

Full Research Paper

On the Extraction of Aromatic Compounds from Hydrocarbons by Imidazolium Ionic Liquids

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Received: 12 June 2007; in Revised Form: 22 June 2007 / Accepted: 22 June 2007 /

Published: 2 July 2007

Abstract: The liquid-liquid equilibrium for the ternary system formed by *n*-octane and aromatic (alkylbenzenes) and heteroaromatic compounds (nitrogen and sulfur containing heterocycles) and 1-alkyl-3-methylimidazolium ionic liquids (ILs) associated with various anions has been investigated. The selectivity on the extraction of a specific aromatic compound is influenced by anion volume, hydrogen bond strength between the anion and the imidazolium cation and the length of the 1-methyl-3-alkylimidazolium alkyl side chain. The interaction of alkylbenzenes and sulfur heterocycles with the IL is preferentially through CH- π hydrogen bonds and the quantity of these aromatics in the IL phase decreases with the increase of the steric hindrance imposed by the substituents on the aromatic nucleus. In the case of nitrogen heterocycles the interaction occurs preferentially through N(heteroaromatic)-H(imidazolium) hydrogen bonds and the extraction process is largely controlled by the nitrogen heterocycle pKa. Competitive extraction experiments suggest that benzene, pyridine and dibenzothiophene do not compete for the same hydrogen bond sites of the IL.

Keywords: ionic liquid, extraction, fuel, aromatics, hydrogen bonds.

1. Introduction

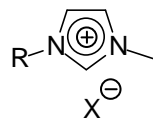
The use of ionic liquids as media for liquid–liquid extractions is growing rapidly, since their hydrophobic or hydrophilic nature can be modulated by modifications in both cation and anion [1-11]. They have been used in the separation of variety substances such as metallic ions, organic molecules, fuel desulfurization and gas separation using different various ionic liquids [12].

The selective extraction of benzene and alkyl-benzenes from *n*-heptane and *n*-octane (benzene/hexane, toluene/heptane, ethylbenzene/octane and *m*-xylene/*n*-octane) by pyridinium based ionic liquids increases at lower concentrations [13-15]. Various ILs have also been tested for the extraction of sulfur compounds from *n*-dodecane (model of diesel oil) [16], model fuel and commercial gasoline [17-21].

The vast majority of the studies reported so far are concentrated on the extraction properties displayed by various imidazolium or pyridinium ionic liquids on mixtures of benzene or toluene and hydrocarbons (heptane, *n*-octane and cyclohexane) [22-24]. Moreover, the tie line compositions between different imidazolium-based ionic liquids, aromatic hydrocarbons (benzene, toluene) and alkanes (heptane, dodecane, hexadecane) have been determined [25,26]. Alternative methods of deep desulfurization, including oxidative desulfurization in liquid–liquid systems using ionic liquids, have been investigated [27].

The aromatic extraction properties of ionic liquids – in particular those based on 1,3-dialkylimidazolium cations – are most probable related to their peculiar structural organization. Indeed, pure 1,3-dialkylimidazolium ILs can be described as hydrogen-bonded polymeric supramolecules of the type $[(\text{DAI})_x(\text{X})_{x-n}]^{n+}[(\text{DAI})_{x-n}(\text{X})_x]^{n-}$ where DAI is the 1,3-dialkylimidazolium cation and X is the anion [28,29]. This structural pattern is a general trend for both the solid and the liquid phase and is apparently maintained to a great extent even in the gas phase [30-33]. The introduction of other molecules and macromolecules occurs with a disruption of the hydrogen bond network, generating nano-structures with polar and non-polar regions where inclusion-type compounds can be formed [34]. This polymeric nature is apparently maintained to a great extent when they are mixed with other substances. 1,3-Dialkylimidazolium ILs/aromatic mixtures form liquid clathrates and in the case of a hexafluorophosphate of 1,3-dimethylimidazolium MMI.PF₆/benzene mixture the inclusion compound $[(\text{MMI.PF}_6)_2(\text{benzene})]_n$ could be trapped and its X-ray structure determined [35]. The stabilization of this process is mainly due to the stereoelectronic effects provided by the nano-structures of the type $[(\text{DAI})_x(\text{X})_{x-n}]^{n+}[(\text{DAI})_{x-n}(\text{X})_x]^{n-}$. Therefore the proper combination of imidazolium cations and anions can lead to highly selective materials for the extraction of aromatic compounds. Moreover, different types of hydrogen bonds may be operative depending on the structural and electronic properties of both the IL and the aromatic compounds. For example, simple aromatic compounds such as benzene interacts via CH (imidazolium)- π bonds with the imidazolium cations whereas those containing hydrogen bond acceptor groups such as pyridine the interaction is through N-H-(imidazolium) hydrogen bonds. We now report the electronic and steric effects of both ILs and aromatic compounds on the extraction of aromatic and heteroaromatic compounds present in aliphatic hydrocarbons. Table 1 schematically presents the main ILs' structures used in this work and their respective acronyms used herein.

Table 1. Structure, names and acronyms of the ILs reported in this work, according to the scheme below.



R	X	IL Name	Acronym
Et	N(CF ₃ SO ₂) ₂	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	EMI.N(Tf) ₂
ⁿ Pr	N(CF ₃ SO ₂) ₂	1- <i>n</i> -propyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	PMI.N(Tf) ₂
ⁿ Bu	BF ₄	1- <i>n</i> -butyl-3-methylimidazolium tetrafluoroborate	BMI.BF ₄
ⁿ Bu	N(CF ₃ SO ₂) ₂	1- <i>n</i> -butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	BMI.N(Tf) ₂
ⁿ Bu	PF ₆	1- <i>n</i> -butyl-3-methylimidazolium hexafluorophosphate	BMI.PF ₆
ⁿ Bu	CF ₃ SO ₃	1- <i>n</i> -butyl-3-methylimidazolium trifluoromethanesulfonate	BMI.CF ₃ SO ₃
ⁿ Bu	PF ₃ (CF ₂ CF ₃) ₃	1- <i>n</i> -butyl-3-methylimidazolium trifluorotris(pentafluoroethyl)phosphate	BMI.FAP
ⁿ Hex	N(CF ₃ SO ₂) ₂	1- <i>n</i> -hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	HMI.N(Tf) ₂
ⁿ Dec	N(CF ₃ SO ₂) ₂	1- <i>n</i> -decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	DMI.N(Tf) ₂

2. Results and Discussion

First we have tested the influence of the ionic liquid on the extraction of benzene present in *n*-octane (10 wt %) with 1:1 mol/mol ionic liquid/benzene ratio and the results obtained with a series of imidazolium cation associated with various anions are summarized in Figure 1.

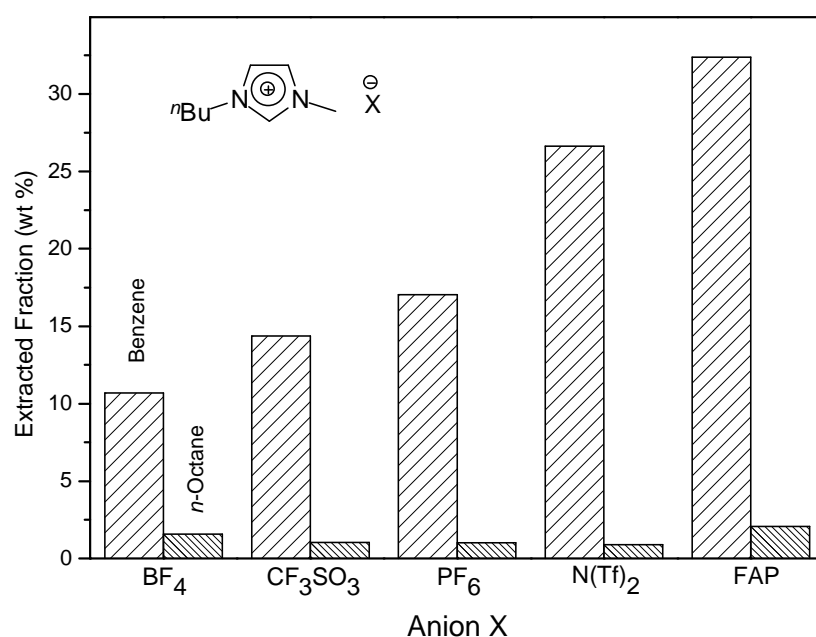


Figure 1. Extracted fraction of benzene and *n*-octane from a 10 wt % benzene solution in *n*-octane (LI:benzene ratio of 1:1, mol/mol) by 1-*n*-butyl-3-methylimidazolium based ILs.

It is clear from the data on Figure 1 that the quantity of benzene extraction depends on the type of the anion and increases in the order $\text{BF}_4 < \text{CF}_3\text{SO}_3 < \text{PF}_6 < \text{N}(\text{Tf})_2 < \text{FAP}$. In the case of the fluorinated anions the benzene extraction increases with the increase of the van der Waals volume of the anion that are *ca.* 39 \AA^3 , 52 \AA^3 , 342 \AA^3 and 484 \AA^3 for BF_4 , PF_6 , $\text{N}(\text{Tf})_2$ and FAP , respectively [36]. Moreover, the quantity of benzene extraction is also related with the strength of C2-H imidazolium hydrogen bond with the anion that follows $\text{BF}_4 > \text{CF}_3\text{SO}_3 > \text{PF}_6 > \text{N}(\text{Tf})_2 > \text{FAP}$ as determined by competitive ESI-MS experiments [32,37,38]. These results can be rationalized assuming that the formation of benzene inclusion type compounds is related with the availability of the C2-H of the imidazolium unity to interact with benzene via $\text{CH} \cdots \pi$ bonds [31] i.e. the facility that benzene has to disrupt the supramolecular clusters formed between the cations and anions of the IL. Therefore, decreasing the strength of C2-H hydrogen bond with the anion increases the benzene extraction capacity of the IL. Indeed, the interaction between benzene and the IL is preferentially via $\text{CH} \cdots \pi$ interactions as observed by the high field NMR shift of the C2-H hydrogen with the increase of benzene concentration in $\text{BML.N}(\text{Tf})_2$. The C2-H of the imidazolium cation exhibits the greatest shielding (up to -0.5 ppm), indicating the existence of $\text{CH} \cdots \pi$ of the cation with benzene (Figure 2).

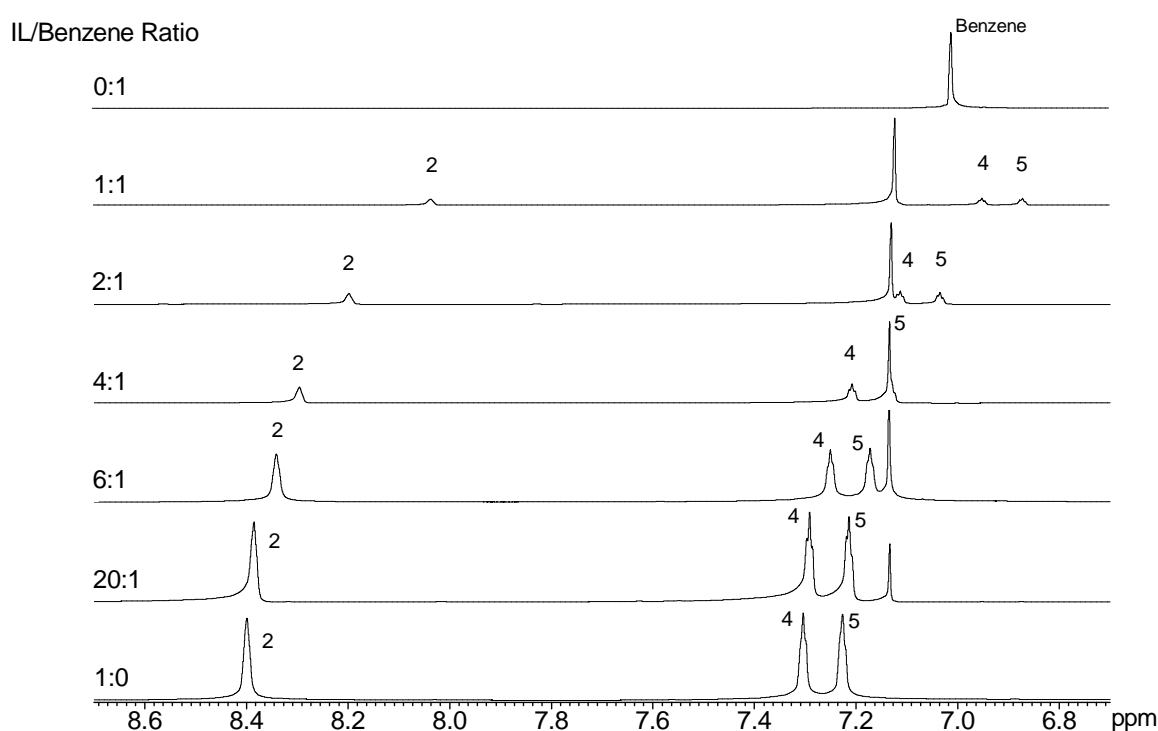


Figure 2. ^1H NMR spectra of different compositions of $\text{BML.N}(\text{Tf})_2$ and benzene at $25 \text{ }^\circ\text{C}$ evidencing the signals shifts due to the interaction between the hydrogens of the IL ring and those of the aromatic ring of benzene.

Notice that the equilibrium is attained after *ca.* 20 min in the extraction of benzene in *n*-octane by $\text{BML.N}(\text{Tf})_2$ (Figure 3a). Moreover, as shown in Figure 3b there is an ideal molar ratio between IL and benzene (IL:benzene = 50:1 mol/mol) in order to attain maximum benzene extraction from the mixture.

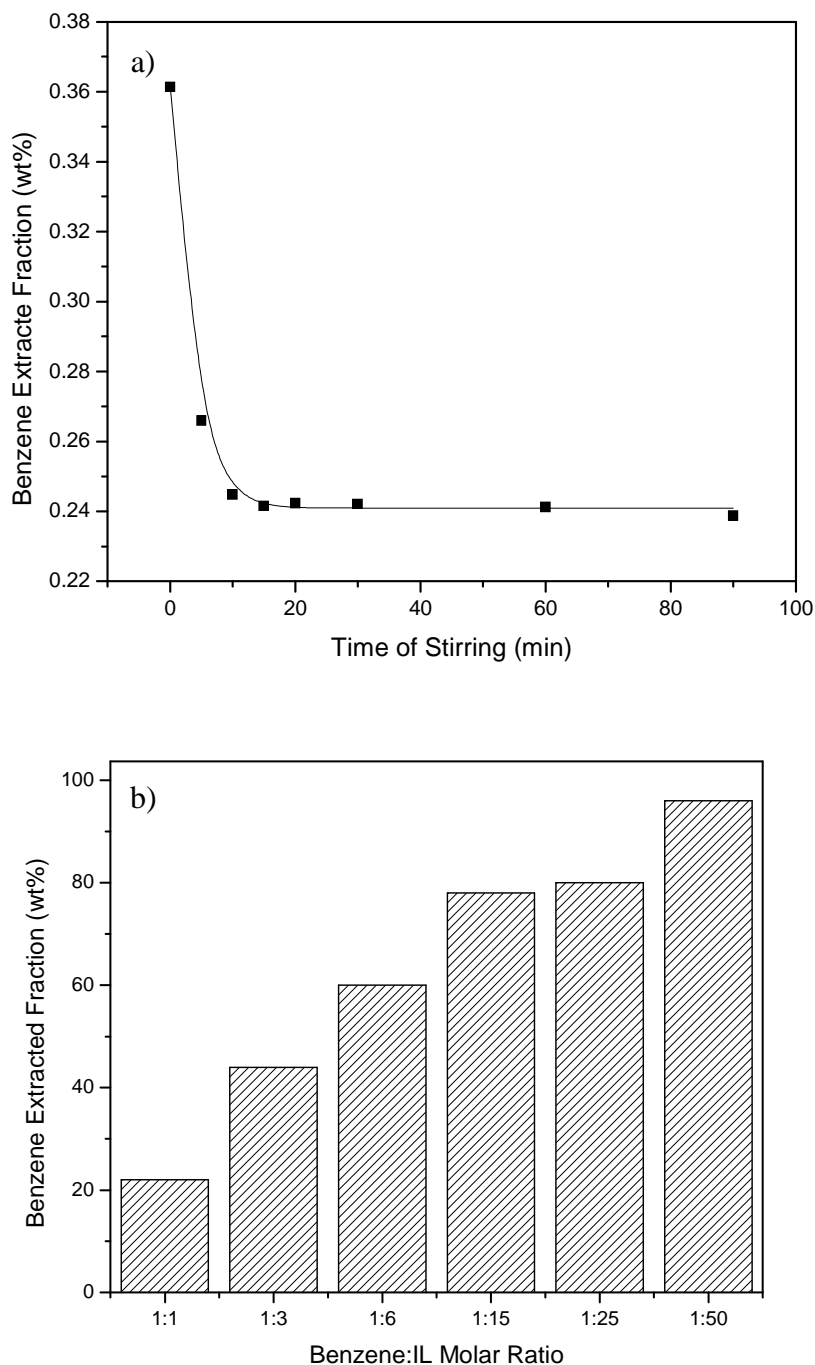


Figure 3. (a) Content of benzene in the organic phase observed after different extraction times, and (b) the extracted fraction of benzene from different ratios of benzene and BMLN(Tf)₂.

The extraction process is also quite sensitive to stereo-electronic effects imposed by the substituents on the *N*-alkyl side chain of the 1-methylimidazolium cation (Figure 4). Indeed, the quantity of benzene extraction [39] increases with the increase of the numbers of the carbons of the *N*-alkyl side chain (from ethyl to *n*-decyl). However, there is also an increase on the *n*-octane content on the ionic liquid phase (from 1 wt % in EMLN(Tf)₂ to 6 wt % in DMLN(Tf)₂ and therefore a reduction on the extraction benzene selectivity from the mixture [40] (from 20:1 in EMLN(Tf)₂ to 35:6 in DMLN(Tf)₂). The

increase of *n*-octane in the ionic liquid phase is much probably related to possibility of van der Waals interactions of this alkane with *N*-alkyl chains of the imidazolium ring [41].

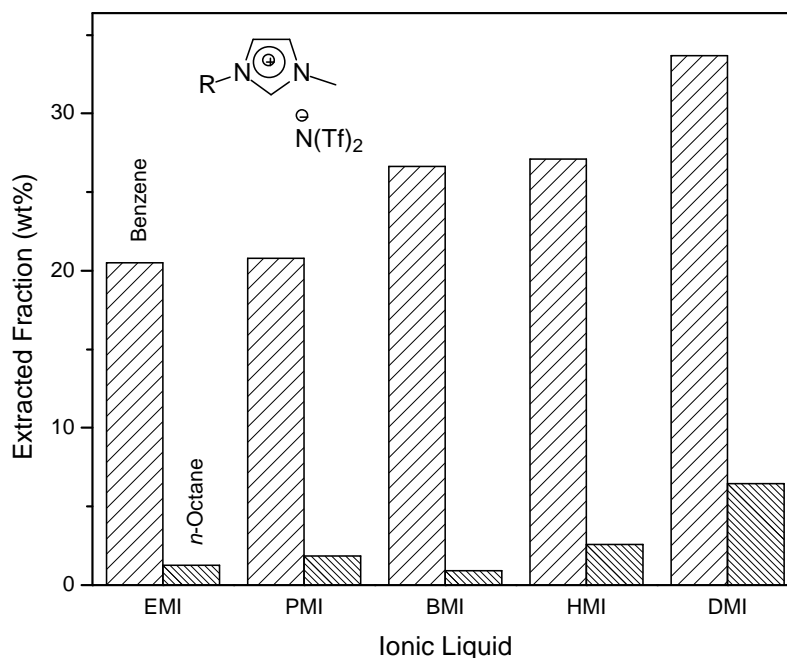


Figure 4. Benzene and *n*-octane extracted fractions from a model fuel (10 wt % of benzene in *n*-octane) by dialkyl imidazolium ILs (IL:benzene ratio of 1:1, mol/mol; 1 ml of IL) with different length side chains.

Moreover, the increase of the *N*-alkylimidazolium side chains increases in size the volume of the channels formed by the interaction of the imidazolium cations with anions and thus facilitates the accommodation of the included benzene molecules.

The liquid-liquid phase diagram of BMI.N(Tf)₂/benzene/*n*-octane at 25 °C was built to better understand the solubility capacity of benzene from *n*-octane by BMI.N(Tf)₂, and is presented in Figure 5 in a right angle triangle.

The methodology used to build the diagram is based on the preparation of biphasic mixtures of the three components, stirring for 20 minutes followed by separation of the upper phase from the lower phase, determination of the mass and composition (via GC analysis) of the upper phase, and finally, the determination of the mass and composition of the lower phase by component mass balance. The IL content in the upper phase (raffinate) was found to be negligible, in such a way that the raffinate composition line is located over the triangle diagonal, where the IL fraction is zero. The upper phase composition line is indicated in the main chart (Figure 5, right side chart). The left chart shown in Figure 6 indicates the relation between the benzene fractions in the lower and upper phases, and the chart-auxiliary diagonal.

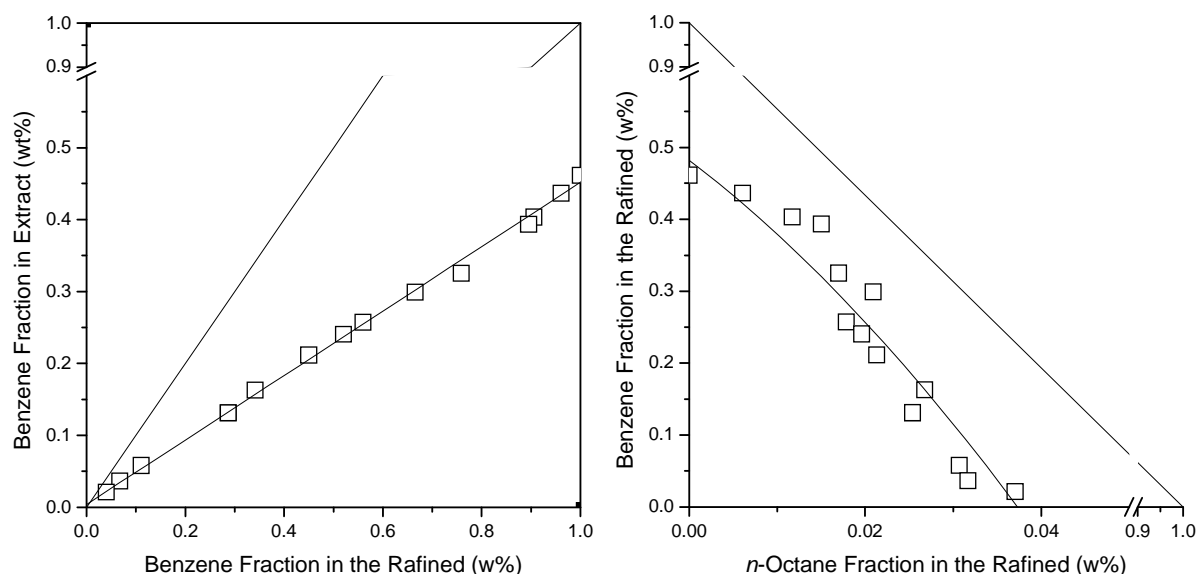


Figure 5. Liquid-liquid phase diagram of BMI.N(Tf)₂/benzene/*n*-octane at 25 °C in right triangle shape. The main chart is shown at right evidencing the extract composition line which divides the chart into the single (under that line) and two phases (over that line) regions. The raffinate composition line is located over the triangle diagonal, since the amount of ionic liquid can be neglected therein. The left chart relates the composition of benzene in the extract and in the raffinate.

Dramatic steric effects are also observed in the extraction process of mono and dialkyl substituted benzenes dissolved in *n*-octane by BMI.N(Tf)₂ (Figure 6). Therefore the extraction of benzene derivatives decreases with the increase of the size of the benzene alkyl side chains (from 24 wt% for benzene to 4 wt% for iso-butylbenzene) under the same extraction conditions.

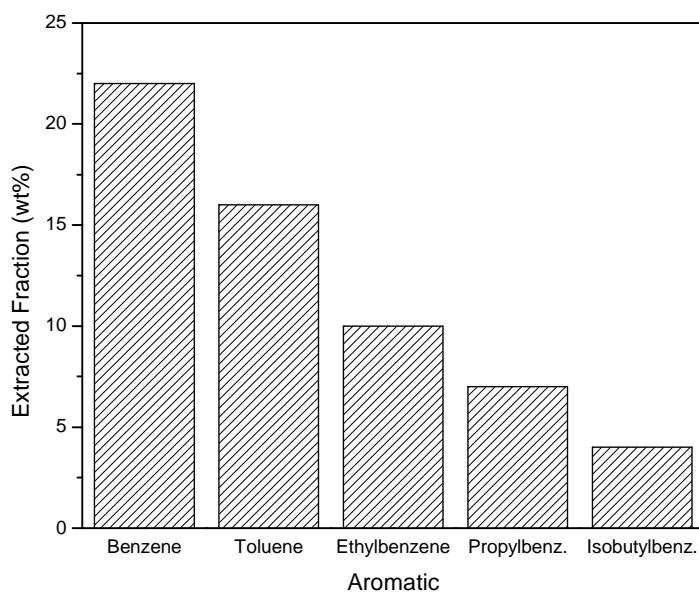


Figure 6. Effect of the alkyl substituents of the benzene ring on the extraction of aromatic compounds from *n*-octane (10 wt % solution of benzene in *n*-octane) by BMI.N(Tf)₂ (IL:benzene ratio of 1:1, mol/mol; 1 ml of IL).

The extraction of sulfur containing aromatic compounds such as 2,5-dimethylthiophene, thiophene, benzothiophene and dibenzothiophene (1 wt %) present in *n*-octane follows the same trend observed by benzene derivatives (Figure 7a). The interaction of these sulfur compounds with the ionic liquid is through CH--- π bonds and the quantity of sulfur compounds extraction increases with the increase of the π -density and decreases with the degree of alkyl substituents as already observed in the extraction procedures by 1-*n*-butyl-3-methylimidazolium *n*-octylsulfate and 1-ethyl-3-methylimidazolium ethylsulfate IIs [16].

The ionic liquid BMI.N(Tf)₂ is also quite effective for the extraction of nitrogen containing compounds such as 7,8-benzo[H]quinoline, pyridine, quinoline and 8-methylquinoline from *n*-octane. (1 wt %) (Figure 7b). In these cases the affinity of the IL with the nitrogen compounds is related to its pKa. The quantity of the nitrogens compounds present in the IL phase increase with the increase of the pKa. In these cases the interaction of the ionic liquid with the *N*-heterocycles is through C-H---N(*N*-heterocycles) bonds as opposed to the *S*-heterocycles and alkyl-benzenes that occurs through CH--- π interactions.

We have also performed the extractions of benzene (10 wt % in *n*-octane), DBT (1 wt % in *n*-octane) and pyridine (1 wt % in *n*-octane) by BMI.N(Tf)₂ in three separated experiments and again in a mixture containing the same 10 wt % of benzene, 1 wt % of DBT and 1 wt % of pyridine in *n*-octane. The results presented in Figure 8 reveal that the extraction amount of those contaminants are equal either when mixed and isolated from the others, suggesting that aromatic hydrocarbons, *S*- and *N*-heterocycles occupy different sites in the IL structure and do not compete with each other under those concentrations.

In summary we have shown that aromatic compound extraction capacity of 1-alkyl-3-methylimidazolium IIs increases with the anion volume and decreases with the increase of the hydrogen bond strength between the anion and the imidazolium cation. The increase on the length of the imidazolium alkyl side increases the concentration of aromatics in the IL phase but reduces the selectivity. The CH- π hydrogen bonds are preferential in the interaction of alkylbenzenes and sulfur heterocycles with the IL. The quantity of these aromatics in the IL phase decreases with the increase of the steric hindrance imposed by the substituents on the aromatic nucleus. In the case of nitrogen heterocycles the interaction occurs preferentially through N(heteroaromatic)-H(imidazolium) hydrogen bonds and the extraction process is largely controlled by the nitrogen heterocycle pKa. Benzene, pyridine and dibenzothiophene do not compete for the same hydrogen bond sites of the IL in molar ratio > 3. The use of these ionic liquids as materials for gas separation, purification, capture and storage are currently under investigation in our laboratories.

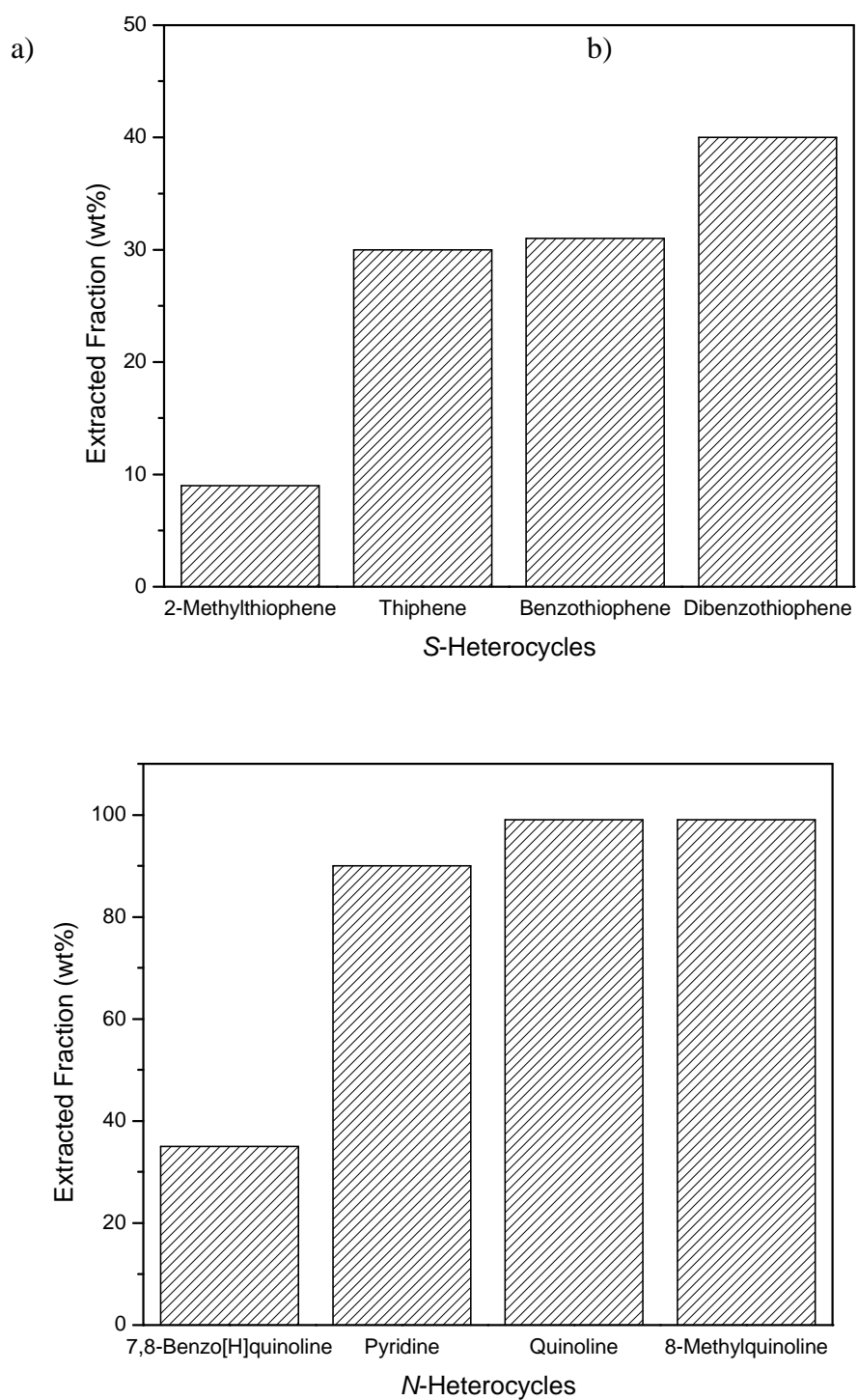


Figure 7. Extracted fractions of (a) *S*- and (b) *N*-heterocycles from a 1 wt % solution in *n*-octane.

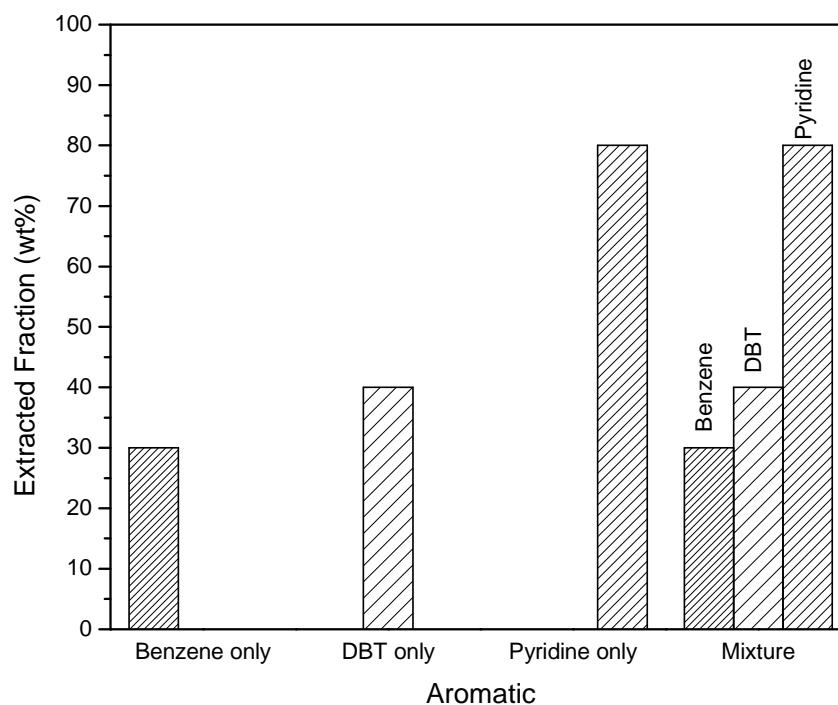


Figure 8. Extraction of benzene (10 wt %), dibenzothiophene (1 wt %) and pyridine (1 wt %) from *n*-octane (a) in separated solutions and (b) in a solution containing all three contaminants by BMI.N(Tf)₂, (IL:benzene= 1:1 mol/mol, DBT:IL = 1:10 mol/mol, pyridine:IL = 1:10 mol/mol; using 1 ml of IL).

3. Experimental Section

All solvents were dried with suitable drying agents and distilled under argon prior to use. All other chemicals were purchased from commercial sources (Acros or Aldrich) and used without further purification. All ILs have been prepared as previously described [42]. GC analyses were performed on an Agilent 6820 gas chromatograph equipped with a 30 meters capillary column HP-5, all products were resolved within a 60 °C isotherm at 10 psi pressure on the column head. ¹H-NMR spectra of the ILs were performed on a Varian XL-300 MHz using a D₂O capillary tube as reference.

Ternary diagram BMI.N(Tf)₂/benzene/*n*-octane. Liquid-liquid biphasic mixtures were prepared from known amounts of those three components, and stirred for 20 minutes. The upper phase (raffinate) was removed and its mass and compositions determined by GC. No IL was detected in the upper phase, even in larger scale experiments. The composition of the lower phase was determined by mass balance. All bench procedure was performed at 25 °C.

Extraction of aromatic hydrocarbons from *n*-octane by ILs. 10 wt % solution of benzene in *n*-octane was stirred with the IL (IL:benzene = 1:1 mol/mol) for 20 minutes at 25 °C. Compositions of the lower and upper phases were determined as described above.

Extraction of *S*- and *N*-heterocycles from *n*-octane by ILs. 1 wt % solution of benzene in *n*-octane was stirred with the IL (IL:benzene = 1:1 mol/mol) for 20 minutes at 25 °C. Compositions of the lower and upper phases were determined as described above.

Acknowledgements

Thanks are due to PETROBRAS and CNPq for partial financial support and to CAPES for scholarships.

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