Permeation of coal tar absorption oil

through ionic liquid supported liquid membrane

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1. Introduction

Coal tar absorption oil (AO) is one of distillation fractions of a coal tar (b.p. = 470~550K) which is obtained coal carbonization. There are many kinds of chemical compounds contained in it, the nitrogen heterocyclic compounds such as quinoline (Q), isoquinoline (IQ), indole (I); the homocyclic compounds such as 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), etc. The mass fraction of some main compounds in AO is shown in **Table 1**. These compounds are useful as raw materials for agricultural chemicals, medicines, perfumes, and many other useful chemicals. Generally, the current method mainly used to separate these compounds in AO is carried out in two steps: first step is a rough separation of AO into several fractions by acidic and basic extraction; and second step are further separation and purification of these fractions into respective products by other methods. The separation for this first step in the industrial fields has some drawbacks, e.g., corrosion of the equipments and difficulties in solvent recovery. To solve these problems, several alternative methods, such as liquid-liquid extraction method and O/W/O supported liquid membrane method (SLM) have been studied[1,2,3].

Ionic liquids (ILs) are emerging as alternative green solvents to the volatile organic compounds typically used in separation processes because they are air and water stable, have a non-measurable vapor pressure. ILs are organic salts that are liquid close to room temperature, constituted by an organic cation and either an organic or an inorganic anion.

It has been already reported that the organic nitrogen compounds by supported liquid membranes based on ionic liquids, etc. However there is no report of the separation from an actual multi-component like AO.

In this work, the separation of AO by the ionic liquid supported liquid membrane was conducted. The permeation rate process through the ionic liquid supported liquid membrane was investigated.

2. Experimental
2.1. Preparation of ionic liquid supported liquid membrane

The structure of the ionic liquid used in this work is described in **Fig. 1** and the properties of it are shown **Table 2**. 1-butyl-3-methylimidazolium tetrafluoroborate [bmim$^+$][BF$_4^-$] was selected as the membrane liquid due to the property of solubility[4]. This ionic liquid was purchased from Wako Chemical Co., Ltd. 3 kinds of the membrane liquid were prepared (C_{IL}=0,0.5,1).

The specifications of the hydrophilic filter paper (cellulose, advantec filter paper no.5B) used as a supporter in the previous work[2] are shown in **Table 3**. The filter paper was purchased from Toyo Roshi Kaisha, Ltd.

The filter paper was impregnated with the ionic liquid by dropping carefully. Then, the excess of the ionic liquid from the membrane surface was removed and the mass of the liquid membrane was adjusted.

2.2. Batch permeation

Figure 2 illustrates a permeator for the supported liquid membrane (SLM). The liquid membrane was placed between two Pyrex glass vessels. The operation temperature was kept constant by the constant-temperature water passing through the tube coiled around the permeator. The principal conditions of permeation runs are shown in **Table 4**. The 12 permeation runs on 12 conditions were conducted by varying the following factors; the mass fraction of the
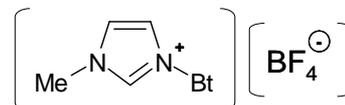
Fig. 1 Structure of [bmim$^+$][BF$_4^-$]

Table 2 Physicality and miscibility of [bmim$^+$][BF$_4^-$]

m.p.	density	viscosity (298K)	T_d	electrical conductivity
[K]	[kg/m^3]	[cP]	[K]	[mS/m]
202	1370	118.3	573	343

solubility with traditional solvents						
H$_2$O	MeOH	EtOH	Acetone	THF	Heptane	Toluene
					×	×

Table 3 Specifications of the filter paper

material	mass	diameter	thickness	mean pore size	real density
	[kg/m^2]	[m]	[m]	[μm]	[kg/m^3]
cellulose	0.104	0.07	2.2×104	4	1550

Table 1 Mass fractions of some main compounds 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
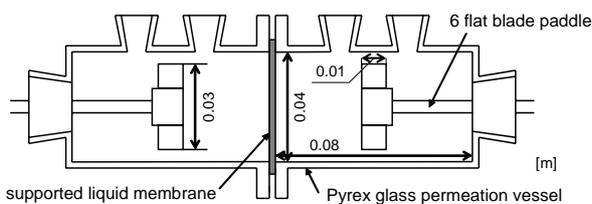
Fig. 2 Schematic diagram of experimental apparatus

Table 4 Material systems and experimental conditions

Feed	AO (V_F=1.2×10⁻⁴ m³)		
	model solution ($x_{Q,0}$=0.08, $x_{2MN,0}$=0.25, $x_{Hp,0}$=0.67)		
	AO-heptane solution ($v_{AO,0}$=0.5, $v_{Hp,0}$=0.5) (V_F=1.2×10⁻⁴ m³)		
Solvent	toluene (V_E=1.2×10⁻⁴ m³)		
Number of supporters	n = 1, 2, 3		
Membrane Liquid	water, ionic liquid([bmim⁺][BF₄⁻]) aqueous (C_{IL}=0, 0.5, 1)		
Stirring Velocity	N_{SLM}	[h⁻¹]	6000 or 12000
Temperature	T	[K]	298
Time	t	[h]	12

membrane liquid (C_{IL}=0, 0.5, 1), the stirring velocity in both phases (N_{SLM}=6000, 12000), the number of supporters (n=2, 3). The feed and solvent were poured into the respective vessels simultaneously and quickly, and then the agitation of the feed and solvent phases were started (t=0) to begin the batch permeation run. The raffinate and extract phases were sampled at specified operating times, for analysis by a gas chromatograph (GC-2010, Shimadzu Corp.).

3. Results and Discussion
3.1. Composition of extract phase
For all permeation runs, the membrane remained stable during the operation run because of low solubility in the raffinate and extract phases and the affinity for the supporter sheet[5]. **Figure 3** shows examples of time courses of mass fractions in the extract phases. The mass fraction of each component increased linearly with time. The permeation rates, especially for I, drastically increased with the addition of the ionic liquid, because the addition of the ionic liquid widely increased solubilities of all components. The permeation rates of Q were largest in the case without the ionic liquid and those of I were largest in the case with the ionic liquid. The overall mass transfer from raffinate to extract phase was governed by the permeation through the membrane, because the permeation rate was not affected by the stirring velocity and was inversely proportional to the number of membrane supporter sheets.

3.2. Yield
The yield of component i, Y_i, was defined as,

$$Y_i = \frac{E \cdot y_i}{R_0 \cdot x_{i,0}} \tag{1}$$

Figure 4 shows the examples of time courses of Y_Q. Under all conditions, Y_i of nitrogen heterocyclic compounds were larger than those of other compounds, namely, it was confirmed that these compounds were separated into each other by the ionic liquid membrane. The yields of Q were the largest in the case without the ionic liquid and those of I were the largest in the case with the ionic liquid. The yields, especially for I, drastically increased with the addition of the ionic liquid.
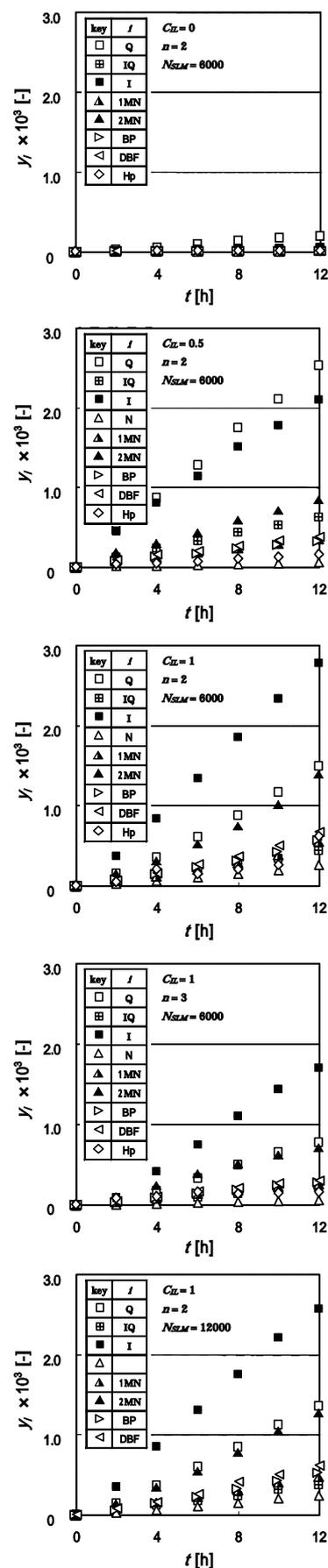
Fig.3 Time courses of mass fraction in extract phase

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3.3. Overall permeation coefficient

Since the mass fraction of each component increased linearly with time, namely, it could be assumed that the permeation rates were proportional to the mass fraction of the feed and the overall permeation coefficients were constant in each component, the permeation rate was expressed by[2],

$$E_0 \cdot \frac{dy_i}{dt} = P_{x,i} \cdot A \cdot x_{i,0} \qquad (2)$$

Figure 5 shows the examples of the effects of C_{IL} on $P_{x,i}$ calculated by Eq. (1). Regardless of the concentration of the ionic liquid, P_x of the nitrogen heterocyclic compounds was higher than those of other compounds, which means that the nitrogen heterocyclic compounds were selectively permeated through the liquid membrane to extract phase and could be separated from other compounds. The overall permeation coefficient was expressed by[2],

$$P_{x,i} \propto \frac{\rho_{ML} \cdot D_i \cdot m_i}{n} \qquad (3)$$

where ρ_{ML}, D_i and m_i denote the density of the membrane liquid, diffusivity of component i in the liquid membrane and distribution coefficient, respectively. The results that $P_{x,i}$ widely increased with the addition of the ionic liquid and P_x of I decreased with the increase of C_{IL} are most affected by m_x.

3.4. Separation selectivity

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

$$\beta_{i,2MN} = \frac{P_{x,i}}{P_{x,2MN}} \qquad (4)$$

Figure 6 shows examples of the effects of C_{IL} on $\beta_{i,2MN}$. Whereas $\beta_{i,2MN}$ of Q and IQ decreased with the addition of the ionic liquid into the membrane, $\beta_{I,2MN}$ increased. The effect of the addition of the ionic liquid on the other components was not observed and $\beta_{i,2MN}$s of them are about 1. The number of the supporter sheets had no effect on $\beta_{i,2MN}$. The highest $\beta_{I,2MN}$ was about 18 in the case of C_{IL}=0.5.

4. Conclusions

The nitrogen heterocyclic compounds were separated from AO by the 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 and the yields of all components dramatically increased with an addition of the ionic liquid. The yields of nitrogen heterocyclic compounds were larger than those of other compounds. The separation selectivities of each nitrogen heterocyclic compound were affected by the mass fraction of the ionic liquid.

Nomenclatures

A	= contact area	[m^2]
C_{IL}	= mass fraction of an ionic liquid in membrane liquid	[-]
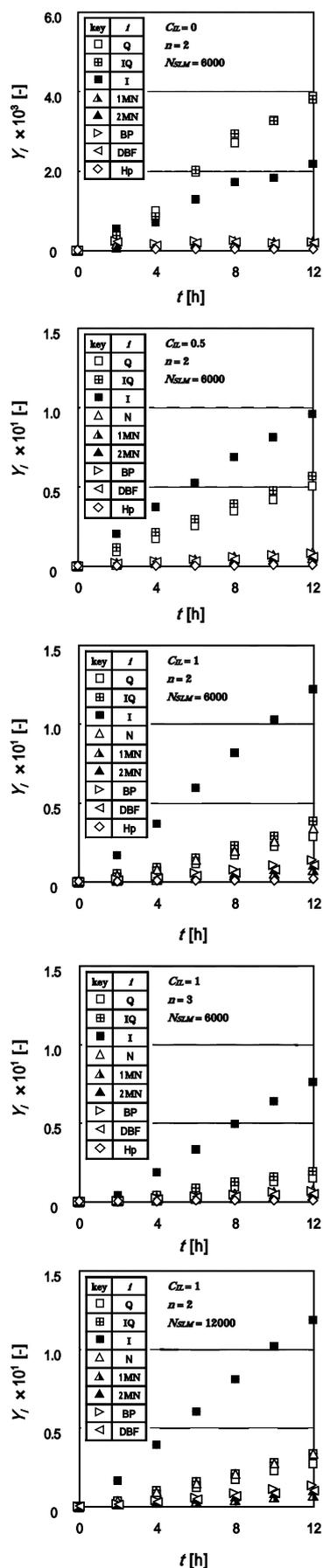
Fig.4 Time courses of yields in extract phase

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D_i = diffusivity of component i in the liquid membrane $\quad$ [m²h⁻¹]
E = mass of extract phase $\quad$ [kg]
m_i = distribution coefficient of component i $\quad$ [-]
N_{SLM} = stirring velocity in permeation vessel $\quad$ [h⁻¹]
n = number of supporters $\quad$ [-]
P_x = overall permeation coefficient based on mass fraction in raffinate phase $\quad$ [kgh⁻¹m⁻²]
R = mass of raffinate phase $\quad$ [kg]
V = volume $\quad$ [m³]
v = volume fraction in feed solution $\quad$ [-]
x = mass fraction in raffinate phase $\quad$ [-]
y = mass fraction in extract phase $\quad$ [-]
<Greek>
$\alpha_{i,2MN}$ = separation selectivity of component i relative to 2-methylnaphthalene $\quad$ [-]
ρ_{ML} = density of the membrane liquid $\quad$ [kgm⁻³]
<Subscript>
0 = at initial state
1MN = 1-methylnaphthalene
2MN = 2-methylnaphthalene
AO = absorption oil
BP = biphenyl
DBF = dibenzofuran
E = extraction solvent
F = feed solution
Hp = heptane
I = indole
IQ = isoquinoline
N = naphthalene
Q = quinoline

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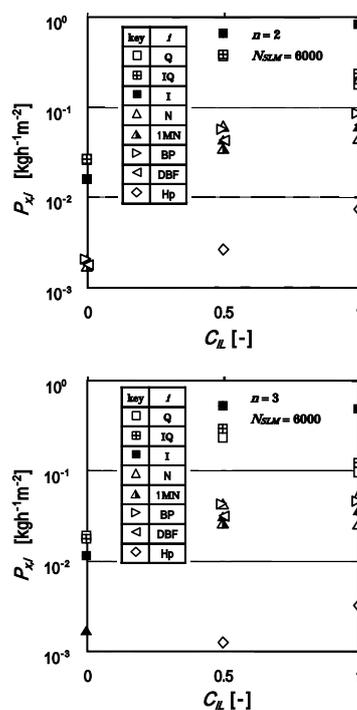
Fig.5 Effects of IL concentration on the overall permeation coefficient based upon raffinate concentration
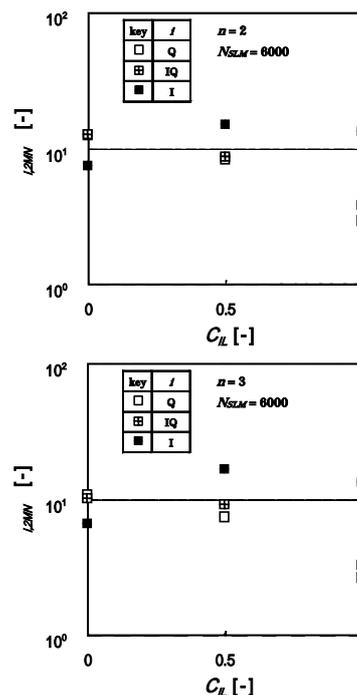
Fig.6 Effects of IL concentration on separation selectivity of nitrogen heterocyclic compounds relative to 2MN