**Aromatic/aliphatic separation by liquid-liquid extraction with ionic liquids: an overview process analysis with the COSMO-based/Aspen Plus approach**

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**Highlights**

* More than 100 ionic liquids evaluated in the whole extraction + recovery process.
* Close relationship found between extractive properties and process insights.
* Cyano-based ionic liquids stand as the most potential solvents.
* The separation is enhanced but the costs are increased with the number of cyano groups.

**1. Introduction**

Ionic liquids (ILs) are non-conventional salts that are liquid below 373 K, showing negligible vapor pressure and an interesting liquid range of use only limited by their thermal stability [1]. Among other purposes, ILs have been frequently evaluated in a high number of separation cases as solvents in liquid-liquid extraction processes [1]. Focusing the attention in the aromatic/aliphatic separation, which is one of the most prolific and hopeful research lines using ILs [2], a feasible process was evidenced in the literature referring not only to the core separation (liquid-liquid extraction) but also including side-separations and purifications to enhance aromatic standards and recycle the solvent [3,4]. The aforementioned claim is supported by experimental data at laboratory and pilot plant scales [3-5] but also by process simulation [6,7]. Although large experimental liquid-liquid equilibrium data is available, vapor-liquid equilibrium data is scarce and simultaneous modelling liquid-liquid and vapor-liquid equilibria was not revealed to be easy; thus, a proper overview process analysis lighting the more convenient IL-based solvents is still not available in the literature.

According to this, a systematic process analysis for the aromatic/aliphatic separation seems to be interesting to evaluate, for this example, the real applicability of these neoteric solvents at industrial scale. To do this, COSMO-based/Aspen Plus methodology was selected because of its outstanding power and availability to deal with more than 100 ILs in a wide range of conditions, all in the framework of a commercial process simulator. After validating COSMO predictions against all reliable experimental data regarding liquid-liquid extraction and distillation units involved in the process, the methodology was deployed to better understand the aromatic/aliphatic separation.

**2. Methods**

Integrated COSMO-based-Aspen Plus methodology was deployed to simulate the aromatic/aliphatic separation process, which involves the extractor and three flash distillation units; the first two flashes are destined to purify the aromatics, whereas the last one is aimed at separating the aromatics and the IL. The COSMOSAC property model was selected to calculate the activity coefficients in the simulations, specifically the modification to the Lin and Sandler model (mode 3 of COSMOSAC model) developed by Lin, Mathias et al. (2002) because that approach better represented available experimental data. Regarding the modules, EXTRACT and FLASH 2 were selected in the simulation.

**3. Results and discussion**

After properly selecting the input/output matrix and executing more than 5000 simulations, the results were summarized and analyzed. As exemplified in Fig 1 to representative ILs, it is difficult to find an IL with good performance in both aromatic recoveries and purities, even more complex considering recycling streams. Although [4mbpy][TCM] shows a very competitive performance in the more realistic conditions, the direct proportionality between aromatic distribution ratio and utilities costs makes the analysis even more complex. Taking into account process simulation performance, utilities costs and typical ILs’ limitations as viscosity and thermal stability, cyano-containing ILs stand as the more potential ILs nowadays.



**Figure 1.** Aromatic recovery and purity with selected ILs in several scenarios. Toluene/n-heptane separation: only extraction, blue; whole process, grey. BTX removing from pyrolysis gasoline: only extraction, red; whole process, yellow.

**4. Conclusions**

The overview process analysis of the aromatic/aliphatic separation by liquid-liquid extraction with ILs has provided a useful guide to evaluate the global and partial impact of the extractive and physical properties related to available and future IL species on relevant process insights. A clear correlation between ILs features and process simulation insights, such as utilities costs, recoveries and purities, has permitted to give recommended standards for the solvents that will easy the search of even better solvents than cyano-containing ILs for the petrochemical industry.

**References**

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