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Experimental Study on Enrichment of Indole in Wash Oil by a Combined Process of Extraction and Re-Extraction

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Abstract: Wash oil, one of the by-products of coal tar distillation, contains useful nitrogen heterocyclic compounds (NHC) such as indole (IN), which is used as a raw material for perfume, essential amino acid, and pharmaceuticals. In this study, as a pre-treatment step for purification of IN, which is about 5.75% contained in wash oil, the enrichment of IN in wash oil was examined by combining formamide extraction (FE) and n-hexane re-extraction (HRE). The raw material for the re-extraction was a mixture of the preceding formamide extract phase acquired through batchwise 5-stage co-current extraction trial under fixed FE condition. As the 5-stage FE and HRE progressed, the IN yield based on IN in the wash oil was approximately 73.3%, and the IN concentration in the raffinate oil acquired from the re-extraction run was highly enriched to about 92.4%. In addition, the IN enrichment efficiency of the FE-HRE combined process (FHC) employed in this study was compared with methanol extraction (ME)-hexane re-extraction (HRE) combination (MHC).

Keywords: indole; wash oil; extraction; re-extraction; enrichment combination



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1. Introduction

Wash oil, one of the by-products of coal tar distillation, contains useful nitrogen heterocyclic compound (NHC) such as indole (IN), which is used as a raw material for perfume, essential amino acid, and pharmaceuticals [1–7]. Therefore, if it is possible to separate and purify IN contained in wash oil used only as fuel, it is very meaningful in terms of resource utilization.

Although it depends on the manufacturer from which the wash oil is produced, wash oil used in this study contained approximately IN of 5.75%. From Table 1, we see that the boiling points of the various compounds present in the wash oil are almost the same, so separation between components through distillation operation is very difficult. From this fact, we think that the following multi-step procedure is required for purification of IN in wash oil: (i) The recovery of IN contained in wash oil by the solvent extraction method etc.; (ii) Enrichment of IN presenting in extract phase through distillation [6] or re-extraction method [3] etc.; (iii) The purification of IN using as a raw material, which are IN-enriched distillate acquired through distillation operation or IN-enriched raffinate recovered through re-extraction operation.

Until now, the separation of NHC contained in coal tar distillation by-products has been mainly achieved by reaction extraction using acid and base substances, but this separation method uses both a strong alkaline solution (e.g., NaOH) and an acidic solution (e.g., H₂SO₄) [8,9]. It has the disadvantage of being expensive, corroding the metal separation apparatus and seriously polluting the environment, and also complicating the separation process because the separation agent cannot be regenerated. Therefore, it is of great significance to find a novel alternative separation method that is simpler and more efficient than reactive extraction.

Table 1. Physical property and composition of each compound in feed.

Compound	Physical Property		Composition (wt%)	
	b.p. * [K]	m.p. ** [K]	Extraction	Re-Extraction
Naphthalene (<i>NA</i> , C ₁₀ H ₈)	491	351–353	0.960	0.013
Quinoline (<i>QU</i> , C ₉ H ₇ N)	511	257	1.379	0.157
Indole (<i>IN</i> , C ₈ H ₇ N)	526	325	5.753	0.993
2-Methylnaphthalene (<i>2MNA</i> , C ₁₁ H ₁₀)	514–515	307–309	53.251	0.391
1-Methylnaphthalene (<i>1MNA</i> , C ₁₁ H ₁₀)	513–516	251	21.854	0.165
Biphenyl (<i>BP</i> , C ₁₂ H ₁₀)	528	342	11.339	0.074
Others			5.464	98.207 (with solvent)

*: boiling point, **: melting point.

For the development of a novel separation method, until now the recovery and enrichment of *IN* contained in coal tar fraction was reviewed through separation operations, such as traditional extraction methods [1,3–6,10] using organic solvents, supercritical extraction [9,11,12], extraction using ionic liquids [2,7,13–18], and azeotropic distillation etc. The purification of *IN* using the *IN*-enriched distillate acquired by distillation operation of the extract oil was examined by purification operations such as crystallization [19], adsorption [20], and inclusion complexation [21,22].

In the previous study [3], we examined the recovery and enriching of *IN* in wash oil through methanol extraction (ME)-hexane re-extraction (HRE) combination (MHC) as a pre-treatment operation to purify 5.75% *IN* contained in the wash oil. As a result of the review, the solubility of *IN* is really excellent, but the selectivity is very low, so the concentration of *IN* (about 12.4 wt%) in the extract phase recovered by ME run was very low. In addition, when the extract phase finally acquired through ME run is distilled, methanol flows out as an overhead product, and water and extracted oil remain as bottom products. Therefore, in order to recover the extracted oil, a phase separation process for the bottom product is required. As the phase separation is added, the process for *IN* enrichment becomes more complicated. To solve the disadvantages of ME, that is, the low selectivity of *IN* and the complexity of the *IN* enrichment process, this study first examined the recovery of *IN* in wash oil by using formamide as the solvent, which shows relatively high selectivity of *IN* [1,5] and does not cause phase separation during distillation operation for solvent recovery. Next, the enrichment of *IN* by re-extraction was studied using extract phase which is acquired from formamide extraction (FE) as a raw material and n-hexane as a solvent, respectively. For this, we examined the effects of operation factors and conditions of FE and n-hexane re-extraction (HRE) on the enrichment of *IN*. Furthermore, we compared the experimental results of this study obtained by FE-HRE combination (FHC) with those of the previous study [3] obtained by MHC in terms of the enrichment efficiency of *IN*.

2. Experimental Method and Conditions

2.1. Equilibrium Extraction

In this study, equilibrium extraction of batch 1-stage and co-current 5-stage was performed by the same method as MHC in the previous study [3]. The formamide was mixed with tap water (electrical conductivity: 86 μ S/cm, pH: 7.3) to make a solvent of a certain concentration. In order to reach liquid-liquid equilibrium, the 1 L Erlenmeyer flask containing a constant volume of feed and fresh solvent was placed in a shaking water bath maintained at a constant temperature and shaken for a constant time. After equilibrium was reached, it was allowed to settle for a certain time, and the extract phase and the raffinate phase were separated using a 1 L separatory funnel, and then the masses of the two phases were measured. The raffinate phase separated from each stage and a fresh solvent were

used as the feed and a solvent of the next stage, respectively. The analysis conditions of two phases by the gas chromatography (GC) are shown in Table 2. The concentration of each compound contained in the two phases was determined using a calibration curve for each compound obtained using six standard reagents, which were selected considering the constituent compounds of wash oil [3].

Table 2. Equipment and conditions of analysis by gas chromatography (GC).

Gas Chromatograph	HP 6890 (Hewlett Packard Co., Palo Alto, CA, USA)
Column	Capillary column HP-1
length [m]	60
inner diameter [mm]	0.32
film [μm]	0.25
Carrier gas	N_2
split ratio [-]	0.025
flow rate in column [mL/min]	2
Sample volume [μL]	1
Injection temperature [K]	523
Column temperature [K]	383–593
temperature program [K/min]	0 (for 0–3 min) 5 (383–523 K) 14 (523–593 K)
Detector (FID) temperature [K]	593

Table 3 shows the material systems and experimental conditions. Wash oil (provided by OCI Company Ltd., Seoul, Republic of Korea), and the raffinate phases which recovered from each stage run, were used as feed for extraction operation, and aqueous formamide solution was used as extraction solvent. The volume fraction of water in solvent in initial ($y_{w,0}$), the volume ratio of solvent to feed in initial (E_0/R_0 , E_0 and R_0 : volume of fresh solvent and feed put into $n = 1$), the stage number of batch co-current equilibrium extraction (n), and the shaking time (t) were changed, the temperature (T) and the volume of solvent added to each stage (E_0 – E_4) were fixed.

Table 3. Material systems and experimental conditions.

Equilibrium Extraction	Equilibrium Re-Extraction	
Feed: wash oil or raffinate phase *	<i>MFEP</i> ** or raffinate phase ***	
Solvent: aqueous solution of formamide	n-hexane	
Shaking time, t (h)	72	72
Stage number of batch co-current Equilibrium extraction, n (-)	1–5	1–5
Temperature, T (K)	303	303
Volume of fresh solvent (E_0 – E_4), (mL)	320	320
Volume fraction of water in solvent in initial, $y_{w,0}$ (-)	0.1–0.3	–
Volume ratio of solvent to feed in initial, E_0/R_0 (-)	0.5–3	0.5–3

* raffinate phase acquired from FE run of each stage, ** mixed formamide extract phase (*MFEP*, $\sum_{n=1}^5 E_n$), which is a mixture of each formamide extract phase acquired from FE run of each stage, *** raffinate phase acquired from HRE run of each stage.

All experimental data acquired from extraction and re-extraction operation of this study were obtained by performing the experiment only once, rather than repeating it 2–3 times under the same conditions.

2.2. Equilibrium Re-Extraction

Liquid-liquid equilibrium was reached in the same method as the above-mentioned FE using a certain amount of raw materials and a fresh solvent, and then separated into a raffinate phase and an extraction phase. The analysis conditions of two phases by GC were the same as the FE described above (see Table 2).

Material system and experimental conditions are shown in Table 3. A mixed formamide extract phase ($MFEP, \sum_{n=1}^5 E_n$), which is a mixture of each extract phase acquired from FE run of each stage ($n = 1-5$), and *n*-hexane were used as feed and solvent, respectively. T, t , and E_0-E_4 were fixed, E_0/R_0 and n were varied in this study.

3. Results and Discussion

3.1. Calculation Formula

In extraction and re-extraction, the distribution coefficient of compound i ($m_{i,n}$) was calculated using Equation (1).

$$m_{i,n} = y_{i,n}/x_{i,n} \quad (n = 1-5) \quad (1)$$

$x_{i,n}$ and $y_{i,n}$ in Equation (1), respectively, represent the mass fraction of component i in a raffinate phase and an extract phase which acquired at the n th stage.

The yield of IN ($Y_{IN,5}$) in FE run of $n = 5$ was calculated using the Equation (2).

$$Y_{IN,5} = \sum_{n=1}^5 E_n \times y_{IN,n} / (R_0 \times x_{IN,0}) \times 100\% \quad (n = 1-5) \quad (2)$$

$x_{IN,0}$ and R_0 represent the mass fraction of IN in wash oil, and the mass of wash oil, respectively. Additionally, E_n and $y_{IN,n}$ denote the mass of the extract phase and the mass fraction of IN in the extract phase acquired from the n th stage extraction, respectively.

$Y_{IN,5}$, the yield of IN obtained after HRE run of $n = 5$, was calculated using the Equation (3).

$$Y_{IN,5} = (R_5 \times x_{IN,5}) / (R_0 \times x_{IN,0}) \times 100\% \quad (n = 1-5) \quad (3)$$

in the denominator of Equation (3), R_0 and $x_{IN,0}$ represent the mass of the wash oil and the mass fraction of IN in the wash oil, respectively. In addition, R_5 and $x_{IN,5}$ in the numerator, respectively, represent the mass of the raffinate phase acquired from the 5th re-extraction run and the mass fraction of IN presenting in the raffinate phase.

The selectivity of compound i in reference to 2-methylnaphthalene (2MNA) or IN acquired from each operation of the n th stage, $(\beta_{i,2MNA})_n$ or $(\beta_{i,IN})_n$, were calculated using the following equation, respectively.

$$(\beta_{i,2MNA})_n = m_{i,n}/m_{2MNA,n}, \quad (\beta_{i,IN})_n = m_{i,n}/m_{IN,n} \quad (n = 1-5) \quad (4)$$

where $m_{i,n}$, $m_{2MNA,n}$, and $m_{IN,n}$ represent the distribution coefficients of compound i , 2MNA, and IN obtained from each operation of the n th stage, respectively.

3.2. Equilibrium Extraction

3.2.1. GC Chromatogram of Wash Oil (Extraction Feed)

Figure 1a shows the GC chromatogram of wash oil and the names of the identified compounds [3]. We have added a small amount of six standard reagents purchased from Sigma Aldrich Korea, Seoul, Republic of Korea, one compound each, to the wash oil and accurately identified each compound presented in the wash oil based on the change in height of the GC chromatogram peak. From identification by GC, we found that wash oil contained 2MNA, 1-methylnaphthalene (1MNA), and biphenyl (BP) in large amounts

compared to naphthalene (*NA*), quinoline (*QU*), and *IN*. Table 1 shows the composition of the quantified compounds. The composition of *IN* was about 5.75%.

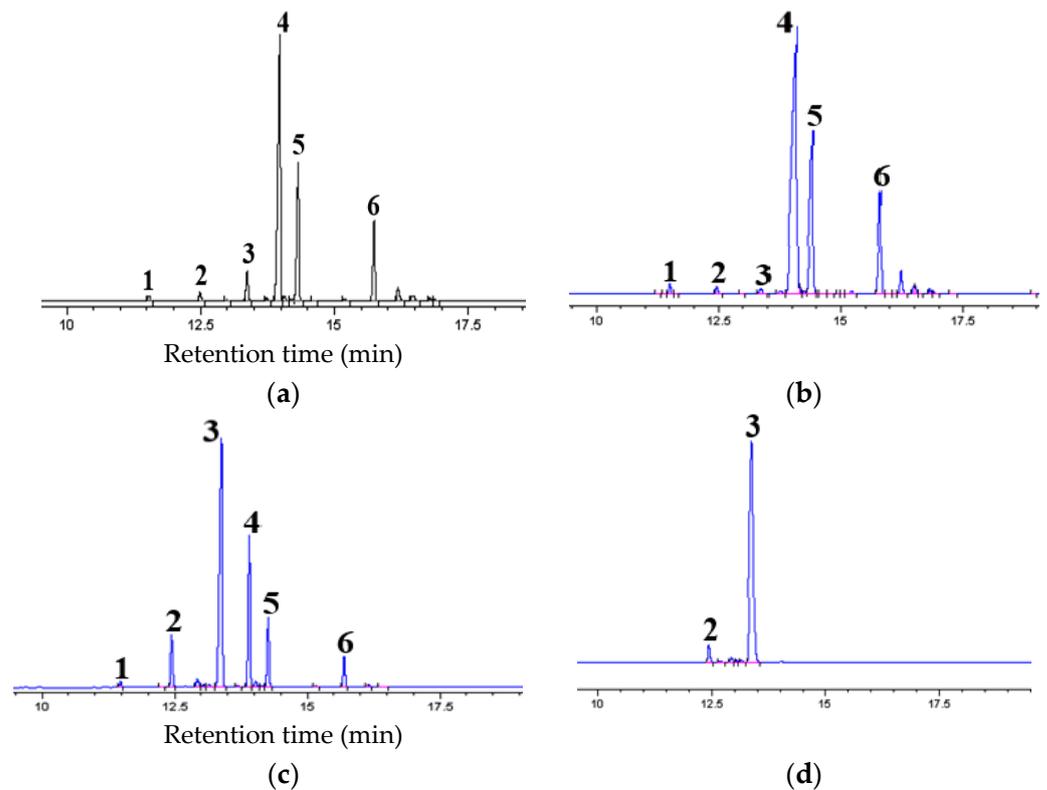


Figure 1. GC chromatograms of (a) wash oil [3], (b) raffinate phase (R_5) acquired from FE run of $n = 5$, (c) *MFEP* ($\sum_{n=1}^5 E_n$, re-extraction feed), (d) raffinate phase (R_5) acquired from HRE run of $n = 5$ using *MFEP* as feed. Extraction conditions: $n = 1-5$, $y_{w,0} = 0.1$, $E_0/R_0 = 1$, $T = 303$ K, $t = 72$ h; Re-extraction conditions: $n = 1-5$, $E_0/R_0 = 0.5$, $T = 303$ K, $t = 72$ h. Peak number 1: *NA*, 2: *QU*, 3: *IN*, 4: *2MNA*, 5: *1MNA*, and 6: *BP*.

3.2.2. Confirmation of Equilibration Time

Although the figure was omitted, the two phases obtained from contact between the feed and fresh solvent (shaking times 24, 48, 72, and 96 h) were analyzed to confirm the time taken to reach equilibrium. Regardless of shaking time and operation, the compositions of the two phases acquired contacting 72 and 96 h were almost identical. For this reason, all experiments in this study were performed with the shaking time maintained at 72 h.

3.2.3. Recovery Performance of *IN*

Figure 2a,b, respectively, show the solvent comparison results for the effect of $y_{w,0}$ on the distribution coefficient of compound i ($m_{i,1}$), the selectivity of compound i in reference to *2MNA* ($(\beta_{i,2MNA})_1$), the ratio of $m_{i,1}$ in ME run to FE run ($\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$) and the ratio of $(\beta_{i,2MNA})_1$ in FE run to ME run ($\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$) obtained in $n = 1$. The abbreviations FE and ME refer to the formamide extraction and methanol extraction, respectively. For comparison of solvents, the recovering performance data of *IN* obtained from a previous study [3] using methanol aqueous solution as an extraction solvent are added to this figure. For two solvents used, the $m_{i,1}$ and $(\beta_{i,2MNA})_1$ values of *2MNA* and *1MNA*, which are structural isomers, are almost identical in Figure 2a, so the keys of *2MNA* and *1MNA* overlap, the key of *2MNA* is not visible. Under the same $y_{w,0}$, the $m_{i,1}$ of two kinds of *NHC* was much higher when methanol, which is a greater polar than formamide, was used as the extraction solvent, but on the contrary, the $(\beta_{i,2MNA})_1$ when formamide was used was

much higher than that of methanol. Regardless of the extraction solvent, compared to *NA*, *1MNA*, *2MNA* and *BP*, $m_{i,1}$ of *NHC* with high polarity was much larger. Additionally, an increase in $y_{w,0}$ increased the polarity of the extraction phase, so $m_{i,1}$ of each compound decreased. Conversely, $(\beta_{i,2MNA})_1$ of two kinds of *NHC* decreased as $y_{w,0}$ decreased in the two solvents used. These results for each compound suggest that the selectivity of entire *NHC* based on entire bicyclic aromatic compound (*BAC*) contained in the wash oil may be very high. Consistent with the previously published methanol results [3], for each compound using formamide, $m_{i,1}$ and $(\beta_{i,2MNA})_1$ showed the order $IN > QU > NA > 1MNA = 2MNA > BP$. As predicted from the results of Figure 2a, we can see in Figure 2b that $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$ rapidly increase as $y_{w,0}$ decreases. In the range of $0.1 \leq y_{w,0} \leq 0.3$, we found that $(m_{i,1})_{ME}$ of all compounds was about 2 to 30.7 times greater than $(m_{i,1})_{FE}$, whereas $(\beta_{i,2MNA})_{1,FE}$ was about 1 to 9.8 times greater than $(\beta_{i,2MNA})_{1,ME}$. The $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$ of $i = IN$, which is the compound for recovery and enriching in this study, showed about 3.1 and 9.8 at $y_{w,0} = 0.1$ and about 2 and 3.9 at $y_{w,0} = 0.3$. Considering the balance between $m_{i,1}$ and $(\beta_{i,2MNA})_1$ of *IN*, the FE run of $y_{w,0} = 0.1$ was thought to be the most appropriate condition.

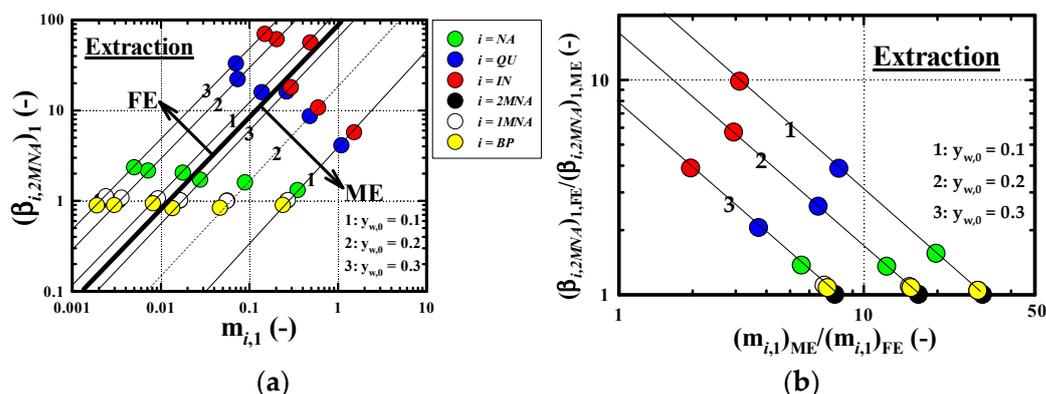


Figure 2. Solvent comparison for effect of $y_{w,0}$ on (a) $m_{i,1}$ and $(\beta_{i,2MNA})_1$, (b) $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$. FE: formamide extraction, ME: methanol extraction [3]. Experimental conditions: $n = 1$, $y_{w,0} = 0.1$ – 0.3 , $E_0/R_0 = 0.1$, $T = 303$ K, $t = 72$ h. Keys: *NA* naphthalene, *QU* quinoline, *IN* indole, *2MNA* 2-methylnaphthalene, *1MNA* 1-methylnaphthalene, *BP* biphenyl.

Figure 3a,b, respectively, present the solvent comparison results for the effect of E_0/R_0 on $m_{i,1}$ and $(\beta_{i,2MNA})_1$, $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$ obtained in $n = 1$. Irrespective of the solvent used, the effects of E_0/R_0 on $m_{i,1}$ and $(\beta_{i,2MNA})_1$ are not significant for all compounds. In addition, in $0.5 \leq E_0/R_0 \leq 3$, we found that $(m_{i,1})_{ME}$ for all compounds was about 2.5 to 30.7 times greater than $(m_{i,1})_{FE}$, whereas $(\beta_{i,2MNA})_{1,FE}$ was about 1 to 9.8 times greater than $(\beta_{i,2MNA})_{1,ME}$. The $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$ of $i = IN$, which is the compound for recovery and enriching in this study, showed about 2.5 and 9.3 at $E_0/R_0 = 0.5$ and about 3.2 and 9.8 at $E_0/R_0 = 3$. $E_0/R_0 = 1$ was thought the optimal condition for FE run when considering the recovery efficiency of *IN* per unit solvent volume.

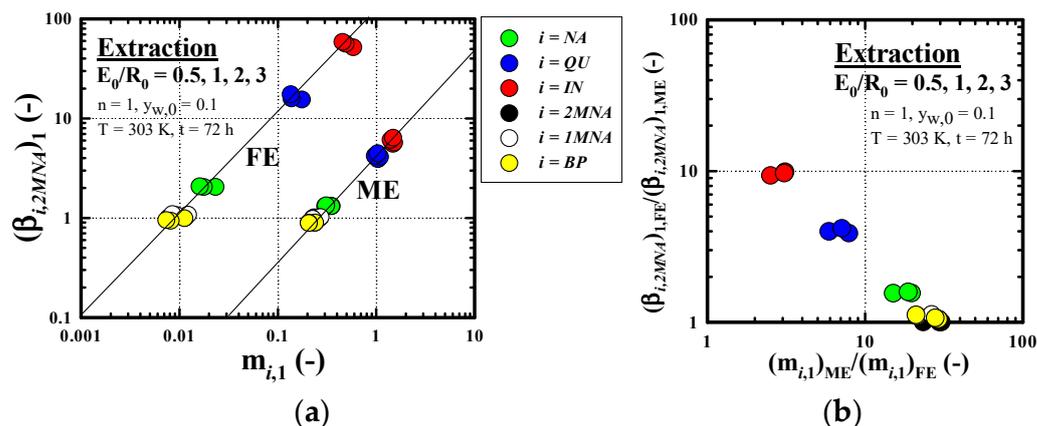


Figure 3. Solvent comparison for effect of E_0/R_0 on (a) $m_{i,1}$ and $(\beta_{i,2MNA})_1$, (b) $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$. FE: formamide extraction, ME: methanol extraction [3].

Figure 4a–c, respectively, show the solvent comparison results for the effect of n on $x_{i,n}$ (without solvent), $m_{i,n}$ and $(\beta_{i,2MNA})_n$, $\frac{(m_{i,n})_{ME}}{(m_{i,n})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{n,FE}}{(\beta_{i,2MNA})_{n,ME}}$ obtained in the n th FE run. The $n = 0$ shown in Figure 4a represents wash oil. Regardless of the solvent used, as n increases, large amounts of highly polar *NHC* transferred into the extract phase, resulting in a sharp decrease in the $x_{i,n}$ of *NHC* in the raffinate phase. In ME run of $n = 5$, the key did not appear because *IN* was not contained within R_5 . Conversely, except for *NHC*, *BAC* (*NA*, *2MNA*, *1MNA*) and *BP* showed almost constant $x_{i,n}$ values regardless of n and solvent. It is considered that this is the result of reflecting the content of each compound included in the wash oil [3]. In the range of $n = 1$ – 5 , $x_{IN,n}$ ($i = IN$) showed the ranges of about 0.73–3.93% in the case of FE and about 0–3.3% in the case of ME [3], respectively. Irrespective of the solvent used, improvement in wash oil quality is expected from $x_{IN,5}$. In addition, from Figure 4b,c, for all the compounds in this study, $m_{i,n}$ and $(\beta_{i,2MNA})_n$, $\frac{(m_{i,n})_{ME}}{(m_{i,n})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{n,FE}}{(\beta_{i,2MNA})_{n,ME}}$ show almost the same value regardless of used solvent and n , therefore, there is no considerable difference by using different solvents for the extraction. Furthermore, $\frac{(m_{i,n})_{ME}}{(m_{i,n})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{n,FE}}{(\beta_{i,2MNA})_{n,ME}}$ of *IN*, showed about 3 and 11 at the ranges of $n = 1$ – 5 .

The GC chromatogram of R_5 recovered through FE is presented in Figure 1b. As a result of comparing R_5 and wash oil, we found that the peaks of *QU* and *IN* were very small in R_5 , but the peak heights of other compounds were almost the same as those of wash oil. From this fact, we were able to reconfirm that the quality of wash oil (raffinate oil) was improved through FE run by confirming the reduction of *NHC* (*QU*, *IN*), undesirable impurities in wash oil due to their contribution to air pollution and unpleasant odors [12,14]. In addition, when the GC chromatogram of the *MFEP* in Figure 1c was compared with those of wash oil or R_5 , the peak heights of *NHC* in Figure 1c were much higher than that of wash oil or R_5 . From this result, it can be seen that FE is a very good solvent in terms of selective separation between the *NHC* (particularly *IN*) and the *BAC* and *BP* contained in the wash oil.

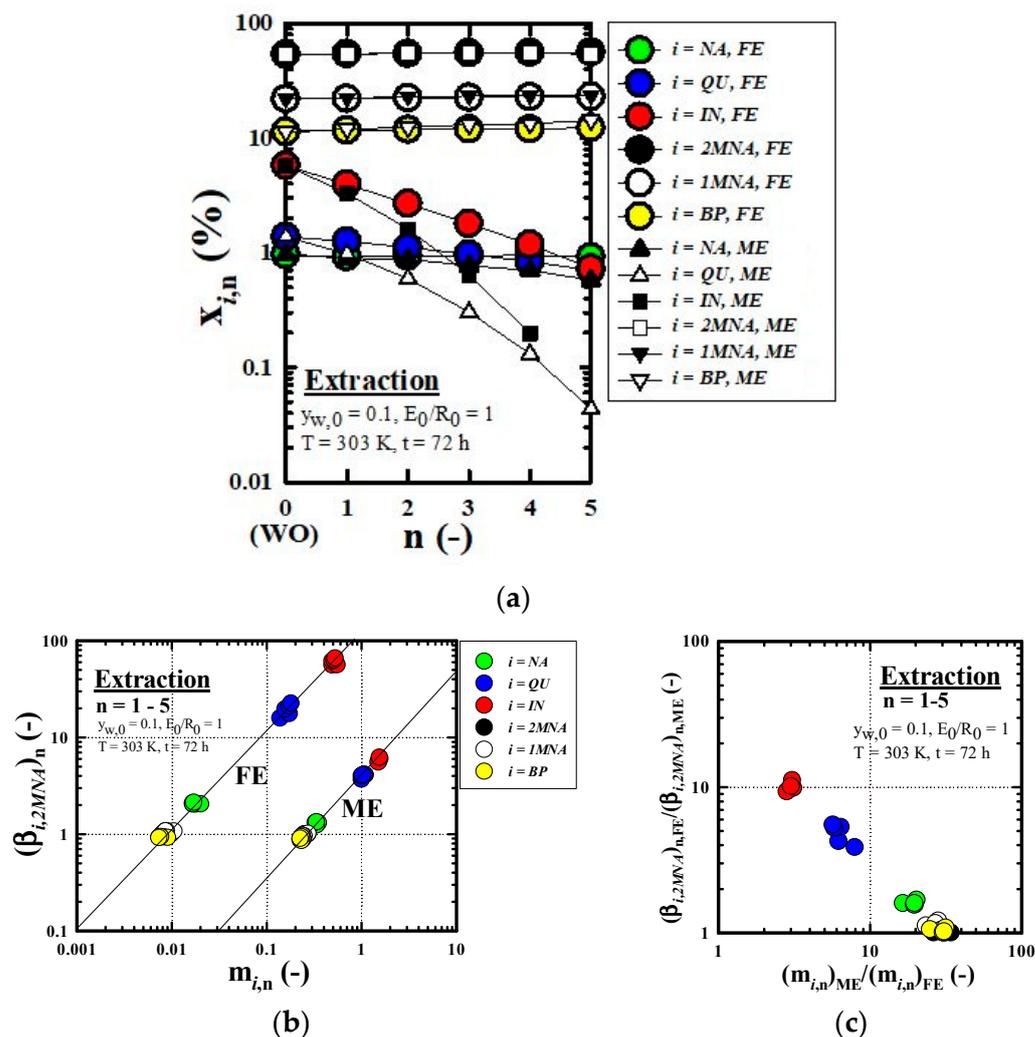


Figure 4. Solvent comparison for effect of n on (a) $x_{i,n}$ (without solvent), (b) $m_{i,1}$ and $(\beta_{i,2MNA})_1$, (c) $\frac{(m_{i,1})_{ME}}{(m_{i,1})_{FE}}$ and $\frac{(\beta_{i,2MNA})_{1,FE}}{(\beta_{i,2MNA})_{1,ME}}$. WO: wash oil, FE: formamide extraction, ME: methanol extraction [3].

3.3. Equilibrium Re-Extraction

3.3.1. GC Chromatogram of MFEP (Re-Extraction Feed)

A MFEP of above-mentioned Figure 1c was used as the feed. The composition of the MFEP including the extraction solvent is shown in Table 1. The concentration in feed of *IN*, the target compound for enrichment of this study, was approximately 1%.

3.3.2. Enrichment Performance of *IN*

Figure 5a,b, respectively, present the effect of E_0/R_0 and the re-extraction feed on $m_{i,1}$ and $(\beta_{i,2MNA})_1$, $\frac{(m_{i,n})_{MFEP}}{(m_{i,n})_{MMEP}}$ and $\frac{(\beta_{i,IN})_{1,MFEP}}{(\beta_{i,IN})_{1,MMEP}}$ obtained in $n = 1$. The abbreviations MFEP and MMEP refer to the mixed formamide and methanol extract phases used as feed, respectively. In Figure 5a, when MFEP was used as the feed, $x_{i,n}$ for four compounds except NHC did not appear in above $E_0/R_0 = 1$. This is because the concentration of the four compounds contained in the raffinate phase was too low to analyze under conditions of $E_0/R_0 = 1$ or higher. Irrespective of feed used from Figure 5a, contrary to the above-mentioned FE run, $m_{i,1}$ and $(\beta_{i,IN})_1$ of NHC showed much smaller values compared to BAC and BP. From this fact, it can be seen that compounds easily acquired from wash oil by FE run are enriched in raffinate phase by re-extraction. Therefore, contrary to the results of FE run, $m_{i,1}$ and $(\beta_{i,IN})_1$ of each compound showed the order $2MNA = 1MNA > BP > NA > QU > IN$. The effect of raw material type and E_0/R_0 on $m_{i,1}$ and $(\beta_{i,IN})_1$ was not differentiable for all compounds.

Through Figure 5b, for all compounds of the range of $0.5 \leq E_0/R_0 \leq 3$, $(m_{i,1})_{MFEP}$ was about 0.6 to 22 times greater than $(m_{i,1})_{MMEP}$ and $(\beta_{i,IN})_{1,MFEP}$ was 1 to about 21 times greater than $(\beta_{i,IN})_{1,MMEP}$. Since $m_{IN,1}$ ($i = IN$) showed the smallest value among the six components, it was found that IN was highly enriched in the raffinate phase. Considering the enrichment efficiency of IN per unit solvent volume, $E_0/R_0 = 0.5$ was thought to be the optimal condition for HRE run.

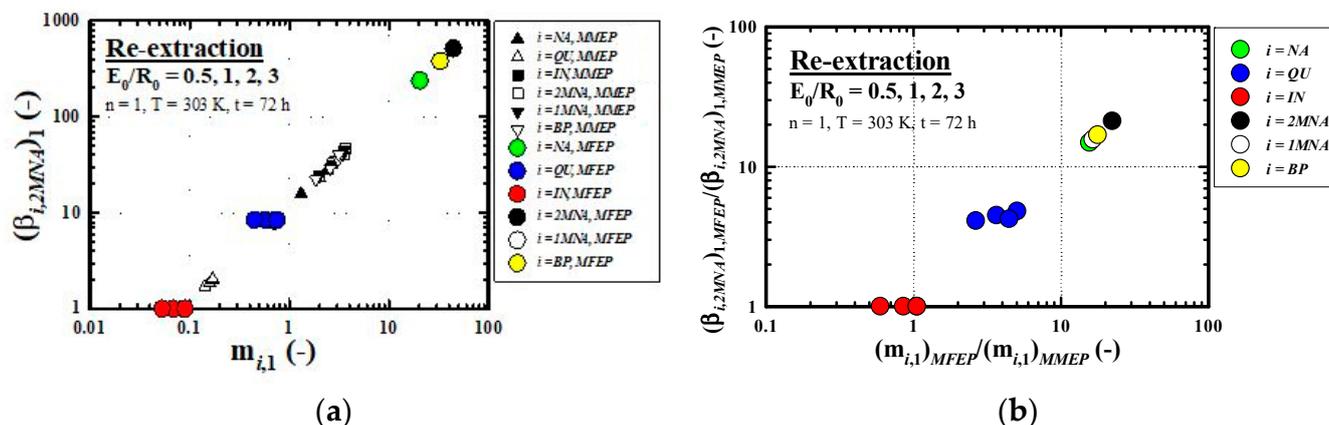


Figure 5. Effects of E_0/R_0 and re-extraction feed on (a) $m_{i,1}$ and $(\beta_{i,2MNA})_1$, (b) $\frac{(m_{i,1})_{MFEP}}{(m_{i,1})_{MMEP}}$ and $\frac{(\beta_{i,2MNA})_{1,MFEP}}{(\beta_{i,2MNA})_{1,MMEP}}$. MFEP: mixed formamide extract phase, MMEP: mixed methanol extract phase [3].

Figure 6a–c, respectively, show the effects of n and the re-extraction feed on $x_{i,n}$ (without solvent), $m_{i,n}$ and $(\beta_{i,IN})_n$, $\frac{(m_{i,n})_{MFEP}}{(m_{i,n})_{MMEP}}$ and $\frac{(\beta_{i,IN})_{n,MFEP}}{(\beta_{i,IN})_{n,MMEP}}$ obtained in the n th HRE run. The $n = 0$ shown in Figure 6a represents the re-extraction feed (REF). In the case of using MFEP, IN with strong polarity compared to the other five compounds are enriched in the raffinate phase, and it can be seen that the $x_{IN,n}$ ($i = IN$) increases as n increases. Conversely, the $x_{i,n}$ of the four compounds with strong hydrophobic properties, except NHC , decreased rapidly as n increased. In MFEP, $x_{i,n}$ for four compounds except for NHC did not appear after $n = 1$. This is the result of four compounds not being detected in the GC analysis of the raffinate phase recovered after $n = 1$. At $n = 5$, $x_{IN,n}$ ($i = IN$) was about 92.4% in MFEP and about 73.3% in MMEP, respectively. In Figure 6b,c, for all compounds in this study, $m_{i,n}$ and $(\beta_{i,IN})_n$, $\frac{(m_{i,n})_{MFEP}}{(m_{i,n})_{MMEP}}$ and $\frac{(\beta_{i,IN})_{n,MFEP}}{(\beta_{i,IN})_{n,MMEP}}$ show almost the same values regardless of the re-extraction feed used and n , so the effect of re-extraction feed and n is not considerable.

Figure 1d shows the GC chromatograms of R_5 recovered through the 5th re-extraction run with MFEP. Comparing Figure 1d with Figure 1c, which is the re-extraction feed, it can be seen that the four compounds except NHC (IN , QU) are almost absent in R_5 . Through this, we were able to reaffirm the feasibility of HRE run regarding the enrichment of IN present in the MFEP.

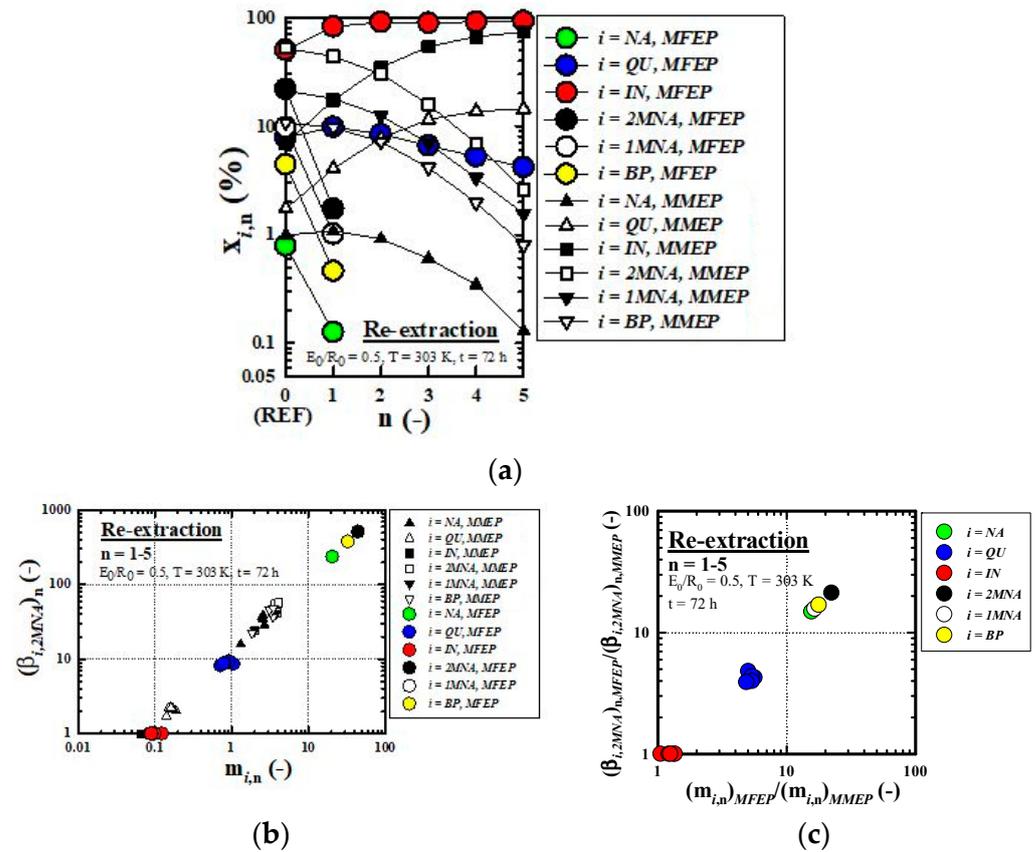


Figure 6. Effects of n and re-extraction feed on (a) $x_{i,n}$ (solvent-free), (b) $m_{i,n}$ and $(\beta_{i,2MNA})_n$, (c) $\frac{(m_{i,1})_{MFEP}}{(m_{i,1})_{MMEP}}$ and $\frac{(\beta_{i,2MNA})_{1,MFEP}}{(\beta_{i,2MNA})_{1,MMEP}}$. REF: re-extraction feed, MFEP: mixed formamide extract phase, MMEP: mixed methanol extract phase [3].

3.4. Comparison of Combined Enrichment Efficiency

Figure 7a,b respectively, present the yield ($Y_{IN,5}$) and concentration ($y_{IN,5}$) changes of *IN* by two types (FHC and MHC (3)) of enrichment combination after extraction and re-extraction run of $n = 5$. $Y_{IN,5}$ in each combination is based on the mass of *IN* contained in the wash oil, and this was calculated by Equations (2) and (3). $Y_{IN,5}$ by FHC and MHC decreased as enrichment run progressed, showing almost the same value (about 78%) regardless of the combination, but $y_{IN,5}$ conversely increased rapidly as enrichment run progressed by the two combinations. The concentration of *IN* in the wash oil was about 5.75%, but the $y_{IN,5}$ of the extract phase, which recovered by FE and ME of $n = 5$, was 50.1% and 12.4%, respectively. And the $y_{IN,5}$ of the raffinate phase (without solvent), which recovered by HRE of $n = 5$ was it showed high enrichment efficiency of 92.4% in the case of FHC and 73.3% in the case of MHC, respectively. Therefore, we evaluated FHC as a much more useful combination than MHC in terms of the enrichment efficiency of *IN* as well as the simplicity of enrichment process of *IN*. The enrichment efficiency of *IN* by FHC of this study showed really excellent results compared to the combination of FE and distillation [1], the combination of ME and distillation [6], and reaction extraction using acid and base [8,9].

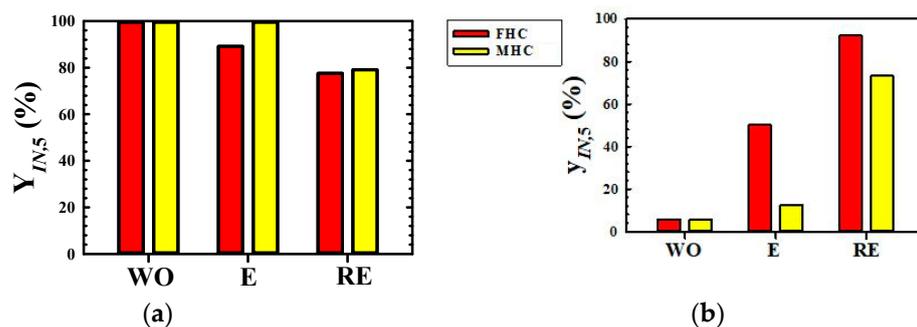


Figure 7. Comparison of enrichment combination for (a) $Y_{IN,5}$ and (b) y_{IN} of IN. WO: wash oil, E: extraction, RE: re-extraction, FHC: formamide-hexane combination, MHC: methanol-hexane combination [3]. Extraction conditions: $n = 1-5$, $y_{w,0} = 0.1$, $E_0/R_0 = 1$, $T = 303$ K, $t = 72$ h; Re-extraction conditions: $n = 1-5$, $E_0/R_0 = 0.5$, $T = 303$ K, $t = 72$ h.

4. Conclusions

To develop an efficient new process for high-purity purification of IN contained in wash oil, this study first experimentally investigated the enrichment performance of IN contained in wash oil by FHC, and then compared the results with those obtained by MHC previously reported. Yield of IN using FHC and MHC showed almost the same value, but the concentration of IN is significantly higher with FHC than with MHC. FHC adopted in this study was expected to be a more effective combination than MHC not only in terms of the enrichment efficiency of IN included in wash oil but also in terms of simplicity of the enrichment process. For high-purity purification of IN in wash oil, it is necessary to remove QU, etc. presenting as impurity in the 92.4% IN concentrate recovered from FHC of this study. Since the melting point difference between IN and QU is 68 K, the purification method using this melting point difference is expected to be highly feasible for further purification of IN. Therefore, we would like to report the research results on the high purity purification of IN in a future paper by adopting crystallization as a separation method using the melting point difference.

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