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Abstract: Ionic liquids were found to be highly selective for the extractive removal of aromatic sulfur compounds from fuels at room temperature. The efficiency of ionic liquids for the removal of aromatic sulfur compounds is dependent on the properties and structure of the ionic liquids. In this work, the Lewis-acidic ionic liquid 1-butyl-3-methylimidazolium tetrahalogenoferrate(III) ([BMIM] [$FeCl_4$]) was synthesized and demonstrated to be more effective for the removal of aromatic sulfur compounds from diesel over ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] [BF_4]) because of its Lewis-acidic property. The ionic liquids favorably extracted organic compounds with a higher density of aromatic π-electrons. [BMIM][$FeCl_4$] ionic liquid can be regenerated through reextraction by hexane, and could be used in multiple steps for the removal of sulfur compounds from diesel.

Keywords: Desulfurization, diesel, extraction, ionic liquid, lewis-acidic

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INTRODUCTION

In the last decade, much attention has been paid to the deep desulfurization of fuels due to more stringent environmental regulations (1). Although hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides, and disulfides, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives to an ultra-low level. Therefore, the development of alternative ultra-deep desulfurization processes, such as adsorption (2,3), biodesulfurization (4,5), oxidation (6,7), is desired.

Ionic liquids (ILs) have attracted intensive interest because of their unique chemical and physical properties (8) such as negligible vapor pressure, low toxicity, high chemical and thermal stabilities, and the ability to dissolve a wide range of organic and inorganic compounds. Ionic liquids have been used as alternatives to classical molecular solvents in a range of fundamental researches and applications, including synthesis, catalysis, separation, and so on (9–12).

An extractive desulfurization process using ionic liquids can be a complementary technology for the HDS process, and some studied work has been reported (13–23). Most of them are neutral ionic liquids, and their efficiencies of sulfur removal are rather low. Although $AlCl_3$-based Lewis-acidic ionic liquids have excellent desulfurization results, they are sensitive to moisture and air. In this work, a kind of Lewis-acidic ionic liquid 1-butyl-3-methylimidazolium tetrahalogenoferrate(III) ([BMIM][$FeCl_4$]) and other two ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]), are studied for the extraction of sulfur compounds from model diesel and diesel fuel, and the feasibility of [BMIM][$FeCl_4$] regeneration is also investigated. Unlike $AlCl_3$-based ionic liquids, [BMIM][$FeCl_4$] is air and moisture stable, and is immiscible with water (24). The electronic configuration of Fe^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$. According to π-complexation mechanism the cations with empty s-orbitals and the electron density can form the usual σ bonds with their s-orbitals and, in addition, their d-orbitals can back-donate electron density to the anti-bonding π-orbitals of the sulfur rings. Fe^{3+} can form π-complexation bonding with aromatic sulfur compounds (25). [BMIM][$FeCl_4$] might be used as a promising solvent for the desulfurization of diesel by an extractive desulfurization process.

MATERIALS AND EXPERIMENTAL

The following reagents were purchased from Beijing Chemical Company: chlorobutane, ethyl acetate, dichloromethane, sodium tetrafluoroborate, iron(III) chloride anhydrous, *n*-octane, naphthalene, all of which were analytical grade reagents. *N*-methylimidazole (purity, >99%) was purchased from the Zhejiang Kaile Chemical Plant. Potassium hexafluorophosphate was purchased from Jiangsu Zhang Jiagang Chemical Plant and purified through a twice recrystallization process with deionized water. Dibenzothiophene (DBT) was purchased from Acros Organics, USA. Diesel fuel with 65.7% aromatics was kindly provided by Research Institute of Petroleum Processing.

Preparation of Ionic Liquids

[BMIM][BF_4] and [BMIM][PF_6] ionic liquids were prepared and purified according to the method described in a literature procedure (26,27). [BMIM][$FeCl_4$] was prepared according to a literature procedure (24). ^{1}H NMR spectra data of the [BMIM][BF_4] and [BMIM][PF_6] ionic liquids was determined by using a Bruker AV-400 Spectrometer, and it is in good agreement with that reported in literature (28). The yields of [BMIM][BF_4] and [BMIM][PF_6] ionic liquids are 76% and 81% respectively. The water content of the ionic liquid was determined by Karl Fisher titration, and it is 0.04%, 0.02%, and 0.01% in [BMIM][BF_4], [BMIM][PF_6] and [BMIM][$FeCl_4$] ionic liquids. The chloridion content was determined by chloride-selective electrode, and it is 0.034 mol/kg, 0.012 mol/kg in [BMIM][BF_4] and [BMIM][PF_6] ionic liquids.

Extractive Desulfurization Process

All the extractive desulfurization experiments were conducted in a 50 mL flask. The mass ratios of ionic liquids to model diesel or diesel fuel were 1:3. The ionic liquids were added into model diesel or diesel fuel, magnetically stirred for 15 min at room temperature to reach thermodynamic equilibrium, and then laid aside for 5 min for phase splitting and settling.

Analytical Methods

High-performance liquid chromatography (HPLC) was used for the quantitative assay of DBT and naphthalene in the *n*-octane phase. HPLC was performed on a Agilent 1100 (HP1100, Agilent, USA) liquid chromatography 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 DBT and naphthalene, the external standard method was used at 280 nm.

The total sulfur content (by weight) in diesel fuel was measured in triplicate for each sample by combustion of samples and measurement of the released sulfur dioxide with a micro-coulomb analyzer (RPA-200, JiangHuan Electroanalysis, China).

RESULTS AND DISCUSSION

Extractive Desulfurization Equilibrium

In order to investigate the time needed to reach the extraction equilibrium, a model diesel containing 160 ppm sulfur in the form DBT in the *n*-octane was treated with [BMIM][PF_6], [BMIM][BF_4] and [BMIM][$FeCl_4$]. The sulfur content in the model diesel was measured for 5, 10, 15, 20, and 30 min. Figure 1 showed that the extraction process proceeded quickly, and the equilibrium was reached after 10 min of the extraction process. Consequently, the sulfur content in the model diesel was reached after 10 min and longer stirring did not result in lower sulfur content. The result was in agreement with that reported by Zhang et al. (16). The extraction equilibrium for the DBT between the *n*-octane and the ionic liquids was established so rapidly that the extraction process is rather simple to carry out. In addition, the ionic liquids used in this work are stable to water and are liquid at room temperature.

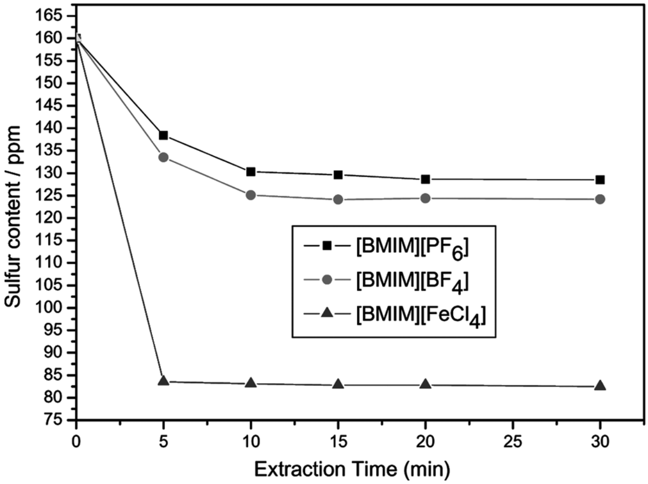

Figure 1. Sulfur content versus extraction time.

Effect of Mass Ratio of Ionic Liquids to Model Diesel on Sulfur Content

To investigate the effect of the mass ratio of ionic liquids to model diesel on the extraction properties of ionic liquids, the extraction of DBT in *n*-octane by ionic liquids under various mass ratio of ionic liquids to model diesel was carried out at room temperature. The sulfur content in Fig. 2 at zero of the mass ratio of ionic liquids to model diesel reflects the original sulfur content in *n*-octane. As shown in Figure 2, the mass ratio of ionic liquids to model diesel has a strong influence on the sulfur content after extraction by ionic liquids. When the mass ratio of ionic liquids to model diesel is 1:5, the sulfur content of the model diesel decreases from its original value of 160 ppm to 137.3, 131.4, and 108.6 ppm after extraction by ionic liquids [BMIM][PF_6], [BMIM][BF_4] and [BMIM][$FeCl_4$]. Thus, the amount of DBT in the model diesel that extracted by [BMIM][PF_6], [BMIM][BF_4] and [BMIM][$FeCl_4$] is 14.2%, 17.9%, and 32.1%, respectively. The result is similar to the literature reported by Bösmann et al. (13). The literature reported that the sulfur removal is 12% and 16%, when the model diesel was prepared by adding DBT to *n*-dodecane, and the mass ratio of [BMIM][PF_6] and [BMIM][BF_4] to model diesel is 1:5. In this work, when the the mass ratio of ionic liquids to model diesel increased to 1:3 and 1:1. The sulfur removal of DBT in the model diesel that extracted by [BMIM][PF_6], [BMIM][BF_4] and [BMIM][$FeCl_4$] is 19.7%, 22.4%, 48.4%, 32.9%,

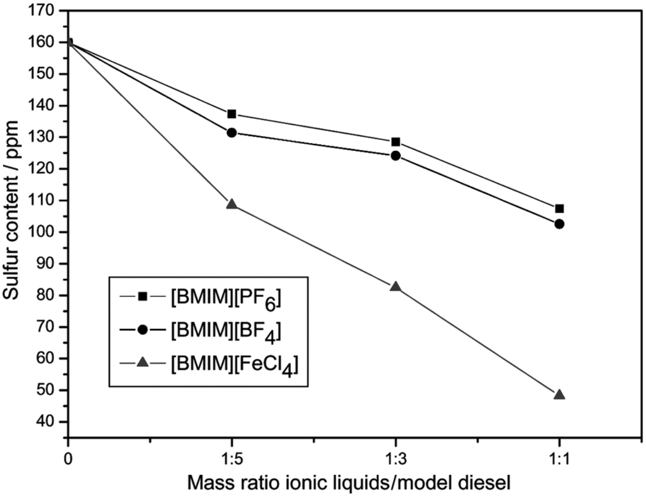

Figure 2. Sulfur content versus mass ratio of ionic liquids to model diesel.

35.9%, and 69.8%, respectively. The sulfur content in *n*-octane decreased rapidly when the extraction solvent was [BMIM][$FeCl_4$]. In contrast, the sulfur content in *n*-octane decreased slightly when the extraction solvents were [BMIM][PF_6] and [BMIM][BF_4].

[BMIM][PF_6] and [BMIM][BF_4] are neutral ionic liquids, the extraction capacity of them for sulfur compound is sensitive to the structure of both anion and cation of the ionic liquids, especially the structure of the cation. The effects of cation and anion sizes on the interaction of absorbed thiophene and ionic liquids have been confirmed by Su et al. (29) Molecules with highly polarizable π-electron density preferably insert into the molecular structure of the ionic liquids. Holbrey et al. (30) also indicated that liquid clathrate could form due to the interaction between the ionic liquids and aromatics through π-π interaction. This work further confirms these results. There is π-π interaction between the cation of the ionic liquids and the DBT, because the cation of the ionic liquids and the DBT possess higher density of aromatic π-electrons. The results also showed that [BMIM][BF_4] has a little better removal of DBT from the model than [BMIM][PF_6], though they have the same cations. The molecule DBT can not interact better with [BMIM][PF_6] than [BMIM][BF_4] due to the anion of [BMIM][PF_6] is larger than that of [BMIM][BF_4]. Though [BMIM][$FeCl_4$] ionic liquid possesses the same cation as [BMIM][PF_6] and [BMIM][BF_4] ionic liquids, it exhibited much better desulfurization performance than [BMIM][PF_6] and [BMIM][BF_4] ionic liquids. [BMIM][$FeCl_4$] is a Lewis-acidic ionic liquid, Lewis-acid-base interactions enhance the extraction power of the ionic liquid (13). Moreover, Fe^{3+} can form π-complexation bonding with the aromatic sulfur compound (25). The electronic configuration of Fe^{3+} is $1s^22s^22p^63s^23p^63d^54s^0$. According to π-complexation mechanism the cations with empty s-orbitals and the electron density can form the usual σ bonds with their s-orbitals and, in addition, their d-orbitals can back-donate electron density to the anti-bonding π-orbitals of the sulfur rings. These interactions further enhance the extraction power of [BMIM][$FeCl_4$].

Effect of Multistage Extraction Steps on Sulfur Content

Although the sulfur removal is not very high in a single extraction, the feasibility for ionic liquids regeneration and reuse makes them attractive for process involing multiple extraction steps. In order to prove the feasibility of ionic liquids for a deep desulfurization process, we tried to reach very low sulfur levels by application of a multistage extraction process. The ionic liquids [BMIM][PF_6], [BMIM][BF_4], and [BMIM][$FeCl_4$]

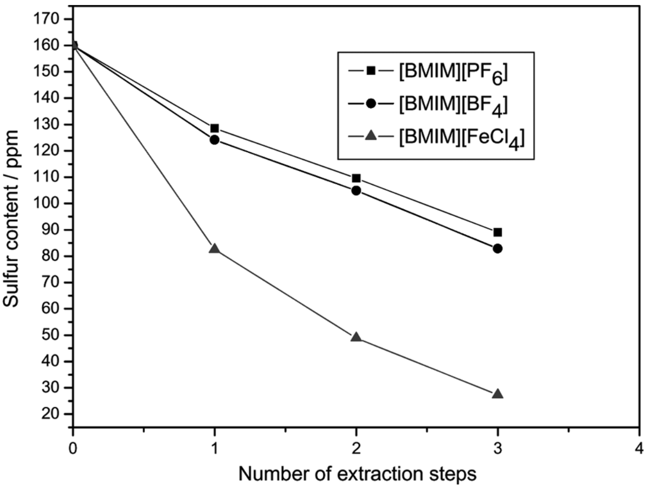

Figure 3. Sulfur content versus number of extraction steps.

were used as the extraction solvents, and the *n*-octane contained some amount of DBT was chosen model diesel. The mass ratio of ionic liquids to model diesel was 1:3. The desulfurized model diesel from the first extraction step was again treated with fresh ionic liquid. This process was repeated up to three times, and the results are shown in Fig. 3.

Figure 3 shows that after three times extractive desulfurization by [BMIM][PF$_6$], [BMIM][BF$_4$], and [BMIM][FeCl$_4$], the sulfur content decreased from 160 ppm to 89.1, 82.9, 27.3 ppm respectively. Thus, the amount of DBT in the model diesel that was removed by [BMIM][PF$_6$], [BMIM][BF$_4$], and [BMIM][FeCl$_4$] is 48.2%, 44.3%, and 82.9%, respectively. It appears that the desulfurization efficiency of [BMIM][FeCl$_4$] was best among these three ionic liquids. The reason is that the Lewis acid-base interaction and Fe^{3+} can form π-complexation bonding with aromatic sulfur compound.

Effect of Aromatic on Sulfur Content

Model diesel with 5.0 mmol/L DBT and 5.0 mmol/L naphthalene were also treated with [BMIM][BF$_4$] and [BMIM][FeCl$_4$] ionic liquids. The results are shown in Fig. 4. The two ionic liquids showed the extraction of a small amount of naphthalene and a relatively larger amount of DBT. Because of the interaction of the aromatic ring with the cation of the ionic liquids, naphthalene also can be extracted by ionic liquids. The two ionic liquids

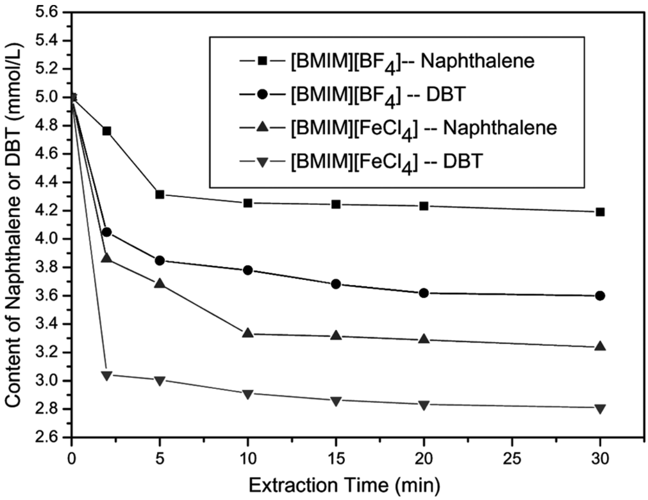

Figure 4. Effects of aromatic on the extractive desulfurization of ionic liquids.

favorably extracted molecules with a higher density of aromatic π-electrons, and the density of aromatic π-electrons of DBT is higher than naphthalene. It is evident that the ionic liquids showed remarkable selectivity for the removal of DBT over naphthalene. For the DBT and naphthalene [BMIM][$FeCl_4$] has higher extraction capacities than does [BMIM][BF_4]. The results suggest that the structure and property of the anion of ionic liquids affect extraction capacity. The interactions of Lewis acid-base interaction and π-complexation bonding between Fe^{3+} with aromatic sulfur compounds further enhance the extraction capacity of [BMIM][BF_4].

Extractive Desulfurizatin of Sulfur Compounds from Diesel Fuel

Diesel fuel with 65.7% aromatics was also treated with these ionic liquids, and its original sulfur content was 122.8 ppm. The diesel fuel was treated by these ionic liquids three times, respectively. The sulfur content and the sulfur removal of the diesel treated every time were shown in Table 1. The results were not better than those of treating model diesel because diesel fuel has complex chemical composition including many different sulfur compounds and higher content aromatic. The ionic liquid [BMIM][$FeCl_4$] showed a remarkable capacity for the removal of sulfur compounds from diesel. This also indicated that Lewis acid-base interactions further enhance its extraction capacity, and if the number of extraction steps is high enough, the deep desulfurization could be obtained.

Table 1. Sulfur removal from diesel fuel by three ionic liquids through three extraction steps at room temperature

Ionic liquids	Step	Sulfur content after treatment	Sulfur removal (%)
[BMIM][BF_4]	1	112.5	8.4
	2	104.9	14.6
	3	99.3	19.1
[BMIM][PF_6]	1	110.4	10.1
	2	101.5	17.3
	3	96.2	21.7
[BMIM][$FeCl_4$]	1	100.4	18.2
	2	85.5	30.3
	3	73.6	40.1

Regeneration of Ionic Liquids

For the technical application of an ionic liquid extraction, the regeneration and subsequently recycling of ionic liquid is of vital importance. Removal of sulfur compounds from an ionic liquid can be done by a few methods, such as (a) Heating the ionic liquid to remove the sulfur compounds (16). (b) Precipitating the sulfur compounds by a water dilution process (18,20). (c) Reextraction sulfur compounds with low-boiling hydrocarbons pentane or hexane (17). In this work, because [BMIM][$FeCl_4$] ionic liquids exhibited good desulfurization performance, regeneration of [BMIM][$FeCl_4$] ionic liquid was investigated. The used [BMIM][$FeCl_4$] ionic liquid was regenerated through reextraction by hexane two times, then the ionic liquid was dried under vacuum at 60°C for 12 h to remove the remaining hexane. The data shown in Table 2 indicates that the [BMIM][$FeCl_4$] ionic liquid can be recycled 3 times without

Table 2. Results of recycle of [BMIM][$FeCl_4$] ionic liquid in desulfurization of model diesel[a]

Cycle	Sulfur removal (%)	Cycle	Sulfur removal (%)
1	48.4	4	46.2
2	47.8	5	43.7
3	47.5		

[a] Model oil: 160 ppm S as sulfur compound in *n*-octane; mass ratio of ionic liquid to model diesel = 1:3, mixing time 15 min, room temperature.

a significant decrease in the desulfurization performance. When 4 cycles had finished, the desulfurization performance decreased slightly with the increase of the cycle. The mass of [BMIM][$FeCl_4$] ionic liquid dropped from 4 g to 3.4 g after 5 operation cycles. When [BMIM][$FeCl_4$] ionic liquid was separated from the model diesel and regenerated, some [BMIM][$FeCl_4$] ionic liquid was lost.

CONCLUSIONS

The ionic liquids [BMIM][PF_6], [BMIM][BF_4], and [BMIM][$FeCl_4$] showed a good ability for the extraction of sulfur compounds from diesel. The extraction process proceeded quickly, and the equilibrium was reached within 10 min. The structure and property of anion of ionic liquids affect their extraction capacity. [BMIM][$FeCl_4$] is a Lewis-acidic ionic liquid, and Fe^{3+} can form π-complexation bonding with aromatic sulfur compound. These interactions further enhance the extraction power of [BMIM][$FeCl_4$], so the extraction efficiency of [BMIM][$FeCl_4$] is better than other two ionic liquids. The ionic liquids favorably extracted DBT with higher density of aromatic π-electrons over naphthalene. [BMIM][$FeCl_4$] ionic liquid can be recycled 3 times without a significant decrease in the desulfurization performance.

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