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Extractive Desulfurization of Fuel Using 3-Methylpyridinium-Based Ionic Liquids

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Abstract:

3-Methylpyridinium-based ionic liquids (ILs) were demonstrated to be effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel at room temperature. The results indicated that the extractive performance using 3-methylpyridinium-based ILs followed the order of 1-octyl-3-methylpyridinium tetrafluoroborate ($[C_8^3MPy][BF_4]$) > 1-hexyl-3-methylpyridinium tetrafluoroborate ($[C_6^3MPy][BF_4]$) > 1-butyl-3-methylpyridinium tetrafluoroborate ($[C_4^3MPy][BF_4]$). For a given IL, the sulfur removal selectivity of sulfur compounds followed the order of dibenzothiophene (DBT) > benzothiophene (BT) > thiophene (TS) > 4,6-dibenzothiophene (4,6-DMDBT) under the same conditions except for $[C_8^3MPy][BF_4]$ IL followed the order of DBT > BT > 4,6-DMDBT > TS. The 3-methylpyridinium-based ILs are insoluble in diesel, while diesel has a certain solubility in 3-methylpyridinium-based ILs with the content varying from 6.1 wt % for $[C_4^3MPy][BF_4]$ to 9.5 wt % for $[C_8^3MPy][BF_4]$. The spent IL saturated sulfur compounds could be regenerated by a water dilution process. Considering these results, ILs studied in this work are more competitive and feasible for extractive desulfurization applications. Moreover, the extractive desulfurization using 3-methylpyridinium-based ILs could be used at least as a complementary process to the hydrodesulfurization (HDS).

Keywords: desulfurization, extraction, ionic liquids, diesel

1 Introduction

In the past decade, air pollution has been a major public concern. The combustion of sulfur compounds in gasoline and diesel fuel results in emission of SO_x and sulfate particulate matter, which is major cause of air pollution and acid rain. In order to reduce atmospheric pollution by sulfur oxides, governments around the world have established stringent environmental regulations ([Song, 2003](#)). Hydrodesulfurization (HDS) is a conventional method to remove sulfur compounds for industrial purposes. However, the main drawbacks of HDS include high temperature (> 300 °C), high pressure (> 4 MPa), high-energy cost and difficulty-to-remove aromatic heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives. In order to meet the new environmental regulations, various alternative deep desulfurization processes have been extensively investigated in the past few years, including biodesulfurization ([Shan, 2005](#)), adsorption ([Li, 2007](#)), oxidation ([Otsuki, 2000](#)), and extractive desulfurization ([Shiraishi, 2001](#)).

Recently, various ionic liquids (ILs) have been used as extractants for the removal of sulfur compounds from the fuel due to their unique chemical and physical properties such as

negligible vapor pressure, high chemical and thermal stabilities, and ability to dissolve a wide range of organic and inorganic compounds (Welton, 1999). The extractive desulfurization process using ionic liquids can be a complementary technology for the HDS process (Bösmann, 2001; Eßer, 2004; Gao, 2008; Nie, 2006; Nie, 2008; Zhang, 2002; Zhang, 2004). These studies indicated that the ILs have high extraction ratios and greater selectivity compared to molecular solvents because of the unique solvent characteristics of ILs. The sulfur compounds mainly studied are aromatic sulfur compounds, such as BT and DBT dissolved in dodecane as a model oil system. All those studied focused only on *N*-methylimidzole-based ILs. For the IL extractive desulfurization process, the attention is focused on finding an effective IL which is thermally stable, is non-sensitive to moisture and air, has a low cost for commercial application, and has high extractive performance. In our previous study (Gao, 2008), pyridinium-based ILs, *N*-butylpyridinium tetrafluoroborate ([C₄Py][BF₄]), *N*-hexylpyridinium tetrafluoroborate ([C₆Py][BF₄]) and *N*-octylpyridinium tetrafluoroborate ([C₈Py][BF₄]) were synthesized and used for treating model diesel and real diesel, and they all showed good extractive desulfurization performance for fuel. In order to have a better insight into the structure-property relationship of this series of ILs and design a promising extractant, the structure of the cation of pyridinium-based ILs were altered. Therefore, another three 3-methylpyridinium-based ILs [C₄³MPy][BF₄], [C₆³MPy][BF₄], and [C₈³MPy][BF₄] were investigated for the feasibility to desulfurize of diesel according to the Nernst partition coefficient (*K_N*) values.

2 Experimental Section

2.1 Preparation of Ionic Liquids

The ionic liquids [C₄³MPy][BF₄], [C₆³MPy][BF₄] and [C₈³MPy][BF₄] were prepared according to the published procedure (Bonhote, 1996; Wang, 2005). The structure of these ILs, as shown in Figure 1, has been identified by ¹H NMR, and the ¹H NMR data agree with IL structures.

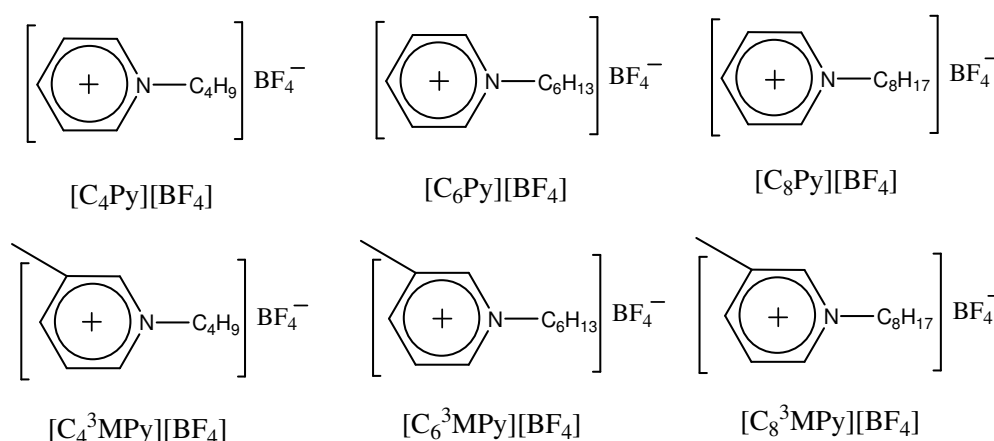


Figure 1. Chemical structures of the pyridinium-based ILs

2.3 Extractive Desulfurization Process

All the extractive desulfurization experiments were conducted in a 50 mL flask. The mass ratios of ILs to model diesel or diesel fuel were 1:1 or 1:3. The ILs were added to the model diesel or diesel fuel, magnetically stirred for 15 min at room temperature to reach

thermodynamic equilibrium, and then allowed to settle for 5 min to obtain phase splitting and settling.

2.4 Analytical Methods

HPLC was used for the quantitative assay of TS, BT, DBT and 4,6-DMDBT in the *n*-dodecane phase. HPLC was performed on a Agilent 1100 (HP1100, Agilent, USA) liquid chromatograph equipped with an autosampler, a reversed-phase Zorbax SB-C18 column (4.6 mm×150 mm; 3.6 μm), and a diode array detector. The mobile phase was 90% of methanol in water (v/v, %) with a flow rate of 1.0 mL/min. For the quantification of TS, the external standard method was used at 230 nm, and for BT, DBT and 4,6-DMDBT the external standard method was used at 280 nm.

3 Results and Discussion

3.1 Cross-Solubility of the ILs and Diesel

Table 1. Solubility of diesel in ILs at 298.15 K in mass percentage

ILs	[C ₄ Py][BF ₄]	[C ₆ Py][BF ₄]	[C ₈ Py][BF ₄]
Oil solubility in IL, wt%	0.49	1.3	1.97
ILs	[C ₄ ³ MPy][BF ₄]	[C ₆ ³ MPy][BF ₄]	[C ₈ ³ MPy][BF ₄]
Oil solubility in IL, wt%	6.1	7.6	9.5

The cross-solubility is an important factor in evaluating the applicability of an extractant, because the variation of diesel composition and quality can be affected by the cross-solubility of the ILs and diesel. If the ILs have negligible solubility in the diesel, the diesel was never contaminated with ILs. If 3-methylpyridinium-based ILs in diesel have noticeable solubility, they may on one hand contaminate the fuel and further lead to a NO_x pollution, as well as increase the cost of recycling ILs. By analyzing the ILs-saturated diesel sample using HPLC, no IL peak was found. Therefore, the 3-methylpyridinium-based ILs studied here have negligible solubility in the diesel. The solubility of diesel in ILs was measured using a gravimetric method by weighing the mass difference of a given amount of ILs and the ILs saturated with diesel. As seen in Table 1, the diesel has a certain solubility in 3-methylpyridinium-based ILs, and its solubility in 3-methylpyridinium-based ILs varies to a large extent for different IL species and follows the order [C₈³MPy][BF₄] > [C₆³MPy][BF₄] > [C₄³MPy][BF₄] with the maximum solubility being 9.5 wt % for [C₈³MPy][BF₄], which is smaller than that reported earlier in the literature (Nie, 2006; Nie, 2008). This diesel solubility order could be mainly attributed to the hydrophobic increase from [C₄³MPy][BF₄] to [C₈³MPy][BF₄], as the alkyl substituents in the ILs increase from butyl to octyl. The results also indicate that the diesel solubility in 3-methylpyridinium-based ILs studied in this paper is larger than our previous study (Gao, 2008). The reason may be that hydrophobicity of these three 3-methylpyridinium-based ILs is stronger than those mentioned in our previous reports due to alkyl substituent in the ring of pyridine.

3.2 Effect of Sulfur Species, and IL Species on Extractive Performance with 3-Methylpyridinium-Based ILs

Table 2. Sulfur partition coefficients (K_N) for extraction of sulfur compounds with different pyridinium-based ILs

IL	K_N in mg(S) kg(IL) ⁻¹ /mg(S) kg(Oil) ⁻¹			
	TS	BT	DBT	4,6-DMDBT
[C ₄ Py][BF ₄]	0.53	0.74	0.77	0.16
[C ₆ Py][BF ₄]	0.70	1.28	1.42	0.48
[C ₈ Py][BF ₄]	0.79	1.40	1.79	0.83
[C ₄ ³ MPy][BF ₄]	0.85	1.75	2.08	0.56
[C ₆ ³ MPy][BF ₄]	1.00	2.08	2.89	0.93
[C ₈ ³ MPy][BF ₄]	1.07	2.16	3.11	1.29

Model oil: 160 ppm S as sulfur compound in *n*-dodecane; mass ratio 1:1, mixing Time 15 min, room temperature.

In order to study the effect of sulfur species on the extraction properties of ILs, the extraction of different sulfur compounds, namely TS, BT, DBT and 4,6-DMDBT in *n*-dodecane by ILs, was carried out at room temperature. Table 2 shows the K_N values for selected sulfur compound typically found in diesel. It also indicates that, for each sulfur compound studied, the extractive performance using 3-methylpyridinium-based ILs followed the order of [C₈³MPy][BF₄] > [C₆³MPy][BF₄] > [C₄³MPy][BF₄]. For a given IL, the sulfur removal selectivity of sulfur compounds followed the order of DBT > BT > TS > 4,6-DMDBT under the same conditions except for the [C₈³MPy][BF₄] ionic liquid that followed the order of DBT > BT > 4,6-DMDBT > TS. The mechanism for the extraction of sulfur compounds with 3-methylpyridinium-based ILs can be explained as the formation of liquid-clathrates and π - π interaction between aromatic structures of sulfur compounds and the pyridinium ring system. The formation of liquid-clathrates due to the interaction between the ionic liquids and aromatics through π - π interaction has been confirmed by Holbrey (Holbrey, 2003). Su also indicated that the cation and anion sizes of ILs played an important role in determining the interaction of absorbed thiophene and ionic liquids (Su, 2004). This work further confirms these results. The 3-methylpyridinium-based ILs studied in this work have the same anions, and their cations, with the substitution of a longer alkyl group, have better extractive performance. It is known that the alkyl group on the pyridine ring is an electron-donting group, which makes the cations *N*-alkylpyridinium highly polarizable aromatic π -electron densities compared to pyridine. Therefore, the interaction of sulfur compounds and the ILs would be expected to be strong. The polarizable aromatic π -electron densities increase from [C₄³MPy][BF₄] to [C₈³MPy][BF₄], as the alkyl substituents in the ILs increase from butyl to octyl. The results also suggest that these 3-methylpyridinium-based ILs have better extractive desulfurization performance than our previous research (Gao, 2008), which could be mainly attributed to the cations size of ILs becoming larger and higher polarizable aromatic π -electron densities because of two methyl group on the pyridine ring. On one hand, as the increase of the cation size, the Coulombic interaction between cation and anion decreases, and π - π interaction between aromatic structures of sulfur compounds and the pyridinium ring system increases. On the other hand, alkyl is an electron donating group, as the size of cation increases, the polarizable aromatic electron densities increase, and π - π interaction between aromatic structures of sulfur compounds and the pyridinium ring system would be strong

(Zhang, 2004). Su further proved that molecules with highly polarizable π -electron density preferably insert into the molecular structure of the ILs (Su, 2004). Zhang also stated that the sulfur compounds with higher density of aromatic π -electron are favorably absorbed by ILs (Zhang, 2002; Zhang, 2004). In our work, the relatively large differences in the partition coefficients of the individual sulfur compounds may be due to the difference of aromatic π -electron density of sulfur compounds. As calculated by Otsuki et al. (Otsuki, 2000), the electron density on the sulfur atoms is 5.760 for 4,6-DMDBT, 5.758 for DBT, 5.739 for BT, and 5.696 for TS, and this difference may further cause the relatively large differences of the sulfur compounds partition coefficients. For sulfur compounds DBT, BT and TS, these results indicate that extractive performance becoming better with the increase of aromatic π -electrons density. However, for 4,6-DMDBT, the methyl substitution at 4 and 6-positions of DBT remarkably retards the extractive performance of 3-methylpyridinium-based ILs.

The sulfur removal performance of 3-methylpyridinium-based ILs [C_4^3MPy][BF_4], [C_6^3MPy][BF_4], and [C_8^3MPy][BF_4] was superior to most ILs reported in the literature except ionic liquid [C_4MIM][$Cl/AlCl_3$] (Eßer, 2004; Nie, 2006), as can be seen from the K_N values for DBT. Considering the fact that [C_4MIM][$Cl/AlCl_3$] is very sensitive to water and thus incompatible with a water environment, the 3-methylpyridinium-based ILs studied in this work are more competitive and feasible for extractive desulfurization applications. Moreover, the extractive desulfurization using 3-methylpyridinium-based ILs could be used at least as a complementary process to the HDS.

3.3 Regeneration of ILs

For the industrial application of an IL extraction process, the regeneration and subsequent recycling of IL are of vital importance. Removal of sulfur compounds from an IL can be done by (a) heating the IL to remove the sulfur compounds (Zhang, 2004), (b) reextraction of sulfur compounds with the low-boiling hydrocarbons pentane or hexane (Eßer, 2004), (c) precipitating the sulfur compounds by a water dilution process (Gao, 2008; Nie, 2006). In this work, regeneration of ILs was obtained through a water dilution process (Gao, 2008), and the used ILs could be nearly recovered by adding about 80% water, and 1H NMR analyses indicated that the ILs also maintained their original structures after regeneration. However, considering the high energy costs for water evaporation, this method for regeneration of ILs is only suitable for laboratory-scale experiments, not in industry. Some efficient techniques for separating water and ILs need further investigation.

4. Conclusions

The 3-methylpyridinium-based ILs were found to be effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel at room temperature. The results suggested that the structure and size of the cation greatly affect the extractive performance of ILs. The extractive performance using pyridinium-based ILs followed the order [C_8^3MPy][BF_4] > [C_6^3MPy][BF_4] > [C_4^3MPy][BF_4], and for the ILs, the sulfur removal selectivity of sulfur compounds followed the order DBT > BT > TS > 4,6-DMDBT under the same conditions except for the [C_8^3MPy][BF_4] ionic liquid that followed the order of DBT > BT > 4,6-DMDBT > TS. The mechanism for the extraction of sulfur compounds with 3-methylpyridinium-based ILs could be explained as the formation of liquid-clathrates and π - π interaction between aromatic

structures of sulfur compounds and the pyridinium ring system. According to the results, $[C_4^3MPy][BF_4]$, $[C_6^3MPy][BF_4]$ and $[C_8^3MPy][BF_4]$ can be used as potential extractants for the extractive desulfurization of diesel.

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