



# Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy][Tf<sub>2</sub>N] and [emim][DCA] ionic liquids



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## ARTICLE INFO

### Article history:

Received 17 December 2014

Received in revised form 20 February 2015

Accepted 13 March 2015

Available online 8 April 2015

### Keywords:

Liquid–liquid extraction

Dearomatization

Ionic liquids

Pyrolysis gasoline

Simulation of a countercurrent column

## ABSTRACT

In Europe and Japan, benzene, toluene, and xylenes (BTX) are usually obtained by liquid–liquid extraction from pyrolysis gasolines using organic solvents such as sulfolane. In the last few years, ionic liquids (ILs) have been studied as potential substitutes of conventional solvents in the extraction of BTX from alkanes. In this paper, we have studied the dearomatization of pyrolysis gasolines obtained by mild and severe cracking using the binary IL mixture composed of the 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf<sub>2</sub>N]) and the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) and also employing sulfolane to compare the performance of both extraction solvents. To choose the most appropriate conditions of temperature and solvent to feed ratio to perform the extraction of BTX from pyrolysis gasolines, several extractive properties have been estimated from the experimental results employing the IL mixture and sulfolane. Simulations of countercurrent extraction columns in the dearomatization of both pyrolysis gasolines have also been made using the Kremser equation. The dearomatization of pyrolysis gasolines by the {[4empy][Tf<sub>2</sub>N] + [emim][DCA]} IL mixture would require a higher number of equilibrium stages in the extractor than that employing sulfolane. By contrast, the purity of extracted aromatics would be substantially greater using the IL-based solvent, simplifying the subsequent purification of the BTX.

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## 1. Introduction

Benzene, toluene, and xylenes (BTX) are mainly obtained from pyrolysis and reformer gasolines and coke oven benzole. In the USA, reformer gasoline is the major raw material for BTX, whereas the pyrolysis gasoline is the most important source of aromatics in Japan and Europe [1]. Recovery of aromatics is performed by liquid–liquid extraction, the UOP Sulfolane Process being the most widely used method at industrial scale [2,3]. However, the Sulfolane Process has several drawbacks such as the high energy consumption in the solvent regeneration and the need to recover the sulfolane dissolved in the raffinate stream [4].

ILs have been extensively studied in the dearomatization, denitrogenation, and desulfuration of liquid fuels, showing good extractive properties and a nonvolatile nature that could reduce investment and operating costs of the extraction units [4–16]. A wide number of pure ILs have been specifically applied in the liquid–liquid extraction of benzene, toluene, or xylenes from binary mixtures with an aliphatic hydrocarbon [4,11]. However, only a very limited number of pure ILs have exhibited extractive and physical properties comparable to sulfolane values. For that reason, we have proposed the use of binary IL mixtures in order to obtain

an IL-based solvent with intermediate extractive and physical properties between those of the ILs forming the mixture and comparable or higher than the sulfolane values [17–19].

In our previous works, we studied 34 pure ILs and 6 binary IL mixtures in the separation of an aromatic hydrocarbon from an aliphatic hydrocarbon, studying the liquid–liquid equilibria data of systems (aliphatic + aromatic + IL). Among the IL mixtures studied so far in the liquid–liquid extraction of BTX, the mixture composed of {[4empy][Tf<sub>2</sub>N] and [emim][DCA]} ILs has been the most promising mixed solvent considering its extractive and physical properties. The {[4empy][Tf<sub>2</sub>N] + [emim][DCA]} mixture with a [4empy][Tf<sub>2</sub>N] mole fraction ( $x_1$ ) equal to 0.3 showed extractive properties higher or similar to sulfolane values in the separation of toluene from binary mixtures with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, 2,3-dimethylpentane, or cyclohexane, and in the extraction of benzene, ethylbenzene, or xylenes from *n*-heptane [18,20,21]. Moreover, this IL mixture has shown densities, viscosities, surface tensions, and thermal stability comparable to those of sulfolane [18,22,23].

In our most recently published work, we have studied the performance of the {[4empy][Tf<sub>2</sub>N] + [emim][DCA]} IL mixture with a  $x_1$  of 0.3 in the extraction of benzene, toluene, ethylbenzene, and *p*-xylene from a reformer gasoline model. The IL mixture exhibited yields of extraction of aromatics slightly lower than the sulfolane values and purities of extracted aromatics considerably higher than those using sulfolane [24].

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In this paper, we have studied the liquid–liquid extraction of BTX from two pyrolysis gasoline models obtained by mild and severe cracking using the {[4empy][Tf<sub>2</sub>N] + [emim][DCA]} mixture with a  $x_1$  of 0.3. To analyze the influence of temperature on the extractive properties of the IL-based solvent, the liquid–liquid extraction has been performed at 303.2 K, 313.2 K, and 323.2 K and atmospheric pressure, being these temperature values the most common in the separation of BTX from alkanes using IL-based solvents [4,11]. The effect of the solvent to feed ratio (S/F) on the BTX extraction has also been studied performing liquid–liquid extraction experiments at S/F ratios between 1.0 and 5.0. The extraction of BTX from the pyrolysis gasoline models have also been made employing sulfolane as extraction solvent to perform a comparative analysis between the extractive properties of both solvents.

## 2. Materials and methods

### 2.1. Materials

The ILs [4empy][Tf<sub>2</sub>N] and [emim][DCA] were supplied by Iolitec GmbH (Germany) with a mass fraction purity higher than 0.99 and 0.98, respectively. The presence of halides was lower than 100 ppm in the ([4empy][Tf<sub>2</sub>N]) and lower than 2% in the [emim][DCA], whereas the water content was 42 ppm in the case of the [4empy][Tf<sub>2</sub>N] and 1790 ppm for the [emim][DCA]. *n*-Hexane, *n*-heptane, *n*-octane, benzene, toluene, *p*-xylene, and sulfolane were purchased from Sigma-Aldrich (USA). Chemicals were employed as received without further purification. The ILs were handled in a glovebox filled with dry nitrogen and all chemicals were stored in a desiccator to prevent water absorption. In Table 1, mass fractions purities of the chemicals are listed along with the abbreviations of the compounds used in this paper.

### 2.2. Pyrolysis gasoline models

Franck and Stadelhofer [1] published the composition in mass basis of the pyrolysis gasolines as a function of the severity of the cracking. A typical pyrolysis gasoline obtained by mild cracking has the following composition: benzene (22.0 wt.%), toluene (17.5 wt.%), ethylbenzene, xylenes and styrene (11.5 wt.%), and non-aromatics (49.0 wt.%). On the other hand, according to Franck and Stadelhofer the composition of a typical pyrolysis gasoline obtained by severe cracking is: benzene (33.8 wt.%), toluene (19.4 wt.%), ethylbenzene, xylenes and styrene (13.0 wt.%), and non-aromatics (33.9 wt.%) [1]. To simplify the experimental procedure and the analytical method, the content of ethylbenzene, xylenes, and styrene were represented in the models by *p*-xylene. In addition, the non-aromatic content in the gasoline from mild cracking was formed by a 16.3 wt.% of *n*-hexane, 16.3 wt.% of *n*-heptane, and 16.3 wt.% of *n*-octane, whereas the non-aromatics were

represented by an 11.3 wt.% of each *n*-alkane in the gasoline model from severe cracking. Compositions of the pyrolysis gasoline models obtained by mild and severe cracking employed in this work are presented in Table 2. In the preparation of the gasoline models, aromatic and aliphatic hydrocarbons were added using a Mettler Toledo XS 205 balance with a precision of  $\pm 1 \cdot 10^{-5}$  g to determine the composition of the model by mass.

### 2.3. Dearomatization by liquid–liquid extraction. Experimental procedure and analysis

To study the performance of the {[4empy][Tf<sub>2</sub>N] + [emim][DCA]} IL mixture with a [4empy][Tf<sub>2</sub>N] mole fraction of 0.3 as aromatic extraction solvent, liquid–liquid equilibria (LLE) experiments were made in 8 mL vials with screw caps using a Labnet Vortemp 1550 shaking incubator at 303.2 K, 313.2 K, and 323.2 K for 5 h at 800 rpm. To achieve a complete separation of the extract and raffinate phases in LLE, vials were then placed in a Labnet Accublock dry bath for 12 h at the LLE temperature controlled with a precision of  $\pm 0.1$  K. At each experimental temperature, vials were gravimetrically prepared at S/F ratios in mass basis of 1.0, 2.0, 3.0, 4.0, and 5.0 using a Mettler Toledo XS 205 balance. LLE experiments using sulfolane under the same conditions were also performed to be used as benchmarks.

Raffinate phases were analyzed in triplicate by gas chromatography (GC) employing an Agilent 7890A gas chromatograph coupled with a liquid autosampler Agilent 7693 and a flame ionization detector (FID). In the experiments using sulfolane as solvent, the compositions of both raffinate and extract phases were also determined by GC. A complete description of the analytical method can be found elsewhere [18, 25].

In our recently published papers on the liquid–liquid extraction of aromatics using the {[4empy][Tf<sub>2</sub>N] + [emim][DCA]} IL mixture, signals corresponding to ILs were not found in <sup>1</sup>H NMR spectra from samples of raffinate phases and, therefore, the presence of ILs in this phase was considered negligible [18,20,21].

Samples from extract phases in the LLE experiments using the IL mixture as extraction solvent were analyzed by the multiple headspace extraction (MHE) technique. Three samples of approximately 100 L from each extract phase were added to 20 mL vials to be analyzed in an Agilent 7890A GC coupled with an Agilent 7697A Headspace Sampler. A detailed description of the MHE method used in this work can be found elsewhere [18,25,26]. Standard uncertainties of the compositions are listed in SI Tables 1 to 4 in the supplementary data.

**Table 1**  
Suppliers, purities of chemicals, and abbreviations.

Chemical	Supplier	Mass fraction purity	Analysis method	Abbreviation
[4empy][Tf <sub>2</sub> N] <sup>a</sup>	Iolitec GmbH	0.99	NMR <sup>b</sup> and IC <sup>c</sup>	ILs
[emim][DCA] <sup>d</sup>	Iolitec GmbH	0.98	NMR <sup>b</sup> and IC <sup>c</sup>	
<i>n</i> -Hexane	Sigma-Aldrich	0.99	GC <sup>e</sup>	hexa
<i>n</i> -Heptane	Sigma-Aldrich	0.997	GC <sup>e</sup>	hepta
<i>n</i> -Octane	Sigma-Aldrich	0.99	GC <sup>e</sup>	octa
Benzene	Sigma-Aldrich	0.995	GC <sup>e</sup>	benz
Toluene	Sigma-Aldrich	0.995	GC <sup>e</sup>	tol
<i>p</i> -Xylene	Sigma-Aldrich	0.99	GC <sup>e</sup>	<i>p</i> -xyl
Sulfolane	Sigma-Aldrich	0.99	GC <sup>e</sup>	sulf

<sup>a</sup> [4empy][Tf<sub>2</sub>N] = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide.

<sup>b</sup> Nuclear magnetic resonance.

<sup>c</sup> Ion chromatography.

<sup>d</sup> [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.

<sup>e</sup> Gas chromatography.

**Table 2**  
Composition of the pyrolysis gasoline models obtained by mild and severe cracking in mass basis.

Model of pyrolysis gasoline obtained by mild cracking	
Hydrocarbon	$w_i$
<i>n</i> -Hexane	0.163
<i>n</i> -Heptane	0.163
<i>n</i> -Octane	0.163
Benzene	0.220
Toluene	0.176
<i>p</i> -Xylene	0.115
Model of pyrolysis gasoline obtained by severe cracking	
Hydrocarbon	$w_i$
<i>n</i> -Hexane	0.113
<i>n</i> -Heptane	0.113
<i>n</i> -Octane	0.113
Benzene	0.338
Toluene	0.193
<i>p</i> -Xylene	0.130

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