

# Separation of Benzene and Hexane by Solvent Extraction with 1-Alkyl-3-methylimidazolium Bis{(trifluoromethyl)sulfonyl}amide Ionic Liquids: Effect of the Alkyl-Substituent Length<sup>†</sup>

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Received: September 28, 2006; In Final Form: December 8, 2006

The influence of the alkyl-substituent chain in 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}-amide ionic liquids ( $[C_n\text{mim}][\text{NTf}_2]$ , where  $n$  is the length of a linear alkyl chain) as solvents for the separation of benzene and hexane by liquid extraction was investigated. The liquid–liquid equilibrium (LLE) at 25 °C for the ternary systems ( $[C_n\text{mim}][\text{NTf}_2]$  + hexane + benzene), with  $n$  taking the values 4, 8, 10, and 12, were determined. These data were analyzed and compared to those previously reported for the system ( $[C_2\text{mim}][\text{NTf}_2]$  + hexane + benzene). The results show that short alkyl chains on the imidazolium cation of the ionic liquid lead to a better extractive separation of benzene and hexane, and reveal the influence of the relative degree of ordering in the ionic liquids on the extraction parameters.

## Introduction

For the past decade, with the development of ionic liquids,<sup>1</sup> solvent extraction has been found to be one of the fields in which the application of these families of compounds looks promising.<sup>2,3</sup> Throughout this time, a considerable amount of research has focused on the features of ionic liquids as solvents to perform the extraction of a wide diversity of compounds (see, for instance, the review recently published by Heintz<sup>3</sup>). In addition, ionic liquids have also been shown to be partially miscible with themselves, hydrocarbons, and water, resulting in three- and four-phase systems.<sup>4</sup> Among the separations of mixtures of industrial importance, an improved separation process for the systems involving aromatic and aliphatic hydrocarbons is of considerable interest.<sup>5</sup> To date, a few studies have explored the possibility of using ionic liquids for the separation of these hydrocarbons; an interesting compilation has been recently published by Meindersma et al.<sup>6</sup>

One of the general advantages offered by ionic liquids is their tunability, which has led them to be also known as “designer solvents”: different types of cations and anions can be combined, and their respective structures tailored, to modify the properties of the resulting ionic liquid according to the interest in each specific application.<sup>7</sup> The number of potential ionic liquids and ternary mixtures thereof is well over 1 trillion ( $10^{18}$ ).<sup>8</sup> Therefore, in order to find the best one for a particular application, it is desirable not just to collect examples of how individual ionic liquids function but also to analyze series of similar or homologous ionic liquids. Then, it would be possible to set up guidelines on the effects of structural variations in ionic liquids related to properties of interest. Eventually, this procedural pattern can be useful in building improved predictive models.

Here, we combine the use of ionic liquids as extraction solvents to separate aromatic and aliphatic hydrocarbons with a

study on how the modification of the cation structure of the ionic liquid (in particular its chain length) affects the characteristic parameters of the extraction process. Benzene and hexane were chosen as the representatives of the aromatic and aliphatic hydrocarbon families. As solvents, the hydrophobic 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ionic liquids ( $[C_n\text{mim}][\text{NTf}_2]$ ) were selected. Thus, this work reports liquid–liquid equilibrium (LLE) data at 25 °C for the ternary systems formed by benzene, hexane, and  $[C_n\text{mim}][\text{NTf}_2]$ , with  $n$  ranging from 2 to 12. The results where  $n = 2$  are also being reported separately.<sup>9</sup>

## Experimental Detail

Hydrocarbons, benzene (LabScan, 99.0%), and hexane (BDH, 97.0%, the remaining 3% being isomers of hexane) were used as received, without further purification. The ionic liquids  $[C_n\text{mim}][\text{NTf}_2]$  were synthesized in our laboratory. First, the salts  $[C_n\text{mim}]\text{Cl}$  were prepared by direct alkylation of 1-methylimidazole with the corresponding chloroalkane, in a similar manner to that reported elsewhere.<sup>10</sup> These chloride ionic liquids were mixed with  $\text{Li}[\text{NTf}_2]$  in deionized water, thus obtaining the hydrophobic  $[C_n\text{mim}][\text{NTf}_2]$  by ion metathesis, which forms a dense non-aqueous phase.<sup>11</sup> Dichloromethane was added, and the organic phase was washed several times, until there was no observance of a precipitate by adding silver(I) nitrate to the residual aqueous phase, thus indicating the absence of chloride in significant levels.<sup>12</sup> The dichloromethane was removed in a rotary evaporator, and the purification of the ionic liquids was completed by heating them under high vacuum for at least 24 h (1 mbar, 80 °C). The final products were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy,<sup>11</sup> and their water contents were found to be in the range 95–625 ppm by Karl Fischer titration.<sup>12</sup> Overall, the water content of the combined ionic liquid–benzene–hexane mixtures can have a maximum value of ~0.07%.

The determinations of the experimental tie-lines for the liquid–liquid equilibria were performed by preparation of immiscible mixtures of the three compounds involved in the system, or just two when determining the tie-lines corresponding to the

<sup>†</sup> Part of the special issue “Physical Chemistry of Ionic Liquids”.

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immiscible pairs. Special care was taken in covering the whole immiscibility region and getting well-distributed tie-lines through-out it. The immiscible mixtures were placed inside a specially designed glass cell, which was then sealed and placed in a thermostatted oil bath, keeping the temperature constant at 25.0 °C (with a precision of  $\pm 0.1$  °C). Each mixture was stirred for 1 h, and then allowed to settle for no less than 4 h, to ensure complete phase separation and thermodynamic equilibrium. Then, a sample from each phase was taken with a syringe to carry out the compositional analysis.

A technique based on  $^1\text{H}$  NMR spectroscopy was used to determine the composition of the equilibrium phases. Details on the procedure and the validation of the technique have already been reported in the literature.<sup>9,13</sup> The composition of each phase was calculated by integrating specific peaks in the  $^1\text{H}$  NMR spectrum. In order to select these peaks, miscible samples with overall compositions covering the area in the proximities of the heterogeneous region were prepared by weight (Mettler Toledo AT261 balance, precise to within  $\pm 10^{-4}$  g). The best quantitative agreement between the actual known composition and the integration of the NMR spectra was found when choosing, for the ionic liquid, the peaks corresponding to the methyl and methylene groups bonded to the nitrogen atoms of the imidazolium ring. For benzene, there was a sharp singlet peak in the spectrum between 7.2 and 7.3 ppm. For hexane, the peak of the methylene groups was not desirable, as it was overlapped by signals from the ionic liquid, especially for those ionic liquids with a long side chain, thus losing quantitative accuracy; therefore, the peak of the terminal methyl groups was selected, despite also overlapping with the peak of the terminal methyl group of the alkyl-substituent chain for the systems containing  $[\text{C}_8\text{mim}][\text{NTf}_2]$ ,  $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ , or  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ . This involved subtraction of 3H due to the ionic liquid terminal methyl group from the total peak integration to give the contribution of hexane to the peak integration. The accuracy of the method was investigated. The largest deviation between the actual and calculated compositions, for any compound and in any proportion, was found to be 0.017 in mole fraction. However, an acceptable level of accuracy was achieved, both for scientific and practical purposes. The NMR experiments were performed with a Bruker Avance DPX-500 spectrometer.

## Results and Discussion

The experimental LLE data for the ternary systems (hexane + benzene +  $\{[\text{C}_4\text{mim}][\text{NTf}_2], [\text{C}_8\text{mim}][\text{NTf}_2], [\text{C}_{10}\text{mim}][\text{NTf}_2], \text{ or } [\text{C}_{12}\text{mim}][\text{NTf}_2]\}$ ), at 25 °C, are reported in Table 1. The triangular diagrams with the tie-lines for each system are plotted in Figure 1, along with the diagram for the ternary system (hexane + benzene +  $[\text{C}_2\text{mim}][\text{NTf}_2]$ ).<sup>9</sup> This set of plots provides a clear visualization of the change in the size and shape of the immiscibility region as a result of the increase in the length of the hydrocarbon side chain of the solvent cation. It is notable how the mutual solubility of both hydrocarbons and the ionic liquid increases as the length of the alkyl chain becomes longer, with the pair (benzene +  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ ) eventually being found to be completely miscible; thus, this is a possible indication that a transformation from a type II to a type I system has occurred.<sup>14</sup>

An interesting fact observable from Figure 1 is that, for all of the diagrams, the tie-lines show a positive slope throughout most of the immiscibility region, which is a desirable feature for an extracting solvent. For the cases in which the ionic liquid and the benzene have a certain degree of immiscibility, the systems show solutropy;<sup>15</sup> that is, the sign of the tie-line slopes changes, becoming negative as the mole fraction of benzene

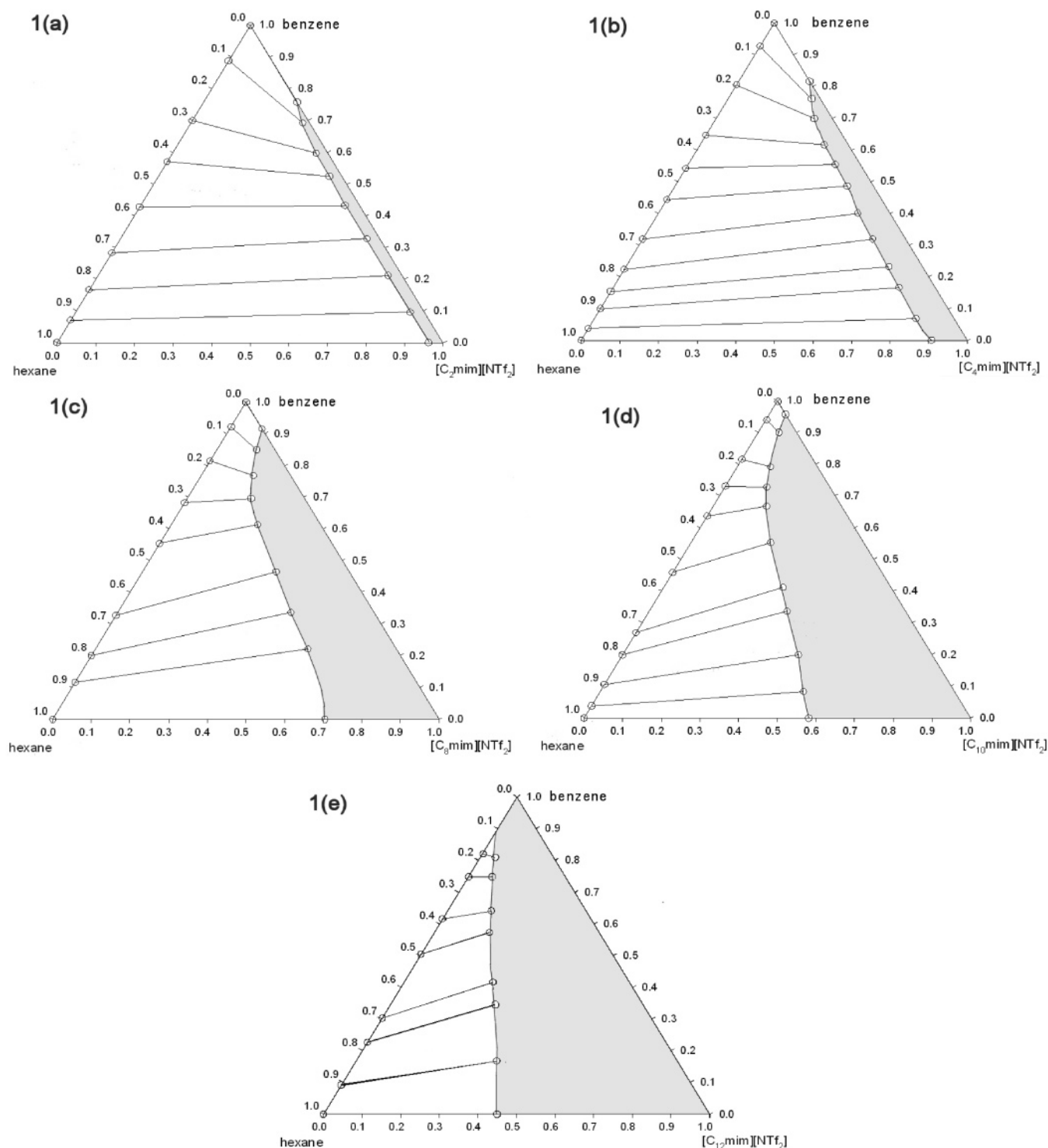
**TABLE 1: Composition of the Experimental Tie-Line Ends and Values of the Solute Distribution Ratio ( $\beta$ ) and Selectivity ( $S$ ) for the Ternary Systems (Hexane + Benzene +  $[\text{C}_n\text{mim}][\text{NTf}_2]$ ) ( $n = 4, 8, 10, \text{ or } 12$ ) at 25 °C<sup>a</sup>**

organic-rich phase			ionic-liquid-rich phase			$\beta$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$		
(hexane + benzene + [C <sub>4</sub> mim][NTf <sub>2</sub> ])							
1.000	0.000	0.000	0.093	0.000	0.907		
0.962	0.038	0.000	0.099	0.068	0.833	1.79	17.39
0.900	0.100	0.000	0.094	0.166	0.740	1.66	15.89
0.846	0.154	0.000	0.087	0.232	0.681	1.51	14.65
0.777	0.223	0.000	0.086	0.319	0.595	1.43	12.92
0.681	0.319	0.000	0.083	0.401	0.516	1.26	10.31
0.556	0.444	0.000	0.068	0.486	0.446	1.09	8.95
0.458	0.542	0.000	0.065	0.554	0.381	1.02	7.20
0.353	0.647	0.000	0.062	0.616	0.322	0.95	5.42
0.195	0.805	0.000	0.047	0.699	0.254	0.87	3.60
0.073	0.927	0.000	0.022	0.762	0.216	0.82	2.73
0.000	1.000	0.000	0.000	0.816	0.184	0.82	
(hexane + benzene + [C <sub>8</sub> mim][NTf <sub>2</sub> ])							
1.000	0.000	0.000	0.295	0.000	0.705		
0.883	0.117	0.000	0.228	0.222	0.550	1.90	7.35
0.799	0.201	0.000	0.215	0.337	0.448	1.68	6.23
0.672	0.328	0.000	0.189	0.465	0.346	1.42	5.04
0.446	0.554	0.000	0.163	0.613	0.224	1.11	3.03
0.317	0.683	0.000	0.138	0.696	0.166	1.02	2.34
0.186	0.814	0.000	0.097	0.768	0.135	0.94	1.81
0.077	0.922	0.001	0.047	0.850	0.103	0.92	1.51
0.000	0.999	0.001	0.000	0.915	0.085	0.92	
(hexane + benzene + [C <sub>10</sub> mim][NTf <sub>2</sub> ])							
1.000	0.000	0.000	0.419	0.000	0.581		
0.962	0.038	0.000	0.390	0.084	0.526	2.21	5.45
0.895	0.105	0.000	0.346	0.199	0.455	1.90	4.90
0.801	0.199	0.000	0.306	0.337	0.357	1.69	4.43
0.731	0.269	0.000	0.280	0.411	0.309	1.53	3.99
0.542	0.458	0.000	0.240	0.553	0.207	1.21	2.73
0.363	0.637	0.000	0.194	0.667	0.139	1.05	1.96
0.269	0.731	0.000	0.163	0.728	0.109	1.00	1.64
0.184	0.815	0.001	0.121	0.792	0.087	0.97	1.48
0.057	0.940	0.003	0.046	0.900	0.054	0.96	1.19
0.000	0.997	0.003	0.000	0.957	0.043	0.96	
(hexane + benzene + [C <sub>12</sub> mim][NTf <sub>2</sub> ])							
1.000	0.000	0.000	0.551	0.000	0.449		
0.908	0.092	0.000	0.468	0.168	0.364	1.83	3.54
0.773	0.227	0.000	0.383	0.345	0.272	1.52	3.07
0.697	0.303	0.000	0.353	0.416	0.231	1.37	2.71
0.496	0.504	0.000	0.284	0.573	0.143	1.14	1.99
0.385	0.615	0.000	0.245	0.641	0.114	1.04	1.64
0.251	0.748	0.001	0.189	0.748	0.063	1.00	1.33
0.177	0.820	0.003	0.151	0.809	0.040	0.99	1.16

<sup>a</sup> The mole fractions of hexane, benzene, and ionic liquid are represented by  $x_1$ ,  $x_2$ , and  $x_3$ , respectively.

becomes greater, and the tie-lines approach the binary system formed by just benzene and the ionic liquid. The system of type I, with  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$  as the solvent, also seems to be solutropic, although in this case the slightly negative slope of the last experimental tie-line, close to the supposed solutrope, lays next to the plait point. It is clear that most of the immiscibility region is located below the solutrope (horizontal tie-line) for all of the systems studied. Another remarkable issue to be highlighted after inspection of Figure 1 is that, as a general rule, the ionic liquid does not enter the hydrocarbon-rich phase in equilibrium, at least up to the levels detectable by the measuring technique. This fact would eliminate the need for a further separation unit to recover and recycle the solvent, leaving the extractor within the raffinate stream.

Together with the LLE data, Table 1 includes the corresponding values for the solute distribution ratio ( $\beta$ ) and the selectivity ( $S$ ), which are widely used parameters to characterize



**Figure 1.** Triangular phase diagrams for the LLE data of the ternary systems: (hexane + benzene +  $[C_n\text{mim}][\text{NTf}_2]$ ) ( $n = 2, 4, 8, 10$ , or  $12$ ), at  $25\text{ }^\circ\text{C}$ . The area shaded in gray corresponds to the region of miscibility (1 phase).

the suitability of a solvent in liquid extraction.<sup>16</sup> Their calculation is easily made from the experimental compositions of the tie-line ends, according to the following expressions:

$$\beta = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \quad (1)$$

$$S = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \cdot \frac{x_1^{\text{I}}}{x_1^{\text{II}}} \quad (2)$$

where  $x$  is the molar fraction, the superscripts I and II refer to the organic-rich and solvent-rich (ionic-liquid-rich) phases, respectively, and the subscripts 1 and 2 refer to the inert (hexane) and the solute (benzene), respectively.

The evolution of the solute distribution ratio and the selectivity for each system, as a function of the mole fraction of the solute in the organic phase, are plotted in Figures 2 and 3, respectively. An exponential equation with three adjustable parameters was the simplest expression found in both cases to correlate the data with a good degree of accuracy:

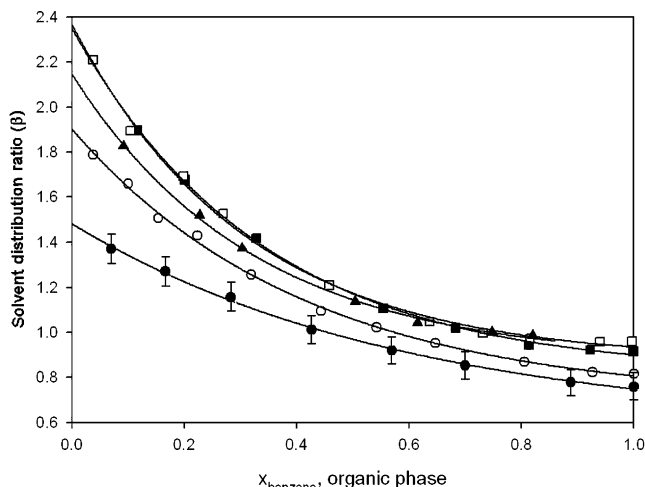
$$\beta = A + B \exp\left(-\frac{x_{2,\text{org}}}{C}\right) \quad (3)$$

$$S = a + b \exp\left(-\frac{x_{2,\text{org}}}{c}\right) \quad (4)$$

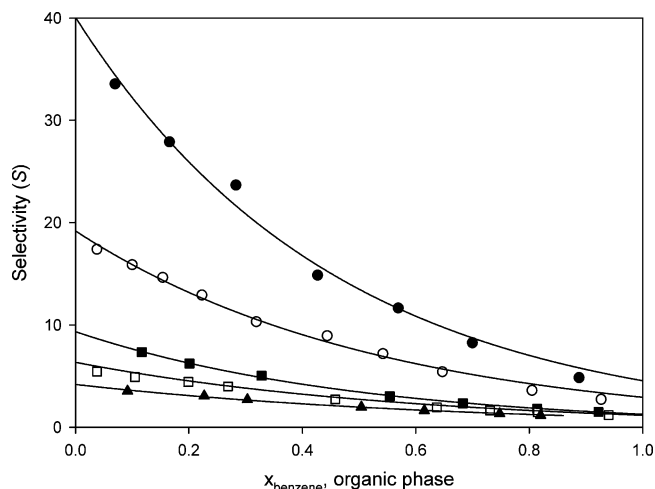
where  $A$ ,  $B$ ,  $C$ ,  $a$ ,  $b$ , and  $c$  are constants and  $x_{2,\text{org}}$  represents the mole fraction of benzene in the organic-rich phase. The values of the parameters, as well as the correlation coefficient and the relative standard deviations of the regressions, are reported in Tables 2 and 3.

From the comparison of Figures 2 and 3, it is noticeable that, contrary to the selectivity series for each system, some of the solute distribution ratio lines cross with others. The use of the ionic liquid with the shortest alkyl side chain,  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ( $n = 2$ ), as the solvent leads to the best selectivity values, which then decrease as the chain of the ionic liquid becomes longer (i.e., as  $n$  increases). However, for the solute distribution ratio,  $[\text{C}_2\text{mim}][\text{NTf}_2]$  has the lowest values, which become higher by moderately increasing the length of the alkyl chain of the ionic liquid. In Figure 4, the plot of the extrapolated values of the solute distribution ratio at infinite dilution ( $\beta_{\text{inf}}$ ) against the number of carbon atoms of the alkyl chain of the cation is shown. The values on the y-axis for this figure were calculated by setting  $x_{2,\text{org}}$  to zero in eq 3, or equivalently from the sum of parameters  $A$  and  $B$  in Table 2. As seen, the value of  $\beta_{\text{inf}}$  increases with an increase in the alkyl chain length and levels off for the octyl and decyl chains. The  $\beta_{\text{inf}}$  value then decreases for the dodecyl chain. However, for high concentrations of benzene in the system, the solute distribution ratios appear to reach a maximum for the dodecyl chain.

It is known that benzene interacts with ionic liquids such as  $[\text{C}_2\text{mim}][\text{NTf}_2]$  to form an inclusion compound,  $[\text{C}_2\text{mim}][\text{NTf}_2] \cdot \text{C}_6\text{H}_6$ .<sup>17</sup> Its stability is derived from the anions clustering around the benzene and due to interactions between the benzene hydrogen atoms and the oxygen atoms of the sulfonyl groups in the anions.<sup>17</sup> There is also a lesser interaction with the benzene hydrogen atoms and the anionic fluorine atoms. The cation–benzene interactions are mainly due to  $\pi$ – $\pi$  stacking. A similar type of behavior is seen in the benzene– $[\text{C}_1\text{mim}][\text{PF}_6]$  crystals.<sup>18</sup> From these, the quadrupolar benzene molecule associates with the anion and the imidazolium part of the cation. In long chain 1-alkyl-3-methyl imidazolium ionic liquids, the cationic imidazolium group remains close to the anion to form a charge-containing region, and the alkyl chains form ordered regions where the alkyl groups line up and form an ordered structure. Examples of this effect are known for imidazolium hexafluorophosphates,<sup>19</sup> and in imidazolium halides.<sup>20</sup> Short chain  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ionic liquids can dissolve benzene fairly well, but for hexane, the ionic interactions would be disrupted if it were to mix. Hence, it mixes with benzene to a greater extent than with hexane. For long chain  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ionic liquids, the hexane can be accommodated in the hydrophobic region of the alkyl side chains and hence its solubility in the ionic phase improves. Benzene can also be accommodated in these nonpolar regions, and hence, its solubility increases to such an extent that it is completely miscible with  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ , as it can enter both the hydrophobic régime (within the chains) and the hydrophilic régime (attracted by the imidazolium head groups). These types of mixtures have also been described as liquid clathrates.<sup>21</sup> It can be seen from Figure 1e that  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$  and benzene are completely miscible, but the best benzene distribution ratios occur at low benzene concentrations (Figure 2). The distribution ratios (Figure 2) fall to 1.0–0.8 at high benzene concentrations with the values being in the order  $\text{C}_{12}$



**Figure 2.** Solute distribution ratio for the ternary systems (hexane + benzene +  $[\text{C}_n\text{mim}][\text{NTf}_2]$ ), at 25 °C, as a function of the mole fraction of benzene in the organic-rich phase. Solvents:  $[\text{C}_2\text{mim}][\text{NTf}_2]$ , ●;  $[\text{C}_4\text{mim}][\text{NTf}_2]$ , ○;  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , ■;  $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ , □; and  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ , ▲. The solid lines correspond to the regressions according to eq 3. The error in the data points is  $\pm 3\%$ , and the error bars are shown in the  $[\text{C}_2\text{mim}][\text{NTf}_2]$  data.



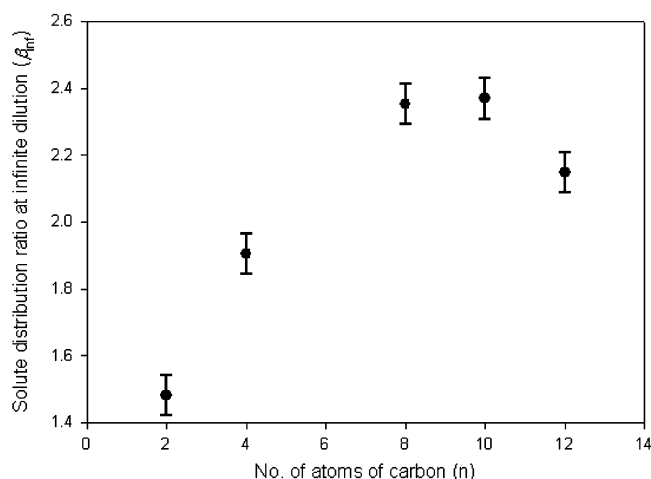
**Figure 3.** Selectivity for the ternary systems (hexane + benzene +  $[\text{C}_n\text{mim}][\text{NTf}_2]$ ), at 25 °C, as a function of the mole fraction of benzene in the organic-rich phase. Solvents:  $[\text{C}_2\text{mim}][\text{NTf}_2]$ , ●;  $[\text{C}_4\text{mim}][\text{NTf}_2]$ , ○;  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , ■;  $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ , □; and  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ , ▲. The solid lines correspond to the regressions according to eq 4.

**TABLE 2: Fitting Parameters of eq 3, Correlation Coefficients ( $R^2$ ), and Relative Standard Deviations ( $\sigma_r$ ) for the Regression of the Solute Distribution Ratio Values as a Function of the Mole Fraction of Solute in the Organic-Rich Phase**

solvent	$A$	$B$	$C$	$R^2$	$\sigma_r$
$[\text{C}_2\text{mim}][\text{NTf}_2]$	0.581	0.901	0.593	0.9982	0.011
$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.698	1.205	0.414	0.9983	0.012
$[\text{C}_8\text{mim}][\text{NTf}_2]$	0.817	1.535	0.341	0.9990	0.013
$[\text{C}_{10}\text{mim}][\text{NTf}_2]$	0.874	1.496	0.311	0.9970	0.021
$[\text{C}_{12}\text{mim}][\text{NTf}_2]$	0.871	1.277	0.324	0.9985	0.013

$> \text{C}_{10} > \text{C}_8 > \text{C}_4 > \text{C}_2$ . At low benzene concentrations (Figure 2), the order changes to  $\text{C}_{12} < \text{C}_{10} = \text{C}_8 > \text{C}_4 > \text{C}_2$ . A plausible explanation is that, for  $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ , hexane is moderately soluble. The benzene can dissolve either in hexane or a phase which is about 50% hexane. The increasing hexane concentration in the ionic liquid as the chain length increases lowers the distribution ratio. The best distribution ratios occur for ionic liquids that are immiscible with benzene, but only just (viz.,





**Figure 4.** Extrapolated values of the solute distribution ratio at infinite dilution, as a function of the number of carbon atoms in the alkyl-substituent chain of the imidazolium ring of the ionic liquid. The error in the data points is  $\pm 3\%$ .

**TABLE 3: Fitting Parameters of eq 4, Correlation Coefficients ( $R^2$ ), and Relative Standard Deviations ( $\sigma_r$ ) for the Regression of the Selectivity Values as a Function of the Mole Fraction of Solute in the Organic-Rich Phase**

solvent	<i>a</i>	<i>b</i>	<i>c</i>	$R^2$	$\sigma_r$
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	−5.411	44.13	0.599	0.9935	0.061
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	−4.270	22.88	0.770	0.9976	0.039
[C <sub>8</sub> mim][NTf <sub>2</sub> ]	−0.257	9.49	0.536	0.9964	0.034
[C <sub>10</sub> mim][NTf <sub>2</sub> ]	−0.869	6.70	0.768	0.9964	0.048
[C <sub>12</sub> mim][NTf <sub>2</sub> ]	−1.612	5.63	1.146	0.9984	0.020

C<sub>8</sub>, or C<sub>10</sub>). Recent simulation work<sup>22</sup> has shown the possible existence of polar and nonpolar domains (regions) in the ionic liquids and that these show different affinities for different solutes (hexane was one of the solutes tested).

## Conclusions

The LLE data at 25 °C for ternary systems involving hexane, benzene, and ionic liquids belonging to the homologous series [C<sub>*n*</sub>mim][NTf<sub>2</sub>] were experimentally determined. These results provide insight on how the modification of the alkyl chain of the ionic liquid influences the ability of the solvent to perform the liquid extraction of aromatic hydrocarbons from their mixtures with alkanes. The change in behavior shown by the selectivity and solute distribution ratio can be rationalized by the different ways in which benzene and hexane interact with the anion and cation of the ionic liquids, with hexane only showing a significant association with long alkyl chains.

In a previous work,<sup>9</sup> [C<sub>2</sub>mim][NTf<sub>2</sub>] was already shown to have a very desirable set of properties, constituting a reliable alternative to volatile organic solvents such as sulfolane<sup>16,23</sup> or other ionic liquids<sup>24</sup> in the solvent extraction processes for the separation of aromatic and aliphatic hydrocarbons. The fresh data reported here indicate that homologous ionic liquids with longer alkyl chains lead to lower selectivities. Conversely, an optimum solute distribution ratio is achieved for the ionic liquids with 8–10 carbon atoms in their alkyl chain, therefore minimizing the amount of solvent required to perform a given extraction.

Nevertheless, their greater viscosity may discourage the use of the latter. Therefore, the most suitable ionic liquid of the series [C<sub>*n*</sub>mim][NTf<sub>2</sub>] to carry out the targeted separation is the one with the shortest alkyl chain in the cation: [C<sub>2</sub>mim][NTf<sub>2</sub>].

**Acknowledgment.** H.R. wants to thank the QUILL Centre for hosting him as a temporary research fellow and the Ministerio de Educación y Ciencia (Spain) for the award of an FPI grant (reference BES-2004-5311) under project PPQ2003-01326. We would also like to acknowledge the QUILL Industrial Advisory Board for their support.

**Supporting Information Available:** Examples of the NMR spectra used in determining the liquid–liquid equilibria. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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