Separation of Organic Nitrogen Compounds by Supported Liquid Membranes Based on Ionic Liquids

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(Received January 10, 2006)

Heterocyclic compounds including nitrogen (quinoline, isoquinoline, and pyridine) were separated from \( \text{n}-\)heptane mixtures through supported liquid membranes using room temperature ionic liquids, based on 1-alkyl-3-methylimidazolium and quaternary ammonium salts. The organic nitrogen compounds selectively permeated the membranes. The differences in the structures of room temperature ionic liquids had little effect on the permeability of organic nitrogen compounds. Liquid membranes that used more hydrophilic room temperature ionic liquids yielded higher selectivity. Lower pyridine concentration and temperature caused increases in selectivity. Application of supported liquid membranes based on ionic liquids has potential for the separation process of organic nitrogen compounds and heptane.

Keywords
Ionic liquid, Supported liquid membrane, Organic nitrogen compound, Denitrogenation, Fuel oil

1. Introduction

Reduction of the sulfur, nitrogen, oxygen, and aromatic contents in petroleum fractions is very important for environmental protection, and removal generally relies on a catalytic hydrogenation process. Recent regulations requiring lower sulfur levels now demand processes for deeper desulfurization. However, organic nitrogen compounds, such as quinoline, indole, and carbazole, are the major inhibitors of sulfur removal through hydrodesulfurization\(^1\)\(^-\)\(^3\). Therefore, the removal of nitrogen is essential for future refinery processes. Generally, hydrodenitrogenation is the most difficult hydrogenation reaction because such deep hydrogenation processes have high energy and hydrogen consumption, so other processes are needed. Methods based on solvent extraction method have been proposed\(^4\)\(^-\)\(^5\) with the advantages of low energy cost, elimination of hydrogen usage, retention of the chemical structures of the fuels, and no special equipment requirements\(^6\). Novel desulfurization processes have been suggested for fuel oils based on photochemical reactions and solvent extraction\(^7\). The suitability of ionic liquids as green solvents for chemical processes has been frequently recognized because of the negligible vapor pressure, as replacements for volatile, conventional organic solvents\(^8\)\(^-\)\(^9\). Ionic liquids have been used to replace organic solvents in the field of separation processes\(^6\). Desulfurization and denitrogenation have been investigated with solvent extraction using ionic liquids\(^10\)\(^-\)\(^13\).

The large amount of ionic liquids used as solvents in liquid-liquid extraction systems is expensive because of the extremely high cost of ionic liquids compared with conventional organic solvents. Recently, studies on a supported liquid membrane (SLM) system have used ionic liquids as membrane solutions. The supported liquid membrane process, which combines extraction and stripping processes, requires less solvent than liquid-liquid extraction systems, but the membrane stability is critical\(^14\). No leakage of ionic liquid was reported from the membrane pores and high operational stability of supported ionic liquid membrane\(^15\). Previously, we reported that aromatic hydrocarbons selectively permeated the supported ionic liquid membrane against aliphatic hydrocarbons\(^16\)\(^-\)\(^17\).

The present study examined the application of ionic liquids to supported liquid membranes for separating organic nitrogen compounds from aliphatic hydrocarbons, as a preliminary investigation for the development of a simultaneous separation process for nitrogen and sulfur from fossil fuels.

2. Experimental

2.1. Materials

Imidazolium-based ionic liquids were prepared from

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the hexafluorophosphates of 1-n-butyl-, 1-n-hexyl-, and 1-n-octyl-3-methylimidazolium, [C₄mim][PF₆], [C₆mim][PF₆], and [C₈mim][PF₆] following the methods of Laszlo and Compton\(^{(18)}\). Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethanesulfone) imide ([T]), and diethyl(2-methoxyethyl)ammonium tetrafluoroborate ([B]) were supplied by Nisshinbo Ind., Inc. (Tokyo, Japan). The structures of these ionic liquids are shown in Fig. 1. All other reagents were of analytical grade and were used without further purification.

### 2.2. Permeation through Supported Liquid Membranes

The membrane material was porous polyvinylidene fluoride film (PVDF, Millipore), with a pore size of 0.45 μm and membrane thickness of 125 μm.

The supported liquid membranes were prepared at room temperature by impregnating the porous film with ionic liquid for 24 h. Penetration of ionic liquid into the membrane was confirmed by measuring the weight difference before and after the immersion treatment.

The feed solutions were a mixture of organic nitrogen compounds and n-heptane. Quinoline, isoquinoline, and pyridine were used as the organic nitrogen compounds. n-Hexadecane was used as the receiving solution. The experimental apparatus is shown in Fig. 2. A membrane with an effective area \( A \) of 12 cm\(^2\) was fixed in the apparatus. The transport experiment was initiated by adding 100 ml of each solution into the respective compartments at 30°C. The stirring speed of the magnetic bar in each cell was controlled at 300 rpm. Samples of hydrocarbon were withdrawn at regular time intervals. n-Heptane concentrations were determined by GLC (gel permeation chromatography) analysis using an internal standard method, and the concentrations of organic nitrogen compounds were determined by UV (ultraviolet) spectrophotometry.

### 3. Results and Discussion

The permeation flux \( J \) through the supported ionic liquid membrane can be expressed by the following equations\(^{(16,17)}\) in the initial stage:

\[
J = - \frac{V}{A} \frac{dC_t}{dt} = PC_t
\]

\[
\ln \frac{C_t}{C_0} = - \frac{A}{V} Pt
\]

where \( A, V, \) and \( t \) are the area of the membrane, the volume of the feed phase, and time, respectively. Superscript 0 denotes the initial state. Here, we discuss permeability \( P \), obtained from the plots on the left hand side of Eq. (2) versus \( t \) in the initial period. Furthermore, we calculated the selectivity of permeability of organic nitrogen compound from heptane, as defined by Eq. (3).

\[
S = \frac{P_{\text{nitrogen compound}}}{P_{\text{heptane}}}
\]

### 3.1. Permeation through Supported Ionic Liquid Membrane

Figures 3(a)–3(c) show the transport of organic nitrogen compounds, quinoline, isoquinoline, and pyridine, and heptane through the SLMs based on [C₄mim][PF₆], respectively. Organic nitrogen compounds selectively permeated the SLM based on [C₄mim][PF₆]. The plots on the left hand side of Eq. (2) versus \( t \) are
shown in Fig. 4, which indicate a linear relationship in the initial period.

First, we examined the effects of organic nitrogen compounds on permeability. Table 1 lists the permeability of organic nitrogen compounds, heptane, and selectivity. Permeation rates increased in the order of heptane < isoquinoline < quinoline ≤ pyridine for all SLMs based on organic liquids investigated and water. This order corresponds to the hydrophobicity of the organic nitrogen compounds, isoquinoline (log $P_{0/w} = 2.08$, where log $P_{0/w}$ is the logarithm of the partition coefficient of the organic nitrogen compounds in 1-octanol and water and is a measure of the hydrophobicity), quinoline (2.00), and pyridine (0.65). However, in this study the permeation rates of these compounds, including heptane, were about ten times higher than those of aromatic compounds benzene (1.99), toluene (2.54), and $p$-xylene (3.09), as well as heptane from a mixture of heptane and aromatic compounds reported in a previous study$^{16}$. Hydrophilicity was found not to be a key factor in the permeation process. The difference in permeation rates between organic nitrogen and aromatic compounds is considered to be caused by polarity differences. The values of solvent polarity $E_{\text{rit}}(30)^{19}$ for organic nitrogen compounds are about 40 kcal/mol and about 34 kcal/mol for aromatic compounds, suggesting that organic nitrogen compounds are more polar than aromatic compounds. The values of $E_{\text{rit}}(30)$ for ionic liquids$^{29}$ are larger than 50 kcal/mol, suggesting that ionic liquids interact well with more polar compounds. Therefore, the present study found that permeation rates through the SLM based on ionic liquids were mainly controlled by the polarity of the permeating species; but species hydrophilicity should be considered if the polarities are similar.

Next we examined the effect of ionic liquids on permeability and selectivity. [T] gives the highest permeability because, as described previously$^{17}$, the viscosity is much lower than those of other ionic liquids. The differences in permeabilities between ionic liquids are relatively small, whereas for aromatic hydrocarbons$^{16}$, permeability through a SLM based on [T] is 2-5 times higher than [Cmim][PF6]. This may be due to the high affinity of organic nitrogen compounds with ionic liquids as described above. [B] and [Cmim][PF6] gave the highest selectivity. Generally, higher permeability caused lower selectivity. Therefore, the selectivity of organic nitrogen compounds from heptane was not as high as that from aromatic hydrocarbons. However, if the viscosities of the ionic liquids were
similar, selectivity increased as the hydrophilicity of the ionic liquids increased, corresponding to the smaller log $P_{\text{QW}}$ values listed in Table 1.

<table>
<thead>
<tr>
<th>Pyridine concentration [mol/dm$^3$]</th>
<th>$10^3P_{\text{pyridine}}$ [mbar]</th>
<th>$10^3P_{\text{heptane}}$ [mbar]</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.619</td>
<td>5.95</td>
<td>0.0240</td>
<td>248</td>
</tr>
<tr>
<td>1.24</td>
<td>6.11</td>
<td>0.0402</td>
<td>152</td>
</tr>
<tr>
<td>6.20$^a$</td>
<td>7.74</td>
<td>0.859</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 2: Effects of Pyridine Concentration on Permeability $P$ and Selectivity $S$ Using [C$_{4}$mim][PF$_6$] as an Impregnating Liquid

$^a$) corresponds to 1:1 volume ratio of pyridine and heptane.

The permeability and selectivity of membranes are functions of feed concentration$^{21}$ in membrane separation. Permeation experiments of pyridine into liquid membranes containing [C$_{4}$mim][PF$_6$] were conducted. 

Table 2 shows the effects of feed concentration on permeation behavior. As pyridine content increased in the feed, pyridine permeability gradually increased and selectivity sharply decreased. Decline in benzene selectivity was observed in the separation of benzene/cyclohexane with polymeric membranes and can be explained by the plasticization effect of benzene on the membrane$^{21}$. As benzene content increases, the membrane is swollen and relaxed polymer chains allow for enhanced permeation of cyclohexane. However, this idea does not apply to our study because the solutes permeate the ionic liquid. Pyridine content in the membrane increased with increasing pyridine concentration in the feed. This may cause changes in membrane characteristics such as polarity and hydrophilicity to promote the heptane permeation. This idea can explain the higher permeability of heptane in the presence of organic nitrogen compounds than in the presence of aromatic hydrocarbons because of the high affinity of organic nitrogen compounds with ionic liquids.

### 3.3. Temperature Effects on Permeability and Selectivity

One disadvantage of SLMs using conventional organic solvent and water is the loss of membrane liquid caused by volatilization or dissolution in the contacting phase$^{141}$. Therefore, temperature increases cause destabilization of the membrane. On the other hand, ionic liquids have extremely high thermal stability and immeasurably low vapor pressure properties, so the temperature effect (5-90°C) on the permeability and selectivity of the supported ionic liquid membrane was examined.

Figure 5 shows the Arrhenius plot and selectivity for the permeability of pyridine and heptane through the SLM based on [C$_{4}$mim][PF$_6$]. Permeability increased and selectivity decreased with increasing temperature as in other membrane separation systems$^{221}$. The permeability logarithm decreased linearly with the reciprocal of temperature, and permeation behavior followed an Arrhenius type relation. The apparent activation energy for permeation was 4.46 kJ/mol for pyridine and 10.4 kJ/mol for heptane. According to the dissolution-diffusion model, membrane selectivity is influenced by the membrane's affinity to components of the feed and the ease of diffusion of molecules through the membrane matrix. Since diffusivity is generally insensitive to temperature and the diffusivity of pyridine is not so different from heptane, the temperature dependency of the affinity between pyridine and ionic liquid may differ from heptane. Unfortunately, we did not confirm the solubility temperature dependency since the solubility of pyridine is immeasurable because of the complete miscibility between pyridine and ionic liquid within the investigated temperature range.

### 4. Conclusion

Supported liquid membranes impregnated with ionic
Initial pyridine concentration was 10 vol%.

Fig. 5 Arrhenius Plot and Selectivity for Permeability of Pyridine and Heptane through SLM Based on [Cmin][PF6]

liquids were investigated to separate organic nitrogen compounds such as pyridine, quinoline, and isoquinoline, as well as heptane. Organic nitrogen compounds selectively permeated the membrane. Permeation rates through the SLM were mainly controlled by the polarity of the permeating species, but the hydrophilicity of the species should be considered if the polarities are similar. The difference in structure of the room-temperature ionic liquids had little effect on the permeability of organic nitrogen compounds. The liquid membrane containing more hydrophilic room-temperature ionic liquids had higher selectivity. Lower pyridine concentrations and temperature increased selectivity. These experimental results indicate that the application of supported ionic liquid membranes to the separation process of organic nitrogen compounds and heptane is potentially applicable to the deep denitrogenation process of fuel oils.

Acknowledgments

The authors wish to thank Nissinbo Ind., Inc. for providing ionic liquids [B] and [T] for this research. This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 17560670) from the Japan Society for the Promotion of Science.

Nomenclatures

\[ A : \text{area of the membrane} \ [m^2] \]

\[ C : \text{concentration} \ [\text{mol/dm}^3] \]

\[ J : \text{flux} \ [\text{mol/(m}^2\cdot\text{s})] \]

\[ P : \text{permeability} \ [\text{m/h}] \]

\[ P_{ow} : \text{partition coefficient of ionic liquids between 1-octanol and water} \ [\text{—}] \]

\[ S : \text{selectivity} \ [\text{—}] \]

\[ t : \text{time} \ [\text{h}] \]

\[ V : \text{volume of reet phase} \ [\text{m}^3] \]

<Subscripts>

\[ f : \text{feed phase} \]

\[ r : \text{receiving phase} \]

<Superscript>

\[ 0 : \text{initial} \]

References

要 旨

イオン液体含浸波膜による有機窒素化合物の分離

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石油の水素化脱硫において、有機窒素化合物は反応の障害物質として知られており除去しなければならないが、有機窒素化合物の水素化反応は条件が厳しいため代替法が求められていた。本研究では、イオン液体を含浸させた高分子膜を用いて、脂肪族炭化水素からの有機窒素化合物の除去を検討した。具体的にはイミダゾリウム塩型および4級アンモニウム塩型のイオン液体を含浸波膜を用いて有機窒素化合物（キノリン、イソキノリン、ピリジン）をヘプタンの分離を行った。これらの有機窒素化合物はヘプタンに対して選択性的に膜を透過した。ピリジンの透過性および選択性に及ぼすイオン液体の種類、ピリジン濃度および温度の影響を検討した。イオン液体の種類はピリジンの透過速度にほとんど影響を及ぼさなかったが、選択性はより親水的なイオン液体を用いることで増加した。ピリジン濃度および温度の減少は選択性の増加をもたらした。以上の点から、イオン液体含浸波膜は有機窒素化合物の分離手段として有効であることが分かった。