ECONOMIC CRITERIA IN DESIGN/SELECTION OF IONIC LIQUIDS USING COSMO-BASED PROCESS SIMULATIONS. AROMATICS REMOVAL FROM NAPHTHA

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Introduction: The room temperature ionic liquids (ILs) have gained popularity in the last years as suitable green solvents. A main advantage of these new solvents is that the cation (C) and the anion (A) can be selected among a huge diversity to obtain an appropriate IL for a specific purpose. Computational approaches [1] have been developed to design new ILs with specific properties. The optimization criteria used in the IL design and selection for uses in separation operations are usually related to the extension of the corresponding equilibria. Nevertheless, the development of ILs with real applicability in industrial processes needs information on the operational conditions, energy consumptions, operating and capital costs, etc. of the corresponding processes. This information can be retrieved *via* process simulation but, this is not a trivial question because the ILs are not available as conventional components in the process simulators databanks. Furthermore, predictive thermodynamic models are needed for computing the thermo-physical properties of the fluids. COSMO-RS model [2] has shown to yield good qualitative and satisfying quantitative predictions for the activity coefficients of neutral compounds in ionic liquids and for binary mixtures of ionic liquids and neutral solvents. Since this success was achieved predictively, COSMO-RS has become a widely used and efficient tool for the prediction and screening of ionic liquids properties. Thus, it has been applied with reasonable achievement to the prediction of thermo-physical, transport and equilibrium properties of the pure ILs and their mixtures with organic solvents. This has supported the decision adopted in the present work related to the use of COSMO-RS to generate the information needed both for creating IL non-databank components and for specifying COSMOSAC property model [3] implemented in Aspen Plus process simulator.

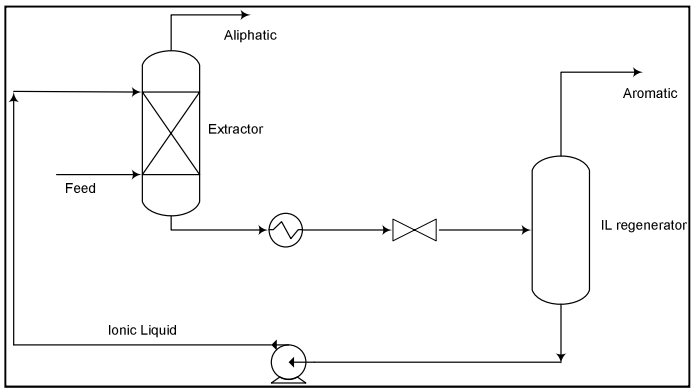

Figure 1. Simplified flowsheet of the process for removing aromatics from naphtha.

Aromatics removal from naphtha is, probably, one of the most extensively studied separation process using ILs. It has been the subject not only of basic studies devoted to elucidate the equilibrium conditions [4] but also of process developments [5]. It has a great technological and economical significance in naphtha cracking processes as shown in [5b].

In the present communication a process for removing benzene from its mixture with hexane using 1-alkyl-3-methylimidazolium NTf_2 ILs is taken as model for studying the capacity of the COSMO-based process simulations to both support process conceptual designs and generate economical and technological information about the process. It essentially consist of two stages: firstly the aromatic hydrocarbon is separated from its mixture with the aliphatic one by LL extraction using an IL, further the IL is recovered by vacuum distillation [5] and recycled (Fig. 1).

Simulations: In process simulations ILs have been created as pseudo-components through Aspen Plus (v 7.3) specifying their molecular weights, normal boiling temperatures and densities. Their unknown properties were estimated by the methods and models used implicitly by the program. The organic solvents were selected as conventional components from its database. The COSMOSAC property model as implemented by default in Aspen Plus was selected to estimate the activity coefficients of the components in the mixtures. The molecular volumes and σ-profiles of the ILs, needed to define the COSMOSAC property model, were specified by the user whereas those corresponding to the organic solvents were taken from the database of the simulator. The information used for both creating IL pseudo-components and for specifying the COSMOSAC property model were obtained from the previous COSMO-RS calculations using the C21_0111 version of the COSMOthermX program package. In COSMO-RS calculations of the ILs were used their ion-paired (CA) structures optimized at B3LYP/6-31++G(d,p) computational level in the gas phase using quantum chemical Gaussian03 package.

Results and discussion: Simulated LLEs (Fig. 2) of the ternary mixtures hexane/benzene/$C_{2,4,6,8,10}$mimNTf_2 overestimates the mutual solubility of both hydrocarbons and the IL respect to the experiments but, successfully reproduces its increasing as the length of the alkyl chain becomes longer [4b]. The VLEs (Fig. 2) of the binary mixtures benzene/$C_{1,2,4}$mimNTf_2 have mean relative deviations respect to the experiment of *c.a*. 5.5%.

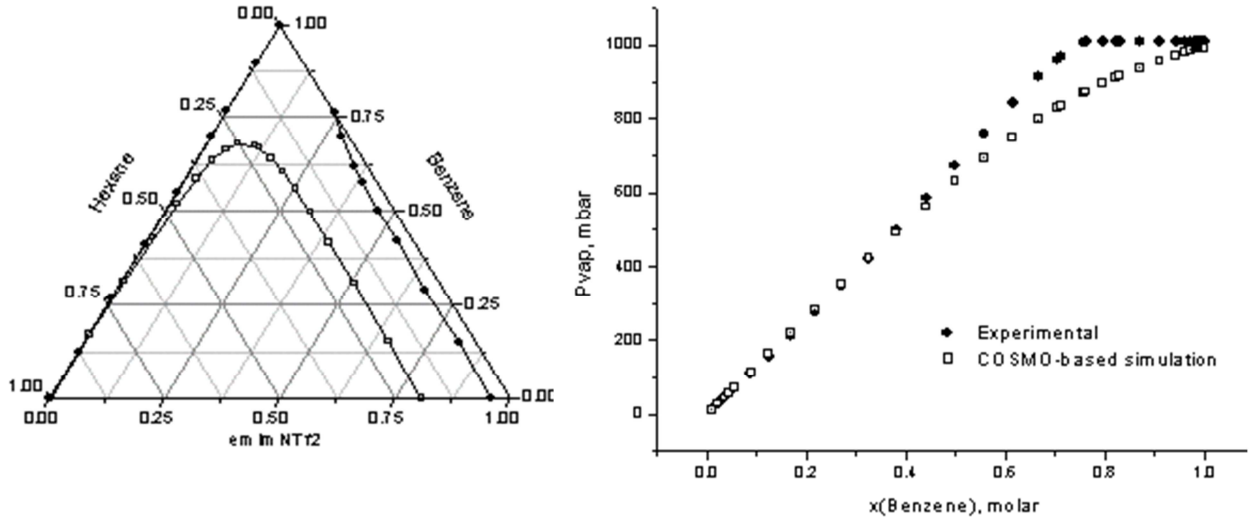

Figure 2. LLE for the ternary mixture hexane/benzene/emimNTf_2 (left) and VLE of the binary mixture benzene/emimNTf_2 (right). Experimental (•) and calculated (□) values by Aspen Plus calculations using COSMOSAC property model.

These results as all show the capability of COSMO-based process simulations to reproduce the main tendencies of the experimental LL and LV behaviours of the aliphatic/aromatic/IL selected mixtures and, correspondingly, to support screenings for selecting ILs with desired properties. For the individual extraction operation, the calculated molar $(S/F)_{min}$ rises linearly (R^2 = 0.984) with the chain length from 0.68 in mmimNTf_2 to 0.73 in bmimNTf_2. Furthermore, the 99.5 wt% purity hexane recovery decreases from 84% to 67% in the same sequence. For the process developed in [5b] (feed mass flow 300 ton/h, 10 wt% of aromatic, IL mass flow 1600 ton/h and a 12-theoretical stages LL extractor) the purity of the hexane varies in the range between 99.7 wt% with mmimNTf_2 to 96.2 wt% with dcmimNTf_2 whereas its recovery fall from 73.5% to 6.8% in the same sequence. This agrees with the experimental findings [4b] that short alkyl chain on the imidazolium cation of the IL lead to a better extractive separation of benzene from hexane. VLE calculations of the IL recovery from its mixtures with benzene give the results shown in Table 1 considering that operating temperature is limited to 450 K for avoiding the thermal decomposition of the IL.

IL	**Operating pressure, kPa**	**$Q_{Vaporization}$, kJ/kg IL recovered**
mmimNTf_2	9.7	179
emimNTf_2	11.3	162
bmimNTf_2	11.9	153

Table 1. Operating pressure and heat necessities of the IL recovery from its mixtures with benzene. TOper. = 450 K.

These results suggest that IL recovery is not a trivial question being necessary a whole process optimization considering not only thermodynamical but also technical and economical criteria. In fact, preliminary economical evaluation of the process (Fig. 1) using Aspen Process Economic Evaluator (v 7.3) shows that this operation represents 35 - 50 % of the overall (capital plus operating) process costs.

Summary: COSMO-supported process simulation is suitable for giving operational and/or economical information to be used in design and selection of ILs to specific uses. This could support rational decisions in the conceptual design of new processes including the solvent selection. If needed in more accurate uses (in basic engineering, for example) these calculations could be improved using, for instance, activity thermodynamic models their binary interaction parameters being regressed from experimental data for a limited group of the more perspective systems.

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