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Insights for Designing the Hydrocarbon Recovery from Ionic Liquids by Distillation in the Aliphatic/aromatic Separation by Liquid-liquid Extraction

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Nowadays the aliphatic/aromatic separation by liquid-liquid extraction using ionic liquids (ILs) is an interesting topic in the search of a new class of separation processes for the oil industry. The wide majority of papers published until now has focused in maximizing the IL extractive properties as can be found in a recent review by Canales and Brennecke (2016); in addition, in the recent past, this search was also oriented to find a commitment election between IL extractive and physical properties, with especial focus on reducing the viscosity to limit its impact on mass transfer and pumping (Larriba et al., 2013a). However, the challenge in the development of this new liquid-liquid extraction technology based on ILs is the selective recovery of aromatics from the solvent. Although IL non-volatile character is suggested as a clear advantage for separation purposes, this is truly a limitation in the vapor-liquid separation as was reported in last papers dealing with the vapor-liquid equilibria involving aliphatics, aromatics, and ILs due to the pretty low equilibrium pressures (Navarro et al., 2015). In addition, the thermal stability of ILs is another drawback since scarce species could be used at industrial scale over 473 K (Navarro et al., 2013). Finally, extracted aromatics have not commercial purity and further purification is mandatory before the aromatic/IL separation (Larriba et al., 2013a). In this work, the simulation of three different recovery sections based on vapor-liquid separations was performed to give some remarks that can help to design distillation processes involving large amounts of ionic liquids. Seven ionic liquids among the most promising species proved so far were selected to completely cover the transferability between liquid-liquid and vapor-liquid equilibria (LLE and VLE, respectively). Aspen Plus commercial simulator was used implementing the Non-Random Two Liquids (NRTL) models from the experimental data regressions for the corresponding *n*-heptane + toluene + ionic liquid ternary systems. Aromatic recoveries and purities for three different process configurations were analysed in order to stablish the impact of the ionic liquid extractive and thermal properties on the design of a suitable recovery section from an industrial point of view.

1. Introduction

ILs are commonly used as alternative solvents in a wide number of extraction processes. The use of ILs as solvents mainly aim in the replacement of organic solvents in high industrial interest cases, i.e. aromatics or metals (Larriba et al., 2013a, Ola et al., 2017) or in the isolation of natural compounds in the search of new sustainable processes (Rahman et al., 2017). Among a more extend collection of uses, the research community has specially focused on the aromatic/aliphatic separation by liquid-liquid extraction using ILs as an interesting way to replace volatile organic compounds, i.e. sulfolane or ethylene glycol (Canales and Brennecke, 2016). There is a wide number of ILs that have been proved in this separation case. Cyano-based ILs stand as the most suitable alternative to separate toluene from *n*-heptane and, thus, to be used in the BTEX removing from refinery streams as pyrolysis and reformer gasolines, the aromatic main sources.

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Cyano-based ILs have shown good extractive and adequate physical properties (Canales and Brennecke, 2016) and interesting thermal stability (Navarro et al. 2013). Both thiocyanate and dicyanamide-based ILs have shown quite higher toluene/*n*-heptane selectivity than that using sulfolane (Larriba et al., 2013a, Gonfa et al., 2013), whereas tricyanomethanide-based ILs have increased the toluene distribution ratios of toluene with even higher toluene/*n*-heptane selectivities (Larriba et al., 2013a; Larriba et al., 2016a). Considering these results, the IL selection will respond to the required aromatic purity in the extract stream and the solvent price. In this search, an IL with high and compensate selectivity and capacity seems to achieve the best performance (Larriba et al., 2015). Nevertheless, as Meindersma claimed years ago, an unrealistic toluene/*n*-heptane selectivity of over 440 would be necessary to avoid further purification of the aromatics after the extraction (Meindersma, 2005). Therefore, the aromatics purity in the extract stream must be increased during its recovery from the solvent.

Flash distillation was recently proposed to take advantage of the high aliphatic/aromatic relative volatility seen for the extract stream-type compositions and selectively remove the aliphatics from the extract stream and, accordingly, increase the aromatic purity. It is commonly found the use of ILs as mass agent in vapor-liquid separations to break azeotropes (Kulajanpeng et al., 2014) with good separation performance but with lower relative volatilities due to much lower IL concentration. Therefore, a series of flash distillation units was found to be enough to fulfil the aromatic commercial grade at the end of the process as well as quantitatively separate the aromatics from the IL (Navarro et al. 2017). However, the influence of the IL in the recovery and purification section was not deeply evaluated until now.

As a result, the aim of this work is evaluating the IL impact on the whole process with special attention to the recovery and purification section. To do this, three process configurations were tested as well as seven cyano-based ILs, namely, 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]), 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), 1-allyl-3-methylimidazolium dicyanamide ([amim][DCA]), 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]), 1-butyl-3-methylimidazolium tricyanomethanide ([bmim][TCM]), and 1-butyl-4-methylpyridinium tricyanomethanide ([4bmpy][TCM]).

2. Simulation

The NRTL models obtained from the experimental liquid-liquid equilibria and vapor-liquid equilibria data regressions were used to simulate the extractor and the flash distillation units involved in the three configurations detailed in Figure 1.

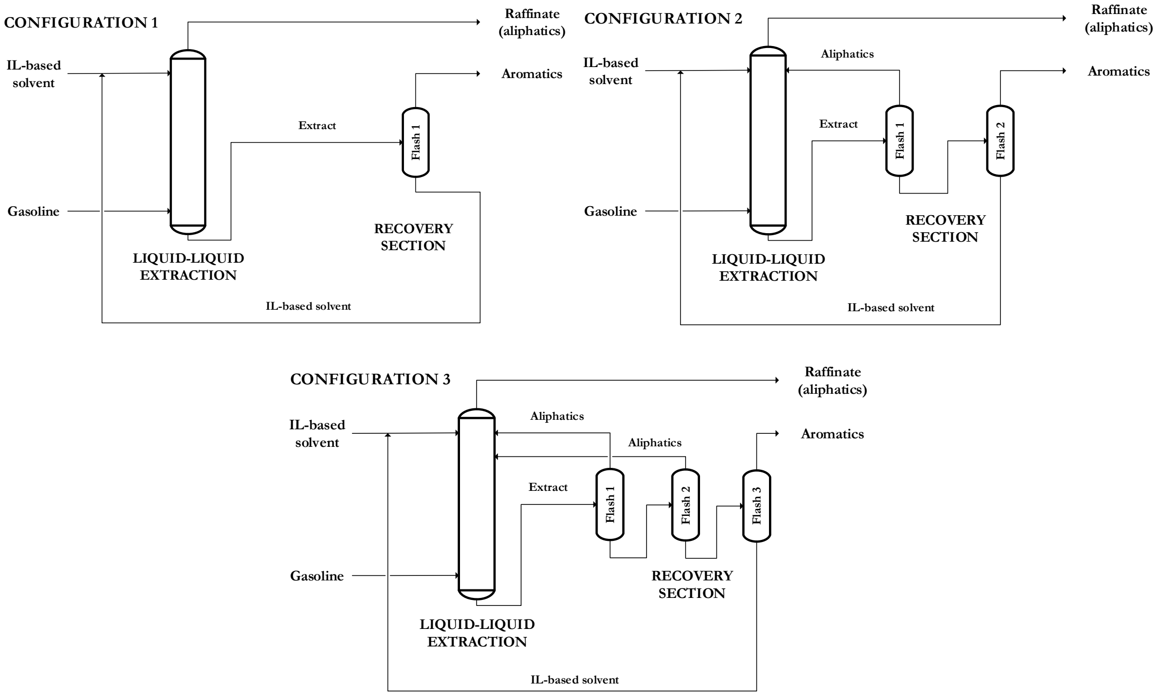

Figure 1: Process configurations to separate and purify aromatics from gasolines using ILs.

The models were implemented in the commercial Aspen Plus simulator software as thermodynamic basis of calculation. Further details can be found in the references indicated in Table 1. The extract model from Aspen Plus was selected to simulate the extractor, whereas Flash 2 model was used for the flash distillation case. These models are commonly used in this kind of simulation studies as can be found elsewhere (Larriba et al. 2018). The hydrocarbon extractor feed has the pyrolysis gasoline composition (i.e. 66 wt. % of toluene) and the solvent to feed ratio was fixed to 5 to ensure a total toluene recovery although from a process point of view this is an optimizable variable. The counter current extractor has ten equilibrium steps and works at 313.2 K. All these conditions are based on previous simulation works on the same separation case (Larriba et al., 2018).

The last flash distillation unit in each configuration was simulated fixing the maximum operation temperature (MOT) estimated for each IL listed also in Table 1, whereas the pressure was varied to find an IL purity of 99.0 wt. %. In configurations 2 and 3, Flash 1 was simulated at 333.2 K and 10 kPa, whereas Flash 2 in configuration 3 operated at 333.2 K and 5 kPa. Mild temperature conditions fixed in the flash units destined to selectively separate *n*-heptane from the extract stream are based on the enhance observed in the *n*-heptane/toluene relative volatility at low temperatures (Navarro et al., 2015; Navarro et al., 2017).

Table 1: Literature source of the NRTL models for LLE and VLE used in the simulations and MOTs for the ILs.

IL	LLE Source	VLE Source	*MOT*/ K
[emim][SCN]	Larriba et al. 2014	González et al. 2015	360 (Navarro et al., 2013)
[bmim][SCN]	Larriba et al. 2014	González et al. 2015	403 (Navarro et al., 2013)
[emim][DCA]	Larriba et al. 2013a	Navarro et al. 2015	412 (Navarro et al., 2013)
[amim][DCA]	Larriba et al. 2016b	Larriba et al. 2016b	418 (Larriba et al., 2016b)
[emim][TCM]	Larriba et al. 2013a	González et al. 2016	452 (Navarro et al., 2013)
[bmim][TCM]	Larriba et al. 2016a	Larriba et al. 2016a	455 (Larriba et al. 2016a)
[4bmpy][TCM]	Larriba et al. 2016a	Larriba et al. 2016a	447 (Larriba et al. 2016a)

3. Results

Firstly, the extractor was simulated as a required first step for the analysis of the three recovery section, obtaining the results presented in Figure 2. As expected, there is a clear correlation between the toluene purity obtained in the counter current extractor and toluene/*n*-heptane selectivity of the solvent. On the other hand, there was no toluene in the raffinate since an S/F ratio of 5 was enough to extract all toluene from the feed using selected ILs, as advised above.

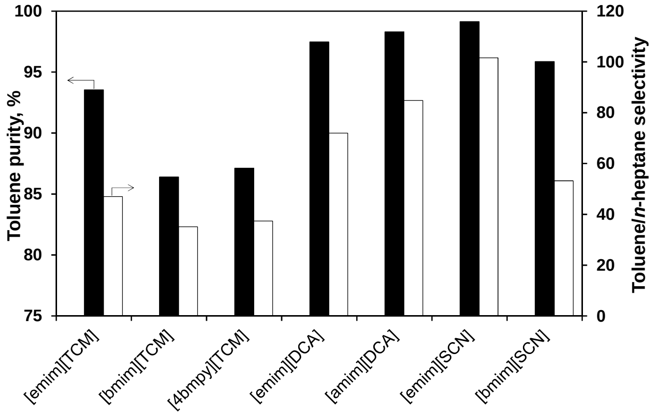

Figure 2: Toluene purities in the extract stream and toluene/n-heptane selectivity of the ILs

Regarding the different configurations, toluene purity and recovery at the end of each configuration are graphically shown in Figure 3 as a function of the used IL. As seen, using just one flash distillation unit (configuration 1), only [emim][SCN] is not far from the commercial grade for toluene but achieved purity is not enough to fulfil industrial standards; then, although toluene/*n*-heptane selectivity enhances toluene purity, process configuration must be improved. Configuration 2 destined one flash distillation unit (Flash 1) for this purpose and, although only [emim][SCN] gets toluene commercial grade, several remarks can be given.

Both dicyanamide-based ILs have shown toluene purities over 99.0 wt. % and recoveries over 80 %, whereas [emim][SCN] has shown higher purities but with a very low toluene recovery (53 %). Although ILs with high toluene/*n*-heptane selectivity and low toluene capacity seems to be the best option to enhance toluene purity and assay the best toluene recovery, toluene distribution ratios and MOTs also play an important role. [emim][SCN] shows low toluene distribution ratios and its MOT is 360 K. Thus, although [emim][SCN] has shown the best purities, its low capacity and thermal stability are not appropriate.

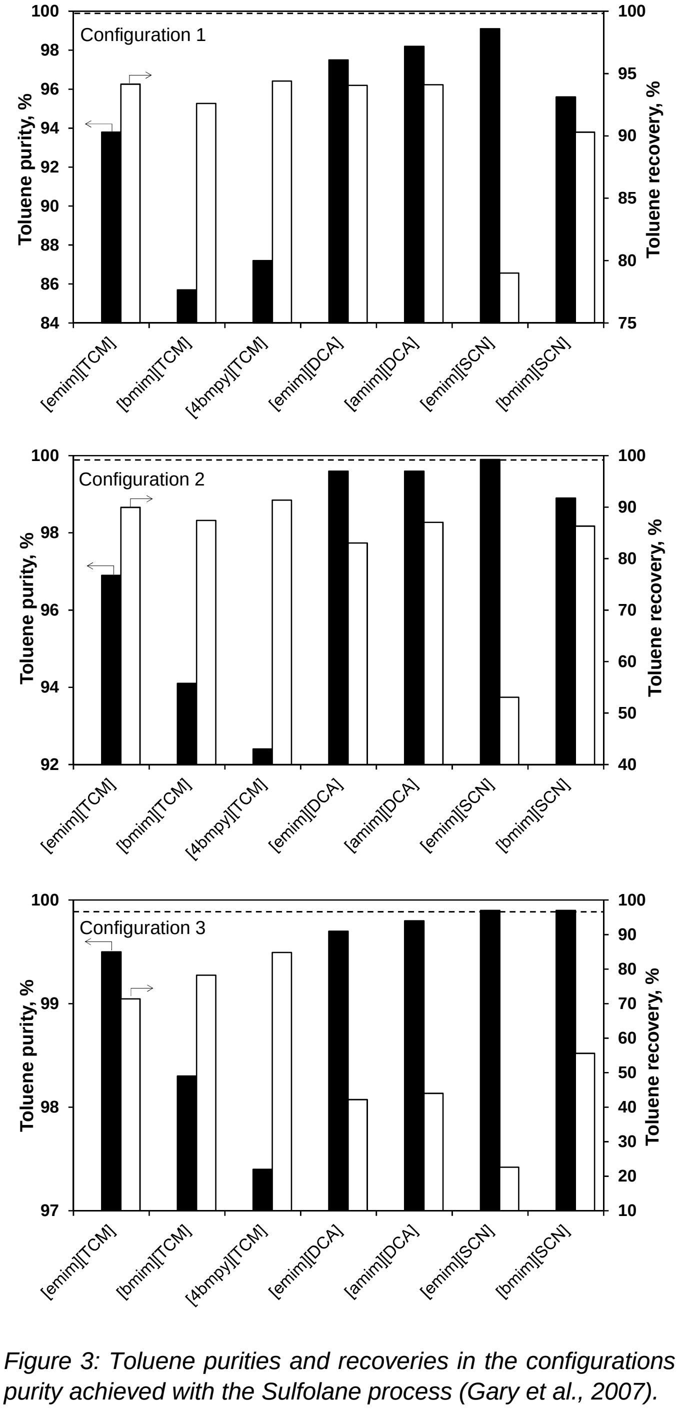

Figure 3: Toluene purities and recoveries in the configurations 1, 2 and 3. Dashed line denotes the aromatic purity achieved with the Sulfolane process (Gary et al., 2007).

As the other ILs do not achieve toluene commercial, it seems to be necessary to deeply inspect configuration 3. On the one hand, [bmim][SCN] has shown toluene commercial grade as all thiocyanate and dicyanamide-based ILs checked in this work, but with higher toluene recovery (56 %). On the other hand, [emim][TCM] has enhanced a toluene purity of 99.5 wt. %, close to industry requirements, but with a very good toluene recovery

(73 %) due to its higher capacity. A high recovery means lower recycles to the extractor, which implies lower S/F ratios and extractor size (Steltenpohl and Graczová, 2014; Graczová et al., 2014). In Figure 4, operation pressure is milder in Flash 3 using [emim][TCM] instead of [bmim][SCN] because [emim][TCM] has a very good combination of MOT and *n*-heptane/toluene relative volatility ($\alpha_{\text{n-heptane/toluene}}$). Therefore, the use of a solvent with the same or even better properties than [emim][TCM] seems to ensure good performance not only in the toluene extraction from *n*-heptane but also in the selective recovery of toluene from the extract stream using configuration 3. Testing ILs in this separation process started by sustainable criteria but both separation performance and operating conditions show competitive values in comparison with industrial solvents, i.e. sulfolane, that work at higher temperatures and required more steps in the recovery section (Gary et al., 2007).

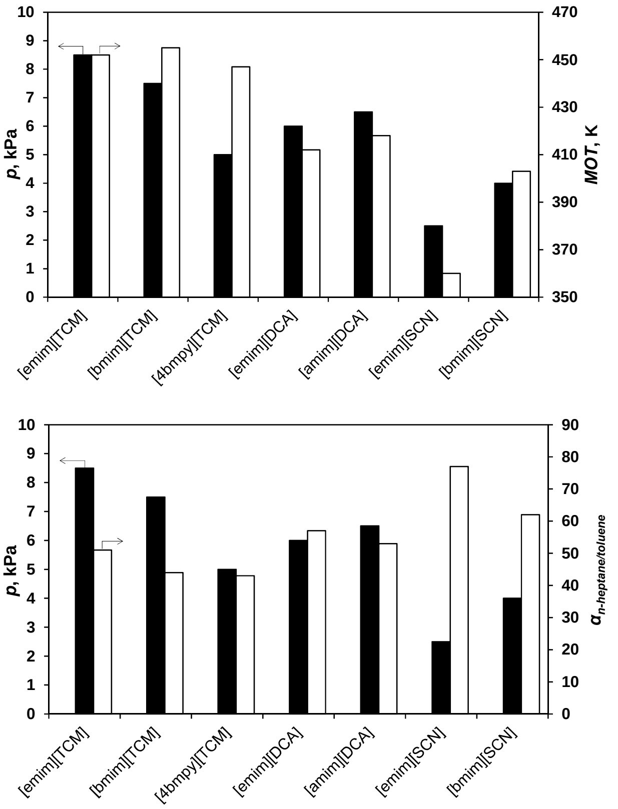

Figure 4: Operation pressure (flash 3, configuration 3) explained by MOT and $\alpha_{\text{n-heptane/toluene}}$.

4. Conclusions

In this work the relevance of the IL nature was demonstrated in the recovery and purification of the extracted aromatics from gasolines using ILs as solvents since pure ILs have shown only one highlighted extractive property. The toluene/*n*-heptane selectivity has revealed as the essential variable to enhance high values of aromatic purity and easy the aromatics recovery from the IL but commitment election with aromatic distribution ratio is essential to enhance a best overall performance (aromatic purity and recovery). The MOT value has conditioned the vacuum required in the final aromatics/IL separation and it is a key value for the recovery section design. Considering all results, the use of [emim][TCM] IL in configurations 3 was revealed as the most suitable combination obtaining an aromatic-rich stream with purities near to commercial grade, low hydrocarbon recycles to the extractor, and milder vacuum conditions in the final aromatic/IL separation.

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