

## Ionic Liquids as Benign Solvents for the Extraction of Aromatics

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Ionic liquids (ILs) have been extensively investigated as promising alternatives to conventional organic solvents such as sulfolane and *N,N*-dimethylformamide for the selective extraction of aromatic hydrocarbons from the C<sub>6</sub>-C<sub>10</sub> hydrocarbon mixtures produced from the cracking processes of naphtha and light oils. The most important advantage of ILs over conventional organic solvents is that they are immiscible with aliphatic hydrocarbons, and thus the back extraction of ILs from the raffinate phases and top hydrocarbon-rich layers is not necessary. In this paper, a brief review on the state of the art in the utilization of ILs for aromatics separation is presented.

**Key Words** : Aromatics separation, Ionic liquids, Liquid-liquid extraction, Sulfolane process

### Introduction

Aromatics are mostly obtained by separating aromatic-rich fractions produced from gasoline reforming and naphtha cracking processes for olefin manufacture.<sup>1,2</sup> A number of processes were developed and employed industrially for recovering aromatics from hydrocarbon mixtures, including azeotropic distillation, extractive distillation, liquid-liquid extraction, crystallization by freezing, and adsorption on solids.<sup>3,4</sup> Of these, liquid-liquid extraction is most widely used process for separating aromatics from hydrocarbon mixtures.

The liquid-liquid extraction of aromatics from reformed petroleum naphtha (reformate) is commercially accomplished through solvent extractions using conventional molecular solvents such as sulfolane,<sup>5-9</sup> *N*-methyl pyrrolidone (NMP),<sup>8</sup> *N*-formyl morpholine (NFM), ethylene glycol,<sup>10-12</sup> propylene glycol,<sup>13</sup> *N,N*-dimethylformamide. However, the extraction processes using these solvents suffer from several drawbacks. First of all, substantial amounts of solvents are present in raffinates, especially for the extraction from feeds with high aromatic content. The recovery of these solvents from the raffinates must be carried out by energy intensive distillation, which results in an additional burden in the installation and operational costs of the overall extraction process. Apart from this, residual non-aromatics are always contained in the extract due to the co-extraction of aliphatic compounds along with aromatics arising from the relatively low selectivities of molecular solvents for aromatics over non-aromatics. Also degradation of solvents always takes place during the recovery of solvents by vacuum distillation at elevated temperatures due to the relatively low thermal stability of solvents, which causes equipment corrosion.

As a means of overcoming the problems associated with the use of molecular solvents, ionic liquids (ILs) have been

intensively investigated as alternative solvents due to their favorable physical and chemical properties suitable as aromatic extractants.

Herein, we present a brief overview on the state of the art in the current and future alternative technologies for the separation of aromatics from aliphatic mixtures.

### Current Technologies for Aromatics Recovery

The separation of aromatics from reformate and pyrolysis gasolines consists essentially of stages for the separation of the non-aromatics followed by separation of the aromatic mixture into its individual components. For technological and economic reasons, fractional distillation is rarely used for the aromatics separation. For example, cyclohexane, *n*-heptane, and other alkanes tend to form azeotropes with benzene or toluene which are not separable by distillation. In addition, the distillation of aromatic mixture with close boiling points, for example, xylenes and ethylbenzene, demand a highly energy-intensive distillation which cannot be economically justified. Thus distillations are usually limited to the production of mixed cuts.

Therefore, the separation of aromatic/non-aromatic mixtures is carried out by means of special separation processes.

As listed in Table 1, five different processes were developed and commercialized for recovering aromatics from hydrocarbon mixtures, including azeotropic distillation, extractive distillation, liquid-liquid extraction, crystallization by freezing, and adsorption on solids. The characteristics of each process are briefly summarized in Table 1.

**Liquid-liquid Extraction.** Of those five processes, liquid-liquid extraction is more widely applied than the other four methods. The aromatics in a mixture with varying concentrations can be simultaneously extracted. The most striking feature of the liquid-liquid extraction is that a readily separable two liquid-phase system is retained at all stages.<sup>14,15</sup> This is a fundamental difference from the extractive distillation pro-

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**Table 1.** Current processes used for aromatics recovery<sup>5</sup>

| Process                     | Application   | Requirements for basic or economical operation  |
|-----------------------------|---|---|
| Azeotropic distillation     | Benzene/toluene/xylenes from pyrolysis gasoline         | High aromatic content (> 90%)   |
| Extractive distillation     | Benzene/toluene/xylenes from pyrolysis gasoline         | Medium aromatic content (65-90%)  |
| Liquid-liquid extraction    | Benzene/toluene/xylenes from reformat gasoline          | Lower aromatic content (20-65%)   |
| Crystallization by freezing | <i>p</i> -xylene from <i>m/p</i> -mixtures              | Distillative pre-separation of <i>o</i> -xylene and ethylbenzene from C <sub>8</sub> aromatic fractions |
| Adsorption on solids        | <i>p</i> -xylene from C <sub>8</sub> aromatic fractions | Continuous, reversible, and selective adsorption  |

**Table 2.** Commercially used solvent extractions for production of aromatics<sup>5</sup>

| Process (Company)      | Solvent  |
|------------------------|--|
| Udex (UOP-Dow)         | Aqueous solution of monoethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), or tetraethylene glycol |
| Tetra (UCC)            | Aqueous solution of tetraethylene glycol   |
| Sulfolane (Shell-UOP)  | Non-aqueous, sulfolane (Tetrahydrothiophene 1,1-dioxide)   |
| Arosolvan (Lurgi)      | Aqueous solution of <i>N</i> -methylpyrrolidone  |
| DMSO (IFP)             | Aqueous solution of dimethyl sulfoxide   |
| Duo-Sol (Milwhite Co.) | Non-aqueous, propane/cresol or phenol  |
| Formex (Snamprogetti)  | Aqueous solution of <i>N</i> -formylmorpholine   |
| Aromex (Koppers)       | Aqueous solution of <i>N</i> -formylmorpholine   |

cess, in which only one liquid phase exists. To maintain two phases, highly polar solvents should be used. Some of the solvents and solvent mixtures used in commercial processes are summarized in Table 2.<sup>5</sup>

The liquid-liquid extraction is characterized by counter-current operation. In an extraction column, the solvent is added at the top of the extractor, and the mixture to be separated is introduced in the middle. The non-aromatics leave the extractor at the upper end, while the aromatic-rich solvent is removed in the lower part. To increase the separation, part of the pure aromatics is introduced into the lower part of the column to force the non-aromatics completely from the extract. After the extraction, the non-aromatics are obtained as raffinate, while the aromatics and the solvent comprise the extract. The extract can either be directly distilled with a steam strip or removed from the selective solvent by stripping, and separated from the extraction solvent by distillation. In stripping, the aromatics are dissolved out of the extract with a light hydrocarbon such as pentane, and freed from the paraffinic solvent by simple distillation.<sup>16</sup>

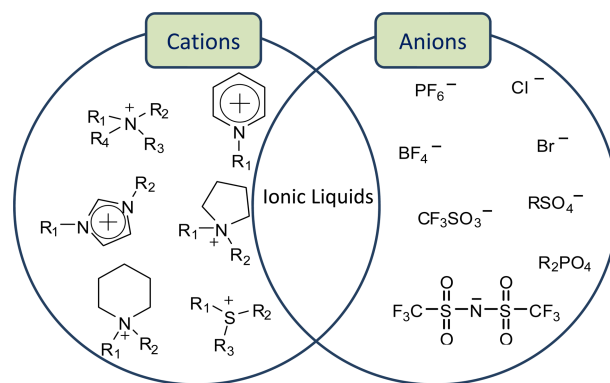
**Sulfolane Process.** Among various liquid-liquid extraction processes so far developed, the Sulfolane process is most widely used for extracting aromatics from aliphatic hydrocarbon mixtures. Usually the Sulfolane process is applied for feed streams with high-content aromatics. The Sulfolane process combines liquid-liquid extraction with extractive distillation to recover high-purity aromatics from hydrocarbon mixtures obtained from reformat, pyrolysis gasoline or coke oven light oils (COLO).<sup>17</sup>

This hybrid combination of techniques allows Sulfolane

units to process feedstocks of much broader boiling range than would be possible by either liquid-liquid extraction or extractive distillation technique alone. A single Sulfolane unit can be used for simultaneous recovery of high purity C<sub>6</sub>-C<sub>10</sub> aromatics, with individual aromatic components recovered downstream by simple fractionation.

The Shell Oil company developed the Sulfolane process in the early 1960s, using sulfolane (tetrahydrothiophene 1,1-dioxide) as a solvent. Because sulfolane has the higher selectivity and capacity for aromatics than any other commercial extraction solvent, Sulfolane units can be operated at the lowest available solvent-to-feed ratio for any given reformat feedstock. The Sulfolane unit is less expensive for building and operation than any other type of extraction unit in case of reformat applications.<sup>18</sup>

**Ionic Liquids as Alternative Solvents.** ILs are organic molten salts consisting of cations and anions, and thus there exist medium to strong electrostatic interactions between cations and anions, depending on the types of ILs.<sup>18,19</sup> For this reason, ILs behave quite differently from common organic solvents. Besides the ionic character, ILs also possess several unique properties suitable for the application as aromatic extractants, including high thermal and chemical stability, non-corrosiveness, and non-flammability, wide liquid temperature range, negligible vapor pressure, and immiscibility with hydrocarbons.<sup>20,21</sup> More advantageously, their physical and chemical properties can easily be tuned by varying cations and/or anions. Among various properties of ILs, ionic character is of pivotal importance in the separation of aromatics from aliphatic mixtures because the driving force for the separation is the electrostatic interaction between aromatics and ILs.<sup>22</sup>

**Figure 1.** Representative cations and anions of ILs used for the extraction of aromatics from hydrocarbon mixtures.

One of the general prediction about the solubilities in ILs is that aromatic compounds are more soluble than aliphatic compounds of the same size due to the existence of the  $\pi$ -electrons in the orbitals above and below an aromatic ring that causes the much stronger electrostatic field around an aromatic molecule compared to a saturated aliphatic molecule.<sup>23,24</sup> Usually alkanes and alkyl side chains give very small electrostatic fields. On the contrary, benzene has a significant quadrupole moment than that of the cyclohexane.<sup>25</sup> Another distinguishable matter is that benzene is more polarizable than cyclohexane. So, these differences cause the enhanced stabilization of the aromatic solutes in the ILs. Consequently, one can predict that the difference in the average electrostatic field is good enough to explain the difference in solubilities of aromatic and aliphatic compounds: any fluctuation in the electronic structure of the aromatic system due to the local fields would just exacerbate such difference.

For instance, in benzene molecule, the  $\pi$ -electron cloud located above and below the benzene molecule creates negatively charged region above and below the molecule, while a net positively charged region exists around the equator.<sup>26</sup> For this reason, cations of ILs are able to interact with the electron-rich  $\pi$ -system, while anions orient themselves around the equator. This is why aromatic compounds are more soluble in ILs than the aliphatic compounds. With this electrostatic interactions, ILs exhibit higher capacities and selectivities for aromatics over aliphatic hydrocarbons than conventional molecular solvents.

**Effect of Cation.** The degree of interaction between IL and the aromatic molecule is more strongly dependent on the type of cation than on the type of anion. The stronger the interaction is, the lower the activity coefficient of aromatics would be.<sup>27</sup> The interaction can be enhanced either by increasing the polarizability of an IL or by increasing the number of IL molecules in the vicinity of an aromatic molecule. This indicates that an efficient IL should possess high polarizability and small molar volume.<sup>28</sup>

Considering all these features, pyridinium- and imidazolium-based ILs with aromatic characters can be regarded as the most promising alternatives to conventional organic solvents. Pyridinium-based ILs were shown to exhibit slightly higher selectivities and aromatics capacities than imidazolium analogues with the same anion. This is because pyridinium cations are more aromatic in character than imidazolium cations.<sup>26</sup>

The IL containing a cation like quaternary phosphonium or ammonium shows relatively low toluene/heptane selectivity, but relatively high toluene distribution coefficient.

Two factors should be considered in determining the performance of ILs for the separation of aromatics from aliphatic hydrocarbon mixtures: capacity and selectivity. As mentioned earlier, the aromaticity of the cation of an IL is an important factor in determining the capacity of an IL to extract aromatics and the selectivity of aromatics over aliphatic compounds. However, molar volume of the IL should also be considered for better performance of the IL.<sup>26</sup>

For example, in the separation of benzene from a hexane mixture, the increase of the molar volume by increasing the alkyl chain length on the cation results in a significant selectivity drop due to the interaction of hexane with the alkyl group of the cation.<sup>26</sup> The activity coefficient of hexane decreases tremendously with increasing alkyl chain length of the cation than that of the benzene. Such a selectivity drop cannot be seen in case of hexane-hexene system as hexene is equally capable of interacting with the alkyl chain of the IL.<sup>26</sup>

**Effect of Anion.** The separation performance of an IL is also affected by the type of anion. However, the effect of the anion is rather complicated and thus cannot be explained by molar volume alone.

Hanke *et al.* reported that the solute-solvent interaction of benzene with the chloride ion of the IL, dimethylimidazolium chloride ([DMIm]Cl) is much stronger than that with the [DMIm] cation and that this interaction is dominated by the electrostatic terms.<sup>29</sup> With benzene, a difference of interaction was found between the ILs, [DMIm]Cl and [DMIm]PF<sub>6</sub>.

The toluene distribution coefficient is very low with the anion, HSO<sub>4</sub><sup>-</sup> at 40 °C with the concentration of 10% toluene for both ILs, 1-hexyl-3-methylimidazolium hydrogen sulfate ([HMIm]HSO<sub>4</sub>) and 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIm]HSO<sub>4</sub>).<sup>22</sup> With the [EMIm]-based ILs, the distribution coefficient of both toluene and heptane increase in the following order at 40 °C: HSO<sub>4</sub><sup>-</sup> < C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub><sup>-</sup> < BF<sub>4</sub><sup>-</sup> < CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> < (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Since the solubility of heptane increases more in this series than that of toluene, the toluene/heptane selectivity decreases in the following order: HSO<sub>4</sub><sup>-</sup> ~ CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> > C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub><sup>-</sup> > C<sub>7</sub>H<sub>7</sub>SO<sub>3</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> > (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>PO<sub>4</sub><sup>-</sup>.<sup>20</sup> For the separation of hexene from a hexane-hexene mixture using an imidazolium-based IL, the selectivity was found in the following order: R-SO<sub>4</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup> > Tf<sub>2</sub>N<sup>-</sup> > X<sup>-</sup>.<sup>26</sup>

From these results, it is obvious that both the size of anion (molar volume) and the degree of cation-anion interaction need to be considered in the selection of ILs as extractants for the aromatics separation. For example, in the extraction of benzene from a hexane mixture, the anion with a localized negative charge like Cl<sup>-</sup> interacts strongly with the cation, thereby limiting the interaction of the cation with the negatively charged region of benzene. Consequently, the activity coefficient of benzene is increased, resulting in the drop of benzene capacity and selectivity.

Delocalized anion like Tf<sub>2</sub>N<sup>-</sup> interacts much weakly with the cation compared with the localized anion. Accordingly, the interaction of the cation with benzene gets larger, resulting in the reduction of benzene activity coefficient. This is demonstrated by the higher benzene capacity in ILs with Tf<sub>2</sub>N<sup>-</sup> than in ILs with a strongly coordinating anion like Cl<sup>-</sup>. For the extraction using ILs with a large-sized, non-coordinating anion like Tf<sub>2</sub>N<sup>-</sup>, the interaction of anion with the non-aromatics is also significant. As demonstrated in the extraction of benzene from *n*-hexane mixtures with ILs bearing a Tf<sub>2</sub>N anion, the activity coefficients of both benzene and *n*-hexane were significantly low in these types of ILs, indicating that substantial amounts of *n*-hexane were co-

extracted along with benzene. As a result of such co-extraction of benzene and *n*-hexane, the selectivity of benzene over *n*-hexane becomes reduced. The ILs with a non-coordinating and smaller-sized anion like BF<sub>4</sub> or alkylsulfate anion show higher selectivity for benzene over *n*-hexane than those bearing a non-coordinating and larger-sized Tf<sub>2</sub>N<sup>-</sup>. This can be attributed to smaller molar volumes of the ILs with a BF<sub>4</sub> or alkylsulfate anion. This is because a number of IL molecules are present in the vicinity of the benzene molecule when the molar volume of IL is smaller.

In summary, to achieve high aromatics capacity and high selectivity of aromatics over non-aromatics, the anion of an IL should be non-coordinating and small-sized as long as other properties such as thermal and chemical stability and immiscibility with hydrocarbons are fully satisfied.

**Effect of Alkyl Chain Length.** As discussed earlier, the chain length of the alkyl substituent on the cation affects both the selectivity of aromatic/aliphatic and the aromatics capacity (capacity to extract aromatics, distribution coefficient). As the alkyl chain length increases, the electron donation from the alkyl group to the cation of IL increases. As a result, the positive character of the cation decreases and thus the interaction between cation and aromatics is weakened, resulting in the reduction of selectivity. Moreover, the increase of alkyl chain length also increases the extraction of non-aromatics, *i.e.* higher distribution coefficient of non-aromatics, thereby further decreasing the selectivity.<sup>30</sup>

On the contrary, the increase of the chain length of the alkyl substituent on the anion mostly affects the distribution coefficient of aliphatic compounds. For the extraction of toluene from *n*-heptane mixture using [RMIm]RSO<sub>4</sub>, it was found that the amount of *n*-heptane extracted (distribution coefficient) increases with the increase of the alkyl chain length, whereas the amount of toluene extracted remains almost unchanged.<sup>30</sup>

From these results, it is concluded that, for the extraction of toluene from heptane mixtures, a shorter alkyl chain on the imidazolium cation is more favorable for higher aromatic/aliphatic selectivities, although the distribution coefficient of toluene is slightly lower than that with a longer alkyl chain.<sup>30,31</sup>

**Color of ILs.** Usually the colored materials are considered as impure. In fact, most of the ILs themselves are colorless liquids. However, they become colored when thermally treated for a long time. An interesting thing is that the color persists in ILs and usually cannot be extracted into the organic products or solvents. In general, the quantity of colored materials present in ILs is too small to characterize. In case of imidazolium-based ILs, it is assumed that the color of the ILs is originated from the oligomerization of the imidazole moiety or from the generation of radical ions. Since the extraction and the products thus obtained are not affected by the colored materials presents in ILs, the use of colored ILs in the commercial sector may not be a problem.<sup>32</sup>

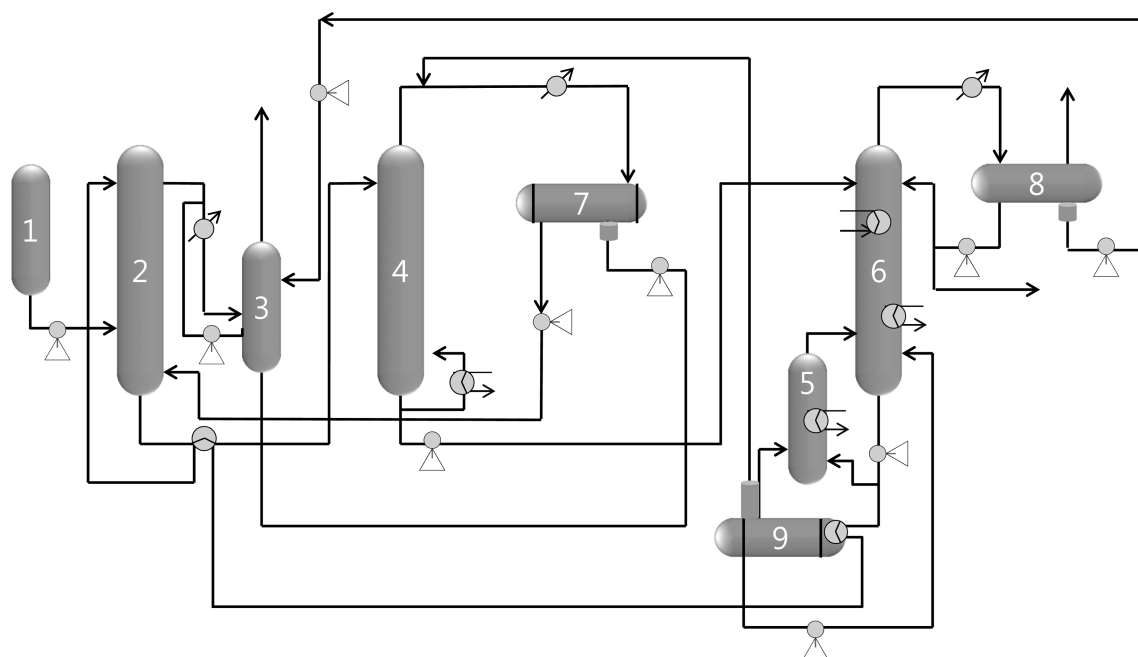
**Thermal Stability of ILs.** For the extraction of aromatics from hydrocarbon mixtures, thermal stabilities of ILs are extremely important because the recovery of aromatics from

ILs layers requires distillation at elevated temperatures. Most of ILs exhibits high thermal stabilities up to 200 °C, and some ILs bearing a Tf<sub>2</sub>N<sup>-</sup> ion remain stable over 400 °C determined by thermogravimetric analysis (TGA).<sup>33</sup> In general, ILs with a non-coordinating anion like Tf<sub>2</sub>N<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and SCN<sup>-</sup> show higher thermal stabilities than those with a strongly coordinating anion.<sup>34</sup> In some cases, the decomposition is observed especially for the ILs with a highly nucleophilic anion at temperatures above 200 °C. For instance, 1,3-dialkylimidazolium-based ILs bearing a Cl anion, was found to decompose into 1-alkylimidazole and chloroalkane at temperatures over 200 °C. Decomposition temperatures of representative ILs are listed in Table 3.<sup>35,36</sup>

**Solvent Loss in the Raffinates.** Although ILs are known to be immiscible with aliphatic hydrocarbons, there is always a possibility that small amounts of ILs dissolve and become entrained in the raffinate stream. Since the recovery of ILs from raffinates is a costly process, the solubility of ILs in the raffinates should be minimized to a great extent by a proper selection of ILs. For the extraction of toluene from *n*-heptane mixtures using 4-methyl-1-butylpyridinium tetra-

**Table 3.** Decomposition temperatures of representative ILs<sup>35,36</sup>

| Ionic liquid  | T <sub>onset</sub> (°C) |
|---|-------------------------|
| 1-ethylpyridinium ethylsulfate ([EPy][EtSO <sub>4</sub> ])  | 303                     |
| 1-ethyl-3-methylpyridinium ethylsulfate ([EMPy][EtSO <sub>4</sub> ])                                  | 281                     |
| 1-ethyl-2,3-dimethylpyridinium ethylsulfate ([EMMPy][EtSO <sub>4</sub> ])                             | 297                     |
| 1-butylpyridinium bromide ([Bpy]Br)   | 237                     |
| 1-butyl-3-methylpyridinium bromide ([BMPy]Br)   | 235                     |
| 1-butyl-3-methylpyridinium bis(trifluoromethane sulfonyl) imide ([BMPy]Tf <sub>2</sub> N)             | 397                     |
| 1-butyl-3-methylpyridinium tetrafluoroborate ([BMPy]BF <sub>4</sub> )                                 | 364                     |
| 1-butyl-2,3-dimethylpyridinium bromide ([BMPMPy]Br)   | 239                     |
| 1-hexylpyridinium bromide ([Hpy]Br)   | 238                     |
| 1-hexylpyridinium bis(trifluoromethane sulfonyl) imide ([Hpy]Tf <sub>2</sub> N)                       | 392                     |
| 1-hexyl-3-methylpyridinium bromide ([HMPy]Br)   | 237                     |
| 1-hexyl-3-methylpyridinium bis(trifluoromethane sulfonyl) imide ([HMPy]Tf <sub>2</sub> N)             | 399                     |
| 1-hexyl-2,3-dimethylpyridinium bromide ([HMPMPy]Br)   | 239                     |
| 1-hexyl-2,3-dimethylpyridinium bis(trifluoromethane sulfonyl) imide ([HMPMPy]Tf <sub>2</sub> N)       | 405                     |
| 1-ethyl-3-methylimidazolium chloride ([EMim]Cl)   | 285                     |
| 1-ethyl-3-methylimidazolium bromide ([EMim]Br)  | 311                     |
| 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF <sub>4</sub> )                                | 450                     |
| 1-ethyl-3-methylimidazolium (trifluoromethyl)trifluoroborate ([EMim]CF <sub>3</sub> BF <sub>3</sub> ) | 246                     |
| 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide ([EMim]Tf <sub>2</sub> N)            | 455                     |
| 1-ethyl-3-methylimidazolium dicyanamide ([EMim]DCA)   | 240                     |
| 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMim]PF <sub>6</sub> )                              | 481                     |



**Figure 2.** Schematic diagram of Sulfolane process.<sup>3</sup>

1: Feed; 2: Extractor; 3: Raffinate wash column; 4: Stripper; 5: Solvent regenerator; 6: Recovery column; 7, 8, 9: Separators.

fluoroborate ( $[\text{MBPy}]\text{BF}_4$ ), it was observed that the solubility of  $[\text{MBPy}]\text{BF}_4$  in heptane was negligible at 40 °C although the solubility of molecular solvent, sulfolane in heptane was found to be as high as 0.6 mol%.<sup>26</sup> The negligible or extremely low solubility of ILs in aliphatic compounds is one of the most striking advantage of ILs over molecular solvents like sulfolane.

**Purification of Extracted Aromatics.** The purity of extracted aromatics depends on the amounts of co-extracted non-aromatics. In the Sulfolane process, the purity of aromatics from the extraction process never exceeds 90% due to the co-extraction of considerable amounts of non-aromatics. Therefore, an extractive stripper column is almost always required to remove residual non-aromatics to achieve the aromatic purity above 98%.

It has been reported that, in the extraction of toluene from *n*-heptane mixture, the extraction curve for IL is very close to the toluene-IL binary axis.<sup>22,37</sup> This indicates that the extract would be much purer for IL than for conventional solvents. Preliminary analysis of the LLE diagram for the same feed composition with  $[\text{MBPy}]\text{BF}_4$  indicates that an aromatic product with a purity of 99% on solvent free basis is possible. Therefore, in case of the aromatic separation using ILs, extractive stripping step may not be needed as long as an appropriate IL is selected.

**Recovery of Aromatics from ILs.** ILs are entirely consists of ions and they do not have the sufficient vapor pressure below their decomposition temperature. It is reported that most of ILs decompose before reaching their boiling point. For example, the vapor pressure of the  $[\text{OMIm}]\text{PF}_6$  at the 75 °C is as low as  $1.0 \times 10^{-6}$  mbar.<sup>38</sup> Therefore, aromatics contained in ILs can be easily separated from ILs by a simple distillation process as long as ILs are stable at the

distillation temperature.

On the other hand, the vapor pressure of sulfolane is 0.42 mbar, and thus the separation of aromatics from sulfolane requires a rather complicated distillation process, especially for the separation of high boiling aromatics such as  $\text{C}_{10}$  aromatics, mostly consisting of *n*-butyl benzene with a normal boiling point of 183 °C.

Though it was mentioned earlier that some ILs bearing a  $\text{Tf}_2\text{N}$  anion are stable up to 400 °C, but long term stability tests show that  $[\text{EMIm}]\text{Tf}_2\text{N}$  is stable up to 234 °C.<sup>39</sup> Obviously, the ILs with an anion other than  $\text{Tf}_2\text{N}$  would be much less thermally stable. Considering this, it is safe to assume that the practical upper limit is around 200 °C. Nonetheless, the temperature of 200 °C is enough to separate most of aromatics by distillation because this is higher than the boiling point of the heaviest aromatics.

Another method to separate aromatics from ILs is the extraction of ILs by water when ILs are water-miscible. However, there is a danger of degradation of ILs during the separation of ILs from water because water-miscible ILs tend to undergo hydrolysis at elevated temperatures.<sup>26</sup> Re-extraction method using an aliphatic hydrocarbon can also be used to separate aromatics from ILs, especially when the ILs have low thermal stabilities. In this case, the boiling point of the aliphatic hydrocarbon should be much lower or higher than that of the targeted aromatics. The re-extracted aromatic-aliphatic mixtures are subsequently separated by distillation.

The re-extraction of aromatics from ILs using dodecane is being practiced in a few commercial units to avoid subjecting the extraction solvent to high temperatures.<sup>26</sup>

**Economic Feasibility.** For the use of ILs as alternatives to molecular solvents, economic feasibility must be consider-

**Table 4.** Comparison between extraction with sulfone and ILs<sup>3</sup>

| Equipment                | Temperature (°C)<br>of process using<br>Sulfolane | Temperature (°C)<br>of process using<br>[MEBPy]BF <sub>4</sub> |
|--------------------------|---|--|
| Extractor                | 100   | 40   |
| Raffinate wash           | 40  | 40   |
| Extractive stripper      | 190   | 135  |
| Recovery column          | 190   | -  |
| Solvent regenerator      | 190   | -  |
| Flash column or stripper | -   | 135  |
| Total heat load, MW      | 160   | 32   |

**Table 5.** Comparison of estimated investment and variable cost in \$1,000<sup>3</sup>

|                                       | Sulfolane<br>(UOP) | [MBPy]BF <sub>4</sub> |
|---------------------------------------|--------------------|-----------------------|
| Materials and labor                   | 5,758              | 32,546                |
| Engineering                           | 18,777             | 7,510                 |
| Inside battery limits                 | 76,359             | 33,798                |
| Outside battery limits                | 25,036             | 11,266                |
| Solvent inventory                     | 6,259              | 25,036                |
| Total investment costs                | 107,655            | 70,100                |
| Annual costs, 40% of total investment | 43,062             | 28,040                |
| Energy costs                          | 30,043             | 6,259                 |
| Total annual costs                    | 73,105             | 34,299                |

ed. Meindersma *et al.* compared the economic feasibility of the IL-based aromatic extraction using [MEBPy]BF<sub>4</sub> as the extractant with that of the Sulfolane process, although the estimation still requires more detailed investigation.<sup>22</sup>

In Tables 4 and 5, the comparison of the above two processes is shown. The most notable difference in Table 4 is that the solvent regeneration step of the IL-based process is much simpler than that of the Sulfolane process. In the Sulfolane process, two distillation columns are required for the recovery of the aromatics and the regeneration of sulfolane. On the contrary, only one flash column or stripper is required for the IL process.

Investment cost between the Sulfolane process and the IL process is also compared by assuming that the investments on the heat exchangers, reboilers, and coolers are proportional to the duty. As shown in Table 5, the investment cost in heat equipments for the IL process is estimated 20% of that of the Sulfolane process. This is because the recovery column and the solvent regenerator can be replaced by one flash column for the IL process. Taken together, they predicted that the total investment for the IL process is about 45% of that of the Sulfolane process.

### Conclusions

Although the industrial application of ILs for aromatic extraction from aliphatic hydrocarbon mixtures has not yet been materialized, ILs have many advantages over conventional molecular solvents due to their high thermal stabi-

lities, negligible vapor pressures, and the immiscibility with aliphatic hydrocarbons. With such unique properties of ILs, the solvent regeneration step could be greatly simplified, resulting in the reduction of investment cost. However, for the industrial application of ILs, the performances of ILs need to be further improved and the cost of ILs should be much lowered through the development of new synthetic processes.

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