



Original article

Extractive desulfurization of fuel oil with metal-based ionic liquids

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ABSTRACT

Several metal-based ionic liquids (ILs) were synthesized and used as extractants for the desulfurization of dibenzothiophene (DBT) in simulated fuel oil. The effects of several anion and metal ions, $n(\text{ILs})/n(\text{metal})$ as mole ratio, $V_{\text{IL}}/V_{\text{oil}}$ and extractive times on the removal ratio of DBT were investigated in detail. The results showed that [BMIM]HSO₄/FeCl₃ (BMIM was short for 1-butyl-3-methyl imidazole) was superior to the other ILs for the extractive desulfurization. A total of 100% of DBT was removed at room temperature in 5 min with $V_{[\text{BMIM}]\text{HSO}_4/\text{FeCl}_3}/V_{\text{oil}} = 1 : 1$. The extractive activity of [BMIM]HSO₄/FeCl₃ IL did not change almost after five runs. Extractive desulfurization of different sulfur compounds and commercial diesel fuel oil were also examined. The removal ratios of the sulfur compounds as the reaction substrates were all over 90% and the sulfur content of commercial diesel oil decreased to 120 ppm from 12,400 ppm.

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1. Introduction

With the number automobiles increasing rapidly in the world, organic sulfur compounds present in diesel fuel oils lead to more emission of SO_x by combustion, which not only heavily pollutes the atmosphere, but also irreversibly poisons the noble-metal catalysts in automobile exhaust systems [1–3]. Therefore, the sulfur content specifications in fuels are becoming more and more stringent worldwide. In the petroleum refining industry, catalytic hydrodesulfurization (HDS) is the conventional and commonly used method to reduce sulfur in fuels. However, it is difficult to remove organic sulfur compounds exhibiting steric hindrance at the sulfur atom, such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) [4]. Severe HDS conditions are required to remove these compounds, such as temperatures about 643 K, pressures in the range of 50–100 bar and a liquid hourly space velocity (LHSV) below 1.5 h⁻¹, which inevitably leads to high capital expenditure [5]. Thus, alternative methods that operate at moderate conditions without requiring H₂, such as oxidative desulfurization [6–9], biosulfurization [10], extractive desulfurization [11–13] and adsorptive desulfurization [14] have been investigated. Among these technologies, extractive desulfurization has been studied

extensively because of its facile and simple operation. A number of organic solvents, such as polyalkyleneglycol and polyalkyleneglycol ether, were tested as extractants for the removal of sulfur-containing compounds from fuel oils, but their performances were never satisfactory. Recently, ionic liquids (ILs) have been employed in the extractive desulfurization of fuel oils because of their unique properties, such as the immiscibility with fuel oils, high affinity to sulfur-containing compounds, nonvolatility, and high thermal stability [15–18]. However, the efficiencies of various kinds of ionic liquids used as extractants on sulfur removal were rather low [19,20]. Based on published papers [21,22], metal-based ionic liquids drew our attention and interest due to their obvious advantages. Zhang *et al.* [23] found AlCl₃-based ionic liquids were effective for the removal of S-containing compounds, however, the application of AlCl₃-based ionic liquids was limited to the absorption of certain aromatic compounds, such as DBT. Huang *et al.* [24], found that a CuCl-based ionic liquid exhibited remarkable desulfurization ability in the desulfurization of gasoline; however, the extraction was carried out at relative high temperature 80 °C. Nan Hee Ko *et al.* [25] found Fe^{III}-containing ionic liquids were effective extractants for the desulfurization of a model (simulated) oil consisting of dibenzothiophene (DBT) dissolved in *n*-octane at room temperature.

In this work, we synthesized several different metal-based ionic liquids (ILs) with 1-butyl-3-methyl imidazole (BMIM) as cation, which were used as extractants for the desulfurization of DBT in simulated oil. Additionally, the reaction conditions were optimized

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and the extraction effectiveness of the optimal IL in the extractive desulfurization of different sulfur compounds and actual diesel oil were investigated.

2. Experimental

2.1. Materials

Dibenzothiophene (99%), *n*-octane (analytical pure grade), benzothiophene (97%), ferric chloride (analytical pure grade) and *N*-methylimidazole (99%) were purchased from Aladdin, China, and were used without any further treatment, actual diesel oil (12,400 $\mu\text{g}/\text{mL}$ S) was purchased from Shijiazuang refinery.

2.2. Analysis

A magnetic stirrer (DF-II, Ronghua Instrument Manufacturing Co., Ltd.) under the reactor flask was used to vigorously stir the solution. Concentrations of sulfur compounds were determined by gas chromatography (GC-7900, Shanghai Tianmei Scientific Instruments Co., Ltd.) equipped with Flame Photometric Detector. The prepared ILs were characterized by Fourier transform infrared spectrophotometry (FT-IR) (IRPrestige-21, Shimadzu, Japan) and electrospray ionization mass spectrometry (ESI-MS) (MS-2010EV, Shimadzu, Japan).

2.3. Preparation of ionic liquids

[BMIM]Br/FeCl₃, [BMIM]Cl/FeCl₃, [BMIM]OH/FeCl₃, [BMIM]HSO₄/FeCl₃, [BMIM]BF₄/FeCl₃, [BMIM]HSO₄/CuCl₂, [BMIM]HSO₄/CoCl₂, [BMIM]HSO₄/ZnCl₂, [BMIM]HSO₄/MoCl₂, [BMIM]HSO₄/MnCl₂, [BMIM]HSO₄/FeCl₃ were prepared by the procedures described in published literature [26–28]. The first step is to synthesize the intermediate ([BMIM]Cl), which could be converted to the ILs with different anions, and then followed by the addition of an equal-molar quantity of the corresponding metal salt in a round-bottom flask maintained for 5 h at room temperature (300 K). The residual reactant and water were removed by a rotary evaporator. The ILs were dried in vacuum to yield the products as colorless liquids. In the case of [BMIM]HSO₄/FeCl₃ for example, Scheme 1 shows the synthesis route of [BMIM]HSO₄/FeCl₃. The structures of the prepared ILs were identified by FT-IR and ESI-MS.

2.4. Extractive desulfurization procedure of simulated oil

Simulated oil (1000 $\mu\text{g}/\text{mL}$ S) was prepared by dissolving DBT in *n*-octane. The extractive desulfurization of model oil was conducted in a 50 mL flask. In a typical run, certain volumes of ionic liquid and model oil were added to the flask and the mixture stirred for a certain period of time at a room temperature (300 K). The clarified oil sample was withdrawn periodically and analyzed for sulfur content by gas chromatography with flame photometric detector.

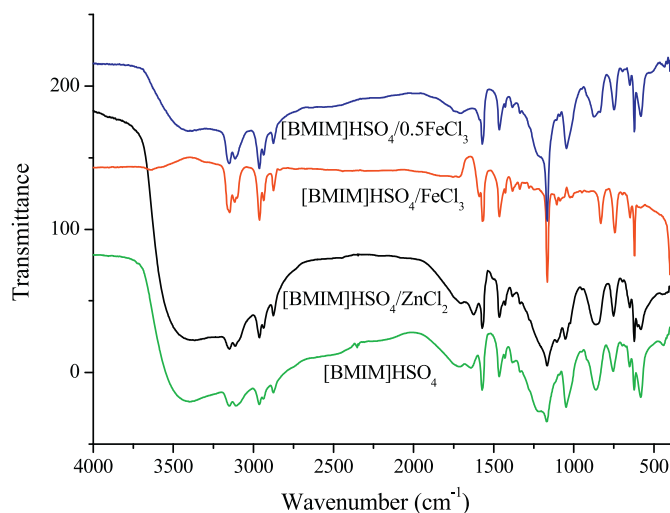


Fig. 1. FT-IR spectra of ionic liquids.

3. Results and discussion

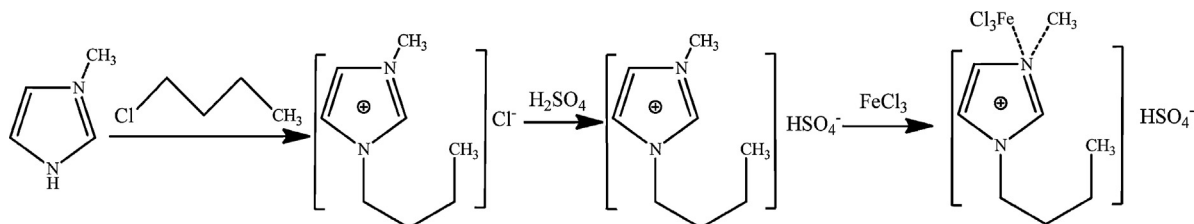
3.1. Characterization of the ILs

The FT-IR spectra of [BMIM]HSO₄/FeCl₃, [BMIM]HSO₄/0.5FeCl₃, [BMIM]HSO₄/ZnCl₂ and [BMIM]HSO₄ ILs are shown in Fig. 1. It is commonly acknowledged that the characteristic absorption peaks of [BMIM]HSO₄ appear at 3148 cm⁻¹, 2961 cm⁻¹, 1573 cm⁻¹, 1170 cm⁻¹, 847 cm⁻¹. The peak could be assigned to the hydrogen bonding between N–H of imidazole with Cl in FeCl₃ [29]. In addition, as demonstrated in Fig. 1, an increase in the amount of FeCl₃ increased the strength of the hydrogen bond because of the existence of the larger FeCl₄⁻ anion [25].

The ESI-MS spectrum of [BMIM]HSO₄/FeCl₃, as a typically representative extractant, was conducted to detect the anions of the IL. From the ESI-MS spectrum of [BMIM]HSO₄/FeCl₃, intensive peaks can be observed at *m/z* = 96.9, 160.84 and 197.8, which correspond to HSO₄⁻, FeCl₃ and FeCl₄⁻, respectively. Thus, the anions of the [BMIM]HSO₄/FeCl₃ IL could be demonstrated conclusively.

3.2. Effect of anions in ILs on the extractive desulfurization of DBT

As seen in Table 1, the nature of the anion in ILs, indeed, had an influence on the extraction activity for DBT when the molar ratio of the metal salt and imidazolium cation are the same. As is well known, the lone pair of electrons on the S atom results in DBT displaying Lewis base properties, while metal-based ILs are Lewis acids. The extractive desulfurization was actually accomplished by the acid-base complexation reaction. Metal-based ILs are the complexes formed by the anions of ILs and metal salts. The complexing powers of various ILs with FeCl₃ are different, which leads to different Lewis acidity. The [BMIM]HSO₄/FeCl₃ IL exhibited



Scheme 1. The synthesis route of [BMIM]HSO₄/FeCl₃ IL.

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