PERMEATION OF NITROGEN HETEROCYCLIC COMPOUNDS THROUGH SUPPORTED LIQUID MEMBRANE

Norio Hara[†1)] and Ryuichi Egashira[†2)]

[†1)]Student I.D. No 97-2317-7,[†2)] Supervisor

1.INTRODUCTION:

Nitrogen heterocyclic compounds, e.g., quinoline etc, are industrially valuable as raw materials for agricultural chemicals, medicines, perfumes, and so forth. A part amount of these compounds are roughly separated from coal tar absorption oil and are purified to be respective products. The technique used in the first rough separation is so complicated that there has been several studies on simpler alternative methods, e.g., a liquid-liquid extraction[1)], a liquid membrane separation[2)], and the like. In this thesis, the liquid membrane permeations of quinoline, a nitrogen heterocyclic compound, and 2-methylnaphthalene, a homocyclic compound from which the nitrogen compounds should be separated were studied with the supported liquid membrane[3)] in terms of various operation conditions.

2.EXPERIMENTAL:

The experimental permeator is shown in Fig.1[3)]. The hydrophilic filter paper impregnated with the aqueous membrane liquid was placed between two Pyrex glass vessels. The feed and solvent were poured into respective vessel simultaneously and quickly, and then the stirrings of the feed and solvent phases were started (t =0) to begin the batch permeation run. The solvent phase was sampled from time to time for the analysis by a gas chromatograph.

Table 1 shows the principal experimental conditions. The absorption oil and the model mixtures are used as a feed. The membrane liquid was water or frequently used in the study of an emulsion liquid membrane. Heptane and 2,2,4-trimethylpentane were used as a solvent.

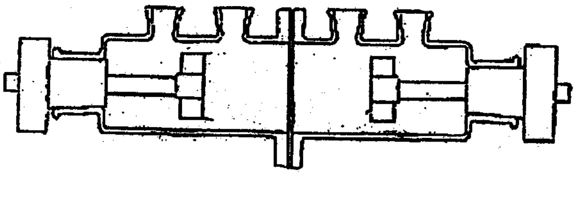

Fig.1 The experimental permeator

System		
System	Feed mixtures	Model mixture (Q-2MN-H Q-H Q-2MN) absorption oil
	Membrane	
	main component	Water
	additive	Saponin
	supporter	Advantec filter paper ;No.5B Diameter=5.5cm, Mean pore size= 4 μ m
	Solvent	Heptane Model mixture (Q-2MN-H)
Cell	Diameter of the cell	4.0 cm
	Impeller	Flat-blade turbine Dia.=3cm
Operating condition	Liquid Volumes	Feed Mixture:120cm^3 Solvent:120cm^3 Membrane:
	Agitation Speed	3.33,6.67 [1/s]
	Temperature	30 [℃]

Table 1 Experimental Conditions

3. RESULTS AND DISCUSSION:

Figure 2 shows the schematic diagram of the concentration profile around an ideal liquid membrane. The permeation rate of component i was represented by,

$$d(E \cdot y_i)/dt = P_i A(x_i - y_i) \qquad (1)$$

with the assumption that the distribution coefficients at the respective interfaces are equivalent with each other. The separation selectivity of quinoline relative to 2-methylnaphthalene, $\beta_{Q,2MN}$, was defined with the overall permeation coefficient, P_i, in Eq.(1), as folliws:

$$\beta_{Q,2MN} = P_Q / P_{2MN} \qquad (2)$$

Figure 3 shows the effect of the stirring rate, N_p, and the number of the membrane on the time courses of the mass fractions in the extract, y_i. Quinoline whose mass fraction in the feed was lower than that of 2-methylnaphthalene permeated preferentially to 2-methylnaphthalene and was separated. y_i increased linearly with time. The stirring velocities of both the feed and solvent phases did not influenced the permeation rates. 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. The effects of the surfactant, saponin, in the membrane are shown in Fig.4. The permeation rates were not affected by the surfactant. y_Q and y_{2MN} are plotted along time for various feed system in fig.5. Although the mass fraction of quinoline was constant independently of the feed system, the permeation rate of quinoline varied with feed system. The distribution coefficient of quinoline might change with feed system. The separation selectivities calculated by Eq.(2) were about 60 to 320.

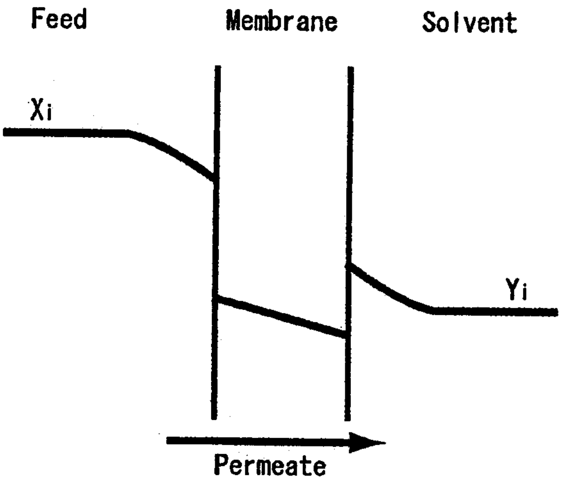

Fig.2 Schematic diagram of the concentration profile around an ideal liquid membrane

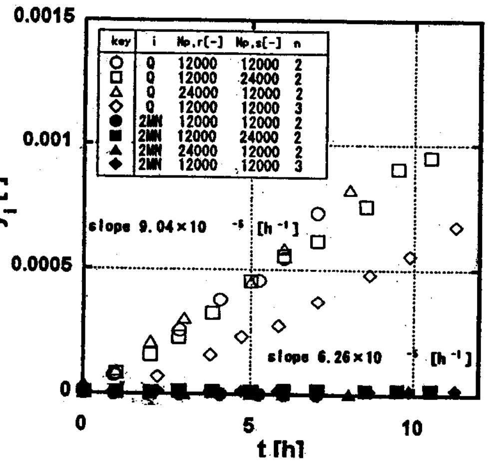

Fig.3 The effect of stirring rate and number of membrane supporter.

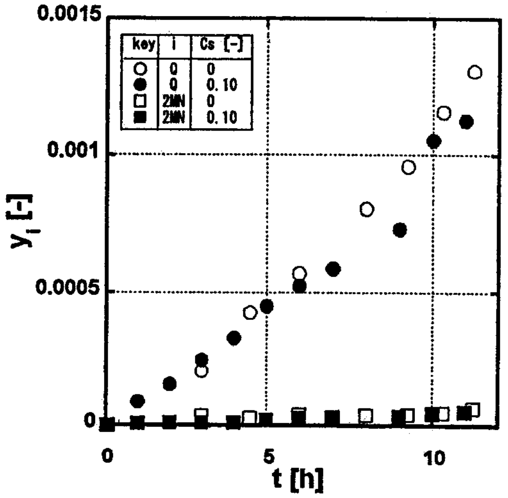

Fig.4 The effect of surfactant

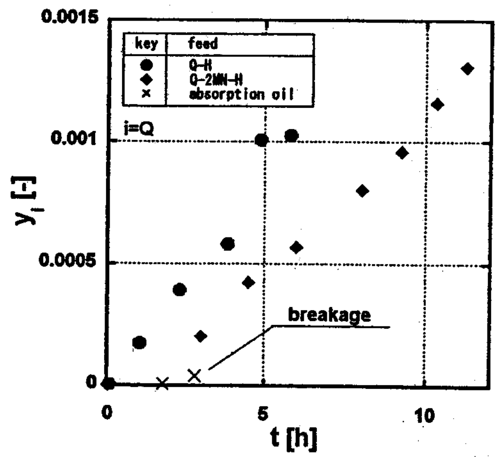

Fig.5 The effect of feed composition

4.CONCLUSION:

Quinoline could be separated from 2-methylnaphthalene by the supported liquid membrane. The effects of a variety of operation conditions on the permeation rates were clarified.

Nomenclature: A: contact area, Cs :mass concentration of surfactant, E : mass of extract, H:heptane, i : component i , Np : stirring velocity, x: mass fraction of raffinate, y: mass fraction, P : permeation coefficient, Q : quinoline, 2MN: 2-methylnaphtalene, β : selectivity

Reference: 1) Egashira, R. and M. Nagai; "Separation of Nitrogen Heterocyclic Compounds Contained in Coal Tar Absorption Oil Fraction by Solvent Extraction," Sekiyu Gakkaishi (Journal of The Petroleum Institute, 43, (5), 339 ～ 345 (September, 2000)), 2)永井政澄,江頭竜一; "コールタール吸収油留分に含まれる含窒素化合物の液膜分離," 石油学会東京大会講演要旨, E16, p.269 (2000年11月6,7日),, 3)Egashira, R., H. Tanno, S. Kato and J. Kawasaki;" A Simple Way for the Improvement of Separation Selectivity of Hydrocarbons by O/W/O Emulsion Liquid Membrane," Journal of Chemical Engineering of Japan, 28, (1), 38～45 (February, 1995)