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Liquid-liquid Equilibrium Extraction of Aromatic Compounds from Model Hydrocarbon Mixtures for Separation of Cracked Oils

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Model hydrocarbon mixtures, consisting of alkene or alkane and/or aromatic components, were utilized as feed oils with methanol, furfural or sulfolane as solvents to evaluate solvent extraction for the separation of aromatic components from cracked oils. Aromatic components were selectively extracted relative to alkane or alkene components with all solvents. The distribution coefficients increased in the order of alkane, alkene and aromatic components. Among the aromatic components, the distribution coefficients of tri cyclic components were the highest, followed by those for di and mono cyclic components. For each aromatic components of the same number of benzene rings, the distribution coefficients generally decreased with the carbon number in the molecule. The separation selectivities of aromatic components relative to nonane were higher with sulfolane than those with the other solvents, and sulfolane has the ability to enhance separations among aromatic components.

1. Introduction

The demand for fossil fuel oil products has been shrinking recently in the developed countries. Especially the consumption of gasoline has decreased for several years due to the development of hybrid or electric vehicles, popularization of biofuels, escalation of the crude oil price, and so on. Then to reduce gasoline production, the operating conditions for the cracking processes in the refineries had to be modified, and accordingly large amounts of surplus cracked oil fractions will be generated as byproducts. The effective utilization of the surplus cracked oil fractions, generally rich in aromatic components, has been suggested [1]. The aromatic components should be recovered from the cracked oils as feed stocks for the chemical industry, and the dearomatized fractions could be utilized as fuels other than gasoline, such as kerosene and diesel fuels, which are required to contain aromatic components at a lower level for effective combustion. For the aromatic recovery process, sulfolane is one of the most popular extraction solvents and it is used in the commercial Sulfolane Process [2]. Furfural is commercially utilized for the refining of lubricant base oil[3]. Methanol has been studied for the separation of coal tar fractions [4, 5]. For the separation of the cracked oils, liquid-liquid equilibrium extraction with methanol and sulfolane was studied using cracked kerosene. The cracked kerosene used in the study contained various kinds of mono and polycyclic aromatic components. The extraction behavior of these components have not been fully discussed in previous studies.

In this study model hydrocarbon mixtures were used as feed oils to simulate the cracked oils, and liquid-liquid equilibrium extraction was measured to study the separation of cracked oils by solvent extraction. Some types of aromatic components were chosen from mono, di, and tri cyclic aromatic hydrocarbons, and some kinds of alkane and alkene components were also chosen as the components in the cracked oils. Sulfolane, furfural and methanol were used as the solvent phases. The distributions of the hydrocarbon components between the feed oil and solvent phases were qualitatively studied.

2. Experimental

Four types of model hydrocarbon mixtures were used as the feed oil phases. Three types of solvents, namely methanol, furfural and sulfolane, were employed as the solvent phases. The hydrocarbon components in the model feed oils were selected from ordinary cracked oil fractions. The compositions of the model feed oils, $x_{\mathrm{i,0}}$s, are shown in Table 1. The components in the model feed oils 1 and 2 were determined to study the distribution behaviors of alkane and alkene components with the selected solvents. The carbon numbers of the alkane and alkene components in the model feed oils 1 and 2 ranged from 7, heptane, to 22, docosane, and from 10, 1-decene, to 20, 1-eicosene, respectively.

Table 1 Compositions of model feed oils

model feed oil 1:

i	$x_{i,0}$	*i*	$x_{i,0}$	*i*	$x_{i,0}$	*i*	$x_{i,0}$
heptane	0.06	undecane	0.06	pentadecane	0.06	nonadecane	0.06
octane	0.06	dodecane	0.06	hexadecane	0.06	eicosane	0.06
nonane	0.06	tridecane	0.06	heptadecane	0.06	heneicosane	0.06
decane	0.06	tetradecane	0.06	octadecane	0.06	docosane	0.06

model feed oil 2:

i	$x_{i,0}$	*i*	$x_{i,0}$
1-decene	0.06	1-hexadecene	0.06
1-dodecene	0.06	1-octadecene	0.06
1-tetradecene	0.06	1-eicosene	0.06
		Nonane	0.64

model feed oil 3:

i	$x_{i,0}$
toluene	0.06
1-methylnaphthalene	0.06
phenanthrene	0.06
nonane	0.82

model feed oil 4:

i	$\mathrm{x}_{\mathrm{i,0}}$	*i*	$\mathrm{x}_{\mathrm{i,0}}$	*i*	$\mathrm{x}_{\mathrm{i,0}}$
toluene	0.06	tetraline	0.06	fluorene	0.06
o-xylene	0.06	1-methylnaphtalene	0.06	phenanthrene	0.06
mesitylene	0.06	hexylbenzene	0.06	nonane	0.5

The model feed oil 3 was prepared to contain aromatic and alkane components, in which toluene, 1-methylnaphthalene, phenanthrene and nonane represent mono, di and tri cyclic aromatic components and alkane components. The model feed oil 4 also consisted of mono, di and tri cyclic aromatic components and nonane, to study the effects of carbon numbers in the aromatic components for each ring number in the molecules. Then the effects of the molecular structure of the aromatic components on the equilibrium conditions were studied. The principal experimental conditions are shown in Table 2. The feed oil and solvent phases were brought into contact in an erlenmeyer flask using a constant temperature shaker. After equilibrium, the raffinate and extract phases were separated using a separation funnel, and analyzed by gas chromatograph (GC-2010, SHIMADZU) with capillary column (ULBON HR-1).

Table 2 Experimental conditions for liquid-liquid equilibrium mesurement

Feed		model hydrocarbon mixtures
mass	[kg]	0.02
Solvent		methanol, furfural, sulfolane
Mass ratio of solvent to feed	[-]	1
Operating temperature	[K]	303
Contacting time by shaker	[h]	48
Amplitude of shaking	[m]	0.04
Frequency of shaking	[h^{-1}]	5400

3. Results and Discussion

All combinations of the feed oil and solvent in this study formed two phases, and so liquid-liquid extraction could be carried out. In GC analysis, the peaks of sulfolane and dodecane overlapped and the mass fractions of dodecane could not be appropriately measured in the presence of sulfolane.

The distribution coefficient of component *i*, m_i, and the separation selectivity of component *i* relative to component *j*, $\beta_{i,j}$, were defined by,

$$m_i = y_i / x_i \quad (1)$$

$$\beta_{i,j} = m_i / m_j \quad (2)$$

where x_i and y_i stand for the mass fraction of component *i* in the raffinate and extract phases at equilibrium, respectively. The effects of the carbon number of the component, *CN*, on the distribution coefficients of the alkane and alkene components, m_i, are shown in Figures 1 and 2. For both of alkane and alkene components, m_i simply decreased as *CN* increased, and the m_i values for the alkene components were larger than those for the alkane components. This difference is probably mainly because alkene molecules have π bonds and show higher polarity than alkane molecules. The slopes of m_i for the alkene components against *CN* were lower than those of alkane components. Among the three solvents, methanol showed the largest m_i values, followed by furfural and sulfolane.

Figure 3 shows the effects of the number of benzene rings in the aromatic components on their distribution coefficients, when the model feed 3 was used. With all solvents, the m_i values for the tri cyclic phenanthrene were the largest, followed by di cyclic 1-methylnaphthalene and mono cyclic toluene.

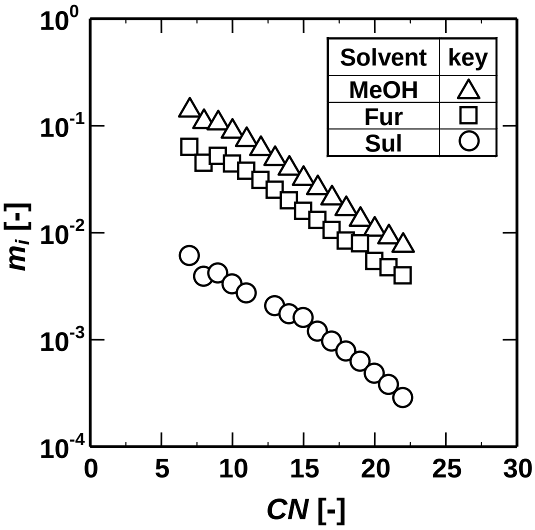

Figure 1. Effects of solvents on m_i of alkanes with model feed 1.

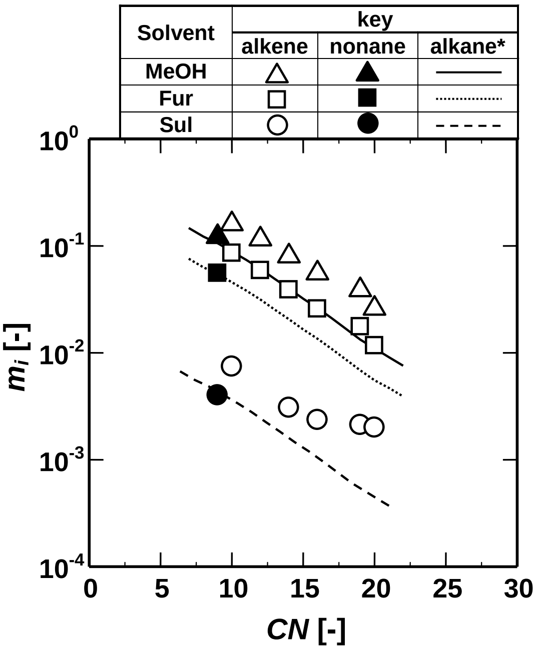

Figure 2. Effects of solvents on m_i of alkenes with model feed 2, *results with model feed 1.

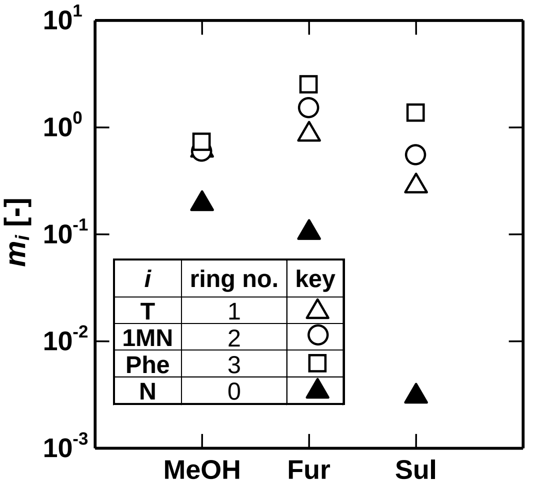

Figure 3. Effects of solvents on m_i of aromatics with model feed 3.

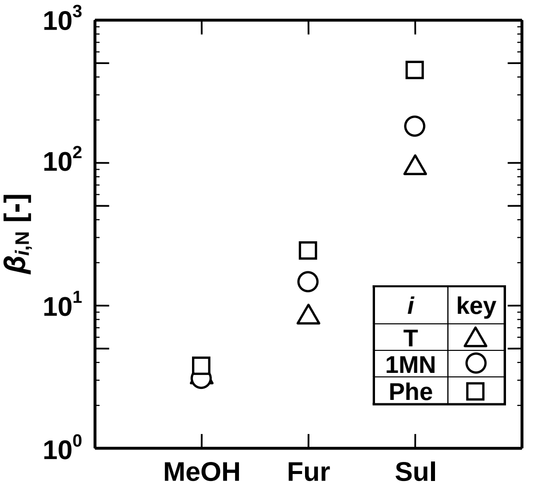

Figure 4. Effects of solvents on $\beta_{i,\mathrm{N}}$ of aromatics with model feed 3.

Furfural showed higher m_i values for aromatic components, and the m_i values for methanol and sulfolane were comparable. The m_i values for nonane were much smaller than those for aromatic components and the m_i value for sulfolane was notably small. Figure 4 shows the separation selectivity of aromatic components relative to nonane, $\beta_{i,\mathrm{N}}$ (j=nonane), which was estimated using Eq.(2) from the results for the model feed 3.

For any solvent, aromatic components could be selectively extracted relative to nonane, and the selectivities increased in the order of methanol, furfural and sulfolane. This trend is mainly affected by the m_i value for nonane. In the case of methanol, the separation selectivities of respective aromatic components were similar. On the other hand, for furfural and sulfolane, the selectivity clearly increased in the order of mono, di, and tri aromatic compounds. Therefore furfural and sulfolane can be used not only for the recovery of aromatic components but also for the separation among the aromatic components; i.e. separation of mono, di and tri cyclic aromatic compounds.

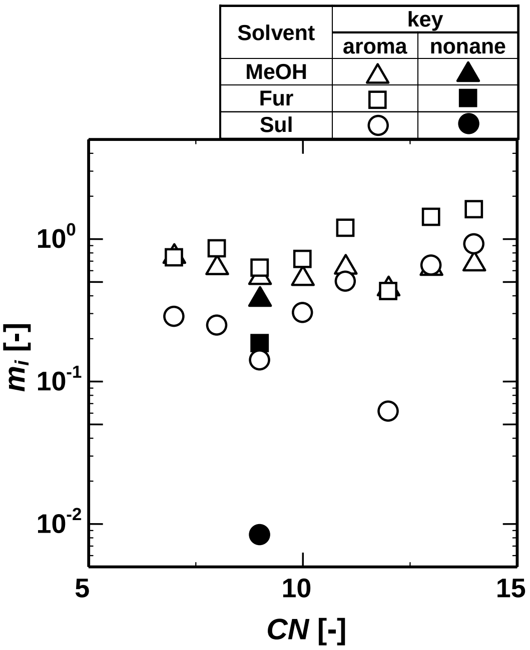

Figure 5. Effects of solvents on m_i of aromatics with model feed 4.

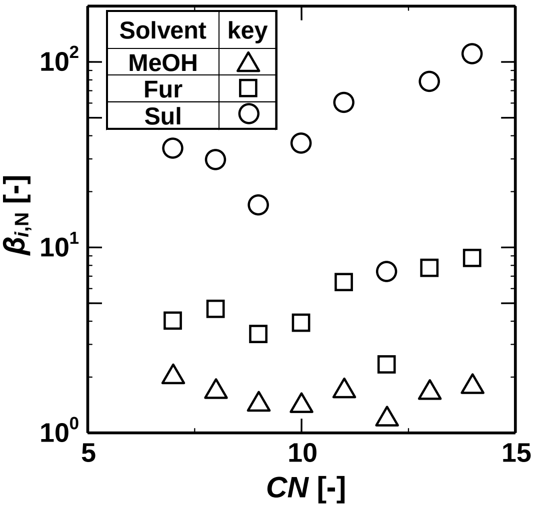

Figure 6. Effects of solvents on $\beta_{i,\mathrm{N}}$ of aromatics with model feed 4.

The effects of *CN* on m_i in the case of the model feed oil 4 are shown in Figure 5. With any solvent, the m_i values for the aromatic components were higher than that of nonane, and the aromatic components in the feed oil were selectively extracted. The m_i values for the aromatic components were relatively high with furfural, followed by those for methanol and sulfolane. The effects of the different solvents on the m_i values for aromatic components were not so evident. The m_i value for nonane was much lower with sulfolane than those with methanol or furfural. Among the aromatic components, m_i increased with the number of benzene rings in the molecule, as shown in Figure 3, and the m_i values for mono cyclic aromatics generally decreased as *CN* increased, except for tetraline which has a cyclohexyl ring in the molecule. Similarly, the m_i value for fluorene which has a fluorine ring in the molecule was higher than that for 1-methylnaphthalene though *CN* for fluorene (*CN*=13) was higher than that for 1-methylnaphthalene (*CN*=11). The effects of ring structure and number of benzene rings on the increment of m_is were smaller for methanol than those for furfural or sulfolane. Figure 6 shows the effects of CN on the separation selectivity of component i relative to nonane, $\beta_{i,\mathrm{N}}$ (j=nonane), which was estimated using Eq.(2) from the results for the model feed 4. $\beta_{i,\mathrm{N}}$ increased in the order methanol, furfural and sulfolane. The difference was caused largely by m_N for each solvent. $\beta_{i,\mathrm{N}}$ for sulfolane was approximately ten times higher than that for furfural. The $\beta_{i,\mathrm{N}}$ values for tri cyclic aromatic components were very large relative to the mono and di cyclic aromatic components with sulfolane. As mentioned above, the separation of the aromatic components can be achieved with sulfolane as the solvent.

4. Conclusion

Four types of model feed oils and three types of solvents, methanol, furfural and sulfolane, were used to determine the liquid-liquid equilibrium extraction for the separation of cracked oils by solvent extraction. The aromatic components were selectively extracted into the solvent phases used relative to the alkane component. The distribution coefficients of aromatic and alkane components were larger and smaller with sulfolane than those with the other solvents, and sulfolane could be an effective solvent for recovery of the aromatic components. Moreover with sulfolane, the distribution coefficients of tri cyclic aromatic components were larger than those of the di and mono cyclic aromatic components. Therefore separation of the aromatic components is possible using sulfolane. In these measurements, three types of possible solvents were used. However it would be necessary to study the effects of water addition on the aromatic separation for the further development.

Nomenclature

CN = carbon number in molecule [–]
m_i = distribution coefficient of component i [–]
x_i = mass fraction of component i in raffinate phase [–]
y_i = mass fraction of component i in extract phase [–]
$\beta_{i,j}$ = separation selectivity of component i relative to component j [–]
<Subscript>
0 = at initial state
Fur = furfural
i = component i
MeOH = methanol
2MN =2-methylnaphthalene
N = nonane
Phe = phenanthrene
Sul = sulfolane
T = toluene

References

1) H. Habaki, K. Miyazaki, and R. Egashira, *J. Jpn. Pet. Inst.*, 55, 241-249 (2012).
2) G. H. Deal, H. D. Evans, E. D. Oliver and M. N. Papadopoulos, *Petroleum Refiner*, 38, 185-192 (1959).
3) Sequeria, P. B. Sherman, J. U. Douciere and E. O. McBride, *Hydrocarbon Processing*, 58, 155-160 (1979).
4) R. Egashira and M. Nagai, *J. Jpn. Pet. Inst.*, 43, 339-345 (2000).
5) A. Matsumura, Y. Kodera, T. Kondo, K. Ukegawa, H. Tanabe, S. Yoshida, Y. Mito, *Shigen to Kankyo* (*J. of NIRE*), 4, 43–47 (1995).