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# Deep Separation of Benzene from Cyclohexane by Liquid Extraction Using Ionic Liquids as the Solvent

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## Supporting Information

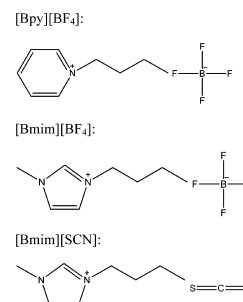
**ABSTRACT:** Separation of benzene and cyclohexane is one of the most important and difficult processes in the petrochemical industry, especially for low benzene concentration. In this work, three ionic liquids (ILs), [Bmim][BF<sub>4</sub>], [Bpy][BF<sub>4</sub>], and [Bmim][SCN], were investigated as the solvent in the extraction of benzene from cyclohexane. The corresponding ternary liquid–liquid equilibria (LLE) were experimentally determined at  $T = 298.15$  K and atmospheric pressure. The LLE data were correlated with the nonrandom two-liquid model, and the parameters were fitted. The separation capabilities of the ILs were evaluated in terms of the benzene distribution coefficient and solvent selectivity. The effect of the IL structure on the separation was explained based on a well-founded physical model, COSMO-RS. Finally, the extraction processes were defined, and the operation parameters were analyzed. It shows that the ILs studied are suitable solvents for the extractive separation of benzene and cyclohexane, and their separation efficiency can be generally ranked as [Bmim][BF<sub>4</sub>] > [Bpy][BF<sub>4</sub>] > [Bmim][SCN]. The extraction process for a feed with 15 mol % benzene was optimized. High product purity (cyclohexane 0.997) and high recovery efficiency (cyclohexane 96.9% and benzene 98.1%) can be reached.

## 1. INTRODUCTION

As an important industrial chemical, cyclohexane is generally produced by the catalytic hydrogenation of benzene. The unreacted benzene is entrained in the product stream and must be removed for an economically viable process. The separation of benzene and cyclohexane is one of the most challenging processes in the chemical industry because of their extremely close boiling points ( $\Delta T_b = 0.6$  °C at 1 atm). The recommended process for this separation is extraction or extractive distillation using volatile organic solvents, such as sulfolane, dimethyl sulfoxide, *N*-methylpyrrolidone, and *N*-formylmorpholine. Typically, for benzene and cyclohexane separation, extraction is suitable for the range of 20–65 wt % benzene content and extractive distillation for 65–90 wt %.<sup>1</sup> There is usually no desirable separation process for the mixtures with lower benzene concentration. However, in practice, the unreacted benzene in cyclohexane production is normally lower than 20 wt %.

Ionic liquids (ILs) are organic salts with negligible vapor pressure, high thermal stability, and tunable properties. They are found to be promising solvents in chemical separation because of their high solution capacity and nonvolatile nature.<sup>2–6</sup> Compared with conventional solvent extraction, IL extractive processes are considerably simplified and the solvents are highly recyclable. Many researchers have investigated the features of using ILs as the solvent to perform the extraction of aromatic compounds from their aliphatic mixtures.<sup>7–19</sup> It is proved that, combined with the anion [BF<sub>4</sub>]<sup>−</sup>, most imidazolium- and pyridinium-based ILs are good solvents for aromatic/aliphatic hydrocarbon separation.<sup>11–14</sup> Additionally, Hansmeier et al.<sup>15</sup> has confirmed the separation capability of thiocyanate-based ILs in the extraction of toluene from heptane.

In this work, three ILs, 1-butylpyridinium tetrafluoroborate ([Bpy][BF<sub>4</sub>]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>]), and 1-butyl-3-methylimidazolium thiocyanate ([Bmim][SCN]), were investigated as solvents for the benzene/cyclohexane extractive separation. Their structures are given in Figure 1. The ILs were chosen with the same cation



**Figure 1.** Structures of ILs [Bpy][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>], and [Bmim][SCN].

or anion and thus can be helpful for studying the influence of different ionic species on the extraction. The corresponding liquid–liquid equilibria (LLE) for these ILs with cyclohexane and benzene were experimentally measured and correlated with the nonrandom two-liquid (NRTL) equation. The suitability of these solvents in the extraction of benzene from cyclohexane was evaluated, and the effect of the IL structure on the

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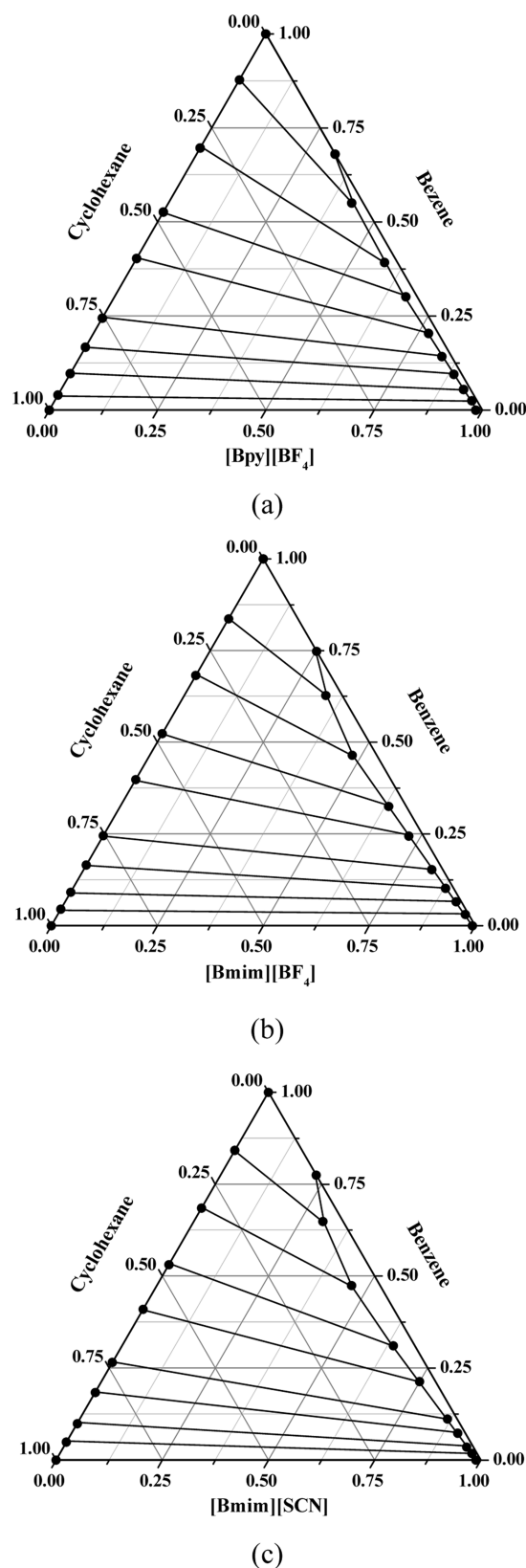
separation was analyzed with the aid of the COSMO-RS model. Finally, the extraction process was proposed, and the operation parameters were optimized, which can act as a preliminary study for industrial scaling up.

## 2. LLE

**2.1. Experimental Section.** **2.1.1. Chemicals.** The ILs 1-butylpyridinium tetrafluoroborate ([Bpy][BF<sub>4</sub>]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>]), and 1-butyl-3-methylimidazolium thiocyanate ([Bmim][SCN]) were purchased from the Lanzhou Institute of Chemical Physics, Chinese Academy of Science, with quoted mass fraction purities higher than 0.990. Prior to use, the ILs were treated by vacuum evaporation to remove possible traces of volatile organics and water. Benzene and cyclohexane were supplied by Lingfeng Co., Ltd., Shanghai, China, with the mass fraction purity higher than 0.995.

**2.1.2. Apparatus and Procedure.** The LLE experiments for the three studied systems were carried out in a cellular culture utensil with a volume of 10 mL. The culture utensil was tightly sealed with a poly(vinyl chloride) cover in order to prevent environmental moisture. First, the IL, benzene, and cyclohexane, with total compositions lying inside the immiscible zone, were, in turn, introduced into the utensil. The overall compositions of the mixtures were obtained gravimetrically on a Sartorius BSA224S-CW balance with a precision of  $\pm 0.0001$  g. To ensure complete thermodynamic equilibrium, the liquids inside were mixed vigorously with a magnetic stirrer for at least 4 h and then were left to settle overnight at the specified temperature. The equilibrium liquid temperature was controlled by a water bath (Huber Ministat 230, Offenburg, Germany) equipped with a temperature controller with a fluctuation of  $\pm 0.1$  K. Samples from the lower and upper layers were carefully taken with syringes and analyzed by a gas chromatograph (GC 7890A from Agilent) equipped with a flame ionization detector and a PEG-20 M column (30 m, 0.32 mm id, 0.25  $\mu$ m film thickness). The ILs cannot be analyzed by gas chromatography (GC) because of their negligible vapor pressure. They were collected in a precolumn (5 m  $\times$  0.250 mm, uncoated fused silica). An area normalization method was applied to determine the mole ratio of benzene-to-cyclohexane of each layer. Samples from the upper layers were confirmed to be totally free of ILs by <sup>1</sup>H NMR analysis (Bruker Avance 500). This is in accordance with previous findings that can be found elsewhere.<sup>8,10–12,16,17</sup> Thus, the phase compositions can finally be determined based on the GC results plus an overall mass balance for the hydrocarbons in the mixtures. The estimated uncertainties of the determined mole compositions in the upper and lower phases were less than 0.001 and 0.003, respectively. A detailed description of the analysis conditions and approaches can be found elsewhere.<sup>11</sup>

**2.2. Experimental LLE Data.** The experimental LLE data for the systems in the study at  $T = 298.15$  K and atmospheric pressure are given in Table S1 (see the Supporting Information) and displayed in the triangular diagram shown in Figure 2. It is clear that the tie-lines for all of the studied systems present a negative slope, and this slope is more negative as the benzene composition increases. As depicted, benzene shows a considerable solution affinity in the IL-rich phase, and this concentration increases substantially as its total composition in the mixtures increases. On the other hand, a much lower hexane concentration is found in the IL-rich phase, and this concentration shows a very limited variation in the



**Figure 2.** Triangular phase diagrams for the LLE data of the ternary systems {cyclohexane (1) + benzene (2) + IL (3)} at  $T = 298.15$  K where IL = [Bpy][BF<sub>4</sub>] (a), [Bmim][BF<sub>4</sub>] (b), and [Bmim][SCN] (c).

whole composition range. It is illustrated that the ILs studied are suitable solvents for the extraction of benzene from

cyclohexane and, moreover, the fact that no IL was detected in the raffinate phase can significantly facilitate the recovery of solvents.

**2.3. Thermodynamic Correlation.** The experimentally determined phase equilibrium data were correlated with the NRTL model;<sup>20</sup> the activity coefficient  $\gamma_i$  for the component  $i$  of the system is given by

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} x_j G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left[ \tau_{ij} - \frac{\sum_m \tau_{mj} x_m G_{mj}}{\sum_k x_k G_{kj}} \right] \quad (1)$$

with

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad (2)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (3)$$

where  $\Delta g_{ij}$  is an energy parameter that characterizes the interactions between species  $i$  and  $j$ ,  $x_i$  is the mole fraction of component  $i$ ,  $\alpha_{ij}$  is a nonrandomness parameter related to the mixture,  $R$  is the gas constant, and  $T$  is the absolute temperature.

The model parameters were optimized using an objective function that minimizes the overall differences between the experimental and calculated mole fractions of the components in both phases. For each system, the nonrandomness parameter  $\alpha_{ij}$  was initially fixed as 0.30 and the binary interaction parameters  $\Delta g_{ij}$  were achieved. After that, the obtained  $\Delta g_{ij}$  values were fixed and the parameters  $\alpha_{ij}$  were finally optimized to ensure the best fit. The estimated NRTL model parameters for systems in this study are given in Table 1. Because the

**Table 1. NRTL Parameters Regressed from the Experimental LLE Data for the Ternary Systems {Cyclohexane (1) + Benzene (2) + IL (3)} at  $T = 298.15$  K**

components $i-j$	NRTL parameters			$\sigma$
	$(\Delta g_{ij}/R)/K$	$(\Delta g_{ji}/R)/K$	$\alpha_{ij}$	
Cyclohexane (1) + Benzene (2) + [Bpy][BF <sub>4</sub> ] (3)				
1–2	577.22	332.89	0.3879	0.0085
1–3	2308.9	1038.7	0.2503	
2–3	2406.3	824.79	0.3560	
Cyclohexane (1) + Benzene (2) + [Bmim][BF <sub>4</sub> ] (3)				
1–2	383.12	−2.0089	0.5998	0.0098
1–3	2325.7	1200.5	0.2443	
2–3	2353.5	378.94	0.4122	
Cyclohexane (1) + Benzene (2) + [Bmim][SCN] (3)				
1–2	−719.96	182.64	0.5242	0.0038
1–3	2334.5	1087.5	0.2569	
2–3	2192.2	−316.59	0.4842	

liquid–liquid system is strongly nonideal, the interaction parameters between cyclohexane and benzene are significantly affected by the introduction of the solvent. This may explain why the fitted NRTL parameters are quite different among the three studied systems.

The consistency between the experimental and calculated compositions was evaluated by the root-mean-square deviation (rmsd), which is defined as

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

where the subscripts  $i$ ,  $l$ , and  $m$  provide designations for the component, phase, and tie-line, respectively, and  $k$  represents the total number of the tie-lines. The calculated rmsd values are also listed in Table 1. The small values confirm the good agreement of the experimental LLE data with the NRTL model.

### 3. EXTRACTION PROCESS

**3.1. Evaluation of the Solvent Capability.** For benzene/cyclohexane separation, a good solvent must show high solubility for benzene and meanwhile satisfying selectivity through a much lower dissolving capability with cyclohexane. The separation performance of a solvent in liquid extraction can be evaluated by the solute distribution coefficient ( $\beta$ ) and solvent selectivity ( $S$ ), as defined in eqs 5 and 6, respectively.

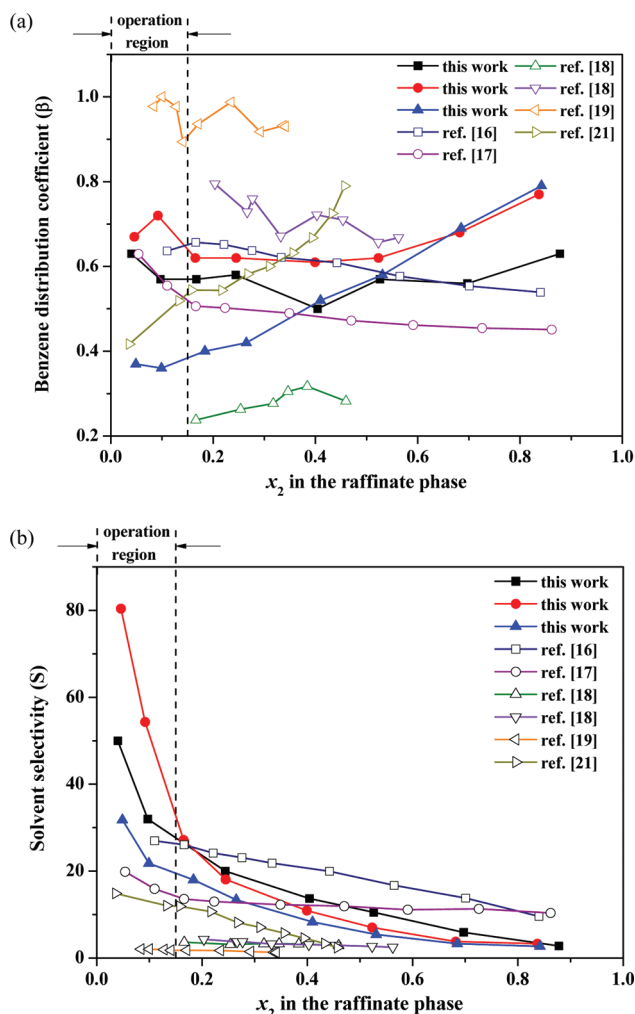
$$\beta = \frac{x_2^E}{x_2^R} \quad (5)$$

$$S = \frac{x_2^E/x_2^R}{x_1^E/x_1^R} \quad (6)$$

The values of  $\beta$  and  $S$  were calculated and are presented in Table S1 in the Supporting Information. Their variations are plotted with the benzene mole fraction in the raffinate phase, shown in parts a and b of Figure 3, respectively. It is found that the selectivities of all solvents are higher than 1, which confirms the suitability of the studied ILs as solvents for the separation of benzene and cyclohexane mixtures. In order to further evaluate the extraction efficiency of the studied ILs, a comparison with the reported  $\beta$  and  $S$  values of sulfolane and other ILs was also carried out. Currently, the sulfolane process licensed by UOP is one of the most important extraction processes for industrial aromatic separation.

In this work, the separation of low-concentration benzene (<15 mol %) was focused on. The corresponding benzene composition in the raffinate phase is indicated as the operation region (see Figure 3). It can be observed that, apart from the IL [Mim][DBP],<sup>19</sup> [Bmim][BF<sub>4</sub>] shows the highest benzene distribution coefficient among all of the reported values in the extractive operation region. The  $\beta$  values of the three studied ILs can be generally ranked as [Bmim][BF<sub>4</sub>] > [Bpy][BF<sub>4</sub>] > [Bmim][SCN]. With respect to the solvent selectivity, it decreases significantly as the benzene concentration in the raffinate phase increases (see Figure 3b). As depicted, the selectivities of the studied ILs are obviously among the highest ones in the operation region. Particularly, it can reach 50 with [Bpy][BF<sub>4</sub>] and even exceed 80 with [Bmim][BF<sub>4</sub>] at very low benzene composition, which suggests their superior suitability for the deep separation of benzene from its mixtures with cyclohexane. From analysis of the  $\beta$  and  $S$  values, it is clear that the overall separation efficiency of the studied ILs follows the sequence [Bmim][BF<sub>4</sub>] > [Bpy][BF<sub>4</sub>] > [Bmim][SCN].

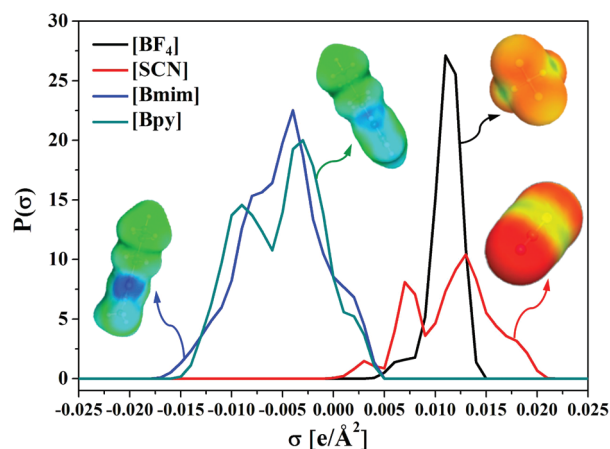
In order to understand the influence of different ionic species of the three ILs studied, the theory of COSMO-RS is applied for determining the polarities of cations and anions investigated. The full description of the theory has been given elsewhere.<sup>22</sup> According to COSMO-RS, a less-polar character of compounds always results in a relatively narrow  $\sigma$ -profile (distribution of charge densities) compared with more-polar ones. From the  $\sigma$ -profiles and COSMO cavities of [BF<sub>4</sub>]<sup>−</sup>, [SCN]<sup>−</sup>, [Bmim]<sup>+</sup>, and [Bpy]<sup>+</sup> (see Figure 4), [Bmim]<sup>+</sup> has a more concentrated positive charge density than [Bpy]<sup>+</sup>.



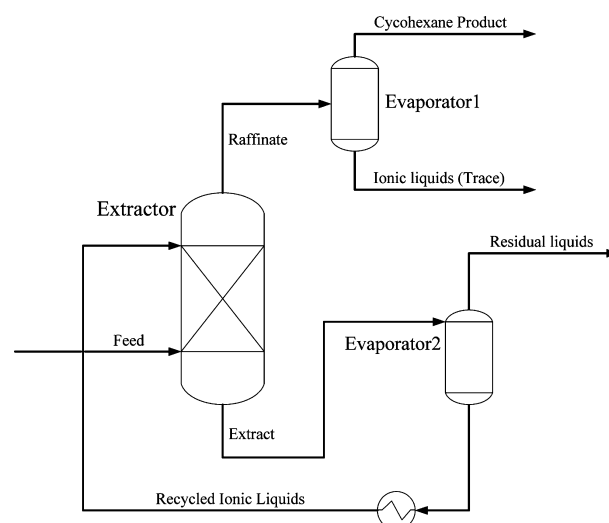
**Figure 3.** (a) Benzene distribution coefficient and (b) solvent selectivity for the ternary systems {cyclohexane (1) + benzene (2) + solvent (3)} at  $T = 298.15$  K. Solvent: (■) [Bpy][BF<sub>4</sub>] (this work); (●) [Bmim][BF<sub>4</sub>] (this work); (▲) [Bmim][SCN] (this work); (□) 1-ethyl-3-methylpyridinium ethylsulfate (from ref 16); (○) 1-ethyl-3-methylimidazolium ethylsulfate (from ref 17); (Δ) 1-methyl-3-methylimidazolium dimethylphosphate (from ref 18); (▽) 1-ethyl-3-methylimidazolium diethylphosphate (from ref 18); (◀) N-methylimidazolium dibutylphosphate (from ref 19); (▶) sulfolane (from ref 21).

Therefore, interaction of the electron cloud of a benzene-conjugated  $\pi$  bond with [Bmim]<sup>+</sup> is much stronger, which is in good agreement with the experimental separation efficiency of [Bmim][BF<sub>4</sub>] > [Bpy][BF<sub>4</sub>]. With regard to the anion here, it is demonstrated that [BF<sub>4</sub>]-based IL shows a higher separation capability than [SCN]-based IL. As proven in Figure 4, [BF<sub>4</sub>]<sup>−</sup> is much less polar than [SCN]<sup>−</sup>. The more decentralization of the [BF<sub>4</sub>]<sup>−</sup> charge density leads to a weaker cation–anion electrostatic force, which finally results in a stronger interaction affinity of the cation toward the benzene molecule. Therefore, the separation efficiency of [Bmim][BF<sub>4</sub>] is higher than that of [Bmim][SCN].

**3.2. Process Analysis.** On the basis of the obtained NRTL thermodynamic model, the conceptual process for the extractive separation of benzene from cyclohexane was designed (Figure 5). As mentioned before, this study especially focuses on the removal of low-concentration benzene. Here the feed stream with 15 mol % benzene is specified, which is added



**Figure 4.**  $\sigma$ -profiles and COSMO cavities of ions [BF<sub>4</sub>]<sup>−</sup>, [SCN]<sup>−</sup>, [Bmim]<sup>+</sup>, and [Bpy]<sup>+</sup>.



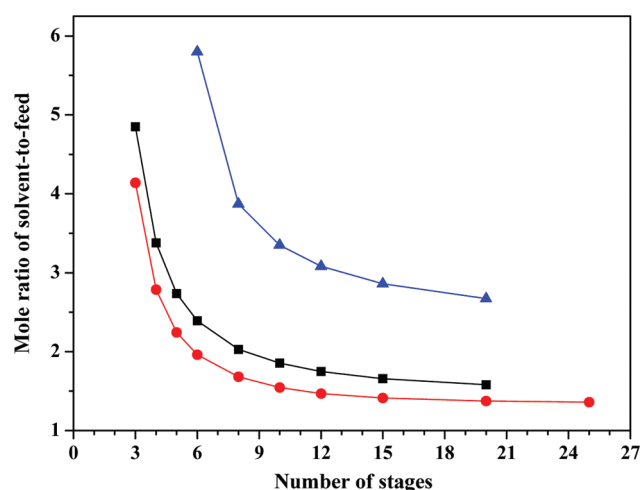
**Figure 5.** Simulation process for the separation of benzene and cyclohexane.

to the bottom of the extractor. The raffinate and extract phases are collected and delivered into the evaporators to remove the solvents. The ILs are recycled and fed to the top of the extractor. Unlike the conventional separation process, which usually contains serial units, the IL extraction process only consists of an extractor and two evaporators.

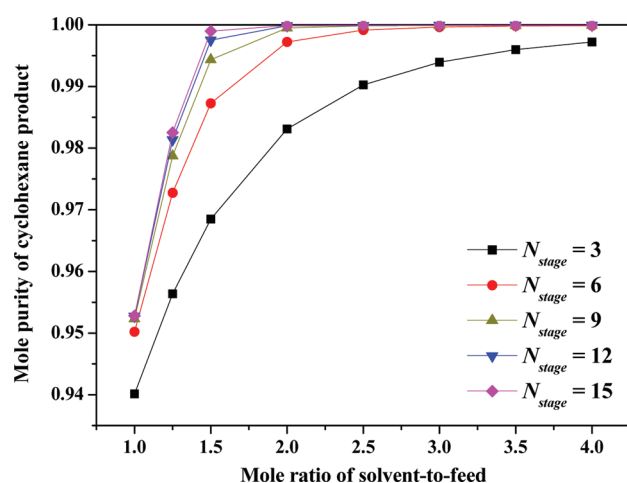
The extraction process at 298.15 K and 101.3 kPa was simulated by *ASPEN Plus 12.1*. In order to achieve a high-purity cyclohexane product of at least 0.995 (moles) and meanwhile to ensure a high benzene recovery rate of at least 98%, the required number of stages and the corresponding mole ratio of solvent-to-feed ( $S/F$ ) for the studied ILs are plotted in Figure 6. As illustrated, the number of stages for [Bmim][SCN] must be higher than 6 and the  $S/F$  ratio should be higher than 2.60. For [Bmim][BF<sub>4</sub>], the minimal number of stages is 3 and the minimal  $S/F$  value is about 1.30. The overall separation performances of the studied ILs can be ranked as [Bmim][BF<sub>4</sub>] > [Bpy][BF<sub>4</sub>] > [Bmim][SCN].

For [Bmim][BF<sub>4</sub>], the purity of the cyclohexane product and the benzene recovery efficiency as a function of the  $S/F$  ratio at different numbers of stages are given in Figures 7 and 8, respectively. Considering the separation demands and overall investment, the number of stages and the  $S/F$  ratio for the

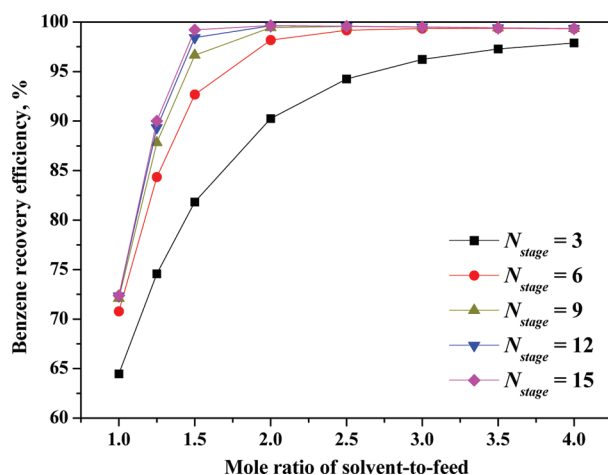




**Figure 6.** Mole ratio of solvent to feed plotted with the number of stages for the separation demands of the cyclohexane mole purity >0.995 and the benzene recovery rate >98%: (■) [Bpy][BF<sub>4</sub>]; (●) [Bmim][BF<sub>4</sub>]; (▲) [Bmim][SCN].



**Figure 7.** Purity of the cyclohexane product plotted with the mole ratio of solvent to feed at different numbers of stages for the solvent [Bmim][BF<sub>4</sub>].



**Figure 8.** Benzene recovery efficiency plotted with the mole ratio of solvent to feed at different numbers of stages for the solvent [Bmim][BF<sub>4</sub>].

solvent [Bmim][BF<sub>4</sub>] were optimized to 6 and 2.0, respectively. The achieved purity of the cyclohexane product and the recovery rate of benzene are 0.997 and 98.1%, respectively. The same procedure was carried out with the other two ILs, [Bpy][BF<sub>4</sub>] and [Bmim][SCN], for which the optimal number of stages and the S/F ratio are recommended. With these optimized operation parameters, the extraction processes using different ILs as solvents were compared (see Table 2), where

**Table 2. Simulation Results for the Extraction of Benzene with the ILs [Bpy][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>], and [Bmim][SCN] at  $T = 298.15$  K and  $P = 101.3$  kPa**

parameters	feed	solvent	product	residual liquids
Case 1: [Bpy][BF <sub>4</sub> ], 8 Stages				
mass flow (kg/h)	8310.0	49064.4	6844.9	1459.6
cyclohexane	7140.0	0.0	6832.6	306.8
benzene	1170.0	0.0	12.3	1152.8
[Bpy][BF <sub>4</sub> ]	0.0	49064.4	0.0	0.001
Case 2: [Bmim][BF <sub>4</sub> ], 6 Stages				
mass flow (kg/h)	8310.0	45204.0	6934.7	1369.7
cyclohexane	7140.0	0.0	6917.4	222.3
benzene	1170.0	0.0	17.3	1147.4
[Bmim][BF <sub>4</sub> ]	0.0	45204.0	0.0	0.022
Case 3: [Bmim][SCN], 12 Stages				
mass flow (kg/h)	8310.0	65109.0	6717.1	1574.0
cyclohexane	7140.0	0.0	6711.6	427.4
benzene	1170.0	0.0	5.5	1146.6
[Bmim][SCN]	0.0	65109.0	0.0	0.051

the total molar flow rate of the cyclohexane/benzene feed stream was set to 100 kmol/h. It is worth mentioning that, considering the relatively high price and molecular weights of ILs, even for [Bmim][BF<sub>4</sub>], a considerable amount of the initial cost is required to carry out the extraction. However, the total investment can be considerably reduced because of the much simplified processes and highly recycled solvents. The economic evaluation confirms that, with a suitable IL solvent, the total investment costs of the aromatic/aliphatic extraction process are reduced by 35% compared with those of the conventional sulfolane process.<sup>14</sup>

#### 4. CONCLUSIONS

The potential of three ILs, [Bpy][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>], and [Bmim][SCN], as alternative solvents for the extraction of benzene from cyclohexane mixtures is explored and evaluated. The extraction process with ILs as solvents is proposed and simulated with a feed stream of 15 mol % benzene. The overall separation performances can be ranked as [Bmim][BF<sub>4</sub>] > [Bpy][BF<sub>4</sub>] > [Bmim][SCN]. For solvent [Bmim][BF<sub>4</sub>], the stage number is 6, and the corresponding mole ratio of solvent to feed is 2.0. The achieved mole purity of the cyclohexane product is 0.997, and the recovery rates of cyclohexane and benzene are 96.9% and 98.1%, respectively.

It is proven that the studied ILs are promising solvents for the deep separation of benzene from cyclohexane mixtures, which is very helpful for achieving a high purity of the cyclohexane product. Moreover, the IL extraction processes are economically applicable because of the considerably simplified apparatus units and highly recyclable solvents. Thus, it can be potentially used as the alternative of the conventional benzene/cyclohexane extractive separation process.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Supplementary table as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

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### Notes

The authors declare no competing financial interest.

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