

# Separation of Coal Tar Absorption Oil with O/W/O Emulsion Liquid Membrane –Effect of Additive in Membrane Liquid–

Dejin Bi  
 Student ID No.: 02\_20049  
 Supervisor: EGASHIRA RYUICHI  
 Department of International Development Engineering, School of Engineering,  
 Tokyo Institute of Technology, Tokyo 152-8552, Japan

## 1. Introduction

Coal tar absorption oil is mainly composed of nitrogen heterocyclic compounds, such as quinoline (Q), isoquinoline, indole, and homocyclic compounds, such as 1-methylnaphthalene, 2-methylnaphthalene (2MN), biphenyl, and so forth. These compounds are useful as raw materials for agricultural chemicals, medicines, perfumes, and many other useful chemicals. The separation of these compounds from absorption oil is carried out in two steps: separation of absorption oil 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 liquid membrane separation method, have been proposed<sup>1)-8)</sup>.

In this work, it was tried to improve the separation performance by the additive into aqueous membrane phase for the absorption oil separation by emulsion liquid membrane.

## 2. Experimentals

### 2.1. Liquid-liquid equilibrium

Absorption oil (abbr. to AO hereafter) and aqueous solution of 1,3-butanediol were brought into contact to be equilibrated using Erlenmeyer flask and commercial constant temperature bath. The principal experimental conditions are shown in **Table 1**.

### 2.2. Batch separation with emulsion liquid membrane

The feed AO and membrane liquid were stirred by a commercial high-speed homogenizer to prepare the emulsion.

The experimental apparatus for the membrane permeation run is demonstrated in **Figure 1**. The prepared emulsion was brought into contact with the solvent by an impeller in a vessel made of Pyrex glass equipped with four baffles as shown in the figure. Stirring was started to begin a permeation run ( $t=0$ ) and was 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. **Table 2** gives the experimental conditions. The membrane liquid was aqueous solution of saponin with methanol or 1,3-butanediol as an additive. All the oil phases were analyzed by a gas chromatograph to determine the compositions.

## 3. Results and Discussion

### 3.1. Liquid-liquid equilibrium

Distribution coefficient of component  $i$ ,  $m_i$ , was defined

as,

$$m_i = \frac{y_i}{x_i} \quad (1)$$

**Figure 2(a)** shows the relation between  $m_i$  of quinoline and 2-methylnaphthalene and the mass fraction of 1,3-butanediol added to water,  $y_{13B,1}$ . The previous results in the case with methanol<sup>5)</sup> are given in **Figure 2(b)**, as well. Quinoline and 2-methylnaphthalene are selected as representative components of nitrogen heterocyclic compounds and homocyclic compounds, respectively, here. The  $m_i$  of the nitrogen compounds were larger than those of the other components. The  $m_Q$  in the case with 1,3-butanediol was slightly lower than that with methanol.

### 3.2. Batch separation with emulsion liquid membrane

The fractional yield of component  $i$  in a batch permeation run,  $Y_i$ , was defined by the following equation:

$$Y_i = \frac{E \cdot y_i}{R_0 \cdot x_{i,0}} \quad (2)$$

Table 1 Experimental conditions for liquid-liquid equilibrium

Mass of AO [g]	50
Mass ratio of aqueous 1,3-butanediol solution relative to AO at initial [-]	1
$y_{w,0}$ [-]	0.2-1
Temperature [K]	298
Contact time [h]	72

Table 2 Experimental conditions for batch separation with emulsion liquid membrane

Feed	AO		
Membrane	Aqueous solution of saponin and additive (1,3-butanediol or methanol)		
Solvent	Toluene		
$C_s$ [-]	$N_c$ [ $h^{-1}$ ]	$N_p$ [ $h^{-1}$ ]	$V_T$ [ $m^3$ ]
0.03	$1.1 \times 10^6$	18000, 36000	$4.0 \times 10^{-4}$
$f_{0,w,0}$ [-]	$f_{0,o,0}$ [-]	$t$ [h]	$T$ [K]
0.25	0.5	0-0.044	$298 \pm 5$

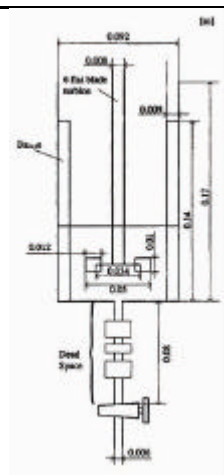


Fig.1 Permeation experimental equipment

Received on February 16, 2006. Correspondence concerning this article should be addressed to D. Bi (E-mail address: dbi@ide.titech.ac.jp)

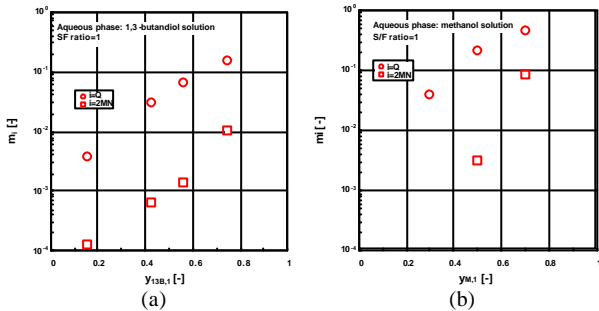


Figure 2 Effect of additive to water phase on distribution coefficient: (a) additive of 1,3-butandiol; (b) additive of methanol<sup>5)</sup>

Figure 3 shows the time courses of these yields of quinoline and 2-methylnaphthalene. The yield increased by adding 1,3-butandiol or methanol to the membrane liquid, before the yield reached the plateau. The yields in the case with methanol were higher than those with 1,3-butandiol. These results are attributed to the effects of additives to the membrane liquid on the distribution coefficient between oil phase and aqueous phase as shown in Figure 2. Higher stirring velocity gave higher yield, since the interfacial area between emulsion and external oil phase increased.

The separation selectivity of quinoline relative to 2-methylnaphthalene was represented by,

$$\beta_{Q,2MN} = \frac{y_i/y_{2MN}}{x_i/x_{2MN}} \quad (3)$$

This selectivity is plotted against time in Figure 4. Both 1,3-butandiol and methanol in the membrane liquid lowered the selectivity. The selectivity increased with stirring velocity in the case with 1,3-butandiol in the membrane. On the other hand, the selectivity decreased with increasing stirring velocity. This may be attributed to the membrane instability or so forth in the case with methanol in the membrane.

#### 4. Conclusion

The distribution coefficient between absorption oil phase and

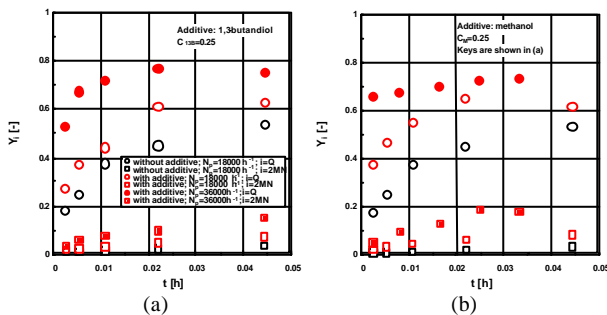


Figure 3 Time courses of fractional yields: (a) 1,3-butandiol in membrane liquid; (b) methanol in membrane liquid

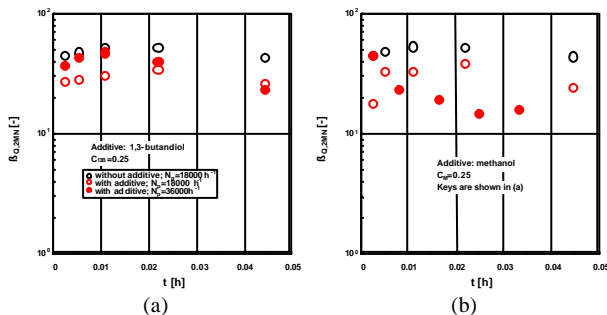


Figure 4 Time courses of separation selectivities of quinoline relative to 2-methylnaphthalene: (a) 1,3-butandiol in membrane liquid; (b) methanol in membrane liquid

aqueous phase increased with additives in the aqueous phase. The additive to the membrane liquid enhanced the permeation through O/W/O emulsion liquid membrane. This was proposed as a method to improve separation performance of this separation technique.

#### Nomenclatures

$C_s$	= mass fraction of the saponin in aqueous membrane phase	[-]
$E$	= mass of extract	[g]
$N_e$	= stirring velocity at emulsification	[h <sup>-1</sup> ]
$N_p$	= stirring velocity in permeation run	[h <sup>-1</sup> ]
$V_T$	= total volume of liquid in permeation vessel	[m <sup>3</sup> ]
$x$	= mass fraction in raffinate phase	[-]
$y$	= mass fraction in extract phase	[-]
$\beta_{Q,2MN}$	= separation selectivity of quinoline relative to 2-methylnaphthalene	[-]
$f_{0,0}$	= volume fraction of inner oil phase in o/w emulsion	[-]
$f_{0,w,0}$	= volume fraction of emulsion in permeation vessel	[-]
<Subscript>		
13B	= 1,3-butandiol	
2MN	= 2-methylnaphthalene	
$i$	= component $i$	
M	= methanol	
Q	= quinoline	

#### References

- 1) Hara, N.; "Permeation of Nitrogen Heterocyclic Compounds through Supported Liquid Membrane," Bachelor Thesis, Tokyo Tech. (2001)
- 2) Hara, N.; "Improvement of Rough Separation with O/W/O Liquid Membrane from Coal Tar Absorption Oil," Master Thesis, Tokyo Tech. (2003)
- 3) Ngai, M.; "Separation of Nitrogen Heterocyclic Compounds Contained in Coal Tar Absorption Oil Fraction by Extraction," Bachelor Thesis, Tokyo Tech. (1999)
- 4) Ngai, M.; "Rough Separation of Heterocyclic Nitrogen Compounds Contained in Coal Tar Absorption Oil Fraction," Master Thesis, Tokyo Tech. (2001)
- 5) Saito J.; "Separation of absorption oil and tar light oil by solvent extraction method," Bachelor Thesis, Tokyo Tech. (2004)
- 6) Salim, C.; "Separation of Coal Tar Absorption Oil Fraction by Extraction with Solvent Containing Metallic Salt," Bachelor Thesis, Tokyo Tech. (2000)
- 7) Salim, C.; "Rough Separation Process of Coal Tar Absorption Oil Using Solvent Extraction Method," Master Thesis, Tokyo Tech. (2002)
- 8) Salim, C.; "Process to Separate Coal Tar Fraction using Solvent Extraction," Doctor Thesis, Tokyo Tech. (2005)