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Gasoline Desulfurization Using Extraction with $[C_8mim][BF_4]$ Ionic Liquid

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Increased reductions of statutory sulfur content on fossil fuels as gasoline or diesel have led to intense research into all possible methods of desulfurization. With the aim to study $[C_8mim][BF_4]$ ionic liquid as extraction solvent for desulfurization, the phase equilibria of different ternary systems involving hydrocarbons present in gasoline formulations, thiophene, and $[C_8mim][BF_4]$, were obtained experimentally. Potential interest of this ionic liquid for desulfurization was confirmed by the phase equilibria determined. As design of a multistage separation process requires knowledge of phase equilibria, simultaneous correlation of liquid–liquid equilibrium data was done using the nonrandom two liquid (NRTL) activity coefficient model. A gasoline formulation was simulated as a mixture of n-hexane, cyclohexane, iso-octane, and toluene with thiophene and dibezothiophene as sulfur-components, and its desulfurization was performed by multistage extraction using the ionic liquid in three successive stages.

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Keywords: desulfurization, extraction, equilibrium, ionic liquids, $[C_8mim][BF_4]$

Introduction

Governmental regulations are getting more stringent on environmental issues. An example could be that for automobile fuels: The European Directive 2003/17/EC lowers the sulfur content (among others) progressively down to 10 ppm in 2009, both for gasoline and diesel. It affects other fuels (like agricultural tractors and nonroad mobile machinery) also limiting their sulfur content. And so does the Environmental Protection Agency (EPA) in the United States. The standard process for sulfur-removal in refinery is hydrotreating, in which the sulfur-containing components of the fuel react with hydrogen in the presence of a suitable catalyst and under severe conditions of temperature (300–400°C) and pressure (over 4 MPa) to produce hydrogen sulfide, H_2S. Hydrogen sulfide is subsequently removed, usually using the classic Clauss process, to produce elemental sulfur. As the sulfur level has to be lowered, the hydrodesulfurization process is less efficient and needs higher temperature and hydrogen pressure, raising the process costs. This lowering of efficiency is mainly due to the low reactivity of some sulfur components[1]: Despite thiols or disulfides have good reaction rates, thiophene, benzothiophene, dibenzothiophene, and their alkylated derivatives are less reactive (specially the aromatic derivatives). Thus, new processes should be envisaged and different alternatives have, so long, appeared published in the literature[2] including adsorption,[3–6] precipitation,[7] biodesulfurization by action of bacteria,[8] oxidation,[9] oxidation using ionic liquids (ILs),[10] and extraction using ILs.[11–17]

ILs are organic salts with melting points around or below ambient temperature. They are getting much attention as some of their properties make them excellent choices as reaction media, extraction solvents, and in other applications. Among these properties we highlight their negligible vapor pressure (which facilitates the recovery of the IL), thermal and chemical stability, wide liquid range, or the possibility to "design" the IL by adding functional groups to meet certain properties.[18,19] For all the above, we have recently started to investigate the

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Table 1. Water Content, Density (ρ) and Refractive Index (n_D) of the Pure Components at 298.15 K and Atmospheric Pressure

			ρ (g cm^{-3})		n_D	
Component	CAS Number	Water (ppm)	Exp.	Lit.	Exp.	Lit.
Cyclohexane	110-82-7	45	0.77376	0.77389[22]	1.42403	1.42354[22]
n-Hexane	110-54-3	75	0.65506	0.65484[22]	1.37287	1.37226[22]
i-Octane	540-84-1	46	0.6774	0.68781[22]	1.38954	1.38898[22]
Thiophene	110-02-1	338	1.05850	1.05887[23]	1.52581	1.52572[23]
Toluene	108-88-3	174	0.86210	0.86219[22]	1.49423	1.49413[22]
[C$_8$mim][BF$_4$]	244193-52-0	51	1.10442	1.103506[24]	1.43329	1.4322[25]

application of ILs as extraction solvents for desulfurization of gasoline or diesel, concentrating the efforts in thiophene and dibenzothiophene as models of the sulfur-containing components, which would be difficult to eliminate using a classic hydrodesulfurization process. Nevertheless, because of the complexity of the composition of these fuels, not only the partition of sulfurated compounds has to be investigated, but also the behavior of others: olefins, aromatics, etc.

Some authors[12,15] pointed out that ILs with longer alkyl chains provided a better extraction of sulfur-containing components. Preliminary experiments in our research group screening different ILs[20] proved that 1-methyl-3-octylimidazolium tetrafluoroborate, [C$_8$mim][BF$_4$], could extract thiophene while most hydrocarbons remained in the raffinate. With the aim to study this IL as extraction solvent for desulfurization, the phase equilibria of different ternary systems involving hydrocarbons present in gasoline formulations, thiophene and [C$_8$mim][BF$_4$] are obtained experimentally. The liquid–liquid equilibrium data are correlated by means of the nonrandom two liquid (NRTL) equation.[21] Finally, a gasoline formulation is simulated as a mixture of *n*-hexane, cyclohexane, iso-octane, and toluene with thiophene and dibenzothiophene as sulfur-components, and its desulfurization was performed by multistage extraction using [C$_8$mim][BF$_4$] in three successive stages.

Experimental

Chemicals

n-Hexane (Fluka, >99.0 wt %), cyclohexane (Riedel-de Haën, purum, >99.5 wt %), iso-octane [Fluka, puriss.p.a.ACS, ≥99.5 wt % (GC)], toluene (Aldrich, 99.5+ wt %, A.C.S.Reagent), dibenzothiophene (Aldrich, 98 wt %) and thiophene (Aldrich, purum, > 99.5 wt %) were used as received from supplier without further purification. The IL 1-methyl-3-octylimidazolium tetrafluoroborate, [C$_8$mim][BF$_4$], was synthesized in our laboratory as explained below. The purities of *n*-hexane, cyclohexane, isooctane, toluene, dibenzothiophene, and thiophene were verified by gas chromatography. The purity of the IL was verified by ^{1}H-NMR spectroscopy. Further information about pure components, experimental densities, refractive indices, and water contents, along with values published by other authors,[22–25] is shown in Table 1.

Synthesis of [C$_8$min][BF$_4$]

1-Methylimidazole was reacted with an excess of 1-bromooctane to produce 1-methyl-3-octylimidazolium bromide. The [C$_8$mim][Br] was then reacted with sodium tetrafluoroborate in aqueous solution to produce [C$_8$min][BF$_4$]. The latter is immiscible with water and thus, two phases appeared. The IL phase was decanted and dissolved in dichloromethane, being this mixture washed several times with water. A rotary evaporator was used to remove the dichloromethane and water, first, and then purification was completed under vacuum. Details of preparation have been published before.[26]

Regeneration of [C$_8$min][BF$_4$]

IL used during this experimentation was recovered and purified using a rotary evaporator first, and then vacuum. The operation is straightforward due to its low vapor pressure when compared with the rest of components. Purity of regenerated IL was analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy. Water content was verified using a Karl–Fischer titration method.

Procedure

All weighing was carried out in a Mettler Toledo AT 261 balance precise to within $\pm 10^{-4}$ g. Water content was measured using a Karl–Fischer titration method in a Metrohm 737 KF coulometer. Densities were measured in an Anton Paar DMA 60/602 densimeter. The uncertainty in the measurement is $\pm 10^{-5}$ g cm^{-3}. Refractive indices were measured in an ATAGO RX-5000 refractometer. The uncertainty in the measurement is $\pm 4 \times 10^{-5}$.

Ternary phase diagrams

Liquid–liquid equilibrium data for ternary systems, ([C$_8$mim][BF$_4$] + thiophene + *i*-octane), ([C$_8$mim][BF$_4$] + thiophene + toluene), and ([C$_8$mim][BF$_4$] + cyclohexane + *n*-hexane), were determined experimentally by analysis of phases at equilibrium. To obtain the tie-lines, mixtures with compositions inside the immiscible region of the systems were introduced into 30 ml glass jacketed vessels, with magnetic stirrers, and closed. The jackets were connected to a thermostat bath (Julabo F12) to maintain a constant temperature of 298.15 K in the vessels. Previous experiments showed that equilibrium was established after about 2 h stirring, to get a good contact between both phases, and a minimum of 4 h to settle down. Then, samples of both layers were withdrawn using syringes and analyzed by gas chromatography using an internal standard method. A Hewlett–Packard 6890N Series gas chromatograph (GC), equipped with a split injection, a thermal conductivity detector and a HP-FFAP capillary column, was used for analysis of ([C$_8$mim][BF$_4$] +

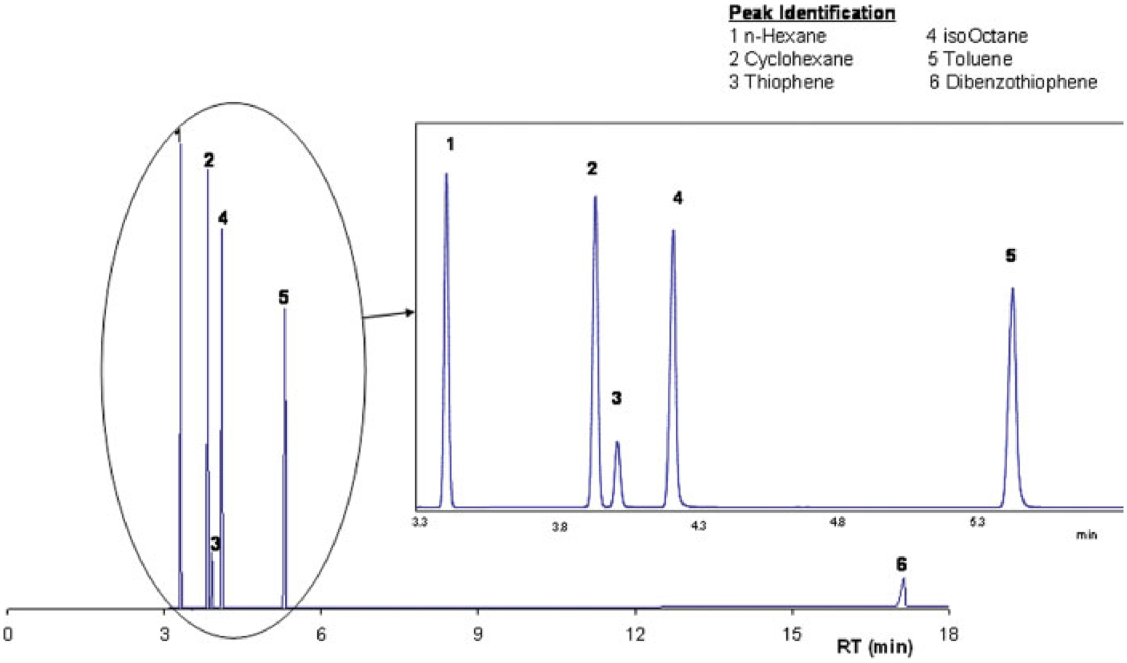

Figure 1. Simulated gasoline chromatogram and peak identification.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thiophene + *i*-octane) and ([C_8mim][BF_4] + cyclohexane + *n*-hexane). For ([C_8mim][BF_4] + thiophene + toluene) samples, a Flame Ionization Detector and a HP-5 capillary column were used. In both cases an empty precolumn was placed between column and injector to protect the column and collect the IL that could not be retained by liner. The GC operating conditions for each system studied are given in supporting material.

Multistage extraction

To analyze the validity of this IL for desulfurization of fuel oils by extraction, a gasoline was simulated with 28 wt % *n*-hexane, 28 wt % cyclohexane, 28 wt % *i*-octane, 10 wt % toluene, 3 wt % thiophene, and 3 wt % dibenzothiophene. A sample of this mixture was introduced into a 30 ml glass jacketed vessel with the IL on a 1:1 mass ratio (Solvent-to-Feed ratio, S/F = 1) following a procedure similar to that explained earlier. Then samples of both layers were withdrawn for composition determination by GC. Chromatographic conditions are given in supporting material. Figure 1 shows a typical chromatogram and peaks for each component are identified. The remaining mixture was decanted: The hydrocarbon phase (raffinate, top phase) was used on a new extraction stage, and the IL phase (extract, bottom phase) was regenerated.

Results and Discussion

Ternary phase diagrams

Table 2 gives the experimental compositions for the tie-lines of the three ternary systems obtained: ([C_8mim][BF_4] + thiophene + *i*-octane), ([C_8mim][BF_4] + thiophene + toluene), and ([C_8mim][BF_4] + cyclohexane + *n*-hexane). The phase diagrams for these systems are shown in Figure 2. This figure also shows the phase behavior for previously studied systems[27] ([C_8mim][BF_4] + thiophene + *n*-hexane) and ([C_8mim][BF_4] + thiophene + cyclohexane) for a better understanding of the multicomponent system behavior. All systems presented here are of the type II, as [C_8mim][BF_4] is partially miscible with all other components. Nevertheless, thiophene solubility in the IL is high (90%). Also, [C_8mim][BF_4] solubility in hydrocarbons is poor (values around or below detection limits), and solubility of hydrocarbons is somehow low in the IL.

Figure 2a shows the IL behavior with *i*-octane, an alkylated alkane. This kind of chemical is likely to be present in gasoline formulations as it increases the octane number. The slope of the tie-lines indicates that [C_8mim][BF_4] is a good solvent for thiophene extraction from a thermodynamic point of view. Moreover, the big immiscibility gap indicates a good selectivity of the solvent: [C_8mim][BF_4] will preferentially extract thiophene and not *i*-octane. On the contrary, Figure 2b shows the high solubility of toluene in [C_8mim][BF_4] (70%) while maintaining a poor solubility of the IL in the hydrocarbon. This fact indicates that in general aromatic compounds would also be extracted, at least to some extent. This fact has been previously found with other ILs[12] and it has to be managed to get a compromise: aromatics enhance the gasoline octane number, but their content is limited by regulations (these limits are referred to benzene particularly, polyaromatics, and total aromatics).

Figure 2c shows the behavior of [C_8mim][BF_4] with a mixture of hydrocarbons (*n*-hexane and cyclohexane) and thiophene. Again, solubility of the IL in the organic phase is poor, but the hydrocarbons have some solubility in the IL

Table 2. Liquid–Liquid Equilibrium Data, Solute Distribution Ratio (β), and Selectivity (S) at 298.15 K for Ternary Systems Involved in Desulfurization

Hydrocarbon-rich Phase			IL-rich Phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
{[C$_8$mim][BF$_4$] (1) + thiophene (2) + *i*-octane (3)}							
0.000	0.000	1.000	0.919	0.000	0.081	–	–
0.000	0.060	0.940	0.790	0.134	0.076	2.23	27.62
0.000	0.124	0.876	0.661	0.258	0.081	2.08	22.50
0.000	0.239	0.762	0.514	0.410	0.076	1.72	17.20
0.000	0.356	0.644	0.418	0.518	0.064	1.46	14.64
0.000	0.516	0.484	0.316	0.615	0.068	1.19	8.48
0.000	0.663	0.337	0.213	0.729	0.058	1.10	6.39
0.000	0.764	0.236	0.155	0.791	0.054	1.04	4.52
0.000	0.829	0.172	0.135	0.818	0.046	0.99	3.69
0.000	0.940	0.060	0.112	0.864	0.024	0.92	2.30
0.000	1.000	0.000	0.100	0.900	0.000	0.90	–
{[C$_8$mim][BF$_4$] (1) + thiophene (2) + toluene (3)}							
0.000	0.000	1.000	0.287	0.000	0.713	–	–
0.003	0.124	0.873	0.255	0.139	0.606	1.12	1.61
0.003	0.235	0.762	0.234	0.218	0.549	0.93	1.29
0.003	0.362	0.635	0.205	0.331	0.464	0.92	1.25
0.003	0.547	0.450	0.174	0.498	0.328	0.91	1.25
0.003	0.671	0.326	0.149	0.605	0.246	0.90	1.19
0.003	0.758	0.239	0.137	0.680	0.182	0.90	1.18
0.003	0.820	0.177	0.127	0.736	0.137	0.90	1.16
0.003	0.889	0.108	0.118	0.786	0.095	0.88	1.01
0.003	0.929	0.068	0.112	0.821	0.066	0.88	0.91
0.003	0.997	0.000	0.100	0.900	0.000	0.90	–
{[C$_8$mim][BF$_4$] + cyclohexane + hexane}							
0.000	0.000	1.000	0.855	0.000	0.146	–	–
0.000	0.101	0.899	0.840	0.023	0.137	0.23	1.49
0.000	0.246	0.754	0.825	0.054	0.121	0.22	1.37
0.000	0.323	0.677	0.816	0.074	0.110	0.23	1.41
0.000	0.457	0.543	0.803	0.102	0.095	0.22	1.28
0.000	0.586	0.414	0.795	0.133	0.073	0.23	1.29
0.000	0.680	0.321	0.793	0.155	0.052	0.23	1.41
0.001	0.837	0.162	0.792	0.179	0.030	0.21	1.15
0.021	0.886	0.094	0.790	0.195	0.016	0.22	1.29
0.052	0.948	0.000	0.792	0.208	0.000	0.22	–

phase (*n*-hexane: 14%; cyclohexane: 20%). The phase diagrams of ([C$_8$mim][BF$_4$] + thiophene + *n*-hexane) and ([C$_8$mim][BF$_4$] + thiophene + cyclohexane) were studied previously[27] and they are similar to that of *i*-octane. Nevertheless, solubility of *n*-hexane and cyclohexane in the IL is slightly higher.

Thiophene distribution ratio, β, and solvent selectivity, S, were calculated to evaluate solvent extraction capacity, according to equations:

$$\beta = \frac{(x_{\text{thiophene}})^{\text{IL-phase}}}{(x_{\text{thiophene}})^{\text{HC-phase}}} \tag{1}$$

$$S = \frac{(x_{\text{thiophene}})^{\text{IL-phase}} \cdot (x_{\text{HC}})^{\text{HC-phase}}}{(x_{\text{thiophene}})^{\text{HC-phase}} \cdot (x_{\text{HC}})^{\text{IL-phase}}} \tag{2}$$

where x is the molar composition of component indicated as subscript, in the phase indicated as superscript. HC stands for hydrocarbon and IL for ionic liquid. The values of both parameters are given in Table 3. It can be seen that thiophene distributes preferentially in the IL, rather than in *i*-octane, especially at low thiophene concentrations. High values of the selectivity are also obtained. Nevertheless, in the toluene system distribution of thiophene is nearly equal between conjugated phases, and selectivity is poor.

The phase diagrams presented here indicate that extraction of thiophene using [C$_8$mim][BF$_4$] seems feasible, with low cross-contamination: The IL is not likely to contaminate the raffinate, and a good selectivity towards hydrocarbons is expected. Aromatics would also be extracted, at least to some extent, and care must be taken for octane number lowering. The problem of cross-contamination (presence of IL in the raffinate and extraction of hydrocarbons together with the sulfur compounds) has been previously pointed out for diesel desulfurization.[12] Thus, not only the distribution of thiophene and its derivatives has to be measured, but also the selectivity of the solvent with the different hydrocarbons present in the fuel.

Data treatment

Correlation of experimental tie-lines was done by means of the NRTL equation.[21] The value of the nonrandomness parameter, α, was previously assigned to 0.1, 0.2, and 0.3. The binary interaction parameters were obtained using a computer program[28] with two objective functions. F_a is used first as it does not require any previous guess for parameters.

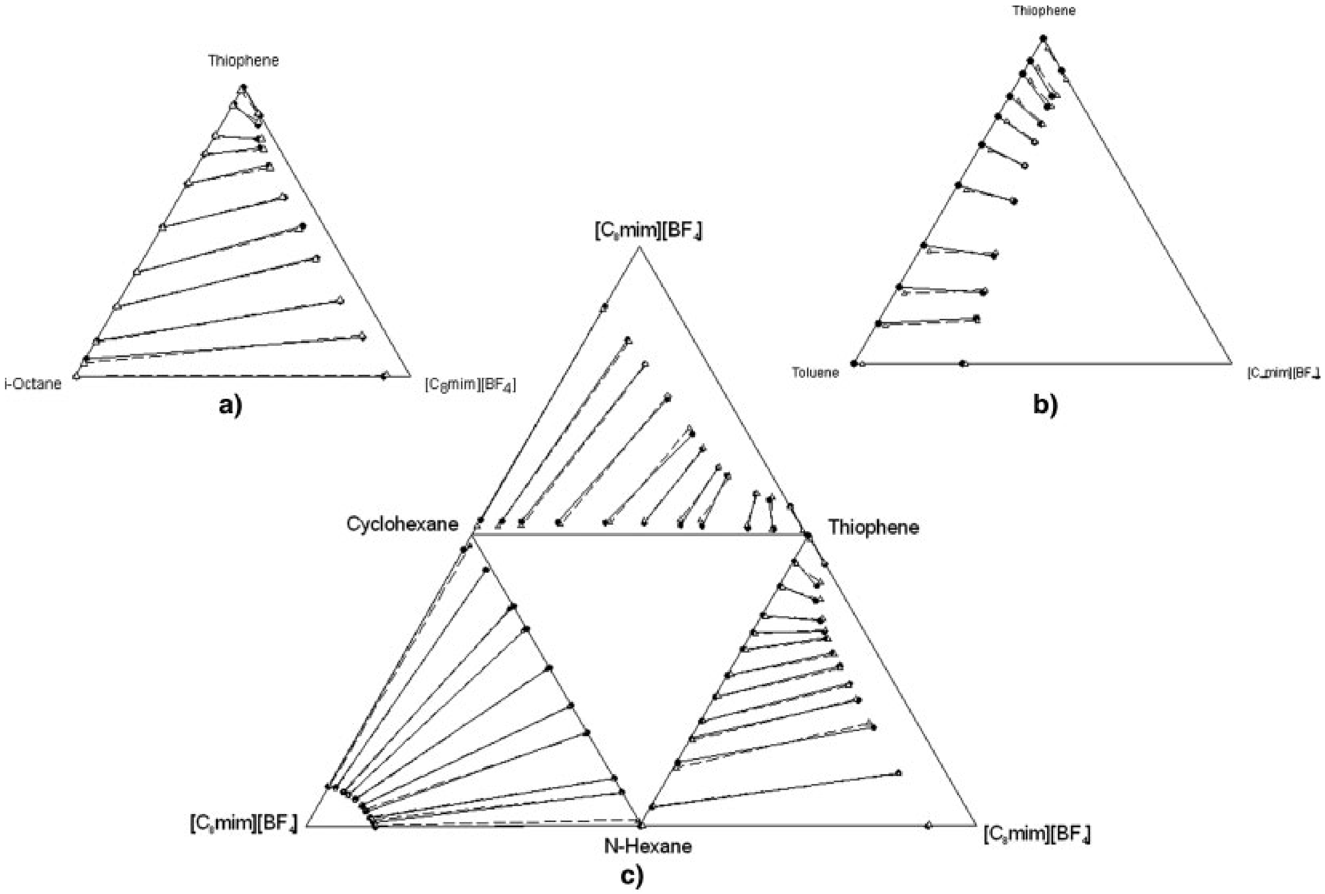

Figure 2. LLE at 298.15 K for ternary systems involved in desulfurization.

●, Experimental; △, correlated.

After convergence, these parameters are used in the second function, F_b, to fit the experimental concentrations:

$$F_\mathrm{a} = \sum_k \sum_i \left[\left(a_{ik}^\mathrm{I} - a_{ik}^\mathrm{II} \right) / \left(a_{ik}^\mathrm{I} + a_{ik}^\mathrm{II} \right) \right]^2 + Q \sum_n P_n^2 \tag{3}$$

$$F_\mathrm{b} = \sum_k \mathrm{mim} \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum P_n^2 + \left[\ln \left(\frac{\hat{\gamma}_{\mathrm{S}\infty}^\mathrm{I}}{\hat{\gamma}_{\mathrm{S}\infty}^\mathrm{II}} \beta_\infty \right) \right]^2 \tag{4}$$

where a is the activity, x is the experimental composition in mole fraction, and $\hat{x}$ the corresponding calculated composition. Subscripts and superscripts are as follows: i for components of the mixture, j for phases (I, II), and k for tie-lines. The second term in both objective functions are penalty terms to reduce the risks of multiple solutions (associated with parameters of high value), in which $Q = 10^{-6}$ for Eq. 3, $Q = 10^{-10}$ for Eq. 4, and P_n stands for the adjustable parameters. F_b also includes a third term to correctly fit experimental distribution ratios when working with low solute concentrations. For this term, $\hat{\gamma}_{\mathrm{S}\infty}^\mathrm{I}$ and $\hat{\gamma}_{\mathrm{S}\infty}^\mathrm{II}$ represent the solute activity coefficients calculated at infinite dilution in both phases and β_∞ is the solute molar distribution ratio at infinite dilution.

The correlation is evaluated using the residual function F and the mean error of the solute distribution ratio, $\Delta\beta$:

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

Table 3. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and Residuals (F, $\Delta\beta$) for the NRTL Correlation of Ternary Systems

r.m.s.d.		Components i–j	Parameters Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
{[C$_8$mim][BF$_4$] (1) + thiophene (2) + *i*-octane (3)}, α = 0.2				
F	0.7053	1–2	−11,935	29,552
$\Delta\beta$	9.4	1–3	2739.0	11,620
		2–3	−739.00	−4675.0
{[C$_8$mim][BF$_4$] (1) + thiophene (2) + toluene (3)}, α = 0.3				
F	1.5664	1–2	−4431.0	13,358
$\Delta\beta$	4.9	1–3	−2305.0	11,464
		2–3	408.50	390.10
{[C$_8$mim][BF$_4$] (1) + cyclohexane (2) + *n*-hexane (3)}, α = 0.2				
F	0.6113	1–2	704.05	8670.4
$\Delta\beta$	3.5	1–3	1398.0	19,471
		2–3	1626.0	−491.00

Table 4. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and Residuals (F, $\Delta\beta$) for the Simultaneous Correlation of all Ternary Systems Involved on Desulfurization Using the NRTL Equation with $\alpha = 0.3$

Components		Parameters	
i	j	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
[C_8mim][BF_4]	Thiophene	−4789.2	14,061
[C_8mim][BF_4]	*n*-Hexane	3052.3	8332.0
Thiophene	*n*-Hexane	3088.8	−461.38
[C_8mim][BF_4]	Cyclohexane	2394.2	7660.4
Thiophene	Cyclohexane	2241.8	−792.92
[C_8mim][BF_4]	*i*-Octane	4348.6	7086.0
Thiophene	*i*-Octane	5829.7	−1293.2
[C_8mim][BF_4]	Toluene	−2317.9	11,391
Thiophene	Toluene	181.53	211.18
n-Hexane	Cyclohexane	214.81	311.53
Ternary System		F	$\Delta\beta$
{[C_8mim][BF_4] + thiophene + *n*-hexane}		1.5033	5.8
{[C_8mim][BF_4] + thiophene + cyclohexane}		0.9681	6.6
{[C_8mim][BF_4] + thiophene + *i*-octane}		1.7404	13.5
{[C_8mim][BF_4] + thiophene + toluene}		1.3245	6.0
{[C_8mim][BF_4] + cyclohexane + *n*-hexane}		1.1753	11.0

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

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

Binary interaction parameters and residuals obtained in the correlation of each system data set are given in Table 3. The comparison of experimental and correlated tie-lines is shown in Figure 2. As indicated by residuals, data reduction is accurate. Biggest errors are in the high-thiophene region. Also, for system ([C_8mim][BF_4] + thiophene + toluene) the model calculates a higher solubility of IL in toluene. This difficulty in the correlation of some type II systems is usually found in bibliography.[28]

A simultaneous correlation of all liquid–liquid equilibria was done using again the NRTL activity coefficient model. This kind of data is necessary to work with multicomponent mixtures (e.g., design of multistage separation process for fuel desulfurization). The nonrandomness parameter α was tested as before and best results were obtained for $\alpha = 0.3$. Table 4 gives the binary interaction parameters and the corresponding residuals for each system. These residuals are slightly higher than in previous correlation. The increased errors are mainly in the high thiophene region and the IL composition in the hydrocarbon phase (the model calculates a higher composition).

Multistage extraction

Figure 3 presents the composition (wt %) of each component in the simulated gasoline formulation and raffinate product after one and three extraction stages. Both thiophene and dibenzothiophene are extracted by [C_8mim][BF_4] and their composition in the raffinate product decreases rapidly:

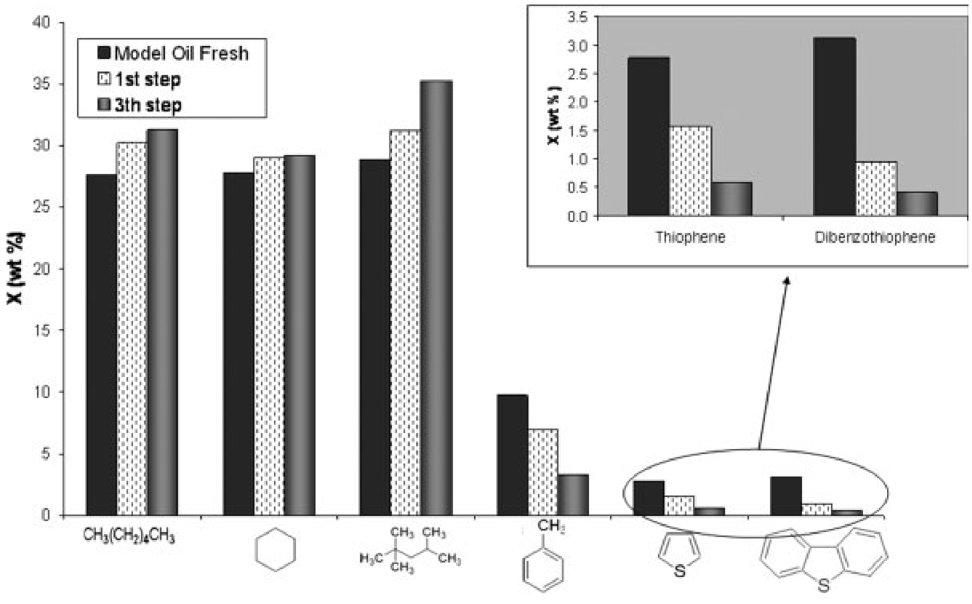

Figure 3. Multistage desulfurization: compositions in initial model oil (gasoline) and after one and three extractions.

40 wt % reduction for thiophene and 70% for dibenzothiophene after one extraction stage. After three extraction stages thiophene composition is reduced 79 wt % and dibenzothiophene is reduced 87 wt %. Figure 3 also shows the co-extraction of toluene, with a toluene composition reduction of 66 wt %. This side effect could be predicted after inspection of ternary diagram in Figure 2b. All other hydrocarbons increase their compositions after each extraction stage. This indicates a high affinity of the IL for aromatics (with and without sulfur), which can be due to CH-π interactions between the hydrogens of the IL ring and those of the aromatic compounds, as it has been evidenced by Dupont et al.[29]

Moreover, the IL composition detected in the raffinate was in all cases less than 2 wt %. Also hydrocarbons in the extract are at low concentration (below 10 wt % each). This confirms the low cross-contamination that was expected from phase diagrams (see Figure 2). Recovery of the IL should be straightforward because of its low volatility (flash or distillation unit). The process was done in our lab in two stages, as explained earlier. The IL could be reused in the experiments after purity verification (see experimental section).

Conclusions

The use of 1-methyl-3-octylimidazolium tetrafluoroborate IL, [C_8mim][BF_4], as solvent for desulfurization of gasoline by liquid–liquid extraction was analyzed. Phase diagrams for ([C_8mim][BF_4] + thiophene + *i*-octane), ([C_8mim][BF_4] + thiophene + toluene) and ([C_8mim][BF_4] + cyclohexane + *n*-hexane) ternary systems were obtained experimentally at 298.15 K. All systems are type II with high solubility of thiophene in the IL.

Essays using [C_8mim][BF_4] showed that solvent extraction of thiophene and dibenzothiophene is possible. Similar conclusions were obtained by Zhang and Zhang[13] using [C_2mim][BF_4] and [C_4mim][BF_4]. This family of ILs has high capacity for extraction of sulfur compounds, which increases with its alkyl chain length.

An extraction process was carried out with the IL 1-methyl-3-octylimidazolium tetrafluoroborate. After three stages the composition of thiophene is reduced by 79 wt % and that of dibenzothiophene is reduced by 87 wt %. As it is well known, the use of a countercurrent operation will increase the separation capacity. By using mass balances and equilibrium data reported on this work, the design of a multistage separation process leading to desulfurization levels in accordance with legislation requirements is possible. Special care must be taken with aromatic compounds since they are also extracted to some extent by the IL. This has to be balanced with regard to the octane number. Some authors[11,12] regard extraction with RTILs as best deployed as a final desulphurization stage following conventional catalytic hydrodesulphurization (a process that eliminates not only sulfur but also nitrogen, oxygen…). A rigorous study of the entire process and its economy would mean a subsequent stage to this work, which is only intended to establish the suitability of using [C_8mim][BF_4] to desulfurizate.

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