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The production of transportation fuels which have a very low content of sulfur has became one of the priority challenges for the oil industry worldwide, due to by strict new regulatory requirements. Ionic liquids (ILs) have been proposed as suitable and promising solvents for this purpose due to their excellent qualities as solvents. In this work a series of ten new ILs derived from pyridinium cation substituted with different alkyl chains have been synthesized from 2-alkyl-3,5-dimethylpyridines. The starting materials were prepared by selective metalation of 2,3,5-trimethylpyridine, which allowed the introduction of different alkyl groups in pyridine position 2 with high yields. To test the ILs sulfur-removal capacity, liquid–liquid equilibrium (LLE) data for ternary systems (heptane + thiophene + IL) were determined at T = 298.15 K and atmospheric pressure. Selectivity and solute distribution ratio, calculated from tie-lines, were used to evaluate whether these new ILs could be used as solvents for the extraction of thiophene from heptane. Finally, the experimental LLE data were correlated with the NRLT thermodynamic model.

Introduction

The combustion of sulfur-containing fossil fuels is the main source of nitrogen and sulfur oxides emission into the atmosphere.¹ The sulfur-bearing compounds are converted to SO_x during the combustion in car engines, and these can be converted to sulfuric acid when reacting with water vapour, causing acid rain. Also, high contents of sulfuric oxides in exhaust fumes lower the efficiency of catalytic converters used for reducing CO and NO_x emissions. During the last decades much attention has been given to the deep desulfurization of transportation fuels such as diesel oil and gasoline since the sulfur-limits for these fuels were gradually lowered. Nowadays EU legislation² sets the upper limit of sulfur content in diesel fuel to 10 ppm while US regulations have established a maximum of 15 ppm for diesel since 2006 and 30 ppm for gasoline from 2005.³

The conventional method used to remove S-compounds in fuel oils is hydrodesulfurization (HDS),⁴ a process in which the S-compounds react with hydrogen and are converted into H₂S and the corresponding hydrocarbons. However, HDS requires high temperatures (300-400 °C) and pressures (20-100 atm of H₂), and presents difficulties in removing aromatic heterocyclic S-compounds such as thiophene, benzothiophene, dibenzothiophene (DBT) or their derivatives, because of the sterically-hindered adsorption of these compounds on the catalyst surface.5 To overcome these drawbacks, it is essential to explore novel approaches to improve HDS technology, and certain alternative deep-desulfuration processes such as absorption,⁶ biodesulfurization,⁷ extraction⁸ and oxidation⁹ have been investigated. Among them, extractive desulfurization (EDS) has been revealed as one of the most promising techniques because it does not involve hydrogen consumption, catalyst, high temperature or high pressure, and operates with mild and simple conditions. A few molecular solvents, such as polyalkylene glycol, imidazolidinone, pyrymidinone and dimethylsulfoxide, were tested in EDS but the results were undesirable, and their mutual solubility led to cross-contamination. Furthermore, these extractants are usually flammable and volatile organic compounds, which result in additional safety and environmental problems. There is an urgent need to find alternative and effective extractants for EDS.

Over the past decade, ionic liquids (ILs) have attracted great interest and their potential and applications as environmentally benign alternative solvents have been extensively reviewed.¹⁰

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Most ILs have several advantages over organic solvents such as chemical and thermal stability, extensive liquid range, nonflammability, compatibility with oxidizing and reducing agents, ability to dissolve a wide range of materials and their negligible vapour pressure, which is the most attractive property from an environmental point of view, allowing its easy regeneration.

The extraction of fuels using ILs to remove S-compounds has been recently reviewed.¹¹ Since 2001,¹² works on EDS using ILs have shown their potential to achieve ultra-low sulfur diesels (ULSDs). The principal focus of these studies is the extraction of S-containing aromatics, such as thiophene, dibenzothiophene (DBT) or 4,6-dimethyldibenzothiophene from heptane or dodecane as a model oil system. By applying NMR studies, Su et al. have demonstrated that thiophene molecules are accommodated into the ionic par structure of the IL in significantly high molar ratios, enabling the selective and extractive removal of aromatic sulfur compounds from fuels.13 Most ILs investigated to remove S-compounds are derived from common anions such as BF₄⁻, PF₆⁻, AlCl₄⁻ or EtSO₄⁻, and conventional aromatic imidazolium and pyridinium cations. Studies of Holbrey and co-workers14 on extraction of DBT from dodecane using ILs with varying cation classes and with a range of anions have revealed that the partition ratio of dibenzothiophene to the ILs shows a clear variation with cation class, following the sequence dimethylpyridinium > methylpyridinium > pyridinium \approx imidazolium \approx pyrrolidinium, with much less significant variation with anion type. Gao and co-workers found that selective removal of aromatic heterocyclic S-compounds from diesel by using pyridinium ILs at room temperature, follows the order $[OPy][BF_4] > [HPy]$ [BF₄] > [BPy][BF₄].¹⁵ More recently, studies of M. Francisco and co-workers have shown that 1-hexyl-3,5-dimethylpyridinium bis(trifluoromethanesulfonyl)imide, [1H3M5MPy][NTf2], affords the best S-compounds removal capacity compared with some previously reported ILs.16

Most of the ILs used to date in EDS show some favorable characteristics, such as negligible miscibility with fuel oil, high affinity for S-compounds, easy regeneration and good reusability. However, they also had some undesirable features such as high viscosity and/or high cost. Moreover, the efficiencies of sulfur removal need to be improved. Therefore, more studies using new IL structures must be developed.

Taking into account the above mentioned results, we have designed and synthesized a series of new ILs derived from pyridinium that incorporate different alkyl chains on the cation, and halides or bis(trifluoromethanesulfonyl)imide (NTf₂) as anions. Two of them have been selected in order to analyze their suitability as solvents in extraction of S-compounds from fuels.

Results and discussion

Synthesis

Our goal was to prepare a series of new ILs derived from 1,2,3,5tetralkylpyridinium and bis(trifluoromethanesulfonyl)imide, $[NTf_2]$, as anion. Quaternization of 2-alkyl-3,5-methylpyridines by treatment with an alkyl halide would afford the corresponding pyridinium halide. $[NTf_2]$ anion would be subsequently introduced by a metathesis reaction with bis(trifluoromethanesulfonyl)imide lithium salt (Scheme 1).



Scheme 1 Synthesis of 1,2,3,5-tetralkylpyridinium ILs.

Synthesis of 2-alkyl-3,5-dimethylpyridines

We first tried to prepare the 2-ethyl-3,5-dimethylpyridine (2) as starting material (Scheme 2). The classical methods described for the synthesis of 2 involve heterocyclization reactions in order to form the pyridine ring.¹⁷ These procedures show many inconveniences, such as low yields, the need for high pressures and high temperatures, and the obtaining of 2 with other non-desired amines.



Scheme 2 Metalation of 2,3,5-collidine (1) and later alkylation.

Taking into account the commercial accessibility of 2,3,5collidine (1), our approach was focused on the selective metalation of 1 on 2-methyl group and subsequent alkylation. A series of methods for the alkylation of methylated pyridine have been described,¹⁸ all of them involving the use of a base for the anion formation and a subsequent alkylation by means of an akylating agent.

At this point, the choice of the base was of high importance. It is well known that methyl groups located in pyridine positions 2 and 4 undergo facile metalation, since the resulting anions are highly resonance stabilized. However, even relatively weakly acidic alkyl groups on position 3 of such molecules can be ionized by strongly basic ions like amide.¹⁹ On the other hand, *n*-BuLi promotes ionization of 2-methyl groups, which is ascribed to prior complexation of lithium cation with the nitrogen ring.²⁰ Consequently, *n*-BuLi was selected as the base to be used for 2,3,5-collidine (1) metalation on position 2 (Scheme 2).

The treatment of **1** with 1 eq. of *n*-BuLi, followed by the addition of 1 eq. of MeI, resulted in the exclusive ionization of 2-methyl group, but the starting material was recovered in 37% yield (Table 1, entry 1). The procedure was then repeated by using different reagent proportions. Unexpectedly, 2-pentyl-3,5-dimethylpyridine (**3**) was obtained when 2 eq. of *n*-BuLi were employed, which can be explained by a metal-halogen exchange reaction between MeI and the excess of *n*-BuLi. These exchanges are rapid reactions even at low temperatures; lithium at equilibrium is preferentially attached to the organic residue being better able to stabilize the negative charge.²¹ Spectroscopic data of **2** were in agreement with those previously reported in the literature.²² No reported data were found for **3**. Its structure was determined by NMR and mass spectrometry.

In order to avoid metal-halogen exchange, an excess of MeI was used keeping 1 eq. of n-BuLi (entry 4). These conditions afforded the desired compound 2 in high yield. When 1-bromobutane was employed instead of MeI, compound 3 was

 Table 1
 Metalation of 2,3,5-collidine (1) and later alkylation^a

Entry	n-BuLi (eq.)	RX (eq.)	$ \begin{array}{l} \mathbf{R}_2 = \mathbf{M}\mathbf{e} \\ \begin{pmatrix} 0 \\ 0 \end{pmatrix} \end{array} $	$\begin{array}{l} \mathbf{R}_2 = \mathbf{E}\mathbf{t} \\ (\%) \end{array}$	$\begin{array}{l} \mathbf{R}_2 = \mathbf{Pen} \\ (\%) \end{array}$
1	1	MeI (1)	37	60	0
2	2	MeI (1)	13	13	69
3	2	MeI(2)	1	27	69
4	1	MeI(2)	8	85	0
5	1	BrBu (2)	9	0	84

^{*a*} All yields are for isolated products by column chromatography on silica gel.

 Table 2
 Quaternization reactions of 2,3,5-trialkylpyridines

Trialkylpyridine	R_1X (eq.)	Solv.	T ^a (°C)	<i>t</i> (h)	Product (%)
1	HexI (2)	Tol.	110	168	4 (99)
1	HexI (3)	Tol.	110	117	4 (99)
1	HexI (5)	Tol.	110	96	4 (99) 5 (25)
2	HexBr (5)	IOL CH CN	110	336 144	5 (25) 5 (98)
3	EtBr(5)	CH ₃ CN	80	312	6 (94)
3	BuBr (5)	CH ₃ CN	80	312	7 (92)
3	HexBr (5)	CH ₃ CN	80	312	8 (85)

obtained (entry 5). With this methodology, we have obtained a procedure for the selective metalation of polymethylated pyridines which permits the introduction of different alkyl groups in position 2 with high yields.

Quaternization of 2,3,5-trialkylpyridines

Quarternization of 1 by treatment with an excess of 1-iodohexane in toluene afforded 1-hexyl-2,3,5-trimethylpyridinium iodide [1H2M3M5MPy][I] (4) in high yield (Scheme 3, Table 2). When the equivalents of 1-iodohexane were increased, a drop in reaction times was observed. However, the treatment of 2 with 1-iodohexane gave rise to a dirty mixture of reaction products. Quaternization of 2 was then carried out using 1-bromohexane, but 2-ethyl-1-hexyl-3,5dimethylpyridinium bromide (5) was only obtained in 25% yield and the reaction was too slow. Several experiments changing solvent and temperature were then carried out (Table 2). The best results were obtained when 5 equivalents of 1bromohexane were used, heating at 80 °C and using acetonitrile as a solvent. Similar conditions were used for the quaternization of 3 with bromoethane, 1-bromobutane and 1-bromohexane, which afforded $[{}^{1}E{}^{3}M{}^{5}M{}^{2}PPy][Br]$ (6), $[{}^{1}B{}^{3}M{}^{5}M{}^{2}PPy][Br]$ (7) and [1H3M5M2PPy][Br] (8) respectively. Due to steric hindrance, the reaction yield decreases as the bromide alkyl chain increases.



Scheme 3 Quaternization of 2-alkyl-3,5-dimethylpyridines.



Scheme 4 Preparation of pyridinium bis(trifluoromethane)sulfonimides.

Anion metathesis

The subsequent metathesis reactions of tetralkylpyridinium halides **4–8** with bis(trifluoromethane)sulfonimide lithium salt,²³ provided the bis(trifluoromethanesulfonyl)imides [${}^{1}H^{2}M^{3}M^{5}MPy$] [NTf₂] (9), [${}^{2}E^{1}H^{3}M^{5}MPy$][NTf₂] (10), [${}^{1}E^{3}M^{5}M^{2}PPy$][NTf₂] (11), [${}^{1}B^{3}M^{5}M^{2}PPy$][NTf₂] (12) and [${}^{1}H^{3}M^{5}M^{2}PPy$][NTf₂] (13) as pure liquids in high overall yields (Scheme 4). Their structures were confirmed by NMR and high resolution mass spectrometry.

LLE data

Among all prepared ILs, $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$ (11) was first selected to be applied on EDS because its low viscosity, which is a key feature in the extraction processes. Secondly $[{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$ (12) was also tested in order to determine the influence of the alkyl chain length linked to the pyridinium nitrogen on the extraction ability. A mixture of heptane and thiophene was selected as the model oil, taking as reference some previous works.²⁴⁻²⁶

The ILs feasibility as solvents for the liquid–liquid extraction of thiophene from heptane was analyzed by determining experimental tie-lines covering the whole immiscibility region of the ternary system (heptane + thiophene + IL). The experimental LLE data for the ternary systems (heptane + thiophene + $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$) and (heptane + thiophene + $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$) are given in Tables 3 and 4 respectively, and the corresponding triangular diagrams are plotted in Fig. 1 and 2.

It is possible to observe that according to the classification proposed by Sørensen,²⁷ both systems correspond to a Type 2 category, in which two of the pairs of compounds (heptane/IL and thiophene/IL) exhibit partial miscibility, while only one pair (thiophene/heptane) is miscible in the whole range of compositions. As expected, it is also shown that heptane is less soluble than thiophene in both ILs, which could be attributable to π - π interactions between the thiophene and the aromatic core of the ILs cation.²⁸ The solubility values of heptane and thiophene in the studied ILs are represented by the first and last tie-lines (IL-rich phase). The large difference between heptane and thiophene solubility in the ILs indicates that both ['E³M⁵M²PPy][NTf₂] and [¹B³M⁵M²PPy][NTf₂] could achieve a good extraction of thiophene from heptane.

Comparison of heptane solubility in both ILs shows that it is more soluble in $[{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$ ($x_{1} = 0.242$) than in $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$ ($x_{1} = 0.156$), which indicates that an increase in the alkyl chain length located in position 1, leads to a higher alkane solubility.

Alkane-rich phase (I)			Ionic liquid-rich phase (II)				
<i>x</i> ₁	<i>X</i> ₂	<i>X</i> ₃	$\overline{x_1}$	<i>X</i> ₂	<i>X</i> ₃	β	S
1.000	0.000	0.000	0.156	0.000	0.844		
0.983	0.017	0.000	0.152	0.077	0.771	4.53	29.29
0.942	0.058	0.000	0.124	0.199	0.677	3.43	26.06
0.924	0.076	0.000	0.124	0.248	0.628	3.26	24.32
0.885	0.115	0.000	0.109	0.325	0.566	2.83	22.95
0.809	0.191	0.000	0.094	0.427	0.479	2.24	19.24
0.740	0.260	0.000	0.094	0.504	0.402	1.94	15.26
0.621	0.379	0.000	0.085	0.590	0.325	1.56	11.37
0.500	0.500	0.000	0.083	0.647	0.270	1.29	7.80
0.356	0.644	0.000	0.078	0.709	0.213	1.10	5.02
0.205	0.795	0.000	0.069	0.775	0.156	0.97	2.90
0.062	0.938	0.000	0.035	0.838	0.127	0.89	1.58
0.000	1.000	0.000	0.000	0.889	0.111	0.89	_

Table 3 Experimental liquid–liquid equilibrium data in mole fraction, and values of the solute distribution ratio (β) and selectivity (*S*) for the ternary systems (heptane (1) + thiophene (2) + [¹E³M⁵M²PPy][NTf₂] (3)) at *T* = 298.15 K and atmospheric pressure

Table 4 Experimental liquid–liquid equilibrium data in mole fraction, and values of the solute distribution ratio (β) and selectivity (*S*) for the ternary systems (heptane (1) + thiophene (2) + [¹B³M⁵M²PPy][NTf₂] (3)) at *T* = 298.15 K and atmospheric pressure

Alkane-rich phase (I)			Ionic liquid-rich phase (II)				
<i>x</i> ₁	<i>x</i> ₂	<i>X</i> ₃	$\overline{x_1}$	<i>X</i> ₂	<i>X</i> ₃	β	S
1.000	0.000	0.000	0.242	0.000	0.758		_
0.987	0.013	0.000	0.225	0.069	0.706	5.31	23.28
0.967	0.033	0.000	0.207	0.139	0.654	4.21	19.68
0.934	0.066	0.000	0.175	0.242	0.583	3.67	19.57
0.883	0.117	0.000	0.141	0.355	0.504	3.03	19.00
0.823	0.177	0.000	0.149	0.426	0.425	2.41	13.29
0.626	0.374	0.000	0.126	0.591	0.283	1.58	7.85
0.499	0.501	0.000	0.120	0.657	0.223	1.31	5.45
0.407	0.593	0.000	0.111	0.694	0.195	1.17	4.29
0.284	0.716	0.000	0.097	0.744	0.159	1.04	3.04
0.130	0.870	0.000	0.064	0.819	0.117	0.94	1.91
0.054	0.946	0.000	0.032	0.867	0.101	0.92	1.55
0.000	1.000	0.000	0.000	0.910	0.090	0.91	_



Fig. 1 Experimental and correlated tie-lines for the LLE at 25 °C for the ternary system (heptane + thiophene + [${}^{1}E^{3}M^{5}M^{2}PPy$][NTf₂]). Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from NRTL model.

The solubility of thiophene is shown to be also higher in $[{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}] (x_{2} = 0.910)$ than in $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}] (x_{2} = 0.889)$, although in this case the difference is not so large. Similar behaviour was shown by Arce *et al.* studying the



Fig. 2 Experimental and correlated tie-lines for the LLE at 25 °C for the ternary system (heptane + thiophene + $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$). Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from NRTL model.

separation of benzene from hexane by extraction with several 1alkyl-3-methylimidazolium bis(trifluoromethanelsulfonyl)imide ILs as solvents.²⁹ Another remarkable fact is that no presence of IL was detected in the alkane-rich phase of either studied systems. This lack of IL in the raffinate stream makes the IL recovery and reuse easier, since a unit for solvent recovery from the alkane-rich phase would be not necessary in an industrial process. Therefore, IL recovery from the IL-rich phase could be carried out by using a flash unit which would reduce installation and operation costs.

Evaluation of ILs capacity as extractants

The ILs potential suitability to separate thiophene from heptane was evaluated by classical parameters, such as the solute distribution ratio, β , and the selectivity, *S*, defined according to the following equations:

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

$$S = \frac{x_2^{II} x_1^{I}}{x_2^{I} x_1^{II}}$$
(2)

where x_1^{I} and x_2^{I} are the mole fractions of heptane and thiophene, respectively, in the alkane-rich phase (upper phase); and x_1^{II} and x_2^{II} are the mole fractions of heptane and thiophene, respectively, in the ionic liquid-rich phase (lower phase).

The calculated values of solute distribution ratio, β , and selectivity, *S*, for the systems (heptane + thiophene + [¹E³M⁵M²PPy][NTf₂]) and (heptane + thiophene + [¹B³M⁵M²PPy][NTf₂]) are also included in Tables 3 and 4, respectively. In all cases, *S* values are higher than unity, which shows that a good degree of extraction of thiophene from heptane can be achieved, especially at those low mole fractions of thiophene in the alkane-rich phase where *S* values are higher.

Solute distribution ratio values, β , are also higher than unity at low thiophene concentrations in the alkane-rich phase, but decrease to values below unity when thiophene concentration increases, showing the solutropic behavior of these systems according to the tie-line slopes, which change from positive to negative along the triangular diagram.

The variation of S and β versus thiophene composition in the alkane-rich phase for the systems (heptane + thiophene + IL) is plotted in Fig. 3 and 4 respectively. For comparison purpose, the S and β values for the system (heptane + thiophene + [¹H³M⁵MPy][NTf₂]¹⁶) were also included.

As can be observed in Fig. 3, S values decrease with increasing composition of thiophene in the alkane-rich phase. Comparing results of the two studied ternary systems, it can be seen that selectivity values decrease in the order $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}] > [{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$, the opposite way to the miscible region. This behaviour indicates that an increase of the cation alkyl chain length results in lower selectivity values because, as mentioned above, the solubility of heptane also increases and a greater amount of this compound is present in the IL-rich phase.

Regarding the solute distribution ratio, β values are very similar for both systems, as is drawn in Fig. 4.

As explained previously, pyridinium ILs achieved great success as an efficient alternative for extractive desulfurization issues. More precisely, alkyldimethyl pyridinium-based ILs showed the best results.¹⁴ When comparing



Fig. 3 Selectivity, as a function of the thiophene mole fraction in the alkane-rich phase, for the ternary systems (heptane + thiophene + $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}])$ (\bigcirc) (heptane + thiophene + $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$) (\bigcirc) and (heptane + thiophene + $[^{1}H^{3}M^{5}MPy][NTf_{2}]$) (\bigcirc)¹⁶ at T = 298.15 K.



Fig. 4 Solute distribution ratio, as a function of the thiophene mole fraction in the alkane-rich phase, for the ternary systems (heptane + thiophene + $[^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$) (\bigcirc); (heptane + thiophene + $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$) (\bigcirc) and (heptane + thiophene + $[^{1}H^{3}M^{5}MPy][NTf_{2}]$) (\bigtriangleup)¹⁶ at T = 298.15 K.

the $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$ and $[{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$ ILs with $[{}^{1}H^{3}M^{5}MPy][NTf_{2}], {}^{16}$ the effect of the number of substituents can be analyzed. Solute distribution ratio and selectivity values are higher at low thiophene concentrations in the case of polysubstituted pyridinium, indicating that the capability of these pyridinium-based ILs to desulfurate increases when increasing the alkyl groups in the aromatic ring.

Taking into account that practical application of desulfurization processes corresponds to low concentrations of sulfurcontaining compounds (lowest part of triangular diagrams) and that the highest S and β values were obtained in this area, the studied ILs could be considered as an alternative for the extraction of thiophene from heptane.

Although at present the ILs are more expensive than conventional solvents, future production of higher quantities and the possibility of their recovery in the process could make their use competitive.

Thermodynamic correlation

LLE data were correlated using the Non-Random Two Liquid (NRTL) thermodynamic model developed by Renon and Prausnitz.³⁰ Although this model was not originally developed for systems involving electrolytes, it has been successfully used to correlate the LLE data of systems involving ILs.³¹

Following a common procedure, the nonrandomness parameter in the NRTL equation, α_{ij} , was set to different values during calculations, and the best results were achieved with $\alpha_{ij} = 0.3$. The objective function used minimizes the differences between the experimental and calculated mole fraction of the components in both phases.

Correlation quality was tested calculating the root-meansquare deviation of the composition, σx , and the mean error of the solute distribution ratio, $\Delta \beta$. These deviations were calculated as:

$$\sigma x = 100 \sqrt{\frac{\sum_{k}^{M} \sum_{i=1}^{N-1} [(x_{ki}^{\text{Lexp}} - x_{ki}^{\text{Lealc}})^{2} + (x_{ki}^{\text{ILexp}} - x_{ki}^{\text{ILealc}})^{2}]}{2MN}}$$
(3)

$$\Delta \beta = 100 \sqrt{\frac{1}{M} \sum_{k=1}^{M} \left(\frac{\beta_k - \beta_k^{\text{calc}}}{\beta_k}\right)^2}$$
(4)

where M is the number of tie-lines and N the number of components in the mixture.

These deviations together with the binary interaction parameters of the correlation model are listed in Table 5. Comparing the values of σx and $\Delta \beta$, it can be inferred that NRTL model gives lower deviations for the system containing [¹E³M⁵M²PPy][NTf₂].

As an example of the obtained correlation, the experimental tie-lines and those obtained from the correlation with the NRTL model, are plotted in Fig. 1 and 2. After inspection of this figure, it can be concluded that the NRTL model fits the experimental data quite satisfactorily at low thiophene concentration, while larger differences between experimental and calculated data were found at high thiophene concentrations, where the model calculates quantities of IL in the alkane-rich phase for the studied systems.

Table 5 NRTL binary interaction parameters and deviations for LLE data for the ternary systems (heptane (1) + thiophene (2) + $[^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$ or $[^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$ (3)) at T = 298.15 K

i—j	$\Delta g_{ij}/\mathrm{J}~\mathrm{mol}^{-1}$	$\Delta g_{jj}/\mathrm{J}~\mathrm{mol}^{-1}$	$lpha_{ij}$	x	$\Delta \beta$
(hepta	ne + thiophene +	[¹ E ³ M ⁵ M ² PPv][N	Tf ₂])		
1-2	-697.77	4519.2	0.30	0.711	2.13
1–3	10111	2857.4			
2–3	14493	-5163.3			
(hepta	ne + thiophene +	[¹ B ³ M ⁵ M ² PPy][N	Tf_2])		
1-2	-835.29	3502.7	0.30	0.765	2.76
1–3	10019	1877.8			
2–3	15966	-6114.0			

Experimental

Synthesis

Acetonitrile (Sigma–Aldrich, ACS reagent, $\geq 99.5\%$), bis(trifluoromethanesulfonyl)imide lithium salt (Fluka, $\geq 99\%$), 1-bromobutane (Sigma–Aldrich, 99%), bromoethane (Sigma– Aldrich, 98%), 1-bromohexane (Aldrich, 98%), n-butyllithium (Aldrich, 1.6 M in hexane), 2,3,5-collidine (Aldrich, 99%), diethyl ether (Merck, GR, $\leq 0.03\%$ H₂O), 1-iodohexane (Acros organics, 98+%, stabilized) and iodomethane (Acros organics, 99%, stabilized) were procured from the commercial supplier and used without any pre-treatment, except diethyl ether, which was dried before its use.

The ¹H, ¹³C and ¹⁹F NMR spectra of the purified products were recorded in CDCl₃ on a Bruker ARX at 400.1621, 100.6314 and 376.5266 MHz respectively, with chemical shifts given in parts per million and coupling constants (J) in hertz. ESI mass spectra were recorded on a micrOTOF Focus spectrometer and on an apex-Qe spectrometer.

General procedures for 2,3,5-collidine (1) alkylation

In a dried, argon-flushed 500 mL flask, anhydrous diethylether (75 mL) was introduced via syringe and a solution of nbutyllithium 1.6 M in hexane (77.4 mL, 123.8 mmol) was added dropwise. A solution of 2,3,5-collidine (16.44 mL, 123.8 mmol) in diethylether (40 mL) was then slowly added over 10 min. After stirring for 1 h, the mixture was cooled to -78 °C by a dry-ice-acetone bath and a solution of the 1-alkyl halide (2 equiv.) in diethylether (75 mL) was added. The reaction progress was monitored by t.l.c. using silica gel 60 GF-254 aluminium sheets and hexane-ethyl acetate (1:1) as eluent. After 1 h of stirring for 2 and 6.5 h of stirring for 3 at room temperature, the mixture was poured into water (50 mL), neutralized with a saturated solution of ammonium chloride (50 mL) and extracted with dichloromethane $(3 \times 50 \text{ mL})$. The organic extracts were combined, dried over Na₂SO₄ and filtered. The solvent was removed on the rotary evaporator and the residue was chromatographed over silica gel using hexane : ethyl acetate (1:1) as eluent.

2-Ethyl-3,5-dimethylpyridine (2). Yield 85%. ¹H NMR (CDCl₃): δ 8.14 (1H, s, 6-H), 7.13 (1H, s, 4-H), 2.70 (2H, q, J = 7.5 Hz, CH_2CH_3), 2.20 (3H, s, Ar- CH_3), 2.18 (3H, s, Ar- CH_3), 1.20 (3H, t, J = 7.6 Hz, CH_2CH_3). ¹³C RMN (CDCl₃): δ 158.5, 146.8, 138.2, 130.1, 129.9, 28.1, 18.4, 17.7, 12.8.

2-Pentyl-3,5-dimethylpyridine (3). Yield: 84%. ¹H NMR (CDCl₃): δ 8.20 (1H, s, 6-H), 7.22 (1H, s, 4-H), 2.74 (2H, dd, $J_1 = 6.3$ Hz, $J_2 = 9.6$ Hz, 1'-Pen), 2.28 (3H, s, Ar-CH₃), 2.26 (3H, s, Ar-CH₃), 1.68 (2H, m, 2'-Pen), 1.38 (4H, m, 3',4'-Pen), 0.91 (3H, t, J = 7.0 Hz, 5'-Pen). ¹³C RMN (CDCl₃): δ 157.8, 146.9, 138.3, 130.1, 130.1, 35.2, 32.0, 28.7, 22.6, 18.6, 17.8, 14.1. Electrospray MS (micrOTOF Focus) m/z (%) 179.2 [(C₁₂H₁₉N) + 2]⁺ (28), 178.15928 [(C₁₂H₂₀N) requires 178.15903 (100)].

General procedures for the synthesis of pyridinium halides

The 1-alkyl halide (5 equivalents) was added dropwise to a solution of the 2-alkyl-3,5-dimethylpyridine in acetonitrile (5 mL per mmol of starting trialkylpyridine). The reaction mixture was stirred at 80 °C until completion. The reaction progress was followed by t.l.c. using silica gel 60 GF-254 aluminum sheets and Cl_2CH_2 : CH_3OH (95:5) as eluent. The mixture was heated under reduced pressure and the resulting IL was washed with ethyl ether (4 × 3 mL per mmol of starting trialkylpyridine). The remaining ethyl acetate was removed by heating under reduced pressure to afford the desired IL that was dried by heating at (373.15 to 383.15 K) and stirring under high vacuum (2 × 10⁻¹ Pa) for 48 h.

1-Hexyl-2,3,5-trimethylpyridinium iodide (4). Yield 99%. ¹H NMR (CDCl₃): δ 9.18 (1H, s, 6-H), 7.97 (1H, s, 4-H), 4.75 (2H, dd, $J_1 = 6.2$ Hz, $J_2 = 9.8$ Hz, NC H_2), 2.77 (3H, s, Ar-CH₃), 2.53 (3H, s, Ar-CH₃), 2.51(3H, s, Ar-CH₃), 1.91 (2H, m, NCH₂C H_2) 1.46 (2H, m, N(CH₂)₂C H_2) 1.32 (4H, m, N(CH₂)₃C H_2 C H_2) 0.86 (3H, t, J = 7.1 Hz, N(CH₂)₅C H_3). ¹³C NMR (CDCl₃): δ 150.5, 147.1, 142.8, 138.6, 136.4, 59.7, 31.2, 30.6, 26.2, 22.5, 20.7, 18.5, 17.5, 14.0. Electrospray MS (apex-Qe) m/z (%) 1206 [(C₁₄H₂₄N)₄ (I)₃ + 1]⁺ (5), 1205 [(C₁₄H₂₄N)₄ (I)₃]⁺ (9), 541 [(C₁₄H₂₄N)₂ (I) + 2]⁺ (3), 540 [(C₁₄H₂₄N)₂(I) + 1]⁺ (26), 539.28492 ([(C₁₄H₂₄N)₂(I)]⁺ requires 539.28567, 100), 207 [(C₁₄H₂₄N) + 1]⁺ (6), 206 [C₁₄H₂₄N]⁺ (49).

2-Ethyl-1-hexyl-3,5-dimethylpyridinium bromide (5). Yield 98%. ¹H NMR (CDCl₃): ¹H NMR (CDCl₃): δ 9.47 (1H, s, 6-H), 7.99 (1H, s, 4-H), 4.76 (2H, dd, $J_1 = 5.7$ Hz, $J_2 = 10.3$ Hz, NCH₂), 3.02 (2H, q, J = 7.6 Hz, 2-CH₂), 2.51 (3H, s, Ar-CH₃), 2.50 (3H, s, Ar-CH₃), 1.91 (2H, m, NCH₂CH₂), 1.45 (2H m, N(CH₂)₂CH₂), 1.28 (7H, m, N(CH₂)₂CH₂, 2-CH₂CH₃), 0.81 (3H, t, J = 7.0 Hz, N(CH₂)₅CH₃). ¹³C NMR (CDCl₃): δ 153.9, 147.2, 144.6, 136.9, 136.6, 57.9, 32.3, 31.2, 26.0, 22.7, 22.3, 19.2, 18.0, 13.9, 12.2. Electrospray MS (micrOTOF Focus) m/z (%) 522 [(C₁₅H₂₆N)₂ (⁸¹Br) + 1]⁺ (11), 521.32829 ([(C₁₅H₂₆N)₂ (⁸¹Br)]⁺ requires 521.32896, 34), 520 [(C₁₅H₂₆N)₂ (⁷⁹Br) + 1]⁺ (12), 519.32939 ([(C₁₅H₂₆N)₂ (⁷⁹Br)]⁺ requires 519.33084, 28), 221 [(C₁₅H₂₆N) + 1]⁺ (18), 220 [(C₁₅H₂₆N)]⁺ (100).

1-Ethyl-3,5-dimethyl-2-pentylpyridinium bromide (6). Yield 92%. ¹H NMR (CDCl₃): δ 9.63 (1H, s, 6-H), 7.97 (1H, s, 4-H), 4.86 (2H, q, J = 7.27 Hz, NCH₂), 2.94 (2H, dd, $J_1 = 9.45$ Hz, $J_1 = 7.11$ Hz, 1'-Pen), 2.52 (3H, s, Ar-CH₃), 2.49 (3H, s, Ar-CH₃), 1.63 (3H, t, J = 7.3 Hz, NCH₂CH₃), 1.56 (2H, m, 2'-Pen), 1.44 (2H, m, 3'-Pen), 1.34 (2H, m, 4'-Pen), 0.89 (1H, t, J = 7.2 Hz, 5'-Pen). ¹³C NMR (CDCl₃): δ 153.0, 147.2, 144.0, 137.2, 136.8, 53.5, 31.8, 29.2, 27.7, 22.2, 19.4, 18.0, 17.4, 13.8. Electrospray MS (micrOTOF Focus) m/z (%) 207 [(C₁₄H₂₄N + 1]⁺ (15), 206.19012 ([(C₁₄H₂₄N]⁺ requires 206.19033, 100).

1-Butyl-3,5-dimethyl-2-pentylpyridinium bromide (7). Yield 91%. ¹H NMR (CDCl₃): δ 9.64 (1H, s, 6-H), 7.96 (1H, s, 4-H), 4.80 (2H, dd, $J_1 = 6.0$ Hz, $J_2 = 9.9$ Hz, NCH₂), 2.92 (2H, dd, $J_1 = 5.8$ Hz, $J_2 = 10.7$ Hz, 1'-Pen), 2.52 (3H, s, Ar-CH₃), 2.50 (3H, s, Ar-CH₃), 1.97-1.87 (2H, m, NCH₂CH₂), 1.64-1.30 (m, 8H, N(CH₂)₂CH₂, 2',3',4'-Pen), 0.96 (3H, t, J = 7.3 Hz, N(CH₂)₃CH₃), 0.90 (3H, t, J = 7.2 Hz, 5'-Pen). ¹³C NMR (CDCl₃): δ 152.9, 147.2, 144.5, 137.1, 136.5, 57.6, 34.0, 31.8, 29.2, 27.7, 22.1, 19.7, 19.4, 18.0, 13.8, 13.6. Electrospray MS (micrOTOF Focus) m/z (%) 235 [(C₁₆H₂₈N) + 1]⁺ (17), 234.22137 ([(C₁₆H₂₈N)]⁺ requires 234.22163, 100).

1-Hexyl-3,5-dimethyl-2-pentylpyridinium bromide (8). Yield 85%. ¹H NMR (CDCl₃): δ 9.76 (1H, s, 6-H), 7.89 (1H, s, 4-H), 4.85 (2H, dd, $J_1 = 6.1$ Hz, $J_2 = 10.0$ Hz, NCH₂), 2.93 (2H, dd, $J_1 = 5.9$ Hz, $J_2 = 10.6$ Hz, 1'-Pen), 2.56 (3H, s, Ar-CH₃), 2.51 (3H, s, Ar-CH₃), 1.95 (2H, m, NCH₂CH₂), 1.61 (2H, m, 2'-Pen), 1.55–1.25 (10H, m, N(CH₂)₂CH₂CH₂CH₂, 2',3',4'-Pen), 0.90 (3H, t, J = 7.2 Hz, 5'-Pen), 0.84 (3H, dt, $J_1 = 3.7$ Hz, $J_2 = 7.1$ Hz, N(CH₂)₃CH₃). ¹³C NMR (CDCl₃): δ 152.9, 147.2, 144.4, 137.1, 136.5, 57.8, 32.1, 31.8, 31.2, 29.2, 27.6, 26.0, 22.4, 22.1, 19.4, 18.0, 13.9, 13.8. Electrospray MS (micrOTOF Focus) m/z (%) 263 [(C₁₈H₃₂N) + 1]⁺ (18), 262.25261 ([(C₁₈H₃₂N)]⁺ requires 262.25293, 100).

General procedures for the synthesis of pyridinium bis(trifluoromethanesulfonyl)imides

The tetraalkylpyridinium halide (21 mmol) was dissolved in water (20 mL) and treated with an aqueous solution of bis(trifluoromethane)sulfonimide lithium salt (6,64 g, 23 mmol) in water (20 mL). The obtained solution was stirred at rt for 10 min. The product was isolated by solvent extraction using CH_2Cl_2 (2 × 10 mL). The extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to yield the required product. The ILs obtained were dried by heating at (343.15 to 353.15 K) and stirring under high vacuum (2 × 10⁻¹ Pa) for 48 h.

1-Hexyl-2,3,5-trimethylpyridinium bis(trifluoromethanesul-fonyl)imide (9). Yield 99%. ¹H NMR (CDCl₃): δ 8.29 (1H, s, 6-H), 7.96 (1H, s, 4-H), 4.47 (2H, dd, $J_1 = 5.9$ Hz, $J_2 = 10.3$ Hz, NCH₂), 2.69 (3H, s, Ar-CH₃), 2.50 (3H, s, Ar-CH₃), 2.46 (3H, s, Ar-CH₃), 1.88 (2H, m NCH₂CH₂), 1.43 (2H, m N(CH₂)₂CH₂), 1.33 (4H, m, N(CH₂)₃CH₂CH₂), 0.88 (3H, t, J = 7.1 Hz, N(CH₂)₅CH₃). ¹³C NMR (CDCl₃): δ 150.6, 146.7, 142.2, 138.6, 136.3, 119.77 (q, $J_{CF} = 321.4$ Hz), 59.2, 31.0, 30.4, 25.9, 22.3, 19.9, 17.7, 16.1, 13.8. ¹⁹F RMN (CDCl₃): δ –78.92. Electrospray MS (apex-Qe) m/z (%) 693.30 [(C₁₄H₂₄N)₂ (C₂F₆NO₄S₂) + 1]⁺ (4), 692.29730 ([(C₁₄H₂₄N) + 1]⁺ (12), 206.19 [(C₁₄H₂₄N)]⁺ (100).

2-Ethyl-1-hexyl-3,5-dimethylpyridinium bis(trifluoromethanesulfonyl)imide (10). Yield 97%. ¹H NMR (CDCl₃): δ 8.36 (1H, s, 6-H), 7.98 (1H, s, 4-H), 4.49 (2H, dd, $J_1 = 6.1$ Hz, $J_2 =$ 10.1 Hz, NCH₂), 3.05 (2H, q, J = 7.6 Hz, 2-CH₂), 2.54 (3H, s, Ar-CH₃), 2.49 (3H, s, Ar-CH₃), 1.93 (2H, m, NCH₂CH₂), 1.46 (2H, m, N(CH₂)₂CH₂), 1.35 (7H, m, N(CH₂)₃CH₂CH₂, 2-CH₂CH₃), 0.91 (3H, t, J = 6.9 Hz, N(CH₂)₅CH₃). ¹³C NMR (CDCl₃): δ 154.6, 147.5, 142.7, 137.8, 136.7, 119.8 (q, $J_{CF} = 321.4$ Hz), 58.4, 31.8, 31.0, 26.0, 22.7, 22.3, 19.0, 17.7, 13.8, 11.7. ¹⁹F RMN (CDCl₃): δ -78.92. Electrospray MS (micrOTOF Focus) m/z(%) 722 [(C₁₅H₂₆N)₂ (C₂F₆NO₄S₂) + 2]⁺ (10), 721 [(C₁₅H₂₆N)₂ (C₂F₆NO₄S₂) + 1]⁺ (22), 720.32735 ([(C₁₅H₂₆N)₂ (C₂F₆NO₄S₂)]⁺ requires 720.32979, 57), 637 [(C₂₆H₃₉F₆N₃O₄S₂) + 2]⁺ (2), 636 [(C₂₆H₃₉F₆N₃O₄S₂) + 1]⁺ (10), 221 [(C₁₅H₂₆N) + 1]⁺ (18), 220 [(C₁₅H₂₆N)]⁺ (100).

1-Ethyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl)imide (11). Yield 89%. ¹H NMR (CDCl₃): δ 8.39 (1H, s, 6-H), 7.97 (1H, s, 4-H), 4.58 (2H, q, *J* = 7.3 Hz, NC*H*₂), 2.98 (2H, dd, *J*₁ = 7.2 Hz, *J*₂ = 9.5 Hz, 1'-Pen), 2.53 (3H, s, Ar-CH₃), 2.49 (3H, s, Ar-CH₃), 1.64 (5H, m, NCH₂C*H*₃, 2'-Pen), 1.51–1.35 (4H, m, 2',3'-Pen), 0.95 (3H, t, J = 7.2 Hz, 5'-Pen). ¹³C NMR (CDCl₃): δ 153.8, 147.5, 142.3, 138.0, 136.9, 119.81 (q, $J_{C-F} = 321.5$ Hz), 53.7, 31.8, 29.3, 27.5, 22.1, 19.1, 17.7, 16.7, 13.8. ¹⁹F RMN (CDCl₃): δ –78.94. Electrospray MS (micrOTOF Focus) m/z (%) 692.29877 ([(C₁₄H₂₄N)₂ (C₂F₆NO₄S₂)]⁺ requires 692.29849, 2), 207 [(C₁₄H₂₄N + 1]⁺ (19), 206.19070 ([(C₁₄H₂₄N]⁺ requires 206.19033, 100).

1-Butyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl)imide (12). Yield 95%. ¹H NMR (CDCl₃): δ 8.38 (1H, s, 6-H), 7.97 (1H, s, 4-H), 4.48 (2H, dd, J₁ = 6.2 Hz, J₂ = 10.0 Hz, NCH₂), 2.96 (2H, dd, J₁ = 5.8 Hz, J₂ = 10.9 Hz, 1'-Pen), 2.53 (3H, s, Ar-CH₃), 2.49 (3H, s, Ar-CH₃), 1.92 (2H, tt, J₁ = 6.3 Hz, J₂ = 9.3 Hz, NCH₂CH₂), 1.64 (2H, m, 2'-Pen), 1.50 (4H, m, N(CH₂)₂CH₂, 3'-Pen), 1.41 (2H, m, 4'-Pen), 1.02 (3H, t, J = 7.3 Hz, N(CH₂)₃CH₃), 0.95 (3H, t, J = 7.2 Hz, 5'-Pen). ¹³C NMR (CDCl₃): δ 153.7, 147.4, 142.7, 137.9, 136.7, 119.81 (q, J_{C-F} = 321.4 Hz), 58.2, 33.6, 31.8, 29.3, 27.4, 22.1, 19.7, 19.2, 17.7, 13.8, 13.4. ¹⁹F RMN (CDCl₃): δ -78.92. Electrospray MS (micrOTOF Focus) m/z (%) 749 [(C₁₆H₂₈N)₂ (C₂F₆NO₄S₂) + 1]⁺ (2), 748.35789 ([(C₁₆H₂₈N)₂ (C₂F₆NO₄S₂)]⁺ requires 748.36209, 5), 236 [(C₁₆H₂₈N) + 2]⁺ (2), 235 [(C₁₆H₂₈N) + 1]⁺ (32), 234.22145 ([(C₁₆H₂₈N)]⁺ requires 234.22163, 100).

1-Hexyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl)imide (13). Yield 93%. ¹H NMR (CDCl₃): δ 8.41 (1H, s, 6-H), 7.96 (1H, s, 4-H), 4.49 (2H, dd, $J_1 = 5.9$ Hz, $J_2 = 10.4$ Hz, NC H_2), 2.96 (2H, dd, $J_1 = 5.8$ Hz, $J_2 = 11.0$ Hz, 1'-Pen), 2.54 (3H, s, Ar-CH₃), 2.50 (3H, s, Ar-CH₃), 1.93 (2H, m, NCH₂C H_2 C H_2 C H_2 , 3',4'-Pen), 0.97 (3H, t, J = 7.2 Hz, 5'-Pen), 0.92 (3H, t, J = 6.9 Hz, N(CH₂)₅C H_3). ¹³C NMR (CDCl₃): δ 153.7, 147.5, 142.6, 137.9, 136.6, 119.81 (q, $J_{CF} = 321.6$ Hz), 58.4, 31.8, 31.7, 31.0, 29.3, 27.4, 26.0, 22.3, 22.1, 19.1, 17.7, 13.8, 13.7. ¹⁹F RMN (CDCl₃): $\delta -78.87$. Electrospray MS (micrOTOF Focus) m/z (%) 805 [(C₁₈H₃₂N)₂ (C₂F₆NO₄S₂) + 1]⁺ (2), 804.41966 ([(C₁₈H₃₂N)₂ (C₂F₆NO₄S₂)]⁺ requires 804.42369, 4), 264 [(C₁₈H₃₂N) + 2]⁺ (2), 263 [(C₁₈H₃₂N) + 1]⁺ (32), 262 [(C₁₈H₃₂N)]⁺ (100).

Liquid-liquid equilibrium

The experimental LLE for the two studied systems were carried out at T = 298.15 K and atmospheric pressure. For the experimental determination of tie-lines, immiscible mixtures of the three components (or only two components, in the case of binary tie-lines for the pair heptane + ionic liquid and thiophene + ionic liquid) were prepared. Heptane (Fluka, ≥99.5%) and thiophene (Sigma-Aldrich, ACS reagent, >99%), were used as received, without further purification. The mixtures were placed into 10 mL round bottomed flasks together with a magnetic stirring bar under argon atmosphere. Flasks were sealed to avoid losses by evaporation or water absorption from the atmosphere. The temperature within the flask was kept at a constant 25.0 °C by means of an IKA RCT Basic thermostatic water bath. The mixtures were first magnetically stirred for 4 h, and then allowed to settle down overnight to achieve phase separation. Samples of both layers were withdrawn using syringes connected to long stainless steel needles, without disturbance of the interface.

Composition of the equilibrium phases was determined by applying ¹H-NMR spectroscopy. The molar fraction of each component was calculated by the integration of some selected peaks corresponding to the heptane methyl group and the pyridinium and thiophene aromatic protons. The accuracy of the method was investigated. For each study system several miscible samples were prepared by weighting with a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \times 10^{-4}$ g. Their compositions were then calculated by ¹H-NMR as described above. The upper phase error was determined by preparing miscible samples of the binary system heptane/thiophene, while the lower phase error was determined by preparing miscible samples of the ternary system, all of them at the vicinity of the tie-lines. The largest deviation between the real and calculated compositions was 0.013 for the binary system, 0.018 for the $[{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$ system and 0.008 for the $[^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$ system.

All the experiments were performed with a 400 MHz Bruker ARX spectrometer using CDCl₃ as a solvent.

Due to the small amount of IL available, the determination of several tie-lines was carried out using recovered ionic liquid. The recovery of the ionic liquid was performed under vacuum and moderate temperature, and then its purity was confirmed by ¹H NMR spectroscopy. Moreover, in order to confirm the purity of the recovered IL, the tie-lines of the binary systems were repeated using new and recovered IL. The obtained results were similar with both ILs, showing a maximum difference of ± 0.003 in mole fraction.

Conclusions

In this work a series of new ILs derived from pyridinium cation substituted with different alkyl chains were synthesized, and its sulfur-removal capacity were tested.

The polyalkylated pyridines used as starting materials were prepared by selective metalation of 2,3,5-collidine on 2-methyl group and subsequent alkylation. With this methodology, we obtained a procedure for the selective metalation of polymethylated pyridines, which allows the introduction of different alkyl groups in position 2 with high yields.

Liquid–liquid equilibria for the ternary systems (heptane + thiophene + [${}^{1}E^{3}M^{5}M^{5}PPy$][NTf₂]) and (heptane + thiophene + [${}^{1}B^{3}M^{5}M^{2}PPy$][NTf₂]) were determined at *T* = 298.15 K and atmospheric pressure. In order to evaluate the extraction capacity of these ILs as solvents on a desulfurization process *via* liquid extraction, the experimental LLE compositions, selectivity and solute distribution ratio, were calculated.

All studied systems present high values of selectivity and solute distribution ratio, which implies that both $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$ and $[{}^{1}B^{3}M^{5}M^{2}PPy][NTf_{2}]$, could be used as solvents for the extraction of thiophene from heptane. Nevertheless, it is observed that an increase of the cation alkyl chain length leads to lower selectivity values, achieving a higher selectivity when using $[{}^{1}E^{3}M^{5}M^{2}PPy][NTf_{2}]$.

The β and S values obtained for these ionic liquids are higher than those of [¹H³M⁵MPy][NTf₂], implying a greater extractive ability when having substituents in position 2 of the cationic ring.

The NRTL thermodynamic model was satisfactorily applied to correlate the experimental LLE data. The best adjustment was obtained when fixing $\alpha_{ij} = 0.3$. The correlated tie-lines fitted better at low thiophene concentrations.

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