JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Sulfonate-Based Ionic Liquids in the Liquid−Liquid Extraction of Aromatic Hydrocarbons

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

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

ABSTRACT: The liquid−liquid equilibrium (LLE) data for the systems heptane + toluene + 1-ethyl-3-methylimidazolium methanesulfonate ([emim][CH_3SO_3]), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF_3SO_3]), or 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate ([emim][$CHF_2CF_2SO_3$]) at T = 313.2 K and atmospheric pressure were determined. To evaluate the suitability of these three ionic liquids for the extraction of aromatics from their mixtures with aliphatic hidrocarbons, the distribution ratios and separation factor curves from the LLE data were plotted and compared to those for the conventional solvent sulfolane. The degree of quality of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation. In addition, the phase diagrams for the ternary systems were plotted, and the experimental tie lines were satisfactorily correlated with the nonrandom two-liquid (NRTL) model.

INTRODUCTION

The liquid−liquid extraction of aromatic hydrocarbons by the Sulfolane Shell UOP process combines high yield in the recovery of aromatic compounds and a good balance of solvent properties. However, the regeneration of sulfolane requires high investment and energy costs.[1] As a consequence of this, in recent years, ionic liquids (ILs) have begun to be studied as an eco-friendly alternative to replace sulfolane.[2−31] The nonvolatile nature of ILs would facilitate their recovery using techniques as simple as flash distillation or stripping.[1] Hence, the aromatic extraction process should be simpler and less expensive. Even with a lower capacity of extraction than sulfolane, a process with an IL could still be profitable because, in spite of being the investment costs in the same range as those for the sulfolane process, the annual costs would be much lower as a result of the lower regeneration costs of the IL.[32]

However, an industrial extraction process based on ILs as extractive solvents has not been yet developed because none of the ILs thus far investigated has been yet considered suitable for the aromatic/aliphatic separation. The purpose of the present work was to measure new ternary LLE data for the system heptane + toluene + 1-ethyl-3-methylimidazolium methanesulfonate ([emim][CH_3SO_3]). Blahut et al.[33] concluded that, because of its capacity for specific interactions, [emim][CH_3SO_3] turns out to be a potentially very good solvent for separation of aromatic from satured hydrocarbons. Nevertheless, selectivities for this IL were derived from activitiy coefficients at infinite dilution of aromatics and saturated hydrocarbons in the IL determined by gas−liquid chromatography. Distribution coefficients and selectivities calculated from activity coefficients at infinite dilutions of ILs can be useful for screening purposes but are not at all reliable for the design of an industrial separation process.

In this work, we have also determined new LLE data for the ternary systems heptane + toluene + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF_3SO_3]) or 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate ([emim][$CHF_2CF_2SO_3$]). Thus, the effect of the fluorination of the sulfonate anion was also studied. A comparison with literature data for the ternary system heptane + toluene + sulfolane[5] is also made. The degree of quality of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation. The phase diagrams for the ternary systems were plotted, and the experimental tie lines were satisfactorily correlated with 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 ILs 1-ethyl-3-methylimidazolium methylsulfonate ([emim][CH_3SO_3]), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF_3SO_3]), and 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate ([emim][$CHF_2CF_2SO_3$]) were provided by Iolitec GmbH with quoted mass fraction purities greater than 0.99 and halides and water mass fractions less than 0.0001. 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 ([emim][CH_3SO_3], [emim][CF_3SO_3], or [emim][$CHF_2CF_2SO_3$]) 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 the complete insoluble phases separation, the vials were left to settle overnight at a constant temperature of 313.2 K in a dry bath.

Received: March 18, 2011
Accepted: June 7, 2011
Published: June 17, 2011

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) + [emim][CH_3SO_3] (3)								
0.5011	0.0000	1.0000	0.0000	0.0020	0.0000	0.002		
0.4868	0.0267	0.9546	0.0454	0.0019	0.0072	0.002	0.159	79.7
0.4756	0.0546	0.9045	0.0955	0.0017	0.0133	0.002	0.139	74.1
0.4439	0.1151	0.8112	0.1888	0.0016	0.0277	0.002	0.147	74.4
0.4073	0.1893	0.6979	0.3021	0.0014	0.0408	0.002	0.135	67.3
0.3521	0.2978	0.5514	0.4486	0.0013	0.0582	0.002	0.130	55.0
0.3144	0.3700	0.4744	0.5256	0.0014	0.0732	0.003	0.139	47.2
0.2806	0.4417	0.4009	0.5991	0.0013	0.0818	0.003	0.137	42.1
0.2331	0.5359	0.3082	0.6918	0.0012	0.0965	0.004	0.139	35.8
0.1794	0.6416	0.2210	0.7790	0.0009	0.1076	0.004	0.138	33.9
0.1244	0.7507	0.1432	0.8568	0.0009	0.1184	0.006	0.138	22.0
Heptane (1) + Toluene (2) + [emim][CF_3SO_3] (3)								
0.5026	0.0000	1.0000	0.0000	0.0082	0.0000	0.008		
0.4876	0.0268	0.9614	0.0386	0.0076	0.0131	0.008	0.339	42.9
0.4749	0.0545	0.9199	0.0801	0.0073	0.0276	0.008	0.345	43.4
0.4452	0.1143	0.8388	0.1612	0.0078	0.0622	0.009	0.386	41.5
0.4210	0.1591	0.7640	0.2360	0.0085	0.0791	0.011	0.335	30.1
0.3585	0.2870	0.6051	0.3949	0.0071	0.1332	0.012	0.337	28.7
0.3110	0.3794	0.4852	0.5148	0.0051	0.1416	0.011	0.275	26.2
0.2794	0.4429	0.4153	0.5847	0.0053	0.1570	0.013	0.269	21.0
0.2341	0.5333	0.3332	0.6668	0.0054	0.2076	0.016	0.311	19.2
0.1775	0.6474	0.2301	0.7699	0.0045	0.2433	0.020	0.316	16.2
0.1250	0.7515	0.1494	0.8506	0.0033	0.2718	0.022	0.320	14.5
0.0000	0.8513	0.0000	1.0000	0.0000	0.3586		0.359	
Heptane (1) + Toluene (2) + [emim][$CHF_2CF_2SO_3$] (3)								
0.5009	0.0000	1.0000	0.0000	0.0049	0.0000	0.005		
0.4880	0.0265	0.9605	0.0395	0.0056	0.0124	0.006	0.314	53.8
0.4737	0.0544	0.9196	0.0804	0.0056	0.0247	0.006	0.307	50.4
0.4427	0.1155	0.8279	0.1721	0.0049	0.0473	0.006	0.275	46.4
0.4043	0.1932	0.7165	0.2835	0.0049	0.0754	0.007	0.266	38.9
0.3534	0.2963	0.5786	0.4214	0.0045	0.1073	0.008	0.255	32.7
0.3099	0.3798	0.4794	0.5206	0.0043	0.1313	0.009	0.252	28.1
0.2786	0.4436	0.4091	0.5909	0.0038	0.1497	0.009	0.253	27.3
0.2310	0.5395	0.3164	0.6836	0.0035	0.1761	0.011	0.258	23.3
0.1773	0.6463	0.2232	0.7768	0.0026	0.1929	0.012	0.248	21.3
0.1244	0.7527	0.1451	0.8549	0.0022	0.2173	0.015	0.254	16.8
0.0000	0.8506	0.0000	1.0000	0.0000	0.2714		0.271	

Every weighing involved in the experimental work was carried out on a Mettler Toledo AB104 balance with a precision of ± 0.0001 g. Errors in calculating feed mole fractions were estimated to be less than 0.001. The uncertainties in the temperature measurements were ± 0.1 K.

Compositions of the two insoluble phases were determined by ^{1}H NMR spectroscopy. Samples from the upper (heptane-rich phase) and lower layers (IL-rich phase) were analyzed using a Bruker Avance 500 MHz NMR spectrometer. Three drops from the lower and upper layers were carefully taken with disposable Pasteur micropipets and dissolved in 700 μL of deuterated methanol in NMR tubes. The deuterated methanol was purchased by Sigma-Aldrich (methanol-d_4 99.8 atom %D). For acquisition and processing the ^{1}H NMR spectra, the TopSpin software was used. A ^{1}H NMR spectrum shows a peak for each type of hydrogen in the sample. A peak selection for each component was made. The quantitative integration under the selected peaks is proportional to hydrogen moles associated to each peak. Thus, an area proportional to the moles of the referred component is obtained by dividing the peak area by the number of hydrogen atoms. Finally, the mole fraction of the component is calculated by dividing this last area by the sum of the areas. To select the peaks and estimate the uncertainty of the analytical technique, samples were gravimetrically prepared, and then their ^{1}H NMR spectra were determined. Hydrogen atoms from the aromatic and imidazolium rings were not considered. The maximum standard deviation on mole compositions was estimated to be ± 0.003.

RESULTS AND DISCUSSION

The mole fraction compositions for the feed, heptane-rich phase (raffinate), and IL-rich phase (extract) for the ternary systems toluene + heptane + [emim][CH_3SO_3], [emim][CF_3SO_3], or [emim][$CHF_2CF_2SO_3$] at T/K = 313.2 and atmospheric pressure are shown in Table 1 and plotted on the triangular diagrams in Figure 1. The ^{1}H NMR spectra of the samples from the heptane-rich phase showed no detectable signals arising from the IL, so the IL mole fractions in the heptane-rich phases appear to be negligible, as can be observed in the triangular diagrams from Figure 1. This situation is desirable since it would eliminate the need of an extra unit to purify the raffinate phase for recovering the solvent.

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

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

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 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 capacity of extraction and selectivity of these three ILs for the separation 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}) is calculated from the experimental data 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 to 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.

The distribution ratios and separation factors for the three 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. A comparison with literature data for the ternary system heptane + toluene + sulfolane at 313.2 K[5] is also made. As Figure 2 shows, the distribution ratios of heptane for the three ILs are lower than those of sulfolane on the whole range of compositions. The lowest values of D_1 are for the [emim][CH_3SO_3] IL. On the other hand, the distribution ratios of toluene for the three ILs are lower than those of sulfolane practically on the whole range of composition (Figure 3). Similar values of D_2 to those of sulfolane at low compositions of toluene in the heptane-rich phase for the

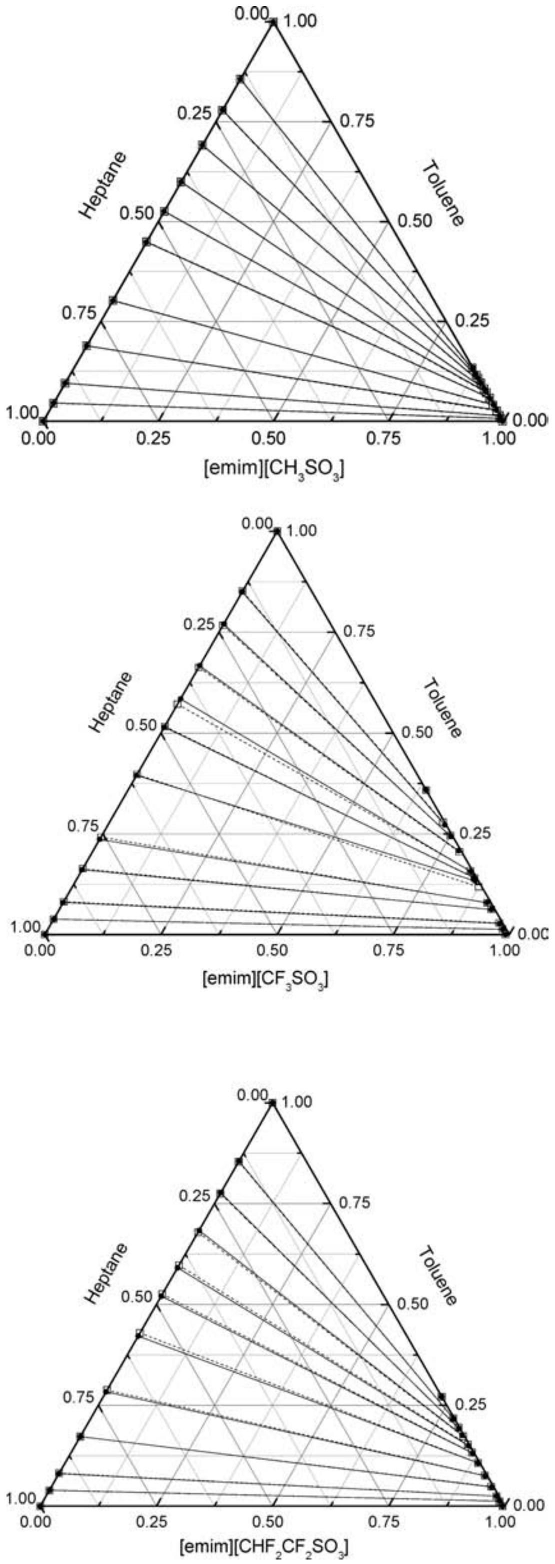

Figure 1. Experimental and calculated LLE for the ternary systems heptane (1) + toluene (2) + IL (3) at T = 313.2 K. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data by the NRTL model.

Table 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) + [emim][CH_3SO_3] (3)			
−3.5038	0.5783	0.9684	0.2090
Heptane (1) + Toluene (2) + [emim][CF_3SO_3] (3)			
−2.7702	0.5793	0.9745	0.1811
Heptane (1) + Toluene (2) + [emim][$CHF_2CF_2SO_3$] (3)			
−3.1271	0.5641	0.9763	0.1588

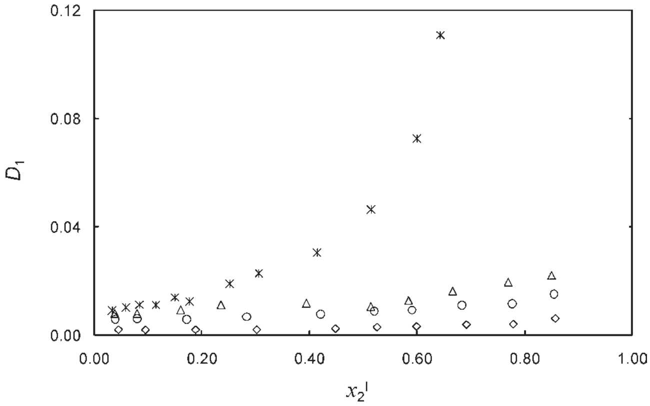

Figure 2. Heptane distribution ratio for the ternary systems at T = 313.2 K: ◊, heptane (1) + toluene (2) + [emim][CH_3SO_3] (3); △, heptane (1) + toluene (2) + [emim][CF_3SO_3] (3); ○, heptane (1) + toluene (2) + [emim][$CHF_2CF_2SO_3$] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 5).

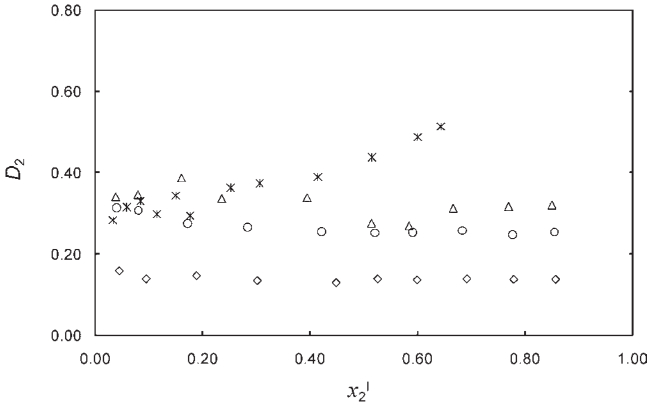

Figure 3. Toluene distribution ratio for the ternary systems at T = 313.2 K: ◊, heptane (1) + toluene (2) + [emim][CH_3SO_3] (3); △, heptane (1) + toluene (2) + [emim][CF_3SO_3] (3); ○, heptane (1) + toluene (2) + [emim][$CHF_2CF_2SO_3$] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 5).

[emim][CF_3SO_3] and [emim][$CHF_2CF_2SO_3$] ILs can be observed. Finally, as can be seen in Figure 4, the values of the separation factors for the three ILs are higher than those of sulfolane on the whole range of compositions. The highest values correspond to the [emim][CH_3SO_3] IL, which is therefore the most selective among them.

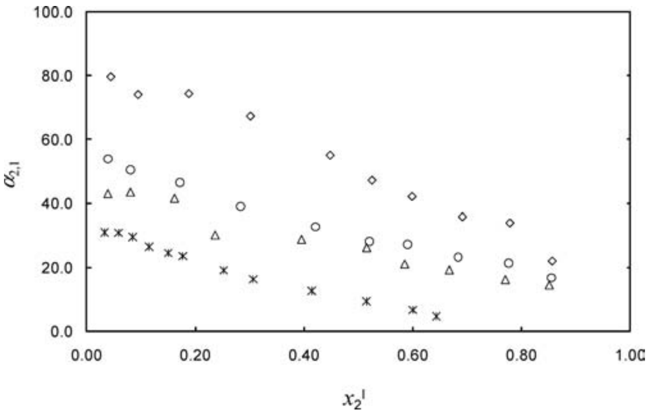

Figure 4. Separation factor for the ternary systems at T = 313.2 K: ◊, heptane (1) + toluene (2) + [emim][CH_3SO_3] (3); Δ, heptane (1) + toluene (2) + [emim][$CHF_2CF_2SO_3$] (3); ○, heptane (1) + toluene (2) + [emim][$CHF_2CF_2SO_3$] (3); ∗, heptane (1) + toluene (2) + sulfolane (3) (from ref 5).

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) + [emim][CH_3SO_3] (3)				
1–2	769.77	1215.7	0.4280	0.0006
1–3	−1592.4	3199.5	0.2786	
2–3	−129.83	1088.1	0.0715	
Heptane (1) + Toluene (2) + [emim][CF_3SO_3] (3)				
1–2	817.94	637.62	0.6140	0.0038
1–3	−1072.2	1556.8	0.3565	
2–3	862.67	298.97	0.3172	
Heptane (1) + Toluene (2) + [emim][$CHF_2CF_2SO_3$] (3)				
1–2	729.08	431.41	0.8324	0.0023
1–3	−2280.6	4250.4	0.1463	
2–3	1014.8	63.910	0.1976	

As Blahut et al. pointed in a previous work,[33] the solute—-[emim][CH_3SO_3] IL interactions are weaker for aliphatic compounds than for aromatic hydrocarbons, leading to a high values of selectivity and low values of distribution ratio of solute, toluene in this case. The inclusion of fluoride atoms in the sulfonate anion of the ILs seems to enforce the IL–aromatic hydrocarbon interactions and therefore increasing the capacity of extraction of toluene. On the other hand, the fluorination of the anion may also increase the amount of dissolved heptane in the ILs reducing the selectivity in the separation of toluene from heptane. In this study, despite the reduction in the selectivity observed with the [emim][CF_3SO_3] and [emim][$CHF_2CF_2SO_3$] ILs, the values of separation factor are still higher than sulfolane. Moreover, it could be also takes into account that some fluorinated ILs usually presents viscosity and chemical stability appropriated for liquid–liquid extraction.[31,35]

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 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.

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 2. The values of the root-mean-square deviation (rmsd) for the three ternary systems are also listed in Table 3. The rmsd is defined as

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

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 rmsd and the virtually identical experimental and calculated data observed in the triangular diagrams give an idea of the goodness of the NRTL model.

CONCLUSIONS

In this work, the experimental determination of the LLE data for the ternary systems toluene + heptane + [emim][CH_3SO_3], [emim][CF_3SO_3], or [emim][$CHF_2CF_2SO_3$] at 313.2 K and atmospheric pressure was carried out. A comparison with literature data for the ternary system heptane + toluene + sulfolane at 313.2 K was also made. The NRTL model was found to correlate satisfactorily the experimental LLE data for the three studied ternary systems.

Our results show higher values of separation factors for the three ILs than those of sulfolane. However, the distribution ratios of toluene are lower. Moreover, the fluorination of the anion seems to enforce the toluene−IL and heptane−IL interactions, increasing the amount of dissolved toluene and heptane. Hence, the greatest selectivity is observed for the [emim][CH_3SO_3] IL, and the highest capacity of extraction corresponds to [emim][CF_3SO_3] and [emim][$CHF_2CF_2SO_3$] ILs. Although none of the three ILs shows simultaneously values of selectivity and capacity of extraction higher than sulfolane, [emim][CF_3SO_3] and [emim][$CHF_2CF_2SO_3$] could be considered as an alternative to sulfolane at low compositions of toluene in the feed.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +34 91 394 51 19. Fax: +34 91 394 42 43. E-mail address: jgarcia@quim.ucm.es (Julián García).

Funding Sources

The authors are grateful to the Ministerio de Ciencia e Innovación of Spain (MICINN) and the Comunidad Autónoma de Madrid (CAM) for financial support of Projects CTQ2008-01591 and S2009/PPQ-1545, respectively. S.G. also thanks MICINN for awarding her an FPI Grant (Reference BES-2009-014703) under the same project.

REFERENCES

(1) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures. *Fuel Process. Technol.* **2005**, *87*, 59–70.

(2) 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.

(3) Letcher, T. M.; Deenadayalu, N. Ternary Liquid−Liquid Equilibria for Mixtures of 1-Methyl-3-octyl-imidazolium Chloride + Benzene + an Alkane at T = 298.2 K and 1 atm. *J. Chem. Thermodyn.* **2003**, *35*, 67–76.

(4) Letcher, T. M.; Reddy, P. Ternary (Liquid + Liquid) Equilibria for Mixtures of 1-Hexyl-3-methylimidazolium (Tetrafluoroborate or Hexafluorophosphate) + Benzene + an Alkane at T = 298.2 K and p = 0.1 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415–421.

(5) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary Liquid−Liquid Equilibria for Mixtures of Toluene + *n*-Heptane + an Ionic Liquid. *Fluid Phase Equilib.* **2006**, *247*, 158–168.

(6) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary Liquid−Liquid Equilibria for Mixtures of an Aromatic + an Aliphatic Hydrocarbon + 4-Methyl-*N*-butylpyridinium Tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1814–1819.

(7) Deenadayalu, N.; Ngcongo, K. C.; Letcher, T. M.; Ramjugernath, D. Liquid−Liquid Equilibria for Ternary Mixtures (an Ionic Liquid + Benzene + Heptane or Hexadecane) at T = 298.2 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2006**, *51*, 988–991.

(8) Domanska, U.; Pobudkowska, A.; Zolek-Tryznowska, Z. Effect of an Ionic Liquid (IL) Cation on the Ternary System (IL + *p*-Xylene + Hexane) at T = 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2345–2349.

(9) 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.

(10) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R. Separation of Aromatic Hydrocarbons from Alkanes using the Ionic Liquid 1-Ethyl-3-methylimidazolium Bis{(trifluoromethyl)sulfonyl}amide. *Green Chem.* **2007**, *9*, 70–74.

(11) 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-Substituent Length. *J. Phys. Chem. B* **2007**, *111*, 4732–4736.

(12) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R.; Soto, A. 1-Ethyl-3-methylimidazolium Bis{(trifluoromethyl)sulfonyl}amide as Solvent for the Separation of Aromatic and Aliphatic Hydrocarbons by Liquid Extraction - Extension to C_7- and C_8-Fractions. *Green Chem.* **2008**, *10*, 1294–1300.

(13) 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.

(14) 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.

(15) Wang, R.; Wang, J.; Meng, H.; Li, C.; Wang, Z. Ternary Liquid−Liquid Equilibria Measurement for Benzene + Cyclohexane + *N*-Methylimidazole, or *N*-Ethylimidazole, or *N*-Methylimidazolium Dibutylphosphate at 298.2 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2008**, *53*, 2170–2174.

(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) Arce, A.; Early, M. J.; Rodríguez, H.; Seddon, K. R.; Soto, A. Bis{(trifluoromethyl)sulfonyl}amide Ionic Liquids as Solvents for the Extraction of Aromatic Hydrocarbons from their Mixtures with Alkanes: Effect of the Nature of the Cation. *Green Chem.* **2009**, *11*, 365–372.

(18) Pereiro, A. B.; Rodriguez, A. Application of the Ionic Liquid Ammoeng 102 for Aromatic/aliphatic Hydrocarbon Separation. *J. Chem. Thermodyn.* **2009**, *41*, 951–956.

(19) 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.

(20) García, J.; Fernández, A.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Liquid−Liquid Equilibria for {Hexane + Benzene + 1-Ethyl-3-methylimidazolium Ethylsulfate} at (298.2, 313.2 and 328.2) K. *Fluid Phase Equilib.* **2009**, *282*, 117–120.

(21) García, J.; Fernández, A.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Ternary Liquid-liquid Equilibria Measurement for Hexane and Benzene with the Ionic Liquid 1-Butyl-3-methylimidazolium Methylsulfate at T = (298.2, 313.2, and 328.2) K. *J. Chem. Eng. Data* **2010**, *55*, 258–261.

(22) 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.

(23) 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.

(24) 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.

(25) González, E. J.; Calvar, N.; González, B.; Domínguez, A. Separation of Toluene from Alkanes using 1-Ethyl-3-methylpyridinium Ethylsulfate Ionic Liquid at T = 298.15 K and Atmospheric Pressure. *J. Chem. Thermodyn.* **2010**, *42*, 752–757.

(26) Hansmeier, A. R.; Jongmans, M.; Meindersma, G. W.; de Haan, A. B. LLE Data for the Ionic Liquid 3-Methyl-*N*-butylpyridinium Dicyanamide with Several Aromatic and Aliphatic Hydrocarbons. *J. Chem. Thermodyn.* **2010**, *42*, 484–490.

(27) García, J.; García, S.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Liquid-Liquid Equilibria for the Ternary Systems {Heptane + Toluene + *N*-Butylpyridinium Tetrafluoroborate or *N*-Hexylpyridinium Tetrafluoroborate} at T = 313.2 K. *J. Chem. Eng. Data* **2010**, *55*, 2862–2865.

(28) García, J.; García, S.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Separation of Toluene and Heptane by Liquid-Liquid Extraction using *z*-Methyl-*N*-butylpyridinium Tetrafluoroborate isomers (z = 2, 3, or 4) at T = 313.2 K. *J. Chem. Thermodyn.* **2010**, *42*, 1004–1008.

(29) García, J.; García, S.; Torrecilla, J. S.; Rodríguez, F. 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. *J. Chem. Eng. Data* **2010**, *55*, 4937–4942.

(30) García, J.; García, S.; Torrecilla, J. S.; Rodríguez, F. *N*-Butylpyridinium bis-(trifluoromethylsulfonyl)imide ionic liquids as solvents for the liquid-liquid extraction of aromatics from their mixtures with alkanes: isomeric effect of the cation. *Fluid Phase Equilib.* **2010**, *301*, 62–66.

(31) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Liquid−Liquid Extraction of Toluene from Heptane Using 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 113–118.

(32) 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.

(33) Blahut, A.; Sobota, M.; Dohnal, V.; Vrbka, P. Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate. *Fluid Phase Equilib.* **2010**, *299*, 198–206.

(34) Othmer, D. F.; Tobias, P. E. Toluene and Acetaldehyde Systems, Tie Line Correlation, Partial Pressures of Ternary Liquid Systems and the Prediction of Tie Lines. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

(35) 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.

(36) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

(37) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling Liquid-Liquid Equilibrium of Ionic Liquid Systems with NRTL, Electrolyte-NRTL, and UNIQUAC. *Ind. Eng. Chem. Res.* **2008**, *47*, 256–272.

(38) Britt, H. I.; Luecke, R. H. The Estimation of Parameters in Nonlinear, Implicit Models. *Technometrics* **1973**, *15*, 233–238.