Solvent Search using UNIFAC Method for Separation of Coal Tar Distillate by Liquid-Liquid Extraction

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UNIFAC法によるコールタール蒸留留分の液液抽出分離に対する溶媒の探索

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まず，コールータール蒸留留分(CT留分)と、各種官能基から構成される仮想的な溶媒との間における液液平衡関係を推算し，溶媒中の官能基の種類，数，などの影響を明らかにした。ついで，これらの結果に基づいて，CT留分の抽出に適切と考えられる実在の溶媒を選定し，CT留分－溶媒間の液液平衡関係を推算した。アルコール類を溶媒とした場合においてはCH_2基の数の増加とともに分配係数は低下する ,OH基の数の増加とともに他の化合物に対する含窒素化合物の分離の選択性は向上する、などの結果を得た。以上は本分離法における溶媒選定の指針となる。

1. Introduction

Coal tar distillates, such as tar light oil (TLO), absorption oil (AO), contain such useful compounds as nitrogen heterocyclic compounds, homocyclic compounds, and so on. Although the separation of coal tar fraction by solvent extraction has been studied[1,2,9)] to obtain these compounds, the study to select the extracting solvent appropriate for this separation is not enough.

UNIFAC[4)] is a method for estimating the activity coefficient of components in liquid phase. Since the parameters used in UNIFAC method are given for respective functional groups, the number of the parameters is much less than those used in other methods using parameters of molecules. In UNIFAC method, there are three kinds of parameters related with volumes, areas, and interactions of functional groups as follows:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \qquad (1)$$

$$\ln \gamma_i^{\mathrm{C}} = \psi^{\mathrm{C}}(Q_1,.., Q_k,.., R_1,.., R_k,.., x_1,.., x_i,.., \nu_{1,1},.., \nu_{k,i},..) \qquad (2)$$

$$\ln \gamma_i^{\mathrm{R}} = \psi^{\mathrm{R}}(Q_1,.., Q_k,.., a_{1/1},.., a_{k/l},.., x_1,.., x_i,.., \nu_{1,1},.., \nu_{k,i},.., T) \qquad (3)$$

where γ_i is the activity coefficient of component i, Q_k is the area parameter for functional group k, R_k is the volume parameter for functional group k, $a_{k/l}$ is the group interaction parameter between functional groups k and l, x_i is the mole fraction of component i, $\nu_{k,i}$ is the number of functional groups k in component i, and T is temperature. In UNIFAC method, functional groups are primarily categorized by their characteristics into “Main groups” and then in each main group, they are sorted into “Sub groups” according to their valencies. For example, CH_3, CH_2, CH, and C are independent sub groups respectively, and they are in same main group “CH_2”. Volume and area parameters, R_k and Q_k, were determined based on the van der Waals volume and the van der Waals radii, and given to every sub group, while interaction parameters were determined based on experimental data of phase equilibria, and given to every main group. The UNIFAC method is used in various manner not only to predict phase equilibria but also to search solvent compounds appropriate for extraction, leaching, extractive distillation, and so forth[3,7)].

The purpose of this study was to search the solvent using UNIFAC method for the extraction separation of coal tar distillates. In the first, the functional groups composing the solvent predicted to be appropriate for this extraction were selected. Secondary, liquid-liquid equilibria (LLE) between coal tar distillates (TLO, AO) and solvent of fictitious component consisting of the above selected functional groups were estimated by UNIFAC. Finally, according to these results, the solvent of real components were selected and were compared with one another.

2. Selection of functional groups

In TLO and AO, there are a number of compounds: pyridine, quinolines, indole, etc. as nitrogen compounds; benzenes, naphthalenes, etc. as homocyclic compounds; dibenzofuran etc. as oxygen compounds; and so forth. The sub groups composing these compounds are summarized in **Table 1**. As UNIFAC parameters for some of these groups, e.g. indene, indole and dibenzofuran have not been given yet, those given for other analogous groups were substituted.

Next, the functional groups predicted to be appropriate for the extracting solvent for separation of coal tar distillate were selected, regarding the polarity of functional groups including oxygen, nitrogen, and the rest. Selected functional groups are shown in **Table 2**.

3. Equilibrium with solvent of fictitious-components

3.1 Conditions for calculation

The equilibrium state obtained by contacting the coal tar distillate and solvent were calculated. The material balances, constraints of mole fractions, and equilibrium relationships can be written as follows:

$$R_0\, x_{i,0} + E_0\, y_{i,0} = R\, x_i + E\, y_i \qquad (4)$$

$$\Sigma_i\, x_i = 1 \qquad (5)$$

$$\Sigma_i\, y_i = 1 \qquad (6)$$

$$x_i\, \gamma_i^{\mathrm{RAF}} = y_i\, \gamma_i^{\mathrm{EXT}} \qquad (7)$$

where γ_i^{RAF} and γ_i^{EXT} denote the activity coefficients of component i in the raffinate and extract phases, respectively. These equations were solved simultaneously to know the equilibrium composition in the raffinate (oil) phase, x_i; in the extract (aqueous) phase, y_i; the amount of the raffinate phase, R; and that of the extract phase, E; under the given temperature; initial composition in the feed, $x_{i,0}$; in the solvent, $y_{i,0}$; the amount of the feed, R_0; and that of the extracting solvent, E_0.

The feed oils were model tar light oil and absorption oil. The compositions of these model mixtures are given in **Table 3**. The compositions were determined according to the previous analysis of real tar light oil and absorption oil[1,2,9)]. The solvent was the aqueous solution of fictitious component composed of the functional groups selected in Table 2. The conditions for calculation are shown in **Table 4**. The mole ratio of solvent to feed and mole fraction of water in solvent were so selected that system would form two liquid phases.

The activity coefficients, γ_i^{RAF} and γ_i^{EXT}, were estimated by UNIFAC. The group interaction parameters which were given by Magnussen *et al.*[8)] for LLE were used mainly. For the groups whose group interaction parameters for LLE were not available, group interaction parameters for vapor-liquid equilibria[5,6,10)] were used.

Table 1 Functional groups composing the compounds in coal tar distillates

Functional group	Example of component
ACH	Benzene: **ACH**×6
AC	Naphthalene: ACH×8, **AC**×2
$ACCH_3$	Toluene: ACH×5, **$ACCH_3$**×1
$ACCH_2$	Ethylbenzene: CH_3×1, ACH×5, **$ACCH_2$**×1
CH_3	Ethylbenzene: **CH_3**×1, ACH×5, $ACCH_2$×1
CH_2	Indene: **CH_2**×1, ACH×6, AC×2
C_5H_5N	Pyridine: **C_5H_5N**×1
C_5H_3N	Quinoline: ACH×4, **C_5H_3N**×1
CHNH	Indole: ACH×5, AC×2, **CHNH**×1
CHO	Dibenzofuran: ACH×8, AC×3, **CHO**×1

Table 2 Selected functional groups predicted to be appropriate for the extracting solvent

Functional group	Example of component
H_2O	Water: **H_2O**×1
OH	Methanol: CH_3×1, **OH**×1
CH_3O	Diethyl ether: CH_3×2, CH_2×1, **CH_2O**×1
CH_3NH	Diethylamine: CH_3×2, CH_2×1, **CH_2NH**×1
CH_3CO	Acetone: CH_3×1, **CH_3CO**×1
CH_2CN	Acetonitrole: **CH_3CN**×1
CH_3	Hexane: **CH_3**×2, **CH_2**×4
ACH	Benzene: **ACH**×6

Table 3 The mole fraction of component *i* in model tar light oil and absorption oil, $x_{i,0}$

Component, *i*	$x_{i,0}$ [−]
Tar light oil	
Benzene,B	0.48
Pyridine,Pyr	0.023
Toluene,T	0.18
Ethylbenzene,EB	0.032
Xylene,X	0.158
Indene,IN	0.12
Naphthalene,Nap	0.007
Absorption oil	
Naphthalene,Nap	0.03
Quinoline,Q	0.13
Isoquinoline,IQ	0.03
Indole,IL	0.08
1-methylnaphthalene,1MN	0.16
2-methylnaphthalene,2MN	0.38
Biphenyl,BP	0.1
Dibenzofuran,DBF	0.09

Table 4 Conditions for calculation of coal tar distillate-fictitious solvent component

Temperature	[K]	303
Mole ratio of solvent to feed	[−]	10
Mole fraction of water in solvent	[−]	0.9

3.2 Results and Discussion

The distribution coefficient of component *i*, m_i, was defined by following equation.

$$m_i = y_i / x_i \tag{8}$$

The main criteria of the appropriate extracting solvent were that the distribution coefficients of nitrogen compounds were large, those of other compounds were small, the selectivity of nitrogen compounds relative to other compounds was high, and the distribution coefficient of solvent component was large.

Fig. 1 (a) shows the distribution coefficient of pyridine and benzene in the case of TLO-fictitious solvent system. **Table 5** shows the relation between the number of functional groups in fictitious component and the distribution coefficient of fictitious component. In all cases, the distribution coefficients of pyridine were larger than those of benzene, that is, pyridine and benzene could be separated by the solvent extraction. The distribution coefficient of pyridine, benzene, and the separation selectivity of pyridine relative to benzene decreased with the number of ACH group in the solvent increased. The separation selectivity of pyridine relative to benzene increased as the number of CH_3 and CH_2CN groups, while the distribution coefficient of fictitious component of these groups were very small. The distribution coefficient of pyridine, benzene and fictitious component increased with the number of OH, CH_3CO, CH_3O and CH_3NH groups. The separation selectivity of pyridine relative to benzene decreased as the number of CH_3CO and CH_3NH groups increased. From these results, the component having ACH group was unsuitable for the solvent of tar light oil extraction.

Fig. 1 (b) shows the distribution coefficient of quinoline, the representative of nitrogen compounds, and that of 2-methylnaphthalene, the representative of homocyclic compounds in AO. Similarly to the case of TLO-fictitious solvent system, the distribution coefficient of quinoline increased as the number of OH, CH_3CO, and CH_3NH groups. The distribution coefficients of quinoline and 2-methylnaphthalene decreased as the number of ACH groups increased. On the other hand, CH_3 and CH_2CN did not affect the separation selectivity of quinoline relative to 2-methylnaphthalene. From these results OH, CH_3CO, CH_3O, CH_2CN, CH_3NH and CH_3 were considered appropriate for the extracting solvent.

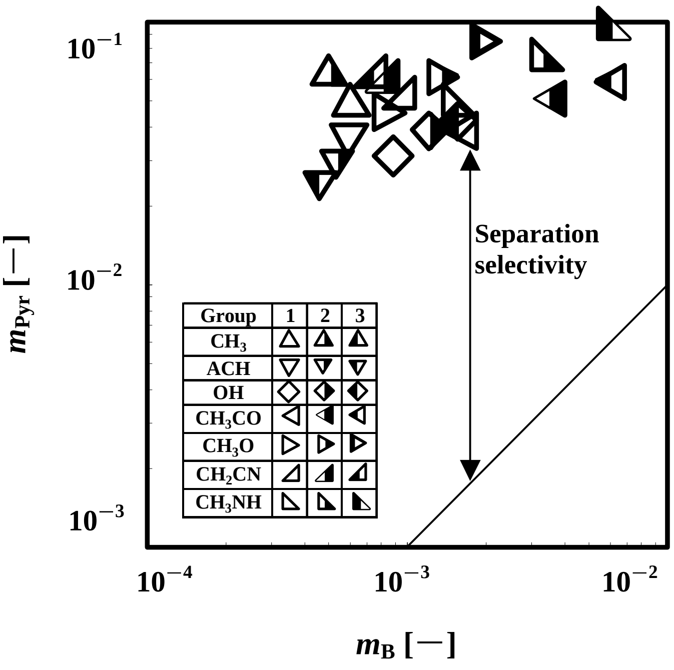

Fig. 1 (a)

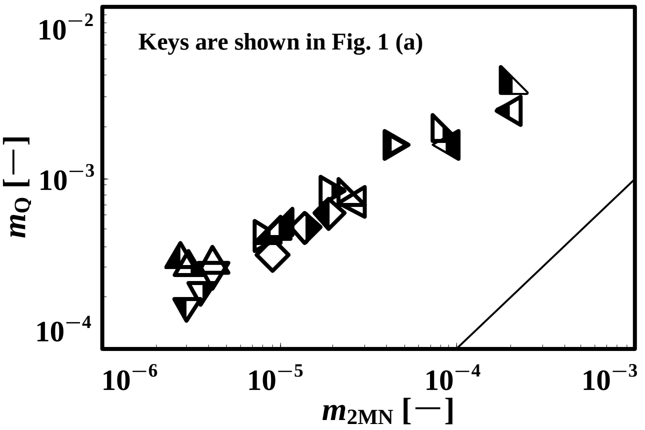

Fig. 1 (b)

Fig. 1 Relation between: (a) the distribution coefficient of benzene, m_B and that of pyridine, m_{Pyr} in TLO-fictitious solvent system; (b) the distribution coefficient of 2-methylnaphthalene, m_{2MN} and that of quinoline, m_Q in AO-fictitious solvent system

Table 5 The relation between the number of functional groups, k in fictitious component, $\nu_{k,\mathrm{fict}}$ and the distribution coefficient of fictitious component, m_{fict}

Functional group, k	$\nu_{k,\text{ fict}}$ [−]	m_{fict}(TLO) [−]	m_{fict}(AO) [−]
CH_3	1	7.7×10^{-2}	6.9×10^{-2}
	2	1.3×10^{-2}	1.4×10^{-2}
	3	−	2.6×10^{-3}
ACH	1	1.2×10^{-1}	9.3×10^{-2}
	2	4.2×10^{-2}	3.3×10^{-2}
	3	1.3×10^{-2}	1.1×10^{-2}
OH	1	1.4×10^{1}	4.7×10^{0}
	2	8.4×10^{2}	1.2×10^{2}
	3	3.9×10^{4}	2.6×10^{3}
CH_3CO	1	2.3×10^{0}	1.5×10^{0}
	2	4.6×10^{1}	2.4×10^{1}
	3	7.2×10^{2}	3.2×10^{2}
CH_3O	1	3.1×10^{-1}	2.5×10^{-1}
	2	3.1×10^{-1}	3.1×10^{-1}
	3	2.8×10^{-1}	4.6×10^{-1}
CH_2CN	1	1.6×10^{-1}	1.4×10^{-1}
	2	3.6×10^{-2}	4.5×10^{-2}
	3	8.0×10^{-3}	1.0×10^{-2}
CH_3NH	1	3.8×10^{0}	3.0×10^{0}
	2	1.7×10^{1}	1.5×10^{1}
	3	4.9×10^{1}	4.8×10^{1}

4. Equilibrium with solvent of real components

4.1 Calculation

Real components examined as solvent components used together with water are summarized in **Table 6**. Monohydric, dihydric, trihydric alcohols, ketones, nitriles, and amine were selected according to the above results of functional groups. The numbers of functional groups were varied in the respective kinds of compounds. The conditions for the calculations are shown in **Table 7**. The results are given on the basis of mass instead of mole. The conditions in the table made immiscible two liquid phases for all material systems. All other conditions and the calculation method were same as those in the preceding section.

Table 6 Selected real solvent components and used functional groups to represent them

Component	Used sub groups
Methanol, MeOH	$CH_3\times1$, $OH\times1$
Ethanol, EtOH	$CH_3\times1$, $CH_2\times1$, $OH\times1$
Propyl alcohol, PrOH	$CH_3\times1$, $CH_2\times2$, $OH\times1$
1,2-propanediol, PrOH2	$CH_3\times1$, $CH_2\times1$, $CH\times1$, $OH\times2$
1,3-butanediol, BtOH2	$CH_3\times1$, $CH_2\times2$, $CH\times1$, $OH\times2$
Ethyleneglycol, EG	$CH_2\times2$, $OH\times2$
Diethyleneglycol, DEG	$CH_2\times3$, $OH\times2$, $CH_2O\times1$
Triethyleneglycol, TrEG	$CH_2\times4$, $OH\times2$, $CH_2O\times2$
Tetraethyleneglycol, TeEG	$CH_2\times5$, $OH\times2$, $CH_2O\times3$
Glycerol, GOH3	$CH_2\times2$, $CH\times1$, $OH\times3$
Acetone, DMK	$CH_3\times1$, $CH_3CO\times1$
Ethylmethylketone, MEK	$CH_3\times1$, $CH_2\times1$, $CH_3CO\times1$
Acetonitrile, ANL	$CH_3CN\times1$
Propiononitrile, PrNL	$CH_3\times1$, $CH_2CN\times1$
Diethylamine, DEA	$CH_3\times2$, $CH_2\times1$, $CH_2NH\times1$

Table 7 Conditions for calculation of coal tar distillate-real solvent component system

Temperature	[K]	303
Mass ratio of solvent to feed	[−]	2
Mass fraction of water in solvent	[−]	0.5

4.2 Results and Discussion

Fig. 2 (a) shows the distribution coefficients of pyridine and benzene in the case of TLO-real solvent system. The distribution coefficient of pyridine decreased in the order of polyhydric alcohol, ketone, nitrile, amine, and monohydric alcohol used as aqueous solvents. The separation selectivity of pyridine relative to benzene decreased in the order of nitrile, amine, ketone, polyhydric alcohol, and monohydric alcohol. In the case of alcohol, as the number of carbon atoms contained in alcohol molecule increased, the distribution coefficient of pyridine decreased. The distribution coefficients of the solvent components are presented in **Table 8**. The distribution coefficients of alcohols were relatively large, whereas those of ketone, nitrile, and amine were small. In the case of alcohol, as the number of carbon atoms in alcohol molecule increased, the distribution coefficient of alcohol decreased.

The distribution coefficients of quinoline, 2-methylnaphthalene, and solvent components in the case of absorption oil system are shown in **Fig. 2 (b)** and Table 8. The effects of the numbers and the kinds of functional groups on the distribution coefficients were similar to those in the case of TLO system but smaller.

These results could be a useful information to select the solvent component appropriate for the extraction of coal tar fraction. On the contrary, it should be noted that there are still a lot of other factors which should be taken into account: extraction rate; properties related to recovery of solvent; those to operation; stability; toxicity; cost; and so forth.

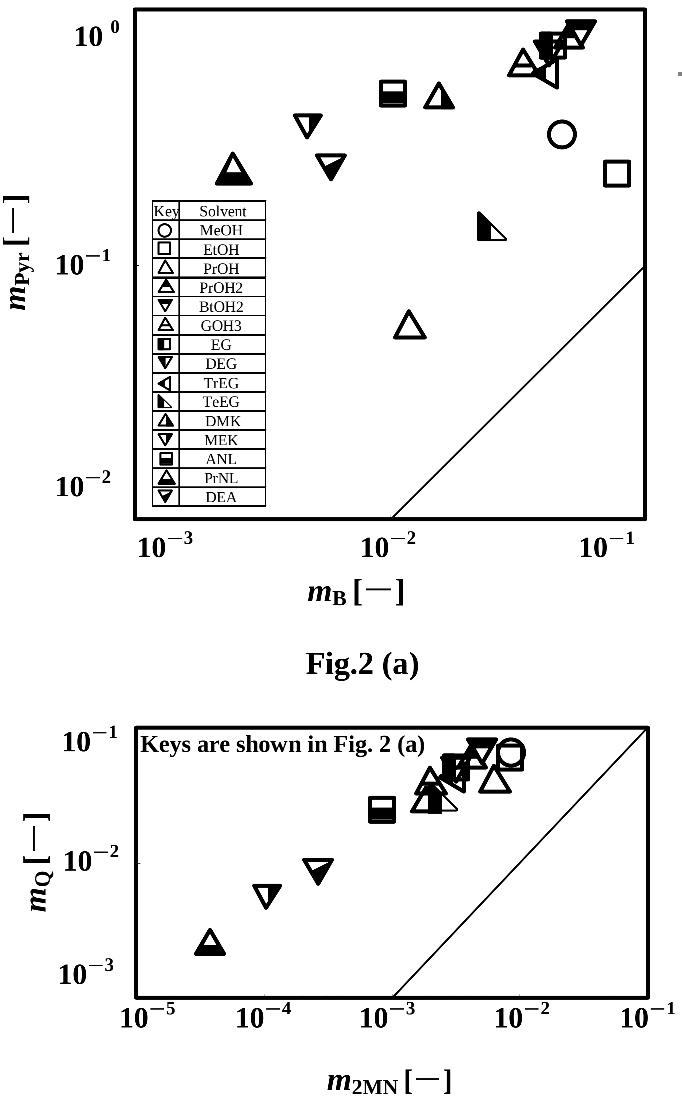

Fig.2 (a)

Fig. 2 (b)

Fig. 2 Relation between: (a) the distribution coefficient of benzene, m_B and that of pyridine, m_{Pyr} in TLO-real solvent system; (b) the distribution coefficient of 2-methylnaphthalene, m_{2MN} and that of quinoline, m_Q in AO-real solvent system

Table 8 The distribution coefficient of solvent component, m_{solv} for the coal tar distillate-real solvent system

Solvent	m_{solv} (TLO) [−]	m_{solv} (AO) [−]
Methanol	1.7×10^1	1.1×10^1
Ethanol	5.4×10^0	5.9×10^0
Propyl alcohol	3.8×10^{-1}	2.5×10^0
1,2-propanediol	2.6×10^2	5.9×10^1
1,3-butanediol	1.3×10^2	3.3×10^1
Ethylene glycol	5.3×10^2	1.1×10^2
Diethylene glycol	1.5×10^2	3.5×10^1
Triethylene glycol	3.8×10^1	1.2×10^1
Tetraethylene glycol	1.4×10^0	3.9×10^0
Glycerol	9.7×10^3	8.5×10^2
Acetone	6.3×10^{-1}	1.2×10^0
Ethyl methyl ketone	1.6×10^{-1}	2.1×10^{-1}
Acetonitrile	6.4×10^{-1}	9.9×10^{-1}
Propiononitrile	1.3×10^{-1}	1.6×10^{-1}
Diethylamine	2.3×10^{-1}	3.9×10^{-1}

5. Conclusions

The functional groups composing the solvent predicted to be appropriate for the separation of coal tar distillate were selected, and effects of these groups on the distribution coefficients were investigated. These results could be useful information to select the appropriate extracting solvent.

Nomenclature

a=group interaction parameter[K], ANL=acetonitrile, B=benzene, BP=biphenyl, BtOH2=1,3-butane diol, DBF=dibenzofuran, DEA=diethyl amine, DEG=diethylene glycol, DMK=acetone, *E*=amount of extract phase[mol], EB=ethylbenzene, EG=ethylene glycol, EtOH=ethanol, GOH3=glycerol, IL=indole, IN=indene, IQ=isoquinoline, *m*=distribution coefficient[-], MEK=ethyl methyl ketone, MeOH=methanol, 1MN=1-methylnaphthalene, 2MN=2-methylnaphthalene, Nap=naphthalene, PrNL=propiononitrile, PrOH=propyl alcohol, PrOH2=1,2-propane diol, Pyr=pyridine, Q=quinoline, Q_k=area parameter of group *k*, *R*=mole of raffinate phase[mol], R_0=mole of feed oil[mol], R_k=volume parameter of group *k*, *T*=temperature[K], T=toluene, TeEG=tetraethylene gylcol, TrEG=triethylene glycol, *x*=mole fraction in liquid phase[-]; mole or mass fraction in the raffinate phase[-], X=xylene, *y*=mole or mass fraction in the extract phase[-], γ =activity coefficient, ν=the number of functional groups in molecule

<Subscripts>

0=at initial, fict=fictitious component, component, *i*=component *i*, *k*=functional group *k*, *l*=functional group *l*, solv=solvent

<Superscripts>

C=combinatorial, EXT=extract phase, R=residual, RAF=raffinate phase

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