Aromatics Extraction. 1. Extraction Characteristics of ILs for the Toluene/Heptane Separation and Equipment Design Aspects

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The study focuses on the separation of aromatic hydrocarbons from aliphatic hydrocarbon mixtures in the presence of new extraction solvents – ionic liquids (ILs). A comparison of various solvents suitable for liquid-liquid extraction of aromatic - aliphatic hydrocarbon mixture is presented. Toluene and heptane were chosen as the representatives of the aromatic and aliphatic hydrocarbon families. As extraction solvents, ILs such as 1-ethyl-3-methylimidazolium ethylsulfate ([EMim][ESO$_4$]), 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([EMim][NTf$_2$]), 3-methyl-N-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)$_4$)], and 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([EMpy][NTf$_2$]) were selected. Selection of ILs from the potential candidates was based on the toluene/heptane selectivity and toluene distribution coefficients in heptane–toluene–IL mixtures published in literature. The effect of extraction properties of the selected IL solvents on the hydrocarbons mixture separation is documented by the results of the counter-current extractor simulation. For a comparison of the selected IL solvents basic extractor design parameters such as the number of theoretical stages, solvent to feed mass ratio, and the purity of the product were determined. The results were compared to those obtained for sulfolane, an extraction solvent considered as a benchmark for the aromatic–aliphatic hydrocarbons mixtures separation. For the thermodynamic description of LLE, the NRTL equation was used.

1. Introduction

Separation of aromatic hydrocarbons C_6-C_8 (benzene, toluene, ethylbenzene and xylenes) from C_4-C_{10} aliphatic hydrocarbon mixtures is one of the most challenging tasks in refinery processes. These hydrocarbons have boiling points in a narrow temperature range and several combinations of the mixture constituents form azeotropes. For the separation of these aromatic and aliphatic hydrocarbon mixtures, the following procedures were developed: liquid-liquid extraction for mixtures with aromatic content from 20 to 65 mass %, extractive distillation for 65-95 mass %, and azeotropic distillation for aromatic content higher than 90 mass % (Perreiro et al., 2012). Typical solvents used in the liquid-liquid (L–L) extraction are polar compounds such as sulfolane, *N*-methyl pyrrolidone, *N*-formyl morpholine, glycols, or propylene carbonate. When these conventional solvents are used, additional distillation steps are required to separate the solvent from both the extract and the raffinate phases, which increases the separation costs (Meindersma and de Haan, 2008).

Recently, ionic liquids (ILs) have been identified as promising solvents to replace conventional solvents in L–L extraction. An IL–based extraction process requires fewer process steps and less energy consumption, provided the aromatic distribution coefficient, D_B, and/or the aromatic/aliphatic selectivity, S_{BA}, are higher than those of sulfolane, one of the most common solvent used for the separation of aromatic and aliphatic hydrocarbons. A higher aromatic/aliphatic selectivity means a purer aromatic product, less extraction of aliphatic hydrocarbons, and a lower number of extraction stages. A high

aromatic distribution coefficient means a lower solvent-to-feed ratio with smaller extraction and regeneration units (lower investment costs including smaller IL inventory, and lower energy consumption). Therefore, information on the aromatic distribution coefficients and selectivities is important when choosing the appropriate extraction solvent. An extensive study of these solvent characteristics was done by Meindersma et al. (2010). Based on the performed analysis, it was concluded that industrial application of ILs for aromatics extraction has not yet been done because only four of the total 121 investigated ILs are considered suitable for aromatic/aliphatic separation. Most of the reported ILs do not provide sufficiently high aromatics distribution coefficients and/or high enough aromatic/aliphatic hydrocarbon selectivity compared to those achieved by conventional solvents such as sulpholane.

2. Theoretical

In liquid–liquid extraction, a solute is distributed between two immiscible liquid phases. For industrial applications it is important to describe the liquid–liquid equilibrium (LLE) of the system to be separated. For LLE in a system of $N = 3$ species at constant T and P, the equilibrium criterion for each component of the mixture is written as:

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \qquad [T,P] \qquad i = A, B, C \tag{1}$$

Superscripts I and II denote the liquid phases; x_i^I and x_i^{II} are mole fractions of component i in the respective equilibrium phases; γ_i^I and γ_i^{II} represent activity coefficients for component i throughout both liquid phases and are expressed in the form of excess molar Gibbs energy dependence on the composition of the liquid phase using the NRTL equation.

The original NRTL equation (Renon and Prausnitz, 1968) is written as follows:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} + \sum_j \frac{x_j G_{ij}}{\sum_l G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_l G_{lj} x_l} \right) \qquad i, j, k, l = A, B, C \tag{2}$$

Binary parameters τ_{ij} and G_{ij} are defined by the following expressions:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \qquad G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \qquad i, j = A, B, C \qquad i \neq j \tag{3}$$

where $\tau_{ij} \neq \tau_{ji}$, $\tau_{ii} = \tau_{jj} = 0$, R is the universal gas constant, $(g_{ij} - g_{jj})$ parameters represent the extent of interactions between molecules i and j; and α_{ij} is the non-randomness parameter of the NRTL equation.

3. Results and discussion

3.1 LLE description of the studied ternary systems

The present study focuses on the separation of aromatics from their mixtures with aliphatic hydrocarbons in the presence of four different ionic liquids. As a model system, the heptane-toluene binary mixture was chosen. As extraction solvents, 1-ethyl-3-methylimidazolium ethylsulfate ([EMim][ESO$_4$]), 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([EMim][NTf$_2$]), 3-methyl-*N*-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)$_4$]), and 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([EMpy][NTf$_2$]) were selected. The results were compared with those obtained for sulfolane, Sources of ternary LLE data are given in Table 1.

Table 1: List of ternary LLE systems

System	Source of NRTL parameters
Heptane–Toluene–Sulfolane at 313.2 K	Meindersma (2005)
Heptane–Toluene–[EMim][NTf$_2$] at 298.15 K	Corderí et al. (2012)
Heptane–Toluene–[EMpy][NTf$_2$] at 298.15 K	Corderí et al. (2012)
Heptane–Toluene–[EMim][ESO$_4$] at 298.15 K	González et al. (2011)
Heptane–Toluene–[3-mebupy][B(CN)$_4$] at 303.2 K	Meindersma et al. (2011)

Table 2: NRTL equation parameters for LLE calculation of the ternary system heptane (A)–toluene (B)–solvent (C) at T = 298.15 K

Binary	$g_{ij} - g_{jj}$ kJ mol^{-1}	$g_{jj} - g_{ii}$ kJ mol^{-1}	α_{ij}
Heptane–Toluene	–1.5661	0.9643	0.30
Heptane–Sulfolane	11.2471	9.3172	0.30
Toluene–Sulfolane	5.7030	–0.2631	0.30
Heptane–Toluene	1.781	1.5898	0.15
Heptane–[EMim][NTf$_2$]	47.4713	7.1305	0.15
Toluene–[EMim][NTf$_2$]	73.9542	3.0348	0.15
Heptane–Toluene	–3.9812	2.3341	0.15
Heptane–[EMpy][NTf$_2$]	55.3848	6.0139	0.15
Toluene–[EMpy][NTf$_2$]	64.1299	–2.8477	0.15
Heptane–Toluene	-5.1741	7.886	0.10
Heptane–[EMim][ESO$_4$]	1143.8	12.329	0.10
Toluene–[EMim][ESO$_4$]	20.412	-4.9679	0.10
Heptane–Toluene	-1.5769	6.6965	0.30
Heptane–[3-mebupy][B(CN)$_4$]	99.7471	8.9856	0.20
Toluene–[3-mebupy][B(CN)$_4$]	11.4879	-2.4987	0.30

To calculate ternary LLE, the original NRTL model was used. Parameters of NRTL equation for the respective ternary systems were taken from literature (Meindersma, 2005) later González et al., 2011; Meindersma et al., 2011) and recently Corderí et al., 2012; and they are summarized in Table 2. In all cases, "binary" NRTL parameters were obtained by direct fitting of ternary LLE data.

The extent of the toluene–heptane mixture separation was deduced using the aromatics distribution coefficient, D_B, and/or the aromatic/aliphatic selectivity of the extraction solvent, S_{BA}.

$$D_B = x_B^{II} / x_B^{I} \tag{4}$$

$$S_{BA} = D_B / D_A \tag{5}$$

The calculated values of the distribution coefficient of toluene and of the toluene/heptane selectivity versus the mole fraction of toluene in the heptane rich-phase are plotted in Figures 1 and 2.

A comparison of the dependencies in Figures 1 and 2 for the system heptane–toluene with various ILs and with sulpholane shows that the capacity, D_B, of the solvent [Emim][ESO$_4$] is the lowest, while it is the highest in case of [3-mebupy][B(CN)$_4$]. Selectivity of IL solvents, S_{BA}, is the highest for [Emim][ESO$_4$] (as it was expected), and the least selective solvent seems to be [Empy][NTf$_2$]. It is clear that the most suitable.
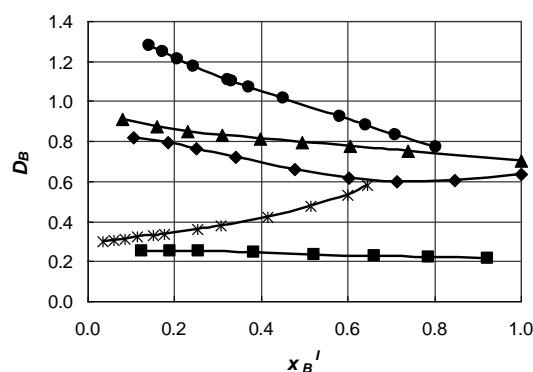

Figure 1: Distribution coefficient, D_B, versus mole fraction of toluene in raffinate, x_B^{I}, for the ternary systems heptane (A)–toluene (B)–solvent (C): sulpholane (✲), [EMim][NTf$_2$] (◆), [EMpy][NTf$_2$] (▲), [EMim][ESO$_4$] (■), and [3-mebupy][B(CN)$_4$] (●).
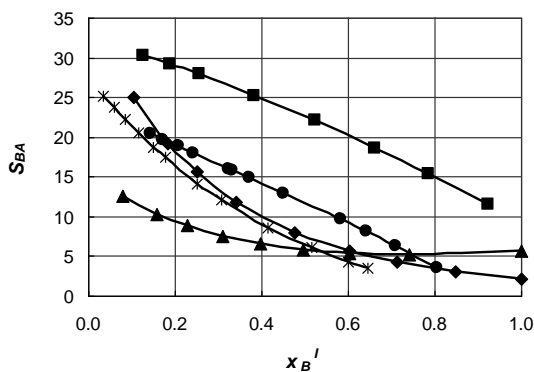
Figure 2: Selectivity, S_{BA}, versus mole fraction of toluene in raffinate, x_B^I, for the ternary systems heptane (A)–toluene (B)–solvent (C): sulpholane (✱), [EMim][NTf$_2$] (◆), [EMpy][NTf$_2$] (▲), [EMim][ESO$_4$] (■), and [3-mebupy][B(CN)$_4$] (●)
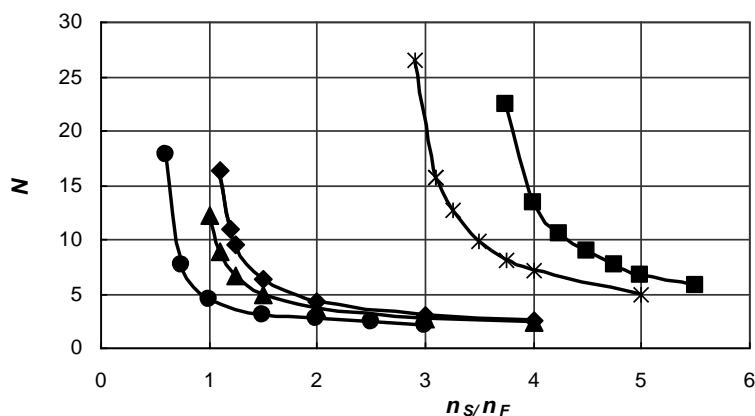

Figure 3: Relation between the number of theoretical stages, N, and the solvent to feed ratio, n_S/n_F. Simulation conditions: concentration of toluene in feed x_{FB} = 0.15, maximum content of toluene in the final raffinate $x_{R/B}$ = 0.005, purity of solvent x_{SC} = 1. Extraction solvent: sulpholane (✱), [EMim][NTf$_2$] (◆), [EMpy][NTf$_2$] (▲), [EMim][ESO$_4$] (■), and [3-mebupy][B(CN)$_4$] (●)

solvent for the toluene–heptane mixture separation with the lowest content of aromatic hydrocarbons in the feed flow (here 0.15 mole %) is [3-mebupy][B(CN)$_4$]. [Emim][NTf$_2$] is an IL comparable with [3-mebupy][B(CN)$_4$].

3.2 Design calculations

Simulation of the toluene/heptane separation in the presence of ILs and sulpholane as the extraction solvents was carried out using the equilibrium model of a counter-current extraction column. The sets of material balances of equilibrium stages combined with the sets of ternary liquid–liquid equilibrium conditions (Eq(1)) were solved simultaneously. The simulations were carried out using the MATLAB program, which corresponds to the Hunter–Nash method (Graczová et al., 2013). The content of toluene in feed was 15 mole %, with the purity of the solvent equal to 1. As the extraction purity criterion, the maximum toluene concentration of 0.5 mole % in the final raffinate was selected.

Results of the simulation are expressed in the form of a relation between the number of theoretical stages, N, and the solvent to feed ratio, n_S/n_F, presented graphically in Figure 3. It is clear that for the separation of the heptane–toluene mixture, the solvent consumption is significantly lower when using ILs as the extraction solvent compared to sulpholane, except for [Emim][ESO$_4$]. Considering a column with ten theoretical stages, the solvent to feed molar ratio, n_S/n_F, when using sulpholane is 3.60. In case of using the remaining three ILs, the solvent consumption was much lower: n_S/n_F = 0.70 for [3-mebupy][B(CN)$_4$], n_S/n_F = 1.05 for [EMpy][NTf$_2$], and n_S/n_F = 1.23 for [EMim][NTf$_2$]. Only in case of [Emim][ESO$_4$], the solvent consumption (n_S/n_F = 4.28) was higher than that obtained using sulpholane as the extraction solvent.

As the separation efficiency criterion, the yield of toluene in the extract, Y_B, and the recovery of heptane in the raffinate, X_A, were used. They were investigated for different consumptions of solvent, calculated as

$$Y_B = \frac{n_{E1B} - n_{SB}}{n_{FB}} \qquad (6)$$

$$X_A = \frac{n_{RNA}}{n_{FA}} \qquad (7)$$

where n_{E1B} is the molar flow of toluene in extract leaving the 1st theoretical stage of the extraction column; n_{RNA} the molar flow of heptane in the final raffinate stream; n_{SB} the molar flow of toluene in the solvent flow; and n_{FA} and n_{FB} are the molar flows of toluene and heptane in the feed.

In Figures 4 and 5, variation of the toluene yield in the extract, Y_B, and the heptane yield in raffinate, X_A, versus the solvent to feed molar flows ratio, n_S/n_F, is presented. It is evident that when using sulpholane as well as the ILs [EMim][NTf$_2$] and [EMim][ESO$_4$] as the extraction solvents, it was impossible to reach toluene yield higher than 97.5 % in the extract even when with larger amounts of the extraction solvents (higher values of the n_S/n_F ratio).

Considering the extraction column with ten theoretical stages and the specific consumption of the solvent, n_S/n_F, corresponding to the preset raffinate purity, $x_{RNB} = 0.005$, toluene yield in the extract for the chosen extraction solvents is comparable ranging between 97.26 % for [EMim][ESO$_4$] and 97.52 % for [3-mebupy][B(CN)$_4$].
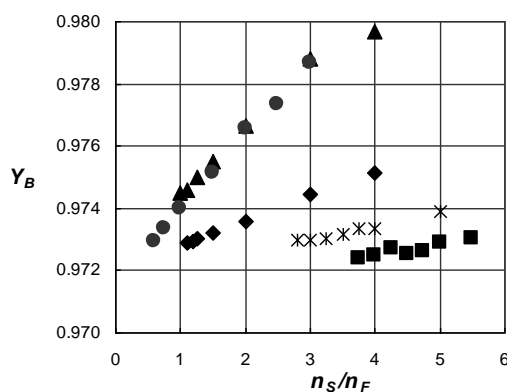

Figure 4. Yield of toluene in the extract, Y_B, versus molar ratio of solvent to feed, n_S/n_F. Extraction solvent: sulpholane (✳), [EMim][NTf$_2$] (◆), [EMpy][NTf$_2$] (▲), [EMim][ESO$_4$] (■), and [3-mebupy][B(CN)$_4$] (●).
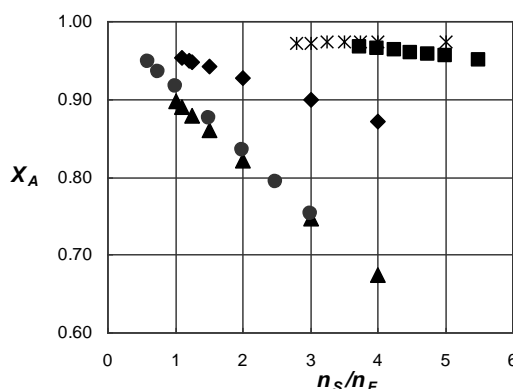

Figure 5. Recovery of heptane in the raffinate, X_A, versus molar ratio of solvent to feed, n_S/n_F. Extraction solvent: sulpholane (✳), [EMim][NTf$_2$] (◆), [EMpy][NTf$_2$] (▲), [EMim][ESO$_4$] (■), and [3-mebupy][B(CN)$_4$] (●).

On the other hand, variation of the heptane recovery in raffinate, X_A, with the solvent to feed mole ratio differs considerably. Assuming the extraction column with ten theoretical stages and the respective solvent consumption to reach the preset raffinate purity, $x_{R/B} = 0.005$, heptane recovery of 93.5 % in the raffinate was computed using [3-mebupy][B(CN)$_4$] as the extraction solvent. [EMpy][NTf$_2$] is even less selective, when approximately 11 % of heptane was transferred to the extract and only about 89 % of the original amount of this component remained in raffinate. The most beneficial situation was observed when sulfolane was used as the extraction solvent. The recovery of heptane in the final raffinate was as high as 97.5 %. Regarding the solvent selectivity, the most advantageous of the ILs chosen is [EMim][ESO$_4$].

4. Conclusions

Various factors influence the selection of ILs as extraction solvents. Firstly, the solvent extraction characteristic, capacity and selectivity, determine the specific consumption of the extraction solvent and the separation efficiency of the equipment used. It was found that the separation efficiency of the extraction column depends, to a certain extent, on the solvent consumption. By increasing the solvent consumption, the yield of toluene in the extract decreases rapidly and, at the same time, the content of heptane in the ILs-rich phase increases. As a consequence, costs of the extract purification increase. The influence of the solvent characteristics on the process economics is discussed in the second part of this paper (Steltenpohl and Graczová, 2014).

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