Separation of aromatic hydrocarbons from alkanes using ammonium ionic liquid $C_2NTf_2$ at $T = 298.15$ K. *Fluid Phase Equilib.* **2007**, *259*, 173–179.

(12) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Liquid-liquid equilibria of toluene from heptane using 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Eng. Data* **2011**, *56*, 113–118.

(13) Hansmeier, A. R.; Jongmans, M.; Meindersma, G. W.; de Haan, A. B. LLE data for the ionic liquid 3-methyl-*N*-butyl pyridinium dicyanamide with several aromatic and aliphatic compounds. *J. Chem. Thermodyn.* **2010**, *42*, 484–490.

(14) Letcher, T. M.; Reddy, P. Ternary (liquid + liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluoroborate) + benzene + an alkane at $T = 298.2$ K and $p = 0.1$ MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415–421.

(15) Lu, Y.; Yang, X.; Luo, G. Liquid-liquid equilibria for benzene + cyclohexane + 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2010**, *55*, 510–512.

(16) Maduro, R. M.; Aznar, M. Liquid-liquid equilibrium of ternary systems 1-butyl-3-methylimidazolium hexafluorophosphate + aromatic + aliphatic. *Fluid Phase Equilib.* **2008**, *265*, 129–138.

(17) Pereiro, A. B.; Rodríguez, A. Application of the ionic liquid Ammoeng 102 for the aromatic/aliphatic hydrocarbon separation. *J. Chem. Thermodyn.* **2009**, *41*, 951–956.

(18) Wang, R.; Wang, J.; Meng, H.; Li, C.; Wang, Z. Liquid-liquid equilibria for benzene + cyclohexane + 1-methyl-3-methylimidazolium dimethylphosphate or + 1-ethyl-3-methylimidazolium diethylphosphate. *J. Chem. Eng. Data* **2008**, *53*, 1159–1162.

(19) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid-liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841–845.

(20) Gómez, E.; Domínguez, I.; González, B.; Domínguez, A. Liquid-liquid equilibria of the ternary systems of alkane + aromatic + 1-ethylpyridinium ethylsulfate ionic liquid at $T = (283.15$ and $298.15)$ K. *J. Chem. Eng. Data* **2010**, *55*, 5169–5175.

(21) Gómez, E.; Domínguez, I.; Calvar, N.; Domínguez, A. Separation of benzene from alkanes by solvent extraction with 1-ethylpyridinium ethylsulfate ionic liquid. *J. Chem. Thermodyn.* **2010**, *42*, 1234–1239.

(22) González, E. J.; Domínguez, I.; González, B.; Canosa, J. Liquid-liquid equilibria for ternary systems of {cyclohexane + aromatic compounds + 1-ethyl-3-methylpyridinium ethylsulfate}. *Fluid Phase Equilib.* **2010**, *296*, 213–218.

(23) González, E. J.; Calvar, N.; González, B.; Domínguez, A. Liquid extraction of benzene from its mixtures using 1-ethyl-3-methylimidazolium ethylsulfate as a solvent. *J. Chem. Eng. Data* **2010**, *55*, 4931–4936.

(24) González, E. J.; Calvar, N.; Gómez, E.; Domínguez, A. Separation of benzene from linear alkanes (C6-C9) using 1-ethyl-3-methylimidazolium ethylsulfate at $T = 298.15$ K. *J. Chem. Eng. Data* **2010**, *55*, 3422–3427.

(25) González, E. J.; Calvar, N.; Canosa, J.; Domínguez, A. Effect of the chain length on the aromatic ring in the separation of aromatic compounds from methylcyclohexane using the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate. *J. Chem. Eng. Data* **2010**, *55*, 2289–2293.

(26) González, E. J.; Calvar, N.; González, B.; Domínguez, A. Measurement and correlation of liquid-liquid equilibria for ternary systems {cyclooctane + aromatic hydrocarbon + 1-ethyl-3-methylpyridinium ethylsulfate} at $T = 298.15$ K and atmospheric pressure. *Fluid Phase Equilib.* **2010**, *291*, 59–65.

(27) González, E. J.; Calvar, N.; González, B.; Domínguez, A. Liquid-liquid equilibrium for ternary mixtures of hexane + aromatic compounds +

[EMpy][ESO$_4$] at $T$ = 298.15 K. *J. Chem. Eng. Data* **2010**, *55*, 633–638.

(28) González, E. J.; Calvar, N.; Gómez, E.; Domínguez, A. Separation of benzene from alkanes using 1-ethyl-3-methylpyridinium ethylsulfate ionic liquid at several temperatures and atmospheric pressure: Effect of the size of the aliphatic hydrocarbons. *J. Chem. Thermodyn.* **2010**, *42*, 104–109.

(29) González, E. J.; Calvar, N.; González, B.; Domínguez, A. (Liquid + liquid) equilibria for ternary mixtures of (alkane + benzene + [EMpy] [ESO$_4$]) at several temperatures and atmospheric pressure. *J. Chem. Thermodyn.* **2009**, *41*, 1215–1221.

(30) Othmer, D. F.; Tobias, P. E. Tie line correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

(31) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamics excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(32) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(33) Esperança, J. M. S. S.; Visak, Z. P.; Plechkova, N. V.; Seddon, K. R.; Guedes, H. J. R.; Rebelo, L. P. N. Density, speed of sound, and derived thermodynamic properties of ionic liquids over an extended pressure range. 4. [C$_3$mim][NTf$_2$] and [C$_5$mim][NTf$_2$]. *J. Chem. Eng. Data* **2006**, *51*, 2009–2015.

(34) Andreatta, A. E.; Arce, A.; Rodil, E.; Soto, A. Physico-chemical properties of binary and ternary mixtures of ethyl acetate + ethanol + 1-butyl-3-methylimidazolium bis(trifluoromethysulfonyl)imide at 298.15 K and atmospheric pressure. *J. Solution Chem.* **2010**, *39*, 371–383.

(35) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(36) Spiteri, W. L.; Letcher, T. M. The excess enthalpies of cyclooctane + n-alkanes. *Thermochim. Acta* **1982**, *59*, 73–80.

(37) Watson, E. P.; McLure, I. A.; Bennett, J. E.; Benson, G. C. Excess Properties of Some Aromatic-Alicyclic Systems. I. Measurements of Enthalpies and Volumes of Mixing. *J. Phys. Chem.* **1965**, *69*, 2753–2758.

(38) González, B.; González, E. J.; Domínguez, I.; Domínguez, A. Excess properties of binary mixtures hexane, heptane, octane and nonane with benzene, toluene and ethylbenzene at $T$ = 283.15 and 298.15 K. *Phys. Chem. Liq.* **2010**, *48*, 514–533.

(39) González, B.; Domínguez, I.; González, E. J.; Domínguez, A. Density, speed of sound, and refractive index of the binary systems cyclohexane (1) or methylcyclohexane (1) or cyclooctane (1) with benzene (2), toluene (2), and ethylbenzene (2) at two temperatures. *J. Chem. Eng. Data* **2010**, *55*, 1003–1011.

(40) Lachwa, J.; Szydlowski, J.; Makowska, A.; Seddon, K. R.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide and arenes. *Green Chem.* **2006**, *8*, 262–267.

(41) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. Liquid-liquid equilibrium data: Their retrieval, correlation and prediction Part I: Retrieval. *Fluid Phase Equilib.* **1979**, *2*, 297–309.

(42) Sorensen, J. M.; Alt, W. *Liquid-liquid equilibrium data collection*; DECHEMA Chemistry Data Series: Frankfurt, 1980.

(43) Kato, R.; Krummen, M.; Gmehling, J. Measurement and correlation of vapor—liquid equilibria and excess enthalpies of binary systems containing ionic liquids and hydrocarbons. *Fluid Phase Equilib.* **2004**, *224*, 47–54.