Liquid−Liquid Extraction of Toluene from Heptane Using 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids

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The good stability and suitable polarity of the 1-alkyl-3-methyl bis(trifluoromethylsulfonyl)imide ionic liquids have prompted their use as solvents for the extraction of mixtures of aromatic and aliphatic hydrocarbons. In this paper, aiming to extend the study of these ionic liquids, the liquid−liquid equilibrium for the systems toluene + heptane + [mmim][Tf_2N], [emim][Tf_2N], [bmim][Tf_2N], or [hmim][Tf_2N] at $T = 313.2$ K were determined. The experiments with [mmim][Tf_2N] and [emim]Tf_2N have shown good results in the separation of toluene from heptane compared with the distribution ratio and separation factor of sulfolane in the whole range of composition. The degree of consistency of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation. The phase diagrams for the ternary systems were plotted, and the tie lines correlated with the NRTL model compare satisfactorily with the experimental data.

Introduction

In recent years, great progresses in the petrochemical industry have been focused on the design of environmentally friendly processes as well as the reduction of high investment and energy consumption. Among these processes, the separation of aromatic hydrocarbons (e.g., toluene, benzene, xylenes, etc.) from petroleum streams by liquid−liquid extraction has aroused a great interest. The research in this field is being driven toward a sustainable green chemistry and less complex processes for the recovery of the aromatic hydrocarbons from their mixtures with aliphatics. In this context, ionic liquids (ILs) have become a novel alternative to replace conventional organic solvents in extraction processes due to their negligible vapor pressure.[1]

In order to assess the feasibility of ILs as nonvolatile solvents for the extraction of aromatics, many authors have determined the thermodynamic and extractive properties for ternary systems containing ILs, aromatic and aliphatic hydrocarbons.[2−29] Among the ILs investigated thus far, only a few have shown both higher selectivity and extractive capacity than those of sulfolane,[30] which is the most common extraction solvent in current industrial processes. In addition, some ILs are highly affected by the presence of water, leading to changes in their properties[31,32] and even decompositions with HF generation.[1] To avoid the drawbacks related to water, we have studied ILs based on the hydrophobic bis(trifluoromethylsulfonyl)imide anion ([Tf_2N]). ILs based on this anion have proved to be practically immiscible in water, insoluble in less polar species such as toluene or *n*-hexane, and chemically stable.[10,33] Furthermore, in previous works published by Arce et al.,[10−12,17] 1-alkyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ILs have shown to be potential alternative solvents for the separation of aliphatic and aromatic mixtures.

Hence, in order to go beyond the study of these ILs in aromatic extraction and as a continuation of our previous work,[20,21,27−29] the objective of this research was the measurement of liquid−liquid equilibrium (LLE) data for the ternary systems toluene + heptane +1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs {[*x*mim][Tf_2N], where *x* refers to methyl (m), ethyl (e), butyl (b), or hexyl (h) group}. The purpose of this study was not only determining LLE data for the former systems, but also observe the effect of the alkyl chain length in the IL on the efficiency of the separation process. The selectivity and the extractive capacity of solvents were calculated from the LLE data. The consistency of the experimental LLE data was tested using the Othmer-Tobias correlation. A comparison of our results with those previously reported in the literature for the ternary systems heptane + toluene + sulfolane[5] and toluene + heptane + [emim][Tf_2N][10] was also done. In addition, the LLE data were correlated by the nonrandom two liquid (NRTL) model.

Table 1. Density ρ at $T = 298.15$ K and Molecular Weight, *M*, of the ILs [mmim][Tf_2N], [emim][Tf_2N], [bmim][Tf_2N], [hmim][Tf_2N] Studied in This Work

IL	ρ / $g \cdot cm^{-3}$	M / $g \cdot mol^{-1}$
[mmim][Tf_2N]	1.570	377.28
[emim][Tf_2N]	1.524	391.31
[bmim][Tf_2N]	1.440	419.37
[hmim][Tf_2N]	1.377	447.42

Experimental Section

Heptane and toluene over molecular sieves were supplied by Sigma-Aldrich with mass fraction purity greater than 0.995 and 0.997, respectively. Their water mass fractions were less than 0.00005. Four ILs based on the cations 1,3-dimethylimidazolium ([mmim]), 1-ethyl-3-methylimidazolium ([emim]), 1-butyl-3-methylimidazolium ([bmim]), and 1-hexyl-3-methylimidazolium ([hmim]), all with the anion bis(trifluoromethylsulfonyl)imide ([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. Water content and purity of the reagents were given by the manufacturer. The molecular weight and density of the ILs are shown in Table 1. The density of the ILs was experimentally determined using a densimeter (model

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Anton Paar DMA 5000). 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 were performed in 8 mL vials with screw caps providing hermetic sealing. Mixtures of known masses of heptane/toluene feed were transferred to tared vials. After the vials were reweighed, the IL ([mmim][Tf_2N], [emim][Tf_2N], [bmim][Tf_2N], or [hmim][Tf_2N]) was gravimetrically added to the feed. The vials were then placed in a shaking incubator at 313.2 K with a shaking speed of 800 rpm for 5 h to reach the thermodynamic equilibrium. Finally, to ensure complete phase separation, the vials were left to settle overnight at a constant temperature of 313.2 K in a dry bath. Every weighing involved in the experimental work was carried out on a Mettler Toledo AB104 balance with a precision of ± 0.0001 g. The error in the mole fraction in the prepared feed mixture was less than 0.001. The uncertainties in the temperature measurements were ± 0.1 K.

Samples from the upper layers (heptane-rich phases) were analyzed using a Bruker Avance 500 MHz NMR spectrometer. The ^1H NMR 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. Approximately 50 μL samples from the lower and upper layers were carefully taken with disposable Pasteur micropipets, dissolved in 1 mL of acetone, and analyzed using a gas chromatograph (model Varian GC 430) equipped with a flame ionization detector (FID), a 30 m × 0.250 mm (film thickness = 0.25 μm) CP-Sil 8CB wall-coated open tubular column (Chrompack), a 5 m × 0.250 mm uncoated fused silica precolumn to collect the ILs present in the lower layers, an isothermal split/splitless injector (model Varian 1177), and an autosampler (model Varian CP-8400). The Varian Galaxie chromatography software was used to obtain the chromatographic areas for the hydrocarbon components. The oven temperature was fixed at 363 K. The injector port and detector temperatures were held at 523 K. The flow rate of the carrier gas (helium) was kept at 2 $mL \cdot min^{-1}$.

An area normalization method with response factors was carried out to determine the hydrocarbon molar 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 the GC. The average compositions are the ones reported here. The estimated uncertainties in the mole compositions, calculated as the standard deviation of the measurements, were less than 0.001.

Results and Discussion

The mole fraction compositions for the toluene/heptane feed, heptane-rich phase (raffinate) and IL-rich phase (extract) for the ternary systems toluene + heptane + [mmim][Tf_2N], [emim][Tf_2N], [bmim][Tf_2N], or [hmim][Tf_2N] at T/K = 313.2 and atmospheric pressure are shown in Table 2 and plotted on the triangular diagrams in Figure 1. The negative slopes of the tie lines at high concentrations of toluene indicate the higher solubility of toluene in heptane than in the IL. However, as well as the amount of toluene decreases, the slopes become horizontal which means a higher solubility of toluene in the IL. No IL was detected in the heptane-rich phase. This situation is desirable since it would eliminate the need of an extra unit to purify the raffinate phase for recovering the solvent.

In order to ascertain the reliability of the experimental LLE data, the Othmer−Tobias correlation[34] was applied

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

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 indicates the degree of consistency of the data. The parameters of the Othmer−Tobias correlation are given in Table 3. The regression coefficients (R^2) very close to unity and the low values of the standard deviation (σ) presented in Table 3 indicate the high degree of consistency of the experimental LLE data.

The potential use of these ILs as solvents for the extraction of toluene from heptane at different concentrations of toluene in the feed has been evaluated by the heptane and toluene distribution ratios D_1 and D_2, respectively, and the separation factor (α_{12}), calculated from the experimental data as follows:

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

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

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

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 refer to heptane and toluene, respectively. The values of D_1, D_2, and $\alpha_{2,1}$ are shown in Table 2 together with the experimental LLE data.

The distribution ratios and separation factors for the four ternary systems as functions of the toluene mole fractions in the heptane-rich phase (x_2^{I}) are plotted in Figures 2, 3, and 4. Comparisons with literature data for the ternary systems heptane + toluene + sulfolane at 313.2 K[5] and heptane + toluene + [emim][Tf_2N] at 298.2 K[10] are also made. As can be seen from Figures 2 to 4, our results for [emim][Tf_2N] IL are similar to those previously reported by Arce et al.[10] in spite of the fact that the temperature of our experiments was higher. This fact could demonstrate the minor effect of the temperature on the liquid−liquid extraction process with ILs as solvents. The results for the heptane distribution ratios for all the four ILs, plotted in Figure 2, are higher than that

Table 2. 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) + [mmim][Tf_2N] (3)								
0.4996	0.0000	1.0000	0.0000	0.0178	0.0000	0.018		
0.4863	0.0255	0.9703	0.0297	0.0186	0.0214	0.019	0.721	37.6
0.4728	0.0555	0.9343	0.0657	0.0162	0.0454	0.017	0.691	39.9
0.4416	0.1156	0.8636	0.1364	0.0174	0.0947	0.020	0.694	34.5
0.4091	0.1810	0.7826	0.2174	0.0164	0.1428	0.021	0.657	31.3
0.3568	0.2851	0.6579	0.3421	0.0154	0.2205	0.023	0.645	27.5
0.3065	0.3877	0.5326	0.4674	0.0147	0.2847	0.028	0.609	22.1
0.2792	0.4411	0.4736	0.5264	0.0151	0.3252	0.032	0.618	19.4
0.2299	0.5392	0.3676	0.6324	0.0129	0.3921	0.035	0.620	17.7
0.1764	0.6466	0.2558	0.7442	0.0124	0.4450	0.048	0.598	12.3
0.1259	0.7483	0.1660	0.8340	0.0107	0.5019	0.064	0.602	9.3
0.0000	0.8701	0.0000	1.0000	0.0000	0.5891		0.589	
Heptane (1) + Toluene (2) + [emim][Tf_2N] (3)								
0.5017	0.0000	1.0000	0.0000	0.0251	0.0000	0.025		
0.4875	0.0278	0.9712	0.0288	0.0299	0.0269	0.031	0.934	30.3
0.4745	0.0557	0.9385	0.0615	0.0256	0.0501	0.027	0.815	29.9
0.4440	0.1173	0.8703	0.1297	0.0261	0.1051	0.030	0.810	27.0
0.4056	0.1938	0.7830	0.2170	0.0266	0.1706	0.034	0.786	23.1
0.3534	0.2974	0.6581	0.3419	0.0252	0.2494	0.038	0.729	19.0
0.3138	0.3743	0.5697	0.4303	0.0246	0.3111	0.043	0.723	16.7
0.2805	0.4404	0.4905	0.5095	0.0236	0.3558	0.048	0.698	14.5
0.2328	0.5359	0.3837	0.6163	0.0227	0.4240	0.059	0.688	11.6
0.1797	0.6427	0.2678	0.7322	0.0197	0.4802	0.074	0.656	8.9
0.1254	0.7502	0.1666	0.8334	0.0144	0.5258	0.086	0.631	7.3
0.0000	0.8511	0.0000	1.0000	0.0000	0.6341		0.634	
Heptane (1) + Toluene (2) + [bmim][Tf_2N] (3)								
0.5014	0.0000	1.0000	0.0000	0.0540	0.0000	0.054		
0.4868	0.0288	0.9740	0.0260	0.0584	0.0312	0.060	1.200	20.0
0.4736	0.0556	0.9473	0.0527	0.0538	0.0581	0.057	1.102	19.4
0.4425	0.1168	0.8867	0.1133	0.0509	0.1199	0.057	1.058	18.4
0.4067	0.1892	0.8119	0.1881	0.0537	0.1901	0.066	1.011	15.3
0.3527	0.2973	0.6949	0.3051	0.0531	0.2905	0.076	0.952	12.5
0.3168	0.3679	0.6087	0.3913	0.0481	0.3464	0.079	0.885	11.2
0.2785	0.4441	0.5224	0.4776	0.0492	0.4126	0.094	0.864	9.2
0.2332	0.5349	0.4090	0.5910	0.0477	0.4757	0.117	0.805	6.9
0.1811	0.6387	0.2874	0.7126	0.0407	0.5410	0.142	0.759	5.4
0.1259	0.7488	0.1840	0.8160	0.0332	0.6416	0.180	0.786	4.4
0.0000	0.8511	0.0000	1.0000	0.0000	0.7273		0.727	
Heptane (1) + Toluene (2) + [hmim][Tf_2N] (3)								
0.5015	0.0000	1.0000	0.0000	0.1375	0.0000	0.138		
0.5036	0.0287	0.9772	0.0228	0.1161	0.0335	0.119	1.469	12.4
0.4754	0.0558	0.9530	0.0470	0.1211	0.0623	0.127	1.326	10.4
0.4430	0.1171	0.9051	0.0949	0.1153	0.1328	0.127	1.399	11.0
0.4110	0.1821	0.8406	0.1594	0.1047	0.1984	0.125	1.245	10.0
0.3537	0.2946	0.7308	0.2692	0.1036	0.3115	0.142	1.157	8.2
0.3151	0.3717	0.6422	0.3578	0.0969	0.3809	0.151	1.065	7.1
0.2668	0.4683	0.5186	0.4814	0.0852	0.4588	0.164	0.953	5.8
0.2369	0.5276	0.4490	0.5510	0.0864	0.5110	0.192	0.927	4.8
0.1787	0.6435	0.3018	0.6982	0.0744	0.5971	0.247	0.855	3.5
0.1271	0.7464	0.1879	0.8121	0.0552	0.6685	0.294	0.823	2.8
0.0000	0.8510	0.0000	1.0000	0.0000	0.8068		0.807	

of sulfolane at low values of x_2^{I}. However, at toluene mole fractions above 0.50 the distribution ratios of heptane for [mmim][Tf_2N] and [emim][Tf_2N] ILs were smaller than that of sulfolane. In addition, the amount of heptane dissolved in the ILs grows with longer alkyl chains in the imidazolium cation. Therefore, the highest value of distribution ratio of heptane is for [hmim][Tf_2N] IL.

As illustrated Figure 3, the distribution ratio of toluene for the four ILs assayed are higher than that of sulfolane on the whole range of composition. Long alkyl chains in the imidazolium cation seem to increase the solubility of toluene in the IL-rich phase. Lachwa et al. discussed different types of interactions between dialkylimidazolium cations and aromatic hydrocarbons to justify this behavior.[35] Thus, the [hmim][Tf_2N] IL also shows the highest values of distribution ratio of toluene. Moreover, as the toluene mole fraction is larger, the distribution ratio of toluene for the four ILs decreases. On the other hand, these trends are reversed when comparing the separation factors for the four ILs (Figure 4). Long alkyl chains in the imidazolium cation reduce the aromaticity of the ILs,[1] thereby the amount of dissolved heptane in the IL-rich phase increases more than that of toluene. The [mmim][Tf_2N] IL shows the highest separation factor and the [hmim][Tf_2N] IL the lowest. In addition, only the [mmim][Tf_2N] IL shows values above than that of sulfolane in the whole range of composition. The [emim][Tf_2N] IL has a separation factor similar to that of sulfolane at values of x_2^{I} below 0.20 whereas the results for this IL are favorably at compositions above 0.20.

The NRTL model[36] 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

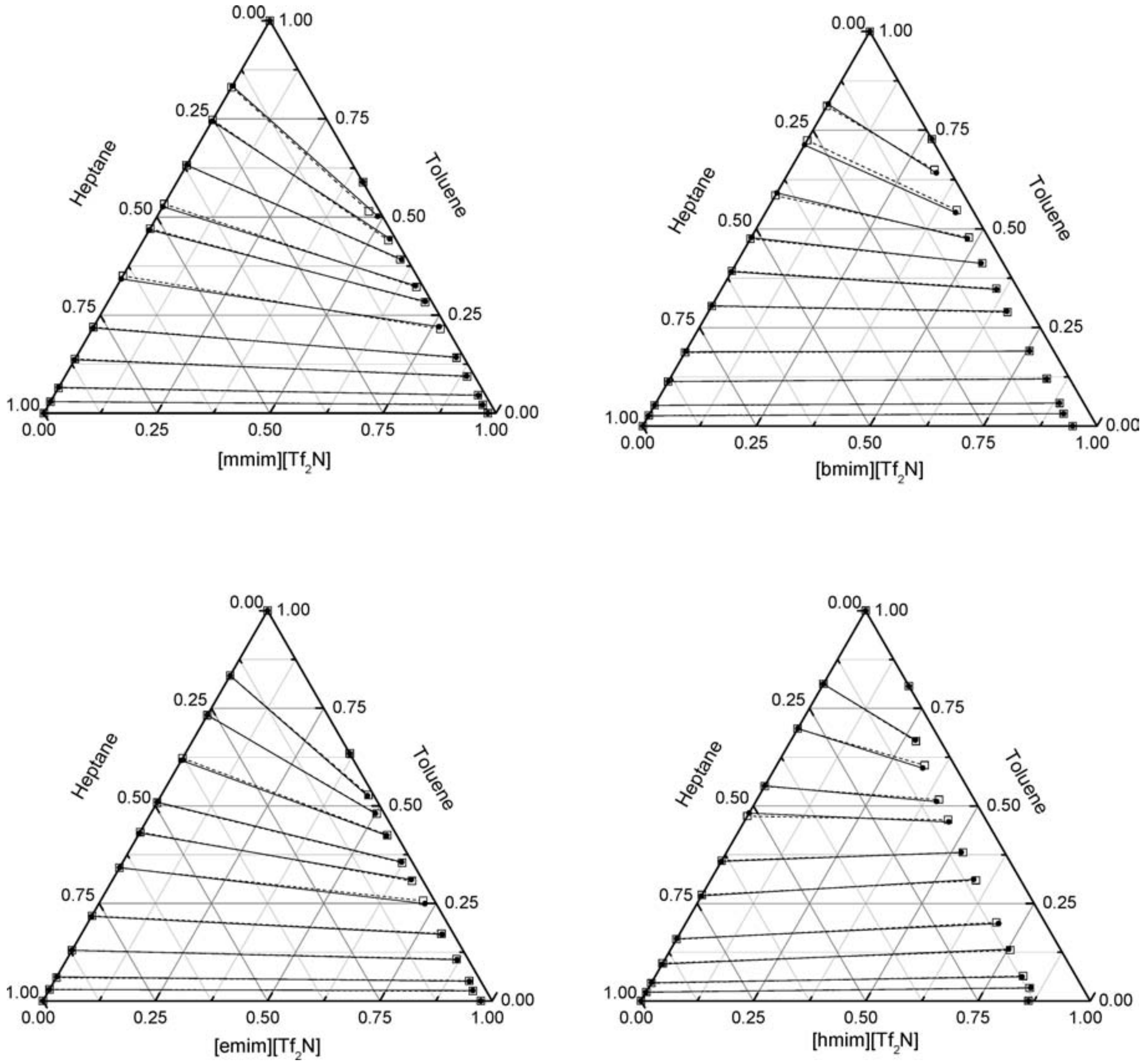

Figure 1. Experimental and calculated LLE for the ternary systems heptane (1) + toluene (2) + IL (3) at $T = 313.2$ K. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data by the NRTL model.

Table 3. Constants of the Othmer−Tobias Correlation (*a* and *b*), Regression Coefficients (R^2), and Standard Deviations (σ) at $T = 313.2$ K

a	b	R^2	σ
Heptane (1) + Toluene (2) + [mmim][Tf$_2$N] (3)			
−2.1832	0.6594	0.9913	0.0818
Heptane (1) + Toluene (2) + [emim][Tf$_2$N] (3)			
−1.9511	0.6551	0.9929	0.0490
Heptane (1) + Toluene (2) + [bmim][Tf$_2$N] (3)			
−1.6331	0.6141	0.9933	0.0550
Heptane (1) + Toluene (2) + [hmim][Tf$_2$N] (3)			
−1.3135	0.5384	0.9923	0.0514

containing ILs.[37] 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 simulator was the generalized least-squares method based on maximum likelihood principles. The Britt-Luecke algorithm[38] was employed to obtain the model parameters with the Deming initialization method. The regression convergence tolerance was set to 0.0001. The value of the third nonrandomness parameter, α_{ij}, in the NRTL model was subject to optimization between 0 and 1.

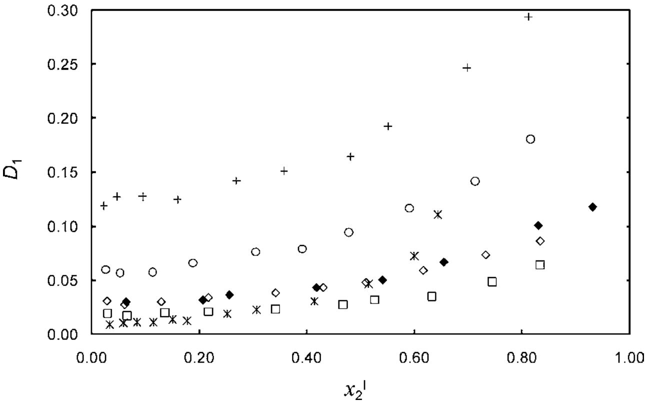

Figure 2. Heptane distribution ratio for the ternary systems at $T = 313.2$ K: □, heptane (1) + toluene (2) + [mmim][Tf$_2$N] (3); ◇, heptane (1) + toluene (2) + [emim][Tf$_2$N] (3); ○, heptane (1) + toluene (2) + [bmim][Tf$_2$N] (3); ○, heptane (1) + toluene (2) + [hmim][Tf$_2$N] (3); *, heptane (1) + toluene (2) + sulfolane (3) (from ref 5); ◆, heptane (1) + toluene (2) + [emim][Tf$_2$N] (3) (from ref 10).

Table 4 shows the values of the fitting parameters obtained using the NRTL model to correlate the experimental LLE data for the four ternary systems. The calculated tie lines from the correlation

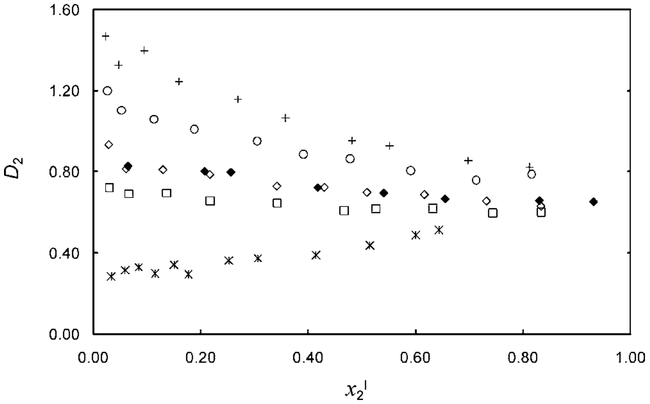

Figure 3. Toluene distribution ratio for the ternary systems at $T = 313.2$ K: □, heptane (1) + toluene (2) + [mmim][Tf_2N] (3); ◇, heptane (1) + toluene (2) + [emim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [bmim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [hmim][Tf_2N] (3); *, heptane (1) + toluene (2) + sulfolane (3) (from ref 5); ◆, heptane (1) + toluene (2) + [emim][Tf_2N] (3) (from ref 10).

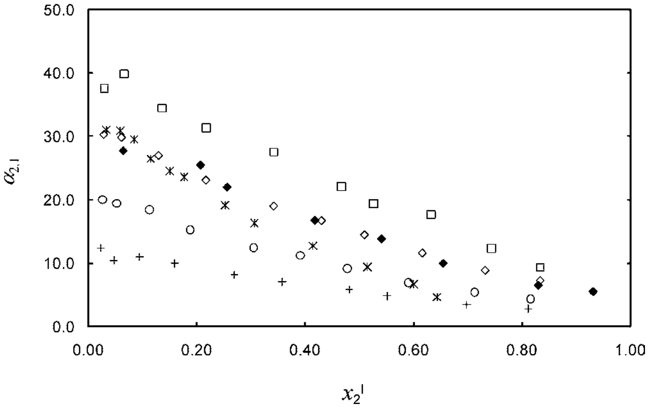

Figure 4. Separation factor for the ternary systems at $T = 313.2$ K: □, heptane (1) + toluene (2) + [mmim][Tf_2N] (3); ◇, heptane (1) + toluene (2) + [emim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [bmim][Tf_2N] (3); ○, heptane (1) + toluene (2) + [hmim][Tf_2N] (3); *, heptane (1) + toluene (2) + sulfolane (3) (from ref 5); ◆, heptane (1) + toluene (2) + [emim][Tf_2N] (3) (from ref 10).

Table 4. Values of the NRTL Parameters Obtained from LLE Data by Regression at $T = 313.2$ K

component	NRTL parameters			
	$\Delta g_{ij}/R$	$\Delta g_{ji}/R$		
$i - j$	K	K	α_{ij}	rmsd
Heptane (1) + Toluene (2) + [mmim][Tf_2N] (3)				
1−2	788.48	390.36	0.4327	0.0044
1−3	3921.6	1089.72	0.4036	
2−3	906.92	49.129	0.1708	
Heptane (1) + Toluene (2) + [emim][Tf_2N] (3)				
1−2	−235.29	493.59	0.1125	0.0019
1−3	2372.1	904.13	0.3917	
2−3	1768.8	−391.26	0.2428	
Heptane (1) + Toluene (2) + [bmim][Tf_2N] (3)				
1−2	704.72	118.63	0.3372	0.0031
1−3	47.016	531.28	0.4520	
2−3	1050.9	14.149	0.2377	
Heptane (1) + Toluene (2) + [hmim][Tf_2N] (3)				
1−2	931.74	−142.75	0.6552	0.0030
1−3	674.39	307.97	0.3913	
2−3	1186.6	336.30	0.5659	

based on the NRTL model are plotted in Figure 1. The values of the root-mean-square deviation (rmsd) for the four ternary systems are also listed in Table 4. The rmsd is defined as

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

where x is the experimental or the calculated 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. The low values for square deviation and the virtually identical experimental and calculated data observed in the triangular diagrams give an idea of the goodness of the NRTL model.

Conclusions

LLE for the systems toluene + heptane + [mmim][Tf_2N], [emim][Tf_2N], [bmim][Tf_2N], or [hmim][Tf_2N] at different concentrations of toluene in the feed were determined experimentally at 313.2 K and atmospheric pressure. The solubility of toluene and heptane 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. The experiments with [mmim][Tf_2N] and [emim][Tf_2N] ionic liquids have shown good results in the separation of toluene from heptane comparing with the distribution ratios and separation factor of sulfolane in the whole range of composition. Hence, they could be considered as suitable solvent for liquid−liquid extraction of toluene from heptane. Moreover, the no detection of ionic liquid in the raffinate phase may improve the liquid−liquid extraction process by remove the purification step for recovering the solvent from the raffinate phase. The NRTL model was found to correlate satisfactorily the experimental LLE data for the four studied ternary systems.

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