Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Nitrogen Heterocyclic Compounds from Model Coal Tar Fraction by Solvent Extraction

Su Jin Kim[a]; Yong Jin Chun[a]
[a] Department of Materials Science and Applied Chemistry, Chungwoon University, Hongsung-Gun, Chungnam, South Korea

To cite this Article Kim, Su Jin and Chun, Yong Jin(2005) 'Separation of Nitrogen Heterocyclic Compounds from Model Coal Tar Fraction by Solvent Extraction', Separation Science and Technology, 40: 10, 2095 — 2109

To link to this Article: DOI: 10.1081/SS-200068488

URL: http://dx.doi.org/10.1081/SS-200068488

Separation Science and Technology, 40: 2095–2109, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200068488

Separation of Nitrogen Heterocyclic Compounds from Model Coal Tar Fraction by Solvent Extraction

Su Jin Kim and Yong Jin Chun
Department of Materials Science and Applied Chemistry, Chungwoon University, Hongsung-Gun, Chungnam, South Korea

Abstract: The separation of four kinds of nitrogen heterocyclic compounds (*NHCs*) from a model mixture comprising *NHCs* [indole (*In*), quinoline (*Q*), iso-quinoline (*iQ*), quinaldine (*Qu*)], three kinds of bicyclic aromatic compounds [*BACs*; 1-methylnaphthalene (*1MN*), 2-methylnaphthalene (*2MN*), dimethylnaphthalene (*DMN*)], biphenyl (*Bp*) and phenyl ether (*Pe*) was examined by a solvent extraction. The model mixture used as a raw material of this work was prepared according to the components and compositions contained in coal tar fraction (the temperature ranges of fraction: 240–265°C). The distribution equilibrium between the coal tar fraction and the solvent was measured with eight kinds of solvents. An aqueous solution of methanol, ethanol, iso-propyl alcohol, N,N-dimethyl acetamide, DMF, formamide, N-methylformamide/methanol, and formamide/methanol were used as solvents. An aqueous solution of formamide was found to be suitable for separating *NHCs* contained in coal tar fraction based on distribution coefficient and selectivity. The effect of operation factors on separating *NHCs* was investigated by the distribution equilibrium using an aqueous solution of formamide. Increasing the operation temperature and the volume ratio of solvent to feed at initial $(S/F)_0$ resulted in improving the distribution coefficients of each *NHC*, but increasing the volume fraction of water in the solvent at initial $(y_{w,0})$ resulted in deteriorating the distribution coefficients of each *NHC*. With increasing $y_{w,0}$ and $(S/F)_0$, the selectivities of each *NHC* in reference to *DMN* increased. Increasing the operation temperature resulted in decreasing the selectivities of each *NHC* in reference to *DMN*. At an experimental condition fixed, the sequence of the distribution coefficient and selectivity in reference to *DMN* for each *NHC* was $In > iQ > Q > Qu$, and also the sequence of the distribution coefficient for each *BAC* was $1MN > 2MN > DMN$. The sequence of the distribution coefficient

Received 29 November 2004, Accepted 8 April 2005

Address correspondence to Su Jin Kim, Department of Materials Science and Applied Chemistry, Chungwoon University, Hongsung-Gun, Chungnam, South Korea. E-mail: sujkim@chungwoon.ac.kr

for entire compounds analyzed by this work was *In*> *iQ* > *Q* > *Qu* > *Bp* > *1MN*> *2MN* > *Pe* > *DMN*.

Keywords: Coal tar fraction, nitrogen heterocyclic compounds, indole, solvent extraction, liquid-liquid equilibrium

INTRODUCTION

There are a lot of valuable nitrogen heterocyclic compounds (*NHC*) in coal tar. Among them, indole has been recognized as an intermediate for fine chemicals such as medicine, perfume, and agricultural chemicals. Therefore, the separation and purification of indole from coal tar is very significant in view of efficient resource utilization.

The separation and purification processes of indole contained in the coal tar consist of the follow: (1) distillation of coal tar in order to recover of an absorption fraction containing rich *NHC*, (2) the reaction extraction using acid and base materials in order to crude separate of *NHC* contained in the absorption fraction, and (3) the downstream process (crystallization etc. (1)) in order to purify indole using extractant containing rich *NHC*. However, the reaction extraction in order to crude separate of *NHC* contained in the absorption fraction is very complicated, also the recovery and recycle of solvents are very difficult. Therefore, there is a need to develop more simple and efficient method of chemical separation.

Up to the present, crude separation of *NHC* from coal tar fraction recovered through distillation of coal tar was investigated by an operation such as inclusion complexation (2, 3), organic solvent extraction (4), adsorption (5) and methanol-water extraction (3, 6), supercritical extraction, azeotropic distillation, and solvent extraction. Egashira (7, 8), Ukegawa (6), and Kodera (9) reported the crude separation of indole by a solvent extraction. They used the methanol as an extraction solvent. This methanol extraction is not satisfactory from a separating point of view, because of low selectivity of indole.

In this work, solvent extraction has been used for the separation of four kinds of *NHC* (*NHCs*) from a model mixture (Feed A) comprising *NHCs* [quinoline (*Q*), iso-quinoline (*iQ*), indole (*In*), quinaldine (*Qu*)], three kinds of bicyclic aromatic compounds [*BACs*; 1-methylnaphthalene (*1MN*), 2-methylnaphthalene (*2MN*), dimethylnaphthalene (*DMN*)], biphenyl (*Bp*) and phenyl ether (*Pe*). Feed A was prepared according to the composition of the coal tar fraction. Distribution equilibrium was measured using Feed A as a raw material and 13 kinds of the aqueous solutions of as solvent, and it was used for surveying optimum solvent for separation between *NHCs* and others (*BACs, Bp* and *Pe*) from Feed A. The effect of operation factors on crude separation of *NHCs* was studied using optimum solvent. To examine the equilibrium states based on the composition of feed, also, we measured the liquid-liquid distribution equilibrium using three kinds of model feeds (Feed A, B, and C) consisting of different composition.

EXPERIMENTAL APPARATUS AND METHOD

A batch-stirred tank (10) (8 cm I.D. and 8 cm height) made of a glass material was used as a contactor for a raw material and a solvent. A six-flatblade 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.

To make solvent normal concentration, city water was added into each solvent, and mixed. An aliquot of solvent was charged to the batch-stirred tank and heated to the experimental temperature. An aliquot of a raw material that was kept at the experimental temperature was added in a batch-stirred tank. After a liquid-liquid contact run of a specified period, stirring stopped, the solution was allowed to settle, and the volumes of the raffinate phase and the extract phase were measured. The raffinate phase and the extract phase were analyzed by adding acetone, and their compositions were determined. An analysis of the raffinate phase and the extract phase were carried out by a gas chromatograph [Hewlett Packard Co., HP 6890: capillary column, HP-5 (50 m × 0.25 mm I.D.)] equipped with flame ionization detector (FID). The analysis conditions of samples were as follows: carrier gas, N_2; flow rate, 1 mL/min; injection port temperature, 150°C; sample size, 1 L; splitting ratio, 100: 1; FID; column temperature, 120°C for 25 min, then increased at 3°C/min to 200°C.

Material systems and experimental conditions used this study were summarized in Table 1. Three kinds of model mixtures (Feed A, B and C) and 13 kinds of aqueous solutions were used feed and solvent, respectively.

Equilibrium extraction experiment of this study was in need of the raw material of vast quantity (more than 20 L). We expected that a lot of time would be required to recover a large amount of coal tar fraction of rich *NHC* (the temperature ranges of fraction: 513–538°C) using a batch distillation apparatus of laboratory scale. Therefore, we used an equilibrium extraction operation making model with raw material that consisted of nine components referred to literature (1, 2, 6).

Material systems and experimental conditions used in this study were summarized in Table 1. Three kinds of model mixtures (Feed A, B and C) and 13 kinds of aqueous solutions were used of feed and solvent, respectively. The compositions of three kinds of model mixtures are listed in Table 2. In Feed A, the sum concentration of *NHCs* and that of *BACs* were about 18.62 wt% and 69.55 wt%, respectively. Feed A, contained about 5.47 wt% of *Bp*, 3.33 wt% of *Pe*, and 3.03 wt% of all others. The composition of *In* was 4.66 wt%. In this work, commercial reagent grade *Q*, *iQ*, *In*, *Qu*, *1MN*, *2MN*, *DMN*, *Bp*, and *Pe* were used without further purification.

The volume fraction of water in a solvent at initial ($y_{w,0}$), the volume ratio of the solvent to a raw material at initial $(S/F)_0$, the liquid-liquid contact time (t), and the operation temperature (T) were varied. The impeller speed (N) was fixed in this work.

Table 1. System and experimental conditions for batch equilibrium extraction

System	
Feed	Three kinds of model mixtures (Feed A, B, and C)
Solvent	1) aqueous solution of methanol 2) aqueous solution of ethanol 3) aqueous solution of iso-propyl alcohol 4) aqueous solution of N,N-dimethyl acetamide 5) aqueous solution of DMF 6) aqueous solution of formamide 7) aqueous solution of 1-pentanol 8) aqueous solution of 1-butanol 9) aqueous solution of iso-amyl alcohol 10) aqueous solution of chloroform 11) 3 : 1 (volume ratio) aqueous solution of N-methylformamide-methanol 12) 7 : 1 (volume ratio) aqueous solution of formamide-methanol 13) 1 : 1 (volume ratio) aqueous solution of chloroform-methanol
Experimental conditions	
Contact time, t (hr)	$0.25 \sim 3$
Impeller speed, N (s^{-1})	5
Operation temperature, T (°C)	$18.5 \sim 60$
Volume of liquid, (m^3)	4×10^{-4}
Volume fraction of water in solvent at initial, $y_{w,0}$ (−)	$0 \sim 0.3$
Volume ratio of solvent to feed at initial, $(S/F)_0$ (−)	$0.25 \sim 7.33$

RESULTS AND DISCUSSION

Definition Equation

The distribution coefficient, m_i, the ratio of composition for component *i* in the extract phase to that in the raffinate phase, is defined as

$$m_i = y_i/x_i \tag{1}$$

where y_i and x_i, respectively, denote the mass fraction of component *i* in the extract phase and that in the raffinate phase after a liquid-liquid contact run.

Table 2. Compositions of three kinds of model feeds

Feed	Group	Component	Composition (mass fraction)	
A	Nitrogen heterocyclic compounds (*NHCs*)	Quinoline (*Q*)	0.0918	0.1862
		Iso-quinoline (*iQ*)	0.0236	
		Indole (*In*)	0.0466	
		Quinaldine (*Qu*)	0.0242	
	Bicyclic aromatic compounds (*BACs*)	2-Methylnaphthalene (*2MN*)	0.3181	0.6955
		1-Methylnaphthalene (*1MN*)	0.1423	
		Dimethylnaphthalene (*DMN*)	0.2351	
	Phenyl	Biphenyl (*Bp*)	0.0547	0.0547
	Ether	Phenyl ether (*Pe*)	0.0333	0.0333
		Others	0.0303	0.0303
			1	1
B	Nitrogen heterocyclic compounds (*NHCs*)	Quinoline (*Q*)	0.1529	0.2935
		Iso-quinoline (*iQ*)	0.0199	
		Indole (*In*)	0.1014	
		Quinaldine (*Qu*)	0.0193	
	Bicyclic aromatic compounds (*BACs*)	2-Methylnaphthalene (*2MN*)	0.2506	0.5490
		1-Methylnaphthalene (*1MN*)	0.1121	
		Dimethylnaphthalene (*DMN*)	0.1863	
	Phenyl	Biphenyl (*Bp*)	0.0729	0.0729
	Ether	Phenyl ether (*Pe*)	0.0572	0.0572
		Others	0.0274	0.0274
			1	1
C	Nitrogen heterocyclic compounds (*NHCs*)	Quinoline (*Q*)	0.0747	0.1878
		Iso-quinoline (*iQ*)	0.0541	
		Indole (*In*)	0.0382	
		Quinaldine (*Qu*)	0.0208	
	Bicyclic aromatic compounds (*BACs*)	2-Methylnaphthalene (*2MN*)	0.2574	0.7071
		1-Methylnaphthalene (*1MN*)	0.1892	
		Dimethylnaphthalene (*DMN*)	0.2605	
	Phenyl	Biphenyl (*Bp*)	0.0477	0.0477
	Ether	Phenyl ether (*Pe*)	0.0274	0.0274
		Others	0.0300	0.0300
			1	1

Yield of component *i*, Y_i, is defined as

$$Y_i = Ey_i/R_0x_{i,0} \tag{2}$$

where $x_{i,0}$ denotes the mass fraction of component *i* in a raw material. E refers to the mass of the extract phase after a liquid-liquid contact run and R_0 denotes the mass of a raw material.

Selectivity of component *i* in reference to component *j*, $\beta_{i,j}$, the ratio of the distribution coefficient for component *i* to that for component *j*, was calculated from Eq. (3).

$$\beta_{i,j} = m_i/m_j \tag{3}$$

Mass balance of component *i* was checked by using Eq. (4) as follows:

$$R_0x_{i,0} - Rx_i = Ey_i - E_0y_{i,0} \tag{4}$$

where E_0 and R, respectively, denote the mass of the extract phase at initial and that of the raffinate phase after a liquid-liquid contact run. Mass balance of all components checked at extraction operation of this work was satisfactory.

Gas Chromatograms of Feed A, Raffinate and Extract Phase

Figure 1(a) through (c) show the gas chromatograms of Feed A, the extract phase and the raffinate phase without a solvent resulted from the formamide extraction and the component names of compounds identified. Though *DMN* of peak number 9 with 10 structural isomers presented five peaks, they were summed and regarded as one component. When the gas chromatogram of the extract phase in Figure 1(b) was compared with that of the Feed A, the peak heights of each *NHC* were considerably increased, but those of each *BAC, Bp* and *Pe* were considerably decreased by the formamide extraction. Figure 1(c) shows that the gas chromatogram of the raffinate phase was very different from that of Feed A. Extracting *NHCs* (*In*, *Q*, *iQ* and *Qu*) by the formamide extraction resulted in decreasing the peaks of each *NHC*, and subsequently increasing those of *BACs*, *Bp* and *Pe*. The gas chromatograms of the raffinate phase and the extract phase could reconfirm the effect of the formamide extraction on the separation of *NHCs* contained in the coal tar fraction.

Equilibrium Extraction

To confirm the time reaching the equilibrium, the raffinate phases and the extract phases obtained through contacting (contact time: 0.25, 1, 2, 3 h) a solvent and Feed A under an identical extraction condition were analyzed.

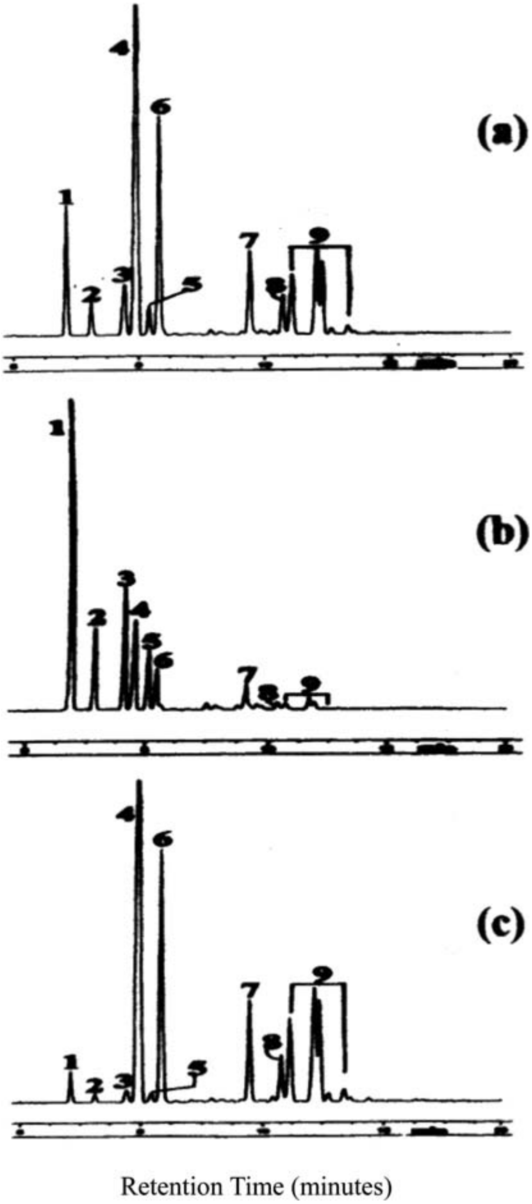

Figure 1. Gas chromatogram of (a) Feed A, (b) the extract phase (without a solvent) and (c) the raffinate phase (without a solvent) obtained by equilibrium extraction operation. Equilibrium extraction conditions of (b) and (c): $y_{w,0} = 0.2$, $(S/F)_0 = 4$ and $T = 30°C$ using Feed A. 1: quinoline (*Q*), 2: iso-quinoline (*iQ*), 3: indole (*In*), 4: 2-methylnaphthalene (2*MN*), 5: quinaldine (*Qu*), 6: 1-methylnaphthalene (1*MN*), 7: biphenyl (*Bp*), 8: phenyl ether (*Pe*), 9: dimethylnaphthalene mixture with ten structural isomers (*DMN*).

The compositions of the raffinate phases and the extract phases obtained through contact for 0.25, 1, 2, and 3 h were the same as each other irrespective of contact time. Therefore, we could know that equilibrium arrival time is within 0.25 h.

Comparison of Solvent

When 13 kinds of the aqueous solutions [methanol, ethanol, iso-propyl alcohol, N,N-dimethyl acetamide, DMF, formamide, iso-amyl alcohol, chloroform, 1-pentanol, 1-butanol, 3 : 1 (volume ratio) N-methylformamide-methanol, 7 : 1 (volume ratio) formamide-methanol and 1 : 1 (volume ratio) chloroform-methanol] were used as solvent, the possibility of forming two liquid phases was investigated. In the case of using five kinds of the aqueous solutions (iso-amyl alcohol, chloroform, 1-pentanol, 1-butanol, 1 : 1 (volume ratio) chloroform-methanol), two liquid phases were unformed under the experimental condition of this work.

Figures 2(a) and (b) show the results of the equilibrium extraction for indole and group consisted of *NHCs* measured by using eight kinds of the aqueous solutions, formed two liquid phases under an identical extraction condition, respectively. In the case of an aqueous solution of formamide, the balance between yield of indole and selectivity of indole in reference to *DMN* as well as that between yield of *NHCs* and selectivity of *NHCs* in reference to group consisted of *BACs* was suitable. Therefore, an aqueous solution of formamide was found to be an optimum solvent for extracting *NHCs* (particularly, indole) from Feed A based on the distribution coefficient and selectivity. When using an aqueous solution of formamide as a solvent for extraction of *NHCs* contained in a model mixture, it can recover solvent easily by distillation because at differences of boiling point of the model mixtures and formamide (b.p.: 210°C) and the model mixture and water are big enough.

Under the experimental conditions of this work, our value of $\beta_{\mathrm{In,2MN}}$ is gotten by using an aqueous solution of formamide as a solvent compared with the value of $\beta_{\mathrm{In,2MN}}$ of Egashira (7, 8) using an aqueous solution of methanol as a solvent. Our value, $\beta_{\mathrm{In,2MN}} = 33$, was big, more than three times than Egashira's, $\beta_{\mathrm{In,2MN}} = 10$.

Equilibrium Extraction with an Aqueous Solution of Formamide

Figure 3(a) through (c) show the effect of the volume fraction of water in the solvent at initial ($y_{w,0}$) on the distribution coefficient (m_i) of component *i*, the yield (Y_i) of component *i*, and the selectivity of component *i* based on *DMN* ($\beta_{i,\mathrm{DMN}}$). The distribution coefficients and yields of each *NHC* were much higher than those of *BACs* (*1MN*, *2MN*, *DMN*), *Bp* and *Pe* due to the solubility of each component in the solvent. Increasing $y_{w,0}$ resulted in decreasing the distribution coefficient of each component because the polarity of an extract phase increased with increasing its moisture. Therefore, the distribution

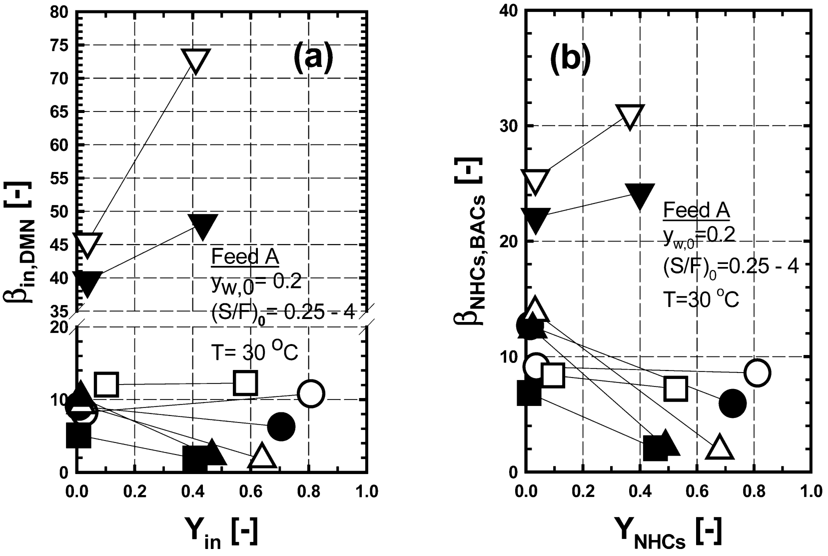

Figure 2. Solvent comparison for (a) the yield of indole and the selectivity of indole in reference to dimethylnaphthalene, (b) the yield of *NHCs* and the selectivity of *NHCs* in reference to *BACs*.

NHCs: group of four kinds of nitrogen heterocyclic compound (*In*, *iQ*, *Q*, *Qu*), *BACs*: group of three kinds of bicyclic aromatic compound (*1MN*, *2MN*, *DMN*), *In*: indole, *iQ*: iso-quinoline, *Q*: quinoline, *Qu*: quinaldine, *1MN*: 1-methylnaphthalene, *2MN*: 2-methylnaphthalene, *DMN*: dimethylnaphthalene.

Keys: ○ aqueous solution of methanol, ● aqueous solution of ethanol, □ aqueous solution of N-methylformamide and methanol (volume ratio 3 : 1), ■ aqueous solution of iso-propyl alcohol, △ aqueous solution of N,N-dimethylacetamide, ▲ aqueous solution of DMF, ▽ aqueous solution of formamide, ▼ aqueous solution of formamide and methanol (volume ratio 7 : 1).

coefficients and yields of each component decreased sharply, accordingly, as $y_{w,0}$ increased. $\beta_{i,DMN}$ increased with increasing $y_{w,0}$. This phenomenon, also, indicated that the increase of $y_{w,0}$ produced the sharp increase of $\beta_{i,DMN}$ because *DMN* is much more hydrophobic than two kinds of *BAC* (*1MN*, *2MN*), *Bp* and *Pe*. These results suggested that the selectivity of *NHCs* in reference to *BACs* in the model coal tar fraction could be very high. The sequence of *NHCs* for m_i, Y_i and $\beta_{i,\,DMN}$ were *In* > *iQ* > *Q* > *Qu* and the sequence of entire component analyzed at this work for m_i, Y_i and $\beta_{i,\,DMN}$ were *In* > *iQ* > *Q* > *Qu* > *Bp* > *1MN* > *2MN* > *Pe* > *DMN*. The values of $\beta_{Q,DMN}$ and $\beta_{iQ,DMN}$, also, those of $\beta_{1MN,DMN}$ and $\beta_{2MN,DMN}$ were observed to be almost the same, and it was difficult to separate between isomer components.

Figure 4(a) through (c) show the effect of $y_{w,0}$ on m_i of group or component *i*, Y_i of group or component *i* and $\beta_{i,BACs}$ of group or component

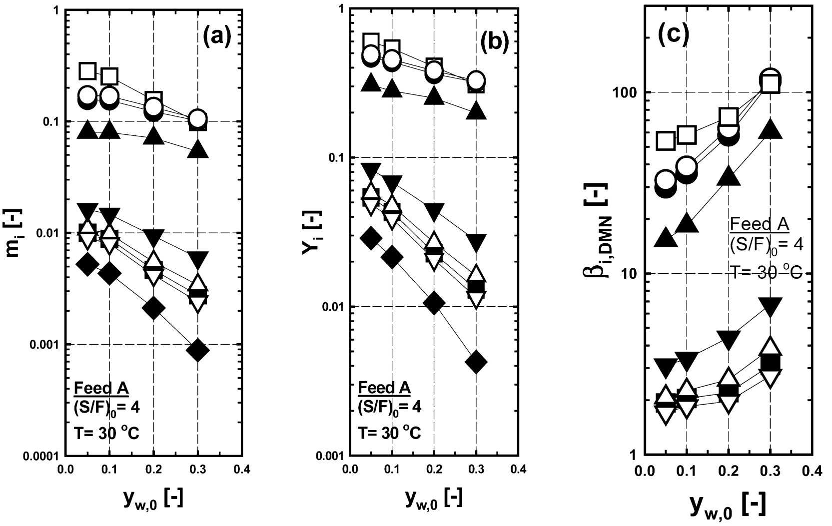

Figure 3. Effects of volume fraction of water in solvent at initial for (a) the distribution coefficient of component *i*, (b) yield of component *i*, and (c) the selectivity of component *i* in reference to component *DMN*.
Keys: □ $i = In$, ○ $i = iQ$, ● $i = Q$, ▲ $i = Qu$, ■ $i = 2MN$, △ $i = 1MN$, ◆ $i = DMN$, ▼ $i = Bp$, △ $i = Pe$.

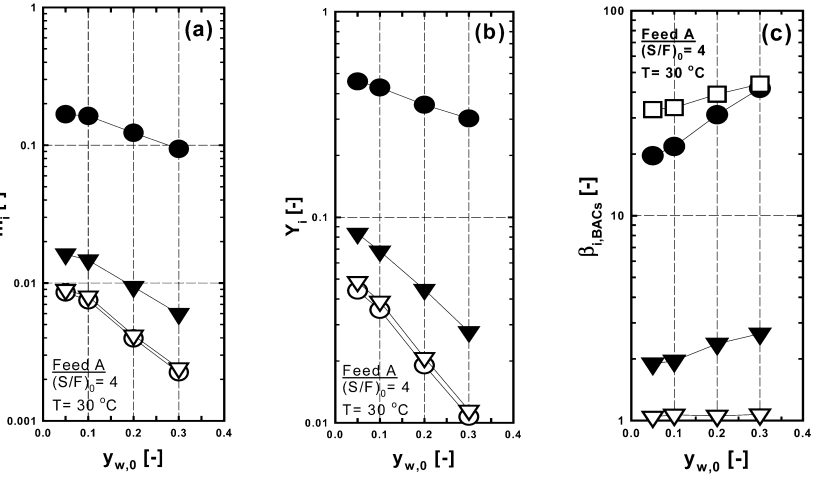

Figure 4. Effects of volume fraction of water in solvent at initial for (a) the distribution coefficient of group or component *i*, (b) yield of group or component *i*, and (c) the selectivity of group or component *i* in reference *BACs*.
Keys: □ $i = In$, ● $i = NHCs$, ○ $i = BACs$, ▼ $i = Bp$, ▽ $i = Pe$.

i in reference to *BACs*. With increasing $y_{w,0}$, m_i and Y_i decreased sharply. The distribution coefficient and yield of *NHCs* were much higher than those of *BACs, Bp* and *Pe*. The sequence of m_i and Y_i were *NHCs* > *Bp* > *Pe* > *BACs*. With increasing $y_{w,0}$, the selectivity of *In*, *NHCs* and *Bp* in reference to *BACs* increased sharply, but the selectivities of *Pe* in reference to *BACs* were observed almost 1. Therefore, it was difficult to separate between *Pe* and *BACs*. With decreasing $y_{w,0}$, as shown in Fig. 4(c), the difference between the selectivity of *In* in reference to *BACs* and that of *NHCs* in reference to *BACs* was much higher. The selectivities of *In* and *NHCs* in reference to *BACs* at $y_{w,0} = 0.05$, respectively, were found to be 33.9 and 19.6. The selectivities of *In* and *NHCs* in reference to *BACs* at $y_{w,0} = 0.3$, respectively, were found to be 43.8 and 41.8.

Figure 5(a) through (c) show the effect of the volume ratio of a solvent to a raw material at initial $(S/F)_0$ on m_i, Y_i and $\beta_{i,DMN}$. m_i of each *NHC* increased slightly with increasing $(S/F)_0$, but m_i of each *BAC*, *Bp* and *Pe* decreased slightly with increasing $(S/F)_0$. This tendency is considered to have been caused by chemical change such as salvation between a solute and a solvent by $(S/F)_0$ change.

The yields of each component increased sharply according to increase $(S/F)_0$. The lower the carbon number in *BACs*, the higher the yield. $\beta_{i,DMN}$ for each *NHC* increased with increasing $(S/F)_0$, but $\beta_{i,DMN}$ for two kinds of *BAC* (*1MN* and *2MN*), *Bp* and *Pe* almost fixed, irrespective of $(S/F)_0$. This result indicated that each *NHC* could be easily separated from the *BACs*, *Bp*

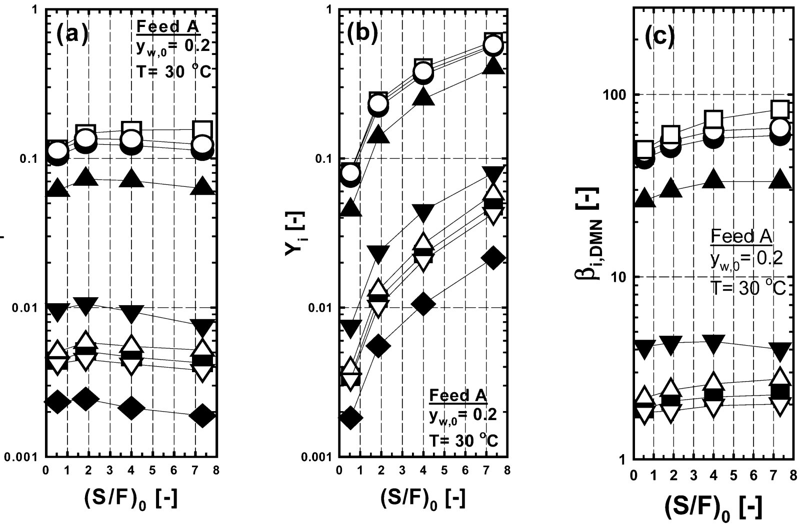

Figure 5. Effects of volume ratio of solvent to feed at initial for (a) the distribution coefficient of component *i*, (b) yield of component *i*, and (c) the selectivity of component *i* in reference to component *DMN*. (Keys are shown in Fig. 3.)

and *Pe* with increasing $(S/F)_0$. The values of $\beta_{Q,DMN}$ and $\beta_{iQ,DMN}$, also, those of $\beta_{1MN,DMN}$ and $\beta_{2MN,DMN}$ were observed almost the same, irrespective of $(S/F)_0$ and it was difficult to separate between isomer components.

Graph for Y_{NHCs} and $\beta_{NHCs,BACs}$ omitted, Y_{NHCs} at $(S/F)_0 = 0.54$ and $(S/F)_0 = 7.33$ were found to be 0.07 and 0.55, respectively. $\beta_{NHCs,BACs}$ at $(S/F)_0 = 0.54$ and $(S/F)_0 = 7.33$, respectively, were found to be 26.7 and 31.4. The selectivity of *Pe* in reference to *BACs* was about 1, irrespective of $(S/F)_0$. Therefore, it was difficult to separate between *Pe* and *BACs*.

Figure 6(a) through (c) show the effect of the operation temperature (T) on m_i, Y_i, and $\beta_{i,DMN}$. As shown in Figs. 6(a) and (b), increasing the operation temperature resulted in increasing m_i and Y_i. $\beta_{i,DMN}$ decreased sharply with increasing the operation temperature.

Graph for Y_{NHCs} and $\beta_{NHCs,BACs}$ omitted, Y_{NHCs} at T = 18.5°C and T = 60°C were found to be 0.35 and 0.40, respectively. $\beta_{NHCs,BACs}$ at T = 18.5°C and T = 60°C, respectively, were found to be 34.7 and 22.1. From the results of the yield and selectivity for each *NHC* and *NHCs* based on operation temperature, it is expected that the formamide extraction of *NHCs* (particularly, indole) in coal tar fraction can be operated at room temperature.

The distribution equilibrium result measured using three kinds of model feeds (Feed A, B, and C) consisted of different composition as shown in Fig. 7. m_i, Y_i, and $\beta_{i,DMN}$ were almost the same, irrespective of composition of feed.

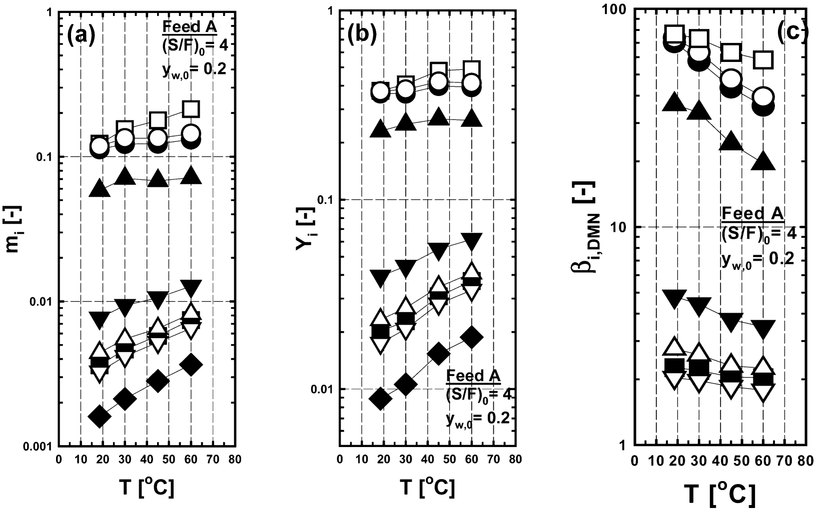

Figure 6. Effects of operation temperature for (a) the distribution coefficient of component *i*, (b) yield of component *i*, and (c) the selectivity of component *i* in reference to component *DMN*. (Keys are shown in Fig. 3.)

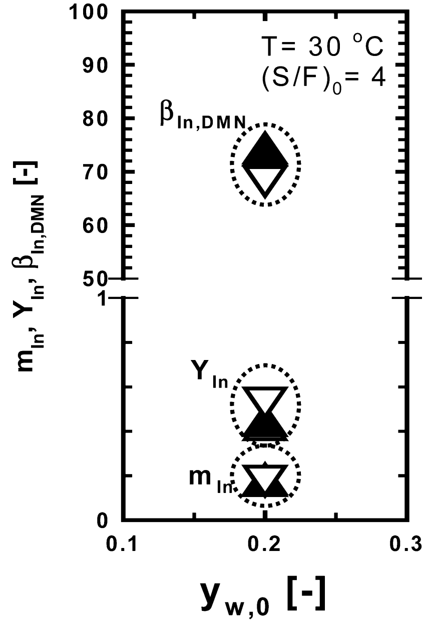

Figure 7. Comparison of separation efficiencies based on composition of feed. Keys: △ feed A, ▲ Feed B, ▽ Feed C.

From the results of this work for the effect of the extraction parameters on the yield and the selectivity of *NHCs*, the extraction operation using an aqueous solution of formamide as the extraction solvent seemed to be the optimal method for recovering of *NHCs* in coal tar fraction.

CONCLUSION

The separation of *NHCs* (particularly, indole) from a model mixture prepared according to the components and compositions contained in coal tar fraction (the temperature ranges of fraction: 240–265°C) was examined by a solvent extraction. The following conclusions resulted from the present examination.

1. The distribution equilibrium between a model mixture and the extraction solvent was measured with eight kinds of solvents (an aqueous solution of methanol, ethanol, iso-propyl alcohol, N,N-dimethyl acetamide, DMF, formamide, N-methylformamide/methanol, and formamide/methanol). An aqueous solution of formamide was found to be suitable for separating *NHCs* contained in coal tar fraction. At $(S/F)_0 = 4$, the yield of indole and selectivity of indole in reference to *DMN* measured by using an aqueous solution of formamide as solvent were 41.1% and 33.3, respectively.

2. The effect of operation factors on recovering *NHCs* was investigated by the distribution equilibrium using an aqueous solution of formamide as solvent. Increasing the operation temperature and $(S/F)_0$ resulted in improving the yield of *NHCs*, but increasing $y_{w,0}$ resulted in deteriorating the yield of *NHCs*. With increasing $y_{w,0}$ and $(S/F)_0$, the selectivity of *NHCs* in reference to *DMN* increased sharply. Increasing operation temperature resulted in decreasing the selectivity of each *NHC* in reference to *DMN*.
3. At an experimental condition fixed, the distribution equilibrium was measured by using three kinds of model feeds consisting of different composition. Independently of feed used, the distribution coefficient, yield, and selectivity in reference to *DMN* for each *NHC* agreed fairly well.
4. At an experimental condition fixed, the sequence of the distribution coefficient, yield, and selectivity in reference to *DMN* for each *NHC* was $In > iQ > Q > Qu$ and, also the sequence of the distribution coefficient, yield for each component of *BAC* was $1MN > 2MN > DMN$. The sequence of the distribution coefficient, yield for all components of this work was $In > iQ > Q > Qu > Bp > 1MN > 2MN > Pe > DMN$.
5. Independently of the extraction conditions, it was difficult to separate the isomer component because the selectivity of the isomer component (*Q* and *iQ*, *1MN* and *2MN*) in reference to *DMN* was roughly equal to 1. The selectivity of two kinds of *BAC* and *Pe* in reference to *DMN* was roughly equal.

ACKNOWLEDGMENTS

This work was supported by grant No. R01-2003-000-11750-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

REFERENCES

1. Yamamoto, Y., Sato, Y., Ebina, T., Yokoyama, C., Takahasi, S., Mito, Y., Tanabe, H., Nishiguchi, N., and Nagaoka, K. (1991) Separation of high purity indole from coal tar by high pressure crystallization. *Fuel*, 70: 565–566.
2. Uemasu, I. and Nakayama, T. (1989) Concentration of indole in coal tar using α-cyclodextrin as the host for inclusion complexation. *J. Inclus. Phenom. Molec. Recogn. Chem.*, 7: 327–331.
3. Uemasu, I. (1991) Effect of methanol-water mixture solvent on concentration of indole in coal tar using α-cyclodextrin as complexing agent. *Sekiyu Gakkaishi*, 34 (4): 371–374.
4. Fei, Y.Q., Sakanishi, K., and Sun, Y.N. (1990) Concentration of pyrroles and phenols from coal tar pitch by organic solvent extraction. *Fuel*, 69 (2): 261–262.
5. Mochida, I., Fei, Y.Q., and Sakanishi, K. (1990) Capture and recovery of basic nitrogen species in coal tar pitch, using nickel sulfate as adsorbent. *Chem. Lett.*, 515–518.

6. Ukegawa, K., Matsumura, A., Kodera, Y., Kondo, T., Nakayama, T., Tanabe, H., Yoshida, S., and Mito, Y. (1990) Solvent extraction of nitrogen compounds from a coal tar fraction (Part I) Effect of extraction conditions on the extraction rate and the selectivities of nitrogen compounds. *Sekiyu Gakkaishi*, 33 (4): 250–254.
7. Egashira, R. and Nagai, M. (2000) Separation of nitrogen heterocyclic compounds contained in coal tar absorption oil fraction by solvent extraction. *Sekiyu Gakkaishi*, 43 (5): 339–345.
8. Egashira, R. and Salim, C. (2001) Solvent extraction of nitrogen heterocyclic compounds contained in coal tar absorption oil fraction—Improvement of separation performance by addition of aluminum chloride to solvent. *Sekiyu Gakkaishi*, 44 (3): 178–182.
9. Kodera, Y., Ukegawa, K., Mito, Y., Komoto, M., Ishikawa, E., and Nagayama, T. (1991) Solvent extraction of nitrogen compounds from coal liquids. *Fuel*, 70 (6): 765–769.
10. Kim, S.J., Kim, S.C., and Kawasaki, J. (2001) A scale-up of stirred tank contactors for the liquid membrane permeation of hydrocarbons. *Sep. Sci. Techno.*, 36 (16): 3585–3598.