Separation of Model Petroleum Heavy Fraction by Equilibrium Extraction

Hiroaki HABAKI¹, Tomonori MASUDA² and Ryuichi EGASHIRA¹*

¹Department of Transdisciplinary Science and Engineering; ²Department of International Development Engineering, Tokyo Institute of Technology, 12-1, O-okayama-2-chome, Meguro-ku, Tokyo 152-8550, Japan

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For the separation of petroleum-derived heavy fractions by solvent extraction, the liquid-liquid equilibrium extraction of model heavy fractions, binary and multicomponent model oils, with aqueous methanol solutions was measured, and the effects of nitrogen heterocyclic and other coexisting compounds on the equilibrium extraction were studied. The distribution coefficient increased in the following order of the group compounds; alkanes, aromatics and heterocyclic compounds when the carbon numbers in the molecules of interest were same, and it decreased with an increase in the carbon number of the compound among the respective groups. The coefficients for indoles and quinolines were comparable, and those of carbazoles were smaller. The liquid-liquid equilibrium of nitrogen heterocyclic compounds with the multicomponent system was similar with that with the binary system, and the approximate trend of liquid-liquid equilibrium in the multicomponent system could be evaluated based on the results of simpler systems.

1. Introduction

Some nitrogen heterocyclic compounds are unfavorably contained in petro-derived fractions in the refinery process and cause deactivation of the catalysts used in the reforming and cracking processes. Although the concentrations of the heterocyclic compounds present in the heavy fractions were relatively low, the compounds in the product fuel oils will degrade the fuel oil quality and result in atmospheric pollution after their combustion. Thus, the removal of these heterocyclic compounds from the heavy fractions has been studied for the stable operation of the catalytic reaction and control of the quality of the fuel oil.

The solvent extraction technique is subject to considerable research as one of the promising separation methods, and some solvent extraction processes for the recovery or removal of aromatic compounds are fit for practical use, such as the Furfural Process [1], Udex Process [2], Arosolvan Process [3], Sulfolane Process [4], and so on. Methanol has also been studied as a potential solvent to recover nitrogen heterocyclic compounds from coal tar absorption oil [5-10]. The nitrogen heterocyclic compounds, such as indoles and quinolines, were selectively extracted relative to alkane or homocyclic compounds, and
the addition of water to the methanol solvent enhanced the separation selectivity of nitrogen heterocyclic compounds over homocyclic compounds.

This study aims at the separation of nitrogen heterocyclic compounds from petroleum-derived heavy fractions by solvent extraction. The liquid-liquid equilibrium extraction of model heavy fractions with aqueous solutions of methanol was measured, and the effects of species of heterocyclic and other coexisting compounds on the liquid-liquid equilibrium were studied with the model feeds of binary and multicomponent systems.

2. Experimental

The compounds used for the model feed mixtures in this study are summarized in Table 1. The nitrogen heterocyclic compounds, homocyclic compounds and alkanes were selected as objective components. The 3 types of nitrogen heterocyclic compounds, such as indoles, quinolines, and carbazoles, and 2 types of hydrocarbon compounds, such as aromatics and alkanes, were used, and totally 16 compounds were used to prepare the model feed oils. For each type of nitrogen heterocyclic compound, the number of carbon and nitrogen atoms in a component $i$, $n_{C_i}$, ranged from 9 to 15. All chemicals used were of analytical grade, purchased from Fujifilm Wako Pure Chemical Corporation.

| Compounds     | Indoles                                      | Quinolines                                  | Carbazoles                                | Hydrocarbons                  |
|---------------|----------------------------------------------|---------------------------------------------|-------------------------------------------|------------------------------|
| N hetero compounds | Indole ($n_{C_j} = 9$) | Quinoline ($n_{C_j} = 10$) | Carbazole ($n_{C_j} = 13$) | Aromatics                    |
|               | 2-Methyl indole ($n_{C_j} = 10$)             | 2-Methyl quinoline ($n_{C_j} = 11$)         | 9-Methyl carbazole ($n_{C_j} = 14$)       | Butyl benzene ($n_{C_j} = 10$) |
|               | 7-Ethyl indole ($n_{C_j} = 11$)              | 2,6-Dimethyl quinoline ($n_{C_j} = 12$)     | 9-Ethyl carbazole ($n_{C_j} = 15$)        | 1-Methyl naphthalene ($n_{C_j} = 11$) |
|               | 2,3-Dimethyl indole ($n_{C_j} = 11$)         | 4-Phenyl pyridine ($n_{C_j} = 12$)          |                                           |                              |
|               | 2-Phenyl indole ($n_{C_j} = 15$)             | Benzo[h]quinoline ($n_{C_j} = 14$)          |                                           |                              |
| Alkane        | n-Undecane ($n_{C_j} = 11$)                   |                                             |                                           |                              |

The experimental conditions are given in Table 2. Two types of model feed oils, binary and multicomponent model mixtures, were used. The binary model feed oil contained one each of a nitrogen heterocyclic and hydrocarbon compound, and the multicomponent model feed oil consisted of 11 nitrogen heterocyclic compounds, i.e. 5 indoles, 4 quinolines, and 2 carbazoles, and 1-methyl naphthalene. Aqueous solutions of methanol were used as the solvents, which have been reported to show favorable extraction
performance in the separation of coal tar absorption oil to recover nitrogen heterocyclic compounds [5-8]. The specified amounts of the feed oil and solvent were put in a conical flask and equilibrated by shaking. After equilibrium was achieved, the raffinate and extract phases were separated using a separatory funnel. The liquid phases were analyzed by gas chromatograph (Shimadzu GC-2010) to determine their compositions.

Table 2. Experimental conditions of liquid-liquid equilibrium.

| Feed | Binary model feed oils  
| N-heterocyclic compound and hydrocarbon  
| mass fraction of N-hetero: 0.01 – 0.2  
| mass fraction of hydrocarbon: 0.8 – 0.99  
| Multicomponent model feed oil (12 components)  
| mass fraction of each N-hetero: 0.01  
| mass fraction of 1-MN: 0.89 |
| Solvent | Aqueous solution of methanol  
| mass fraction of methanol: 0.8 – 1.0 |
| Mass of feed | [kg] | 0.02 |
| Mass ratio of solvent to feed | [-] | 1.0 |
| Operating temperature | [K] | 303 |
| Operating time | [h] | 48 |

3. Results and Discussion

When pure methanol was used as the solvent, the mixture of the binary feed oil and solvent formed a homogeneous phase in most cases, and the measurement of liquid-liquid equilibrium was impossible. Therefore, the results of the measurements would be hereafter presented wherein the mass fraction of methanol in the solvent was 0.8. Then, to confirm the attainment of the liquid-liquid equilibrium condition, the change of the compositions in both raffinate and extract phases along with the contacting time was measured with the binary system of feed oil; quinoline and 1-methyl naphthalene mixture. Both compositions of the raffinate and extract phases became constant after 24 hrs to attain the equilibrium condition, and the contacting time was set at 48 hrs for all the measurements to ensure the equilibrium condition. In all cases, the systems of feed and solvent mixtures were in the liquid-liquid two phase region. The phase separations were easily carried out, and none of the systems investigated in this study formed stable emulsions.

The distribution coefficient of component $i$, $m_i$, was defined as,

$$ m_i = \frac{y_i}{x_i} \quad (1) $$

where $x_i$ and $y_i$ are the mass fractions of component $i$ in the raffinate and extract phases, respectively. The separation selectivity of component $i$ relative to component $j$, $\beta_{i,j}$, was defined as,

$$ \beta_{i,j} = \frac{y_i}{x_i} \frac{x_j}{y_j} \quad (2) $$
Figure 1 shows the distribution coefficient of component $i$, $m_i$, with the binary model feed oils, where the solid lines represent the rough trends of $m_i$ by $n_{C,i}$. In most cases, $m_i$ for the nitrogen heterocyclic compounds decreased with an increase in $n_{C,i}$. The $m_i$s of indoles and quinolines were relatively high and comparable, followed by those of carbazoles and hydrocarbons. The $m_i$s of carazes with large $n_{C,i}$ were almost the same as those of 1-methyl naphthalene or butyl benzene. The $m_i$ for 1-methyl naphthalene was the largest among these hydrocarbons, followed by butyl benzene and undecane, i.e. $m_i$ of the hydrocarbon decreased with the number of rings in the hydrocarbon molecule. The $m_i$s of nitrogen heterocyclic compounds increased in the order of 1-methyl naphthalene, butyl benzene and undecane, which was the decreasing order of the number of rings in the hydrocarbon molecule. The feed oil containing alkane compounds at a higher level should be preferable to separate heterocyclic and other compounds.
Figure 2 shows the effects of the hydrocarbon compound on the separation selectivity of the nitrogen heterocyclic compound $i$ relative to the hydrocarbon compound $j$, $\beta_{i,j}$, with the binary model feed oils. Generally $\beta_{i,j}$ decreased as $n_{C,i}$ increased. The $\beta_{i,j}$s of indoles and quinolines were comparable, and were greater than those of carbazoles. The hydrocarbon compounds were so influential that the $\beta_{i,j}$s were much larger with undecane than those with other hydrocarbons. The maximum $\beta_{i,j}$ exceeded two thousand with undecane. The polarity of the hydrocarbon should have an influence on the distribution of the nitrogen heterocyclic compounds [10]. More polar hydrocarbon compounds should dissolve in the solvent phase and the other polar compounds of nitrogen heterocyclic compounds have limited solubilities. The solubility of a less polar hydrocarbon such as undecane was much smaller than the other hydrocarbon compounds and this could enhance the $\gamma$s of the nitrogen heterocyclic compounds, causing high separation selectivities. The $\beta_{i,j}$s of the nitrogen heterocyclic compounds of higher $n_{C,i}$ relative to the homocyclic compounds were close.
to unity. Thus, the separation of the feed containing such nitrogen heterocyclic and homocyclic compounds with a wide $n_{CJ}$ range should be difficult in this system. Therefore, it should be necessary to find a more effective solvent or employ a different method for the separation.

Figure 3 shows the effects of the mass fraction of quinoline in the extract phase, $y_Q$, on the $m_i$ of quinoline and 1-methyl naphthalene when $x_{Q,0}$ was varied from 0.01 to 0.2 with the binary model feed oils of quinoline–1-methyl naphthalene. Although the quinoline $m_i$ was independent of the composition of the extract phases, the $m_i$ of 1-methyl naphthalene increased with $y_Q$. This might be because the solubility of the less polar component, i.e. 1-methyl naphthalene, should be enhanced by dissolution of the other more polar component, i.e. quinoline, in the extract phase. This trend was also reported in the previous study [7].

![Figure 3. Effects of mass fraction of quinoline on distribution coefficient.](image)

Figure 4 shows the comparison of the extraction equilibrium with binary and multicomponent feed oils. For the binary feed oils, the mass fractions of nitrogen heterocyclic compounds were set at 0.01 (Binary 1: results shown in Figure 1) and 0.1 (Binary 2: quinoline - 1-methyl naphthalene mixture and one of the results shown in Figure 3). The mass fraction of the nitrogen heterocyclic compound in Binary 2 was almost the same as that in the multicomponent feed oil (0.11). The $m_i$ of nitrogen heterocyclic compounds measured with the multicomponent feed oil were approximately the same as those with both Binary 1 and Binary 2 feed oils. The $m_i$ of 1-methyl naphthalene with the multicomponent feed oil was slightly greater than those with the Binary 1 feed oils, and almost the same as that with the Binary 2 feed oil. The multicomponent feed oil contained more nitrogen heterocyclic compounds than that of the Binary 1 feed oil, and the mass fraction of total nitrogen heterocyclic compounds in the extract phase was larger with the multicomponent system than that with the Binary 1 feed oils. Then, as mentioned above, the $m_i$ of 1-methyl naphthalene might be enhanced due to the dissolution of other more polar components, such as nitrogen heterocyclic compounds, in the extract phase. On the other hand, the mass fraction of quinoline in the
Binary 2 feed oil was almost the same as that in the multicomponent feed oil and the m/s of 1-methyl naphthalene were same for both cases. The liquid-liquid equilibrium in the multicomponent system could be estimated roughly with the results measured in binary model feed oils in this range of measurement.

![Figure 4. Comparison of distribution coefficients between binary and multicomponent systems. Binary 1: nitrogen heterocyclic compound – 1-methyl naphthalene, mass fraction of nitrogen heterocyclic compound was 0.01 Binary 2: quinoline – 1-methyl naphthalene, mass fraction of quinoline was 0.1 Multicomponent: 11 nitrogen heterocyclic compounds – 1-methyl naphthalene mass fraction of each nitrogen heterocyclic compound was 0.01](image)

4. Conclusion

The liquid-liquid equilibria of nitrogen heterocyclic and hydrocarbon compounds were measured with binary and multicomponent model feed oils, in which three types of nitrogen heterocyclic compounds and three types of hydrocarbons were used. The distribution coefficient of each component decreased as the carbon number in the molecule increased. The coefficients of indoles and quinolines were comparable and larger than those of carbazoles, followed by those of aromatics and alkane. However the coefficients of large carbon number carbazoles were comparable with that of 1-methyl naphthalene, and the separation between these components by extraction would be difficult. The hydrocarbon component had a large effects on the distribution coefficients of nitrogen heterocyclic components, and the separation selectivity of the nitrogen heterocyclic compound against undecane was the largest, followed by those with butyl benzene and 1-methyl naphthalene. The distribution coefficients of nitrogen heterocyclic compounds were smaller with aromatics than those with alkane. The solubility of the less polar component enhanced the dissolution of the other more polar component in the extract phase. In this study, the trend of the liquid-liquid equilibria with the multicomponent system could be approximately estimated based on the equilibria with the binary model feed oils, and accordingly it was expected that the separation of the real petro-derived
fractions could be roughly evaluated based on the results measured with binary systems.

### Nomenclature

\[
\begin{align*}
m_i & = \text{distribution coefficient of component } i \quad [-] \\
nc_{i} & = \text{number of carbon and nitrogen atoms in component } i \quad [-] \\
x_i & = \text{mass fraction of component } i \text{ in raffinate phase} \quad [-] \\
y_i & = \text{mass fraction of component } i \text{ in extract phase} \quad [-] \\
\beta_{ij} & = \text{separation selectivity of component } i \text{ relative to component } j \quad [-]
\end{align*}
\]

\[\begin{align*}
in_c & = \text{distribution coefficient of component } i \quad [-] \\
_i & = \text{number of carbon and nitrogen atoms in component } i \quad [-] \\
x_i & = \text{mass fraction of component } i \text{ in raffinate phase} \quad [-] \\
y_i & = \text{mass fraction of component } i \text{ in extract phase} \quad [-] \\
\beta_{ij} & = \text{separation selectivity of component } i \text{ relative to component } j \quad [-]
\end{align*}\]

\[
\begin{align*}
0 & = \text{at initial state} \\
i & = \text{component } i \\
MeOH & = \text{methanol} \\
W & = \text{water}
\end{align*}
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