

Stability of emulsion in separation of coal tar absorption oil by O/W/O emulsion liquid membrane

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1. Introduction

Coal tar absorption oil (AO) is one of the coal tar distillate fractions (b.p. =470~550K), which contains various kinds of chemical compounds: the nitrogen heterocyclic compounds such as quinoline (Q), isoquinoline (IQ), indole (IL); the homocyclic compounds such as 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), etc. **Table 1** shows examples of the mass fractions of constituents in AO. These compounds are useful as raw materials for agricultural chemicals, medicines, perfumes, and many other uses. The current method to separate these compounds from AO is performed in two steps: separation of AO into several fractions by acidic and basic extractions; and further separation and purification of these fractions into respective components by other methods. This first step 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 studied¹.

The separation of organic compounds by LMP is based mainly upon the difference of solubilities in aqueous membrane phase between compounds to be separated. Although this separation technique gives quite high separation selectivity, instability of liquid membrane is a defect characteristic of this technique. Instability of liquid membrane is divided into membrane breakage and mechanical entrainment. The membrane breakage is phenomenon that internal oil droplets in the emulsion mechanically leaks directly into external oil phase, while the mechanical entrainment is secondary emulsification of a portion of external oil phase into emulsion. These membrane instabilities lower separation selectivity. When the entrainment is considerable, the O/W/O system entirely becomes O/W emulsion where the separation operation is impossible any longer.

This thesis studied the stability of emulsion, that is, liquid membrane, for the separation of AO using O/W/O emulsion liquid membrane. The effects of the membrane breakage and mechanical entrainment on the separation of AO were examined with varying various operating conditions, such as, surfactant as emulsifying agent, surfactant concentration, etc.

2. Experimental

AO was used as an internal feed oil phase. The membrane liquid was aqueous solution of surfactant. Tween80, polyoxyethylene(20) orel ether (POE) and Tween85 were selected as a surfactant. Toluene was used as an external solvent phase. **Figure 1** shows the photograph of the emulsifier and schematic diagram of the permeator. 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 in stirring vessel. Stirring started to begin a permeation run ($t=0$) and continued for a specified operating time. **Table 2** gives the principal experimental conditions. Decane, whose solubility into aqueous phase are negligible relative to other permeate components in AO, was added to the feed phase to measure the rate of membrane breakage. Similarly, the entrainment was detected using nonane in the solvent phase. The diameter of internal droplet in the emulsion was measured using optical microscope before and after permeation run. The diameter of O/W emulsion drop during the permeation was also measured by a previous method².

3. Results and Discussion

The yield of component i , Y_i and the selectivity of component i , $\beta_{i,2MN}$, were defined as,

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

Figure 2 (a) and (b) show example of time course of yields and selectivities, respectively. Nitrogen heterocyclic compounds were selectively transferred through liquid membrane to extract phase and could be separated from homocyclic compounds. The yields of nitrogen compounds were around 0.6 at highest.

Figure 3 (a) and (b) show example of time course of Sauter mean diameter of inner oil droplet and O/W emulsion,

Table 1 Mass fractions of some main compounds in AO

$x_{Q,0}$	$x_{IQ,0}$	$x_{I,0}$	$x_{N,0}$	$x_{1MN,0}$	$x_{2MN,0}$	$x_{BP,0}$	$x_{DBF,0}$
0.068	0.015	0.029	0.012	0.115	0.267	0.057	0.102

Table 2 Experimental conditions for batch separation with emulsion liquid membrane

Feed	AO with decane		
Membrane	Aqueous solution of the surfactant		
Surfactant	Tween80, POE, Tween85		
Solvent	Toluene with nonane		
C_s [-]	N_e [h^{-1}]	N_p [h^{-1}]	V_T [m^3]
0.01, 0.03, 0.05	1.1×10^5	18000, 36000	4.0×10^{-4}
$\phi_{0,0}$ [-]	$\phi_{w0,0}$ [-]	t [h]	T [K]
0.5	0.25	0~0.044	298 ± 3 (room temp.)

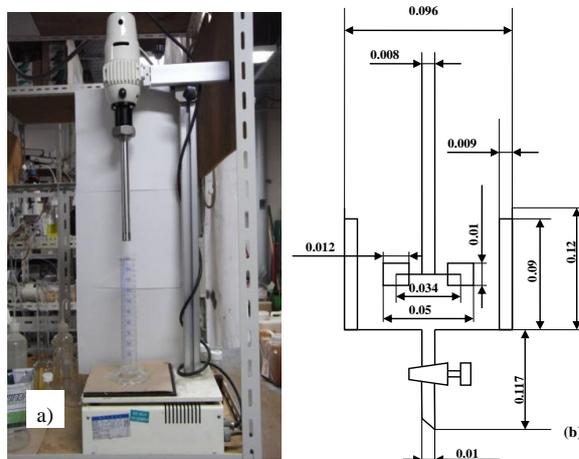


Figure 1 (a) Photograph of emulsifier with high-speed homogenizer; (b) Schematic diagram of stirring vessel

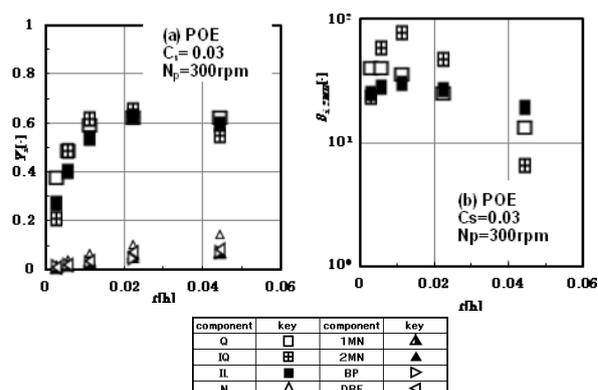


Figure 2 (a) Time courses of yields; (b) Time courses of selectivities

respectively. In all case, Sauter mean diameters of inner oil droplet and O/W emulsion increased with stirring time. It might be because of permeation of toluene to extract phase. And Suter mean diameters of O/W emulsion decreased with stirring velocity. The effects on difference of kind of the surfactant and concentration of the surfactant were not clear.

Figure 4 (a), (b) and (c) show the time courses of $E_{y_{DN}}$. In all case, $E_{y_{DN}}$ increased with stirring time and stirring velocity. $E_{y_{DN}}$ increased in the order of Tween85, Tween80 and POE cases. It is thought that O/W emulsion with Tween85 is unstable because O/W emulsion with Tween85 could not be emulsified by common method of emulsification operation. Time courses of $E_{y_{DN}}$ that concentration of the surfactant is 0.01 was larger than time courses of $E_{y_{DN}}$ that concentration of the surfactant is 0.03 and 0.05. This is attributed to the fact that membrane breakage does not change so much more than a certain concentration of the surfactant. For mechanical entrainment, the effects on difference of stirring velocity, kind of the surfactant and concentration of the surfactant were not clear.

The mass transfer rate of component i was represented by,
$$\frac{d(E \cdot y_i)}{dt} = P_i \cdot a \cdot (x_i - y_i) \cdot V_T + \frac{x_i}{x_{DN}} \cdot \frac{d(E \cdot y_{DN})}{dt} - \frac{y_i}{y_{NO}} \cdot \frac{d(R \cdot x_{NO})}{dt}$$
 with overall permeation coefficient P_i ³⁾. The lefthand side is total mass transfer rate of component i from the raffinate to extract phases, the first term in the righthand side is the permeation rate, the second term is the mass transfer rate by breakage, and the third is that by entrainment. Figures 5 (a) and (b) show the examples of time courses of mass transfer rates. In all case, the mass transfer rate by permeation decreased with stirring time. This reason is that a driving force of permeation, $(x_i - y_i)$, decreased with stirring time. The mass transfer rate by permeation increased with stirring velocity, since contact area increased by reduction of diameter of O/W emulsion. For all permeation runs, regarding the effects of the mass transfer rates by membrane breakage and that by mechanical entrainment on that by permeation, cases of 2MN was larger than cases of Q. Compared with the permeation rate, the mass transfer rate by membrane breakage and that by mechanical entrainment are small.

4. Conclusions

The mass transfer rate by membrane breakage increased with increasing stirring velocity and O/W emulsion with POE was the most stable in the range of this study. Both diameter of inner oil droplet and O/W emulsion increased with stirring time and diameter of O/W emulsion decreased with stirring velocity. Membrane breakage and mechanical entrainment hardly influenced overall permeation.

Nomenclatures

A	= contact area	[m ²]
a	= specific contact area	[m]
C_s	= mass fraction of the surfactant in aqueous membrane phase	[-]
D_p	= sauter mean diameter of O/W emulsion	[μm]
d_p	= sauter mean diameter of inner oil droplet	[μm]
E	= mass of extraction	[kg]
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 h ⁻¹ m ⁻²]
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	[-]
$\phi_{o,0}$	= volume fraction of inner oil in O/W emulsion	[-]
$\phi_{w,0}$	= volume fraction of O/W emulsion in total liquid	[-]

<Subscript>

- 1MN = 1-methylnaphthalene
- 2MN = 2-methylnaphthalene
- BP = biphenyl
- DBF = dibenzofuran
- DN = decane
- IL = indole
- IQ = isoquinoline
- i = component i
- NO = nonane
- Q = quinoline

Reference

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- 3) Egashira, R., H. Tanno, S. Kato and J. Kawasaki; J. Chem. Eng. Japan, 28, 38-45 (1995b)

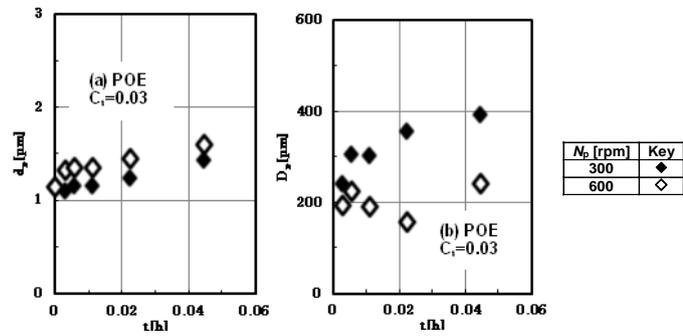


Figure 3 (a) Time courses of Sauter mean diameters of inner oil droplet; (b) Time courses of Sauter mean diameters of O/W emulsion drop

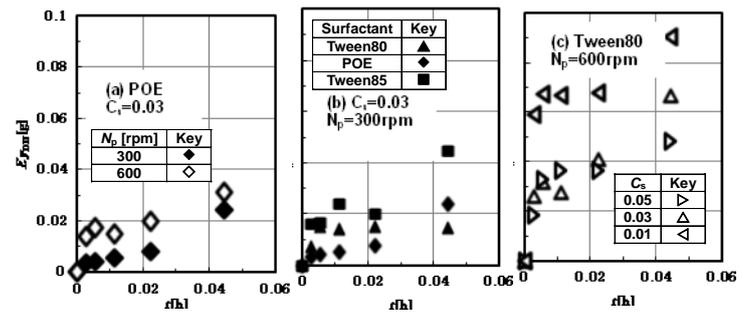


Figure 4 Time courses of $E_{y_{DN}}$: (a) effect of N_p ; (b) effect of surfactant; (c) effect of C_s

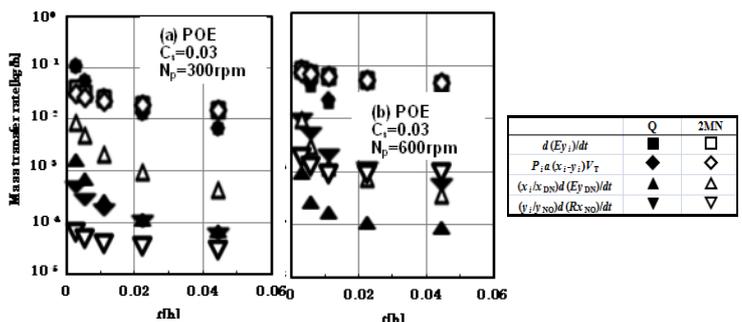


Figure 5 Time courses of mass transfer rates of Q and 2MN: (a) $N_p = 300$ rpm; (b) $N_p = 600$ rpm