Extraction of liquid organic multi-component mixture with ionic liquids as solvents

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イオン液体を溶媒とした液状有機系多成分混合物の抽出
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吸収油中の同素環式化合物(ナフタレンなど)に比較して含窒素複素環式化合物(インドールなど)の, 改質ガソリン中の飽和鎖式化合物(ヘキサン)に比較して芳香族化合物(ベンゼンなど)が選択的にイオン液体中に抽出された. 従来用いられている抽出溶媒に比較して, イオン液体を溶媒とした場合においては収率が高く, 分離の選択度は低かった. どちらの原料混合物においても, 抽出相中からの抽出成分の分離に関して, イオン液体の分解点が抽出成分の沸点範囲より高いことから, 蒸留を用いた分離操作が可能であった.

1. Introduction

Ionic liquids are organic salts that are liquid under 373 K. Ionic liquids have quite low volatility and flammability[4], they are inactive against water and the oxygen.

It has been already reported that the nitrogen compounds and the aromatic hydrocarbons were separated with ionic liquids as solvents from nitrogen/homocyclic compound model mixtures[5], aromatic/aliphatic hydrocarbon model mixtures[2] respectively. However there is no report of the separation from an actual multi-component mixture.

In this work, the ionic liquids were applied to the separation of the actual liquid organic multi-component mixtures as extraction solvents. This would be done by the confirmation of the thermal stability of the ionic liquids and the equilibrium extraction of the organic multi-component oil mixtures. And the separation process in which the extracted components were separated from the extract phase was considered.

## 2. Experimental
2.1. Material System

Four types of ionic liquids were selected as extraction solvents. 1-butyl-3-methyl-imidazolium tetrafluoroborate, [Bmim][BF$_4$]; 1-butyl-3-methylimidazolium hexafluoro-phosphate, [Bmim][PF$_6$], were purchased from Wako Chemical Co. Ltd.

N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate, [Et$_2$MeMeON][BF$_4$]; and N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide, [Et$_2$MeMeON][Tf$_2$N], were provided by Nisshinbo Ind. Inc. (Tokyo, Japan). The structure of these ionic liquids is shown in Figure 1. The actual organic multi-component mixtures were coal tar absorption oil (AO), reformate gasoline (reformate) and light cycle oil (LCO).

2.2. Thermal stability of ionic liquids

The thermal stabilities of ionic liquids were measured by thermogravimetry (TG8120, Rigaku Denki Co. Ltd.) (TG).
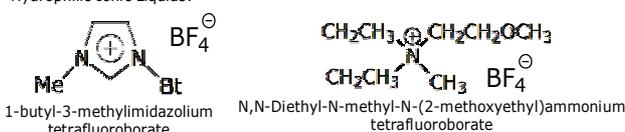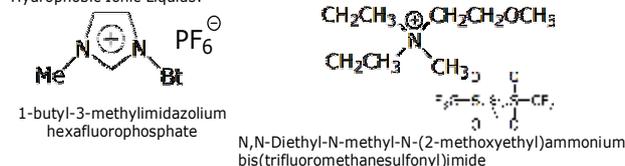

Figure1: The structure of ionic liquids used in this research

2.3. Equilibrium Extraction

All organic multi-component mixtures were brought into contact with each ionic liquid in a 3.5 x 10^{-6} m^3 vial. They were agitated intensely. After settlement, the miscibility between organic multi-component mixtures and the ionic liquids were observed. The immiscible combinations of organic multi-component mixtures and ionic liquids were employed in extraction experiments. The experimental conditions are shown in Table 1. The samples were stirred for 120 hours at room temperature to attain the equilibrium.

Table 1: Experimental Conditions

Feed, R_0	[kg]	0.0010 - 0.0017
Solvent, E_0	[kg]	0.0015 - 0.0023
E_0/R_0	[-]	0.5 - 1.0
Time	[h]	120
Temperature	[K]	296 ± 1

The compositions in the liquid phase were determined by gas chromatography (GC17A, Shimazu) (GC) and Karl-Fisher Titration (Metrohm. Ltd.) (KF). Those in the extract phase were also determined by GC and KF after the reverse extraction was carried out with organic solvents.

3. Results and Discussion
3.1. Thermal stability of ionic liquids

Figure 2 shows the results of the TG analysis. The ionic liquids began to decompose around 600 K. All ionic liquids were thermally stable upto around 600 K.
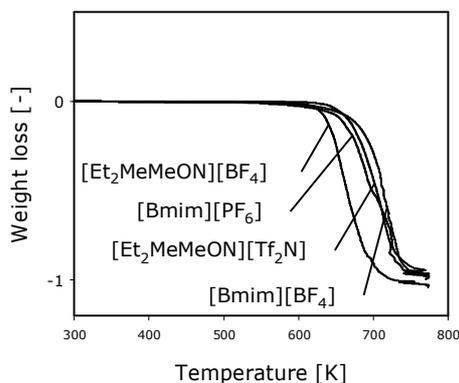
Figure 2: TG diagram of ionic liquids; the ordinate is the weight loss of samples and the transverse is the temperature.

3.3. Equilibrium Extraction

The results of the miscibility were listed in Table 3. The hydrophilic ionic liquids; [Bmim][BF$_4$] and [Et$_2$MeMeON][BF$_4$] were miscible with water, while the hydrophobic ionic liquids; [Bmim][PF$_6$] and [Et$_2$MeMeON][Tf$_2$N] were immiscible with water. All the ILs were immiscible with reformate and LCO.

Table 3: The miscibility Y_i of ionic liquids
with water, absorption oil, reformate and light cycle oil
(O-miscible, X-immiscible)

cation	anion	traditional solvents							
		H$_2$O	AO	reformate	LCO	MeOH	EtOH	Acetone	nC$_6$	Toluene
[BMIM]	[BF$_4$]	O	X	X	X	O	O	O	X	X
[BMIM]	[PF$_6$]	X	O	X	X	O	X	O	X	X
[Et$_2$MeMeON]	[BF$_4$]	O	X	X	X	O	△	O	X	N.A.
[Et$_2$MeMeON]	[Tf$_2$N]	X	O	X	X	O	O	O	X	N.A.

The compositions of feed oils are shown in Table 2, and the gas chromatograms of feed oils are shown in Figure 3. The feed oils contain a lot of components. Among those, the components listed in Table 2 were selected to be identified and studied. And the mass fractions of water were 0.001 and 0.0005 in AO and reformate respectively.

Table 2: The compositions of feed oils; AO and reformate

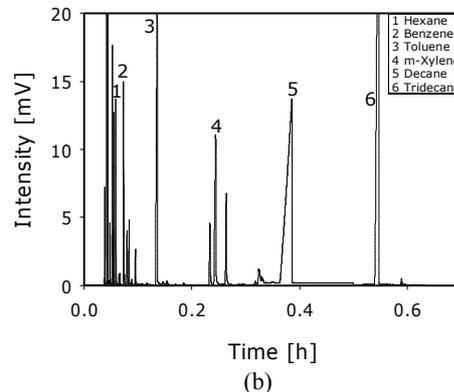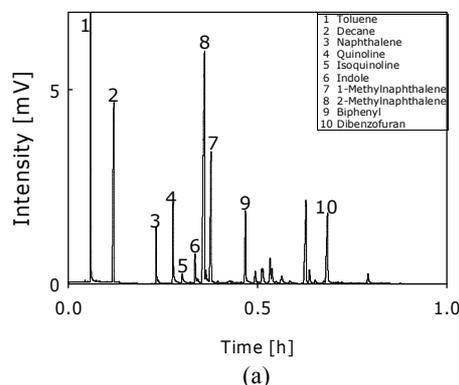| Absorption Oil			Reformate		
constituent	abbrev.	mass fra.	constituent	abbrev.	mass fra.
Quinoline	Q	0.08	Benzene	B	0.05
Isoquinoline	IQ	0.02	Toluene	T	0.23
Indole	I	0.05	m-Xylene	X	0.19
Naphthalene	N	0.03	n-Hexane	H	0.04
1-Methylnaphthalene	1MN	0.11			
2-Methylnaphthalene	2MN	0.25			
Biphenyl	BP	0.07			
Dibenzofuran	DBF	0.12			

(a)

(b)

Figure 3: the gas chromatograms of feed oils
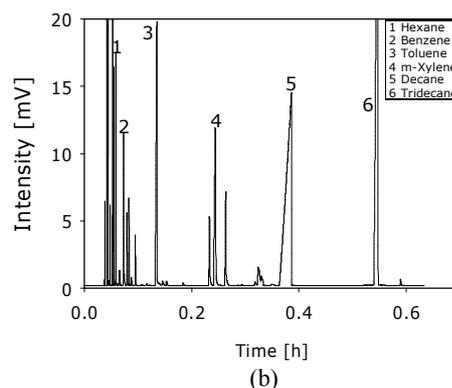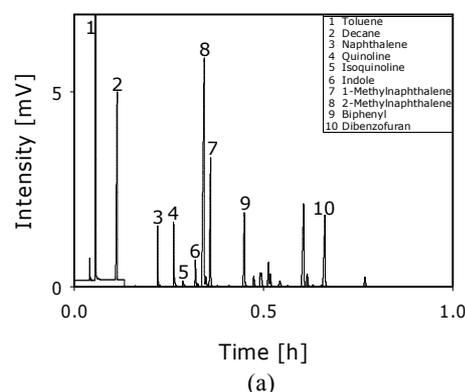(a) AO; (b) reformate

(a)

(b)

Figure 4: the gas chromatograms of the raffinate
(a) AO; (b) reformate

The gas chromatograms of the raffinate are shown in Figure 4. Compared with the gas chromatograms of feed oils, the peaks of nitrogen compounds in AO and those of aromatic hydrocarbons in reformate became smaller, hence the nitrogen compounds and aromatic hydrocarbons preferentially transferred into the extract phase.

It was difficult to analyze the extract phase by means of reverse extraction method, because of the polarity, the structures of ionic liquids and so on, so that the material balance relationship during the runs was not sound. The discussion was based on the composition in the raffinate hereafter. Figures 5 and 6 show the yields of each

component, Y_i, plotted against solvent component in the case of AO and reformate respectively. The yield was defined by equation 1.

$$Y_i = 1 - \frac{Rx_i}{R_0 x_0}$$

Equation 1

In case of AO, the yields with the solvent of ionic liquids were higher than those with the aqueous methanolic solution[1]. The yields of indole with both ionic liquids reached up to 90 percents. In case of reformate, the yields of hexane using ionic liquids were much higher than using sulfolane[3]. The yields of aromatic hydrocarbons with ionic liquids were in the range from 30 to 50 percents.
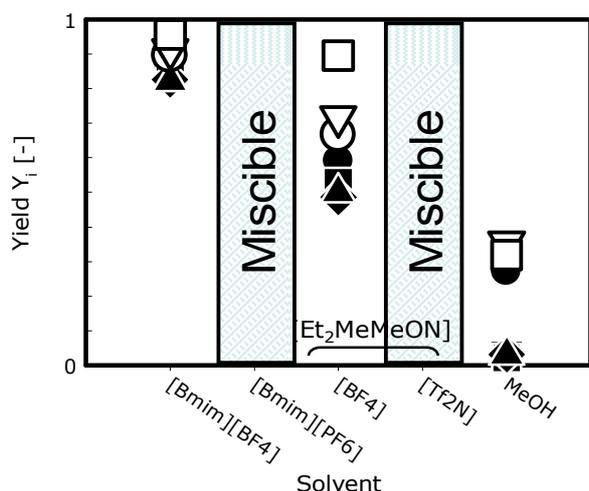
The definition of the separation selectivity is shown in equation 2. The separation selectivities of each compounds in AO and reformate are shown in Figure 7 and 8 respectively.

$$\beta_{i,j} = Y_i / Y_j$$

Equation 2

Since the separation selectivities of nitrogen compounds and aromatic hydrocarbons were higher than the unity in case of AO and reformate respectively, the nitrogen compounds and aromatic hydrocarbons could be separated selectively from AO and reformate respectively. The selectivities with ionic liquids were lower than those with conventional solvents. In AO, indole was extracted more preferentially into the extract phase than the other nitrogen compounds. The separation selectivities of the nitrogen compounds with the ionic liquids constituted a reversal unexpectedly from those with the aqueous methanolic solution, which means the indole had a higher selectivity than the others using the ionic liquids, on the other, hand it had a lower using the aqueous methanolic solution. In reformate, the selectivities with hydrophobic ionic liquids were higher than those with hydrophilic ionic liquids.

Figure 5: the yields, Y_i of AO compositions
○-Quinoline, ▽-Isoquinoline, □-Indole,
●-Naphthalene, ▼- 1-Methylnaphthalene,
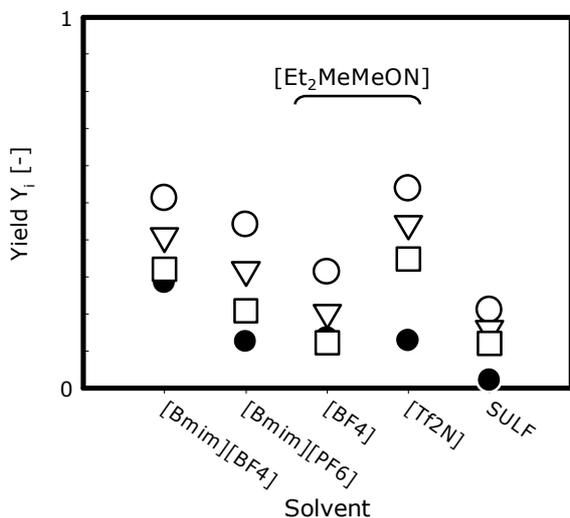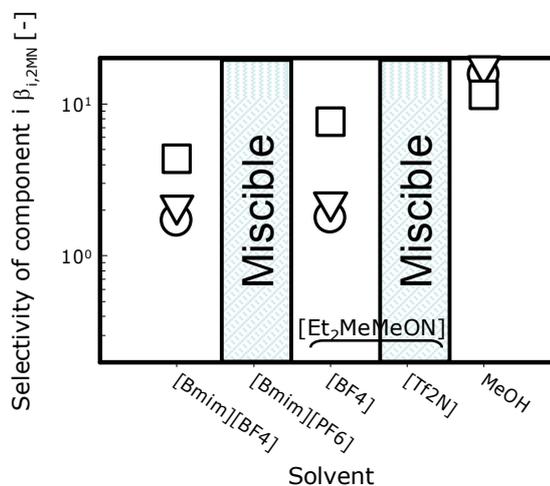■-2-Methylnaphthalene, ◆-Biphenyl,
▲-Dibenzofuran

Figure 7: the separation selectivity in case of AO.
○-Quinoline, ▽-Isoquinoline, □-Indole

Figure 6: the yields, Y_i of reformate compositions
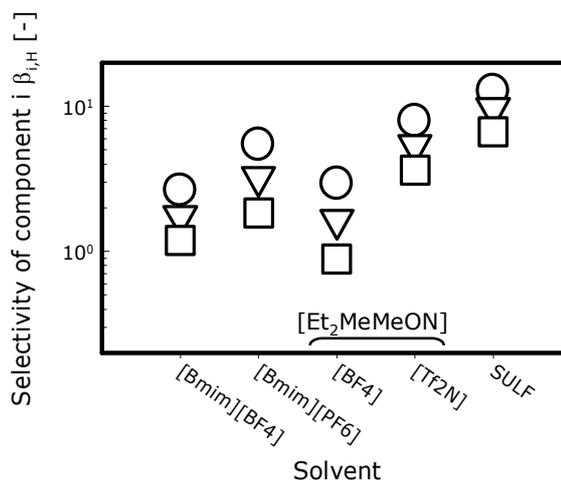○-Benzene, ▽-Toluene, □-m-Xylene, ●-Hexane

Figure 7: the separation selectivity in case of reformate
○-Benzene, ▽-Toluene, □-m-Xylene

3.3. Extraction Process

The separation of the extracted components from the extract phase is required after the extraction. The simple scheme of the separation process is shown in Figure 8. The According to TG results, ionic liquids were remarkably thermally stable upto around 600 K. And there is the difference between the decomposition temperature of the ionic liquids and the boiling range of extracted components. The extracted components in extract phase could be separated from extract phase and the ionic liquid could be recovered by the distillation.
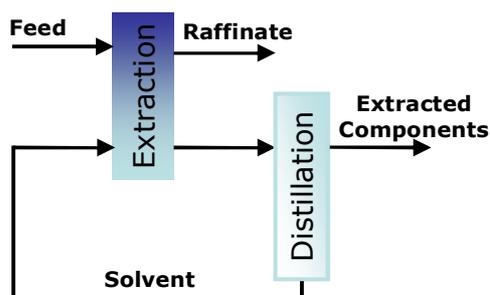

Figure 8: the simple scheme of the separation process

4. Conclusions

The nitrogen compounds and the aromatic hydrocarbons were separated from actual organic multi-component mixtures. The ionic liquids used in this research have the thermal stability upto around 600 K. The solvent extraction could be operated owing to the immiscibility of the ionic liquids. The nitrogen compounds and the aromatic hydrocarbons were separated preferentially from AO and reformate respectively. The yields with ionic liquids were higher than with the conventional solvents. The separation selectivities with ionic liquids were inferior to those with conventional solvents. The selectivities with hydrophobic ionic liquids were higher than with hydrophilic ionic liquids in case of reformate. After the extraction, it could be possible to separate the components in extract and to recover ionic liquids by the distillation

5. Acknowledgment

6. Nomenclatures

R: mass of raffinate   [kg]
R_0: mass of feed   [kg]
x_i: mass fraction of component i in raffinate phase   [-]
$x_{0,i}$: mass fraction of component i in feed   [-]
Y_i: yield of component i   [-]
<subscripts>
i: component i
j: component j
w: water
<greek>
β: separation selectivity   [-]

7. Literature Cited

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