

Liquid Membrane Permeation of Nitrogen Heterocyclic Compounds Contained in Model Coal Tar Fraction

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We investigated the separation of nitrogen heterocyclic compound (NHC) contained in a model coal tar fraction comprising four kinds of NHC [indole (In), quinoline (Q), iso-quinoline (iQ), quinaldine (Qu)], three kinds of bicyclic aromatic compound (BAC) [1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), dimethylnaphthalene (DMN) mixture with ten structural isomers (DMNs; regarded as one component)], biphenyl (Bp) and phenyl ether (Pe) by liquid membrane permeation (LMP). A batch-stirred tank was used as the permeation unit. An aqueous solution of saponin and n-hexane were used as the liquid membrane and the outer oil phase, respectively. Yield and selectivity of individual NHC was much larger than that of BAC, Bp and Pe. Increasing the initial mass fraction of the saponin to the membrane solution ($C_{sap,0}$) and the initial volume fraction of O/W emulsion to total liquid in a stirred tank ($\phi_{OW,0}$) resulted in deteriorating the yield of individual NHC, but increasing the stirring speed (N) resulted in improving the yield of each NHC. With increasing $C_{sap,0}$, the selectivity of each NHC based on DMNs increased. Increasing $\phi_{OW,0}$ and N resulted in decreasing the selectivity of individual NHC based on DMNs. At an experimental condition fixed, the sequence of the yield and selectivity in reference to DMNs for each NHC was $Q > Qu = iQ > In$. Furthermore, we compared LPM method with methanol extraction method in view of the separation efficiency (yield, selectivity) of NHC.

Key Words: Coal tar fraction, Indole, Nitrogen heterocyclic compound, O/W/O Emulsion, Liquid membrane permeation

Introduction

Coal tar, a mixture of approximately 500 compounds, contains many valuable compounds. Among them, nitrogen heterocyclic compound (NHC) such as indole (In), quinoline (Q), iso-quinoline (iQ), quinaldine (Qu) have been recognized as an intermediate for the productions of essential amino acids, medicines, agricultural chemicals and perfumes. There, the separation and purification of valuable NHC from coal tar is very significant in view of effective resource utilization.

The separation and purification processes of a target NHC contained in the coal tar consist of the follow; (1) distillation of coal tar in order to recover of an absorption fraction containing NHC, (2) the reaction extraction using acid and base materials in order to crude separate of NHC in the absorption fraction, and (3) the downstream process (crystallization¹ etc.) in order to purify a target NHC using extract containing rich NHC. However, the reaction extraction in order to crude separate of NHC contained in the absorption fraction is complicated, also the recovery and recycle of solvents are very difficult. Therefore, a new technique for crude separation of NHC in the coal tar absorption fraction might be extensively studied and developed for widespread use as an alternative to the conventional separation processes such as the reaction extraction.

Up to the present, crude separation of NHC from the fraction recovered by distillation of coal tar was investigated by operation such as inclusion complexation,^{2,3} solvent extraction,³⁻⁹

adsorption¹⁰ and supercritical extraction and azeotropic distillation. These crude separation methods, also, are not satisfactory from a separating point of view, because of low separation efficiency of NHC.

The liquid membrane permeation (LMP) method, which was developed by N. N. Li,¹¹⁻¹³ is considered to be a promising technique for crude separation of NHC from the absorption fraction because it separates mixture oils with relatively high separation efficiency and it might be a less energy-consuming operation. Although several studies¹⁴⁻¹⁹ on LMP of petroleum system such as naphtha, kerosene and light cycle oil have been published since Li, the study on LMP of NHC from the coal tar system have not published yet.

A liquid membrane is a film formed at an oil/water interface by a surfactant solution. Such films are formed by dispersing the solution to be separated in the form of droplets in a surfactant solution. The droplets covered with liquid membranes are then contacted with an organic solvent phase to receive the permeates.²⁰ During this process one of the components of the mixture transfers from the droplets through the liquid membrane and into the organic solvent at a faster rate than the other.²⁰ The organic solvent becomes rich in the more permeable component, and the droplets become rich in the less permeable component, thus achieving a separation of the components.

We applied LMP method to separate NHC from the coal tar system. The effects of the permeation time (t), the stirring speed (N), the initial volume fraction of O/W emulsion to total liquid

in a stirred tank ($\phi_{O/W,0}$) and the initial mass fraction of the saponin to the membrane solution ($C_{sap,0}$) on separation of NHC from a model coal tar fraction were investigated. Furthermore, we compared LPM method with methanol extraction method in view of the separation efficiency of NHC.

Experimental

Apparatus and method.

Emulsification: The apparatus and methods for the emulsification operation were the same as those described in our previous report.²⁰ A known amount of a model coal tar fraction (inner oil phase) and the membrane solution were placed in the stirrer (15 cm I.D. and 15 cm height) and emulsified at 10 s^{-1} of stirring speed for ten minutes. Resultant O/W emulsion was circulated with the pump equipped, and simultaneously, emulsified by the high-speed homogenizer (stirring speed: 333 s^{-1}) and the stirrer for ten minutes to make O/W emulsion further particulate.

Permeation: A schematic diagram and the dimensions of a batch-stirred tank (8 cm I.D. and 8 cm height) are presented in Figure 1.²¹ A batch-stirred tank made of a glass material was used as a contactor for O/W emulsion and the outer oil phase. A six flat blade turbine type, impeller was located at the center of the liquid. Four baffle plates were equipped with the tank to prevent free interfaces from forming.

A known amount of the outer oil phase was placed in the batch stirred tank and heated to the experiment temperature (303 K). An aliquot of O/W emulsion that was kept at the experiment temperature was added and stirred in the stirred tank. After the permeation time elapsed, stirring stopped, O/W/O emulsion was allowed to settle, and volume of the O/W emulsion phase and the outer oil phase was measured. The outer oil phase was analyzed by adding acetone, and their compositions were determined. An analysis of the outer oil phase was carried out by a gas chromatograph [Hewlett Packard Co., HP 6890: capillary column, HP-5 (50 m \times 0.25 mm I.D.)] equipped with flame ionization detector (FID). The analysis conditions⁴ of samples were as follows: carrier gas, N_2 ; flow rate, 1 mL/min; injection port temperature, 423 K; sample size, 1 μ L; splitting ratio, 100 : 1; FID; column temperature, 393 K for 25 min, then increased at 3 K/min to 473 K. The compositions of the inner oil phase in O/W emulsion phase were determined by calculation using the mass balance equation (4) mentioned later.

Material system and conditions: Material system and experimental conditions were summarized in Table 1. Permeation experiment of this study was in need of the inner oil of vast quantity (more than 10 L). We expected that a lot of times be required to recover a large amount of coal tar fraction of rich NHC (the temperature ranges of fraction: 513–538 K) using a batch distillation apparatus of laboratory scale. Therefore, we used the permeation operation making a model mixture that is consisted of nine components referred to literature.^{1,2,6} The membrane solution consisted of city water and saponin using generally as an emulsifying agent of O/W emulsion. Hexane was used as the outer oil phase, not only because its solubility in water is so low that its permeation through liquid membrane can be neglected but also because it can be safely used in experiments owing to its low vapor pressure.

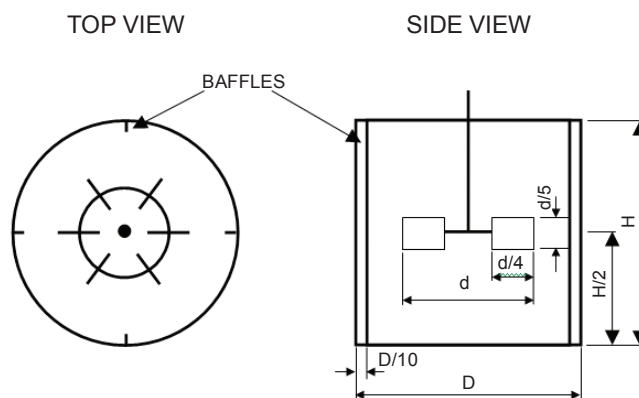


Figure 1. A schematic diagram and the dimensions of a batch stirred tank.²¹ $D = 8\text{ cm}$, $H = 8\text{ cm}$, $d = 5\text{ cm}$.

Table 1. Material system and experimental conditions

Material system	
Feed (inner oil phase)	model coal tar fraction
Membrane	aqueous solution of saponin
Solvent (outer oil phase)	n-Hexane
Experimental conditions	
Initial mass fraction of saponin to membrane solution, $C_{sap,0}$ (—)	0.015 ~ 0.03
Stirring speed, N (s^{-1})	7.33 ~ 15
Permeation temperature, T (K)	303
Permeation time, t (s)	10 ~ 150
Total liquid volume, V (m^3)	3.2×10^{-4}
Initial volume fraction of inner oil to O/W emulsion, $\phi_{O,0}$ (—)	0.5
Initial volume fraction of O/W emulsion to total liquid in a stirred tank, $\phi_{O/W,0}$ (—)	0.1 ~ 0.4

Table 2. Composition of model coal tar fraction⁴

Component	Composition (wt %)
Quinoline (C_9H_7N)	0.092
Iso-quinoline (C_9H_7N)	0.024
Indole (C_8H_7N)	0.047
Quinaldine ($C_{10}H_9N$)	0.024
2-Methylnaphthalene ($C_{11}H_{10}$)	0.318
1-Methylnaphthalene ($C_{11}H_{10}$)	0.142
Dimethylnaphthalene ($C_{12}H_{12}$) mixture with ten structural isomers (regarded as one component)	0.235
Biphenyl ($C_{12}H_{10}$)	0.055
Phenyl ether ($C_{12}H_{10}O$)	0.033
Others	0.030

The permeation temperature (T) and the initial volume fraction of the inner oil phase to O/W emulsion ($\phi_{O,0}$) were fixed in this work. $\phi_{O/W,0}$, t , N , and $C_{sap,0}$ were varied. The composition of a model mixture is listed in Table 2.⁴ In this work, commercial reagent grade Q, iQ, In, Qu, 1MN, 2MN, DMN mixture with ten

structural isomers, Bp and Pe were used without further purification.

Results and Discussion

Gas chromatogram. Figures 2(a) through (c), respectively, are shown the gas chromatograms of a model mixture,⁴ the outer oil phase and the inner oil phase in O/W emulsion without solvent resulted from the permeation operation and the component names identified. Though DMN (peak number 9) with ten structural isomers presented five peaks in (a), they were summed and regarded as one component (DMNs). When the gas chromatogram of the outer oil phase in (b) was compared with that of the model mixture, the peak heights of individual NHC were increased, but those of individual BAC, Bp and Pe were considerably decreased by the permeation operation. (c) is shown that the gas chromatogram of the inner oil phase in O/W emulsion was very different from that of the model mixture. Permeating NHC resulted in decreasing the peaks of individual NHC. The gas chromatograms of the inner oil phase in O/W emulsion and the outer oil phase, it could be reconfirmed that the effect of the permeation operation on the separation of NHC contained in the coal tar fraction.

Definition equation.

Yield and permeation rate: Yield of component i , Y_i , defined by Equation (1), was calculated for each component in order to investigate the permeation.²⁰

$$Y_i = \frac{E y_i}{R_0 x_{i,0}} \quad (1)$$

where $x_{i,0}$ and y_i , respectively, denote the mass fraction of component i in the inner oil phase at initial and that in the outer oil phase after the permeation operation. R_0 refers to the mass of the inner oil phase at initial and E denotes the mass of outer oil phase after the permeation operation.

From Equation (1), the permeation rate ($dE y_i/dt$) of component i was correlated with the slope of the time course curve of the yield (dY_i/dt) as follows:

$$\frac{d(E y_i)}{dt} = R_0 x_{i,0} \frac{dY_i}{dt} \quad (2)$$

Selectivity: To investigate the separation between the compounds, the selectivity of the random component i based on component j , $\beta_{i,j}$, was calculated from Equation (3):

$$\beta_{i,j} = \frac{(y_i/x_i)}{(y_j/x_j)} \quad (3)$$

where x_i denotes the mass fraction of component i in the inner oil phase after the permeation operation.

Mass balance: To confirm that the values observed by the experiment were reasonable, we examined the mass balance of the component i at the random permeation time by the following Equation (4).

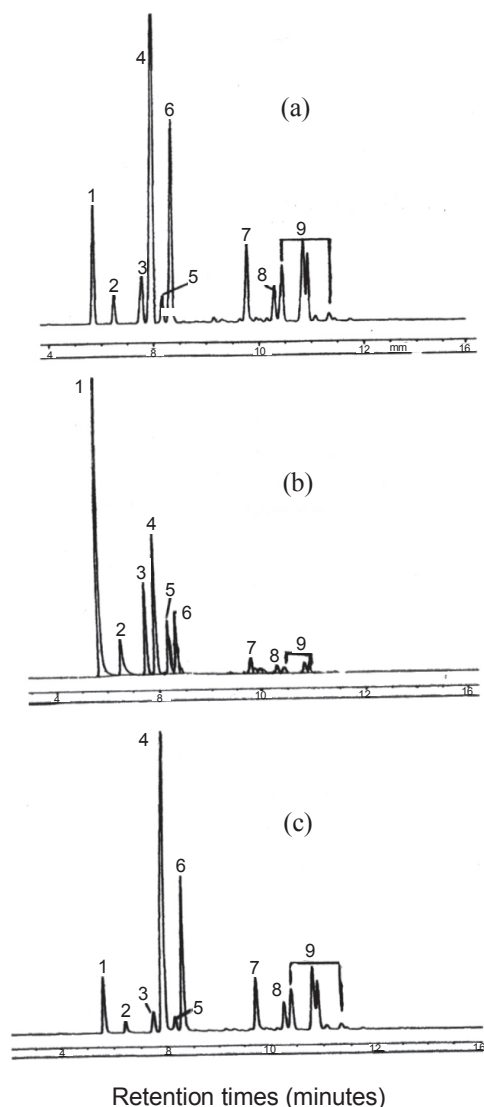


Figure 2. Gas chromatograms of (a) a model coal tar fraction⁴, (b) the outer oil phase (without solvent), and (c) the inner oil phase in O/W emulsion phase (without solvent) obtained by the permeation operation. Permeation conditions of (b) and (c): $\phi_{O/W,0} = 0.1$, $C_{sap,0} = 0.02$, $N = 10 \text{ s}^{-1}$, $T = 303 \text{ K}$ and $t = 40 \text{ sec}$. 1: quinoline (Q), 2: iso-quinoline (iQ), 3: indole (In), 4: 2-methylnaphthalene (2MN), 5: quinaldine (Qu), 6: 1-methylnaphthalene (1MN), 7: biphenyl (Bp), 8: phenyl ether (Pe), 9: dimethylnaphthalene (DMN) mixture with ten structural isomers (DMNs; regarded as one component)

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

where R is the mass of the inner oil phase at the random permeation time and E_0 is the mass of the outer oil phase at initial. $y_{i,0}$ denotes the mass fraction of component i in the outer oil phase at initial. The mass of components i in the inner oil phase at the random permeation time, $R x_i$, found from analyzing the outer oil phase was compared with $R x_i$ that resulted from analyzing the inner oil phase after the demulsification of O/W emulsion. Both were found to be comparable within $\pm 10\%$, and the values of this work were thought to be reasonable. Also, the experiments were replicated twice or three times at the same condition to confirm the reproducibility of the measured value.

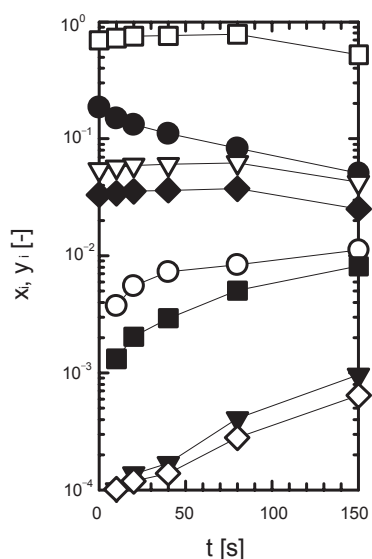


Figure 3. Time course curves for the concentration of component (or group) i in the inner oil and the outer oil phase. Permeation conditions: $\phi_{OW,0} = 0.1$, $C_{sap,0} = 0.02$, $N = 10 \text{ s}^{-1}$ and $T = 303 \text{ K}$. NHCs: NHC group summed four kinds of NHC (Q, iQ, In, Qu), BACs: BAC group summed three kinds of BAC (2MN, 1MN, DMNs), Bp: biphenyl, Pe: phenyl ether. Keys: \bullet x_i ($i = \text{NHCs}$), \square x_i ($i = \text{BACs}$), ∇ x_i ($i = \text{Bp}$), \blacklozenge x_i ($i = \text{Pe}$), \circ y_i ($i = \text{NHCs}$), \blacksquare y_i ($i = \text{BACs}$), \blacktriangledown y_i ($i = \text{Bp}$), \blacklozenge y_i ($i = \text{Pe}$).

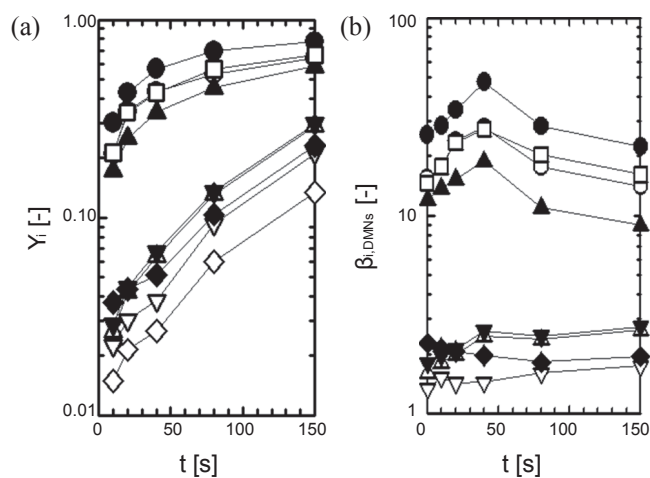


Figure 4. Time course curves for (a) yield, (b) selectivity in reference to DMNs of component i . Permeation conditions: $\phi_{OW,0} = 0.1$, $C_{sap,0} = 0.02$, $N = 10 \text{ s}^{-1}$ and $T = 303 \text{ K}$. In: indole, iQ: iso-quinoline, Q: quinoline, Qu: quinaldine, 1MN: 1-methylnaphthalene, 2MN: 2-methylnaphthalene, Bp: biphenyl, Pe: phenyl ether, DMN: dimethylnaphthalene, DMNs: DMN mixture with ten structural isomers regarded as one component. Keys: \bullet $i = \text{Q}$, \circ $i = \text{iQ}$, \blacktriangle $i = \text{In}$, \triangle $i = \text{2MN}$, \square $i = \text{Qu}$, \blacksquare $i = \text{1MN}$, ∇ $i = \text{Bp}$, \blacklozenge $i = \text{Pe}$, \diamond $i = \text{DMNs}$.

The range of mass variation of individual component in the inner or the outer oil phase was within $\pm 5\%$.

Time course curves. Figure 3 shows the time course curves for concentration of entire NHC (NHCs) summed four kinds of NHC (Q, iQ, In, Qu), entire BAC (BACs) summed three kinds of BAC (1MN, 2MN, DMNs), Bp and Pe in the inner and outer oil phases. The permeation rate of a component through the liquid membrane depends on the diffusivity and, in par-

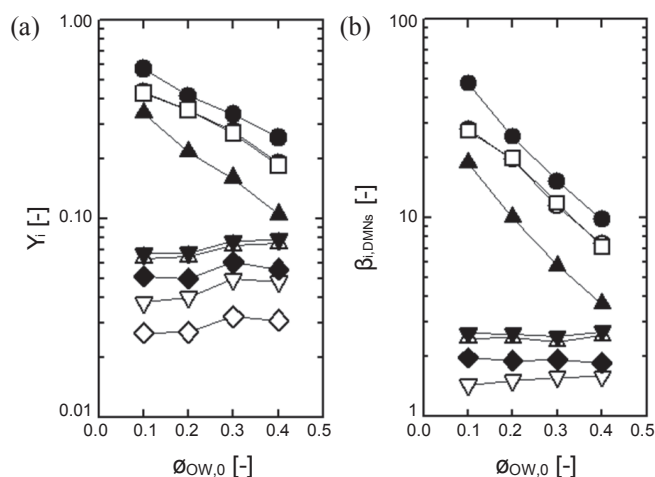


Figure 5. Effect of $\phi_{OW,0}$ for (a) yield, and (b) selectivity based on DMNs of component i . Permeation conditions: $t = 40 \text{ sec}$, $C_{sap,0} = 0.02$, $N = 10 \text{ s}^{-1}$ and $T = 303 \text{ K}$. (Keys are shown in Figure 4)

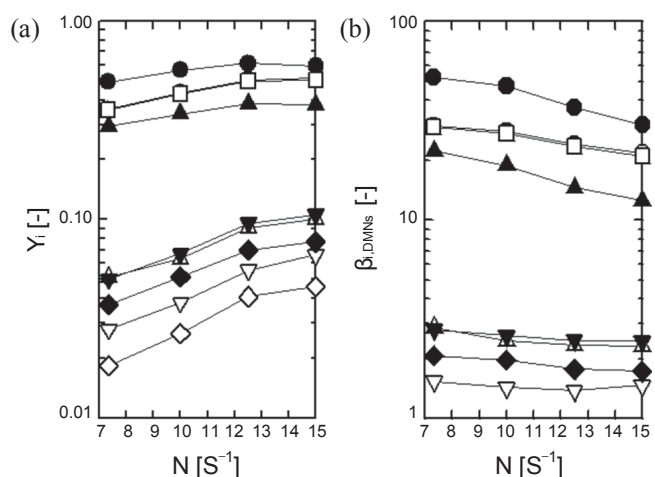


Figure 6. Effect of N for (a) yield, and (b) selectivity based on DMNs of component i . Permeation conditions: $t = 40 \text{ sec}$, $\phi_{OW,0} = 0.1$, $C_{sap,0} = 0.02$ and $T = 303 \text{ K}$. (Keys are shown in Figure 4)

ticular, on the solubility of a component through the liquid membranes.¹⁶ The concentration of NHCs in the outer oil phase was higher than that of BACs, Bp and Pe. It was anticipated that the solubility in liquid membrane of NHC was higher than that of BAC, Bp and Pe. NHCs concentration of the inner oil phase decreased rapidly with increasing permeation time, but concentration of BACs, Bp and Pe of the inner oil phase increased until it reached a maximum, and then decreased with increasing permeation time. This tendency indicated that the permeation of individual BAC, Bp and Pe is much slow than that of individual NHC.

Figure 4(a) shows yield of component i (Y_i), which is derived from Equation (1) to investigate the permeation rate through liquid membranes for the components included in the inner oil phase, according to the permeation time. Y_i increased with the permeation time elapsing. The permeation rate of individual NHC was much higher than that of individual BAC, Bp and Pe. It was expected that the solubility in liquid membrane of

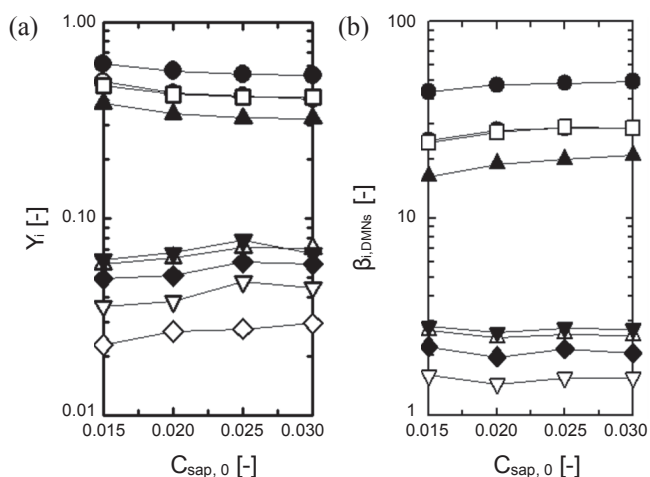


Figure 7. Effect of $C_{\text{sap},0}$ for (a) yield, and (b) selectivity in reference to DMNs of component i . Permeation conditions: $t = 40$ sec, $\phi_{\text{O/W},0} = 0.1$, $N = 10$ s $^{-1}$ and $T = 303$ K. (Keys are shown in Figure 4)

individual NHC is higher than that of individual BAC, Bp and Pe.

Graph for the slope of the time course curve of yield to each component omitted, the permeation rate of Q at $t = 10$ sec, 0.043 g/sec, which was derived from Equation (2) substituted for the slope (0.03) of the time course curve of yield to Q (Y_Q), was about eight times faster than that of DMNs. The sequence of yield for NHC was $Q > iQ = Qu > In$. Y_Q at $t = 10$ sec and 150 sec, were found to be 0.3 and 0.77, respectively. Yield of In (Y_{In}) at $t = 10$ sec and 150 sec, also, were found to be 0.17 and 0.58, respectively. These results suggested that the yield of NHCs (Y_{NHCs}) could be very high. Graph for Y_{NHCs} omitted, Y_{NHCs} at $t = 10$ sec and 150 sec, respectively, were found to be 0.25 and 0.65.

The selectivity, $\beta_{i,\text{DMNs}}$, of the random component i calculated from Equation (3) based on DMNs as the reference component ($j = \text{DMNs}$) according to the permeation time to study the separation between the components is shown in Figure 4(b). Generally, the selectivity represented in the separation method of the rate difference through the batch operation like this work went through maximum value due to the difference of the permeation rate of individual component, and then approached unity after the permeation time sufficiently elapsed. There was the maximum selectivity in only the NHC in the range of the permeation time of this work. The maximum selectivity of individual NHC presented at $t = 40$ sec, respectively, were Q 47, iQ 28, Qu 27 and In 19. $\beta_{i,\text{DMNs}}$ of 1MN, 2MN, Bp and Pe were almost 1-3 irrespective of the permeation time. This result suggested that the individual separation of 1MN, 2MN, Bp and Pe could be very difficult.

Since the ratio of the slope of the yield curve for the random component i to that for DMNs at the starting point of the permeation ($t = 0$ sec) was equal to $\beta_{i,\text{DMNs}}$ at $t = 0$ sec.¹⁶ The selectivity at $t = 0$ sec, $(\beta_{i,\text{DMNs}})_{t=0}$, resulted from Figure 4(a) was represented simultaneously in Figure 4(b). In this study, $(\beta_{i,\text{DMNs}})_{t=0}$ was used as an index for the selectivity of LMP. Using $(\beta_{i,\text{DMNs}})_{t=0}$, and the separation between NHC and BAC in a model mixture was studied. $(\beta_{i,\text{DMNs}})_{t=0}$ of Q, Qu, iQ and In, respec-

tively, were 26, 15, 16 and 12. Graph for $(\beta_{\text{NHCs,BACs}})_{t=0}$ omitted, $(\beta_{\text{NHCs,BACs}})_{t=0}$ was found to be 12. These results suggested that LMP could be a new promising technique to separate NHC in coal tar fraction. However, $(\beta_{Q,iQ})_{t=0}$ and $(\beta_{1\text{MN},2\text{MN}})_{t=0}$ were found to be unity, and subsequently it was difficult to separate between isomer components by LMP.

Our values of $(Y_{\text{NHCs}})_{\text{am}}$, arithmetic mean of Y_{NHCs} obtained at each permeation time, and $(\beta_{\text{NHCs,BACs}})_{t=0}$ compared with the values of Y_{NHCs} and $\beta_{\text{NHCs,BACs}}$ of the previous work⁴ using methanol extraction. Our values, $(Y_{\text{NHCs}})_{\text{am}} = 0.46$ and $(\beta_{\text{NHCs,BACs}})_{t=0} = 12$, were bigger than methanol extraction,⁴ $Y_{\text{NHCs}} = 0.36$ and $\beta_{\text{NHCs,BACs}} = 9$.

Effect of operation factors and experimental conditions. Figures 5(a) and (b), respectively, show the effect of $\phi_{\text{O/W},0}$ for yield and selectivity. The yield of individual NHC decreased sharply with increasing $\phi_{\text{O/W},0}$. The increase of $\phi_{\text{O/W},0}$ resulted in increasing a diameter of O/W emulsion and a mechanical entrainment, and reducing the driving force for the permeation, and subsequently it seemed that they had an effect on decreasing the yield of individual NHC. Also, the selectivity of individual NHC based on DMNs decreased with increasing $\phi_{\text{O/W},0}$. The yield of individual BAC, Bp and Pe, and selectivity of 1MN, 2MN, Bp and Pe in reference to DMNs, however, almost fixed irrespective of $\phi_{\text{O/W},0}$.

The permeation operation at more than $\phi_{\text{O/W},0} = 0.6$ was impossible because the emulsion of (O/W)/O type was transferred to that of O/W type due to the mechanical entrainment of the outer oil phase.

The effect of N for yield and selectivity is shown in Figures 6(a) and (b). The yield of individual component increased with increasing N. This result was ascribed to increase contact area between the O/W emulsion and the outer oil phase, a turbulent flow around the inner oil phase and the breakage of a liquid membrane due to increasing N. However, because the breakage of a liquid membrane was increased with increasing N, the selectivity of individual NHC decreased with increasing N. Independently of N, the selectivity of 1MN, 2MN, Bp and Pe almost fixed.

Figures 7(a) and (b) show the effect of $C_{\text{sap},0}$ for yield and selectivity. In the ranges of $C_{\text{sap},0}$ of this work, the yield of individual NHC decreased with increasing $C_{\text{sap},0}$. This result was ascribed to decrease the breakage of a liquid membrane due to increasing $C_{\text{sap},0}$. However, the selectivity of individual NHC increased with increasing $C_{\text{sap},0}$, because the breakage of a liquid membrane was decreased with increasing $C_{\text{sap},0}$. Independently of $C_{\text{sap},0}$, the yield and selectivity of 1MN, 2MN, Bp and Pe nearly fixed. O/W emulsion produced at $C_{\text{sap},0} < 0.015$ was separated into an oil phase and an aqueous phase within a short time due to the unstable emulsion.

Conclusion

The separation of NHC from a model coal tar fraction prepared according to the components and compositions contained in coal tar fraction (the temperature ranges of fraction: 513-538 K) was examined by LMP. The following conclusions can be drawn from the experimental results: 1. The permeation rate of individual NHC was faster than that of individual BAC, Bp

and Pe. 2. Increasing N resulted in improving yield of NHC, but increasing $\theta_{OW,0}$ and $C_{sap,0}$, resulted in deteriorating that of NHC. With increasing N and $\theta_{OW,0}$, the selectivity of individual NHC in reference to DMNs decreased sharply, but the selectivity of individual NHC increased with increasing $C_{sap,0}$. 3. At an experimental condition fixed, the sequence of the yield of NHC and selectivity of NHC in reference to DMNs was $Q > Qu = iQ > In$. 4. Independently of the permeation conditions, it was difficult to separate the isomer component. 5. LMP values, $(Y_{NHCs})_{am} = 0.46$ and $(\beta_{NHCs,BACs})_{f=0} = 12$, were bigger than methanol extraction, $Y_{NHCs} = 0.36$ and $\beta_{NHCs,BACs} = 9$. 6. The LMP process proposed by this work is the new one, considering the crude separation of NHCs in the coal tar fraction, also, and the simple one without the re-extraction operation. Therefore, this proposed process would be a feasible process to separate NHCs in coal tar fraction.

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