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## **Separation of Coal Tar Absorption Oil by an Ionic Liquid Supported Liquid Membrane**

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The separation of coal tar absorption oil by an ionic liquid supported liquid membrane was studied to recover nitrogen heterocyclic compounds. Batch permeation runs with the supported liquid membrane were conducted using an absorption oil-heptane solution as the feed, an aqueous solution of the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, as the membrane liquid, and toluene as the solvent. Under all conditions, the nitrogen heterocyclic compounds selectively permeated through the membrane compared to other compounds. The permeation rates, especially for indole, significantly increased with the addition of the ionic liquid. The overall permeation coefficients increased with the addition of the ionic liquid and the separation selectivity of indole to 2-methylnaphthalene increased.

### **1. Introduction**

Coal tar absorption oil (AO) is one of the distillation fractions from a coal tar (b.p. = 470~550K), obtained from coal carbonization. It contains many kinds of chemical compounds such as nitrogen heterocyclic compounds, homocyclic compounds, etc, which are useful as raw materials for agricultural chemicals, medicines, perfumes, and many other useful chemicals. The general method to separate these compounds consists of two steps; the first step is a rough separation of AO into several fractions by acidic and basic extraction, followed by the further separation and purification of these fractions into respective products. The separation for the first step in industrial application has some drawbacks, e.g., corrosion of the equipment and difficulties in solvent recovery. As alternative methods, liquid-liquid extraction [1-4] and O/W/O supported liquid membrane methods [5] have been studied.

Ionic liquids are attracting much attention as alternative green solvents to the volatile organic

compounds typically used in separation processes [6, 7] because they are air and water stable, and have a non-measurable vapor pressure. Ionic liquids are organic salts consisting of by an organic cation and either an organic or an inorganic anion, and are liquid at around room temperature.

In this work, the separation of AO by an ionic liquid supported liquid membrane was carried out under various conditions to study the effects of the conditions on the permeation of targeted compounds through the ionic liquid supported liquid membrane.

## 2. Experimental

1-Butyl-3-methylimidazolium tetrafluoroborate [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] was selected as the membrane liquid mainly due to its solubility in traditional solvents. The properties of [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] are shown in Table 1. [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] dissolves in water but is immiscible with hydrocarbons. This ionic liquid was purchased from Wako Chemical Co., Ltd. A hydrophilic filter sheet (cellulose, advantec filter paper no.5B) was used as the membrane liquid support sheet, purchased from Toyo Roshi Kaisha, Ltd.

Table 1 Physical properties and solubilities of [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>]

m.p. [K]	density(298K) [kg m <sup>-3</sup> ]	viscosity(298K) [Pa s]	conductivity [mS m <sup>-1</sup> ]			
202	1370	0.118	343			
solubilities with traditional solvents						
H <sub>2</sub> O	MeOH	EtOH	Acetone	THF	Heptane	Toluene
○	○	○	○	○	×	×

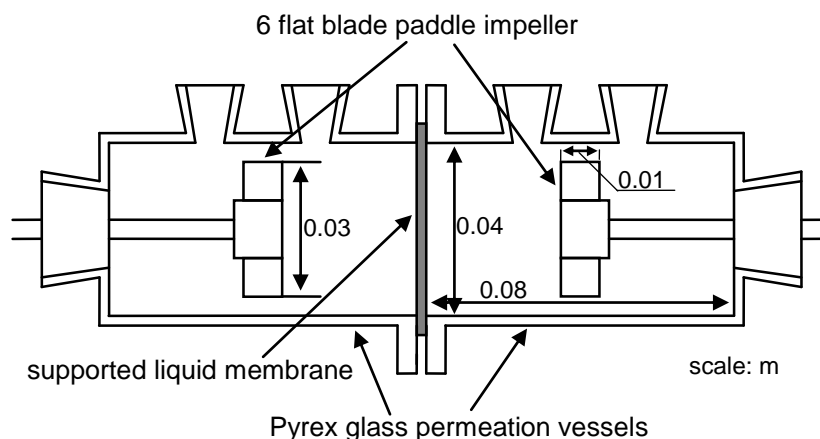


Figure 1. Experimental apparatus for supported liquid membrane permeation.

Table 2 Material systems and experimental conditions

Feed	AO-heptane solution(AO:H <sub>p</sub> =1:1, $1.2 \times 10^{-4} \text{m}^{-3}$ )	
Solvent	Toluene( $1.2 \times 10^{-4} \text{m}^{-3}$ )	
Membrane liquid	Aqueous solution of ionic liquid([bmim <sup>+</sup> ][BF <sup>4-</sup> ]) ( $C_{IL}=0, 0.1, 0.5, 0.9, 1$ )	
Support sheet	Thickness: $2.2 \times 10^{-4} \text{m}$ , Diameter: $7.0 \times 10^{-2} \text{m}$ Mean pore size: $4.0 \times 10^{-6} \text{m}$ , $n: 2, 3$	
Stirring velocity, $N_{SLM}$	[hr <sup>-1</sup> ]	6000, 12000
Temperature	[K]	298
Operation time	[hr]	12

Figure 1 illustrates a permeator for supported liquid membrane permeation. The liquid membrane was placed and held between two Pyrex glass vessels. The operation temperature was kept constant by passing water at a constant temperature through the tube coiled around the permeator. Before placing it in position, the filter sheet was impregnated with the ionic liquid solution adjusted to the specified  $C_{IL}$ . To keep a constant amount of the membrane solution supported in the filter sheet, the excess of the ionic liquid solution was removed from the membrane surface. The feed and solvent were poured into the respective vessels simultaneously and quickly, and then agitation of the feed and solvent phases was started ( $t=0$ ) to begin the batch permeation run. The raffinate and extract phases were sampled at specified operating periods for analysis by a gas chromatograph (GC-2010, Shimadzu Corp.). The principal conditions for the permeation runs are shown in Table 2. The compositions of the membrane liquid ( $C_{IL}=0, 0.1, 0.5, 0.9, 1$ ), the stirring velocities in both phases ( $N_{SLM}=6000, 12000$ ), and the number of support sheets ( $n=2, 3$ ) were varied.

### 3. Results and Discussion

The mass fractions of some of the main compounds in AO are shown in Table 3. Quinoline(Q), isoquinoline(IQ), indole(I) as nitrogen heterocyclic compounds, naphthalene(N), 1- and 2-methylnaphthalenes (1MN and 2MN), biphenyl(BP), and dibenzofuran(DBF) as homocyclic compounds etc. in the absorption oil were identified for quantification.

Table 3 Mass fractions of major components in AO

$x_{Q,0}$	$x_{IQ,0}$	$x_{I,0}$	$x_{N,0}$	$x_{1MN,0}$	$x_{2MN,0}$	$x_{BP,0}$	$x_{DBF,0}$
0.077	0.019	0.036	0.012	0.107	0.263	0.064	0.098

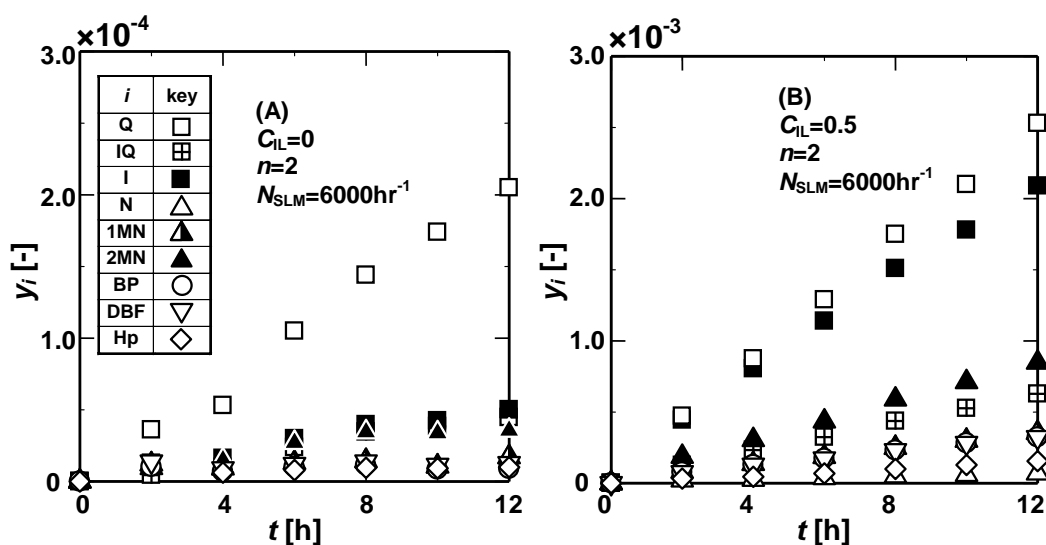


Figure 2. Time courses of  $y_i$  (A)  $C_{IL}=0$ , (B)  $C_{IL}=0.5$ .

For all permeation runs, the membrane solution could be stably supported in the filter during the operation run. Figure 2 shows the examples of the time courses of the mass fractions in the extract phases,  $y_i$ . The addition of the ionic liquid into the membrane solution enhanced the permeation of the components and the  $y_i$  values for most of the components at  $C_{IL}=0.5$  were approximately 10 times higher than those at  $C_{IL}=0$ . The effects of the addition were significant especially for I. Indole and the ionic liquid used have been reported as an acidic compound<sup>8)</sup> and a basic solution<sup>9)</sup>, respectively. The solubility of I in the membrane phase might be enhanced by the addition of the ionic liquid, and consequently permeation was promoted. Most of the nitrogen heterocyclic components selectively permeated through the ionic liquid membrane compared to the other components. Though  $x_{2MN,0}$  was much higher than  $x_{Q,0}$ ,  $x_{IQ,0}$  and  $x_{I,0}$ , the permeation rates of Q, IQ and I were much larger than 2MN and the other components. The effects of  $C_{IL}$ ,  $n$  and  $N_{SLM}$  on the values of  $y_Q$  and  $y_I$  are shown in Figures 3 and 4, respectively. First of all, the addition of the ionic liquid to the membrane solution significantly enhanced the permeation of Q and I. The permeation rate of I simply increased with  $C_{IL}$ . The permeation rate of Q also increased with  $C_{IL}$  up to 0.5. However when  $C_{IL}>0.5$ , the permeation rate of Q decreased. The permeation rate was less affected by the stirring velocity and was inversely proportional to the number of membrane support sheets. Therefore the permeation through the membrane phase was controlling the overall mass transfer in this system.

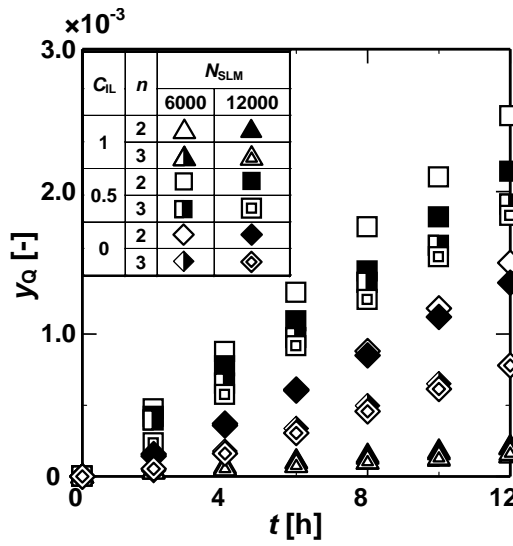


Figure 3. Time courses of  $y_Q$ .

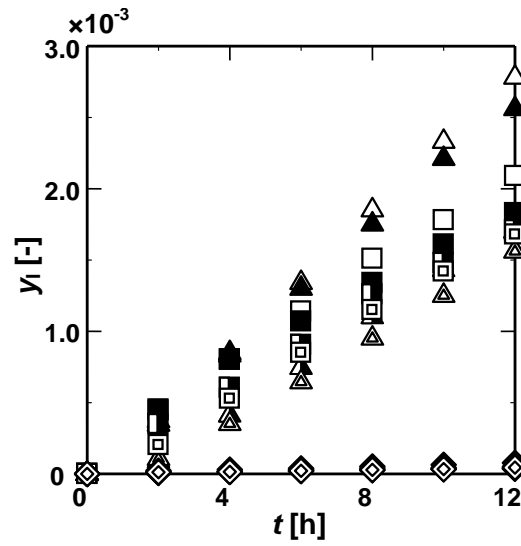


Figure 4. Time courses of  $y_I$   
(keys are the same as in Figure 3).

When the distribution coefficients between the membrane liquid and both phases are in the same range and the mass fraction in the extract phase is substantially small relative to that in the raffinate phase due to small changes in the concentrations in both phases, it can be assumed that the mass fraction of each component should increase linearly with time. The permeation rate can be expressed by [5],

$$E_0 \cdot \frac{dy_i}{dt} = P_{x,i} \cdot A \cdot x_{i,0} \quad (1)$$

Figure 5 shows examples of the effects of  $C_{IL}$  on  $P_{x,i}$ , estimated using Eq.(1). Regardless of the concentration of the ionic liquid, the  $P_{x,i}$  values of the nitrogen heterocyclic compounds were higher than those of other compounds.  $P_{x,i}$  increased with  $C_{IL}$  at lower  $C_{IL}$  values and decreased at higher  $C_{IL}$  values. The effects of  $C_{IL}$  on the  $P_{x,i}$  values were considered as follows. When the overall permeation is governed by the membrane permeation, the overall permeation coefficient can be expressed by a function of  $\rho_{ML}$ ,  $D_i$ ,  $m_i$  and  $n$  as,

$$P_{x,i} \propto \frac{\rho_{ML} \cdot D_i \cdot m_i}{n} \quad (2)$$

where  $\rho_{ML}$ ,  $D_i$  and  $m_i$  denote the density of the membrane liquid, diffusivity of component  $i$  in the membrane liquid and the distribution coefficient of component  $i$  into the membrane liquid, respectively. In the range where the addition of the ionic liquid made  $P_{x,i}$  increase, the effects of  $m_i$  on  $P_{x,i}$  were influential and possibly  $m_i$  increased with  $C_{IL}$ . On the other hand, at higher  $C_{IL}$  values,  $P_{x,i}$  decreased with  $C_{IL}$ . This is probably because  $D_i$  decreased with the addition of the ionic liquid due to an increase in the viscosity of the membrane liquid.

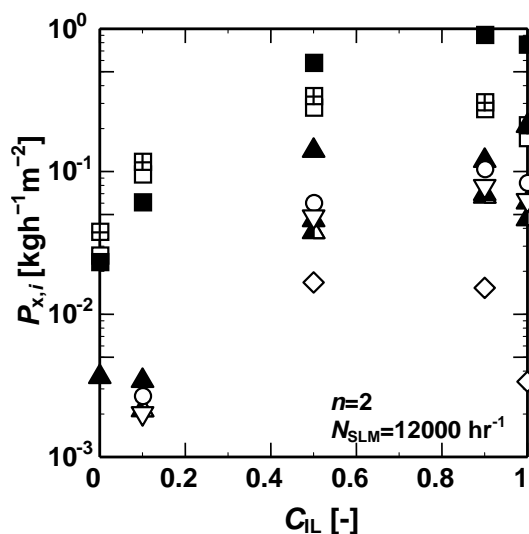


Figure 5. Effects of  $C_{IL}$  on  $P_{x,i}$   
(keys are the same as in Figure 2).

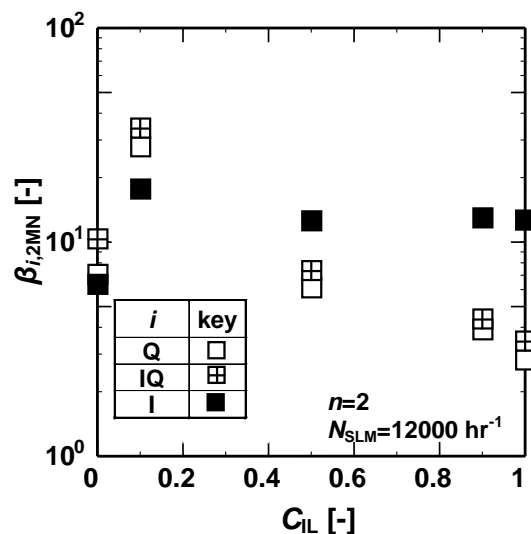


Figure 6. Effects of  $C_{IL}$  on  $\beta_{i,2MN}$  of Q, IQ and I.

The separation selectivity of the nitrogen heterocyclic compounds relative to 2MN,  $\beta_{i,2MN}$ , was defined as,

$$\beta_{i,2MN} = \frac{P_{x,i}}{P_{x,2MN}} \quad (3).$$

Figure 6 shows examples of the effects of  $C_{IL}$  on  $\beta_{i,2MN}$ . The separation selectivity of I relative to 2MN,  $\beta_{I,2MN}$ , slightly increased with addition of the ionic liquid into the membrane whereas the  $\beta_{i,2MN}$  values for Q and IQ decreased. As noted above, both of the  $m_i$  values for the heterocyclic compounds and 2MN might increase with  $C_{IL}$ . Especially the  $m_i$  value for I might greatly increase by the addition of ionic liquid into the membrane phase. However the effects of the ionic liquid addition were larger for 2MN than for Q or IQ, and the  $\beta_{i,2MN}$  values for Q and IQ might decrease. Therefore  $C_{IL}$  should be appropriately adjusted to achieve the favorable permeation.

#### 4. Conclusion

The nitrogen heterocyclic compounds were separated from absorption oil by an ionic liquid supported liquid membrane. The overall mass transfer from raffinate to extract phase was governed by the permeation through the membrane. The permeation rates of all components dramatically increased with the addition of the ionic liquid. The permeation rates of nitrogen heterocyclic compounds, especially for indole, were larger than those of other compounds. The separation selectivity of indole slightly increased with the addition of the ionic liquid into the membrane whereas those of quinoline and isoquinoline decreased. These effects may be attributed largely to the change in the distribution

coefficients. For further study of the permeation through the ionic liquid membrane, it is necessary to obtain equilibrium information, such as distribution coefficients.

### Acknowledgement

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### Nomenclature

$A$	= contacting surface area	$[m^{-1}]$	<Subscript>
$C_{IL}$	= mass fraction of ionic liquid in membrane liquid	$[-]$	
$D_i$	= diffusivity of component $i$ in membrane liquid	$[m^2h^{-1}]$	0 = at initial state
$E$	= mass of extract phase	$[kg]$	1MN = 1-methylnaphthalene
$m_i$	= distribution coefficient of component $i$	$[-]$	2MN = 2-methylnaphthalene
$N_{SLM}$	= stirring velocity	$[h^{-1}]$	BP = biphenyl
$n$	= number of membrane supporter	$[-]$	DBF = dibenzofuran
$P_x$	= overall permeation coefficient	$[kgh^{-1}m^{-2}]$	Hp = heptane
$R$	= mass of raffinate phase	$[kg]$	$i$ = component $i$
$x_i$	= mass fraction of component $i$ in raffinate phase	$[-]$	I = indole
$y_i$	= mass fraction of component $i$ in extract phase	$[-]$	IL = ionic liquid
$\beta_{i,2MN}$	= separation selectivity of component $i$ relative to 2MN	$[-]$	IQ = isoquinoline
$\delta$	= effective thickness of liquid membrane	$[m]$	N = naphthalene
$\rho_{ML}$	= density of the liquid membrane	$[kgm^{-3}]$	Q = quinoline

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