

회분 병류 5단 평형추출에 의한 모델 콜타르 유분 중에 함유된 Indole의 분리 및 회수

김수진[†] · 전용진 · 정화진*

청운대학교 신소재응용화학과, *청운대학교 패션섬유공학과
(2006년 9월 11일 접수, 2007년 3월 7일 채택)

Separation and Recovery of Indole from Model Coal Tar Fraction by Batch Cocurrent 5 Stages Equilibrium Extraction

Su Jin Kim[†], Yong Jin Chun, and Hwa Jin Jeong*

Department of Materials Science and Applied Chemistry, Chungwoon University, Hongsung-Gun, Chungnam, Korea

*Department of Fashion & Textile Engineering, Chungwoon University, Hongsung-Gun, Chungnam, Korea

(Received September 11, 2006; accepted March 7, 2007)

The separation of indole from a model mixture comprising four kinds of nitrogen heterocyclic compounds [indole (*In*), quinoline (*Q*), iso-quinoline (*iQ*), quinaldine (*Qu*)], three kinds of bicyclic aromatic compounds [1-methylnaphthalene (*IMN*), 2-methylnaphthalene (*2MN*), dimethylnaphthalene (*DMN*)], biphenyl (*Bp*) and phenyl ether (*Pe*) was examined by batch cocurrent 4 stages equilibrium extraction. The model mixture used as a raw material in this work was prepared according to the components and compositions contained in coal tar fraction (the temperature ranges of fraction: 240~265 °C). An aqueous solution of formamide was used as a solvent. Indole was recovered more than 99% through 4 stages of the equilibrium extraction. The range of selectivity of indole in reference to *DMN* obtained through the 5 stages equilibrium extraction was found to be 63~118. The process for separation and recovery of indole contained in coal tar was studied by using the experimental results obtained from this work and the previous work.

회분 병류 5단 평형추출에 의해 4종류의 질소고리화합물[indole(*In*), quinoline(*Q*), iso-quinoline(*iQ*), quinaldine(*Qu*)], 3종류의 2환 방향족화합물[1-methylnaphthalene(*IMN*), 2-methylnaphthalene(*2MN*), dimethyl naphthalene(*DMN*)], biphenyl과 phenyl ether로 구성된 모델 혼합물로부터 *In*의 분리를 검토했다. 본 연구의 원료로서 사용된 모델 혼합물은 콜타르 유분(유출온도범위: 240~265 °C)을 구성하고 있는 성분 및 조성을 고려하여 작성했다. 추출용매로서는 Formamide 수용액을 사용했다. 4단 평형추출을 통해 *In*을 99% 이상 회수할 수 있었다. 5단 평형추출을 통해 얻어진 *DMN*을 기준성분으로 한 *In*의 선택도는 63~118의 범위를 나타냈다. 본 연구를 통해 얻어진 실험적 결과와 이전의 연구결과를 이용하여 콜타르 중에 함유된 *In*의 분리 및 회수공정을 검토했다.

Keywords: coal tar, nitrogen heterocyclic compounds, indole, solvent extraction, batch cocurrent multistage equilibrium extraction

1. Introduction

Coal tar contains a lot of valuable nitrogen heterocyclic compounds (*NHC*), including indole that is focused as an intermediate for fine chemicals such as medicine, perfume and agricultural chemicals. Therefore, the separation and purification of valuable hetero compound such as indole contained in 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[1] etc.) 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, 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

[†] 주 저자 (e-mail: sujkim@chungwoon.ac.kr)

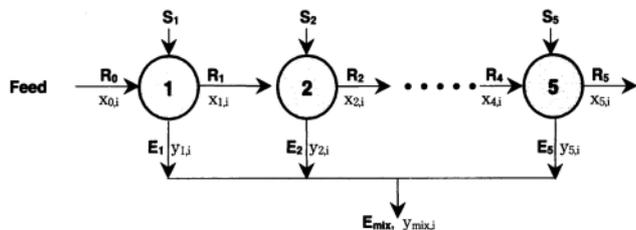


Figure 1. Experimental method of batch cocurrent 5 stages equilibrium extraction.

Table 1. Material Systems and Experimental Conditions for Batch Cocurrent Equilibrium Extraction

System	
Feed	a model mixture
Solvent	an aqueous solution of formamide
Experimental conditions	
Contact time, t (hr)	0.25 ~ 3
Impeller speed, N (s ⁻¹)	5
Number of equilibrium extraction, n(-)	1 ~ 5
Operation temperature, T (°C)	30
Volume of liquid, (m ³)	0.002
Volume fraction of water in solvent at initial, y _{w,0} (-)	0.2
Volume ratio of solvent to a raw material at initial, S ₁ /R ₀ (-)	4

view, because of low selectivity of indole.

In the previous work[10], we investigated the distribution equilibrium between a model coal tar fraction and 8 kinds of extraction solvent (an aqueous solution of methanol, ethanol, iso-propyl alcohol, N,N-dimethylacetamide, N,N-dimethylformamide (DMF), formamide, N-methylformamide/methanol and formamide/methanol). In the case of an aqueous solution of formamide, the balance between yield of indole and selectivity of indole in reference to dimethylnaphthalene was suitable. Therefore, an aqueous solution of formamide was found to be an optimum solvent for extracting indole from a model coal tar fraction based on the distribution coefficient and selectivity. When use an aqueous solution of formamide as a solvent for extraction of indole contained in a model coal tar fraction, we, also, thought that can recover solvent easily by distillation because difference of boiling point of the model coal tar fraction (b.p.: 240~265 °C) and formamide (b.p.: 210 °C) is big enough.

In the present study, the batch cocurrent 5 stages equilibrium extraction has been used for the separation and recovery of indole from a model mixture the same as the present work comprising 4 kinds of NHC [quinoline (Q), iso-quinoline (iQ), indole (In), quinaldine (Qu)], 3 kinds of bicyclic aromatic compounds [1-methylnaphthalene (IMN), 2-methylnaphthalene (2MN), dimethylnaphthalene (DMN)], biphenyl (Bp) and phenyl ether (Pe). The model mixture used as a raw material of this work was prepared by references[1,2,6]. An aqueous solution of formamide used as a solvent. The process for separation and recovery of In contained in coal tar was studied by using the experimental results obtained from this work and the previous work[10].

2. Experimental Apparatus and Method

A batch-stirred tank[11] (15 cm I.D. and 15 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.

The experimental method for cocurrent contact is shown in Figure 1. Formamide was mixed with city water to make a solvent of normal concentration. An aliquot of a solvent was charged to the batch-stirred tank and heated to the experimental temperature. After the solvent reached an experimental temperature, an aliquot of a raw material, kept at the experimental temperature, was added into it. They were stirred for a specified period, and then reached equilibrium. After reaching the equilibrium, the mixture was settled for an aliquot of time and the raffinate phase and the extract phase were split a separatory funnel. The raffinate phase split and a new aqueous solution of formamide were used as a raw material and a solvent of the next stage, respectively. Irrespective of number of stage, 1,600 mL solvent was charged to the batch-stirred tank.

The raffinate phases and the extract phases resulting from equilibrium extraction of each stage were analyzed by adding acetone, and their compositions were determined. The analysis of the raffinate phase and the extract phase was 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, N₂; flow rate, 1 mL/min; injection port temperature, 150 °C; sample size, 1 μL; splitting ratio, 100: 1; FID; column temperature, 120 °C for 25 min, then increased at 3 °C/min to 200 °C.

Experimental conditions and material systems used this work were summarized in Table 1. A model mixture and an aqueous solution of formamide were used a raw material and a solvent, respectively. The volume fraction of water in a solvent at initial (y_{w,0}), the volume ratio of the solvent to model mixture at initial (S₁/R₀), the operation temperature (T) and the impeller speed (N) were fixed in this work according to results of the previous work[10]. The composition of the model mixture is listed in Table 2. In the model mixture, the sum concentration of 4 kinds of NHC and that of 3 kinds of bicyclic aromatic compounds were about 18.62 wt% and 69.55 wt%, respectively. The model mixture, Also, 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, IMN, 2MN, DMN, Bp and Pe were used without further purification.

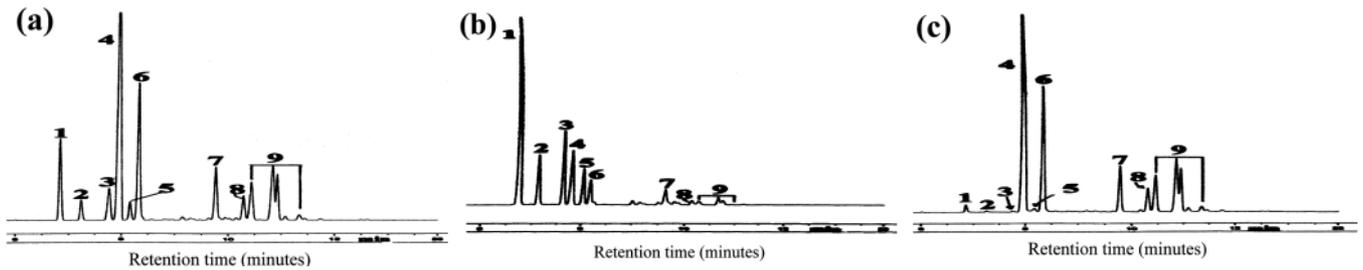
3. Results and Discussion

3.1. Gas Chromatogram

Figure 2(a) through (c) shows the gas chromatograms of the model mixture[10], the extract phase ($\sum_{n=1}^4 E_n$) and the raffinate phase (R₄) without a solvent resulted from 4 stages equilibrium extraction using

Table 2. Compositions of a Model Mixture[10]

Group	Compound	Composition (wt%)
Nitrogen heterocyclic compounds (<i>NHC</i>)	Quinoline (<i>Q</i>)	0.0918
	Iso-quinoline (<i>iQ</i>)	0.0236
	Indole (<i>In</i>)	0.0466
	Quinaldine (<i>Qu</i>)	0.0242
Bicyclic aromatic compounds (<i>BAC</i>)	1-Methylnaphthalene (<i>IMN</i>)	0.3181
	2-Methylnaphthalene (<i>2MN</i>)	0.1423
	Dimethylnaphthalene (<i>DMN</i>)	0.2351
Phenyl	Biphenyl (<i>Bp</i>)	0.0547
Ether	Phenyl ether (<i>Pe</i>)	0.0333
Others	Others	0.0303



Legend

1: quinoline (*Q*), 2: iso-quinoline (*iQ*), 3: indole (*In*), 4: 2-methylnaphthalene (*2MN*), 5: quinaldine (*Qu*), 6: 1-methylnaphthalene (*IMN*), 7: biphenyl (*Bp*), 8: phenyl ether (*Pe*), 9: dimethylnaphthalene mixture with ten structural isomers (*DMN*)

Figure 2. Gas chromatogram of (a) a model mixture, (b) an extract phase ($\sum_{n=1}^4 E_n$), and (c) the raffinate phase (R_n) without a solvent. Extraction conditions: $y_{w,0}$, 0.2; S_1/R_0 , 4; T , 30 °C.

the aqueous solution of formamide as a solvent and the component names of compounds identified. Though *DMN* of peak number 9 with ten structural isomers presented five peaks, they were summed and regarded as one component. When the gas chromatogram of the extract phase in Figure 2(b) was compared with that of a model mixture (Figure 2(a)), the peak heights of 4 kinds of *NHC* were considerably increased, but those of 3 kinds of bicyclic aromatic compounds (*BAC*), *Bp* and *Pe* were considerably decreased by 4 stages equilibrium extraction. In the extract phase, the sum concentration of 4 kinds of *NHC* and that of 3 kinds of *BAC* were about 80.16 wt% and 16.12 wt%, respectively. The extract phase, also, contained about 2.89 wt% of *Bp* and 0.82 wt% of *Pe*. The composition of *In* was 22.53 wt%. Figure 2(c) shows that the gas chromatogram of the raffinate phase was very different from that of the model mixture. Extracting 4 kinds of *NHC* by cocurrent 4 stages equilibrium extraction using the aqueous solution of formamide as a solvent resulted in decreasing the peaks of each *NHC*, and subsequently increasing those of 3 kinds of *BAC*, *Bp* and *Pe*. The gas chromatograms of the raffinate phase and the extract phase, it could be reconfirmed that the effect of the formamide extraction on the separation of *NHC* contained in the model mixture.

3.2. Batch Cocurrent 5 stages Equilibrium Extraction

3.2.1. Confirmation of Equilibrium Arrival Time

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 a model mixture at an identical condition were analyzed. 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.

3.2.2. Definition Equation

The distribution coefficient of component *i* at *n*th stage, $m_{n,i}$, the ratio of composition for component *i* in the extract phase to that in the raffinate phase obtained from *n*th stage, is defined as:

$$m_{n,i} = y_{n,i}/x_{n,i} \quad (1)$$

where $y_{n,i}$ and $x_{n,i}$, respectively, denote the mass fraction of component *i* in the extract phase and that in the raffinate phase after *n*th stage contact run.

Yield of component *i* at *n*th stage, $Y_{n,i}$, is defined as:

$$Y_{n,i} = \left(\sum_{n=1}^n E_n \times y_{n,i} \right) / (R_0 \times x_{0,i}) \quad (n=1,2,\dots, 5) \quad (2)$$

where $x_{0,i}$ denotes the mass fraction of component *i* in a raw material at initial. E refers to the mass of the extract phase after *n*th stage con-

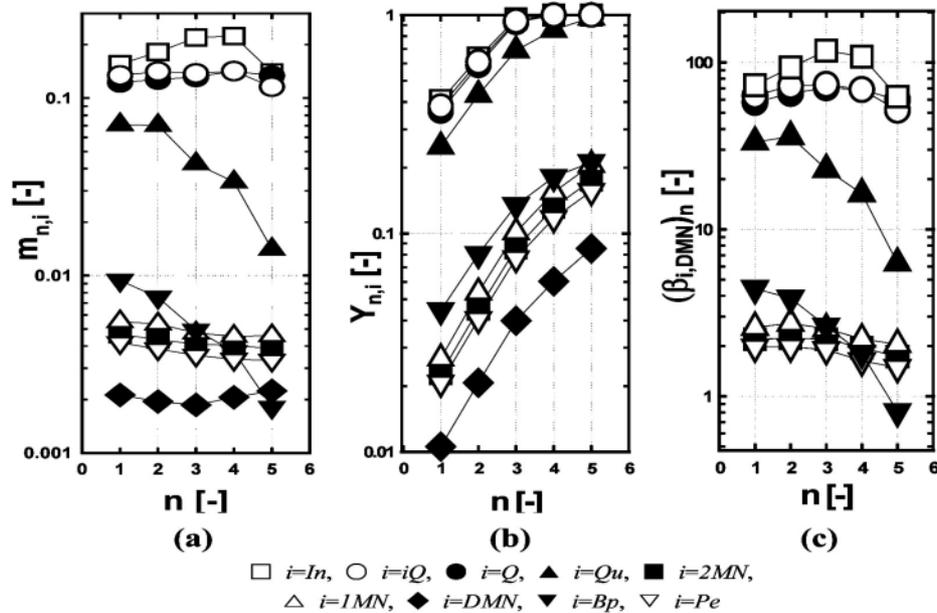
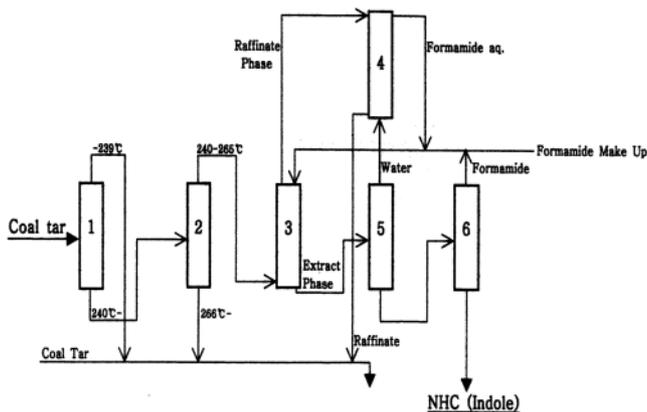


Figure 3. Changes of (a) the distribution coefficient, (b) the yield, and (c) the selectivity in reference to *DMN* based on number of equilibrium extraction. Extraction conditions: $y_{w,0}$, 0.2; S_1/R_0 , 4; T , 30 °C.



1, 2, 5: atmospheric distillation column, 3: extraction tower,
4: washing tower, 6: vacuum distillation column

Figure 4. Separation process of *NHC* (particularly, indole) from coal tar.

tact run. R_0 denotes the mass of a raw material at initial.

Selectivity of component i in reference to *DMN* at n th stage, $(\beta_{i,DMN})_n$, the ratio of the distribution coefficient for component i to that for *DMN*, was calculated from Equation (3).

$$(\beta_{i,DMN})_n = m_{n,i}/m_{n,DMN} \quad (3)$$

3.2.3. Equilibrium Extraction

Figure 3(a) through (c) show the change of the distribution coefficient of component i (m_i), the yield of component i (Y_i) and the selectivity of component i in reference to *DMN* ($(\beta_{i,DMN})_n$) based on number of cocurrent equilibrium extraction (n). The distribution coefficients of each *NHC* were much higher than those of 3 kinds of

BAC (*1MN*, *2MN*, *DMN*), *Bp* and *Pe*. This phenomenon indicated that the polarities of 4 kinds of *NHC* are much higher than those of 3 kinds of *BAC*, *Bp* and *Pe*. The distribution coefficient of *In*, also, was much higher than those of 3 kinds of *NHC* (*Q*, *iQ*, *Qu*). The distribution coefficients of *Qu* and *Bp* decreased sharply with increasing n , but the distribution coefficient of *In* increased inversely with increasing n to 4th stage. The distribution coefficients of *Q*, *Qu*, 3 kinds of *BAC* and *Pe* were almost fixed without regard to n . The reasons for above results are not yet clear. Explaining these results will require further study. The yield of each component increased sharply according to increase n . The sequence of the yield for each component, respectively, was $In > iQ > Q > Qu > Bp > 1MN > 2MN > Pe > DMN$. *In* was recovered more than 99% through 4 stages equilibrium extraction. The selectivity of *In* in reference to *DMN* was much higher than that of *Qu*, 3 kinds of *BAC*, *Bp* and *Pe*. The ranges of selectivity of *In* at $n=1 \sim 5$ were found to be 63-118. The selectivity of *Qu* and *Bp* decreased sharply with increasing n , but the selectivities of *1MN*, *2MN*, and *Pe* was observed almost 1-3, irrespective of n . Therefore, it was difficult to separate between *Pe* and *BAC*. From the investigation for separation efficiency of *NHC* based on n , the extraction operation using an aqueous solution of formamide as a solvent seemed to be optimal method for recovering of *NHC* (particularly, *In*) contained in coal tar fraction.

3.2.4. The Process for Separation and Recovery of Indole from Coal Tar

The process of the separation and recovery of *NHC* (particularly, indole) from coal tar was investigated using the results obtained from this work and the previous work[10]. As shown in Figure 4, the process proposed was composed of four distillation columns, one extraction column and one washing column. Column 1 and 2 were the atmos-

pheric distillation columns for recovering the fraction including indole of high concentration, column 3 the extraction column for separating between *NHC* and all others in the fraction. Column 4 was the washing column for recovering the raffinate, and column 5 was the atmospheric distillation column for recovering water in the extract phase. Column 6, also, was a vacuum distillation column for recovering formamide in the solvent.

4. Conclusion

The separation and recovery of indole from a model mixture prepared according to the components and compositions of fraction (the temperature ranges of fraction: 240~265 °C) obtained by fractional distillation of coal tar was examined by the batch cocurrent 5 stages equilibrium extraction using an aqueous solution of formamide as a solvent. The following conclusions resulted from the present examination.

1) Indole was recovered more than 99% through cocurrent 4 stages equilibrium extraction. The sequence of the yield for each component, respectively, was *In>iQ>Q>Qu>Bp>IMN>2MN>Pe>DMN*.

2) The ranges of selectivity of indole based on *DMN* at $n=1\sim 5$ were found to be 63~118.

3) The process of the separation and recovery of indole from coal tar was investigated using the results obtained from this work and the previous work. The process proposed was composed of four distillation columns, one extraction column and one washing column. The process proposed by this work is the new one, considering the separation efficiency of indole contained in coal tar, also, and the simple one without the re-extraction operation by using an aqueous solution of formamide

as the extraction solvent. Therefore, this proposed process would be a feasible process to recover indole from coal tar.

Acknowledgment

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. Y. Yamamoto, Y. Sato, T. Ebina, C. Yokoyama, S. Takahasi, Y. Mito, H. Tanabe, N. Nishiguchi, and K. Nagaoka, *Fuel*, **70**, 565 (1991).
2. I. Uemasu and T. Nakayama, *J. Inclusion Phenom. Molec. Recogn. Chem.*, **7**, 327 (1989).
3. I. Uemasu, *Sekiyu Gakkaishi*, **34**, 371 (1991).
4. Y. Q. Fei, K. Sakanishi, and Y. N. Sun, *Fuel*, **69**, 261 (1990).
5. I. Mochida, Y. Q. Fei, and K. Sakanishi, *Chem. Lett.*, 515 (1990).
6. K. Ukegawa, A. Matsumura, Y. Koder, T. Kondo, T. Nakayama, H. Tanabe, S. Yoshida, and Y. Mito, *Sekiyu Gakkaishi*, **33**, 250 (1990).
7. R. Egashira and M. Nagai, *Sekiyu Gakkaishi*, **43**, 339 (2000).
8. R. Egashira and C. Salim, *Sekiyu Gakkaishi*, **44**, 178 (2001).
9. Y. Koder, K. Ukegawa, Y. Mito, M. Komoto, E. Ishikawa, and T. Nagayama, *Fuel*, **70**, 765 (1991).
10. S. J. Kim, and Y. J. Chun, *Sep. Sci. Technol.*, **40**, 2095 (2005).
11. S. J. Kim, S. C. Kim, and J. Kawasaki, *Sep. Sci. Technol.*, **36**, 3585 (2001).