Selection of ionic liquids for aromatic/aliphatic separations and determination of LLE data supported by COSMO-RS

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1. Summary

The separation of aromatic and aliphatic hydrocarbons is challenging, due to overlapping boiling points and formation of several azeotropes. Conventional solvents for those separations are polar substances, e.g. sulfolane. Recently it could be shown that ionic liquids can perform considerably better than common extraction solvents. Hence, ionic liquids can be a promising alternative [1].
Ionic liquids (IL) are molten salts composed of large organic cations and various anions. Some of their properties are negligible vapour pressure, wide liquid range (~300K) and the ability to dissolve polar, non-polar, organic and inorganic compounds. Since the properties of an ionic liquid are defined by the combination of cation and anion a great number of combinations ($> 10^{14}$) is conceivable. Hence, it is possible to tailor a specific ionic liquid with the desired properties. In order to be able to make a selection out of all possible combinations COSMO-RS was found to be a suitable screening tool [2].
By comparing the σ-profiles of aromatic and aliphatic compounds and an ionic liquid it is possible to make an assumption whether the ionic liquid is suitable for the separation of the mixture. In this work several ionic liquids have been tested with a simplified naphtha feed consisting of toluene and n-heptane. Based on the preselection made with COSMO-RS, LLE data have been determined and for the ternary mixtures (toluene + n-heptane + [BMIM][DCA]), (toluene + n-heptane + [BMIM][SCN]) and (toluene + n-heptane + [Mebupy][DCA]) ternary diagrams have been derived. It could be shown that COSMO-RS is a useful tool for the selection of ionic liquids.

Keywords: aromatic/aliphatic separation, ionic liquids, σ-profiles

2. Extended Abstract

The COSMO-RS approach is based on unimolecular quantum chemical calculations and, therefore, only limited by the availability of the individual component parameters in which it is different from group contribution methods like UNIFAC.
With this simulation tool ionic liquids have been screened. The screening is based on σ-profiles which describe the surface charge distribution of a molecule.

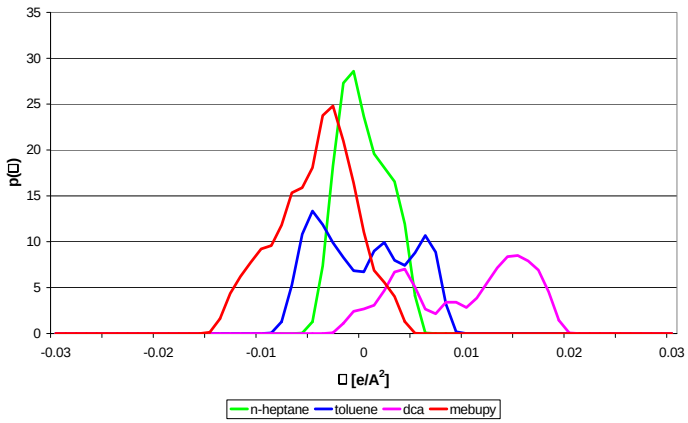

Figure 1: σ-profile of toluene, n-heptane and [Mebupy][DCA]

A typical example for this method is given in Figure 1, which shows the σ-profiles of toluene, n-heptane and the ionic liquid [Mebupy][DCA]. The σ-profile of n-heptane has its maximum at 0[e/A^2] which indicates the similar electron distribution along the whole molecule chain. However, the σ-profile of toluene consists of three overlapping peaks that derive from the p-orbitals of the molecule. In comparison to the aromatic and the aliphatic molecules, the ionic liquid is described by two functions: one for the cation and one for the anion. Since the σ-profile is a mirror inverted image of the molecule's charge, the cation function has negative values and the anion function is positive. From Figure 1 it is visible that the peaks of the ionic liquid are well corresponding with the peaks of toluene but less with n-heptane. Hence, it is tempting to assume that this ionic liquid has very good separation properties for extracting aromatic compounds from aliphatic hydrocarbons. With this method the following ionic liquids were found to be suitable as extraction solvent: [BMIM][SCN], [BMIM][DCA], [Mebupy][DCA].

The screening results have been validated by ternary diagrams of the mixture (toluene + n-heptane + an ionic liquid). As an example the ternary diagram of the mixture (toluene + n-heptane + [Mebupy][DCA]) is shown in Figure 2. As it visible, toluene and the ionic liquid are completely miscible, whereas n-heptane is almost immiscible with [Mebupy][DCA]. For the other ionic liquids mentioned above the same results could be obtained.

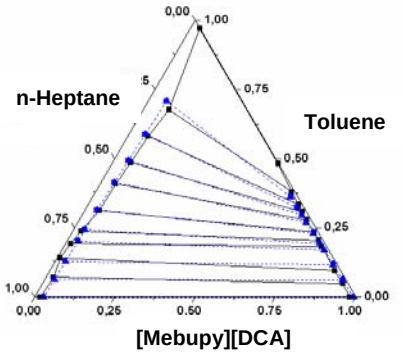

Figure 2: ternary diagram for toluene + n-heptane + [Mebupy][DCA]

3. Conclusion

Conventional simulation tools are difficult to use for mixtures containing ionic liquids. The combination of COMSO-RS screening by comparing the σ-profiles of the components with the σ-profile of an ionic liquid and verification by experimental results allows a qualitative selection of ionic liquids for extraction processes. It could be shown that the obtained screening results are in very good agreement with the experimental values. Hence, COSMO-RS is a suitable screening tool for the selection of ionic liquids.

References

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2. Klamt, A., *COSMO-RS From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, (2005).