



Full Length Article

Synthesis, characterization and application of some non-halogen ionic liquids as green solvents for deep desulfurization of diesel oil



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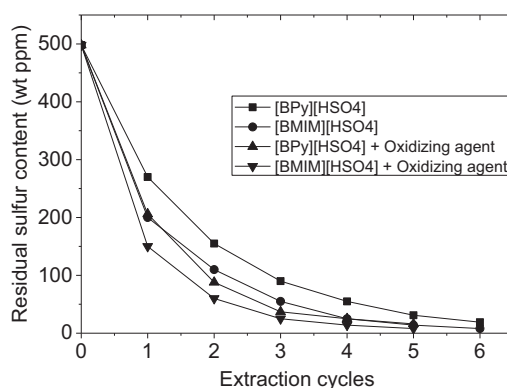
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HIGHLIGHTS

- Five synthesised ILs show high desulfurization efficiency from model and diesel oil.
- Effect of IL and sulfur compound structure on desulfurization was investigated.
- Oxidizing agent increases the desulfurization efficiency of ILs.
- ILs and volatile solvents (used for recovering ILs) show a high reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

Some non-halogen ionic liquids (1-*n*-butyl-3-methylimidazolium hydrosulphates ([BMIM][HSO₄]), 1-*n*-butyl-3-methylimidazolium acetate ([BMIM][CH₃COO]), 1-*n*-butyl-3-methylimidazolium dibutyl phosphate ([BMIM][DBP]), 1-*n*-octyl-3-methylimidazolium hydrosulphates ([OMIM][HSO₄]), and 1-*n*-octyl-3-methylimidazolium acetate ([OMIM][CH₃COO])) were synthesized, characterized, and used as solvents for extraction of sulfur compounds in model oils. All investigated ionic liquids show high desulfurization performance from the model oils. The influence of factors such as the structures of ionic liquid anions and cations, and the structure of sulfur compounds on the deep desulfurization was investigated. Some ionic liquids with high, mild and low desulfurization ability ([OMIM][CH₃COO], [BMIM][DBP], and [BMIM][HSO₄], respectively) were used as solvents to extract sulfur compounds in diesel oil. The residual sulfur contents in diesel oil meet Euro III and Euro IV standards after five or six extraction cycles corresponding to a desulfurization efficiency of approximately 97%. The combination of oxidation reagents and [BMIM][HSO₄] or [BPy][HSO₄] increases the desulfurization efficiency. The used ionic liquids were recovered by re-extraction of sulfur compounds and oxidation products of DBT from ionic liquid

Abbreviations: ASTM, American Society for Testing and Materials; BT, benzothioephene; DBT, dibenzothioephene; [C_nMIM]Cl, 1-methyl-3-alkylimidazolium chloride; [C_nMIM][HSO₄], 1-methyl-3-alkyl imidazolium; [C_nMIM][CH₃COO], 1-methyl-3-alkyl imidazolium acetate; [BMIM]Cl, 1-*n*-butyl-3-methylimidazolium chloride; [BMIM][CH₃COO], 1-*n*-butyl-3-methylimidazolium acetate; [BMIM][DBP], 1-*n*-butyl-3-methylimidazolium dibutyl phosphate; [BMIM][HSO₄], 1-*n*-butyl-3-methylimidazolium hydrosulphate; [BPy][HSO₄], butyl pyridinium hydrosulphate; [C₈MIM][PF₆], 1-*n*-butyl-3-methylimidazolium hexafluorophosphate; COSMO-RS, Conductor like Screening MOdel for Realistic Solvents; DTA, Differential Thermal Analysis; FT-IR, Fourier transform infrared spectroscopy; IL, ionic liquid; ILs, ionic liquids; 4-MDBT, 4-methyl dibenzothioephene; 4,6-DMDBT, 4,6-dimethyl dibenzothioephene; NMR, nuclear magnetic resonance; ODS, oxidative desulfurization; [OMIM][CH₃COO], 1-*n*-octyl-3-methylimidazolium acetate; [OMIM][HSO₄], 1-*n*-octyl-3-methylimidazolium hydrosulphate; TGA, thermogravimetric analysis.

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phase to ethyl acetate or cyclohexane. The formation of sulfones and sulfoxides during oxidative desulfurization was confirmed by FT-IR spectra of ethyl acetate that was used to recover ionic liquids. The slight decrease in desulfurization efficiency of recovered ionic liquids shows their high potential of reusability. Used ethyl acetate and cyclohexane were recovered by distillation and sulfur compounds can be used for other purposes. The extraction process was performed at room temperatures and under normal pressures; no high hydrogen pressure was needed.

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1. Introduction

Sulfur compounds in petroleum lead to equipment corrosion, catalytic deactivation and SO_x emissions that cause air pollution and acid rain. In recent years, regulations on sulfur limits of fuel are increasingly strict [1–3]. The conventional desulfurization method in industry is catalytic hydro desulfurization (HDS). However, benzothiophenes and dibenzothiophenes (DBTs) are highly resistant to hydrogenation and require the processes to be carried out at more severe conditions including the use of more active and high selectivity catalysts and higher consumption of hydrogen, which bring high investment and operating costs [4]. Therefore, extensive research has been carried out during the past decades in industrial and academic research laboratories to deeply desulfurize fuels [5,6].

Some sulfur removing processes operated under moderate conditions without requiring H₂ have been extensively investigated such as biodesulfurization [7], alkyl desulfurization [8], oxidesulfurization [9].

ILs have been examined for effective removal of S-containing aromatic compounds, and these liquids are easy to handle because of nonvolatility, nonflammability, and high thermal stability. The extraction process is based on the fact that sulfur compounds are more soluble in ionic liquids than in hydrocarbons [10–13]. The advantages of desulfurization using ionic liquids are the performance under mild conditions, easy phase separation, high reusability, and adjustable extraction ability by changing the structure of the ionic liquid. However, direct extractive desulfurization by ILs has relatively low desulfurization efficiency in a single extraction and usually requires several continuous extractions (multiple extractions) to reach the stipulated S-content in fuel oils. Oxidative desulfurization (ODS) appears to be particularly promising and is currently receiving increasing attention because it avoids the use of hydrogen, allows the process to be conducted at ambient conditions and brings higher selectivities and desulfurization efficiency. The sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyl dibenzothiophene and their derivatives which are difficult to be removed by the hydrotreating method can be removed by ODS. During the oxidation process, these sulfur compounds could be converted to sulfones and sulfoxides, which have a higher affinity for and have properties considerably differently from those of petroleum compounds. Therefore, they can be easily removed from oil by distillation, extraction, adsorption, and decomposition. For example, dibenzothiophene sulfone (DBTO₂) has higher solubility in IL than this of DBT and is more easily extracted by IL. The nitrogen containing compounds could also be removed during the ODS processes [14]. ODS/extraction using ILs as extractants/catalysts to remove sulfur compounds has been extensively investigated. As an example, the S-content in model diesel fuel composed of DBT and tetradecane is reduced from 758 to 7.8 ppm, a 99% S-removal (70 °C, 1:1 mass ratio of IL/oil, 6 h) when using the [C₄MIM][PF₆]/H₂O₂/CH₃COOH system where [C₄MIM][PF₆] is the extractant, 30 wt% H₂O₂ aqueous solution acts as the oxidant, and acetic acid acts as the catalyst [15]. However, most of the reported ILs are composed of neutral and

the Lewis acidic imidazolium cation and counter anions, such as tetrafluoroborate, copper (II) chloride, chloride or hexafluorophosphate [14–21]. In this research, some non-halogen ionic liquids were synthesized and characterized by infrared and nuclear magnetic resonance spectra. The influence of the structure of ILs and sulfur compounds on the desulfurization of model oil was investigated. Some chosen ILs were used for desulfurization of diesel oil. ILs with lower desulfurization were combined with the oxidizing agent H₂O₂/HCOOH to increase the desulfurization efficiency. The recovery of used ILs and solvents, which were used for recovering them, was investigated. The effort of this work was to develop a mild condition and efficient desulfurization process of diesel oil using ILs. In addition, low-cost available anion based ILs were used in order to reduce the cost of the process.

2. Experimental

1-Methylimidazole (99.5%), 1-chlorobutane (99.8%), 1-chlorooctane (99.8%), dodecane (99.8%), thiophene (99.9%), benzothiophene (99.9%), and dibenzothiophene (99.9%) were purchased from Merck and used without further purification. Sodium acetate (99%), cyclohexane (99.5%), sulfuric acid (99%), and tri butyl phosphate (99%) were purchased from Guangdong Guanghua, China and used as received.

2.1. Preparation of ionic liquids

2.1.1. 1-Methyl-3-alkyl imidazolium chloride ([C_nMIM]Cl)

Equimolar amounts of 1-methylimidazole and 1-chlorobutane (or 1-chlorooctane) were added in a flask containing a magnetic stir bar. The flask was connected to a reflux condenser and immersed in an oil bath. The reaction mixture was stirred for about 100 h at 70 °C. The ionic liquid was washed three times with ethyl acetate to remove any unreacted material and then dried at 110 °C under vacuum (yield = 98%).

2.1.2. 1-Methyl-3-alkyl imidazolium hydrosulphate ([C_nMIM][[HSO₄])

A solution of [C_nMIM]Cl in dichloromethane was added into a round bottomed flask. Then, an equimolar amount of sulfuric acid was added dropwise. The mixture was stirred for 48 h at room temperature and slowly distilled at 80 °C until no HCl released (tested with damp litmus paper), and finally dried at 120 °C under vacuum (yield = 85–88%).

2.1.3. 1-Methyl-3-alkyl imidazolium acetate ([C_nMIM][[CH₃COO])

Ionic liquid 1-methyl-3-alkyl imidazolium acetate was prepared by adding equal molar amounts of [C_nMIM]Cl and sodium acetate to methyl alcohol, and then the mixture was agitated at room temperature for 48 h. The resulting precipitate was then filtered off, and the solvent was removed by evaporation under vacuum to leave a brown liquid (yield = 75–79%).

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