Liquid−Liquid Equilibria for [C_8mim][NTf_2] + Thiophene + 2,2,4-Trimethylpentane or + Toluene

Luisa Alonso, Alberto Arce,* María Francisco, and Ana Soto

Department of Chemical Engineering, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

Tie-line compositions for type II systems of 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide + thiophene + 2,2,4-trimethylpentane or + toluene have been determined at 298.15 K and atmospheric pressure. Solute distribution coefficient and selectivity values have also been determined. The experimental data were correlated with the NRTL and UNIQUAC equations. The best results were found with the UNIQUAC equation. The NRTL equation could not adequately correlate the system with toluene.

Introduction

The products of the Fluid Catalytic Cracking (FCC) tend to contain sulfur impurities even though about half of the sulfur compounds are converted to hydrogen sulfide during the cracking process. The distribution of sulfur in the cracking products is dependent on a large number of factors including feed, type of catalyst, presence of additives, conversion, and other operating conditions, but in any case, a certain proportion of the sulfur tends to enter the light or heavy gasoline fractions.

With the increase of environmental regulations applied to petroleum derivates, the sulfur content of the products has to be reduced in response to concerns about the emissions of sulfur oxides and other sulfur compounds to the air following combustion processes. The conventional process to remove sulfur in fuels is known as catalytic hydrodesulfurization (HDS). Among the various sulfur compounds present in fuel oil, thiophene (TP), benzothiophene (BT), dibenzothiophene (DBT), and its derivatives are the most resistant to hydrogenation and require the use of a modified catalyst and drastic reaction conditions, making deep desulfurization to become an expensive process. Despite recent sulfur reduction technologies,[1–4] there continues the need for effective ways to reduce the sulfur content of gasoline and diesel fuels. Extractive desulfurization (EDS) is considered to be one of the promising new methods for deep desulfurization of fuel oil.[5–7] Compared to conventional HDS, EDS can be carried out under very mild conditions, at room temperature, and under atmospheric pressure.

The EDS technique is very efficient with economical operation conditions, with the key question being to find an effective solvent. Ionic liquids (ILs) are emerging solvents because they have negligible vapor pressure, are nontoxic, are thermally and chemically stable, and are not expensive for commercial applications. ILs seem to be more competitive that conventional solvents considering the fact that they are environmentally benign and designable for desired properties.

The design of extraction processes to accomplish the removal of sulfur compounds requires the knowledge of the liquid−liquid equilibrium (LLE) of sulfur compounds with hydrocarbons and solvent. As part of our study[8–10] about the liquid−liquid equilibrium of thiophene with hydrocarbons and 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide ([C_8mim][NTf_2]) IL, to analyze the viability of using this IL for gasoline desulfurization, in this work phase diagrams at $T = 298.15$ K for [C_8mim][NTf_2] + thiophene + 2,2,4-trimethylpentane and [C_8mim][NTf_2] + thiophene + toluene ternary systems were determined. Also, thiophene distribution ratio coefficients and selectivities were determined. The experimental data were correlated using the NRTL and UNIQUAC equations.

Experimental

Materials. 2,2,4-Trimethylpentane, C_8H_{18},(Fluka, mass fraction > 99.5 %), toluene, C_7H_8 (Sigma-Aldrich, mass fraction > 99.5 %), and thiophene, C_4H_4S (Aldrich, mass fraction > 99.5 %), were used as received from the supplier without further purification. Gas chromatography (GC) analysis did not detect any appreciable peaks of impurities.

1-Methylimidazole was mixed with an excess of 1-chlorooctane to produce [C_8mim][Cl]. This chloride was mixed with Li[NTf_2] salt solvent in deionized water, thus obtaining the [C_8min][NTf_2] by ion metathesis in a similar manner to that reported in a previous paper.[10] After washing, the purification of the ionic liquid was completed by heating it under high vacuum for at least 24 h (1 mbar, 80 °C). The water contain of [C_8min][NTf_2] was measured using Karl Fisher titration and resulted in 21 ppm. Chloride concentration was 413 ppm, measured by means of capillary electrophoresis. The ionic liquid was analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy to confirm the absence of any major impurities.

In Table 1, the experimental density, refractive index, dynamic viscosity, and water content of pure components are compared with values published by other authors.[11–14]

Apparatus and Procedure. Water contents were measured using a Karl Fischer titration method in a Metrohm 737 KF coulometer. Densities were measured with an Anton Paar DMA 5000 densimeter automatically corrected for the viscosity correction associated with this densimeter. The uncertainty in the measurement was $\pm 10^{-5}$ g·cm^{-3}. Refractive indices were measured in an ATAGO RX-5000 refrac-

---

* Corresponding author. Tel.: −34 981 563100 ext. 16790. Fax: +34981528050. E-mail address: eqaaarce@usc.es.

10.1021/je800071q CCC: $40.75

Table 1. Water Mass Fraction (w), Density (ρ), Refractive Index (n_D), and Dynamic Viscosity (η) of the Pure Components at 298.15 K and Atmospheric Pressure

			ρ/g·cm^{-3}		n_D		η/mPa·s	
component	CAS number	$10^6 \cdot w$	exptl	lit.	exptl	lit.	exptl	lit.
C_8H_{18}	540-84-1	4.8	0.68784	0.68782[11]	1.38921	1.38898[12]	0.871	0.886[11]
C_7H_8	108-88-3	174	0.86220	0.86219[12]	1.49393	1.49413[12]	0.577	0.5525[12]
C_4H_4S	110-02-1	13.5	1.05859	1.05884[12]	1.52530	1.52572[12]	0.612	0.613[12]
[C_8mim][NTf_2]	178631-04-4	21	1.31978	1.31[13]	1.43270	Not found	90.37	90.0[14]

Table 2. Operating Conditions for the Gas Chromatography Instrument

	[C_8mim][NTf_2] + C_4H_4S + C_8H_{18}	[C_8mim][NTf_2] + C_4H_4S + C_7H_8
column	HP-FFAP polyethylene glycol TPA (25 m × 200 μm × 0.3 μm)	HP-5 5 % phenyl methyl siloxane (30 m × 320 μm × 0.25 μm)
detector type	TCD	FID
detector temperature	523.15 K	523.15 K
injector temperature	523.15 K	583.15 K
carrier gas	helium	helium
flow rate	1 mL·min^{-1}	1 mL·min^{-1}
T oven	6.5 min at 353.15 K $\xrightarrow{\text{ramp 100 K·min}^{-1}}$ 413.15 K, isothermal for 6 min	3.5 min at 313.15 K $\xrightarrow{\text{ramp 8 K·min}^{-1}}$ 333.15 K $\xrightarrow{\text{ramp 50 K·min}^{-1}}$ 433 K, isothermal for 6 min

tometer with a Heto Therm thermostat to maintain the temperature constant. The uncertainty in the refractive index measurement is ± 4·10^{-5}. The kinematic viscosity was determined by a micro Ubbelohde viscometer technique. The capillaries are calibrated and credited by the company. Flow time measurements were performed by Lauda Processor Viscosity System PVS1. The temperature of the viscometer was kept constant using a Lauda clear view thermostat D 20 KP with a through-flow cooler DLK 10. The dynamic viscosities were calculated from densities with an estimated uncertainty of ± 0.5 %.

The tie-line data were determined by analysis of the two layers of a heterogeneous mixture. Mixtures with compositions inside the immiscible region of the systems were introduced into 30 mL glass wall-jacketed vessels, with magnetic stirrers, and closed. Previous experiments showed that equilibrium was established after about 5 h of stirring, to get a good contact between both phases, and overnight to settle down. Then, one sample of each layer was withdrawn using syringes. The complete process was carried out at constant temperature of 298.15 K using a thermostatic bath (SELECTA 6000382). The uncertainty in the temperature measurement is ± 0.002 K.

Samples of both liquid phases were analyzed by GC using an internal standard method. IL composition was calculated by difference. All weighing to prepare samples for analysis calibration was carried out in a Mettler Toledo AT 261 balance with an uncertainty of ± 10^{-4} g. The uncertainty in the mole fractions of the prepared mixtures was estimated to be ± 2·10^{-4}. The GC used was an HP 6890 Series equipped with a thermal conductivity detector (TCD) and the other with a flame ionization detector (FID), a capillary column, and an empty precolumn to protect the column and collect the ionic liquid that could not be retained by the liner. The GC operating conditions are given in Table 2. To check the uncertainty in the determination of mole fraction compositions, eight samples were prepared by weight, and compositions were calculated using the calibration curves, with the greatest deviations found being ± 0.005.

Table 3. Compositions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivities S for [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_8H_{18} (3) at 298.15 K

IL-rich phase			hydrocarbon-rich phase				
x_1	x_2	x_3	x'_1	x'_2	x'_3	β	S
0.774	0.000	0.226	0.001	0.000	0.999	–	–
0.660	0.135	0.205	0.003	0.044	0.953	3.04	14.17
0.572	0.237	0.191	0.002	0.089	0.909	2.67	12.71
0.441	0.393	0.166	0.006	0.193	0.801	2.04	9.82
0.317	0.525	0.158	0.000	0.328	0.672	1.60	6.79
0.220	0.640	0.140	0.001	0.482	0.517	1.33	4.89
0.163	0.716	0.121	0.002	0.639	0.359	1.12	3.32
0.135	0.758	0.107	0.000	0.740	0.260	1.02	2.49
0.106	0.804	0.090	0.000	0.835	0.165	0.96	1.78
0.074	0.890	0.036	0.000	0.957	0.043	0.93	1.12
0.065	0.935	0.000	0.000	1.000	0.000	0.94	–

Table 4. Compositions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivities S for [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_7H_8 (3) at 298.15 K

IL-rich phase			hydrocarbon-rich phase				
x_1	x_2	x_3	x'_1	x'_2	x'_3	β	S
0.113	0.000	0.887	0.000	0.000	1.000	–	–
0.110	0.069	0.821	0.001	0.074	0.925	0.93	1.05
0.097	0.246	0.657	0.003	0.257	0.740	0.96	1.08
0.095	0.154	0.751	0.000	0.159	0.841	0.97	1.09
0.091	0.341	0.568	0.002	0.381	0.617	0.89	0.97
0.087	0.425	0.488	0.000	0.475	0.525	0.90	0.96
0.086	0.515	0.399	0.000	0.571	0.429	0.90	0.97
0.080	0.654	0.266	0.001	0.727	0.272	0.90	0.92
0.078	0.765	0.157	0.004	0.834	0.162	0.92	0.95
0.065	0.935	0.000	0.000	1.000	0.000	0.94	–

Results and Discussion

Experimental LLE Data. The compositions of the experimental tie-lines at the temperature of 298.15 K for [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_8H_{18} (3) and [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_7H_8 (3) ternary systems are reported in Tables 3 and 4, respectively. Values of solute distribution ratios (β) and selectivities (S) are also shown in those tables. These parameters are defined as follows

$$\beta = \frac{x_2}{x'_2} \tag{1}$$

$$S = \frac{x_2 \cdot x'_3}{x'_3 \cdot x_3} \tag{2}$$

where superscript ′ indicates the hydrocarbon-rich phase and no superscript the IL-rich phase.

Correlation of LLE Data. The NRTL[15] and UNIQUAC[16] equations were used to fit the experimental data, assigning a

Table 5. UNIQUAC Structural (Volume and Area) Parameters[17–19]

	r	q
thiophene	2.8569	2.140
2,2,4-trimethylpentane	5.8463	5.008
toluene	3.9228	2.968
$[C_8mim][NTf_2]$	13.800	9.310

Table 6. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and (Δu_{ij}, Δu_{ji}) and Root Mean Square Deviations (F, $\Delta\beta$) for the NRTL and UNIQUAC Correlation of $[C_8mim][NTf_2]$ (1) + C_4H_4S (2) + C_8H_{18} (3) at 298.15 K

			components	parameters	
model	rmsd		$i-j$	Δu_{ij}/J·mol^{-1}	Δu_{ji}/J·mol^{-1}
NRTL	F	0.7293	1−2	−7659	19173
(α = 0.3)	$\Delta\beta$	10.2	1−3	2253	11051
			2−3	741.6	−1594
UNIQUAC	F	0.5620	1−2	−1489	3248
	$\Delta\beta$	4.40	1−3	−1297	3759
			2−3	−340.4	1367

Table 7. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and (Δu_{ij}, Δu_{ji}) and rmsd (F, $\Delta\beta$) for the NRTL and UNIQUAC Correlation of $[C_8mim][NTf_2]$ (1) + C_4H_4S (2) + C_7H_8 (3) at 298.15 K

			components	parameters	
model	rmsd		$i-j$	Δu_{ij}/J·mol^{-1}	Δu_{ji}/J·mol^{-1}
NRTL	F	14.4682	1−2	−1653	13183
(α = 0.3)	$\Delta\beta$	29.90	1−3	−2106	12832
			2−3	300.9	242.0
UNIQUAC	F	1.6702	1−2	−499.6	1826
	$\Delta\beta$	3.70	1−3	−1163	2545
			2−3	−117.8	76.80

Table 8. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and (Δu_{ij}, Δu_{ji}) and rmsd (F, $\Delta\beta$) for the NRTL and UNIQUAC Correlation of $[C_8mim][NTf_2]$ (1) + C_4H_4S (2) + C_7H_8 (3) at 298.15 K[a]

			components	parameters	
model	rmsd		$i-j$	Δu_{ij}/J·mol^{-1}	Δu_{ji}/J·mol^{-1}
NRTL	F	8.1977	1−2	−2862	12698
(α = 0.3)	$\Delta\beta$	10.90	1−3	−2688	12157
	β_∞	1.14	2−3	1237	1384
UNIQUAC	F	1.4306	1−2	−796.5	2192
	$\Delta\beta$	4.30	1−3	−1238	2685
	β_∞	0.95	2−3	−154.8	222.8

[a] Solute distribution ratio at infinite dilution, β_∞, is fixed.

priori different values for the nonrandomness parameter α in the NRTL equation: 0.1, 0.2, and 0.3. The structural parameters for the application of the UNIQUAC equation were taken from the literature[17–19] and are shown in Table 5.

The binary interaction parameters for both equations were calculated running a computer program designed by Sφrensen and Arlt,[20] which proceeds in two stages. In the first, approximate values of the binary interaction parameters are obtained using an objective function that requires no initial estimate of their values

$$F_a = \sum_k \sum_i [(a'_{ik} - a_{ik})/(a'_{ik} + a_{ik})]^2 + Q \cdot \sum_n P_n^2 \quad (3)$$

where a_{ik} is the activity of component i on tie-line k. Superscript ′ indicates the hydrocarbon-rich phase, and no superscript the IL-rich phase. In P_n, $n = 6$ parameters being optimized and $Q = 10^{-6}$, the factor weighting this contribution to F_a. The effect of the term $Q\sum^{n} P_n^2$ is to minimize the risk of the Gibbs energy surface having more than the required number of minima. In the second stage, the parameter values found in the first stage are used as initial values in minimizing the objective function

$$F_b = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q\sum P_n^2 + \left[\ln\left(\frac{\hat{\gamma}'_{S\infty}}{\hat{\gamma}_{S\infty}}\beta_\infty\right)\right]^2 \quad (4)$$

where x_{ijk} is the experimental mole fraction of component i in phase j on tie-line k; $\hat{x}_{ijk}$ is the value calculated, using the parameters being optimized, for the corresponding end of a tie-line that "min" makes coincide as closely as possible with the experimental tie-line using the Nelder−Mead method. β_∞ is the solute molar distribution ratio at infinite dilution, and $\hat{\gamma}_{S\infty}$ and $\hat{\gamma}'_{S\infty}$ represent the solute (thiophene) activity coefficients calculated at infinite dilution in IL and hydrocarbon phases, respectively. $Q = 10^{-10}$ for eq 4.

The goodness of the fit was quantified by the residual function F and by the mean error of the solute distribution ratio, $\Delta\beta$, defined as

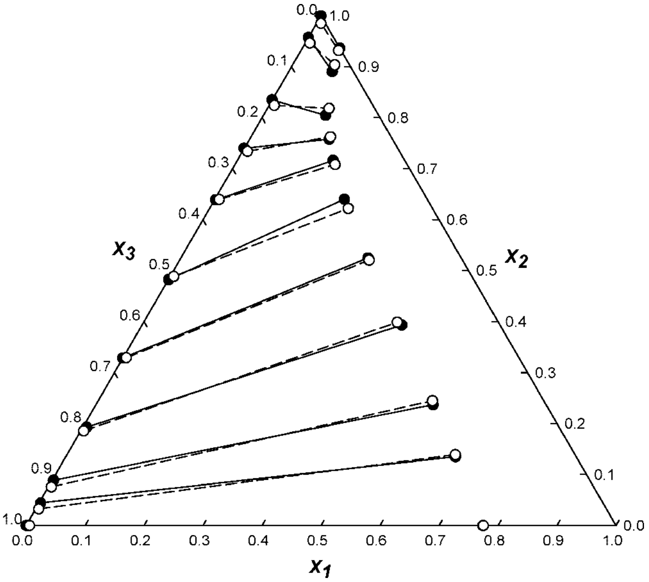

Figure 1. Liquid−liquid equilibria for the ternary system $[C_8mim][NTf_2]$ (1) + C_4H_4S (2) + C_8H_{18} (3) at 298.15 K: ●, solid line, experimental tie-lines; ○, short dash, tie-lines correlated by means of the NRTL equation with α = 0.3.

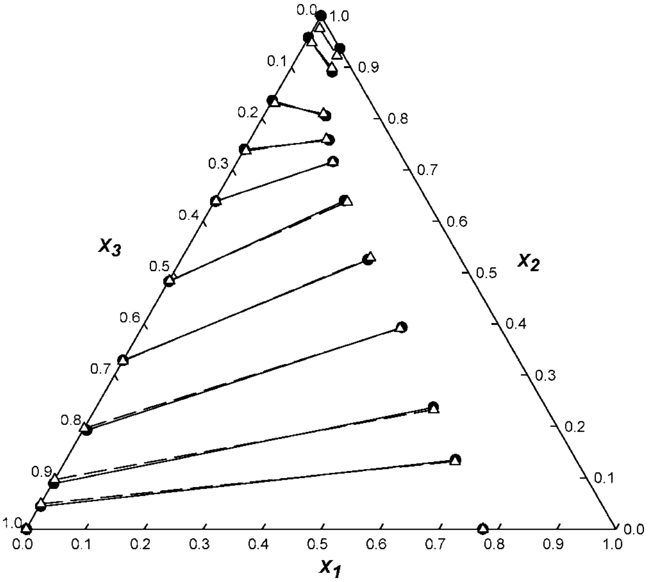

Figure 2. Liquid−liquid equilibria for the ternary system $[C_8mim][NTf_2]$ (1) + C_4H_4S (2) + C_8H_{18} (3) at 298.15 K: ●, solid line, experimental tie-lines; Δ, long dash, tie-lines calculated from UNIQUAC.

$$F = 100 \cdot \left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M} \right]^{0.5} \tag{5}$$

$$\Delta\beta = 100 \cdot \left[\sum_k \frac{((\beta_k - \hat{\beta}_k)/\beta_k)^2}{M} \right]^{0.5} \tag{6}$$

where M refers to the number of experimental tie-lines.

In this work, experimental data were correlated in two ways: without defining an a priori value of β_∞, the last term of eq 4 becoming zero, and specifying an optimal value of this parameter. An appropriate given value of β_∞ can improve the fit at low solute concentrations. Here, the value of β_∞ minimizing the goodness-of-fit index $\Delta\beta$ was found by trial and error.

Tables 6 and 7 show the binary interaction parameters and residuals for the NRTL and UNIQUAC correlations of ternary data, without fixing an optimal value for the solute distribution ratio at infinite dilution. For the NRTL model, the value of the nonrandomness parameter $\alpha = 0.3$ was used because it gives the best results. For the ternary system with toluene, when β_∞ is fixed at its optimal value and the NRTL ($\alpha = 0.3$) equation is used, the residuals F and $\Delta\beta$ decreases extensively. If UNIQUAC equation is used, F decreases, but $\Delta\beta$ slightly increases. Nevertheless, for the system with 2,2,4-trimethylpentane, there is nearly no difference between fixing or not fixing the value of β_∞, and so, the results using the optimal value for β_∞ are not shown. Table 8 shows the values of root-mean-square deviations for the UNIQUAC and NRTL ($\alpha = 0.3$) correlations, by fixing the optimal value of the solute distribution ratio at infinite dilution for the system with toluene.

Figure 1 shows the experimental and correlated NRTL ($\alpha = 0.3$) tie-lines for the 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide + thiophene + 2,2,4-trimethylpentane ternary system. A similar comparison between experimental and correlated data is done in Figure 2 with the UNIQUAC equation. Figures 3 and 4 show the experimental, NRTL, and UNIQUAC correlated (β_∞ fixed) data for bis[trifluoromethylsulfonyl]imide + thiophene + toluene. Despite that the values of β_∞ fixed are used, NRTL is incapable of adequately correlating this system.

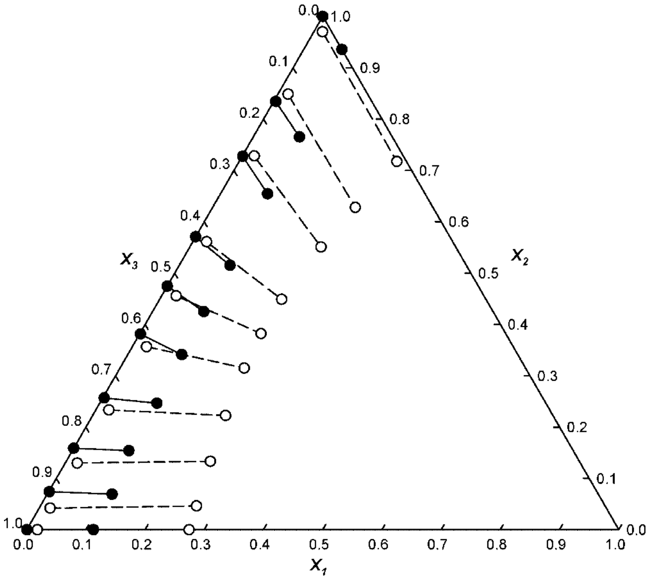

Figure 3. Liquid−liquid equilibria for the ternary system [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_7H_8 (3) at 298.15 K: ●, solid line, experimental tie-lines; ○, short dash,tie-lines correlated by means of the NRTL equation with $\alpha = 0.3$ using the optimal value of the solute distribution ratio at infinite dilution.

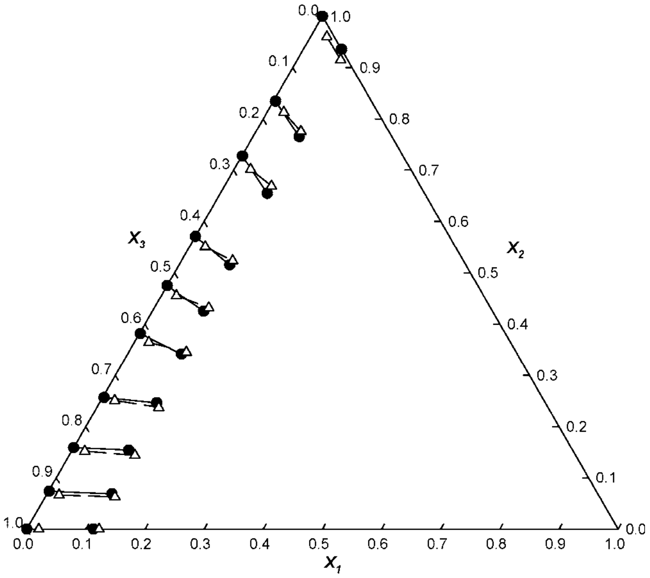

Figure 4. Liquid−liquid equilibria for the ternary system [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_7H_8 (3) at 298.15 K: ●, solid line, experimental tie-lines; Δ, long dash, tie-lines calculated from UNIQUAC using the optimal value of the solute distribution ratio at infinite dilution.

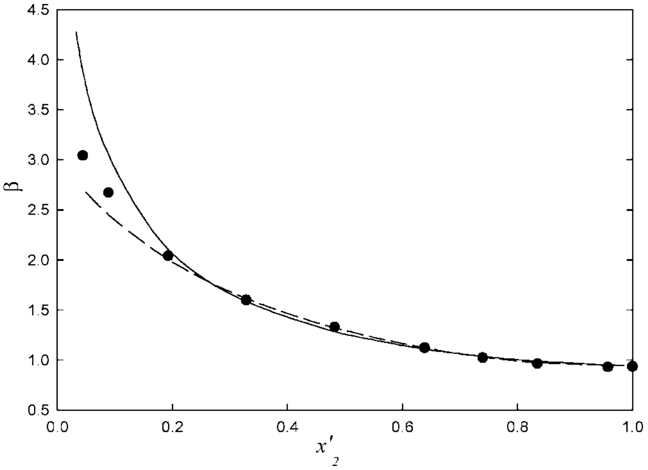

Figure 5. Solute distribution ratio as a function of the mole fraction of solute in the hydrocarbon-rich phase (x'_2) for the [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_8H_{18} (3) ternary system. ●, exptl; −, NRTL; - - -, UNIQUAC model.

Figures 5 and 6 show the correlated solute distribution ratios and selectivities plotted against the mole fraction of solute in the hydrocarbon-rich phase of the [C_8mim][NTf_2] + C_4H_4S + C_8H_{18} ternary system for comparison with experimental values. Solute distribution ratios and selectivities are higher than one at low thiophene concentrations (note that in the desulfurization of fossil fuels the content of sulfur compounds is low, making the ionic liquid an adequate solvent for the extraction of thiophene from 2,2,4-trimethylpentane). Despite that NRTL and UNIQUAC correlate relatively well these parameters, considerable deviations are found to low solute concentrations. Analogously, Figures 7 and 8 present experimental and correlated (β_∞ fixed) solute distribution ratios and selectivities for the [C_8mim][NTf_2] + C_4H_4S + C_7H_8 ternary system. In this case, both parameters are lower or very close to one, extracting the IL important quantities of the aromatic compound. Correlation of these parameters is not adequate, especially with the NRTL equation, as was previously commented.

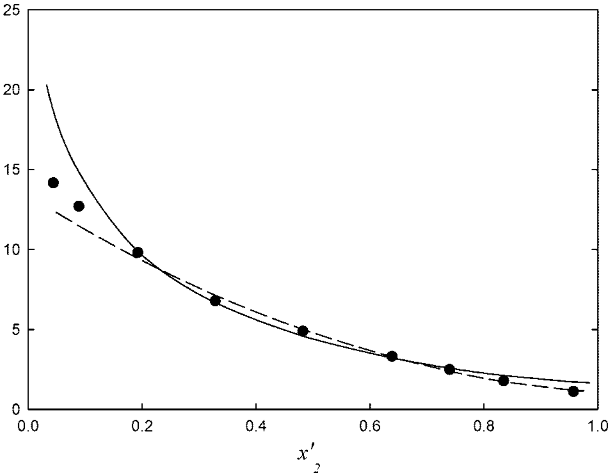

Figure 6. Selectivity as a function of the mole fraction of solute in the hydrocarbon-rich phase (x'_2) for the system [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_8H_{18} (3). ●, exptl; −, NRTL; - - -, UNIQUAC model.

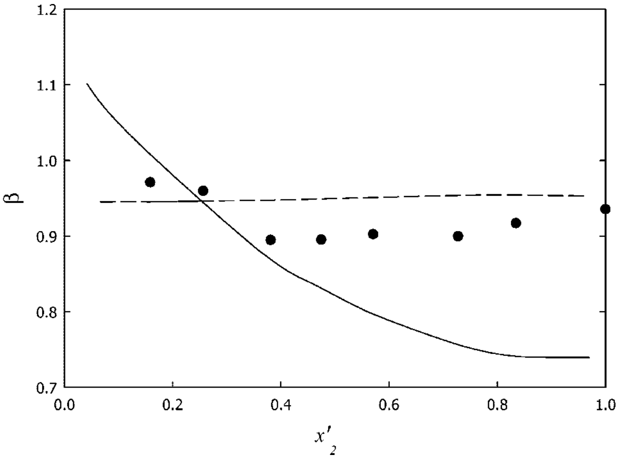

Figure 7. Solute distribution ratio as a function of the mole fraction of solute in the hydrocarbon-rich phase (x'_2) for the [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_7H_8 (3) ternary system. ●, exptl; −, NRTL; - - -, UNIQUAC model.

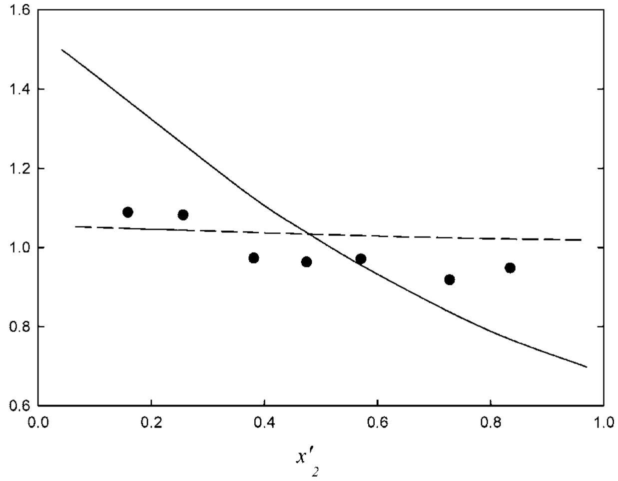

Figure 8. Selectivity as a function of the mole fraction of solute in the hydrocarbon-rich phase (x'_2) for the system [C_8mim][NTf_2] (1) + C_4H_4S (2) + C_7H_8 (3). ●, exptl; −, NRTL; - - -, UNIQUAC model.

Conclusions

The liquid−liquid-phase equilibria for ternary systems 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide + thiophene + 2,2,4-trimethylpentane or 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide + thiophene + toluene have been experimentally obtained at the temperature of 298.15 K and atmospheric pressure. Both systems are type II because [C_8mim][NTf_2] is partially miscible with all other components. Thiophene solubility in the [C_8mim][NTf_2] is high (94 %), and [C_8mim][NTf_2] solubility in hydrocarbons is poor (values around or below detection limits).

Due to the high selectivity values found for the system with 2,2,4-trimethylpentane, separation of the sulfur compound seems to be feasible, but low values of distribution coefficients imply the use of large quantities of solvent. Nonetheless, negligible vapor pressure of IL facilitates solvent recovery without losses. However, low values of both parameters found for toluene indicate that separation of thiophene from toluene using the IL studied is not favorable thermodynamically. The studies would have to focus on a combined desulfurization and dearomatization.

The experimental LLE data were correlated using NRTL and UNIQUAC models. For both systems, the UNIQUAC model gives the best results, NRTL being incapable of adequately correlating the system with toluene.

Literature Cited

(1) Hai, M.; Mei, B. W.; Fu, Y. T. A new method for obtaining ultralow sulfur diesel fuel via ultrasound assisted oxidative desulfurization. *Fuel* **2003**, *82*, 405–414.

(2) Schmitz, C.; Datsevitch, L.; Jess, A. Deep desulfurization of diesel oil: kinetic studies and process-improvement by the use of a two-phase reactor with pre-saturator. *Chem. Eng. Sci.* **2004**, *59*, 2821–2829.

(3) Tailleur, R.; Galiasso, R. J.; Quenza, S.; Valencia, N. Catalyst for ultra-low sulfur and aromatic diesel. *Appl. Catal., A* **2005**, *282*, 227–235.

(4) Babich, I. V.; Moulijn, J. A. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. *Fuel* **2003**, *82*, 607–631.

(5) Nie, Y.; Li, C.; Sun, A.; Meng, H.; Wang, Z. Extractive Desulfurization of Gasoline Using Imidazolium-Based Phosphoric Ionic Liquids. *Energy Fuels* **2006**, *20*, 2083–2087.

(6) Alonso, L.; Arce, A.; Francisco, M.; Rodríguez, O.; Soto, A. Gasoline Desulfurization using Extraction with [C_8min][BF_4] Ionic Liquid. *AIChE J.* **2007**, *53*, 3108–3115.

(7) Holbrey, J. D.; López-Martin, I.; Rothenberg, G.; Seddon, K. R.; Silvero, G.; Zheng, X. Desulfurisation of oils using ionic liquids: selection of cationic and anionic components to enhance extraction efficiency. *Green Chem.* **2008**, *10*, 87–92.

(8) Alonso, L.; Arce, A.; Francisco, M.; Rodríguez, O.; Soto, A. Measurement and correlation of Liquid-Liquid Equilibria of two imidazolium ionic liquids with thiophene and methylcyclohexane. *J. Chem. Eng. Data* **2007**, *52*, 2409–2412.

(9) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. (Liquid-Liquid) Equilibria of C_8mim][NTf_2] ionic liquid with a sulfur-component and hydrocarbons. *J. Chem. Thermodyn.* **2008**, *40*, 265–270.

(10) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Phase behaviour of 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide with thiophene and aliphatic hydrocarbons: The influence of n-alkane chain length. *Fluid Phase Equilib.* **2008**, *263*, 176–181.

(11) Pádua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. Density and Viscosity Measurements of 2,2,4-Trimethylpentane (Isooctane) from 198 to 348 K and up to 100 MPa. *J. Chem. Eng. Data* **1996**, *41*, 1488–1494.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.

(13) Papaiconomou, N.; Yakelis, N.; Salminen, J.; Bergman, R.; Prausnitz, J. M. Synthesis and Properties of Seven Ionic Liquids Containing 1-Methyl-3-octylimidazolium or 1-Butyl-4-methylpyridinium Cations. *J. Chem. Eng. Data* **2006**, *51*, 1389–1393.

(14) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593–19600.

(15) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(16) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(17) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*; Hemisphere: New York, 1989.

(18) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for Multicomponent VLE and LLE*; Prentice-Hall: Englewood Cliffs, New York, 1980.

(19) 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.

(20) Sorensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series: Frankfurt, 1980.

Received for review January 30, 2008. Accepted April 10, 2008. The authors are thankful for the financial support under project CTQ2006-07687/PPQ from the Ministerio of Ciencia y Tecnología (Spain). L. Alonso is grateful to the Ministerio for financial support via "Juan de la Cierva" Programme and M. Francisco for FPI grant (BES-2007-16693).

JE800071Q