An Ionic Liquid Proposed as Solvent in Aromatic Hydrocarbon Separation by Liquid Extraction

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Liquid–liquid extraction is the most common method for extraction of aromatics from their mixtures with aliphatic hydrocarbons. An ionic liquid (IL) 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide [BMpyr][NTf$_2$] was tested as solvent for this separation. The liquid–liquid equilibria (LLE) of the ternary mixtures heptane + benzene, or toluene, or ethylbenzene + [BMpyr][NTf$_2$] were carried out at 298.15 K. The solvent ability of the IL was evaluated in terms of solute distribution ratio and selectivity. The results were compared with those previously reported for the extraction of aromatics from its mixtures with heptane by using ILs. The conventional process using sulfolane as solvent was discussed. The experimental LLE data were correlated by non-random two liquid equation. A proposal of extraction process with this IL as solvent is simulated by conventional software and the results are shown. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 381–386, 2010

Keywords: aromatic hydrocarbons, liquid–liquid equilibria, extraction, ionic liquid, [BMpyr][NTf$_2$]

Introduction

Several processes[1] for the separation of aromatic and aliphatic hydrocarbon mixtures in reformate gasoline distilled from crude has been developed: liquid extraction for aromatic contents from 20 to 65 wt %, extractive distillation for 65–90 wt %, and azeotropic distillation for high aromatic content higher than 90 wt %. The key products of aromatics are benzene, toluene, and ethylbenzene, and they are considered the most widespread and important raw materials in plastic and synthetic fiber manufacture.[2] Aromatics are obtained almost exclusively from the fuels, coal, and oil, however, the most economically feasible process is to remove them from fuels.

Over the last years, ionic liquids (ILs) were suggested as a novel alternative to traditional organic solvents for extractions.[3] In particular, the selection of these new chemicals for the separation of aromatic from their mixtures by solvent extraction was investigated.[4–15] In turn, here, we present an alternative extraction process using an IL as solvent in the separation of aromatic hydrocarbons from its mixture with heptane, which may contain up to 90% aromatics. The application of ILs for extraction processes is promising because a simple flash distillation is required for the solvent recovery.

In this work, the suitability of the selected IL to the separation of aromatics was trying to confirm and the ternary mixtures heptane + benzene, or toluene, or ethylbenzene + 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide [BMpyr][NTf$_2$] have been chosen for experimental determination of the liquid–liquid equilibria (LLE) at 298.15 K. The selection of the temperature was made in the basis of an economical operation cost in this selected process. The extraction of above aromatics from its mixtures with heptane was chosen to expand the research to the separation of hydrocarbons of the C$_7$-fraction of aliphatic hydrocarbons. Preliminary studies of activity coefficients at infinite dilution of [BMpyr][NTf$_2$] has in its favor the low activity coefficients of benzene and high ones of heptane.[16] As this

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result suggest, the IL is selected as solvent in the case of the mixture heptane with benzene.

The experimental data are correlated by applying the nonrandom two liquid (NRTL) equation,[17] thus facilitating their implementation and use in computerized applications as the simulation of the extraction process performed by using the HYSYS software with the aim to optimize operation conditions for continuous extraction of aromatic from their mixture. The optimized conditions were evaluated in practice as a preliminary study for an industrial scaling up.

Experimental

Chemicals

Heptane, benzene, toluene, and ethylbenzene were purchased by Aldrich with a nominal purity ≥99.0 wt % for heptane, ≥99.9 wt % for benzene, and ≥99.8 wt % for toluene and ethylbenzene, respectively. Gas chromatography verified their purities. [BMpyr][NTf$_2$] was acquired at IoLiTec with a nominal purity ≥99.0 wt % and a chloride impurity content (ppm <100) supplier by the company. The IL water content was determined using 831 Karl Fisher coulometer showing 55 ppm.

Experimental LLE procedure

Glass cell was used for the experimental determination of the LLE tie-lines. Ternary mixtures of known composition were placed into the cell and thermostatted by a water jacket connected to a bath controlled to ±0.01 K. The temperature in the cell was measured with an ASL F200 digital thermometer with an uncertainty of ±0.01 K. Each mixture was stirred vigorously for 1 h and allowed to settle for 4 h to guarantee a complete split of the equilibrium phases. Then, samples of both layers were taken with a syringe for composition analysis by means of the densities and refractive indices. The compositions were inferred using calibration curves, which had been previously constructed at 298.15 K. These curves were obtained by fitting the composition on the binodal curve by means of densities and refractive indices at 298.15 K. The uncertainty of the phase composition is estimated as $\pm 4 \times 10^{-3}$ in mass fraction. All weighing was carried out in a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 10^{-4}$ mass fraction. Densities were measured with an Anton Paar DSA-48 digital vibrating tube densimeter with an uncertainty of $\pm 2 \times 10^{-4}$ g/cm^3, and refractive indices with Dr. Kernchen ABBEMAT WR automatic refractometer with an uncertainty of $\pm 4 \times 10^{-5}$.

Results and Discussion

LLE data

LLE data for the ternary mixtures heptane + benzene, or toluene, or ethylbenzene + [BMpyr][NTf$_2$] at 298.15 K are reported in Table 1. In these experiments, no IL was detected in the hydrocarbon equilibrium phase for the tie-lines of the systems. The absence of IL in the upper phase is desirable, since the need of a unit to recover the solvent from the raffinate stream in a continuous extraction process is eliminated.

Table 1. Composition of the Experimental Tie-Lines, Solute Distribution Ratio (*β*), and Selectivity (*S*) for the Ternary Systems at 298.15 K

Hydrocarbon-Rich Phase		Ionic Liquid-Rich Phase			
x_1^{HC}	x_2^{HC}	x_1^{IL}	x_2^{IL}	β	S
{heptane (1) + benzene (2) + [BMpyr][NTf$_2$] (3)}					
1	0	0.071	0		
0.900	0.100	0.063	0.125	1.25	17.91
0.824	0.176	0.063	0.262	1.49	19.54
0.742	0.258	0.062	0.344	1.33	16.01
0.666	0.334	0.062	0.406	1.22	13.17
0.609	0.391	0.060	0.452	1.15	11.79
0.535	0.465	0.053	0.494	1.06	10.76
0.466	0.535	0.052	0.534	1.00	8.97
0.382	0.618	0.045	0.580	0.94	8.00
0.307	0.693	0.041	0.633	0.91	6.88
0.243	0.757	0.033	0.669	0.88	6.50
0.205	0.795	0.028	0.693	0.87	6.42
0.151	0.849	0.022	0.721	0.85	5.98
0.111	0.889	0.020	0.750	0.84	4.74
0.082	0.918	0.015	0.766	0.83	4.67
0.044	0.956	0.010	0.789	0.83	3.80
0	1	0	0.810	0.81	
{heptane (1) + toluene (2) + [BMpyr][NTf$_2$] (3)}					
1	0	0.071	0		
0.901	0.099	0.067	0.098	0.99	13.36
0.807	0.193	0.064	0.183	0.95	12.03
0.665	0.335	0.062	0.321	0.96	10.34
0.547	0.453	0.053	0.422	0.93	9.66
0.448	0.552	0.047	0.487	0.88	8.45
0.360	0.640	0.042	0.537	0.84	7.21
0.337	0.663	0.041	0.549	0.81	6.47
0.308	0.692	0.039	0.563	0.78	5.52
0.247	0.753	0.035	0.591	0.83	6.81
0.215	0.785	0.033	0.607	0.77	5.01
0.179	0.821	0.031	0.622	0.76	4.45
0.145	0.855	0.027	0.638	0.75	3.98
0.115	0.885	0.025	0.650	0.74	3.41
0.088	0.912	0.020	0.662	0.73	3.14
0.032	0.968	0.010	0.693	0.72	2.23
0	1	0	0.732	0.73	
{heptane (1) + ethylbenzene (2) + [BMpyr][NTf$_2$] (3)}					
1	0	0.071	0		
0.890	0.110	0.050	0.082	0.74	13.16
0.791	0.209	0.050	0.163	0.78	12.45
0.706	0.295	0.050	0.218	0.74	10.56
0.632	0.368	0.049	0.259	0.70	9.05
0.563	0.437	0.049	0.295	0.67	7.73
0.499	0.501	0.049	0.329	0.66	6.71
0.451	0.549	0.047	0.356	0.65	6.23
0.377	0.623	0.046	0.396	0.64	5.25
0.314	0.687	0.045	0.432	0.63	4.35
0.248	0.752	0.045	0.471	0.63	3.45
0.193	0.807	0.045	0.507	0.63	2.72
0.159	0.841	0.042	0.532	0.63	2.40
0.126	0.874	0.035	0.560	0.64	2.31
0.075	0.926	0.026	0.596	0.64	1.83
0.033	0.967	0.015	0.634	0.66	1.40
0	1	0	0.684	0.68	

Triangular diagrams with the graphical representation of the ternary LLE data are shown in Figure 1. As can be seen, all ternary systems correspond to the Type 2 category, with two of their constituent pairs showing partial immiscibility and with only an immiscibility region. In accordance with the absence of IL in the hydrocarbon rich phase, the tie-lines

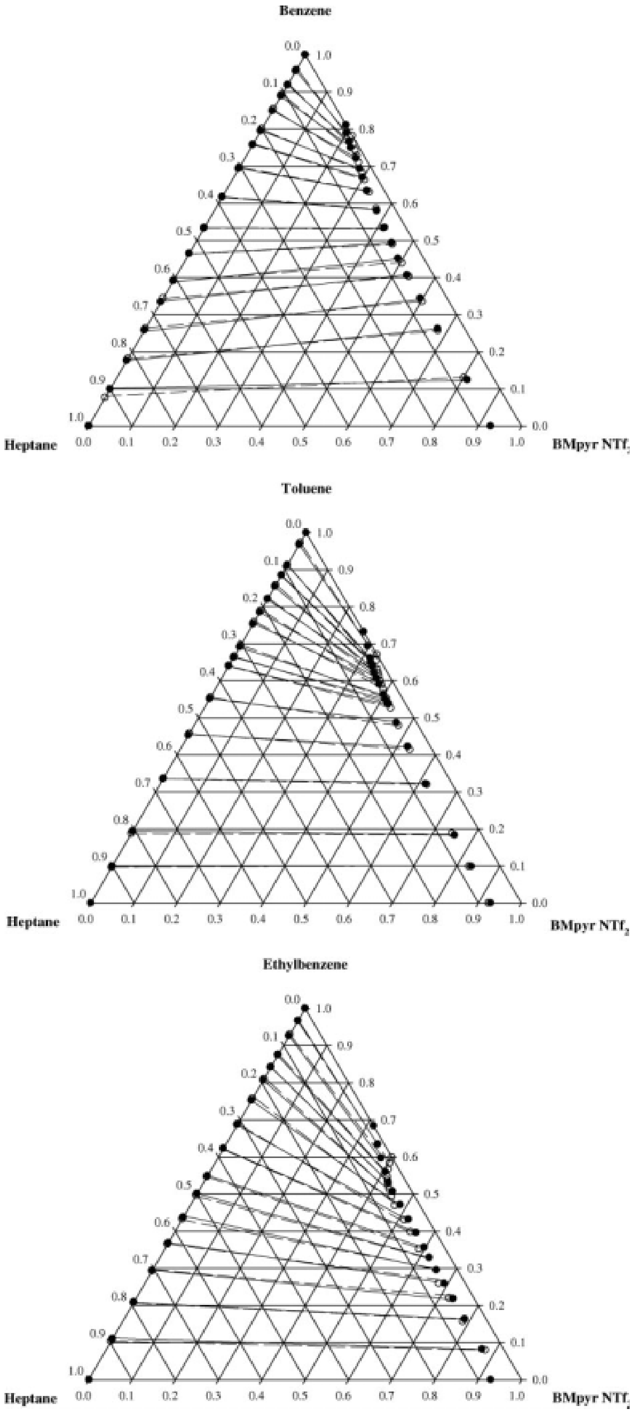

Figure 1. Experimental LLE mole fraction tie-lines of the ternary systems at 298.15 K.

● And solid lines, experimental; ○ and dashed lines, correlated.

performed in the diagrams indicate that the solubility of the aromatic compounds (benzene, toluene, and ethylbenzene) is much higher than that of the heptane. This result is consistent with previously reported experiments.[5–7,14] Moreover, from the results of the miscibility region, it is evident that the substituting groups, methyl and ethyl, influence the solubility of the IL for aromatic hydrocarbons. These results can be observed in terms of solvent capacities of ILs for aromatic hydrocarbons in Figure 2. Apparently, the substituent groups on the benzene ring, methyl and ethyl increase the solvent capacities of different ILs for aromatic hydrocarbons. Such data might result in an excellent alternative of ILs in extractive separation of aromatic hydrocarbons from heptane mixtures.

Solute distribution ratio and selectivity

The solvent ability of [BMpyr][NTf$_2$] as the solvent for the separation of aromatic hydrocarbons from heptane was evaluated by means of the calculation of parameters such as the solute distribution ratio, β, and the selectivity, S.

These parameters were calculated according to the equations:

$$\beta = \frac{w_2^{\text{IL-phase}}}{w_2^{\text{HC-phase}}} \tag{1}$$

$$S = \left(\frac{w_1^{\text{HC-phase}}}{w_1^{\text{IL-phase}}}\right) \cdot \left(\frac{w_2^{\text{IL-phase}}}{w_2^{\text{HC-phase}}}\right) \tag{2}$$

In these equations, w is the mass fraction; subscripts 1 and 2 indicate the heptane and the aromatic hydrocarbon, respectively; and HC-phase and IL-phase indicate the hydrocarbon (top phase) and IL (bottom phase) rich phase, respectively.

The calculated values of β and S for the ternary mixtures at 298.15 K are listed in Table 1. In this table, it can be observed as the β values decrease with an increase in the aromatic content for the ternary systems. On the other hand, S values decrease when the aromatic content is increased.

In Figure 3, the β values of ternary mixtures are represented as a function of the aromatic mole fraction in the heptane rich phase. The values for the analogous system

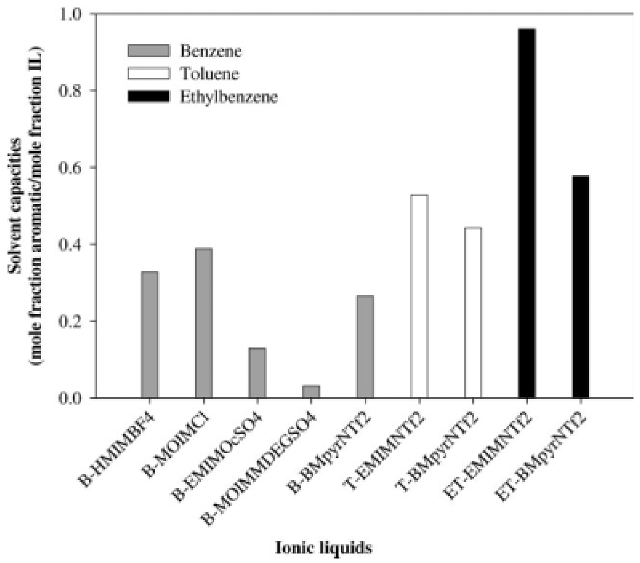

Figure 2. Solvent capacities of ILs for aromatic hydrocarbons.

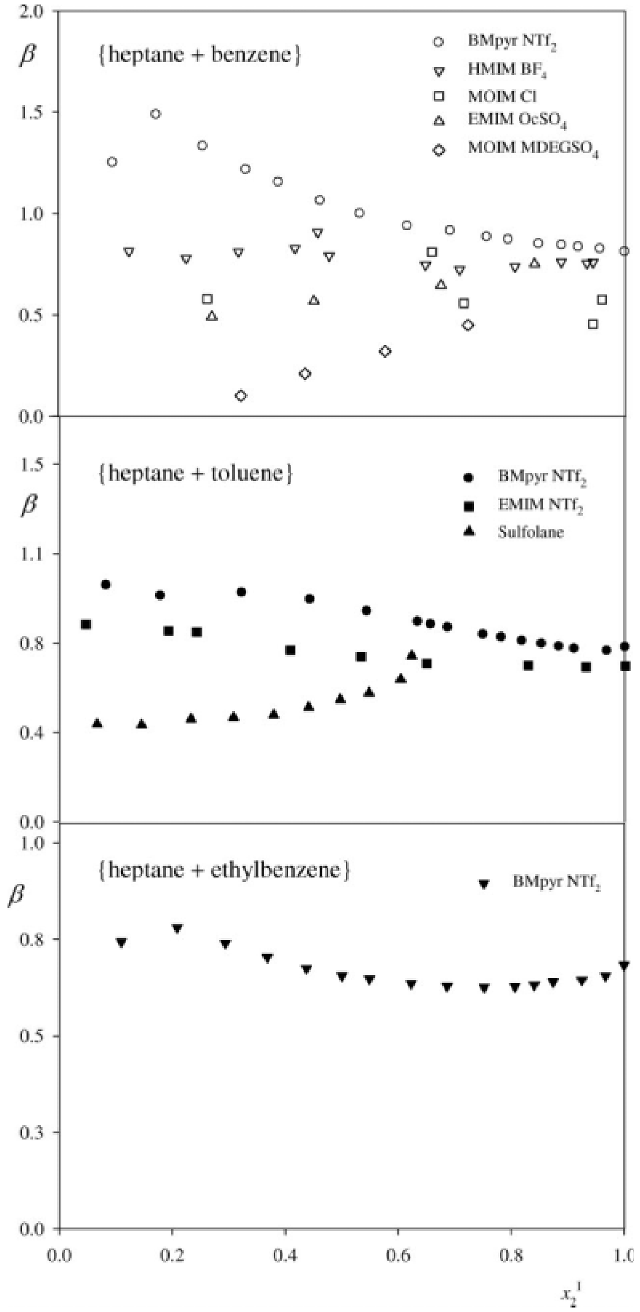

Figure 3. Solute distribution ratio as a function of aromatic mole fraction in the heptane rich phase for the ternary mixtures at 298.15 K.

heptane + aromatic + IL at 298.15 K obtained from the literature are also plotted. Whereas for the mixture heptane + benzene + [BMpyr][NTf$_2$] a notable decrease in β is observed, when the concentration of benzene is increased, the others mixtures remains approximately constant throughout the entire inmiscibility range. Another interesting feature is observed for the ternary mixtures heptane + benzene + other ILs, heptane + toluene + IL or sulfolane and heptane + ethyl benzene + IL contrary to what happens in the above ternary system, the β values are lower than unity; therefore, the solutropy behavior exhibited by the ternary mixture heptane + benzene + [BMpyr][NTf$_2$] disappears in the ternary mixtures with toluene and ethylbenzene as aromatic compounds.

LLE data correlation

With the purpose of a simulation study of the information provided by the experimental LLE data, the experimental tie-lines of the ternary mixtures were correlated. The classical NRTL model was chosen,[16] because it has already used for appropriately correlating the LLE data of analogous ternary systems involving hydrocarbons and ILs.[4–6,8–11,14,15]

The parameters were adjusted to minimize the difference between the experimental and calculated mole fraction defined as:

$$\begin{aligned}\text{O.F.} = \sum_{i=1}^{n}\Bigg[&\left(x_{1i}^{\text{HC-phase}} - x_{1i}^{\text{HC-phase}}(\text{calc})\right)^2 \\ &+\left(x_{2i}^{\text{HC-phase}} - x_{2i}^{\text{HC-phase}}(\text{calc})\right)^2\Bigg] \\ &+\sum_{i=1}^{n}\left(\left(x_{1i}^{\text{IL-phase}} - x_{1i}^{\text{IL-phase}}(\text{calc})\right)^2\right. \\ &\left.+\left(x_{2i}^{\text{IL-phase}} - x_{2i}^{\text{IL-phase}}(\text{calc})\right)^2\right) \quad (3)\end{aligned}$$

where $x_{1i}^{\text{HC-phase}}$, $x_{2i}^{\text{HC-phase}}$, $x_{1i}^{\text{IL-phase}}$, and $x_{2i}^{\text{IL-phase}}$ are the experimental mole fraction; $x_{1i}^{\text{HC-phase}}$ (calc), $x_{2i}^{\text{HC-phase}}$ (calc), $x_{1i}^{\text{IL-phase}}$ (calc), and $x_{2i}^{\text{IL-phase}}$ (calc) are the calculated mole fraction; and superscripts HC-phase and IL-phase indicate the hydrocarbon (top phase) and IL (bottom phase) rich phase phases, respectively.

Table 2 summarizes the fitting parameters together with the deviation which was calculated by applying the following expression:

$$\sigma = \left(\frac{\sum_i \left(x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}}\right)^2}{6k}\right)^{1/2} \quad (4)$$

where x is the mole fraction and the subscripts i, l, and m provide the component, the phase, and the tie-line, respectively. The k value refers to the number of experimental tie-lines.

Following a common procedure, the non-randomness parameter α was optimized for each ternary mixture (from 0.30

Table 2. NRTL Equation Parameters Fitted to the Experimental Data for the Ternary System at 298.15 K

Systems	i,j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)	α	σ
{heptane (1) +	1,2	4852.3	−3229.3	0.30	0.009
benzene (2) +	1,3	6153.0	18,148		
[BMpyr][NTf$_2$] (3)}	2,3	−3787.4	22,661		
{heptane (1)	1,2	6266.6	−2175.4	0.32	0.014
+ toluene (2)	1,3	6685.6	18,273		
+ [BMpyr][NTf$_2$] (3)}	2,3	−870.51	20,683		
{heptane (1)	1,2	5731.2	−653.91	0.35	0.030
+ ethylbenzene (2)	1,3	8954.7	18,622		
+ [BMpyr][NTf$_2$] (3)}	2,3	2198.2	19,561		

to 0.35), covering its most typical values. The correlation of the ternary mixture involving benzene provides the best results and the worst are those achieved for the ternary with ethylbenzene as aromatic. The correlated tie-lines generated from the fitting parameters by the computer software are drawn in Figure 1. In general terms, a visual inspection of the data for the ternary mixtures supports the general validity of the NRTL correlation results. Nonetheless, the model is not able to properly correlate the absence of IL in the hydrocarbon-rich phase, because of the fact that the algorithm used by the program has a handicap at negligible amount of IL.

Simulation results

HYSYS v.3.2 (from Aspen Technology, Cambridge, MA) with NRTL equation fitted to the experimental tie-line data was used to generate accurate data for conceptual process and the flow sheet of the extraction is depicted in Figure 4. The aromatic + heptane stream which contain up to 0.8 mole fraction of aromatic components was fed from the bottom and the raffinate stream was collected from the top liquid–liquid extractor, and recycled to the extractor. The IL used for the extraction of aromatics was fed countercurrent to the top extractor from the solvent evaporator because regenerated IL was used.

The solvent and feed compositions were kept fixed, and flow rates were optimized to maximize aromatic stream purity. With the solvent and feed flow rates listed in the Table 3, an aromatic stream with a purity up to 0.90 mole fraction was achieved. Distillation of the extract stream affords the IL recycled to the first column.

The results of the simulations for extraction of aromatics in heptane feed with the proposed IL are reasonable agreement. The complete recovery of the IL from the extract stream is a prerequisite for an economically feasible process and then the proposal liquid extraction process can be suggested as a potential alternative for azeotropic distillation for high aromatic content.

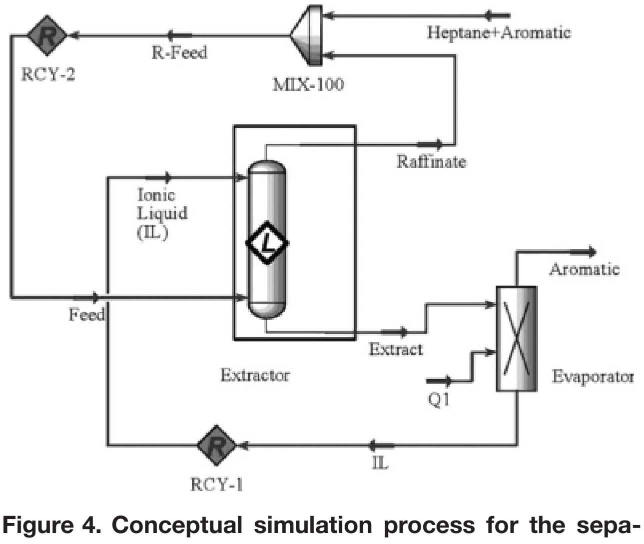

Figure 4. Conceptual simulation process for the separation of aromatic from heptane fraction.

Table 3. Simulation Data for the Extraction of Aromatic with [BMpyr][NTf$_2$] at 298.15 K

{heptane (1) + benzene (2) + [BMpyr][NTf$_2$] (3)}			
Parameters	Feed	IL	Benzene
T (K)	298.15	298.15	298.15
P (kPa)	101.3	101.3	101.3
Flow (mol/h)	55.00	0.79	2.19
Aromatic (mole fraction)	0.8625	0	0.9725
Heptane (mole fraction)	0.1374	0	0.0275
[BMpyr][NTf$_2$] (mole fraction)	0.0001	1	0
{heptane (1) + toluene (2) + [BMpyr][NTf$_2$] (3)}			
Parameters	Feed	IL	Toluene
T (K)	298.15	298.15	298.15
P (kPa)	101.3	101.3	101.3
Flow (mol/h)	55.00	1.02	1.78
Aromatic (mole fraction)	0.8684	0	0.9621
Heptane (mole fraction)	0.1315	0	0.0379
[BMpyr][NTf$_2$] (mole fraction)	0.0001	1	0
{heptane (1) + ethylbenzene (2) + [BMpyr][NTf$_2$] (3)}			
Parameters	Feed	IL	Ethylbenzene
T (K)	298.15	298.15	298.15
P (kPa)	101.3	101.3	101.3
Flow (mol/h)	55.00	0.76	1.05
Aromatic (mole fraction)	0.8684	0	0.9355
Heptane (mole fraction)	0.1315	0	0.0645
[BMpyr][NTf$_2$] (mole fraction)	0.0001	1	0

Conclusions

The IL [BMpyr][NTf$_2$] was tested at 298.15 K as a suitable solvent for extraction of aromatics (benzene, toluene, and ethylbenzene) from heptane (representing C$_7$ fraction in naphthas) mixtures. The corresponding distribution ratios and selectivities were calculated. The comparison of these values for the ternary mixtures with the obtained with sulfolane allowed us to propose the ILs how an efficient solvent in an extraction process for the separation of aromatics from aliphatic hydrocarbons.

In this work, a new proposed process was presented using a simulation software for aromatic purification. The simulation of the process needs the correlation results obtained by applying NRTL equation. The designed process was optimized for a room-temperature countercurrent continuous extraction process including a solvent recycling unit. The results obtained with the solvent extraction process with [BMpyr][NTf$_2$] demonstrate the efficiency of this proposal. Extraction of 0.9 mole fraction aromatic content in the feed achieves more than 0.95 mole fraction extraction yield and the possibility of ready online recovery of [BMpyr][NTf$_2$] is a prerequisite that was confirmed for an economical separation.

The proposed room temperature IL liquid–liquid extraction process is preferred from the economical point of view as alternative of the conventional sulfolane extraction because the energy requirement for the extraction with the IL as solvent is much lower than with sulfolane due to the lower temperature process and the simpler recovery of the IL.

Acknowledgments

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