

Enhancement of Permeation for Emulsion Liquid Membrane Separation of Coal Tar Absorption Oil

Student Number: 06M18197

Name: Dejin BI

Supervisor: Ryuichi EGASHIRA

コールタール吸収油の乳化液膜分離に対する透過促進 畢 徳金

まず、コールタール吸収油とエチレングリコール(EG)、ジエチレングリコール(DEG)、トリエチレングリコール(TEG)の水溶液の液液平衡実験を行い、コールタール吸収油中の含窒素複素環式化合物(キノリン、イソキノリン、インドール)と芳香族炭化水素(1-メチルナフタレン、2-メチルナフタレンなど)化合物の分配係数を実測した。O/W/O 乳化液膜法を用いて、コールタール吸収油中含窒素複素環式化合物と芳香族炭化水素化合物など分離させた。膜液中に EG、DEG、TEG を添加するにより原料コールタール吸収油中各成分の膜透過に対して透過促進させた。その中で DEG による透過促進効果は EG、TEG より優れた傾向を示した。

1. Introduction

Coal tar absorption oil (AO) is one of distillation fractions of coal tar (b.p. =470~550K). There are several kinds of chemical compounds contained in it, the nitrogen heterocyclic compounds such as quinoline (Q), isoquinoline (IQ), indole (IL); the homocyclic compounds such as 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), etc. 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: separation of AO into several fractions by acidic and basic extraction; and 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 emulsion liquid membrane permeation (LMP) method have been proposed¹⁾⁻⁵⁾. In O/W/O emulsion liquid membrane system, water is the main material of aqueous membrane liquid phase. Although water showed a rather highly selective nature in separation but it only allowed quite slow permeation of compounds through liquid membrane because the solubilities of above-mentioned components (Q, IQ, IL, 1MN, 2MN etc.) in water are not so high. EG, DEG, TEG have been widely used as solvent to dissolve organic compounds and would have a high capacity for the dissolution of compounds which contained in AO. Therefore, the addition of one of these substances into an aqueous membrane solution is expected to enhance the permeation⁶⁾⁻⁷⁾.

This work tried to enhance the permeation in separation of AO by O/W/O emulsion liquid membrane. At first the distribution coefficients of compounds which contained in AO, between EG, DEG, TEG aqueous solution and AO were measured. Then an aqueous membrane solution with adding EG, DEG or TEG was used in O/W/O emulsion liquid membrane separation of AO. The effects of these three kinds of additives on yield and separation selectivity were described.

2. Liquid-liquid equilibrium between absorption oil

and aqueous phase

2.1. Experimental

AO and aqueous solution of EG, DEG, TEG were brought into contact to be equilibrated using Erlenmeyer flask and commercial constant temperature bath. Then the solvent phase and raffinate phase were sampled and analyzed by gas chromatography. The principal experimental conditions are shown in **Table 1**.

2.2. Result and Discussion

The mass fractions of the components in absorption oil were described as follows: Q 0.08, IQ 0.02, IL 0.04, 1MN 0.10, 2MN 0.28, BP 0.07, DBF 0.14. The mass fraction of 2MN was highest among homocyclic components, so that 2MN was taken as representative component of homocyclic compounds. The distribution coefficient of component *i* between aqueous phase and oil phase was defined as:

$$m_{i,R} = \frac{C_i}{x_i} \quad (1)$$

where C_i and x_i denote the mass fraction of compound *i* in the extract and raffinate phases, respectively. **Figures 1(a)-(d)** show the relation between $m_{i,R}$ of Q, IQ, IL, 2MN and concentration of TEG/DEG/EG in aqueous phase, C_A . The $m_{i,R}$ of nitrogen heterocyclic compounds Q, IQ, IL were larger than that of 2MN and, in all the cases with additives, distribution coefficients were larger than those without additive. At any case, the $m_{i,R}$ increased with increasing C_A . For example, the maximum $m_{Q,R}$ was 1.8×10^{-1} at $C_{TEG}=0.5$, that was nearly twenty times of that without TEG, and the maximum $m_{2MN,R}$ was 2.8×10^{-3} that was fifteen times of that without TEG. In case with DEG, the maximum $m_{Q,R}$ was 1.1×10^{-3} and $m_{2MN,R}$ was 2.4×10^{-3} ; in case with EG, maximum $m_{Q,R}$ was 5.0×10^{-2} and $m_{2MN,R}$ was 1.2×10^{-3} . $m_{i,R}$ increased in the order of EG, DEG, and TEG cases. This result

Table 1 Experimental condition of liquid-liquid equilibrium

Oil phase	Absorption Oil
mass, R_0 [kg]	0.05
Aqueous phase	Aqueous solution of EG/DEG/TEG
mass, E_0 [kg]	0.05
Mass fraction of EG/DEG/TEG in Aqueous phase C_A [-]	0-0.05
Frequency of shaking	[h ⁻¹] 5400
Amplitude of shaking	[m] 0.04
Shaking time	[h] 72
Temperature, T	[K] 303

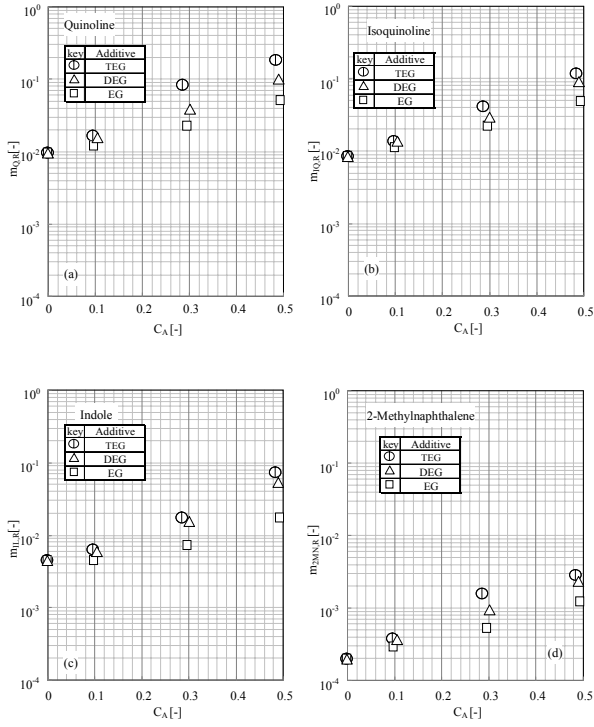


Figure 1 Distribution coefficient of component which contained in AO (a) Quinoline (b) Isoquinoline (c) Indole (d) 2-methylnaphthalene

suggests that EG, DEG, TEG, added to a liquid membrane solution, would enhance the permeation of components. The $m_{i,R}/m_{2MN,R}$ slightly decreased by addition of the additives and also decreased with increasing concentration of additives. The effect of the additive difference was not observed clearly.

3. Batch separation of absorption oil with emulsion liquid membrane

3.1. Experimental

AO was used as inner oil phase; aqueous membrane solution consisted of ion-exchanged water, one of EG, DEG and TEG as permeation enhancing additive, and saponin as an emulsifying agent; toluene was used as external solvent phase. The feed AO and aqueous membrane solution were stirred by a commercial high-speed homogenizer to prepare the emulsion. This prepared emulsion was brought into contact with the solvent by stirring vessel which was made of Pyrex glass equipped with a six-flat-blade turbine type impeller and four baffles. **Figure 2** shows the schematic diagram of high-speed homogenizer and stirring vessel. Stirring started to begin a permeation run ($t=0$) and continued for a specified operating time. This operation was repeated for the several different times to obtain the time courses of the compositions in the extract phase etc. **Table 2** gives the detailed experiment conditions.

3.2. Results and Discussion

3.2.1. Basic Relationships

The permeation rate of component i through ideal one layer liquid membrane was represented by,

$$N = P_i \cdot A \cdot \left[x_i - \frac{m_{i,E}}{m_{i,R}} y_i \right] \quad (2)$$

Table 2 Experimental conditions for batch separation with emulsion liquid membrane

Feed		AO			
Membrane		Aqueous solution of saponin and EG/DEG/TEG			
Solvent		Toluene			
C_s [-]	N_c [h^{-1}]	N_p [h^{-1}]	V_T [m^3]	C_A [-]	
0.03	1.1×10^6	18000, 36000	4.0×10^{-4}	0~0.25	
$\phi_{w,0}$ [-]	$\phi_{o,0}$ [-]	t [h]	T [K]		
0.25	0.5	0~0.044	298±5(room temp.)		

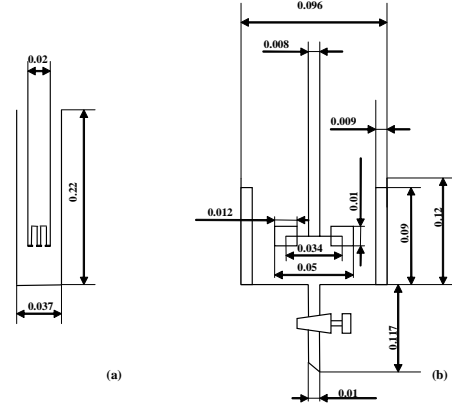


Figure 2 Schematic diagrams of apparatuses for batch separation with emulsion liquid membrane (a) emulsifier with high-speed homogenizer (b) stirring vessel (unit in this figure is meter)

Here, overall permeation coefficient P_i can be expressed by next equation:

$$P_i = m_{i,R} \cdot D_i \cdot \rho / \delta \quad (3)$$

According to these equations the overall permeation coefficient, P_i would be influenced qualitatively by both distribution coefficients, $m_{i,R}$, and diffusion coefficient D_i . x_i can be calculated by mass balance as follows:

$$R_0 x_{i,0} + E_0 y_{i,0} = R x_i + E y_i \quad (4)$$

Here, E and R were obtained from the experimental data. Yield of component i , Y_i , was defined as,

$$Y_i = E y_i / R_0 x_{i,0} \quad (5)$$

where $x_{i,0}$ and y_i denote the mass fraction of component i in the inner oil phase at $t=0$ and that in the external extract oil phase after a run, respectively. R_0 refers to the initial mass of inner oil phase and E expresses the mass of out oil phase after the run. Separation selectivity of component i relative to 2MN was represented by,

$$\beta_{i,2MN} = \frac{y_i / y_{2MN}}{x_i / x_{2MN}} \quad (6)$$

3.2.2. Compositions of raffinate and extract

Figures 3 (a)-(d) show the time courses of x_i and y_i . In any case, x_i decreased and y_i increased with stirring time. In all the cases, y_i of the nitrogen heterocyclic compounds were larger than those of homocyclic compounds, although $x_{i,0}$ of homocyclic compounds were higher than those of nitrogen heterocyclic compounds. Nitrogen heterocyclic compounds were selectively transferred through liquid membrane to extract phase and could be separated from homocyclic compounds. **Figure 3 (d)** shows effect of different additives on x_Q and y_Q . x_Q decreased and y_Q increased in the order of EG, TEG, and DEG cases. $m_{Q,R}$ increased in the order of EG, DEG, and TEG cases, as shown in Figure 1. On the contrary, the diffusion coefficient, D_Q , would increase in the order of

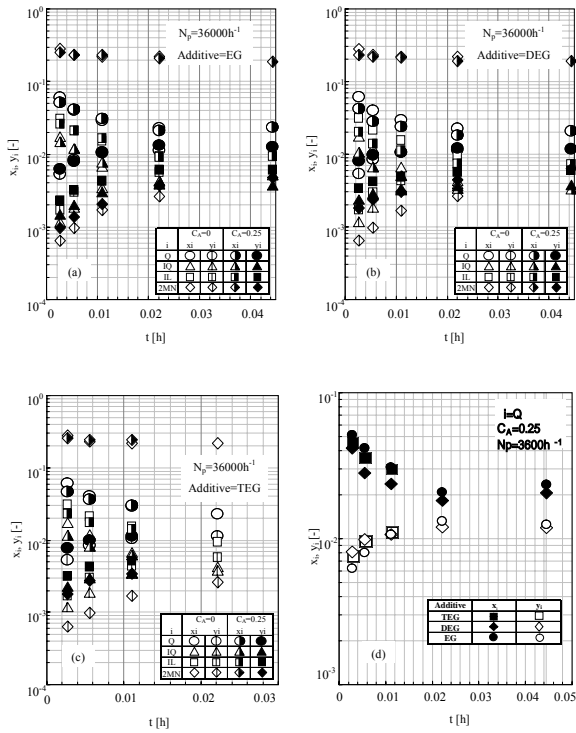


Figure 3 Time course of composition (a) with EG in aqueous membrane solution (b) with DEG in aqueous membrane solution (c) with TEG in aqueous membrane solution (d) compare the effect of different additives (EG, DEG, TEG)

TEG, DEG, and EG cases, based on the Wilke-Chang equation, since the viscosity decreased in the order of TEG, DEG, and EG cases. Both of $m_{Q,R}$ and D_Q affected the permeation rate as Eqs.(1) and (2).

3.2.3 Yield

Figures 4 (a)-(c) are proving that the yields of nitrogen heterocyclic compounds, Q, IQ, and IL were definitely larger than those of 2MN. All kinds of additives did enhance the yields of all the components, obviously. The highest Y_Q , Y_{IQ} , and Y_{IL} in the additive cases were almost as 1.5 times larger than that without additive. These results were attributed to increase of the distribution coefficients as shown in **Figure 1**. The effect of different additives on Y_Q was shown in **Figure 4 (d)**. Y_Q increased in the order of EG, TEG and DEG cases, because $m_{Q,R}$ increased and D_Q decreased as mentioned above. **Figure 4 (e)** indicates the relation between Y_Q and C_A . The Y_Q increased with increasing C_A . This mainly resulted from the increase of distribution coefficients as shown in **Figure 1**. The relation between yields and stirring velocity was shown in **Figure 4 (f)**. Higher stirring velocity gave higher yield, since the interfacial contact area between emulsion and external phase, A , increased.

3.2.4 Separation selectivity

Figures 5 (a)-(c) show the effects of additives EG, DEG, and TEG on separation selectivities of nitrogen heterocyclic compounds. Any kind of additive lowered these separation selectivities, because m_i/m_{2MN} decreased with adding the additives. **Figures 5 (b)-(d)** indicate the relation between additive concentration and separation selectivity of i . In all the cases separation selectivity of

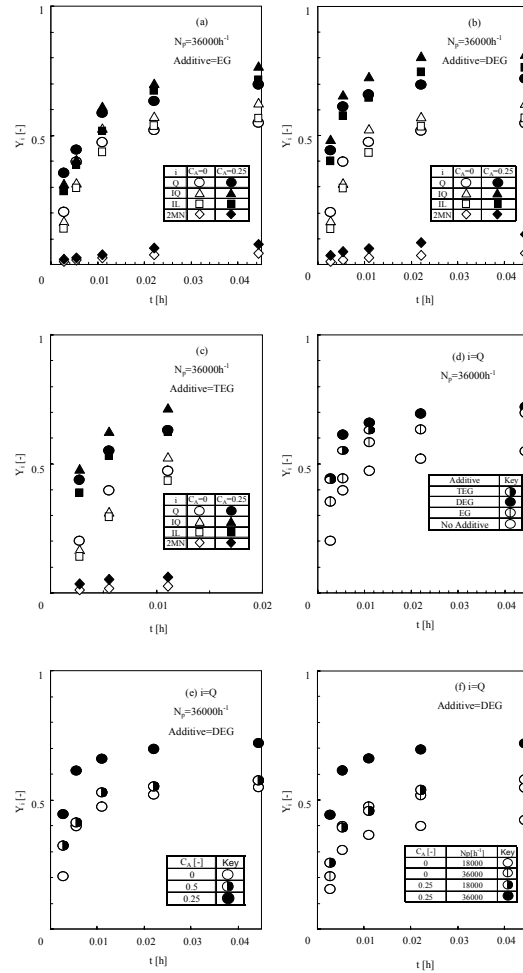


Figure 4 Time course of yields (a) with the EG in aqueous membrane solution (b) with the DEG in aqueous membrane solution (c) with the TEG in aqueous membrane solution (d) compare the effect of different additives (TEG, DEG, EG) (e) relation between yields of Q and additive concentration in aqueous membrane solution (f) relationship between yield of Q and stirring velocity of permeation

component i decreased with increasing concentration of additives in aqueous membrane solution, because the m_i/m_{2MN} decreased.

The relation between stirring velocity and separation selectivity is shown in **Figure 5 (e)**. The separation selectivity of component i increased with stirring velocity. The emulsion drop size and, then, the number of internal oil droplet in a emulsion drop decreased, so that the unfavorable concentration distribution in a emulsion drop disappeared⁸⁾.

4. Conclusions

The distribution coefficients of the components contained in absorption oil between absorption oil and aqueous phases increased by addition and with increasing concentration of the additives, EG, DEG, and TEG. This suggested that these additives would be added into the membrane liquid to improve the performance of emulsion liquid membrane separation. The permeation rates of the components in absorption oil were increased by addition of the additives into the membrane liquid in batch emulsion liquid membrane permeation runs, as predicted from the above liquid-liquid equilibrium.

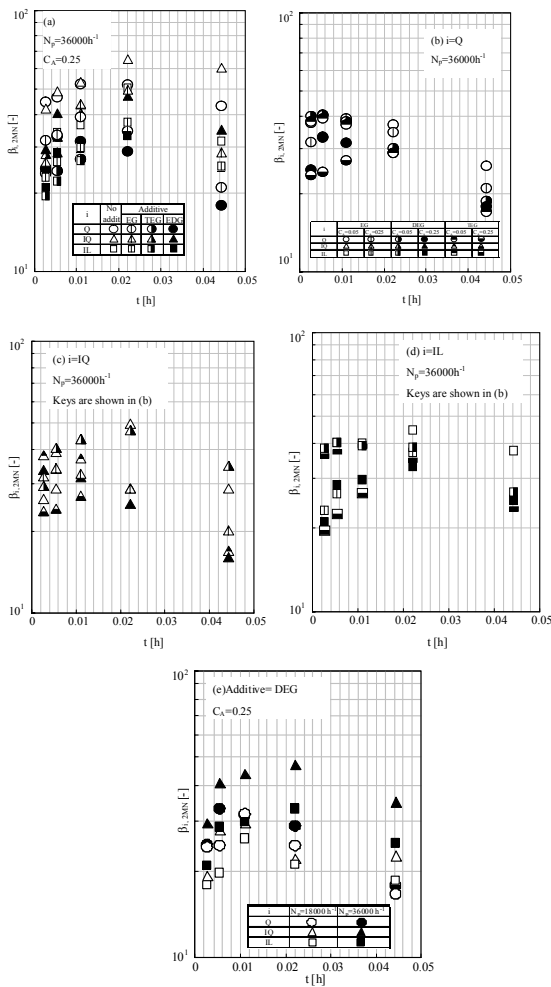


Figure 5 Time course of separation selectivity (a) effect of different additives on separation selectivity (b) relation between additive concentrations and separation selectivity of Q (c) relation between additive concentration and selectivity of IQ (d) relationship between additive concentration and separation selectivity of IL (e) effect of stirring velocity on separation selectivity of Q

Nomenclatures

A	= contact area	[m ²]
C_A	= mass fraction of the additive in aqueous membrane phase	[-]
C_s	= mass fraction of the saponin in aqueous membrane phase	[-]
C_i	= mass fraction in extract phase	[-]
D_i	= diffusivity of component i in liquid membrane	[-]
E	= mass of extraction	[kg]
m	= distribution coefficient	[-]
M	= mass of aqueous phase	[kg]
N_e	= stirring velocity at emulsification	[h ⁻¹]
N_p	= stirring velocity in permeation vessel	[h ⁻¹]
p_i	= permeation coefficient of component i	[kg]
R	= mass of raffinate phase	[g]
V_T	= total volume of liquid in permeation vessel	[m ³]
x	= mass fraction in raffinate phase	[-]
y	= mass fraction in extract phase	[-]
$\beta_{i,2MN}$	= separation selectivity of component i relative to 2-methylnaphthalene	[-]

<Subscript>

i = component i
 A = additive
 Q = quinoline
 IQ = Isoquinoline
 IL = Indole
 1MN = 1-methylnaphthalene
 2MN = 2-methylnaphthalene
 BP = Biphenyl
 DBF = Dibenzofuran
 EG = Ethylene glycol
 DEG = Diethylene glycol
 TEG = Triethylene glycol

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