

IMPROVEMENT OF ROUGH SEPARATION WITH O/W/O LIQUID MEMBRANE FROM COAL TAR ABSORPTION OIL

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O/W/O液膜法によるコールタール吸収油の粗分離における分離性能向上

原典生

まず吸収油に含まれる成分の油相-水相間における分配係数(水相への溶解性)を実測した。同素環式化合物(多環芳香族)等に比較して含窒素複素環式化合物の分配係数は大きく、また油相の種類の変化により多環芳香族の分配係数は影響を受けないのに対し含窒素成分のそれは大きく変化した。これより、適切な溶媒の選定により吸収油の液膜分離における含窒素成分の分離の選択性が向上することを予測した。ついで種々の溶媒を用いて吸収油の回分乳化液膜透過を行った。含窒素成分の分配係数が小さいような溶媒を用いることによりその分離の選択性は向上し、上記の予測を確認した。

1. INTRODUCTION:

Coal tar absorption oil (AO) is mainly composed of heterocyclic nitrogen compounds such as quinoline (Q), isoquinoline (IQ), indole (I), etc, and aromatic hydrocarbons such as 2-methylnaphthalene (2MN), 1-methylnaphthalene (1MN), biphenyl (BP), etc, and a small quantity of heterocyclic oxygen compounds such as dibenzofuran (DBF), etc, as shown in Table 1. These compounds are industrially useful as raw materials for producing agricultural chemicals, medicines, perfumes and many other useful chemicals. The separation of these compounds are carried out in two steps which are rough separation of absorption oil into several parts by acidic and basic extraction method and purification and separation of each part into respective products by other methods. However, the method used industrially for the rough separation has some drawbacks concerning corrosion of the equipments and difficulty in solvent recovery. To counter these problems, some simpler alternative methods such as liquid-liquid extraction method, liquid membrane separation method, etc, have been studied. In this work, using the liquid membrane separation method, the permeations of nitrogen compounds from feed oil to solvent through liquid membrane under various experimental conditions were studied. Also in supported liquid membrane experiments, the effects of various feed oils on the permeations were also studied using measured distribution coefficients.

Table 1 Mass fractions of some main compounds in AO

$x_{Q,0}$ [-]	$x_{IQ,0}$ [-]	$x_{I,0}$ [-]	$x_{2MN,0}$ [-]	$x_{1MN,0}$ [-]	$x_{BP,0}$ [-]	$x_{DBF,0}$ [-]
0.08	0.02	0.05	0.25	0.10	0.06	0.07

2. MEASUREMENT OF DISTRIBUTION COEFFICIENTS

EXPERIMENTAL

a) AO+other compounds mixtures and model mixtures as feed oils

Feed oil and solvent were contacted in a flask at constant temperature until equilibrium is reached. Then the solvent phase was sampled and analyzed by gas

chromatograph. Experimental conditions are shown in Table 2.

Table 2 Experimental Conditions

Feed	AO-Toluene (Tol), AO-Tol-Aniline (Anil), AO-Heptane (Hep)
	$x_{AO,0}$ 0.20 $x_{AO,0}$ 0.10
	Q-2MN-Hep, Q-Hep, 2MN-Hep
	$x_{Q,0}$ 0.08 $x_{2MN,0}$ 0.25
Solvent	Water
Total volume	[m ³] 1×10^{-4}
Volumetric ratio of solvent to feed, V_0/V_f	[-] 2
Shaking time, t	[h] 12
Amplitude of shaking	[m] 0.01
Frequency of shaking	[h ⁻¹] 1200
Temperature	[K] 297 ± 5

b) AO as a feed oil

Figure 1 shows the schematic diagram of apparatus used. A piece of hydrophilic filter paper impregnated with solvent was placed between two Pyrex glass vessels. The feed and solvent were poured into respective vessels quickly and simultaneously, and then the stirrings of the feed and solvent phases were started ($t=0$). The solvent phase was sampled and analyzed by gas chromatograph. Experimental conditions are shown in Table 3.

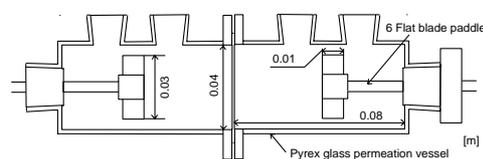


Fig.1 Experimental apparatus

Table 3 Experimental Conditions

Feed	AO	$V_f = 1.20 \times 10^{-4} \text{ m}^3$
Solvent	Water	Supporter: Advantec filter paper no. 58 Thickness = $2.2 \times 10^{-4} \text{ m}$, Diameter = 0.055, $n=1$
N_p	[h ⁻¹]	12000, 24000
T	[K]	297 ± 5
t	[h]	12

RESULTS AND DISCUSSION

Distribution coefficient of component i m_i (selectivity between oil-water phase) is defined as ratio of mass

fraction of component i between water phase and oil phase ($m_i=y_i/x_i$). Table 4 shows the measured distribution coefficients. The comparison of feed oils shows that m_i of nitrogen compounds in the case that Tol-AO and Tol-Ani-AO were used as feed oils were about ten times lower than that in the case of AO-Hep and m_i of 2MN was independent to composition of feed oils except when AO is used as feed oil, m_i of nitrogen compounds in AO-Tol were 2~4 times higher than that in AO while m_i of 2MN in AO-Tol was about 10 times higher than that in AO. Figures 2 and 3 show the comparison of distribution coefficients among three feeds: AO-Tol, AO-Hep, and AO. m_i of nitrogen compounds of feed AO-Hep were the highest which were possibly caused by low polarity of this feed mixture. m2MN was the lowest among three feed.

Table 4 Experimentally measured distribution coefficients

Feed Oil	m_o	m_n	m_i	m_{2MN}
AO-Tol	3.65×10^{-3}	3.11×10^{-3}	2.24×10^{-3}	1.53×10^{-4}
AO-Hep	1.86×10^{-2}	2.01×10^{-2}	2.43×10^{-2}	1.84×10^{-4}
AO-Tol-Ani	3.05×10^{-3}	3.08×10^{-3}	2.14×10^{-3}	1.61×10^{-4}
Q-2MN-H	5.33×10^{-2}			1.86×10^{-4}
Q-H	8.84×10^{-2}			
2MN-H				1.85×10^{-4}
AO	1.94×10^{-3}	8.95×10^{-4}	5.45×10^{-4}	1.54×10^{-5}

3. BATCH PERMEATION WITH SUPPORTED LIQUID MEMBRANE:

EXPERIMENTAL

The experimental apparatus is the same as 2(b) (Fig.1). Table 5 shows the experimental conditions. AO and model mixtures are used as feed oils. Water or saponin which is frequently used in the study of an emulsion liquid membrane was used as membrane liquid. Heptane is used as a solvent.

Table 5 Experimental Conditions

Feed	model mixture (Q-2MN-H, Q-H, Q-2MN) absorption oil $x_{Q,0}=0.08$, $x_{2MN,0}=0.25$ $V_F=1.20 \times 10^{-4} m^3$	
Membrane	aqueous solution of saponin, $C_S=0 \sim 0.10$ Supporter: advantec filter paper no.5B $l=2.2 \times 10^{-4} m$, diameter=0.055m	
Solvent	heptane, quinoline-toluene	
N_p [h ⁻¹]	12000, 24000	
T [K]	303	

RESULTS AND DISCUSSION

Figure 4 shows the schematic diagram of the concentration profile around an ideal liquid membrane. The permeation rate of component i for supported liquid membrane permeation is represented by,

$$\frac{d(E \cdot y_i)}{dt} = P_{x,i} A \left(x_i - \frac{m_{E,i}}{m_{R,i}} y_i \right) \quad (1)$$

$P_{x,i}$ is the overall permeation coefficient based on mass fraction in raffinate phase. If the controlling resistance of permeation reside in the membrane, $P_{x,i}$ of ideal one layer liquid membrane is as follows:

$$P_{x,i} = \rho_W D_i m_{R,i} / \delta \quad (2)$$

D_i is diffusivity and δ is thickness of liquid membrane.

Figure 5 shows the effect of the stirring rate, N_p , and the number of membranes on mass fractions of components in the extract y_i during the course of time. Although the initial mass fraction of Q in the feed oil is lower than that of 2MN in the feed (Table 5), Q permeated preferentially to 2MN (Fig.5), thus both can be

separated. y_i increased linearly with time and the stirring velocities of both the feed and the solvent phases did not influence the permeation rates. However, the permeation rates were in inverse proportion to the thickness of the membrane. The controlling resistance of mass transfer from the feed to solvent, therefore, resided in the membrane. Change of saponin concentration C_S in membrane liquid did not effect the permeation rate of Q (Fig.6). y_Q are plotted along time for various feed systems in fig.7. Although the initial mass fractions of Q were the same for all the feed systems, the permeation rates of Q varied with feed systems. Figure 8 shows correlation of P_i with $m_{R,i}$ and D_i based on Eq.(2). Measured equilibrium data was used as $m_{R,i}$ (Table 4). The distribution coefficient of Q might change with feed system (Table 4), and permeation rate might in turn change with distribution coefficient which implies that selection of more suitable solvent could produce higher selectivity.

4. BATCH SEPARATION WITH EMULSION LIQUID MEMBRANE:

EXPERIMENTAL

a) Emulsification

The feed oil and liquid membrane were stirred with high-speed homogenizer for obtaining emulsion.

b) Permeation

The emulsion from a) and the solvent are then poured into mixing apparatus, and then the stirring was started ($t=0$). Each of this operation was carried under each different t . The solvent phase was sampled and analyzed by gas chromatograph. Table 6 shows the experimental conditions. AO was used as feed and nonane was added as tracer for detection of membrane breakage. Aqueous solution of saponin was used as membrane liquid. Hep, Tol, Tol-Ani were used as solvents. N_e is stirring rate of emulsification, V_{T1} is total volume of emulsion and solvent and ϕ_{OW} is volume fraction of O/W emulsion in total liquid. ϕ_o is volume fraction of inner oil phase in O/W emulsion

Table 6 Experimental Conditions

Feed	AO, AO-nonane ($x_{N,0}=0.05$)			
Membrane	aqueous solution of saponin			
Solvent	Hep, Tol, Tol-Ani ($y_{ani,0}=0.11$)			
C_S [-]	N_e [h ⁻¹]	N_p [h ⁻¹]	V_T [m ³]	
0.03	1.1×10^{-6}	36000	4.0×10^{-4}	
$\phi_{O,W}$ [-]	ϕ_o [-]	t [h]	T [K]	
0.25	0.5	0-0.033	298 ± 5	

RESULTS AND DISCUSSION

The permeation rate of component i for emulsion liquid separation considering membrane breakage transfer from feed to solvent is represented by,

$$\frac{d(E \cdot y_i)}{dt} = P_{x,i} A \left(x_i - \frac{m_{E,i}}{m_{R,i}} y_i \right) V_T + x_i W_B \quad (3)$$

With the assumption that mass fraction transferred by membrane breakage is the same as the average of mass fraction in raffinate phase and that transfer of tracer, nonane, for membrane breakage detection occurred only by membrane breakage, the transfer rate by membrane breakage can be represented by,

$$W_B = \frac{1}{x_N} \cdot \frac{d(E \cdot y_N)}{dt} \quad (4)$$

The yield of component i and the separation selectivity of component i relative to 2MN, $\beta_{i,2MN}$ were respectively defined as follows:

$$Y_i = \frac{E \cdot y_i}{R_0 \cdot x_{i,0}} \quad \beta_{i,2MN} = \frac{y_i/x_i}{y_{2MN}/x_{2MN}}$$

Figure 9 shows the time course of nonane for membrane breakage detection. Membrane breakage was independent of solvent type. Figure 10 shows one of the results of the effect of transfer rate from feed to solvent by membrane breakage on permeation rate. Each member of Eq.(3) was plotted. Permeation rate was only slightly affected by membrane breakage. The changes of mass in raffinate phase, R and extract phase, E with the passage of time are shown in Fig.11 R and E in the case of Hep as solvent were constant at any t, however E of solvent Tol and Tol-Ani decreased with time. This shows that the transfer of solvent from extract to raffinate was taken place. Fig.12 shows that the effect of various solvent systems on the time course of x_Q and y_Q . Permeation of nitrogen compounds in the case of solvent Hep stopped in spite of apparent difference of concentration between feed phase and solvent phase, however that of solvent Tol continued until the $x_i=y_i$ was almost reached. In the case of solvent Tol-Ani the position of x_i and y_i reached the $x_i=y_i$ and continued until the position changed.

Figure 13 shows the effect of various solvent used on the yield of components in solvent Y_i with the passage of time. Obviously nitrogen compounds were separated from other compounds in any case of solvent used. Y_i of solvent Tol was much higher than of solvent Hep. Y_i of solvent Tol-Ani was the highest among these solvents. This resulted from variation of distribution coefficients in Eq.(3) caused by differences of polarities of solvents. Fig.14 shows the time course of i_{2MN} . Nitrogen compounds were selectively separated from other compounds, especially Q which had a maximum Q_{2MN} of about 50. Figure 15 shows the time course of driving force caused by concentration difference x_i-m/y_i which was evaluated using distribution coefficients.

5.CONCLUSION:

Nitrogen compounds were able to be separated from other compounds using liquid membrane. Changes of distribution coefficients were dependent of systems, which in turn influenced the permeation rate. In supported liquid membrane experiments, the permeation mechanism of Q was clarified for various conditions. In emulsion liquid membrane, permeation rate were shown to differ according to solvents used in the experiments. By choosing solvent with small components distribution coefficient between membrane and solvent phase, the selectivity of nitrogen compounds to others can be increased.

Nomenclatures

A: contact area a: specific contact area C: mass fraction in membrane Di: diffusivity of component i E: mass of extract phase m_i : distribution coefficient Ne: Stirring rate of emulsifier Np: stirring rate of permeation $P_{x,i}$: overall transfer coefficient based on mass fraction in raffinate phase R: mass in raffinate phase V_T : total volume of liquid in permeator x_i : mass fraction of component i in raffinate phase Y_i : yield of component i y_i mass fraction of component i in extract phase

References

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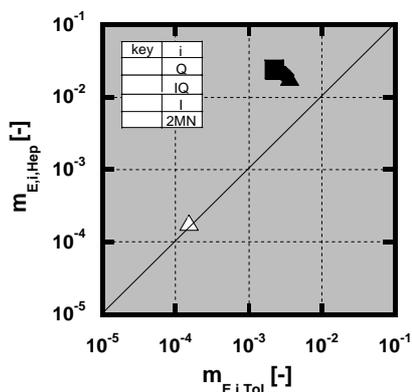


Fig.2 Comparison of distribution coefficients(feedAO-Tol vs feed AO-Hep)

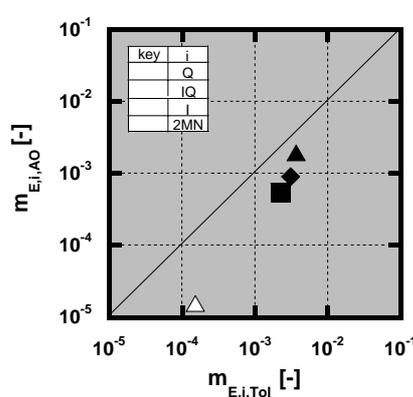


Fig.3 Comparison of distribution coefficients(feedAO-Tol vs feed AO)

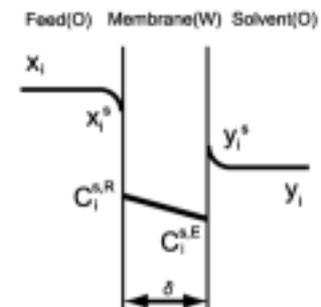


Fig.4 Concentration profile around one ideal liquid membrane

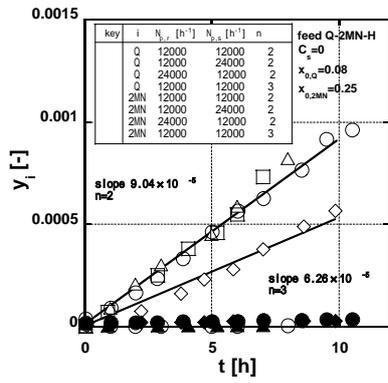


Fig.5 Effect of stirring velocity and number of supporters on permeation rate

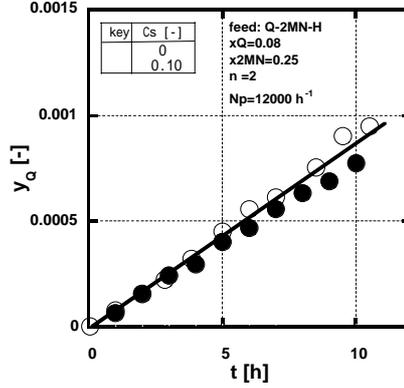


Fig.6 Effect of surfactant on permeation rate

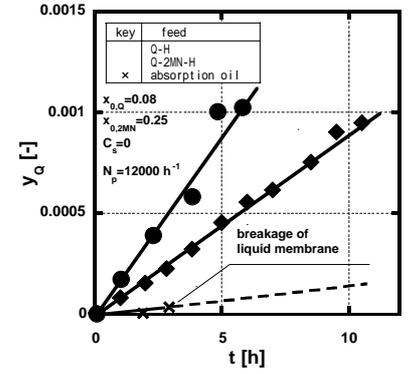


Fig.7 Effect of feed systems on permeation rate

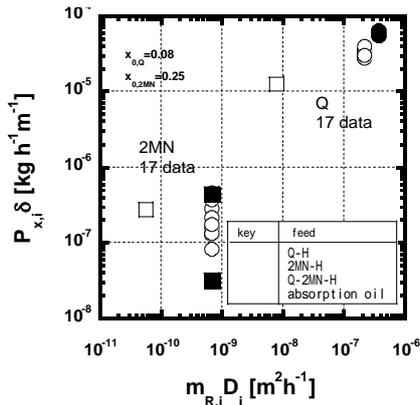


Fig.8 Correlation of m_i and D_i with P_i

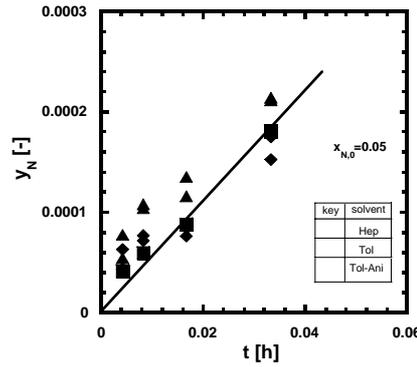


Fig.9 Time course of nonane

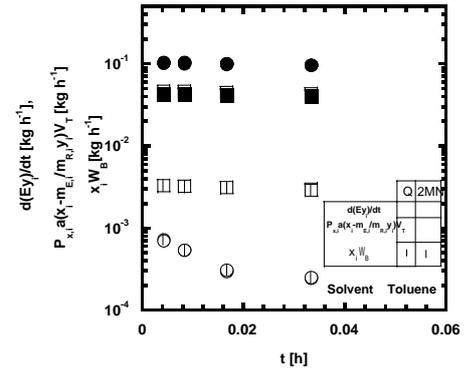


Fig.10 Effect of membrane breakage on permeation rate

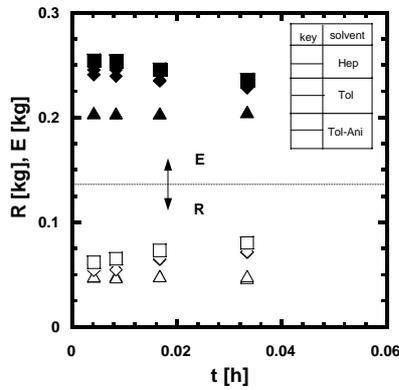


Fig.11 Time course of R and E

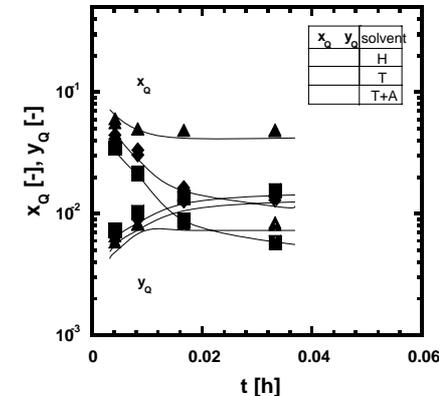


Fig.12 Effect of solvent system on time course of x_Q, y_Q

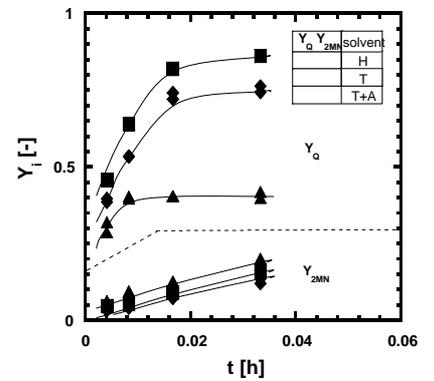


Fig.13 Effect of solvent systems on time course of y_i

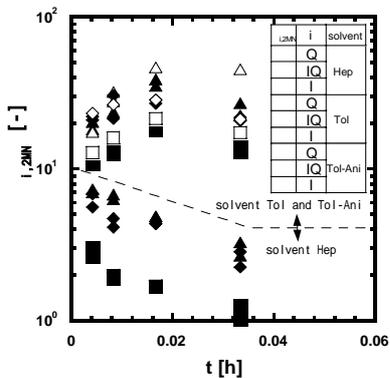


Fig.14 Effect of solvent system on time course of i_{2MN}

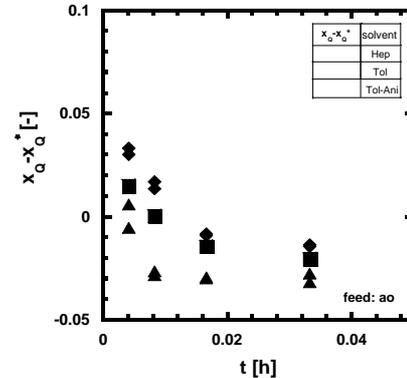


Fig.15(a) Time course of driving force of Q

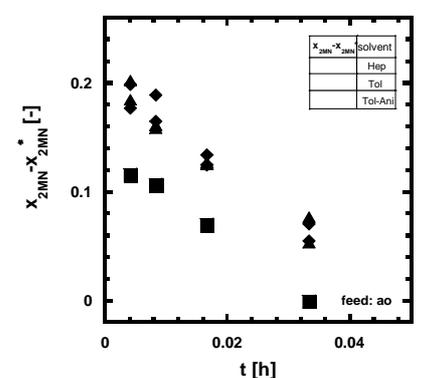


Fig.15(b) Time course of driving force of 2MN