

# Batch Equilibrium Extraction of Model Petroleum Heavy fraction

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## 1. Introduction

Some petroleum-derived heavy fractions contain not only homocyclic but also heterocyclic compounds at certain concentration, and the latter should cause degradation of fuel oil quality and be poisonous for catalysts used in the successive processes, such as hydrocracking, desulfurization and so on. Then the removal of these heterocyclic compounds from the heavy fractions has been studied for the catalytic reaction stably operated or improved, keep the quality of fuel oil.

Solvent extraction has been utilized as a commercialized method to separate aromatic compounds from petro-derived fractions. Separation of nitrogen heterocyclic compounds (Hetero) by solvent extraction has been studied, in which coal tar absorption oil or catalytic cracked oil was used as feed oil [2-4]. However the separation of heterocyclic compounds from the heavy fractions has been insufficiently investigated.

In this study, liquid-liquid equilibrium extraction of model heavy fractions with aqueous solutions of methanol was measured. The effects of species of Hetero and other coexisting components on the liquid-liquid equilibrium were studied.

## 2. Experimentals

### 2.1 Materials

The material systems used in this study are summarized in Table 1. The 3 types of nitrogen heterocyclic compounds (Hetero), such as quinolines (Qs), indoles (INs) and Carbazoles (CBZs), and 2 types of non-heterocyclic compounds (Non-hetero), such as aromatics and alkanes (AL), were selected and totally 21 components were used. For each type of Hetero, the carbon numbers in molecules were varied by changing their functional group. To prepare the model feed solutions of binary system, one each component was chosen from Hetero and Non-hetero components. The carbon number in the molecule, CN, was estimated by regarding heteroatom as carbon in the molecule. Aqueous methanol solution, one of the popular solvents used in the previous studies, was used as the solvent.

### 2.2 Experimental conditions

The experimental conditions are summarized in Table 2. The mass fraction of the Hetero component in the model binary feed solutions was set as 0.01. The specified amounts of feed, and solvent, were put in conical flask and shaken at 303K for 48 hours to be equilibrated. After reaching equilibrium conditions, the raffinate and extract phases and were separated into each other with separatory funnel. The liquid phases were analyzed by gas chromatograph (Shimadzu GC-2010) with capillary column (HR-1) to determine respective compositions of both phases.

Table 1 Compounds in model systems

Hetero	
<b>Quinolines(Qs)</b>	
quinoline(Q, CN = 10),	2-methylquinoline(MeQ, CN = 11),
2,6-dimethylquinoline(DMeQ, CN = 12),	4-phenylpyridine(PhPYR, CN = 12),
benzo[h]quinolone(BeQ, CN = 14)	
<b>Indoles(INs)</b>	
indole(IN, CN = 9),	2-methylindole(MeIN, CN = 10),
7-ethylindole(EtIN, CN = 11),	2,3-dimethylindole(DMeIN, CN = 11),
2-phenylindole(PhIN, CN = 15)	
<b>Carbazoles(CBZs)</b>	
carbazole(CBZ, CN = 13),	9-methylcarbazole(MeCBZ, CN = 14),
9-ethylcarbazole(EtCBZ, CN = 15)	
<b>Non-hetero</b>	
<b>Aromatics</b>	
1-metylnaphthalene(1MeN, CN = 11),	butylbenzene(BuBEZ, CN = 10)
<b>Alkanes(AL)</b>	
decane(C10, CN = 10),	undecane(C11, CN = 11),
dodecane(C12, CN = 12),	tridecane(C13, CN = 13),
tetradecane(C14, CN = 14)	

Table 2 Experimental conditions

System		Model heavy fraction	
Feed		Model heavy fraction	
Solvent		Methanol aqueous solution	
Conditions			
Mass of feed, $R_0$	[kg]	0.02	
Solvent/feed ratio, $E_0/R_0$	[-]	1	
Mass fraction of Hetero $y_{Hetero,0}$	[-]	0.01~0.2	
Mass fraction of methanol in solvent $y_{MeOH,0}$	[-]	0.8	
Temperature	[K]	303	
Time	[h]	48	

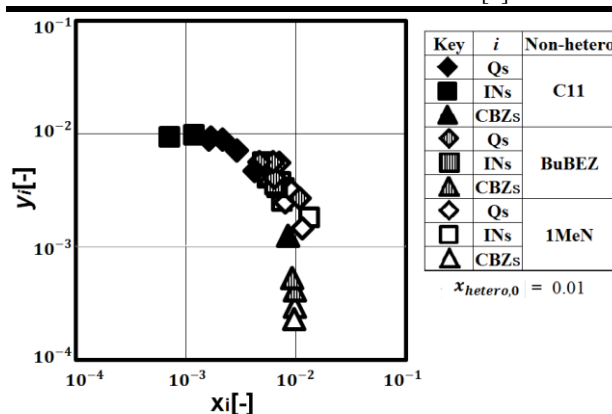


Fig.1 Mass fraction of Hetero in raffinate and extract phase

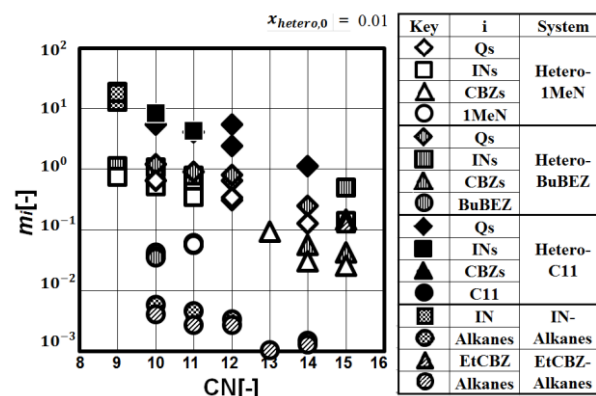


Fig.2 Effect of carbon number on distribution ratio,  $m_i$

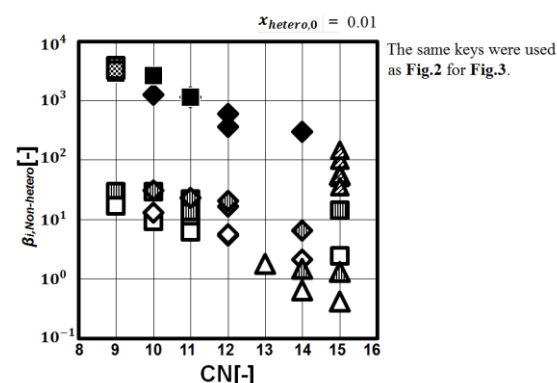


Fig.3 Effect of carbon number on selectivity  $\beta_{i,Non-hetero}$

## 3. Results and Discussion

### 3.1 Definitions

The distribution ratio of component  $i$ ,  $m_i$  and the

selectivity of component  $i$  against Non-hetero,  $\beta_{i,Nonhetero}$  is defined as follow:

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

$$\beta_{i,Nonhetero} = m_i/m_{Non-hetero} \quad (2)$$

Where  $y_{i,1}$  and  $x_{i,1}$  are the mass fractions of component  $i$  in each phases in extraction. Mass fraction excluding solvent in extract phase,  $z$  defined as follow:

$$z = 1 - y_{MeOH,1} - y_{W,1} \quad (3)$$

Where  $k$  is all compounds used in model systems and solvent,  $n$  is compounds used in solvent.

### 3.2 Equilibrium with model binary feed oil systems

In all cases, the liquid-liquid extraction could be stably operated and stable emulsion was not formed. The compounds of Q and C12, or MeQ and 1MeN could not be appropriately analyzed by gas chromatogram since they could not be separated by the used column in the gas chromatogram.

The plots of the mass fractions of Hetero components in the extract phases against those in the raffinate phases are shown in Fig.1. The  $y_{i,1}$  of Hetero components were larger with C11 than in 1MeN-hetero systems. The  $y_{i,1}$  of Qs and INs were relatively high and those of CBZs were small with each Non-hetero component.

The effect of CN on  $m_i$ , is shown in Fig.2. In most case,  $m_i$  decreased as CN increased and  $m_i$  of Hetero components were larger than those of Non-hetero components. Among Hetero components,  $m_i$  of Qs and INs were almost comparable with each other, and were larger than those of CBZs. The  $m_i$  of Hetero components were the largest with C11, followed by those with BuBEZ and 1MeN. The  $m_i$  of Non-hetero components were independent of the coexisting Hetero components to be constant for respective Non-hetero components. The  $m_i$  was the smallest with C11, followed by BuBEZ and 1MeN.

The effect of CN on  $\beta_{i,Non-hetero}$  is shown in Fig.3. The  $\beta_{i,Nonhetero}$  decreased as CN increased. The  $\beta_{i,Nonhetero}$  was the largest with C11, followed by those with BuBEZ and 1MeN, and  $\beta_{i,Nonhetero}$  of IN with C11 attained more than 2800. This so high selectivity might be caused by the water content in extract phase.

Figure 4 shows the effect of  $z$  on  $m_Q$  and  $m_i$  of Non-hetero components when  $x_{Q,0}$  was varied from 0.01 to 0.2. In lower range of  $z$ ,  $m_Q$  decreased and  $m_i$  of Non-hetero component increased as  $z$  increased. With less polar component, such as C11, more polar component, such as Q, preferably dissolved into the solvent phase. The difference between  $m_i$  of Q and C11 was quite large and the ratio,  $m_Q/m_{C11}$ , was more than 1200. This characteristic feature became obscure in the order of C11, BuBEZ, and 1MeN, that is to say, the ascending order of the mass fraction of Non-hetero component in the extract phase. In the higher range of  $z$ , although  $m_Q$  was kept constant,  $m_{1MeN}$  increased with  $z$ . When both components in the binary system are likely to dissolve into solvent phase, the solubility of less polar component should be enhanced by the other more polar component. This trend was also reported in the previous studies[8].

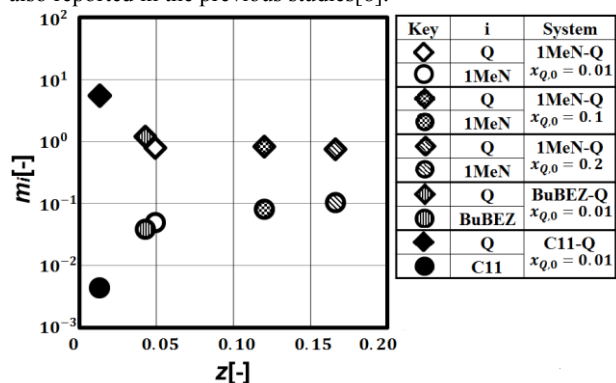


Fig. 4 Effect of mass fraction excluding solvent in extract phase for distribution ratio

### 3.3 Extraction of model multicomponent feed oil system

The results with the multicomponent system are shown in Fig.5, when 1MeN was used as Non-hetero compound. The  $m_i$  of Hetero components were larger than  $m_i$  of Non-hetero in 2 components systems, because total initial mass fraction of Hetero component in multicomponent system was larger than that of Hetero component in 2 components systems. So, the tendency of 2 components systems was same as that of multicomponent system.

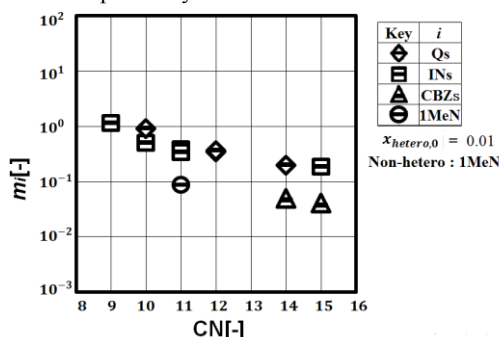


Fig. 5 Effect of CN for distribution ratio in multicomponent system

## 4. Conclusion

Batch Equilibrium of nitrogen heterocyclic compounds, alkanes and aromatics were measured on 2 component systems. As CN increased, distribution ratio of Hetero and alkanes decreased. Distribution ratio of CBZs were smaller with each Non-hetero components than that of INs and Qs. Distribution ratio of Hetero was larger than that of aromatics, and that of aromatics was larger than that of alkanes. The selectivity of Hetero against alkanes was largest, followed by those with BuBEZ and 1MeN.

The distribution ratio of Hetero was smaller with aromatics than that of Hetero with alkanes. The solubility of less polar component was enhanced by the other more polar component.

The liquid-liquid equilibrium in 2 compounds systems and multicomponent system was almost comparable with each other.

### Nomenclature

CN = carbon number of compounds,  $x_i$  = Mass fraction of  $i$  in raffinate phase,  $y_i$  = Mass fraction of  $i$  in extract phase,  $m_i$  = Distribution ratio of  $i$

1MeN = 1-methylnaphthalene, BuBEZ = Butylbenzene, C10 = Decane, C11 = Undecane, C12 = Dodecane, C13 = Tridecane, C14 = Tetradecane, Q = Quinoline, DMeQ = 2,6-dimethylquinoline, MeQ = 2-methylquinoline, PhPYR = 4-phenylpyridine, BeQ = benzo[h]quinoline, IN = Indole, MeIN = 2-methylindole, EtIN = 7-ethylindole, DMeIN = 2,3-dimethylindole, PhIN = 2-phenylindole, CBZ = Carbazole, MeCBZ = 9-methylcarbazole, EtCBZ = 9-ethylcarbazole, MeOH = Methanol, W = Water, Qs = Quinoline compounds, INs = Indole compounds, CBZs = Carbazole compounds, Hetero = Heterocyclic compounds, Non-hetero = alkanes and aromatics, AL = alkanes

### Subscript

$i$  : component  $i$ , 0 : at initial state, 1 : at equilibrium state

### Reference

- [1] Nagai.M 東京工業大学 1999年卒業論文
- [2] Yoshimura.Y Solvent Extraction Research and Development, Japan, 20, 169~174 (April, 2013)
- [3] Chris. S 東京工業大学大学院 2000年卒業論文
- [4] Hasegawa.H, 東京工業大学 2014年卒業論文
- [5] 石油学会;石油精製プロセス,第五章,接触分解 125-138
- [6] Kim. C.J, Won.D.B, Fluid Phase Equilibria 193 (2002) 217~227
- [7] George.W.M, Dennis.R.H, Ind. Eng. Chem. Res. (2008), 47, 2867-2875
- [8] Chris.S et al, J.Jpn. PetInst, 48, 60-66 (2005)