



## Experimental screening towards developing ionic liquid-based extractive distillation in the dearomatization of refinery streams



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### ABSTRACT

Ionic liquids (ILs) are potential neoteric solvents to design new advanced separation processes. Among several separation cases studied so far, the good performance of ILs regarding the dearomatization of liquid fuels, i.e. pyrolysis and reformer gasolines, has received especially attention. Indeed, a wide number of works has been done to characterize the phase equilibria for {aliphatic + aromatic + ILs} systems as well as the IL thermo-physical properties, concluding in the development of a liquid-liquid extraction process. However, this technology seems not to be enough to fulfill current aromatic commercial standards nor potential incoming restrictions for aromatic content in liquid fuels as a result of its low separation effectiveness for extreme aliphatic and aromatic purification. Extractive distillation with ILs stands as a new process configuration to overcome these limitations by enhancing the aliphatic/aromatic relative volatilities. In this work, an IL experimental screening in the *n*-heptane/toluene separation was done to further develop this new IL-based technology. Nine ILs were tested as mass agents in a wide range of conditions, i.e. solvent to feed (S/F) ratios from 1 to 10 and temperatures from 323.2 to 403.2 K. The required vapor-liquid-liquid equilibria (VLE) data were obtained by an experimental procedure based on headspace gas chromatography (HS-GC) developed in the framework of this work. Although all pre-selected ILs have shown good performance, tricyanomethanide-based ILs have been the most promising mass agents.

### 1. Introduction

ILs are non-conventional salts that are liquid under 373 K and have negligible vapor pressure, showing an interesting liquid range of use [1]. Among other purposes, ILs have been successfully used in a high number of separation cases as solvents in liquid-liquid extraction processes or as mass agents in vapor-liquid separation technologies [2–11]. Liquid-liquid extraction processes using ILs have been designed to eliminate non-desirable compounds in final streams (i.e. aromatics or drugs) or to recover high-valuable substances (i.e. metals, proteins, nucleic acids, lipids or amino-acids) from waste streams [12–18]. As mass agents, ILs have been mainly proved in homogeneous {alcohol + water + IL} systems [19–22].

Focusing the attention in the dearomatization of hydrocarbon streams, which is one of the most prolific and hopeful research lines using ILs [23], several remarks can be given from the wide majority of the published works until now. It is important to mention that all these works were aimed in designing a liquid-liquid extraction process with

ILs. From the liquid-liquid equilibrium (LLE) data referring to {aliphatics + aromatics + ILs} systems, it is possible to highlight the suitability of cyano-based and bis(trifluoromethylsulfonyl)imide-based ILs as can be seen in the recent review on the aromatic/aliphatic separation topic by Canales and Brennecke or in previous works based on both experimental data or COSMO-RS prediction studies [23–26]. Thiocyanate-based and dicyanamide-based ILs have shown aromatic/aliphatic selectivities quite higher than those for conventional organic solvents [27–29], whereas tricyanomethanide-based and bis(trifluoromethylsulfonyl)imide-based ILs displayed comparable or even higher aromatic distribution ratios in mass basis in comparison with those exhibited by the conventional solvents such as sulfolane [26,27,30]. In addition to this, all of these ILs present low viscosities and enough densities to ensure two liquid phases splitting [26]. Therefore, by using these pure ILs or a well-selected binary mixture of them in the aromatic extraction from aromatic main sources, i.e. pyrolysis and reformer gasolines, the extractor efficiencies and size would be similar to that in the Sulfolane process and the aromatic purity in the

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extract stream would be increased [31]. However, further purification is mandatory in the extract stream to achieve a commercial purity of aromatics. In fact, Meindersma has advised years ago that an IL with an unrealistic toluene/*n*-heptane selectivity of 440 was necessary to avoid additional purifications [32]. Thus, the feasibility of the liquid-liquid extraction process is completely dependent on the efficiencies in the recovery section destined to selectively separate the aromatics from the extract stream.

To properly design this recovery section, our research group has been focused on determining the vapor-liquid equilibria (VLE) data regarding extract stream compositions [33]. The best process configuration obtained so far for the aromatic recovery section involved three flash distillation units; the first two flashes destined to selectively remove the aliphatics and the third to separate the aromatics from the IL-based solvent [12,34]. Other options as a lower number of flash distillation units or an stripping column were planned in the literature, but aromatic purity was far for commercial grade because it is essential to tune temperature and pressure in each equilibrium step [35]. Flash distillation units were selected to solve the aromatic purification and hydrocarbon remove from the solvent as a result of the high aliphatic/aromatic relative volatility shown in the extract stream compositions and the aforementioned non-volatile character of ILs. The commercial aromatic purities (99.9 wt%) obtained after the recovery section, working at temperatures below the maximum operating temperature (MOT) estimated for the ILs, support the technical feasibility of the process [34].

Nevertheless, there are some limitations that IL-based liquid-liquid extraction technology seems not to be able to solve. Dearomatized gasolines showed a residual amount of aromatics that can vary between 1 and 2 wt% [31,36]. These values are slightly higher than current restrictions for benzene and toluene in liquid fuels [37] and can limit the uses of the outcome gasoline. Liquid-liquid extraction technology is not capable to reduce this residual aromatic content in the raffinate stream because ILs and commercial solvents have shown tie-lines with very low slope in the {aliphatic + aromatic + IL} ternary systems at low aromatic concentration [23]. Hence, the search of a new process configuration is necessary to achieve better aliphatic purities.

On the other hand, the values of aromatic purity obtained in the extract stream range from 97.2 to 98.4 wt% [31,36]. Although this was solved by a series of flashes as mention above, the recovery section has required very low vacuum conditions (near 5 kPa) at temperatures up to 393.2 K [34]. Taking into consideration that the MOTs for the potential ILs in the aromatic/aliphatic separation are below 500 K [29,30,38,39], the recovery section for the extract stream irreparably implies high vacuum costs independently of the nature of the IL. In addition to this, the aromatic purification also implies recycling stream to the extractor, fact that implies a higher IL consumption [35]. Therefore, it is important to develop an IL-based technologies that can

avoid additional separation steps in the way of process intensification and taking also into account that coming directives will probably strengthen impurity limits and future technologies must deal with even lower impurities.

IL-based extractive distillation can overcome the aforementioned limitations by enhancing the aliphatic/aromatic relative volatilities, as previously suggested [40,41]. Extractive distillation takes advantage of the good performance seen in liquid-liquid extraction technology with ILs together with the volatility difference as an additional driving force to separate aromatics from gasolines and jointly purify aromatic-rich and aliphatic-rich streams [41].

In this work, an experimental screening for nine ILs as mass agents in the toluene/*n*-heptane separation by extractive distillation is presented. ILs were selected by their highlighted extractive properties in the toluene separation from *n*-heptane and also by their low viscosity [23]. The VLLE data have been determined by HS-GC in {*n*-heptane + toluene + IL} ternary systems. The {*n*-heptane + toluene} binary system was fixed to a toluene content of 66 wt% due to the typical aromatic content in the pyrolysis gasoline [42], whereas the S/F ratio was studied from 1 to 10 within the (323.2–403.2) K temperature range. S/F ratio has been evaluated in this range to include both the values that were used in previous publications and those use currently at industrial scale [40,42].

## 2. Experimental section

### 2.1. Chemicals

The nine ILs, namely 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]), 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]), 1-butyl-3-methylimidazolium tricyanomethanide ([bmim][TCM]), 1-butyl-4-methylpyridinium tricyanomethanide ([4bmpy][TCM]), 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf<sub>2</sub>N]), and 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4bmpy][Tf<sub>2</sub>N]), were acquired from Iolitec GmbH with purities higher than 98 wt% for cyano-based ILs and higher than 99 wt% for bis (trifluoromethylsulfonyl)imide-based ILs. They have been used as received without further purification and handled into a glove box under an inert atmosphere of dry nitrogen. Hydrocarbons (toluene and *n*-heptane) were supplied by Sigma-Aldrich with purities higher than 99.5 wt% and were kept into their original vessels over molecular sieves. Additional details for the chemicals used in this work can be found in Table 1.

**Table 1**  
Specifications of chemicals.

Chemical	Source	Analysis method	Purity in wt%	Water content in ppm
[emim][SCN]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	1678
[bmim][SCN]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	1831
[emim][DCA]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	1121
[bmim][DCA]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	1760
[emim][TCM]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	537
[bmim][TCM]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	153
[4bmpy][TCM]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	98	304
[4empy][Tf <sub>2</sub> N]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	99	76
[4bmpy][Tf <sub>2</sub> N]	Iolitec GmbH	NMR <sup>a</sup> , IC <sup>b</sup>	99	48
<i>n</i> -heptane	Sigma-Aldrich	GC <sup>c</sup>	99.7	–
toluene	Sigma-Aldrich	GC <sup>c</sup>	99.5	–

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

<sup>b</sup> Ion chromatography.

<sup>c</sup> Gas chromatography.

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