Aromatics Extraction. 2. Economic Aspects

Pavol Steltenpohl, Elena Graczová*

Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
elena.graczova@stuba.sk

Besides the core-equipment design parameters, investment and operational costs of a separation unit are influenced by the down-stream separation apparatuses design. In case of aromatics liquid-phase extraction, down-stream processing is represented by the extraction solvent regeneration carried out in order to obtain pure products, i.e. components of the original mixture, and the solvent that is repeatedly used in the extractor. Solvent regeneration is typically done in a distillation column as the extraction solvent boiling point differs considerably from those of the original mixture components. The presence of a distillation/stripping column and the conditions applied in this equipment show a significant impact on the overall production line profitability. Moreover, purity of regenerated extraction solvents influences the separation efficiency of an extractor. Here, the impact of the extraction solvent nature on the production costs is discussed assuming ionic liquids 1-ethyl-3-methylimidazolium ethylsulfate ([EMim][ESO$_4$]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide ([EMim][NTf$_2$]), 3-methyl-*N*-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)$_4$)]), and 1-ethyl-3-methylpyridinium bis(trifluoromethylsulphonyl)imide ([EMpy][NTf$_2$]), or sulphotane as an extraction solvent used for heptane–toluene mixture separation.

1. Introduction

Separation of aromatics from complex hydrocarbon mixtures is usually carried out using liquid-phase extraction, extractive distillation, or azeotropic distillation. The separation method selection depends on the aromatics content in the hydrocarbons feed (Weissermel and Arpe, 2003).

Concerning liquid-phase extraction, several extractive solvents were proposed and used for the separation of aromatics from their mixtures with less polar hydrocarbons. Due to its high selectivity and fair extraction capacity, sulpholane became a benchmark of the extraction solvents for aromatics separation by the liquid-phase extraction (Rawat and Gulati, 1976). Pure aromatics stream is then obtained from the extract during the solvent regeneration in a distillation column. Non-aromatics are obtained as a raffinate from which the solvent is separated in order to prevent its loss. Simplified flow sheet of a liquid extraction-based aromatics separation with the extraction solvent regeneration is presented in Figure 1.

Recently, imidazolium- and pyridinium-based ionic liquids (ILs) have been shown to possess comparable or even better extractive solvent separation characteristics (aromatics to aliphatic hydrocarbons selectivity and aromatics distribution coefficient) compared to sulphotane (Meindersma, 2005). Moreover, ILs are considered as non-volatile liquids with very low values of saturated vapor pressure even at elevated temperatures (Rocha et al., 2011); thus, they are easy to separate from the mixture with hydrocarbons by simple distillation or stripping. On the other hand, very low solubility of ILs in non-aromatics makes the solvent recovery from a raffinate stream unnecessary (Meindersma, 2005).

According to Meindersma and de Haan (2008), major part of investment and operational costs of an aromatics separation unit are connected with the solvent regeneration and prevention of its loss in the raffinate stream. In case of traditional extraction solvents, e.g. sulphotane, the extract is distilled in a column during the solvent regeneration. Heating and cooling duties of the distillation column reboiler and condenser depend on the amount of extract processed, the value of the reflux ratio and the components vaporization heat. To the regeneration costs, also costs of the solvent recovery from the raffinate should be included. When ionic liquid is used as the extractive solvent for the aromatics separation, IL regeneration by stripping is less energy demanding than distillation.
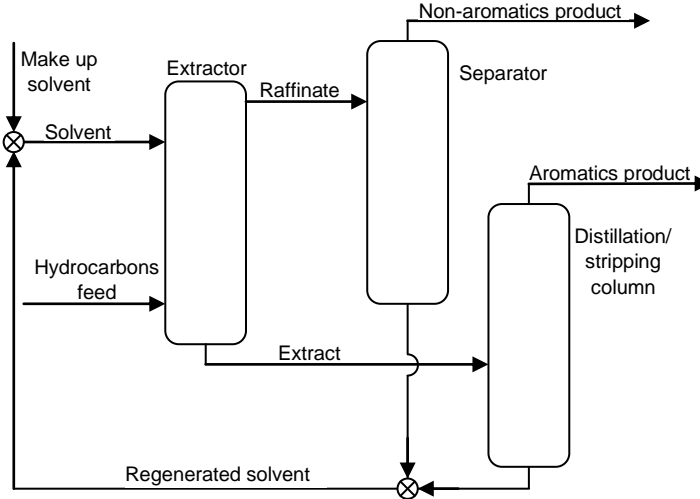
Figure 1: Simplified scheme of the liquid-phase extraction of aromatics from a hydrocarbons mixture with extractive solvent regeneration and recovery

Consequently, overall costs of the aromatics separation using sulphotane are substantially higher than those connected with the use of ionic liquids as the solvent for the liquid-phase extraction. Here, the influence of separation characteristics of the selected ILs on some economic parameters of aromatics separation is presented.

2. Aromatics separation simulation

The model mixture to be separated consisted of heptane and toluene representing aliphatic and aromatic hydrocarbons, . As extractive solvents, 1-ethyl-3-methylimidazolium ethylsulfate ([EMim][ESO$_4$]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide ([EMim][NTf$_2$]), 3-methyl-*N*-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)$_4$]), 1-ethyl-3-methylpyridinium bis(trifluoromethylsulpho-nyl)imide ([EMpy][NTf$_2$]), and sulphotane were chosen. Liquid–liquid equilibria of individual ternary systems were modeled using the NRTL excess Gibbs energy model (Renon and Prausnitz, 1968). Binary parameters of the NRTL equation were obtained from literature. Data for sulphotane were taken from Meindersma (2005), for [EMim][NTf$_2$] and [EMpy][NTf$_2$] from Corderí et al. (2012), for [EMim][ESO$_4$] from González et al. (2011), and for [3-mebupy][B(CN)$_4$)] from Meindersma et al. (2011). Values of the NRTL binary parameters for the chosen systems are summarized in Graczová et al. (2014).

Simulation of the model hydrocarbon mixture separation in the presence of extraction solvents was carried out using the equilibrium model of a counter-current extraction column (Figure 2). Simultaneous solution of material balances of the equilibrium stages was combined with summation equations of mole fractions in equilibrium phases and the ternary liquid–liquid equilibrium description:

$$-\left(\dot{n}_{Rj} + \dot{n}_{Ej}D_{ij}\right)x_{Rij} + \dot{n}_{Ej+1}D_{ij+1}x_{Rij+1} = -\dot{n}_F x_{Fi} \quad i = A,B,C \quad j = 1 \tag{1}$$

$$\dot{n}_{Rj-1}x_{Rij-1} - \left(\dot{n}_{Rj} + \dot{n}_{Ej}D_{2ij}\right)x_{R2i} + \dot{n}_{Ej+1}D_{ij+1}x_{Rij+1} = 0 \quad i = A,B,C \quad j = 2,3,...,N-2,N-1 \tag{2}$$

$$\dot{n}_{Rj-1}x_{Rij-1} - \left(\dot{n}_{Rj} + \dot{n}_{Ej}D_{ij}\right)x_{Rij} = -\dot{n}_S x_{Si} \quad i = A,B,C \quad j = N \tag{3}$$

where x_i is the *i*-th component mole fraction in the extract, feed, raffinate, and solvent (E, F, R, and S) from the *j*-th equilibrium stage and $\dot{n}$ is molar flow. D_{ij} is the *i*-th component distribution coefficient
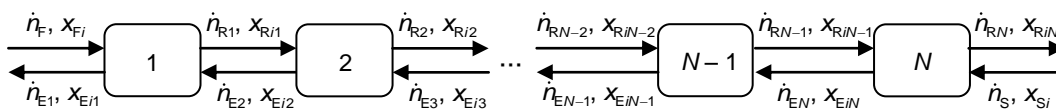

Figure 2: Schematic representation of an extraction column composed of N equilibrium stages

Table 1: Input data for the extractor simulations

$\dot{n}_F$ /(kmol h^{-1})	x_{FA}	x_{FB}	x_{FC}	N	x_{RBN}
10	0.85	0.15	0.00	10	0.005
Solvent composition			x_{SA}	x_{SB}	x_{SC}
Computation set		1	0	0	0
		2	0.0005	0.0005	0.999
		3	0.001	0.001	0.998

at the *j*-th equilibrium stage representing the isoactivity condition:

$$D_{ij} = \frac{x_{Eij}}{x_{Rij}} = \frac{\gamma_{Rij}}{\gamma_{Eij}} \quad i = A,B,C \quad j = 1,2,...,N-1,N \tag{4}$$

γ_{Rij} is the *i*-th component activity coefficient in the heptane-rich phase from the *j*-th equilibrium stage and γ_{Eij} is the *i*-th component activity coefficient in the extraction solvent-rich phase from the *j*-th equilibrium stage.

3. Results and discussion

Three sets of computations were carried out for every extraction solvent using the above-mentioned extractor model assuming different purities of the extraction solvent used. In all simulations, the number of extractor theoretical stages, feed amount and composition, as well as the mole fraction of toluene in the final raffinate were fixed. The input values are presented in Table 1. The output information was the consumption of the extraction solvent relative to the amount of feed and the complete composition of all streams appearing in Figure 2 and also in the set of material balances Eqs (1)–(3).
In Figure 3, extraction solvent selectivity (S_{BA}) versus toluene distribution coefficient (D_B) is presented. The values of both parameters were calculated for the composition of the final raffinate (heptane-rich phase) and its conjugated extract (extraction solvent-rich phase) leaving the last (*N*-th) extractor equilibrium stage. For comparison, also the value corresponding to sulphotane is shown in Figure 3. Solvent selectivity is given by the following equation:

$$S_{BA} = \frac{D_{BN}}{D_{AN}} = \frac{x_{EBN} x_{RAN}}{x_{RBN} x_{EAN}} \tag{5}$$

From Figure 3 it can be deduced that, besides [EMim][ESO$_4$], the chosen ILs posses different extraction selectivity and capacity in the toluene–heptane liquid phase extraction compared to sulphotane.
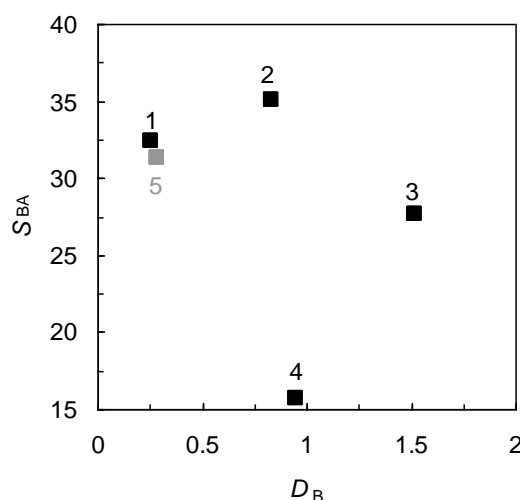

Figure 3: Selectivity of toluene–heptane extraction separation versus the toluene distribution coefficient diagram for the chosen extraction solvents: [EMim][ESO$_4$] (1), [EMim][NTf$_2$] (2), [3-mebupy][B(CN)$_4$] (3), [EMpy][NTf$_2$] (4), and sulphotane (5). The values were computed for fixed value of toluene content in the final raffinate x_{RBN} = 0.005

Figure 4 presents the comparison of extraction solvents consumption relative to that of sulphotane assuming different purity of solvents. It can be seen that the ILs consumption is lower compared to that of sulphotane (values of relative consumption lower than 0.4) with the exception of [EMim][ESO$_4$], which is slightly higher (relative consumption of about 1.2). Moreover, considering solvents which contain different levels of the impurities content, a decrease in the consumption of ILs relative to that of sulphotane was observed. The only exception was the increase in the relative consumption of [EMim][ESO$_4$] when a higher level (0.002 mole %) of impurities content in the extractive solvent was taken into account.

Relative solvent consumption (RSC) values were obtained by comparing the amount of IL used as the extraction solvent to the amount of sulphotane at the same simulation conditions:

$$RSC = \dot{n}_{S(IL)} / \dot{n}_{S(Sulfolane)} \tag{6}$$

Generally, the use of extraction solvent containing impurities causes an increase in the solvent consumption, the excess of which increases exponentially with the decreasing value of the toluene distribution coefficient (Figure 5). In case of [3-mebupy][B(CN)$_4$] (D_B = 1.52), the increase was only about 0.8 % and 1.7 % for the impurities content of 0.001 mole % and 0.002 mole % compared to the consumption of pure solvent. On the other hand, the increase in solvent consumption for [EMim][ESO$_4$] (D_B = 0.26) was about 10.2 % and 22.5 % for the two levels of impurities content considered in this study (Figure 5). The value of the increase in solvent consumption (ISC/%) compares the consumption of regenerated and pure extraction solvent according to the following equation:

$$ISC = \left(\dot{n}_{S(with\ impurities)} / \dot{n}_{S(pure)} - 1 \right) 100\% \tag{7}$$

The increase of the solvent amount used in aromatics liquid-phase extraction can cause an increase in the dimensions both of the extractor and of the down-stream processing equipment. Moreover, energetic equipment (heaters, coolers) dimensions and the consumption of heating and cooling media can be influenced.

In case of ILs used as extraction solvents for aromatics separation from complex hydrocarbons mixtures, extracted aromatics and an unavoidable amount of non-aromatic hydrocarbons are removed from the extract via stripping with permanent gas. The consumption of stripping medium in stripping column can be assumed to be proportional to the amount of hydrocarbons present in the extract. Afterwards, the extracted aromatics with a portion of other hydrocarbons are recollected from the stripping medium in a cooler as the aromatics product. Consumption of the cooling medium is proportional to the amount of the strippant used.
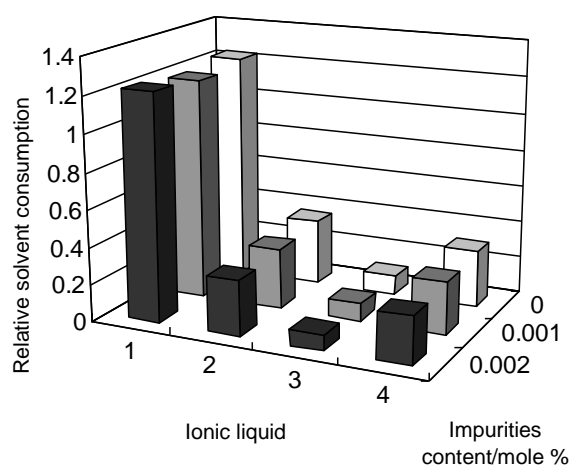

Figure 4: Variation in the solvent consumption relative to that of sulphotane (RSC) versus the extraction solvent purity for: [EMim][ESO$_4$] (1), [EMim][NTf$_2$] (2), [3-mebupy][B(CN)$_4$] (3), and [EMpy][NTf$_2$] (4)
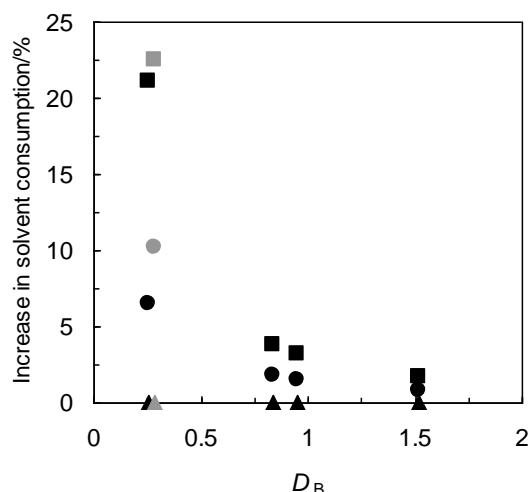
Figure 5: Variation of the extraction solvent consumption increase (ISC) versus the toluene distribution coefficient (D$_B$) for: pure solvent (▲) and solvent containing 0.1 mole % (●) and 0.2 mole % (■) of impurities. Data for sulphotane are given in grey color
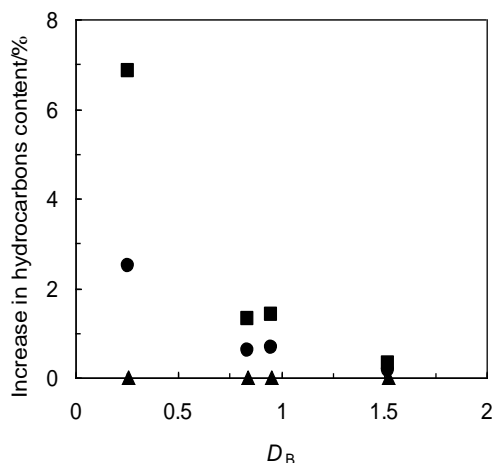
Figure 6: Increase of the amount of hydrocarbons (heptane and toluene) in extract (ICH) versus D_B for: pure solvents (▲) and solvents containing 0.1 mole % (●) and 0.2 mole % (■) of impurities

Thus, the use of solvent with higher content of impurities should be avoided and, therefore, thorough purification of the extraction solvent is recommended during the regeneration step.

Figure 6 shows the influence of the solvents purity on the cumulative amount of heptane and toluene in extracts. An exponential increase of the excess hydrocarbons amount in the extract is observed when plotted against D_B. The increase in the hydrocarbons content (IHC/%) was computed by comparing the amount of hydrocarbons accumulated in the extract when using regenerated and pure extraction solvent:

$$IHC = \left[\frac{\dot{n}_{E(with\ impurities)} \left(x_{EA1} + x_{EB1} \right)}{\dot{n}_{E(pure)} \left(x_{EA1} + x_{EB1} \right)} - 1 \right] 100\% \tag{8}$$

However, from the separation unit economics point of view, the most relevant information is the overall amount of hydrocarbons present in the extract. The values of hydrocarbons yield in the extract for the chosen ionic liquids are shown in Figure 7 with respect to the toluene distribution coefficient. No direct relation between the separation characteristics (S_{BA} and D_B) and the hydrocarbons content in the extract was found, although this chart resembles a mirror reflection of the S_{BA} versus D_B diagram (Figure 3).
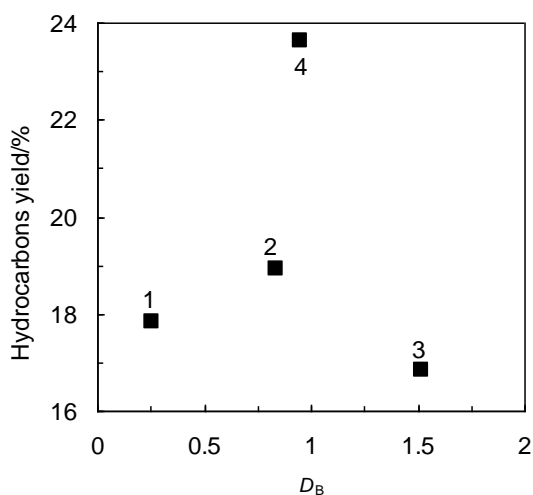

Figure 7: Hydrocarbons (heptane + toluene) yield in extracts obtained by liquid-phase extraction of the model mixture versus D_B using: [EMim][ESO$_4$] (1), [EMim][NTf$_2$] (2), [3-mebupy][B(CN)$_4$] (3), and [EMpy][NTf$_2$] (4) as extraction solvents
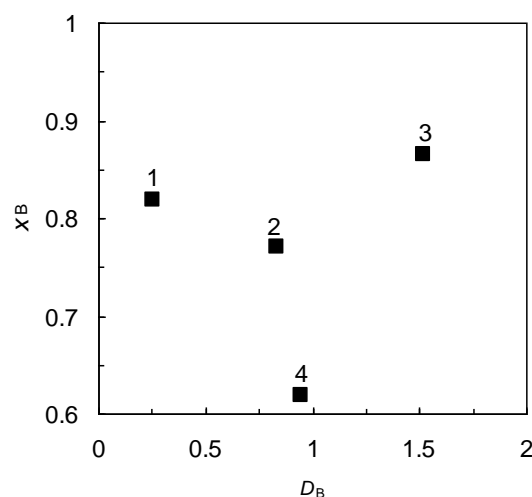
Figure 8: Toluene mole fraction in aromatics product from the model mixture extraction versus D_B using: [EMim][ESO$_4$] (1), [EMim][NTf$_2$] (2), [3-mebupy][B(CN)$_4$] (3), and [EMpy][NTf$_2$] (4) as extraction solvents

The highest yield hydrocarbons in the extract was observed in case of [EMpy][NTf$_2$], the ionic liquid with the second highest value of the toluene distribution coefficient (D_B = 0.95) among the ILs chosen as extraction solvents for aromatics separation. On the other hand, selectivity of this IL computed for the preset raffinate purity value, x_{RBN} = 0.005, was S_{BA} = 15.6, the lowest of all ILs considered in this study.

Also, composition of the aromatics product obtained from the extract by stripping of the whole amount of hydrocarbons from ILs was investigated. Large differences in the composition of this product were observed as shown in Figure 8. Mole fraction of toluene in the aromatics product (x_B) did not exceed the value of 0.90 irrespective of the extraction solvent used. Thus, another purification step (extraction or azeotropic distillation, Weissermel and Arpe (2003)) is required to provide a pure aromatics stream.

4. Conclusions

Simulation results confirmed that high value of D_B is a key parameter influencing the aromatics extraction process (Meindersma and de Haan, 2008). Figures 4 and 5 show that the solvent purity has a significant impact on the solvent consumption (2-22 % increase for the solvent impurities content of 0.2 mole %) and the extraction column size/operation conditions. The excess amount of solvent necessary for the extraction process increases exponentially with the decrease of D_B. The presence of impurities causes an increase of the hydrocarbons amount in the ILs-rich phase, thus increasing the costs of the extract down-stream processing. An exponential increase of the extra amount of hydrocarbons (0.2-2.5 % at the impurity level of 0.1 mole % and 0.5-7 % at 0.2 mole %) with the decreasing value of D_B was observed (Figure 6). Similar extra costs connected with separation of hydrocarbons during ILs regeneration (strippant and cooling medium consumption as well as the equipment size) are to be expected. In order to get a pure aromatics stream, hydrocarbons mixture resulting from the ILs regeneration (toluene mole fraction on the level of 62-87 mole %, Figure 8) requires further purification step irrespective of the IL used as the solvent.

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