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Solvent Extraction of Toluene from Heptane with the Ionic Liquids *N*-Ethylpyridinium Bis(trifluoromethylsulfonyl)imide and *z*-Methyl-*N*-ethylpyridinium Bis(trifluoromethylsulfonyl)imide ($z = 2, 3$, or 4) at $T = 313.2$ K

Julián García,* Silvia García, José S. Torrecilla, and Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

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Four pyridinium-based ionic liquids {*N*-ethylpyridinium ([epy]), 2-methyl-*N*-ethylpyridinium ([2empy]), 3-methyl-*N*-ethylpyridinium ([3empy]), and 4-methyl-*N*-ethylpyridinium ([4empy]), all with the anion bis(trifluoromethylsulfonyl)imide ([Tf_2N])} were investigated for the first time as solvents in the liquid−liquid extraction of aromatics. Liquid−liquid equilibrium (LLE) data for the four ternary systems {heptane + toluene + [epy][Tf_2N], or [2empy][Tf_2N], or [3empy][Tf_2N], or [4empy][Tf_2N]} were determined at T/K = 313.2 and atmospheric pressure. 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 were compared satisfactorily with the experimental data. Finally, the selectivity and extractive capacity, derived from the LLE data, were calculated and compared to those previously reported in the literature for the system {heptane + toluene + sulfolane} to evaluate the feasibility of using these ionic liquids as solvents for the extraction of aromatics from aliphatic hydrocarbons.

Introduction

Ionic liquids (ILs) are becoming increasingly promising as viable media for the separation of aromatic and nonaromatic compounds, which has traditionally been one of the most challenging tasks in the refinery process. Just a decade ago, Selvan et al. reported for the first time ternary liquid−liquid equilibrium (LLE) data to investigate whether the preference of ILs for aromatic compounds could be exploited to extract aromatic compounds from mixtures of aromatics and paraffins.[1] Since then a number of papers have been published dealing with the LLE for the ternary system {aliphatic hydrocarbon + aromatic hydrocarbon + IL}.[2−27] Most of the ILs investigated as extracting solvents in these papers are imidazolium-based ILs.[1−3,6,7,9−11,13−16,19,20] However, in spite of the fact that the pyridinium cation could provide capacity and selectivity superior to that of the imidazolium cation because of its higher aromaticity, only a few pyridinium-based ILs have been assayed for the aromatic/aliphatic hydrocarbon separation.[4,5,12,18,21−27]

The purpose of this paper was to gather experimental LLE data for the four ternary systems {heptane + toluene + *N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide ([epy][Tf_2N]), or 2-methyl-*N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide ([2empy][Tf_2N]), or 3-methyl-*N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide ([3empy][Tf_2N]), or 4-methyl-*N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N])} at 313.2 K and atmospheric pressure. The interest of this study was not only to determine new LLE data but also to observe the effect of the inclusion and position of a methyl group in the *N*-ethylpyridinium cation on the separation of aromatic and aliphatic hydrocarbons. The selectivity and the extractive capacity for the four studied ILs were calculated from the LLE data. The consistency of the experimental LLE data was tested using the Othmer−Tobias correlation. In addition, the LLE data were correlated by the NRTL model.

Experimental Section

Heptane and toluene over molecular sieves, with water mass fractions less than 0.00005, were supplied by Sigma-Aldrich with mass fraction purity greater than 0.995 and 0.997, respectively. Four ILs based on the cations *N*-ethylpyridinium ([epy]), 2-methyl-*N*-ethylpyridinium ([2empy]), 3-methyl-*N*-ethylpyridinium ([3empy]), and 4-methyl-*N*-ethylpyridinium ([4empy]), all with the anion bis(trifluoromethylsulfonyl)imide ([Tf_2N]), were supplied by Iolitec GmbH with quoted mass fraction purities greater than 0.99, bromide mass fractions less than 0.0001, and water mass fractions less than 0.0001. All chemicals were used as received without further purification. To prevent hydration, they were kept in their original tightly closed bottles in a desiccator before use. 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 ([epy][Tf_2N], or [2empy][Tf_2N], or [3empy][Tf_2N], or [4empy][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 uncertainties in the temperature measurements were ± 0.1 K.

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* Corresponding author. Tel.: +34 913945119. Fax: +34 913944243. E-mail: jgarcia@quim.ucm.es.

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Table 1. Experimental LLE Data on Mole Fraction (x_i), Distribution Ratios (D_i), and Separation Factors ($\alpha_{2,1}$)

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) + [epy][Tf$_2$N] (3)								
0.4892	0.0276	0.9737	0.0263	0.0236	0.0289	0.024	1.10	45.3
0.4749	0.0558	0.9432	0.0568	0.0236	0.0549	0.025	0.97	38.6
0.4310	0.1414	0.8483	0.1517	0.0209	0.1312	0.025	0.86	35.1
0.4185	0.1649	0.8247	0.1753	0.0215	0.1546	0.026	0.88	33.8
0.3999	0.2050	0.7774	0.2226	0.0236	0.1875	0.030	0.84	27.7
0.3711	0.2593	0.7252	0.2748	0.0246	0.2441	0.034	0.89	26.2
0.3415	0.3190	0.6425	0.3575	0.0218	0.2781	0.034	0.78	22.9
0.3057	0.3927	0.5718	0.4282	0.0246	0.3552	0.043	0.83	19.3
0.2497	0.5040	0.4400	0.5600	0.0248	0.4379	0.056	0.78	13.9
0.1993	0.6024	0.3459	0.6541	0.0257	0.5411	0.074	0.83	11.1
Heptane (1) + Toluene (2) + [2empy][Tf$_2$N] (3)								
0.4887	0.0283	0.9743	0.0257	0.0254	0.0307	0.026	1.19	45.8
0.4743	0.0558	0.9445	0.0555	0.0237	0.0560	0.025	1.01	40.2
0.4454	0.1168	0.8832	0.1168	0.0243	0.1168	0.028	1.00	36.3
0.4170	0.1680	0.8364	0.1636	0.0269	0.1721	0.032	1.05	32.7
0.3717	0.2586	0.7328	0.2672	0.0241	0.2502	0.033	0.94	28.5
0.3619	0.2779	0.7089	0.2911	0.0241	0.2650	0.034	0.91	26.8
0.3268	0.3493	0.6271	0.3729	0.0239	0.3255	0.038	0.87	22.9
0.3046	0.3947	0.5817	0.4183	0.0261	0.3710	0.045	0.89	19.8
0.2462	0.5087	0.4560	0.5440	0.0277	0.4720	0.061	0.87	14.3
0.1978	0.6069	0.3537	0.6463	0.0248	0.5631	0.070	0.87	12.4
Heptane (1) + Toluene (2) + [3empy][Tf$_2$N] (3)								
0.4888	0.0276	0.9756	0.0244	0.0329	0.0305	0.034	1.25	37.1
0.4734	0.0557	0.9485	0.0515	0.0340	0.0595	0.036	1.16	32.2
0.4433	0.1189	0.8869	0.1131	0.0323	0.1243	0.036	1.10	30.2
0.4214	0.1635	0.8463	0.1537	0.0314	0.1724	0.037	1.12	30.2
0.3978	0.2097	0.7919	0.2081	0.0311	0.2111	0.039	1.01	25.8
0.3702	0.2614	0.7485	0.2515	0.0368	0.2701	0.049	1.07	21.8
0.3439	0.3171	0.6647	0.3353	0.0299	0.2992	0.045	0.89	19.8
0.3041	0.3932	0.5928	0.4072	0.0343	0.3801	0.058	0.93	16.1
0.2460	0.5093	0.4560	0.5440	0.0358	0.4745	0.079	0.87	11.1
0.1976	0.6058	0.3578	0.6422	0.0366	0.5693	0.102	0.89	8.7
Heptane (1) + Toluene (2) + [4empy][Tf$_2$N (3)]								
0.4874	0.0276	0.9760	0.0240	0.0329	0.0310	0.034	1.29	38.3
0.4733	0.0557	0.9480	0.0520	0.0296	0.0591	0.031	1.14	36.4
0.4414	0.1196	0.8845	0.1155	0.0320	0.1233	0.036	1.07	29.5
0.4164	0.1693	0.8383	0.1617	0.0334	0.1761	0.040	1.09	27.3
0.3914	0.2191	0.7859	0.2141	0.0353	0.2236	0.045	1.04	23.3
0.3703	0.2610	0.7276	0.2724	0.0349	0.2503	0.048	0.92	19.2
0.3413	0.3192	0.6836	0.3164	0.0366	0.3216	0.054	1.02	19.0
0.3059	0.3896	0.5754	0.4246	0.0336	0.3543	0.058	0.83	14.3
0.2453	0.5106	0.4668	0.5332	0.0350	0.4891	0.075	0.92	12.2
0.1982	0.6045	0.3706	0.6294	0.0373	0.5812	0.101	0.92	9.2

Samples from the upper layers (heptane-rich phases) were analyzed using a Bruker Avance 500 MHz NMR spectrometer. The ^{1}H 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 $\text{mL} \cdot \text{min}^{-1}$.

An area normalization method with response factors was carried out to determine the hydrocarbon concentration 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 set 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 here reported. The estimated uncertainties in the hydrocarbon molar compositions in the feed, heptane-rich phase, and IL-rich phase were less than 0.0008.

Results and Discussion

The experimental LLE data for the ternary systems {heptane + toluene + [epy][Tf$_2$N], or [2empy][Tf$_2$N], or [3empy][Tf$_2$N], or [4empy][Tf$_2$N]} at $T = 313.2$ K and atmospheric pressure are given in Table 1 and plotted in triangular diagrams in Figure

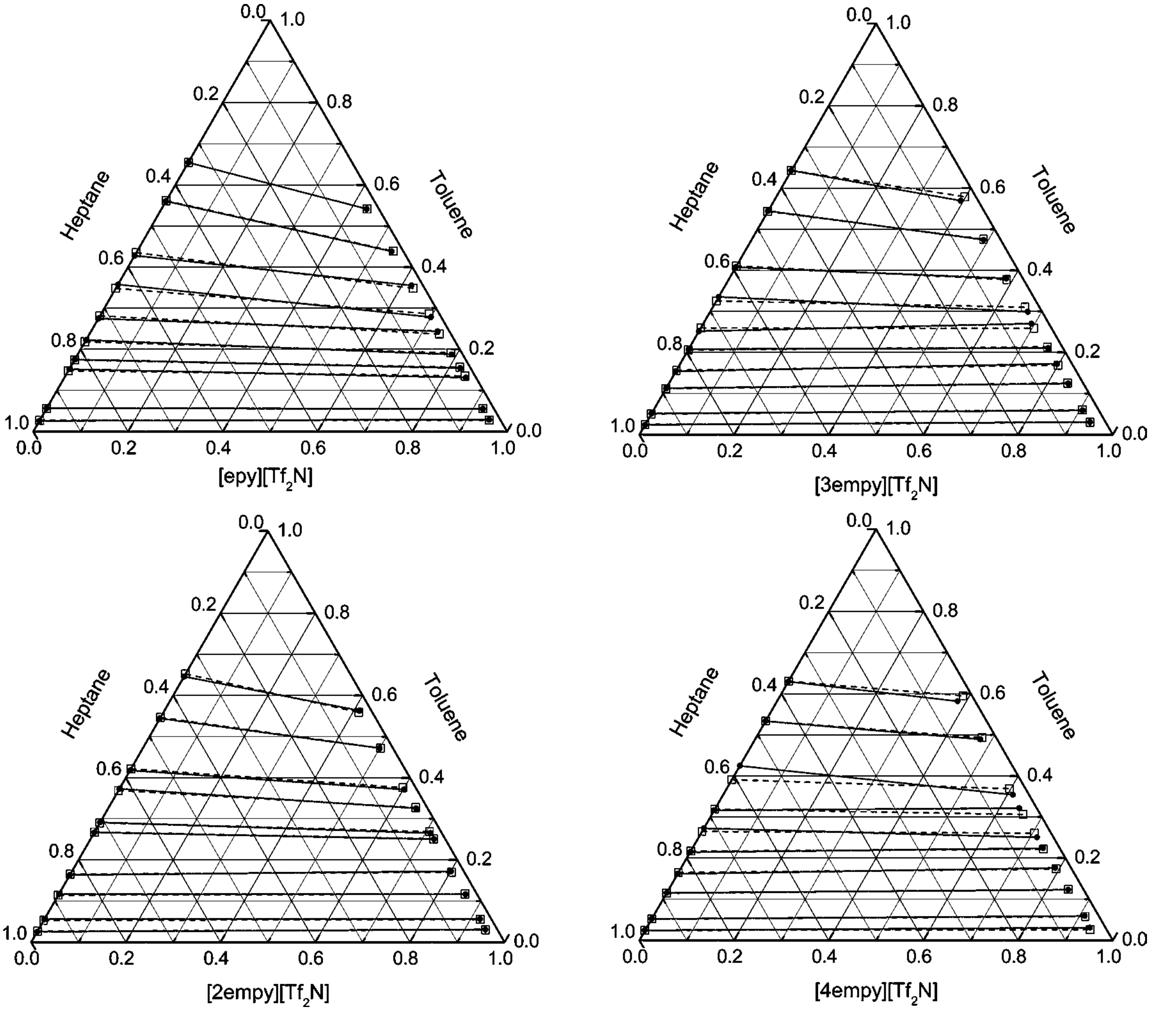

Figure 1. Experimental and calculated LLE data for the ternary systems heptane (1) + toluene (2) + IL (3) at $T = 313.2$ K. Solid lines and solid circles represent experimental tie lines, and dashed lines and open squares represent data calculated using the NRTL model.

1. The reliability of the experimentally measured LLE data can be ascertained by applying the Othmer−Tobias correlation[28]

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

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 indicates the degree of consistency 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 consistency of the experimental LLE data.

The feasibility of using these ILs as solvents to perform the liquid−liquid extraction of toluene from its mixtures with heptane was evaluated using the distribution ratios (D_i) and the separation factor ($\alpha_{2,1}$), which were calculated from the experimental LLE data as follows

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

Table 2. Constants of the Othmer−Tobias Correlation (*a*, *b*), Regression Coefficients (*R*^{2}), and Standard Deviations (*σ*)

a	*b*	*R*^{2}	*σ*
Heptane (1) + Toluene (2) + [epy][Tf$_2$N] (3)			
−1.6968	0.7417	0.9907	0.0942
Heptane (1) + Toluene (2) + [2empy][Tf$_2$N] (3)			
−1.6507	0.7574	0.9935	0.0815
Heptane (1) + Toluene (2) + [3empy][Tf$_2$N] (3)			
−1.5016	0.7260	0.9925	0.0843
Heptane (1) + Toluene (2) + [4empy][Tf$_2$N] (3)			
−1.4784	0.7428	0.9851	0.1211

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

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

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_i and $\alpha_{2,1}$ are shown in Table 1 together with the experimental LLE data.

The distribution ratios and separation factors for the four ternary systems as functions of the toluene mole fraction in

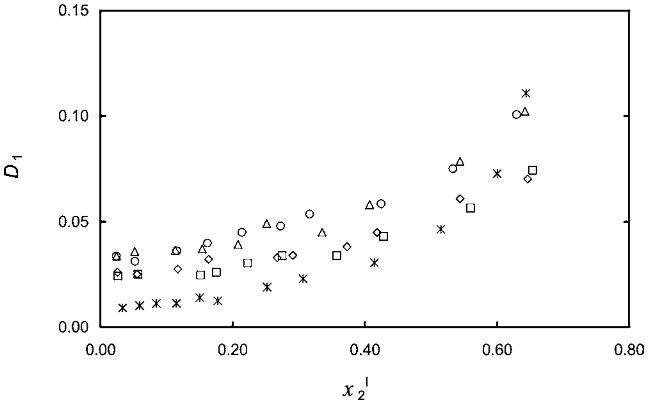

Figure 2. Heptane distribution ratio for the ternary systems at $T = 313.2$ K: □, heptane (1) + toluene (2) + [epy][Tf$_2$N] (3); ◇, heptane (1) + toluene (2) + [2empy][Tf$_2$N] (3); △, heptane (1) + toluene (2) + [3empy][Tf$_2$N] (3); ○, heptane (1) + toluene (2) + [4empy][Tf$_2$N] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 4).

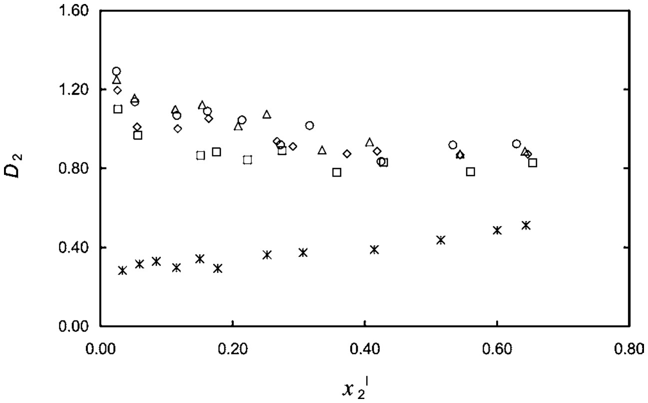

Figure 3. Toluene distribution ratio for the ternary systems at $T = 313.2$ K: □, heptane (1) + toluene (2) + [epy][Tf$_2$N] (3); ◇, heptane (1) + toluene (2) + [2empy][Tf$_2$N] (3); △, heptane (1) + toluene (2) + [3empy][Tf$_2$N] (3); ○, heptane (1) + toluene (2) + [4empy][Tf$_2$N] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 4).

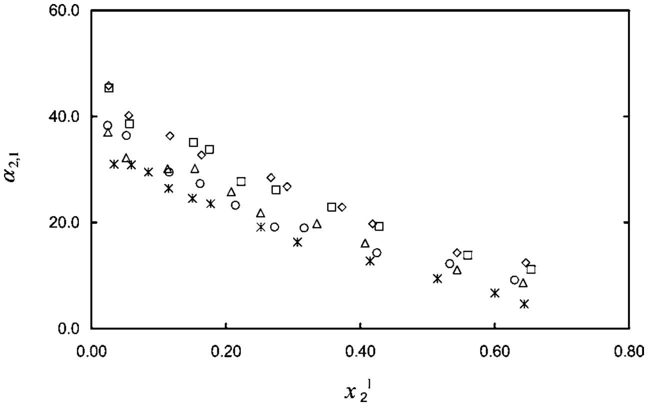

Figure 4. Separation factor for the ternary systems at $T = 313.2$ K: □, heptane (1) + toluene (2) + [epy][Tf$_2$N] (3); ◇, heptane (1) + toluene (2) + [2empy][Tf$_2$N] (3); △, heptane (1) + toluene (2) + [3empy][Tf$_2$N] (3); ○, heptane (1) + toluene (2) + [4empy][Tf$_2$N] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 4).

Table 3. Values of the NRTL Parameters Obtained from LLE Data by Regression

component	NRTL parameters			
$i-j$	$(\Delta g_{ij}/R)$/K	$(\Delta g_{ji}/R)$/K	α_{ij}	rmsd
Heptane (1) + Toluene (2) + [epy][Tf$_2$N] (3)				
1−2	733.01	1261.9	0.3	0.0041
1−3	−1027.9	1177.6	0.3	
2−3	1581.9	−109.90	0.2	
Heptane (1) + Toluene (2) + [2empy][Tf$_2$N] (3)				
1−2	689.25	1112.3	0.3	0.0027
1−3	−938.44	956.62	0.3	
2−3	1694.1	−177.07	0.2	
Heptane (1) + Toluene (2) + [3empy][Tf$_2$N] (3)				
1−2	747.49	981.50	0.3	0.0051
1−3	−915.51	885.85	0.3	
2−3	1717.8	−124.92	0.2	
Heptane (1) + Toluene (2) + [4empy][Tf$_2$N] (3)				
1−2	669.74	1108.0	0.3	0.0094
1−3	−941.37	961.92	0.3	
2−3	1723.7	−203.25	0.2	

the heptane-rich phase (x_2^{I}) are plotted in Figures 2 to 4. Comparisons with literature data for the ternary system {heptane + toluene + sulfolane} are also made.[4] As can be seen from Figures 2 and 3, the heptane distribution ratios for all the four ILs grow with increasing toluene mole fraction in the heptane-rich phase, whereas the toluene distribution ratios decrease with increasing toluene mole fraction in the heptane-rich phase. According to Hansmeier et al., these trends can be explained because the IL cations and toluene organize in a sandwich structure.[25] In line with the effects of toluene concentration on the distribution ratios is the influence of these effects on the separation factor. The grow of D_1 and decrease of D_2 is expressed by a decrease in $\alpha_{2,1}$ as is apparent from Figure 4.

As illustrated Figure 2, the heptane distribution ratios for [epy][Tf$_2$N] and [2empy][Tf$_4$N] seem to be the lowest. They show no significant different values over the whole range of compositions and likewise for those for [3empy][Tf$_4$N] and [4empy][Tf$_4$N]. In addition, the heptane distribution ratios for the four ILs are slightly larger than those reported previously for sulfolane over the low range of compositions. With respect to toluene distribution ratios, Figure 3 shows that the four ILs present larger values than sulfolane over the whole range of compositions. The toluene distribution ratios seem to increase when a methyl group is incorporated to the [epy] cation. However, the influence of cation isomers on the toluene distribution ratio is difficult to ascertain from these data. Finally, the four ILs show also larger separation factors than sulfolane over the whole range of compositions, the highest values being for [epy][Tf$_2$N] and [2empy][Tf$_4$N] (Figure 4). The influence of the methyl group position in the cation of the three IL isomers on the distribution ratios and separation factors would be probably due to differences in polarity and in Kamlet−Taft parameters related to their molecular structure.[29]

The NRTL model[30] 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.[31] 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[32] 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 fixed after checking different values between 0.2 and 0.5.

Table 3 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 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

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

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.

Conclusions

LLE data for the ternary systems {heptane + toluene + [epy][Tf_2N], or [2empy][Tf_2N], or [3empy][Tf_2N], or [4empy][Tf_2N]} were determined experimentally at 313.2 K and atmospheric pressure. A high degree of consistency of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation. The corresponding values of the distribution ratios and separation factor were calculated and compared with those previously reported in the literature for the ternary systems {heptane + toluene + sulfolane}. The four ILs show heptane distribution ratios slightly larger than those for sulfolane over the low range of compositions but toluene distribution ratios and separation factors larger than those for sulfolane over the whole range of compositions. No significant differences in the distribution ratios and separation factors were observed between the ILs [epy][Tf_2N] and [2empy] [Tf_2N] and between the ILs [3empy] [Tf_2N] and [4empy] [Tf_2N]. The NRTL model was used to satisfactorily correlate the experimental LLE data for the four studied ternary systems.

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