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

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(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 (1MN), 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 ℃). 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.

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 view.

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In the previous work[10], we investigated the distribution equilibrium, because of low selectivity of indole.

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

<table>
<thead>
<tr>
<th>System</th>
<th>a model mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental conditions</td>
<td>an aqueous solution of formamide</td>
</tr>
</tbody>
</table>

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, (m³) 0.002
Volume fraction of water in solvent at initial, y_{w,0} (-) 0.2
Volume ratio of solvent to raw material at initial, S₁/R₀(-) 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 solvents easily by distillation because difference of boiling point of each solvent is big enough.

Table 2. Results of the previous work[10].

<table>
<thead>
<tr>
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In this work, commercial reagent grade formamide was used as a raw material and 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 without further purification. 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 NHIC 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, Qh, 1MN, 2MN, 2MN, Dim, 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 (Rₐ) and the raffinate phase (Rₐ) without a solvent resulted from 4 stages equilibrium extraction using...
Table 2. Compositions of a Model Mixture[10]

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

Figure 2. Gas chromatogram of (a) a model mixture, (b) an extract phase \((\sum_{n=1}^{5} E_n)\), and (c) the raffinate phase (R4) without a solvent. Extraction conditions: \(y = 0.2; S = R = 4; T = 30 ^\circ C\).

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

3.1. Batch Cocurrent 5 stages Equilibrium Extraction
3.1.1. 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. 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:

\[
m_{n,i} = \frac{y_{n,i}}{x_{n,i}}
\]

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:

\[
Y_{n,i} = \sum_{n=1}^{5} E_n \times \frac{y_{n,i}}{(R_0 \times x_{0,i})}
\]

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\]

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: $y_{w,0} = 0.2$; $S/R_0 = 4$; $T = 30$ °C.

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

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

$t$ 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 form Equation (3).

$$(\beta_{i,DMN})_n = \frac{m_n,i}{m_n,DMN}$$

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 $n=1$ to 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>1MN>2MN>Pe>DMN.

2) The ranges of selectivity of indole based on DMN at n=1 ∼ 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