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1-Alkyl-2,3-dimethylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids for the Liquid−Liquid Extraction of Toluene from Heptane

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ABSTRACT: The liquid−liquid equilibria (LLE) of three ternary systems formed by toluene, heptane, and 1-alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids {[*x*dmim][Tf_2N], where *x* refers to ethyl (e), propyl (p), or butyl (b)} were determined at T = 313.2 K and atmospheric pressure. The methyl group in position 2 in the imidazolium cation seems to improve the selectivity of the liquid−liquid extraction process of toluene from heptane compared to the results previously obtained for 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids {[*x*mim][Tf_2N], where *x* refers to ethyl (e), propyl (p), or butyl (b)}. [edmim][Tf_2N] and [pdmim][Tf_2N] ILs seem to be alternatives for sulfolane in the extraction of toluene from heptane. The experimental LLE data were satisfactorily correlated by means of the thermodynamic nonrandom two-liquid (NRTL) model.

INTRODUCTION

Ionic liquids (ILs) are salts with a melting point below 100 °C. They are considered an attractive alternative to conventional organic solvents due to their nonvolatile nature, thermal stability, relatively high polarity, and nonflammability. Thus, their use in liquid−liquid extraction of aromatic hydrocarbons has become an important aim in petrochemical industry, especially to solve the drawbacks of this separation at low concentrations of aromatics.[1]

A variety of experimental measurements of liquid−liquid equilibria (LLE) for aromatic/aliphatic mixtures and ILs is available in literature.[2−33] Most of the ILs investigated are imidazolium-based ILs.[2−5,7,8,10−12,14−16,20,21,31−33] Moreover, 1,3-dialkylimidazolium salts are still the most studied and best-characterized ILs.[34] Among all of them, only a few have shown both a higher selectivity and a higher extractive capacity than those of sulfolane, which is the most common organic solvent in current separation processes of aromatics.[35] The combination of some 1,3-dialkylimidazolium cations and the bis(trifluoromethylsulfonyl)imide anion has enhanced not only the selectivity or the extractive capacity of aromatics related to sulfolane but also the chemical stability of the solvent.[10−12,31,32,36] However, the effect of introducing another methyl group in the imidazolium ring has not been studied despite the fact that it could modify the aromaticity of the ILs, improving the selectivity or the extractive capacity in the separation process.

Hence, this work was focused on the separation of toluene from heptane using 1-alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ILs {[*x*dmim][Tf_2N], where *x* refers to ethyl (e), propyl (p), or butyl (b)}. The measurement of LLE data was determined at T = 313.2 K and atmospheric pressure. The purpose of this research was to study the effect of a methyl group inclusion in position 2 in different imidazolium cations on selectivity and extractive capacity. Therefore, the results were compared with those previously reported for the systems toluene + heptane + 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide {[*x*mim][Tf_2N], where *x* refers to ethyl (e), propyl (p), or butyl (b)}[31,32] and also with those for the system toluene + heptane + sulfolane.[5] The selectivity and the extractive capacity were calculated from the LLE data. The quality of the experimental LLE data was tested using the Othmer−Tobias equation. In addition, the LLE data were correlated by the nonrandom two-liquid (NRTL) model.

EXPERIMENTAL SECTION

Heptane and toluene over molecular sieves were supplied by Sigma-Aldrich with a mass fraction purity greater than 0.995 and 0.997, respectively. Their quoted water mass fractions were less than 0.00005. The three ILs 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([edmim][Tf_2N]), 1-propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([pdmim][Tf_2N]), and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([bdmim][Tf_2N]) were provided by Iolitec GmbH with quoted mass fraction purities greater than 0.99 and halides and water mass fractions less than 0.0001. The water content and purity of the reagents were given by the manufacturer. All chemicals were used as received, without further purification. To prevent water hydration, they were kept in their original tightly closed bottles in a desiccator. When any chemicals were used, they were always manipulated inside a glovebox under a dry nitrogen atmosphere.

The LLE experiments with the systems heptane + toluene + [edmim][Tf_2N], [pdmim][Tf_2N], or [bdmim][Tf_2N] were performed in 8 mL vials with screw caps providing hermetic sealing. The gravimetrically prepared feed mixtures of heptane/toluene/IL were shaken at T = 313.2 K with a shaking speed of 800 rpm for 5 h and were settled overnight. This was carried out according to the procedure previously reported.[31] The estimated error in the mole fraction in the prepared feed mixture was less than 0.001.

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Table 1. Experimental LLE Data on Mole Fraction (x), Distribution Ratios (D_i), and Separation Factors ($\alpha_{2,1}$) at T = 313.2 K

feed (global composition)		heptane-rich phase (upper layer)		IL-rich phase (lower layer)				
x_1	x_2	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	D_1	D_2	$\alpha_{2,1}$
			Heptane (1) + Toluene (2) + [edmim][Tf_2N] (3)					
0.5016	0.0000	1.0000	0.0000	0.0264	0.0000	0.026		
0.4883	0.0279	0.9698	0.0302	0.0219	0.0257	0.023	0.851	37.7
0.4634	0.0544	0.9422	0.0578	0.0222	0.0513	0.024	0.888	37.7
0.4386	0.1165	0.8748	0.1252	0.0236	0.1082	0.027	0.864	32.0
0.4074	0.1869	0.7930	0.2070	0.0214	0.1669	0.027	0.806	29.9
0.3505	0.3004	0.6525	0.3475	0.0210	0.2491	0.032	0.717	22.3
0.3100	0.3819	0.5607	0.4393	0.0212	0.3158	0.038	0.719	19.0
0.2781	0.4462	0.4830	0.5170	0.0192	0.3568	0.040	0.690	17.4
0.2334	0.5335	0.3852	0.6148	0.0189	0.4186	0.049	0.681	13.9
0.1791	0.6431	0.2687	0.7313	0.0157	0.4823	0.058	0.660	11.3
0.1274	0.7466	0.1806	0.8194	0.0140	0.5915	0.078	0.722	9.3
0.0000	0.8510	0.0000	1.0000	0.0000	0.6336		0.634	
			Heptane (1) + Toluene (2) + [pdmim][Tf_2N] (3)					
0.5033	0.0000	1.0000	0.0000	0.0295	0.0000	0.030		
0.4826	0.0279	0.9740	0.0260	0.0375	0.0297	0.039	1.142	29.7
0.4740	0.0556	0.9445	0.0555	0.0313	0.0558	0.033	1.005	30.3
0.4446	0.1155	0.8813	0.1187	0.0301	0.1125	0.034	0.948	27.7
0.4078	0.1889	0.7986	0.2014	0.0296	0.1768	0.037	0.878	23.7
0.3559	0.2925	0.6798	0.3202	0.0306	0.2646	0.045	0.826	18.4
0.3138	0.3758	0.5804	0.4196	0.0256	0.3284	0.044	0.783	17.7
0.2800	0.4439	0.4998	0.5002	0.0254	0.3787	0.051	0.757	14.9
0.2348	0.5338	0.3920	0.6080	0.0244	0.4346	0.062	0.715	11.5
0.1792	0.6424	0.2756	0.7244	0.0219	0.5086	0.079	0.702	8.8
0.1254	0.7499	0.1686	0.8314	0.0204	0.5522	0.121	0.664	5.5
0.0000	0.8515	0.0000	1.0000	0.0000	0.6958		0.696	
			Heptane (1) + Toluene (2) + [bdmim][Tf_2N] (3)					
0.5024	0.0000	1.0000	0.0000	0.0439	0.0000	0.044		
0.4878	0.0276	0.9757	0.0243	0.0490	0.0305	0.050	1.255	25.0
0.4749	0.0557	0.9482	0.0518	0.0473	0.0593	0.050	1.145	22.9
0.4429	0.1162	0.8828	0.1172	0.0418	0.1153	0.047	0.984	20.8
0.4073	0.1841	0.8207	0.1793	0.0424	0.1883	0.052	1.050	20.3
0.3545	0.2925	0.7053	0.2947	0.0413	0.2905	0.059	0.986	16.8
0.3125	0.3763	0.6056	0.3944	0.0404	0.3595	0.067	0.912	13.7
0.2804	0.4431	0.5263	0.4737	0.0389	0.4130	0.074	0.872	11.8
0.2306	0.5397	0.4110	0.5890	0.0357	0.4864	0.087	0.826	9.5
0.1778	0.6455	0.2856	0.7144	0.0297	0.5510	0.104	0.771	7.4
0.1258	0.7491	0.1813	0.8187	0.0232	0.6209	0.128	0.758	5.9
0.0000	0.8514	0.0000	1.0000	0.0000	0.7031		0.703	

Samples from the heptane-rich phase were analyzed by ^{1}H NMR. The spectra showed no detectable signals arising from the ILs, so the IL mole fractions in the heptane-rich phases appear to be negligible. Thus, gas chromatographic analyses of each layer plus an overall mass balance on hydrocarbons in the mixture were done to determine the phase compositions. A detailed description of the equipments and the analysis conditions can be found elsewhere.[31]

An area normalization method with response factors was carried out to determine the hydrocarbon mole ratio in each layer. The gas chromatography response factors for the hydrocarbons were calculated by using standard mixture samples of pure heptane and toluene. The compositions of these standard samples were obtained through weighing with an electronic balance having a precision of ± 0.0001 g. Toluene in the mixture was chosen as the standard, and its response factor was set to 1.0. The response factor for heptane was then calculated using the renormalization method before every run of samples to ensure measurement accuracy. Samples were taken in triplicate, and each of them injected six times in gas chromatography (GC). The average compositions are reported here. The estimated uncertainties in the compositions, calculated as the standard deviation of the measurements, were less than 0.001.

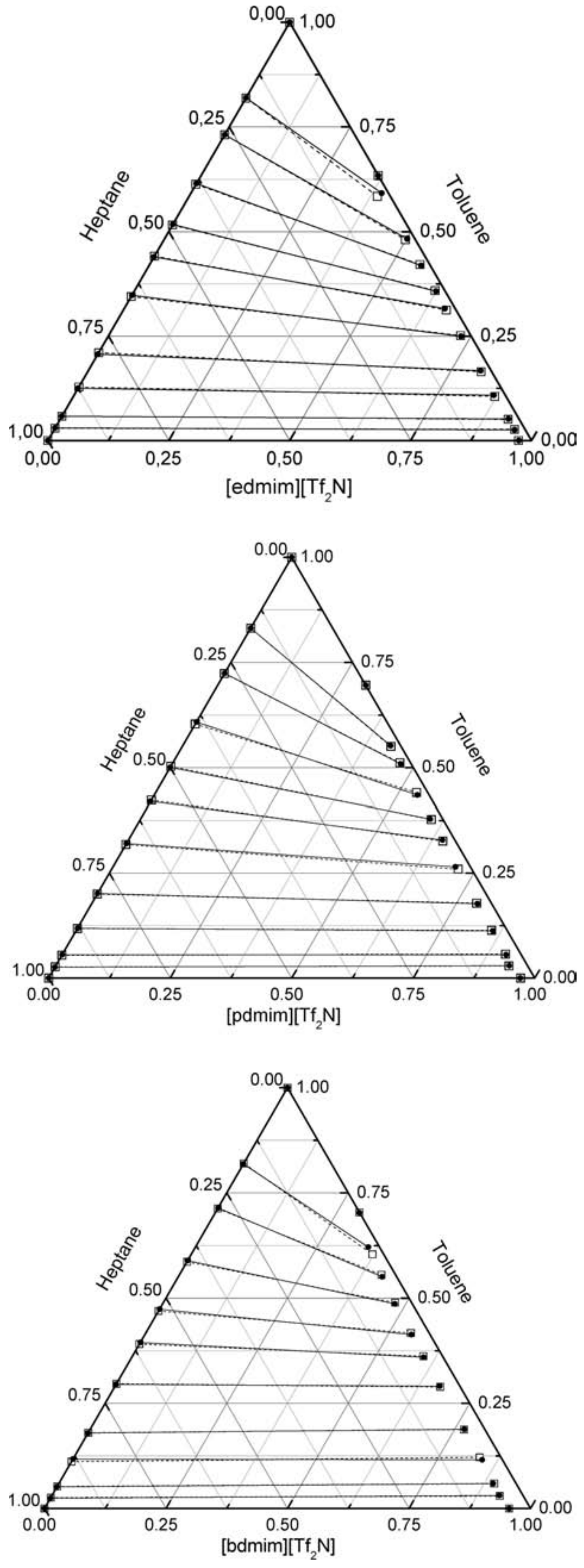

Figure 1. Experimental and calculated LLE for the ternary systems heptane (1) + toluene (2) + IL (3) at $T = 313.2$ K. Solid lines and full points indicate experimental tie lines, and dashed lines and empty squares indicate calculated data by the NRTL model.

RESULTS AND DISCUSSION

The experimental LLE data for the ternary systems heptane + toluene + [edmim][Tf_2N], [pdmim][Tf_2N], or [bdmim][Tf_2N] at $T = 313.2$ K and atmospheric pressure are shown in Table 1 and plotted in triangular diagrams in Figure 1. As can be seen in Table 1, no IL is detected in the heptane-rich phase. Therefore, no extra operation would be needed for purifying the heptane and recovering the solvent. This fact would reduce the cost of the aromatic hydrocarbons extraction process. On the other hand, the negative slopes of the tie lines in the three triangular diagrams (Figure 1) at high concentrations of toluene in the feed show a greater solubility of toluene in the heptane than in the IL. This situation remains the same for [edmim][Tf_2N] IL at low concentrations of toluene. However, [pdmim][Tf_2N] and [bdmim][Tf_2N] ILs show solutropy; that is, the slope from the tie lines changes from negative to positive as the concentration of toluene decreases.

The reliability of the experimentally measured LLE data can be ascertained by applying the Othmer–Tobias correlation[37]

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

where w_3^{II} is the mass fraction of IL (3) in the IL-rich phase (lower layer), w_1^{I} is the mass fraction of heptane (1) in the heptane-rich phase (upper layer), and a and b are the fitting parameters of the Othmer–Tobias correlation. The linearity of the plot, shown in Figure 2, indicates the degree of quality of the data. The parameters of the Othmer–Tobias correlation are given in Table 2. The regression coefficients (R^2) very close to unity, and the low values of the standard deviation (σ) presented in Table 2 indicate the high degree of quality of the experimental LLE data.

The distribution ratio of heptane (D_1) and toluene (D_2) and the separation factor ($\alpha_{2,1}$) were used to establish the suitability of these ILs to perform the liquid–liquid extraction of toluene from its mixtures with heptane. These parameters were calculated as follows

$$D_1 = \frac{x_1^{\mathrm{II}}}{x_1^{\mathrm{I}}} \tag{2}$$

$$D_2 = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \tag{3}$$

$$\alpha_{2,1} = \frac{D_2}{D_1} \tag{4}$$

where x is the mole fraction, superscripts I and II refer to the heptane-rich and IL-rich phases, respectively, and subscripts 1 and 2 denote heptane and toluene, respectively. The values of D_1, D_2, and $\alpha_{2,1}$ are shown in Table 1 together with the experimental LLE data. As expected from the solutropic behavior, the values of D_2 for [pdmim][Tf_2N] and [bdmim][Tf_2N] ILs are higher than unity at low molar fractions of toluene in the heptane-rich phase and then change to values below unity as the concentration of toluene increases. Thus, the horizontal tie line, or solutrope, in the triangular diagrams (Figure 1) corresponds to a molar fraction of toluene (x_2^{I}) in the range of 0.0560 to 0.1200 for both ILs.

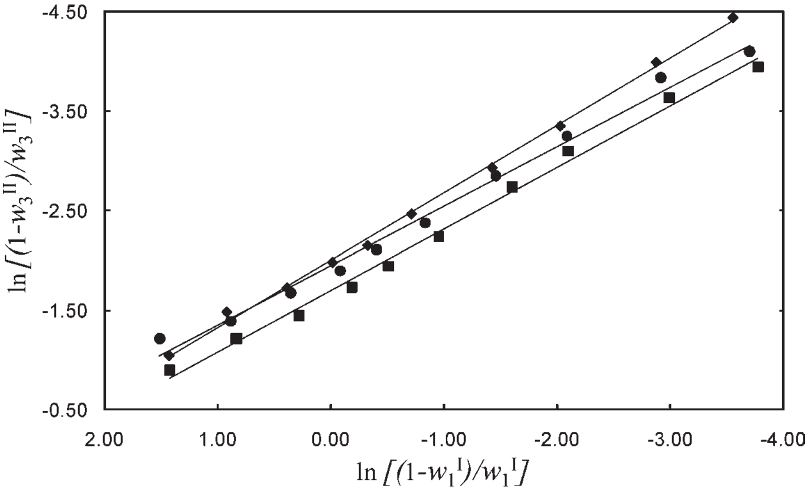

Figure 2. Othmer−Tobias plot for the ternary systems at T = 313.2 K: ◆, heptane (1) + toluene (2) + [edmim][Tf$_2$N] (3); ●, heptane (1) + toluene (2) + [pdmim][Tf$_2$N] (3); ■, heptane (1) + toluene (2) + [bdmim][Tf$_2$N] (3). Solid lines represent the linear Othmer−Tobias fit.

The distribution ratios of heptane (D_1) for the systems heptane + toluene + [edmim][Tf$_2$N], [pdmim][Tf$_2$N], or [bdmim][Tf$_2$N] as a function of toluene mole fraction (x_2^{I}) in the heptane-rich phase are plotted in Figure 3. The results were compared to those previously reported for the system heptane + toluene + sulfolane[5] and the corresponding heptane + toluene + [$x$mim][Tf$_2$N] systems, where x refers to ethyl (e), propyl (p), and butyl (b).[31,32] The distribution ratio of toluene (D_2) and the separation factor ($\alpha_{2,1}$) versus x_2^{I} for these same systems are also plotted in Figures 4 and 5 together with data for sulfolane and [$x$mim][Tf$_2$N] ILs. To facilitate the understanding of the plots, the values for [$x$mim][Tf$_2$N] ILs were represented by empty symbols and the values for [$x$dmim][Tf$_2$N] ILs by solid symbols.

As can be seen in Figures 3, 4, and 5 for [$x$dmim][Tf$_2$N] ILs, the amounts of toluene and heptane dissolved in the IL are higher as it grows the length of the alkyl chain in the imidazolium ring by increasing the distribution ratios and decreasing the selectivity in the extraction of toluene. Thus, [bdmim][Tf$_2$N] IL shows the highest distribution ratios of toluene and heptane and the lowest separation factors. This behavior is the same as previously observed for [$x$mim][Tf$_2$N] ILs.[31,32] On the other hand, the three ILs show distribution ratios of toluene greater than those of sulfolane in the whole range of compositions (Figure 4), but only the separation factors of the [edmim][Tf$_2$N] and [pdmim][Tf$_2$N] ILs are higher than that of sulfolane (Figure 5). The [edmim][Tf$_2$N] and [pdmim][Tf$_2$N] ILs could be considered an alternative for sulfolane in the liquid−liquid extraction of toluene from its mixtures with heptane.

In addition, comparisons were made between each pair of [$x$mim][Tf$_2$N] and [$x$dmim][Tf$_2$N] ILs. The purpose of these comparisons was to study the effect of a methyl group inclusion in position 2 in different imidazolium cations on the selectivity and capacity of the extraction of toluene from its mixtures with heptane. As illustrated in Figure 3, [$x$dmim][Tf$_2$N] ILs show a lower distribution ratio of heptane than the corresponding [$x$mim][Tf$_2$N] ILs. However, no effect was observed in the distribution ratio of toluene (Figure 4). Hence, the separation factors of [$x$dmim][Tf$_2$N] ILs are higher than those of the corresponding [$x$mim][Tf$_2$N] ILs, as Figure 5 shows. Thus, the inclusion of a methyl group in position 2 in a 1-alkyl-3-methylimidazolium cation seems to improve the selectivity of the IL with respect to the corresponding 1-alkyl-3-methylimidazolium, but it maintains the extractive capacity of toluene.

Table 2. Constants of the Othmer−Tobias Correlation (a, b), Regression Coefficients (R^2), and Standard Deviations (σ) at T = 313.2 K

a	b	R^2	σ
Heptane (1) + Toluene (2) + [edmim][Tf$_2$N] (3)			
−2.0032	0.6758	0.9977	0.0223
Heptane (1) + Toluene (2) + [pdmim][Tf$_2$N] (3)			
−1.9489	0.6003	0.9889	0.0906
Heptane (1) + Toluene (2) + [bdmim][Tf$_2$N] (3)			
−1.7128	0.6182	0.9887	0.0972

The NRTL model[38] was used to correlate the LLE data in the present work, as it has proven to have adequate correlating capability with respect to ternary LLE data for systems containing ILs.[39] In this model, the two binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ were calculated using an ASPEN Plus simulator. The regression method used in the ASPEN Plus simulator was the generalized least-squares method based on maximum likelihood principles. The Britt−Luecke algorithm[40] was employed to obtain the model parameters with the Deming initialization method. The regression convergence tolerance was set to 0.0001. The third nonrandomness parameter, α_{ij}, in the NRTL model was subject to optimization between 0 and 1.

Table 3 shows the values of the fitting parameters obtained using the NRTL model to correlate the experimental LLE data for the three ternary systems. The calculated tie lines from the correlation based on the NRTL model are plotted in Figure 1 together with the experimental tie-line data. The values of the root-mean-square deviation (rmsd) for the four ternary systems are also listed in Table 3. The rmsd is defined as

$$\text{rmsd} = \left\{ \frac{\sum_i \sum_l \sum_m (x_{ilm}^{\text{exptl}} - x_{ilm}^{\text{calcd}})^2}{6k} \right\}^{1/2} \qquad (5)$$

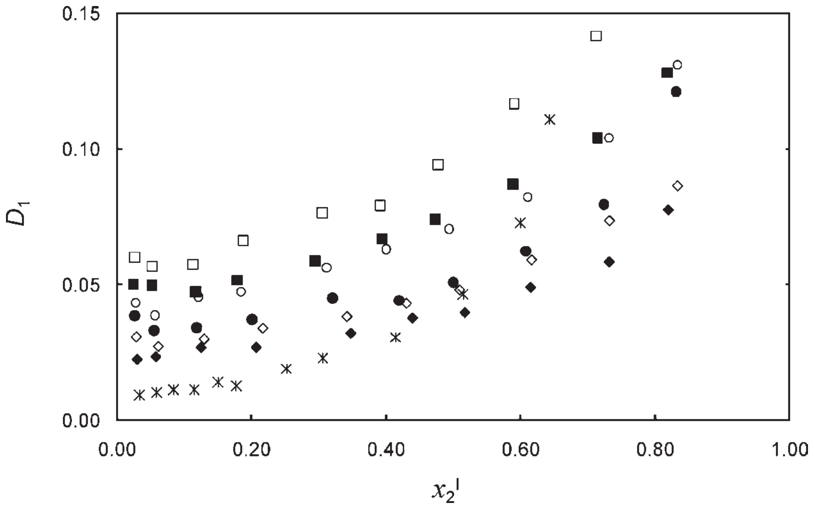

Figure 3. Heptane distribution ratio for the ternary systems at T = 313.2 K: ◇, heptane (1) + toluene (2) + [emim][Tf_2N] (3) (from ref 31); ◆, heptane (1) + toluene (2) + [edmim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [mpim][Tf_2N] (3) (from ref 32); ●, heptane (1) + toluene (2) + [pdmim][Tf_2N] (3); □, heptane (1) + toluene (2) + [bmim][Tf_2N] (3) (from ref 31); ■, heptane (1) + toluene (2) + [bdmim][Tf_2N] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 5).

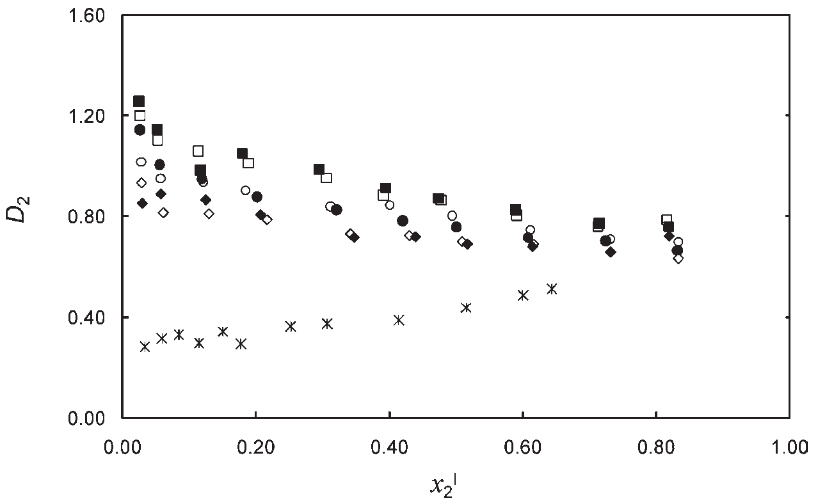

Figure 4. Toluene distribution ratio for the ternary systems at T = 313.2 K: ◇, heptane (1) + toluene (2) + [emim][Tf_2N] (3) (from ref 31); ◆, heptane (1) + toluene (2) + [edmim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [mpim][Tf_2N] (3) (from ref 32); ●, heptane (1) + toluene (2) + [pdmim][Tf_2N] (3); □, heptane (1) + toluene (2) + [bmim][Tf_2N] (3) (from ref 31); ■, heptane (1) + toluene (2) + [bdmim][Tf_2N] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 5).

where x is the mole fraction and the subscripts i, l, and m represent the component, phase, and tie line, respectively. The value of k designates the number of tie lines.

Taking into account the rmsd values shown in Table 3, the NRTL model seems to be adequate to correlate the LLE data.

■ CONCLUSIONS

LLE data for the systems heptane + toluene + [edmim][Tf_2N], [pdmim][Tf_2N], or [bdmim][Tf_2N] were determined experimentally at T = 313.2 K and atmospheric pressure. A high degree of quality of the experimental LLE data was ascertained by applying the Othmer–Tobias correlation. The distribution ratios of heptane and toluene and the separation factors for these ternary systems were calculated and compared with those for the system heptane + toluene + sulfolane and the systems previously reported, heptane + toluene + [emim][Tf_2N], [mpim][Tf_2N], or [bmim][Tf_2N]. The inclusion of a methyl group in the 1-alkyl-3-methylimidazolium cation seems to reduce the amount of heptane dissolved in the IL, but it does not affect the solubility of toluene. Hence, the distribution ratio of toluene is similar between [$x$mim][TF_2N] IL and the corresponding [$x$dmim][Tf_2N] IL, whereas the separation factor of the liquid–liquid extraction of toluene from heptane is improved with [$x$dmim][Tf_2N] ILs with respect to the [$x$mim][TF_2N] ILs. On the other hand, the [edmim][Tf_2N] and the [pdmim][Tf_2N] ILs show a higher distribution ratio of toluene and a higher separation factor than those of sulfolane. Thus, these two ILs would be a possible alternative for the liquid–liquid extraction of toluene from heptane. The NRTL

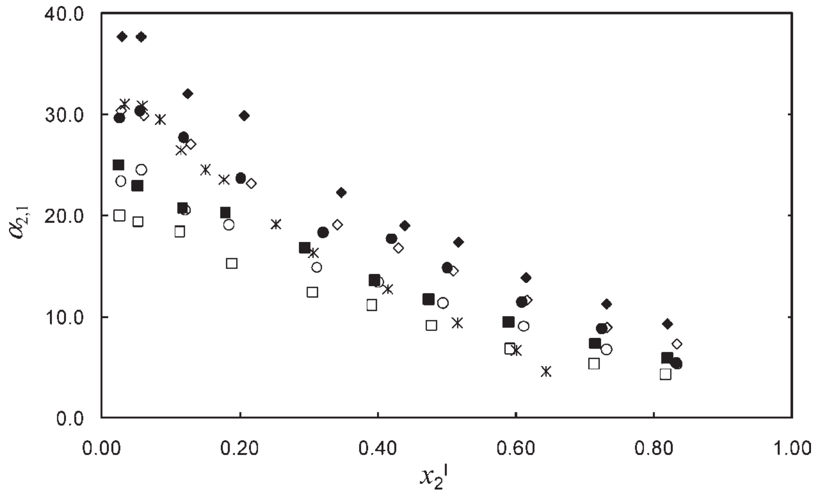

Figure 5. Separation factor for the ternary systems at $T = 313.2$ K: ◇, heptane (1) + toluene (2) + [emim][Tf_2N] (3) (from ref 31); ◆, heptane (1) + toluene (2) + [edmim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [mpim][Tf_2N] (3) (from ref 32); ●, heptane (1) + toluene (2) + [pdmim][Tf_2N] (3); □, heptane (1) + toluene (2) + [bmim][Tf_2N] (3) (from ref 31); ■, heptane (1) + toluene (2) + [bdmim][Tf_2N] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 5).

Table 3. Values of the NRTL Parameters Obtained from LLE Data by Regression at T = 313.2 K

component	NRTL parameters			
$i-j$	$(\Delta g_{ij}/R)$/K	$(\Delta g_{ji}/R)$/K	α_{ij}	rmsd
	Heptane (1) + Toluene (2) + [edmim][Tf_2N] (3)			
1−2	760.98	286.92	0.4645	0.0025
1−3	7902.3	972.89	0.3697	
2−3	1003.9	−11.809	0.2126	
	Heptane (1) + Toluene (2) + [pdmim][Tf_2N] (3)			
1−2	767.90	186.54	0.5618	0.0021
1−3	2758.4	811.65	0.3643	
2−3	1022.4	33.566	0.3186	
	Heptane (1) + Toluene (2) + [bdmim][Tf_2N] (3)			
1−2	−78.051	466.80	0.1524	0.0036
1−3	11848	775.26	0.3140	
2−3	1680.2	−320.75	0.3054	

model was used to satisfactorily correlate the experimental LLE data for the three studied ternary systems.

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