1. SUMARY

As one of the multiple applications of ionic liquids, extraction of sulfur- and nitrogen-containing compounds from fuels has been studied in this thesis.

Three imidazolium-based ionic liquids: 1-octyl-3-methylimidazolium tetrafluoborate ($[C_8mim][BF_4]$), 1-octyl-3-ethylimidazolium bis{(trifluoromethylsulfonyl)imide} ($[C_8mim][NTf_2]$) and 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2mim][EtSO_4]$) and a poly substituted pyridinium ionic liquid, 1-hexyl-3,5-dimethylpyridinium bis{(trifluoromethyl sulfonyl)imide} ($[C_6mmPy][NTf_2]$) were chosen as possible solvents .Thiophene and pyridine were selected as representative sulfur- and nitrogen-containing compounds.

With this aim, liquid-liquid equilibrium data of ternary systems composed by {Ionic liquid (IL) + thiophene/pyridine+fuel representative hydrocarbon} have been determined and discussed in terms of solute distribution ratio (β) and selectivity(S).

Three steps extraction experiments were carried out with two synthetic mixtures simulating gasoline and diesel and following raffinate composition after each one of the steps. Ability of the four ionic liquids to extract sulfur- and nitrogen-containing compounds has been demonstrated. The ionic liquid which gave the greatest extraction yield was $[C_6mmPy][NTf_2]$. Certain degree of dearomatization has been also observed.

Extraction performances using real samples from the refinery previous to desulfurization have been found to be in agreement with the model oil results.

2. PROBLEM ADRESSED

2.1 Environmental Background

Emissions of sulfur gases from both natural and anthropogenic sources strongly influence the atmosphere chemistry. Since the industrial revolution, release of sulfur and nitrogen oxides has increased. Burning of fossil fuels caused the industrial growth and energy-generating facilities, are the main sources. These emissions, plus those from the transportation sector, are the major originators of increased nitrogen and sulfur oxides into the atmosphere which can be transformed to strong acids (sulfuric and nitric acids) causing the undesirable acid rain [1].

In order to endeavour this problem, "The Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Further Reduction of Sulphur Emissions" is an agreement to provide for a further reduction in sulfur emissions or transboundary fluxes [2].

Over the last decade, environmental regulations focus attention on reduction of emissions from the transport sector with the purpose of improving air quality and welfare [3]. According to the Directive of the European Union, gasoline and diesel fuels in Europe should not exceed 10 ppm of total sulfur content starting from 2010 [4]. US regulations established a maximum of 15 ppm for diesel starting from 2006 and 30 ppm for gasoline starting from 2005 [5].

2.2 The problem of fuel desulfurization: an overview

2.2.1 Petroleum technology context

Product improvement in refineries consists on the treatment of petroleum products to ensure that they meet utility and performance specifications. It usually involves changes in molecular shape (reforming and isomerization) or in molecular size (alkylation and polymerization) and it can play a major role in product improvement.

A growing dependence on high-heteroatom heavy oils and residua has emerged as a result of continuing decreasing availability of conventional crude oil, owing to the depletion of reserves in various parts of the World. Thus, the ever-growing tendency to convert as much as possible of lower-grade feedstock to liquid products is causing an increase in the total sulfur content in refined products [6].

There are several valid reasons for removing heteroatoms from petroleum fractions. These reasons include:

- Reduction or elimination of corrosion during refining, handling or use of the various products.
- Production of products having an acceptable degree of specifications.
- Increasing the stability and performance of the transportation fuels.
- Decreasing smoke formation in kerosene.
- Reduction of heteroatom content in fuel oil to a level that improves burning characteristics and is environmentally acceptable.

Sulfur-, nitrogen- and metal-containing compounds have different reactivities and chemistries depending on the boiling ranges of the fractions in which are found. Thus, specific processes have been developed for the removal of each one of these impurities and are classified as hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallization (HDM) processes, respectively.

In general, sulfur impurity is the major concern because S-compounds are often serious poisons and inhibitors for other secondary-process catalysts and their combustion products create serious environmental hazards. Thus, the main hydrotreating processes that have been

developed for distillable feedstock are HDS processes. N-containing compounds are also removed during this process and also HDA reactions are occurred, even though quality requirements often require an HDA procedure after the initial HDS+HDN processes [7].

2.2.2 Current Process: hydrodesulfurization (HDS)

Catalytic HDS of crude oil and refinery streams is carried out at elevated temperature and hydrogen partial pressure, converting organosulfur compounds to hydrogen sulfide (H_2S) and hydrocarbons. The conventional HDS process is usually conducted over sulfided $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts [8]. Their performance in terms of desulfurization level, activity and selectivity depends on the properties of the specific catalyst used (active species concentration, support properties, synthesis route), the reaction conditions (sulfiding protocol, temperature, partial pressure of hydrogen and H_2S), nature and concentration of the sulfur compounds present in the feed stream, and reactor and process design.

Deep desulfurization of refinery streams becomes possible when the severity of the HDS process conditions is increased [9, 10]. Unfortunately, more severe conditions result not only in a higher level of desulfurization but also in undesired side reactions. When FCC gasoline is desulfurized at higher pressure, many olefins are saturated and the octane number decreases. Higher temperature processing leads to increased coke formation and subsequent catalyst deactivation. It is also important to note that in practice the severity of the operating conditions is limited by the HDS unit design. In addition to applying more severe conditions, HDS catalysts with improved activity and selectivity must be used. New improvements related to new HDS-based techniques are being developed and already reviewed in literature [7, 11, 12]

In any case, to carry out the deep HDS processes, the energy and hydrogen consumption should be evidently increased and these severe operation conditions inevitably lead to high increase in capital expenditure.

3. STATE OF THE ART

The production of transportation fuels having very low content of sulfur became one of the priory actual challenges for oil refineries worldwide forced by new strict regulatory requirements. Under this context, many researchers have been developing methods to meet these sulfur regulations based on improving the current HDS process in refineries (highly active catalysts, reactor improvements,…) as it was previously mentioned. But it is also being stringently necessary to explore alternative desulfurization approaches as reactive distillation, several precipitation techniques, reactive alkylation, complexation, selective oxidation, adsorption, biodesulfurization, photochemical desulfurization, several utltrasonic extraction treatments, and their combinations already reviewed in literature [11-17]:

Extractive desulfurization is based on the fact that organosulfur compounds are more soluble than hydrocarbons in an appropriate solvent.

The most attractive feature of the extractive desulfurization is the applicability at low temperature and low pressure. As the equipment used is rather conventional without special requirements, the process can be easily integrated into the refinery. To make the process efficient, the solvent must be carefully selected to satisfy a number of requirements. The organosulfur compounds must be highly soluble in the solvent. The solvent must have a boiling temperature different than that of the sulfur containing compounds, and it must be inexpensive to ensure economic feasibility of the process.

The efficiency of extractive desulfurization is mainly limited by the solubility of the organic sulfur compounds in the solvent. Solubility can be enhanced by choosing an appropriate solvent taking into account the nature of the sulfur compounds to be removed. A lot of organic solvents such as polyalkyleneglycol, polyalkyleneglycol ether, pyrrolidones, imidazolidinones, dimethyl sulfoxide and pyrimidinones were tried as extractants for the removal of sulfur compounds from fuel, but none of them obtaining satisfactory performances. This is usually achieved by using a 'solvent cocktail' such as acetone–ethanol [18] or a tetraethylene glycol–methoxytri glycol mixture [19]. Preparation of such 'solvent cocktail' is rather difficult and intrinsically non-efficient since its composition depends strongly on the spectrum of the organosulfur compounds present in the feed stream.

4. KEY INNOVATIONS

4.1 Selection of ionic liquids as solvents in extractive desulfurization

ILs are promising replacements for conventional non desirable organic solvents [20, 21] to act as entrainers in liquid-liquid extraction. Most of ionic liquids have many attractive properties such as chemical and thermal stability, nonflammability, high ionic conductivity, wide range of potential window and they possess a very low vapor pressure, which may be the single most attractive property for their use as solvents [22]. A key feature of ionic liquids is that their properties can be tailored by judicious selection of cation, anion and substituents so they can be designed to perform selective liquid-liquid separations [22-24]. To improve the safety and environmental friendliness of this conventional separation technique, ionic liquids can be used as ideal substitutes of conventional solvents for the design of novel liquid-liquid extraction systems [20, 25].

In this work, feasibility of the $[C_8mim][BF_4]$, $[C_8mim][NTf_2]$, $[C_2mim][EtSO_4]$, and $[C_6mmPy][NTf_2]$ ionic liquids as solvents for extraction of sulfur- and nitrogen-containing compounds from fuels has been studied. For all chosen solvents, the analysis of their suitability

for our purposes has been evaluated according to thermodynamic criteria. For this reason, the study of liquid-liquid equilibrium of each one of the ternary systems composed by IL, a sulfur or nitrogen-containing compound and a fuel representative constituent is going to be carried out and experimental data are going to be correlated and analyzed.

All equilibria involving the use of each IL as a separating agent will be correlated together. The binary interaction parameters obtained are needed for the design of an extraction column for desulfurization of fuel-oils.

4. 2 Model oil desulfurization

In a next step, two liquid mixtures simulating gasoline and gasoil respectively were subjected to a three stages extraction process employing the selected ionic liquids as entrainers. Composition of feed and raffinate after each one of the extraction steps was analyzed with the aim of following not just the sulfur reduction, but also the evolution of fuel constituents along this extraction process.

4. 3 Real samples desulfurization

As interesting innovation, the study of the desulfurization yield of the ionic liquids has been tested by using real samples of diesel and light naphta previous to desulfurization process in the refinery. Three steps extraction process were carried out with the aim of following sulfur content evolution in raffinate along the different stages. A comparation between the desulfurization ability of the four ionic liquids was analyzed to verify the consistency of the real fuel results with the obtained results in previous sections.

5. APPLICATIONS, IMPLEMENTATIONS AND RESULTS

In this work, feasibility of the $[C_8mim][BF_4]$, $[C_8mim][NTf_2]$, $[C_2mim][EtSO_4]$, and $[C_6mmPy][NTf_2]$ ionic liquids as solvents for extraction of sulfur- and nitrogen-containing compounds from fuels has been studied. Extraction power of these four ionic liquids has been tested by studying liquid-liquid equilibrium data and a three-step extraction process of both synthetic model oils and real fuels previous to HDS process in refinery.

From the obtained liquid-liquid equilibrium data it can be concluded that these four ionic liquids are able to extract sulfur-containing compounds from fuels. Best results in terms of solute distribution ratios (β) were found for $[C_6mmPy]$ $[NTf_2]$ but $[C_2mim]$ $[EtSO_4]$ showed the highest values for selectivity (S). Solubility of aromatic compounds represented by toluene was found high for all the studied ionic liquids. This means that a certain degree of aromatic compounds extraction can be predicted simultaneously to desulfurization process. These results indicate that in the case of a practical application a compromise between desulfurization and

dearomatization must be achieved in order to comply with transportation fuel specifications and keep the octane number of gasoline. All of the four Pyridine-containing ternary systems showed high values for selectivity and solute distribution ratio, for this reason it can be concluded that denitrogenation could be easily reached with any of these ionic liquids.

Liquid-liquid equilibrium data of the ternary systems studied were correlated by means of NRTL and UNIQUAC equations. Figures 1-3 show four representative examples of experimental and correlated LLE data for the selected ionic liquids.

Overall, satisfactory results have been found and no conclusions could be established about what is the best model to correlate LLE data of these ionic liquid-containing systems. When the simultaneous correlation of the ternary systems studied involved in gasoline and diesel desulfurization was carried out with these models, relative large deviations were found, and UNIQUAC seems to give slightly better results than NRTL model.
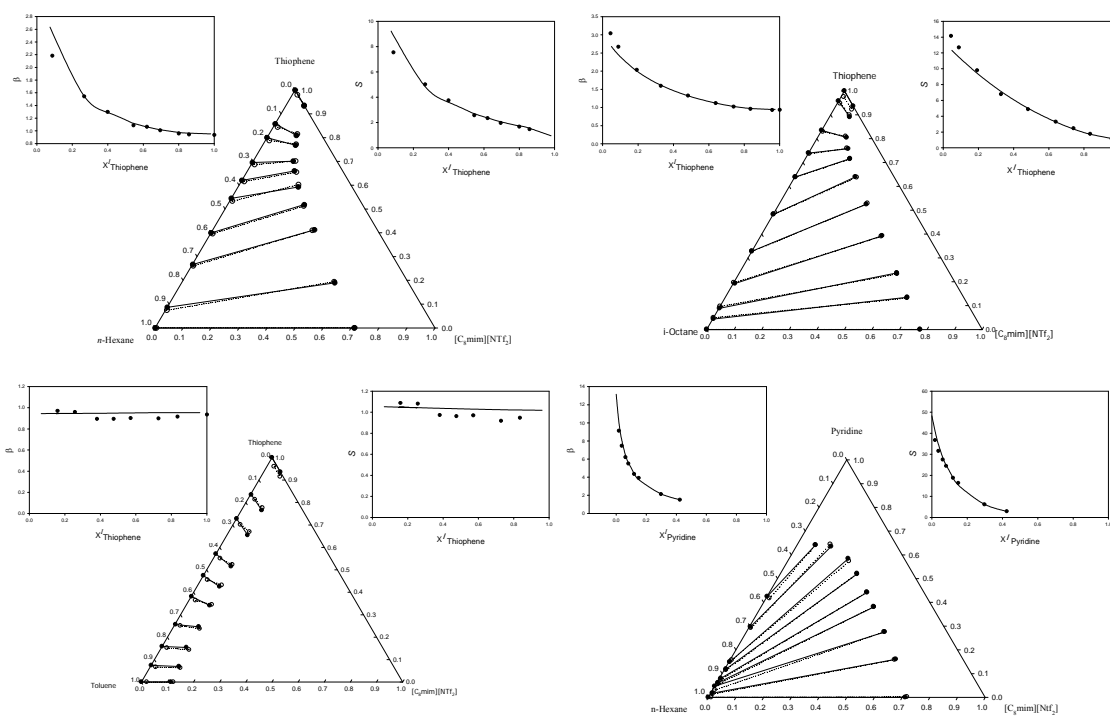

Figure 1. Experimental tie-lines (•, solid line), solute distribution ratio (β) and selectivites (S) for the LLE of the ternary system [C$_8$mim][NTf$_2$] (1) + pyridine/thiophene (2) + hydrocarbon (3) at 298.15 K and atmospheric pressure.

Figure 2. Experimental tie-lines (•, solid line), solute distribution ratio (β) and selectivites (S) for the LLE of the ternary system $[C_8mim][BF_4]$ (1) + pyridine/thiophene (2) + hydrocarbon (3) at 298.15 K and atmospheric pressure.
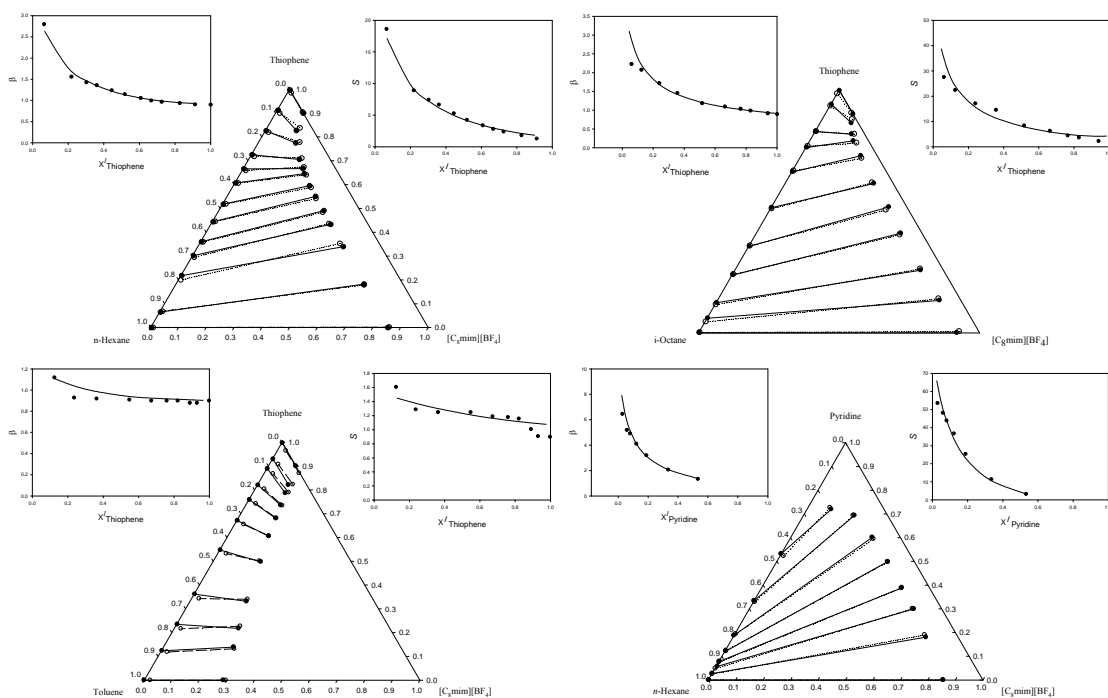

Figure 3. Experimental tie-lines (•, solid line), solute distribution ratio (β) and selectivites (S) for the LLE of the ternary system $[C_2mim][EtSO_4]$ (1) + pyridine/thiophene (2) + hydrocarbon (3) at 298.15 K and atmospheric pressure.
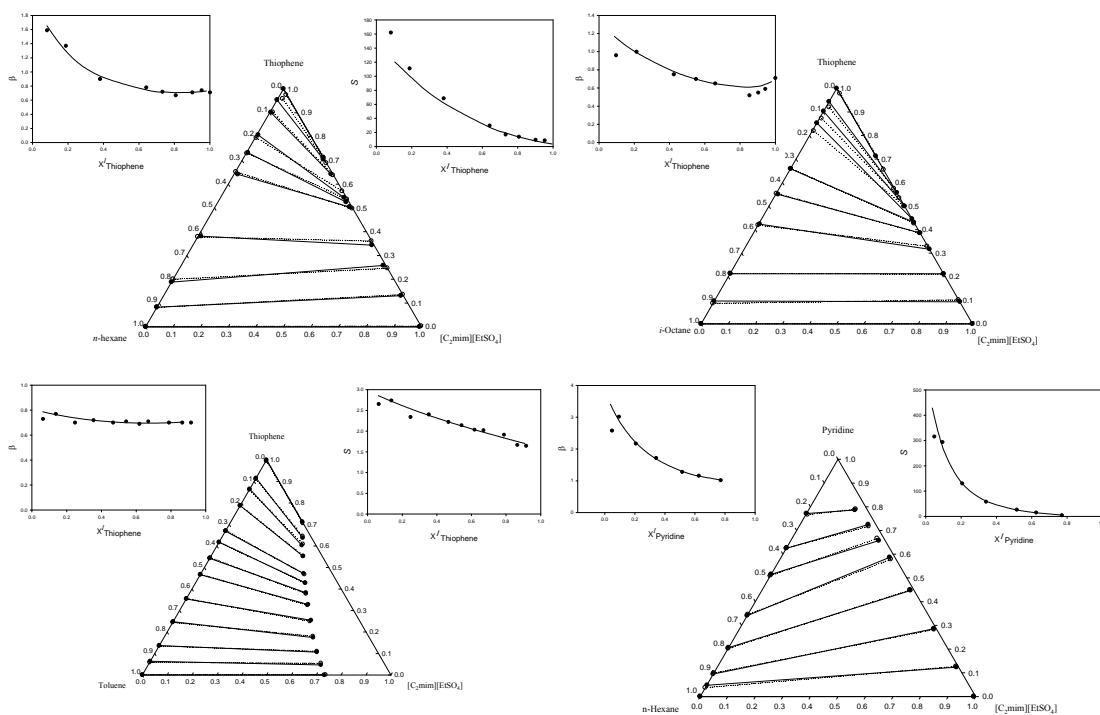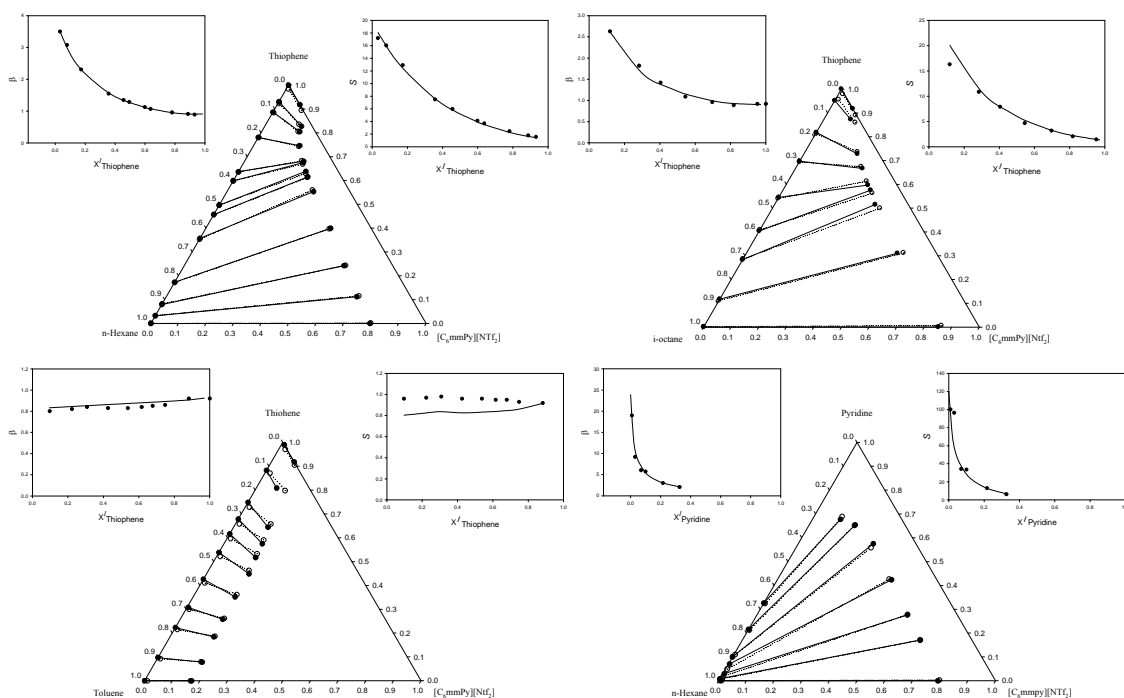
Figure 4. Experimental tie-lines (•, solid line), solute distribution ratio (β) and selectivites (S) for the LLE of the ternary system [C$_6$mmPy][NTf$_2$] (1) + pyridine/thiophene (2) + hydrocarbon (3) at 298.15 K and atmospheric pressure.

Results found in model oil extraction are in agreement with what could be expected from liquid-liquid equilibrium data. In the case of gasoline, the desulfurization yield for the four ionic liquids studied ranks as [C$_6$mmpy][NTf$_2$] > [C$_8$mim][BF$_4$] $\geq$ [C$_8$mim][NTf$_2$] >[C$_2$mim][EtSO$_4$] and in the case of the diesel model oil as [C$_6$mmpy][NTf$_2$] > [C$_2$mim][EtSO$_4$] > [C$_8$mim][NTf$_2$] > [C$_8$mim][BF$_4$]. The [C$_6$mmpy][NTf$_2$] ionic liquid showed the largest desulfurization capacity as it is shown in Figure 5. Aside desulfurization, denitrogenation with all of the ionic liquids is total in the first stage of extraction for diesel models and in the second stage for the case of gasoline except with [C$_2$mim][EtSO$_4$] which needed a third extraction step. Desulfurization and denitrogenation are also accompanied by dearomatization. In all the extractions performed with these model oils, the ionic liquid composition in raffinates was undetectable.

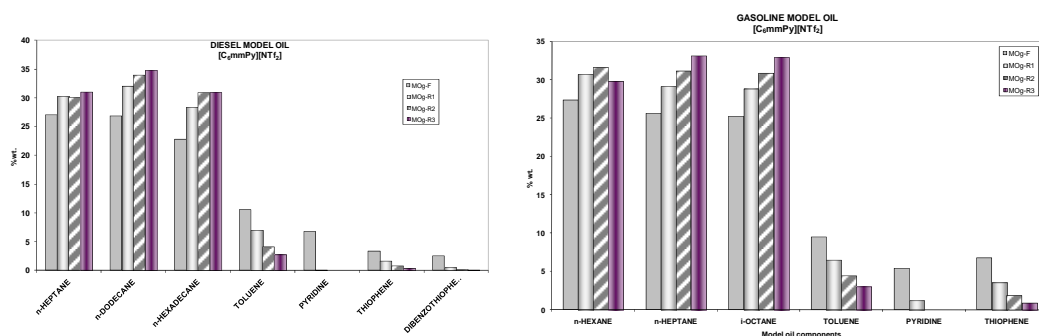**Figure 5** Evolution of simulated gasoline and diesel components in a three step extraction process using [C$_6$mmPy][NTf$_2$] as solvent. MOg represents model oil, F, fresh mixture, and R1, R2, and R3, raffinate composition after each extraction step.

Exactly the same results obtained for model oils were found for real oil samples, light naphtha and diesel obtained previous to desulfurization process in refinery streams, when analyzing sulfur reduction in the three-step extraction. This ensures that in the case of $[C_6mmPy][NTf_2]$ and $[C_2mim][EtSO_4]$, no ionic liquid is solubilized by hydrocarbon phase, because if that would have happened inherent sulfur content of these salts would have increased the total sulfur content of samples.
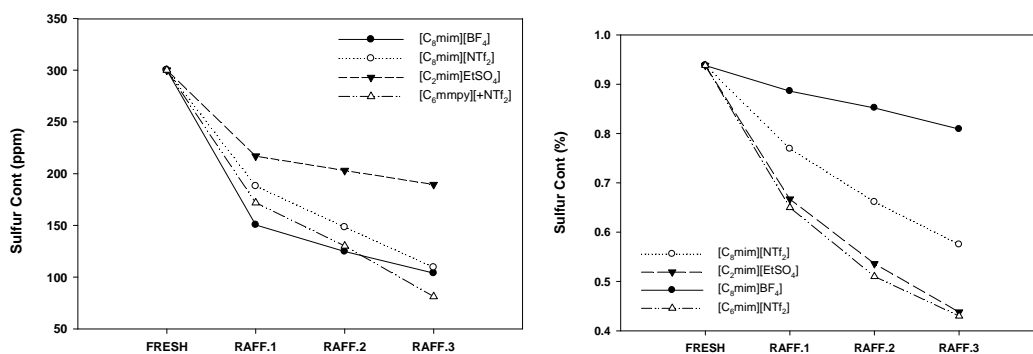

Figure 6 Sulfur content evolution of a light naphtha(left) and a diesel (right) in a three step extraction process.

From all the ionic liquids studied, $[C_6mmPy][NTf_2]$ seems to be the most adequate candidate to carry out fuel-oil desulfurization. Simulation of the extraction process using available process-software confirms the capacity of this ionic liquid to lead to desulfurization levels in accordance with legislation requirements. Nonetheless, due to the order of deviations found with the correlation equations, this can only be understood as a qualitative simulation exercise. Pilot plant testing, economical studies, life cycle assessment…are necessary steps to continue this study.

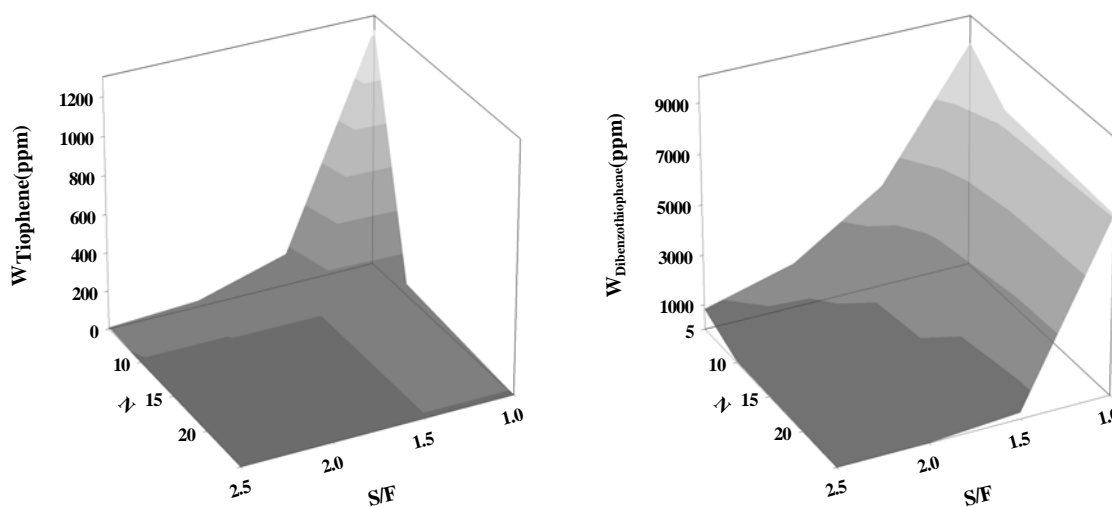
Figure 7 Thiophene and dibenzothiophene mass fractions (ppm) in raffinatte as a function of the solvent-to-feed ratio, *S/F*, and number of equilibrium stages, *N*, when $[C_6mmpy][NTf_2]$is used as solvent in desulfurization of a diesel.

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Gasoline Desulfurization Using Extraction with [C₈mim][BF₄] 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 [C₈mim][BF₄] ionic liquid as extraction solvent for desulfurization, the phase equilibria of different ternary systems involving hydrocarbons present in gasoline formulations, thiophene, and [C₈mim][BF₄], 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. © 2007 American Institute of Chemical Engineers AIChE J, 53: 3108–3115, 2007
Keywords: desulfurization, extraction, equilibrium, ionic liquids, [C₈mim][BF₄]

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

Component	CAS Number	Water (ppm)	ρ (g cm^{-3})		n_D	
			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 tetrafluoro-

borate 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$_4$] +
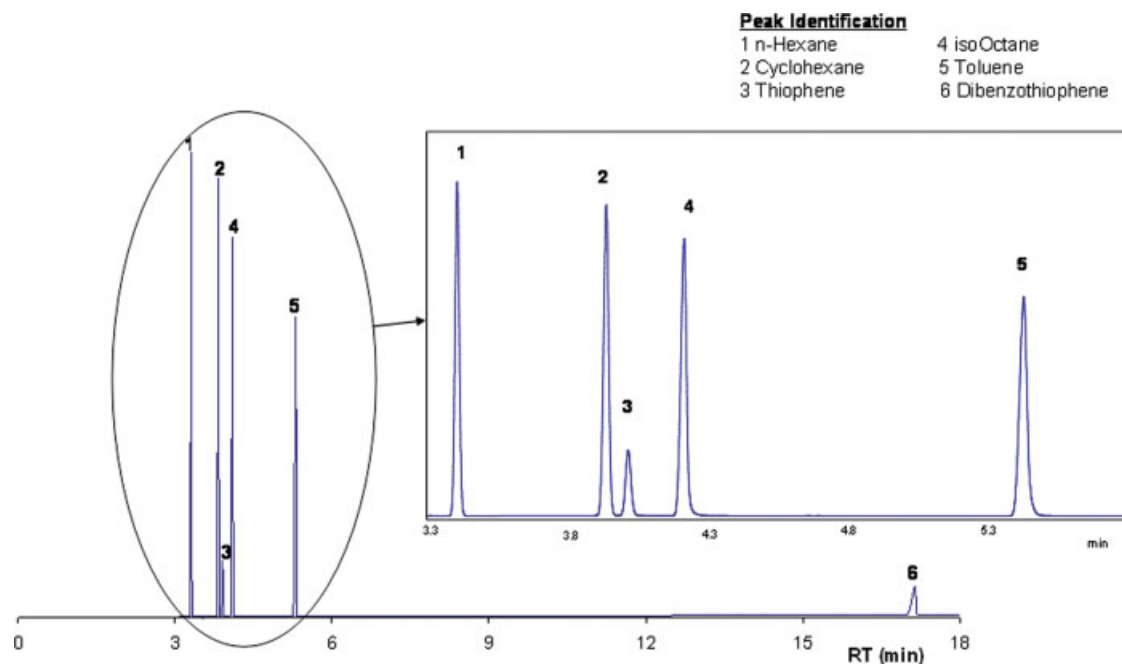
Figure 1. Simulated gasoline chromatogram and peak identification.

[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 + tolu-

ene), 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:

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

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

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.
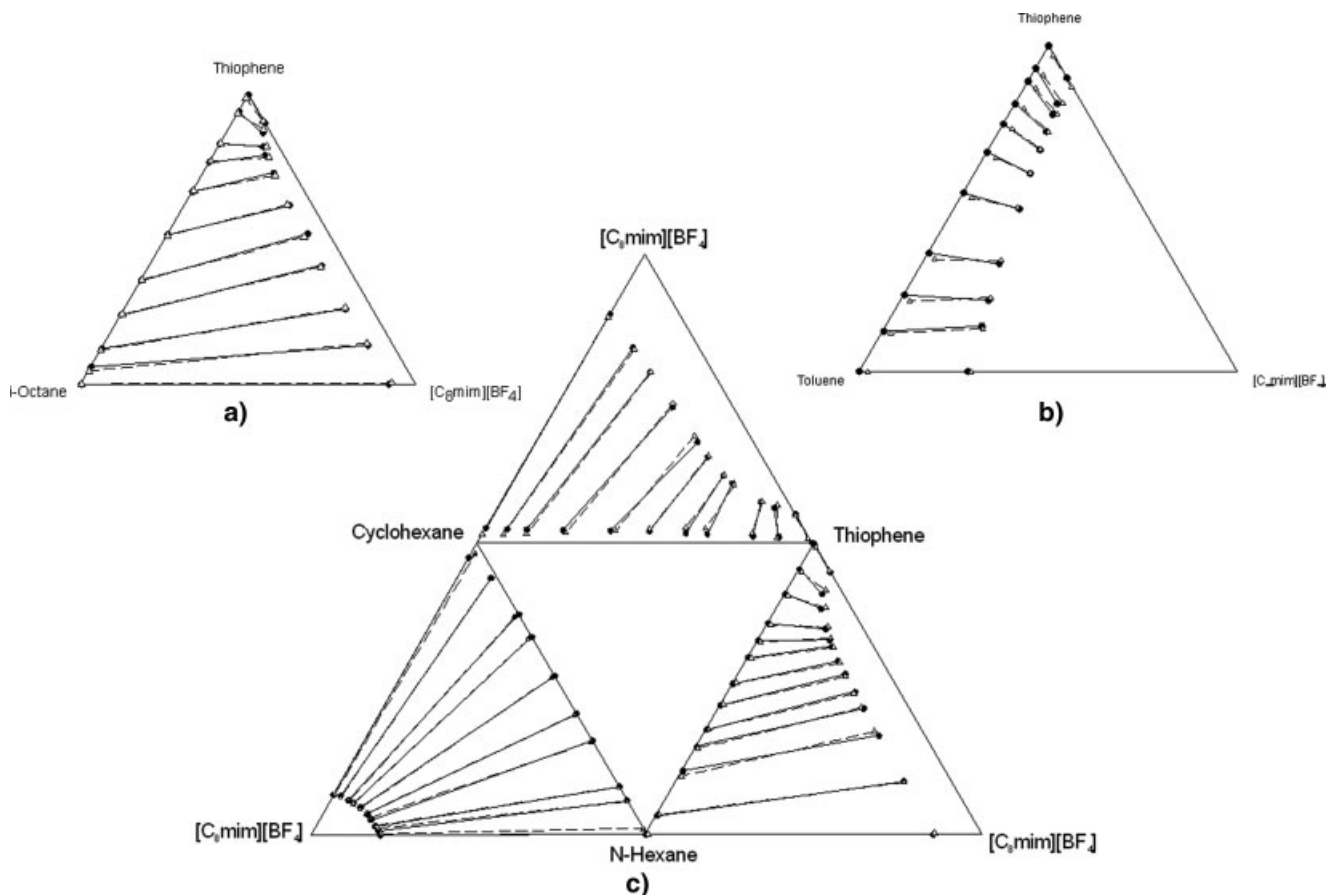
Figure 2. LLE at 298.15 K for ternary systems involved in desulfurization.
●, Experimental; △, correlated.

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

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

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

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, $\hat{\gamma}_{S\infty}^I$ and $\hat{\gamma}_{S\infty}^{II}$ 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, $\Delta\beta$:

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

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

		Parameters	
r.m.s.d.	Components i–j	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
{[C$_8$mim][BF$_4$] (1) + thiophene (2) + i-octane (3)}, $\alpha = 0.2$			
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)}, $\alpha = 0.3$			
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)}, $\alpha = 0.2$			
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$_8$mim][BF$_4$]	Thiophene	−4789.2	14,061
[C$_8$mim][BF$_4$]	n-Hexane	3052.3	8332.0
Thiophene	n-Hexane	3088.8	−461.38
[C$_8$mim][BF$_4$]	Cyclohexane	2394.2	7660.4
Thiophene	Cyclohexane	2241.8	−792.92
[C$_8$mim][BF$_4$]	i-Octane	4348.6	7086.0
Thiophene	i-Octane	5829.7	−1293.2
[C$_8$mim][BF$_4$]	Toluene	−2317.9	11,391
Thiophene	Toluene	181.53	211.18
n-Hexane	Cyclohexane	214.81	311.53
Ternary System		*F*	*Δβ*
{[C$_8$mim][BF$_4$] + thiophene + n-hexane}		1.5033	5.8
{[C$_8$mim][BF$_4$] + thiophene + cyclohexane}		0.9681	6.6
{[C$_8$mim][BF$_4$] + thiophene + i-octane}		1.7404	13.5
{[C$_8$mim][BF$_4$] + thiophene + toluene}		1.3245	6.0
{[C$_8$mim][BF$_4$] + cyclohexane + n-hexane}		1.1753	11.0

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

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$_8$mim][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$_8$mim][BF$_4$] and their composition in the raffinate product decreases rapidly:
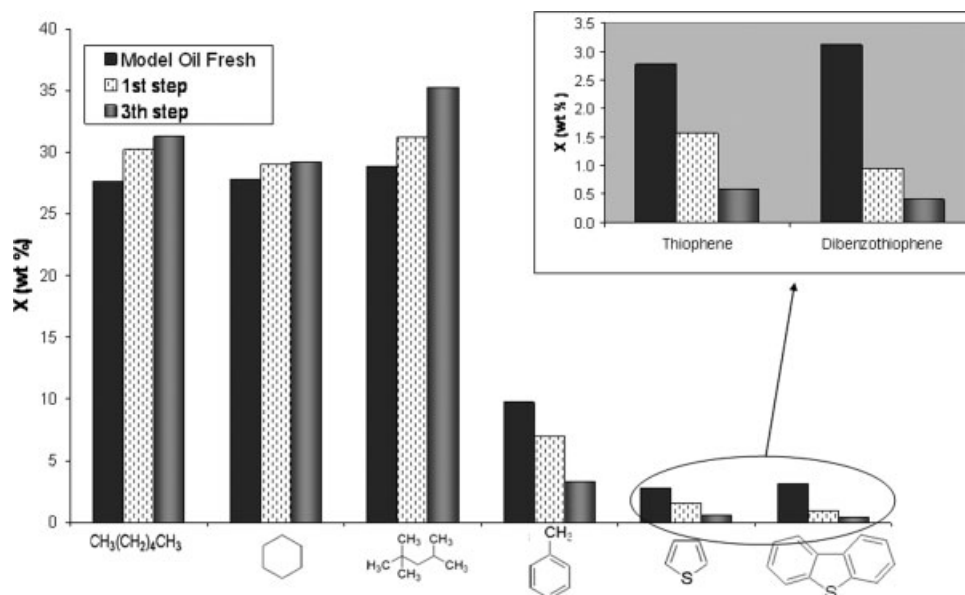

Figure 3. Multistage desulfurization: compositions in initial model oil (gasoline) and after one and three extractions.

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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Ionic liquids on desulfurization of fuel oils

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A R T I C L E   I N F O

A B S T R A C T

In this paper, a review about the role of Ionic Liquids on desulfurization of fuel oils has been done. From these salts, the pyridiniums are showing the most promising results on sulfur reduction by simple liquid–liquid extraction. For this reason, in this work the suitability of a new pyridinium ionic liquid as solvent in the extraction of sulfur- and nitrogen-containing compounds from fuels has been analysed. Liquid + liquid equilibrium data for 1-hexyl-3,5-dimethyl pyridinium {bis[trifluoromethylsulfonyl] imide} + thiophene + n-hexane or n-dodecane or n-hexadecane and 1-hexyl-3,5-dimethyl pyridinium {bis[trifluoromethylsulfonyl]imide} + pyridine + hexane ternary systems have been determined at 298.15 K and atmospheric pressure. High solubility of thiophene and pyridine in ionic liquid but also of toluene, has been found, being this salt practically inmiscible with linear hydrocarbons. Equilibrium data of these systems have been correlated with UNIQUAC and NRTL models driving to high deviations at high solute concentrations. Three steps extraction experiments with simulated gasoline and diesel and also with real samples, previous to refinery desulfurization process, confirmed ability of ionic liquid [hmmpy][Ntf$_2$] as solvent for extractive desulfurization of transportation fuels.

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1. Introduction

Emissions of sulfur gases from both natural and anthropogenic sources strongly influence the chemistry of the atmosphere. Sulfur dioxide is emitted largely from the excessive burning of fossil fuels, petroleum refineries, chemical and coal burning power plants etc. Sulfur dioxide and nitrogen dioxide can suffer a harmful reaction in the atmosphere that cause acid rain. Over the last decade, environmental regulations focus attention on reduction of emissions from the transport sector in order to improve air quality and welfare [1]. According to the Directive of the European Union, gasoline and diesel fuels in Europe should not exceed 10 ppm of total sulfur content starting from 2010 [2]. US regulations established a maximum of 15 ppm for diesel starting from 2006 and 30 ppm for gasoline starting from 2005 [3].

Conventionally, hydrodesulfurization (HDS) has been employed by refineries to remove organic sulfur from fuels. This widely applied process easily allows the elimination of aliphatic and alicyclic sulfur compounds, but removal of many thiophene and dibenzothiophene derivatives turns into a difficult task due to several catalyst surface interactions and stereo hindrance [4–7]. Due to these difficulties to remove some sulfur-containing aromatic compounds highly resistant to hydrotreatment, several attempts to change operation conditions of HDS are under way [8]. Nonetheless, to carry out the deep HDS processes, the energy and hydrogen consumption should be evidently increased and these severe operation conditions inevitably lead to high increase in capital expenditure.

The production of transportation fuels having very low content of sulfur became one of the priority actual challenges for oil refineries worldwide forced by new strict regulatory requirements. Under this context, many researchers have been developing new innovative methods to meet these sulfur regulations based on improving the HDS current process in refineries (high active catalysts, reactor improvements…) [9,10] being stringently necessary to explore the alternative desulfurization approaches as reactive distillation, several precipitation techniques, reactive alkylation, complexation, selective oxidation, adsorption, biodesulfurization, photochemical desulfurization, several utltrasonic treatments extraction… and their combinations already reviewed in literature [11–17].

Among all these new processes, as clean, cheap because of low energy cost, mild operation conditions and facile operation option, extractive desulfurization appears to be especially promising and researching efforts over the last years are being focused on finding the most suitable solvent for desulfurization purposes. Apart from other desired features, an extracting solvent must primarily exhibit high capacity, high solute distribution ratio and high selectivity. A lot of organic solvents such as polyalkyleneglycol, polyalkyleneglycol ether, pyrrolidones, imidazolidinones, dimethyl sulfoxide and pyrimidinones were tried as extractants for the removal of sul-

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fur compounds from fuels, but none of them obtaining satisfactory performances.

Over the past years Ionic Liquids (ILs) became a promising family of substances that have been object of burgeoning research. From the beginning of this decade, they have been defined as salts with melting point below 100 °C [18–20]. ILs are promising replacements for conventional non-desirable organic solvents [21] to act as entrainers in liquid–liquid extraction. Most of ionic liquids have many attractive properties such as chemical and thermal stability, nonflammability, high ionic conductivity, wide range of potential window and they posses a very low vapour pressure, which may be the single most attractive property for their use as solvents [23]. A key feature of ionic liquids is that their properties can be tailored by judicious selection of cation, anion and substituents so they can be designed to perform selective liquid–liquid separations [22–24]. It may be apparent that *ionic liquids may in themselves be suitable and indeed favourable media for the design of novel liquid–liquid extraction systems* [25,26].

The use of ionic liquids for the selective extraction of sulfur compounds from diesel fuel was described by Bössman et al. for the first time [27]. Keeping in mind that the most popular ionic liquids are undoubtedly the di-alkylimidazolium salts, due to their easy synthesis and attractive physical properties, and based on the initial idea of the extraction of sulfur compounds by chemical interaction, these authors investigated the extraction with Lewis- and Brønsted-acidic ionic liquids employing mixtures of *n*-butyl-3-methylimidazolium chloride and *n*-ethyl-3-methylimidazolium chloride with AlCl$_3$. Even though AlCl$_3$ and AlCl$_4$ based ionic liquids are effective for the removal of S-containing compounds [28], they often form dark precipitates and they are sensitive to water presence [29] generating HCl and making them unstable in air and of limited practical utility.

Ionic liquid extraction power for DBT has been proved to be not uniquely based on chemical interactions involving the acid proton, so different cation/anion combinations of neutral ILs were tested [27], showing that desulfurization is hardly affected by the chemical nature of the anion and that the size of ions is important for the extraction effect. A possible explanation for this behaviour may be that solubility of sulfur-containing compounds (DBT and derivates) is dependent on steric factors in the IL.

Several authors studied the use of PF$_6$$^-$ and BF$_4$$^-$ anions for imidazolium-based ionic liquids [30–32] significantly more stable to hydrolysis. Sulfur was preferentially removed from gasoline samples but also a change in the content of aromatics was observed, which can be problematic for maintaining octane number in gasoline. Several liquid–liquid equilibrium studies reinforce this conclusion [33–35] and coulombian interactions between these ionic liquids and S-containing compounds were also studied [36]. Removal of sulfur-containing molecules with high density of aromatic π electrons is favoured due to stronger interactions with this kind of ILs. The extractive removal efficiency for aromatic nitrogen compounds is also high and extraction results indicated that these ILs are particularly selective for aromatic N-containing compounds from fuels. But the use of these PF$_6$ and BF$_4$ ILs as large scale extracting agents is not optimal because of the relative high price of starting material and additionally, the formation of hydrolysis products, especially HF, is observed at elevated temperatures in presence of water [37].

To avoid these stability and corrosion problems, the use of completely halogen-free ILs was suggested [38,39]. N-alkyl-3-methylimidazolium alkylsulfates were tried as readily accessible from cheap starting materials. Several studies of liquid–liquid equilibrium data of different fuel components and S-containing compounds were done strengthening conclusions of suitability of [EMIM][EtSO$_4$] as solvent extractant [40,41]. It might look inconsistent to use S-containing ILs for desulfurization but leaching of

IL into the oil phase is in any case unwanted. Nevertheless, certain degree of cross-solubility of hydrocarbons in the IL was observed. In case of [BMIM][OcSO$_4$] distribution coefficients for S-compounds is two times higher than for [EMIM][EtSO$_4$] but the cross-solubility is by a factor 4–16 times higher.

Also, N-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids were studied and compared to tetrafluoborate or alkylsulfate ones [42–45], not showing definitive conclusions about the better suitability of these ILs for this application. Searching in a different way, Huang et al. [46] proposed the use of CuCl-based ionic liquids, also moisture-insensitive and stable in air. These ILs showed remarkable desulfurization ability attributed to the π-complexation of Cu(I) with aromatic S-containing compounds.

As cheaper option for real industrial application, the use of imidazolium-based phosphoric ionic liquids was also analysed [37,47–49] with encouraging results. It was showed that desulfurization ability of the studied ILs varies following the order [BMIM][DBP] > [EMIM][DEP] ≫ [MMIM][DMP], however fuel solubility in ILs is noticeable following the same tendency. [EMIM][DEP] was the recommended IL. Later on the same authors suggest the use of [EEIM][DEP] [50]. Nie et al. [51] studied the effect of the length of the alkyl group of these cations for alkylphosphate ionic liquids, showing as expected that the longer the alkyl substitute of the anion or cation, the higher the partition coefficient value for the studied ionic liquid.

Within all cation–anion combination options which offer the huge family of ionic liquids Holbrey et al. [52] investigated the DBT extraction power from dodecane for a range of ionic liquids varying cation and anion classes. Polyaromatic quinolinum-based ionic liquids were found to show the best extractive ability, nevertheless, these and other polyaromatic cations, such as 1,3-dibenzimidazolium are technically limited by their high melting points and only tend to form low-melting point ionic liquids when combined with highly flexible perfluorinated anions such as bis(trifluoromethylsulfonyl)amide. This studio ranks ionic liquids desulfurization ability by cation following the secuence *methylpiridinium ≥ pyridinium ≈ imidazolium ≈ pyrrolidinium* with much less significant variation with anion type. Following this line, Gao et al. [53,54] perform several extraction experiments with alkyl- and alkylmethyl-pyridinium-based ionic liquids, but best results were found for [alkyl-dmpy]$^+$ ionic liquids. With these cations, ethanoate and thiocyanate anions gave the best extraction performance (consistent with Domanska et al. [55] conclusions in their equilibrium studies). In this way, these more benign and cheaper anions could be used as alternative to the perfluorinated and tetrafluoborate ones.

Continuum solvation models based on the conductor like screening model (COSMO) along with its extension to real solvents (COSMO-RS) also reinforce the idea of suitability of methylpyridinium ionic liquids as solvents for desulfurization [56].

A more complex option is the use of Oxidative Desulfurization (ODS), which involves in a first step oxidizing sulfur compounds, such as DBT and its derivatives, to transform them into sulfones and sulfoxides [57]. In a second step these oxidized products are removed by selective extraction with polar solvents, such as dimethyl sulfoxide.

Taking a step forward, Lu et al. [58] described in their work a combination of ODS and extraction with BF$_4$ ILs. It was proved that desulfurization yield is increased by about one order of magnitude compared with merely extracting with ILs. Several authors had already tried this idea adding H$_2$O$_2$ as oxidant with several catalysts as acetic acid [59], phosphotungstenic acid [60], decatungstates [61], V$_2$O$_5$ [62], and several different ionic liquids (quaternary ammonium coordinated ionic liquids [63], *n*-methyl pyrrolidinium ionic liquids [64] or even task-specific ionic liquids

Table 1
CAS-register number, water mass fraction (ω_{H_2O}), density (ρ) and refractive index (n_D) of the pure components at 298.15 K and atmospheric pressure.

Component	CAS	ω_{H_2O} (ppm)	ρ (g cm^{-3})		n_D	
			Exp.	Lit.	Exp.	Lit.
n-Hexane	110-54-3	75	0.65506	0.65484 [74]	1.37287	1.37226 [74]
n-Dodecane	112-40-3	31	0.74532	0.74518 [74]	1.42011	1.41952 [74]
n-Hexadecane	544-76-3	7.4	0.77115	0.77008 [74]	1.43232	1.4329 [74]
n-Heptane	142-82-5	4.8	0.67947	0.67946 [74]	1.38517	1.38511 [74]
2,2,4 Trimethylpentane	540-84-1	4.9	0.68784	0.68778 [75]	1.38921	1.3895 [75]
Toluene	108-88-3	174	0.86220	0.86219 [75]	1.49393	1.49413 [75]
Thiophene	110-02-1	314	1.05859	1.05887 [74]	1.52530	1.52572 [74]
Pyridine	110-86-1	177	0.97802	0.97824 [74]	1.50699	1.50745 [74]
[hmmpy][NTf$_2$]	Not found	59.8	1.32814	1.33 [76]	1.44978	Not found

[65]) as extractants. Zhu et al. [64] demonstrated using peroxotungsten and peroxomolybdenum complexes in ILs that when H_2O_2 and catalyst are introduced together, the removal of sulfur increased sharply. Zhao et al. [63,66–68] studied ODS using [HNMP][BF$_4$] and [HNMP][H$_2$PO$_4$] which act also themselves as catalysts. However, imidazolium or pyrrolidinium-based ionic liquids are relatively expensive and impossible to use in ODS for industry. Lewis acidic ionic liquids containing metal halide anions such as AlCl$_4$ [31,69], FeCl$_4$ [70] and CuCl$_2$ [46] or ZnCl$_2$ [71] are being studied.

In this work, suitability of a new pyridinium ionic liquid as solvent in extraction of sulfur- and nitrogen-containing compounds from fuels is analysed. Liquid + liquid equilibrium data for ternary systems composed by 1-hexyl-3,5-dimethyl pyridinium {bis[trifluoromethylsulfonyl]imide}, thiophene and three hydrocarbons representative of fuel (*n*-hexane, *n*-dodecane and *n*-hexadecane), and for the ternary system composed by 1-hexyl-3,5-dimethyl pyridinium {bis[trifluoromethylsulfonyl]imide}, pyridine and hexane were determined at 298.15 K and atmospheric pressure. Experimental data were correlated with UNIQUAC and NRTL models. Three steps extraction experiments with simulated and real, previous to refinery desulfurization process, fuel oils were carried out. Results were compared with previously obtained by using other ILs [35,72]. Study was not focused just on the desulfurization yield but also in the effect of using this ionic liquid, as solvent for extraction, on the rest of the fuel constituents, pointing attention to aromatic compounds.

2. Experimental

2.1. Chemicals

n-Hexane, *n*-dodecane, *n*-hexadecane, and thiophene were supplied by the Aldrich Chemical Company with quoted purities of 0.995, 0.99 and 0.99 mass fraction; pyridine was supplied by Riedel-de Haën with quoted purity of 0.995 mass fraction. Purities were tested by gas chromatography (GC) analysis which did not detect any appreciable peaks of impurities and products were used as received from supplier without further purification.

The ionic liquid [hmmpy][Ntf$_2$] was synthesised in our laboratory following two-steps reaction path previously published [73]. In a first step 3,5-lutidine (Aldrich, 98%+) reacts with an excess of 1-bromohexane (Fluka, purum, >98.0 wt%) to produce 1-hexyl-3,5-dimethylpyridinium bromide. In a second stage, desired final product [hmmpy][Ntf$_2$] is obtained by ion methatesis direct reaction with Li[Ntf$_2$] salt. The purity of the final product was adequately characterised by analysing its ^{1}H NMR and ^{13}C NMR spectra.

In Table 1 water content of pure compounds is reported, and their experimental densities and refractive indices are compared with the available values published by other authors [74–76].

2.2. Procedure

2.2.1. Physical properties of pure compounds

Water contents were determined using a Karl Fischer titration method in a Metrohm 737 KF coulometer. Densities were obtained with viscosity correction in an Anton Paar DMA 5000 densimeter with an uncertainty in the measurement of $\pm 3 \times 10^{-5}$ g cm^{-3}. Refractive indices were measured in an ATAGO RX-5000 refractometer connected to a Heto Therm thermostat to maintain the temperature constant. The uncertainty in the refractive index measurement is $\pm 4 \times 10^{-5}$.

2.2.2. LLE data

Liquid–liquid equilibrium data of ternary systems were obtained introducing mixtures of the three studied components lying into the immiscible region into a 30 ml jacketed glass vessel connected to a thermostatic bath (SELECTA 6000382) maintaining temperature at 298.15 K. Good contact between phases was guaranteed by vigorous stirring, establishing required stirring times to achieve equilibrium state for each one of the studied ternary systems. Overnight settle down allowed phases separation. Samples of both layers were withdrawn using syringes connected to long stainless steel needles. Composition of these equilibrium phases was analysed by gas chromatography. Hydrocarbon, thiophene and pyridine molar fractions were determined using an internal

Table 2
Chromatographic conditions for compositions analysis.

Column	SPB^{TM}-1 SULFUR (30 m × 0.32 mm × 4 μm)
Detector type	FID
Detector temperature	250 °C
Carrier gas	Helium, split ratio 50:1
Injector temperature	275 °C, injection 1 μL

- Ionic liquid + thiophene + *n*-hexane
Flow rate: 1.5 mL min^{-1}
Column oven: 100 °C, 10 min isothermal
- Ionic liquid + thiophene + *n*-dodecane
Flow rate: 1.5 mL min^{-1}
Column oven: 100 °C (4.10 min) → 250 °C (20 °C/min), 2 min
- Ionic liquid + thiophene + *n*-hexadecane
Flow rate: 1.5 mL min^{-1}
Column oven: 100 °C (4.10 min) → 250 °C (20 °C/min), 5 min
- Ionic liquid + thiophene + *n*-hexane
Flow rate: 2 mL min^{-1}
Column oven: 150 °C, 5.5 min isothermal
- Gasoline-model fuel
Flow rate: 1 mL min^{-1}
Column oven: 70 °C, 40 min isothermal
- Gasoil-model fuel
Flow rate: 1.9 mL min^{-1} → 2.5 mL min^{-1}(1 min), 5 min
Column oven: 100 °C (4 min) → 250 °C(20 °C/min), 5 min

standard method and ionic liquid composition was established by difference. The employed gas chromatograph was an HP 6890 Series equipped with an Autosampler 7683 Series, and a Flame Ionization Detector (FID). Used carrier gas was helium. A fused silica capillary column SPB^{TM}-1 sulfur was selected and protected with an empty pre-column to collect ionic liquid that could be not retained by liner. The GC operating conditions are given in Table 2. All weighing in preparation of samples and for analysis calibration was carried out in a Mettler Toledo AT 261 balance with an uncertainty of $\pm 10^{-4}$ g. For improvement of the accuracy, all samples were injected five times. A careful calibration was required during data acquisition to provide estimated experimental uncertainties of ± 0.005 mol fraction in the hydrocarbon-rich phase and ± 0.007 mol fraction in the ionic liquid-rich phase.

2.2.3. Synthetic fuel oils

Commercial gasoline was simulated by means of a mixture of 26 wt% hexane, 26 wt% heptane, 26 wt% isooctane, 10 wt% toluene, 6 wt% thiophene and 6 wt% pyridine, while commercial diesel model oil was composed by 26 wt% heptane, 26 wt% dodecane, 26 wt% hexadecane, 10 wt% toluene, 3 wt% thiophene, 6 wt% pyridine and 3% dibenzothiophene. Both mixtures were introduced into 30 ml glass jacketed vessels adding the ionic liquid and following the same procedure as described for determination of liquid–liquid equilibria. Upper phase samples were withdrawn and their composition was analysed by GC after each extraction step. The remainder mixture was decanted and model-oil phase was used as feed in the next extraction step. GC operation conditions are described in Table 2. All mole fraction compositions were determined with uncertainty of ± 0.001 mol fraction for gasoline and ± 0.003 mol fraction for diesel.

2.2.4. Real fuel extraction experiments

Real light naphtha and diesel samples, previous refinery desulfurization, were provided by Repsol IPF and desulfurization was carried out in three stages, with the same experimental procedure that in the case of synthetic model oils. In this case, the sulfur content was determined with an uncertainty of ± 1 ppm by using a Total Sulfur Analyzer TS 3000 for low sulfur content mixtures and with an uncertainty of ± 20 ppm by using a Oxford Lab-X 3000S sulfur analyzer for high sulfur content mixtures (sulfur content >0.1% mass).

3. Results and discussion

3.1. Experimental LLE data

The LLE data for [hmmpy][Ntf$_2$] + thiophene + hexane, [hmmpy][Ntf$_2$] + thiophene + dodecane, [hmmpy][Ntf$_2$] + thiophene + hexadecane and [hmmpy][Ntf$_2$] + pyridine + hexane ternary systems at 298.15 K are reported in Tables 3–6, showing also values of the solute distribution ratio (β) and selectivity (S) defined by following equations:

$$\beta = \frac{x_2^{II}}{x_2^{I}} \tag{1}$$

$$S = \frac{x_2^{II} \cdot x_1^{I}}{x_2^{I} \cdot x_1^{II}} \tag{2}$$

where x represents mole fraction, subscripts 1 and 2 refer to hydrocarbon and solute (thiophene or pyridine) and superscripts I and II refer to inert-rich phase and IL-rich phase, respectively.

Figs. 1–4 show experimental liquid–liquid equilibrium data represented in four equilateral triangular diagrams. As it can be

Table 3

Experimental LLE data for ternary system {[hmmpy][Ntf$_2$] (1) + thiophene (2) + hexane (3)} at 298.15 K.

IL-rich phase			Hydrocarbon-rich phase			β	S
x_1^{II}	x_2^{II}	x_3^{II}	x_1^{I}	x_2^{I}	x_3^{I}		
0.795	0.000	0.205	0.000	0.000	1.000		
0.691	0.112	0.197	0.000	0.032	0.968	3.50	17.20
0.580	0.243	0.177	0.000	0.079	0.921	3.08	16.03
0.453	0.399	0.148	0.000	0.173	0.827	2.31	12.91
0.314	0.553	0.133	0.000	0.357	0.643	1.55	7.49
0.262	0.615	0.123	0.000	0.456	0.544	1.35	5.97
0.244	0.638	0.118	0.000	0.495	0.505	1.29	2.52
0.216	0.674	0.110	0.000	0.598	0.402	1.13	4.13
0.215	0.680	0.105	0.000	0.637	0.363	1.07	3.70
0.168	0.746	0.086	0.000	0.780	0.220	0.96	2.46
0.138	0.805	0.057	0.000	0.887	0.113	0.91	1.80
0.133	0.828	0.039	0.000	0.931	0.069	0.89	1.57
0.082	0.918	0.000	0.000	1.000	0.000	0.92	

Table 4

Experimental LLE data for ternary system {[hmmpy][Ntf$_2$] (1) + thiophene (2) + dodecane (3)} at 298.15 K.

IL-rich phase			Hydrocarbon-rich phase			β	S
x_1^{II}	x_2^{II}	x_3^{II}	x_1^{I}	x_2^{I}	x_3^{I}		
0.947	0.000	0.053	0.000	0.000	1.000		
0.800	0.145	0.055	0.000	0.125	0.875	1.16	18.45
0.693	0.254	0.053	0.008	0.255	0.737	1.00	13.85
0.614	0.333	0.053	0.000	0.373	0.627	0.89	10.56
0.527	0.417	0.056	0.006	0.521	0.473	0.80	6.76
0.495	0.449	0.056	0.009	0.609	0.382	0.74	5.03
0.423	0.517	0.060	0.006	0.764	0.230	0.68	2.59
0.374	0.567	0.059	0.000	0.830	0.170	0.68	1.97
0.362	0.582	0.056	0.000	0.867	0.133	0.67	1.59
0.341	0.612	0.047	0.000	0.918	0.082	0.67	1.16
0.082	0.918	0.000	0.000	1.000	0.000	0.92	

Table 5

Experimental LLE data for ternary system {[hmmpy][Ntf$_2$] (1) + thiophene (2) + hexadecane (3)} at 298.15 K.

IL-rich phase			Hydrocarbon-rich phase			β	S
x_1^{II}	x_2^{II}	x_3^{II}	x_1^{I}	x_2^{I}	x_3^{I}		
0.968	0.000	0.032	0.000	0.000	1.000		
0.801	0.167	0.032	0.000	0.148	0.852	1.13	30.09
0.662	0.309	0.029	0.000	0.313	0.687	0.99	23.45
0.576	0.393	0.031	0.000	0.417	0.583	0.94	17.68
0.519	0.448	0.033	0.000	0.559	0.441	0.80	10.69
0.475	0.487	0.038	0.000	0.672	0.328	0.71	6.13
0.430	0.522	0.048	0.003	0.754	0.243	0.69	3.49
0.340	0.611	0.049	0.000	0.894	0.106	0.68	1.47
0.269	0.699	0.032	0.000	0.969	0.031	0.72	0.70
0.082	0.918	0.000	0.000	1.000	0.000	0.92	

Table 6

Experimental LLE data for ternary system {[hmmpy][Ntf$_2$] (1) + pyridine (2) + hexane (3)} at 298.15 K.

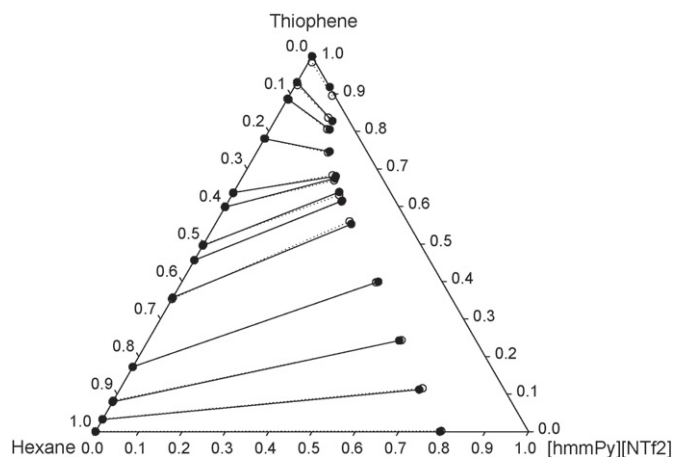| IL-rich phase			Hydrocarbon-rich phase			β	S
x_1^{II}	x_2^{II}	x_3^{II}	x_1^{I}	x_2^{I}	x_3^{I}		
0.791	0.000	0.209	0.005	0.000	0.995		
0.641	0.171	0.188	0.000	0.009	0.991	19.00	100.15
0.544	0.276	0.180	0.005	0.030	0.965	9.20	96.50
0.412	0.424	0.164	0.004	0.070	0.926	6.06	34.22
0.271	0.575	0.154	0.000	0.100	0.900	5.75	33.60
0.166	0.653	0.181	0.000	0.216	0.784	3.02	13.08
0.101	0.678	0.221	0.000	0.326	0.674	2.08	6.34

Fig. 1. Experimental tie-lines (●, solid line) for the LLE of the ternary system {[hmmpy][Ntf₂] (1) + thiophene (2) + hexane (3)} at 298.15 K. The corresponding tie-lines correlated by means of the UNIQUAC model are also plotted (○, dotted).
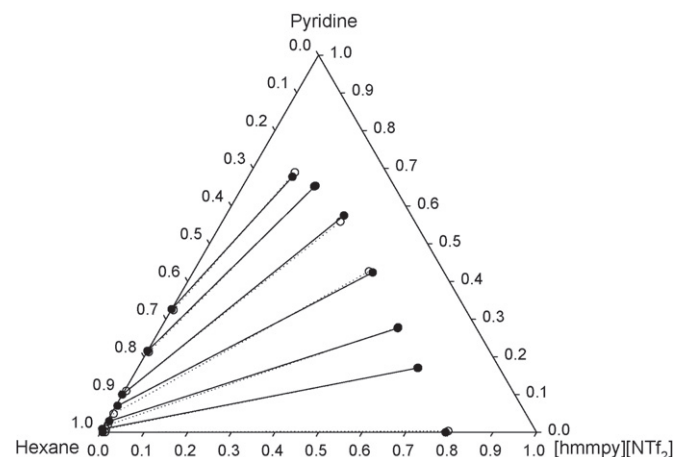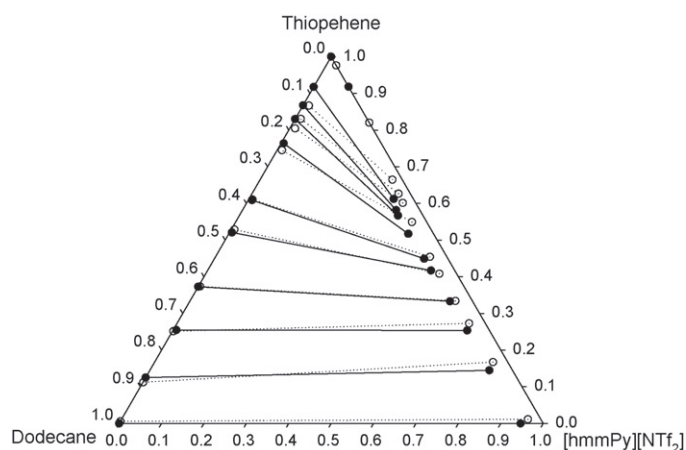

Fig. 2. Experimental tie-lines (●, solid line) for the LLE of the ternary system {[hmmpy][Ntf₂] (1) + thiophene (2) + dodecane (3))} at 298.15 K. The corresponding tie-lines correlated by means of the UNIQUAC model are also plotted (○, dotted).

seen, all of studied ternary systems with thiophene show Type 2 behaviour, with two of their constituent pairs exhibiting partial immiscibility and with only one immiscibility region, but the one which contains pyridine corresponds to Type 1 with only one
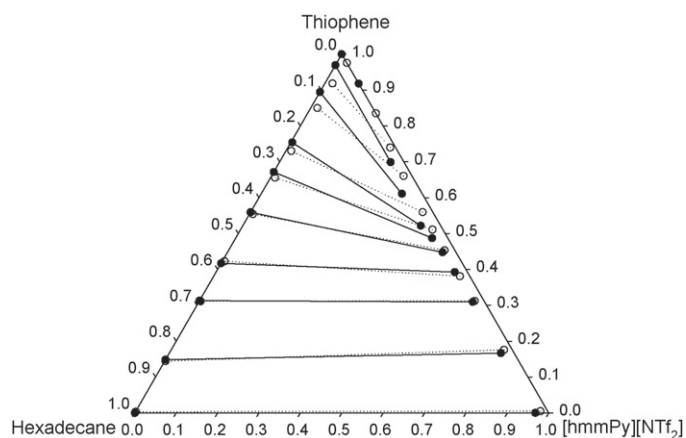

Fig. 3. Experimental tie-lines (●, solid line) for the LLE of the ternary system {[hmmpy][Ntf₂] (1) + thiophene (2) + hexadecane (3))} at 298.15 K. The corresponding tie-lines correlated by means of the NRTL model are also plotted (○, dotted).

Fig. 4. Experimental tie-lines (●, solid line) for the LLE of the ternary system {[hmmpy][Ntf₂] (1) + pyridine (2) + hexane (3))} at 298.15 K. The corresponding tie-lines correlated by means of the UNIQUAQ model are also plotted (○, dotted).

immiscible region and only one pair presenting partial immiscibility.

As practical application of desulfurization process correspond to low concentrations of nitrogen- and sulfur-containing compounds, the lowest part of the diagrams must be analysed. Tie-lines slopes are positive for low solute concentrations in case of thiophene-containing ternary systems, however, all systems present solutropic behaviour changing from positive to negative values of tie-lines slopes when concentration of solute increases. This is also reflected in the solute distribution ratio (β) values, changing from greater to less than one. In the case of pyridine-containing ternary system, the immiscible region is greatly reduced. The slope of the tie-lines is positive for the entire diagram and solute distribution ratio values are always bigger than unit. Lower solute distribution ratio values require greater amounts of ionic liquid in the extraction process. For linear hydrocarbons, it can be concluded in terms of solute distribution ratio, the more large the hydrocarbon chain, the higher amount of solvent is required. [hmmpy][NTf₂] ionic liquid shows high values of solute distribution ratio for extraction of nitrogen-containing compounds, which is more favoured than extraction of thiophene which requires more solvent entrance.

Non-detectable IL concentration was observed in the hydrocarbon-rich phase of any of the studied systems and high selectivity values were found for all fuel constituents, outstanding the more favourable values in case of pyridine ternary system. In the case of extraction of thiophene from linear hydrocarbons, selectivity (and consequently ease of separation) is increased as higher the hydrocarbon chain is.

3.1.1. Correlation
In order to facilitate their use in simulation and design processes, experimental data are correlated using the NRTL [77] and UNIQUAC [78] equations. The value of the non-randomness parameter α in the NRTL equation was pre-fixed at 0.1, 0.2 and 0.3.

Table 7
UNIQUAC structural parameters.

Component	r	q	Ref.
Hexane	4.4998	3.856	[80]
Dodecane	8.5462	7.096	[80]
Hexadecane	11.2438	9.256	[80]
Pyridine	2.9993	2.113	[80]
Thiophene	2.8569	2.140	[80]
[hmmpy][NTf₂]	11.8526	10.0659	[81]

Table 8
Binary interaction parameters and root mean square deviations (F, $\Delta\beta$) for the correlation of {[hmmpy][Ntf$_2$] (1) + thiophene (2) + hexane (3)} at 298.15 K.

NRTL				
Residuals		Components	Parameters	
		i–j	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
		$\alpha = 0.2$; optimized $\beta_\infty = 3.95$		
		1–2	−26,101	3268.5
F	2.6240	1–3	243.20	18,402
$\Delta\beta$	6.9	2–3	30,187	−22,567
UNIQUAC				
Residuals		Components	Parameters	
		i–j	Δu_{ij} (J mol^{-1})	Δu_{ji} (J mol^{-1})
		Not otpimized		
		1–2	−1312.0	2872.4
F	0.7193	1–3	−632.89	3783.2
$\Delta\beta$	6.7	2–3	12.175	1138.44
		Optimized $\beta_\infty = 3.99$		
		1–2	−1287.7	2798.2
F	0.5568	1–3	−974.71	5971.9
$\Delta\beta$	1.1	2–3	−443.78	1895.4

The binary interaction parameters were obtained using a computer program described by Sørensen and Arlt [79], which uses two objective functions to fit the experimental phase compositions. As first step, F_a is employed as objective function to fit data, which does not require any initial guess of parameters, and after convergence the obtained parameters are used in the second fit using, F_b:

$$F_a = \sum_k \sum_i \left[\frac{a_{ik}^{\mathrm{I}} - a_{ik}^{\mathrm{II}}}{a_{ik}^{\mathrm{I}} + a_{ik}^{\mathrm{II}}} \right]^2 + Q \sum_n P_n^2 \tag{3}$$

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

where a_i is the activity, x_i is the experimental composition in mole fraction, and $\hat{x}_i$ the corresponding calculated composition for component i. Other subscripts and superscripts are: j for phases (I, II) and k for tie-lines. Both functions include a penalty term (the second term) to reduce the risks of multiple solutions associated with parameters of high value. Q is set to 10^{-6} in Eq. (3) and to $Q = 10^{-10}$

in Eq. (4). P_n are the adjustable parameters. F_b also includes a third term to correctly fit experimental results when working with low solute concentrations, in which $\hat{\gamma}_{S\infty}^{\mathrm{I}}$ and $\hat{\gamma}_{S\infty}^{\mathrm{II}}$ represent the solute activity coefficients calculated at infinite dilution in both phases and β_∞ is the solute molar distribution ratio at infinite dilution.

In this work, β_∞ is not introduced at the beginning, making the last term of equation (4) zero. In the next step, this is fixed as some given optimized value driving correlation to lower residual values. The quality of correlation is measured by the residual function F and the mean error of the solute distribution ratio, $\Delta\beta$:

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

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

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

Table 9
Binary interaction parameters and root mean square deviations (F, $\Delta\beta$) for the correlation of {[hmmpy][Ntf$_2$] (1) + thiophene (2) + dodecane (3)} at 298.15 K.

NRTL				
Residuals		Components	Parameters	
		i–j	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
		$\alpha = 0.1$; optimized $\beta_\infty = 1.67$		
		1–2	5138.4	−4193.5
F	2.8070	1–3	37,207	−1140.7
$\Delta\beta$	6.6	2-3	20,669	−10,016
UNIQUAC				
Residuals		Components	Parameters	
		i–j	Δu_{ij} (J mol^{-1})	Δu_{ji} (J mol^{-1})
		Not optimized		
		1–2	−44.204	1155.1
F	2.6595	1–3	−222.30	1862.9
$\Delta\beta$	12.2	2–3	−1625.4	3166.4
		Optimized $\beta_\infty = 1.45$		
		1–2	−46.219	1230.8
F	2.8213	1–3	−164.97	2001.3
$\Delta\beta$	9.5	2–3	−1577.6	3257.7

Table 10
Binary interaction parameters and root mean square deviations (F, $\Delta\beta$) for the correlation of {[hmmpy][Ntf$_2$] (1) + thiophene (2) + hexadecane (3)} at 298.15 K.

NRTL				
Residuals		Components	Parameters	
		i–j	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
		$\alpha = 0.2$; optimized $\beta_\infty = 1.51$		
		1–2	−5016.0	15,024
F	3.6611	1–3	4761.7	10,893
$\Delta\beta$	4.9	2–3	4353.5	−2629.5
UNIQUAC				
Residuals		Components	Parameters	
		i–j	Δu_{ij} (J mol^{-1})	Δu_{ji} (J mol^{-1})
		Not otptimized		
		1–2	245.64	868.86
F	2.7083	1–3	−321.91	1859.1
$\Delta\beta$	12.7	2–3	−824.26	1851.3
		Optimized $\beta_\infty = 1.52$		
		1–2	41.725	1086.9
F	2.3808	1–3	−235.64	1918.9
$\Delta\beta$	9.5	2–3	−1446.6	3332.3

The structural parameters for the application of the UNIQUAC equation were taken from the literature [80,81] and are shown in Table 7. Tables 8–11 show the binary interaction parameters and residuals for the NRTL and UNIQUAC correlations of ternary data. For the NRTL equation, the α-values which led to the lowest residual values were selected. With this model, when β_∞ is not optimized, convergence problems have been found in several cases. UNIQUAC correlated tie-lines compositions are showed in Figs. 1–4 together with experimental data. This model has been selected because, despite cases where NRTL provided lower residuals, a slightly better representation of tie-lines compositions at high concentrations of thiophene can be seen.

3.2. Fuel models desulfurization

Figs. 5 and 6 present the composition (wt%) of each component in the simulated gasoline and diesel formulations, respectively, and raffinate product after one, two and three extraction stages when the [hmmpy][NTf$_2$] is used as solvent.
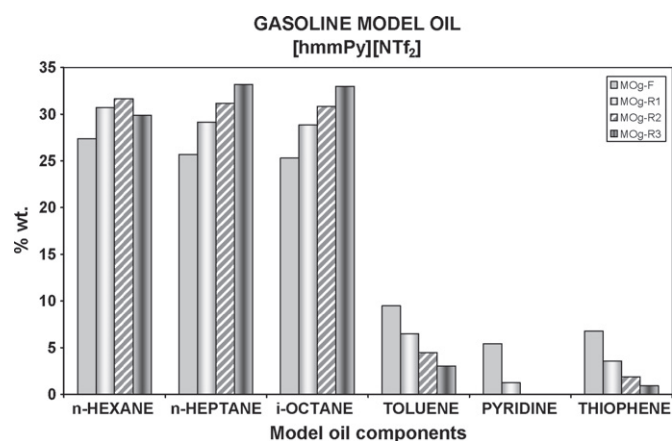

Fig. 5. Evolution of simulated gasoline components in a three-step extraction process using [hmmpy][Ntf$_2$] as solvent. MOg represents gasoline model oil, F, fresh mixture, and R1, R2, and R3, raffinate composition after each extraction step.
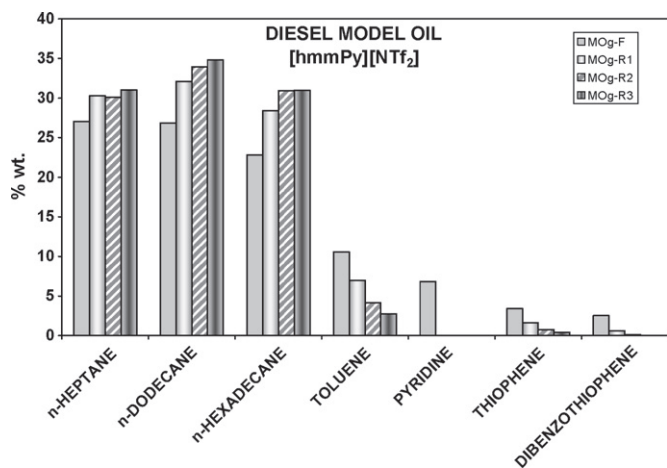
Table 11
Binary interaction parameters and root mean square deviations (F, $\Delta\beta$) for the correlation of {[hmmpy][Ntf$_2$] (1) + pyridine (2) + hexane (3)} at 298.15 K.

NRTL				
Residuals		Components	Parameters	
		i–j	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
		$\alpha = 0.2$; optimized $\beta_\infty = 25$		
		1–2	874.68	3632.6
F	0.6723	1–3	12,463	67.081
$\Delta\beta$	18.5	2–3	1516.3	−6709.5
UNIQUAC				
Residuals		Components	Parameters	
		i–j	Δu_{ij} (J mol^{-1})	Δu_{ji} (J mol^{-1})
		Not otptimized		
		1–2	3602.9	−1354.0
F	0.7995	1–3	5556.0	−1689.1
$\Delta\beta$	20.8	2–3	−922.07	−2162.7
		Optimized $\beta_\infty = 25$		
		1–2	3557.8	−1358.7
F	0.8094	1–3	5745.1	−1711.8
$\Delta\beta$	19.3	2–3	−447.56	−2430.2

Fig. 6. Evolution of simulated diesel components in a three step extraction process using [hmmpy][NTf$_2$] as solvent. MOg represents diesel model oil, F, fresh mixture, and R1, R2, and R3, raffinate composition after each extraction step.
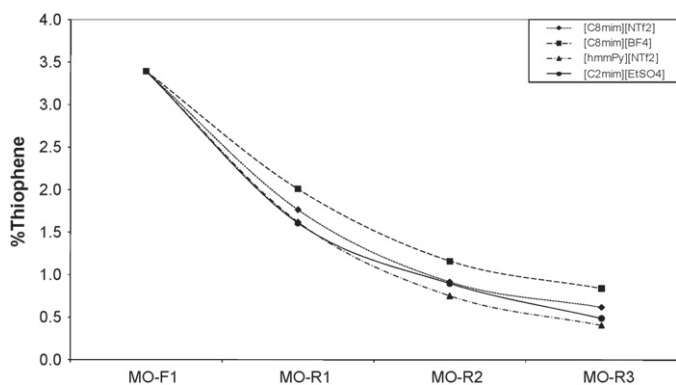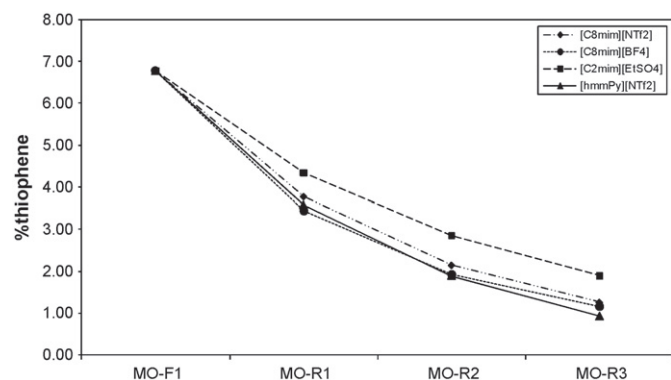

Fig. 7. Evolution of thiophene composition in simulated diesel three-step extraction process using [hmmpy][NTf$_2$] as solvent compared with other stuidied ionic liquids. MO represents diesel model oil, F, fresh mixture, and R1, R2, and R3, raffinate composition after each extraction step.

Thiophene is extracted by the IL and its composition in the raffinate products decreases rapidly. Comparing the behaviour of this IL with several ([C$_8$mim][BF$_4$], [C$_8$mim][NTf$_2$] and [C$_2$mim][EtSO$_4$]) ILs previously studied [35,72], as it is reflected in Figs. 7 and 8, the [hmmpy][NTf$_2$] has showed the largest capacity extraction, being the thiophene composition reduced around the 86 wt% in the case

Fig. 8. Evolution of thiophene composition in simulated gasoline three-step extraction process using [hmmpy][NTf$_2$] as solvent compared with other stuidied ionic liquids. MO represents gasoline model oil, F, fresh mixture, and R1, R2, and R3, raffinate composition after each extraction step.
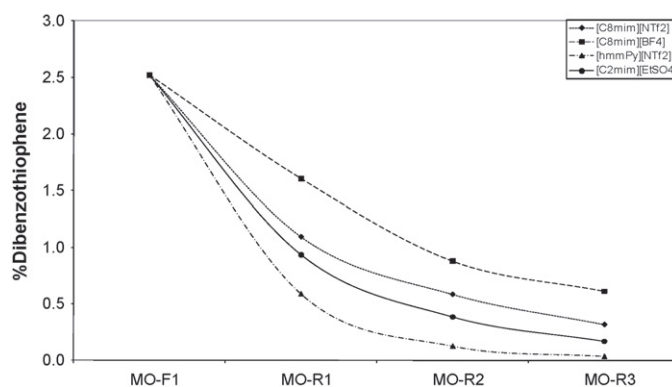
Fig. 9. Evolution of dibenzothiophene composition in simulated diesel three-step extraction process using [hmmpy][NTf$_2$] as solvent compared with other stuidied ionic liquids. MO represents diesel model oil, F, fresh mixture, and R1, R2, and R3, raffinate composition after each extraction step.

of gasoline and 88 wt% in the case of diesel, after three extraction stages.

As it can be seen in Fig. 9, dibenzothiophene of diesel is also extracted by any of the ILs and its composition in the raffinate products is rapidly decreased. For these mixtures of higher molecular weigh components, the [hmmpy][NTf$_2$] has showed the largest capacity extraction, and dibenzothiophene is reduced around 98 wt% after three extraction stages.

As it was expected by the LLE determined in this paper, and repeating qualitative behaviour found with previously studied ILs [35,72] denitrogenation with [hmmpy][NTf$_2$] is total, being the pyridine concentration undetectable after the second stage in case of gasoline and even after the first stage for the case of the diesel model. Desulfurization and denitrogenation also are accompanied by dearomatization, reflected in a toluene composition reduction of 68 wt% in the case of gasoline model and 61% in the case of diesel. Similar toluene reductions were found with [C$_8$mim][NTf$_2$] and [C$_2$mim][EtSO$_4$] ILs [72]. All other hydrocarbons increase their compositions after each extraction stage.

In all cases (fuel models for gasoline and diesel), the ionic liquid composition in raffinates was undetectable.

3.3. Light naphtha and diesel desulfurization

Fig. 10 shows how total sulfur concentration diminishes when a real gasoline is submitted to the same multistage extraction performed for synthetic model oils. Conclusions are coincident with
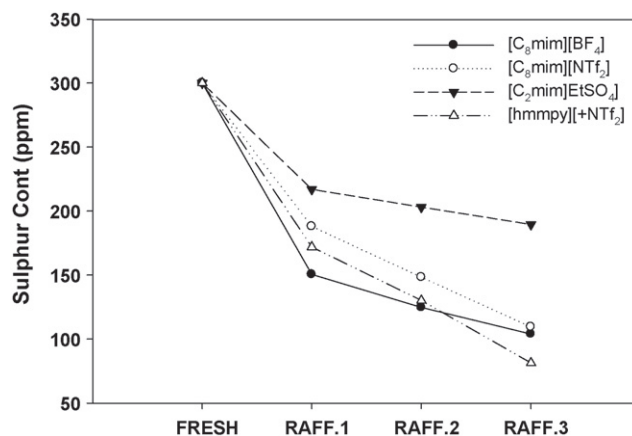

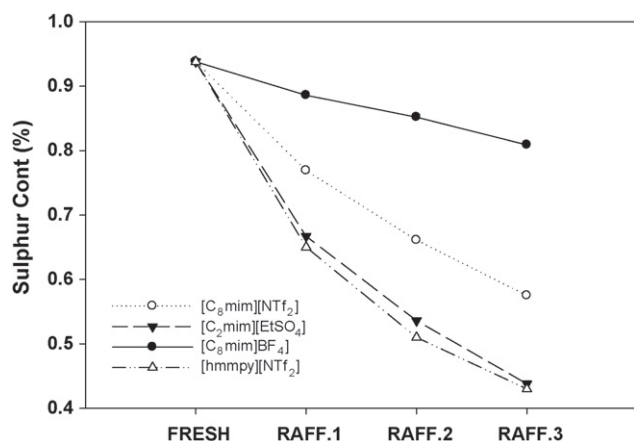**Fig. 10.** Sulfur content evolution of a light naphtha in a three-step extraction process.

Fig. 11. Sulfur content evolution of a diesel in a three-step extraction process.

above section and [hmmpy][NTf$_2$] gives better results than those found for previously studied ILs.

Fig. 11 shows how total sulfur concentration diminishes when a real diesel is submitted to the multistage extraction process. Conclusions are coincident with above section and [hmmpy][NTf$_2$] gives the best results.

4. Conclusions

A large amount of research has been done about the use of ILs for fuel-oils desulfurization. Bibliography focuses on alkylmethyl-pyridinium-based ILs as possible extractant agents to afford legal requirements without the use of more complex techniques as oxidative extraction. In this work suitability of the use of ionic liquid [hmmpy][NTf$_2$] as solvent for extraction of sulfur and nitrogen compounds from fuel oils was analysed.

Liquid + liquid equilibrium data for ternary systems composed by 1-hexyl-3,5-dimethyl pyridinium {bis[trifluoromethyl-sulfonyl]imide}, thiophene and three hydrocarbons representative of fuel (n-hexane, n-dodecane and n-hexadecane), and for the ternary system composed by 1-hexyl-3,5-dimethyl pyridinium {bis[trifluoromethylsulfonyl]imide}, pyridine and hexane were determined at 298.15 K and atmospheric pressure. All ternary systems with thiophene correspond to the Type 2 category, with partial or total inmiscibility of the IL with the thiophene and the hydrocarbons. The one which contains pyridine corresponds to Type 1 category with only one pair of immiscibility.

In base of obtained experimental liquid–liquid equilibrium data, suitability of ionic liquid [hmmpy][Ntf$_2$] has been evaluated in terms of solute distribution ratio and selectivity parameters. At low thiophene concentrations, favourable values of these parameters were found but large quantities of solvent would be required for desulfurization. Extraction of pyridine is much more favoured.

The NRTL and UNIQUAC equations were used to correlate the experimental LLE data. The optimum interaction parameters were determined. In general, the LLE data of the [hmmpy][Ntf$_2$] + thiophene + hydrocarbon ternary systems are poorly correlated with both models, being the best results achieved when β_∞ is optimized. In any case, high deviations between experimental and correlated data are found for high thiophene concentrations, being slightly less with UNIQUAC model. High values of β found for the [hmmpy][Ntf$_2$] + pyridine + hexane ternary system imply high value of this residual in the correlation of the system.

Previously synthetic and real fuel oils experiments of desulfurization done with [C$_8$mim][BF$_4$], [C$_8$mim][NTf$_2$] and [C$_2$mim][EtSO$_4$] ILs were repeated in this paper by using the [hmmpy][Ntf$_2$] IL. This IL afforded the best sulfur compounds

removal capacity. Denitrogenation is practically complete and desulfurization comes also accompanied of a dearomatization process (behaviour also found for previously studied ILs). This has to be balanced with regard to the octane number.

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