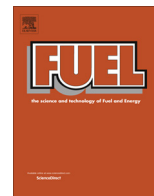




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Temperature-responsive ionic liquid extraction and separation of the aromatic sulfur compounds

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HIGHLIGHTS

- Piperidinium-based ionic liquids were synthesized and applied in extraction desulfurization.
- Temperature-responsive ionic liquid extraction desulfurization was proposed.
- Due to the reversible thermoregulated phase transition of the IL, it was easy for separation of oil and IL.
- The extraction mechanism was studied systematical with experimental and theoretical methods.

ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form 12 September 2014

Accepted 22 September 2014

Available online xxxxx

Keywords:

Temperature-responsive
Extractive desulfurization
Ionic liquid
Fuel

ABSTRACT

Extraction of aromatic sulfur compounds from model oil using a temperature-responsive ionic liquid (IL) N-butyl-N-methylpiperidinium tetrachloroferrate ($[\text{C}_4\text{mpip}]\text{FeCl}_4$) as extractant has been investigated. In the extractive desulfurization process, liquid–liquid equilibrium was obtained at 45 °C for 10 min. After the extraction system was cooled to room temperature, the IL returned to solid due to the reversible thermoregulated phase transition of the IL. Therefore, it was easy for separation of oil and solid $[\text{C}_4\text{mpip}]\text{FeCl}_4$. The extraction efficiency and Nernst partition coefficient (K_N) could get to 45.5% and 2.92, respectively, after a single extraction of DBT. Some important factors, such as extraction temperature, the amount of IL, initial sulfur content, multiple extractions, reusability and the mutual solution were investigated. The extraction ability of different sulfur compounds followed the order $\text{DBT} > \text{BT} > 4,6\text{-DMDBT}$. Finally, the extraction mechanism was studied systematically with experimental and theoretical methods. Compared with the extraction abilities of another three ILs, $[\text{C}_8\text{mpip}]\text{FeCl}_4$, $[\text{C}_{12}\text{-mpip}]\text{FeCl}_4$ and $[\text{C}_4\text{Py}]\text{FeCl}_4$, the size and aromatic structure of cation may be two positive factors but not the main extraction mechanism. The coordination interaction between Fe atom of IL and S atom of DBT was confirmed by IR spectra and theoretical computation.

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1. Introduction

The current oil refineries are facing an increasing technical challenge to remove trace sulfur compounds in transportation fuels due to growing environmental pressures and strict regulatory requirements [1–3]. Hydrodesulfurization (HDS) is viewed as a mature technology in industry, since it is highly efficient in removing thiols, sulfides, and disulfides. However, it requires harsh conditions such as high temperature, high pressure, catalysts with higher activity, and high operating cost to remove aromatic sulfur compounds, particularly alkylated benzothiophenes and dibenzothiophenes [4–6]. Therefore, it is critically important to develop

new desulfurization technologies to minimize the negative health and environmental pollutions from automobile exhaust emissions.

To date, some non-HDS methods based on absorption [7,8], biodesulfurization [9], extraction [10–21], and oxidation [22–26] have been explored. Among them, liquid–liquid extraction desulfurization (EDS) is one of the most promising techniques because it can be performed under mild conditions at low energy consumption and without hydrogen consumption. Furthermore, the process does not change the chemical structure of the fuel components, and the extracted sulfur compounds can be re-used as raw materials. In general, an ideal extractant should have the following properties. Firstly, the partition coefficient for sulfur compounds should be high; secondly, extractants should be absolutely immiscible with oil, easily regenerated, and environmentally benign.

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Compared to the conventional molecular solvents, ionic liquids (ILs) are more desirable for this application due to their unique physicochemical properties, such as the immiscibility with oil, a broad liquid range, negligible vapor pressures, and high thermal stability [27–36]. Jess and his group [11] reported EDS with ionic liquids for the first time, and found that the size of the ions and Lewis acid-base interactions might be important effect for the extraction desulfurization. Then they reported 1,3-dialkylimidazolium alkylsulfates from cheap starting materials, which could be used on a large scale [10]. Zhang et al. [1,12] compared the adsorption capacities of several air- and moisture-stable ILs, [EMIM][BF₄], [BMIM][BF₄] and [BMIM][PF₆], for sulfur-containing compounds, and further elucidated the interaction between thiophene and ILs by multinuclear NMR. Results showed that the chain or the alkyl group on the imidazolium cation and the property and size of the anion determined the absorption capability of thiophene by various ILs. Following these initial reports, there emerged various types of ILs based on some common anions, e.g. BF₄⁻, PF₆⁻, AlCl₄⁻, EtSO₄⁻ [14,16,37,38]. Holbrey and co-workers [18] investigated about 20 kinds of ILs with a range of cation and anion types, and reached a conclusion that the extractive ability of ILs followed the order, methylpyridinium > pyridinium ≈ imidazolium ≈ pyrrolidinium, with much less significant variation with anion type. In addition, they tried to find the solvent group contributions to extraction by quantitative structure–property relationship (QSPR) analysis. However, explaining the differences in the extraction of DBT by the different ILs is challenging. Thus, the mechanism of EDS with ILs is still far from being fully understood.

Up to now, most of the reported ILs in EDS are composed of the conventional imidazolium and pyridinium cations [10,12–16,19,38–47]. Moreover, the oil cannot be separated completely due to the fluidness of the ILs and oil. In this paper, a temperature-responsive ionic liquid extractive desulfurization system was designed, where N-butyl-N-methylpiperidinium tetrachloroferrate ([C₄mpip]FeCl₄) was used as extractant. The solid–liquid transformation temperature of [C₄mpip]FeCl₄ was 41.8 °C, and the extraction temperature was set at 45 °C in extraction process. After cooling the extractive system to room temperature, the solid [C₄mpip]FeCl₄ could be separated easily and efficiently. Some important factors, such as extraction temperature, the amount of IL, initial sulfur content, multiple extractions, reusability and the mutual solution were investigated. The extraction mechanism was investigated through experimental and theoretical methods.

2. Experimental

2.1. Preparation of model oil and ILs

Model oils were prepared by dissolving DBT, BT and 4,6-DMDBT in n-octane to give solutions with a sulfur content of 500, 250 and 250 ppm, respectively. In addition, tetradecane was added into the model oil as an internal standard.

The ILs used in this study was synthesized according to our previous work [48,49]. The structures are shown in Fig. 1. The melting point of [C₄mpip]FeCl₄ is 41.8 °C determined by a digital display microscopic melting point locator X-4 (Beijing Tech Instrument

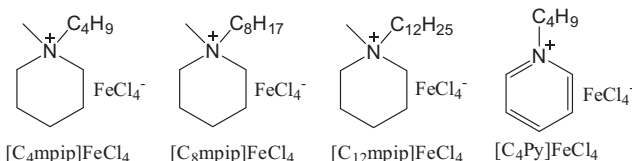


Fig. 1. Structures of the ILs used in this study.

Co., Ltd.). [C₈mpip]FeCl₄ and [C₁₂mpip]FeCl₄ are room temperature ionic liquids.

2.2. Extractive desulfurization

In the general procedure, IL and model oil were placed in a home-made 40 mL two-necked flask. Then the mixture was stirred for 10 min at a given temperature in a water bath. With the same experimental method, the desulfurization reaction was carried out at other reaction conditions.

2.3. Analysis of sulfur content

After the reaction mixture was cooled to room temperature, the ionic liquid changed to solid. Then the upper phase (model oil) was separated by a simple decantation for further analysis via gas chromatography–flame ionization detection (GC-FID) (Agilent 7890A, HP-5 column, 30 m long × 0.32 mm inner diameter (id) × 0.25 μm film thickness). The sulfur extraction efficiency was defined as in Eq. (1), where C₀ (ppm) is the initial sulfur concentration in the model oil, C_f (ppm) is the final sulfur concentration in model oil after extraction. Nernst partition coefficients (K_N) was calculated by Eq. (2)

$$\text{Sulfur removal (\%)} = (1 - C_f/C_0) \times 100 \quad (1)$$

$$K_N = \text{mg (Sulfur) g}^{-1} (\text{IL}) / \text{mg (Sulfur) g}^{-1} (\text{oil}) \quad (2)$$

2.4. Solubility of ionic liquid in n-octane

A high performance liquid chromatography (HPLC) (Agilent Technologies 1200 series equipped with a UV–vis detector under 316 nm wavelength; column, Agilent TC-C18(2) 4.6 × 150 mm 5 μm; column temperature, 35 °C; mobile phase, methanol/water = 85/15; flow-rate, 1 mL min⁻¹) was used to analyze solubility of ionic liquid in n-octane.

3. Results and discussion

3.1. Temperature-responsive extractive behavior of [C₄mpip]FeCl₄

The effect of solid–liquid phase transformation behavior of [C₄mpip]FeCl₄ on extraction is presented in Fig. 2. Under room temperature (30 °C), [C₄mpip]FeCl₄ was solid and the extraction efficiency was 15.8%. When the extraction temperature was increased to 45 °C, [C₄mpip]FeCl₄ transformed to liquid, leading

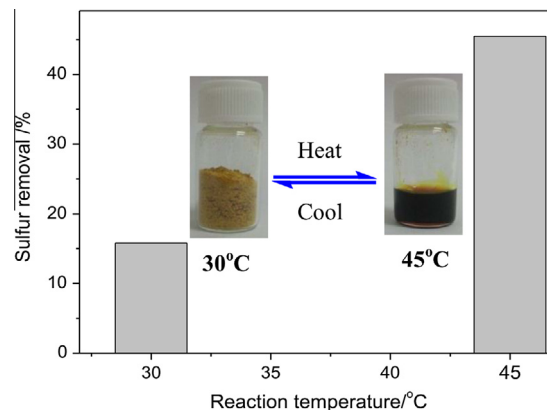


Fig. 2. The solid–liquid phase transformation behavior of [C₄mpip]FeCl₄ and the different extraction efficiencies in this process. Experimental conditions: [C₄mpip]FeCl₄ = 1 g, model oil (DBT) = 5 mL, t = 10 min.

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