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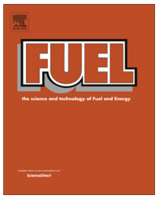

Energy-efficient extractive desulfurization of gasoline by polyether-based ionic liquids

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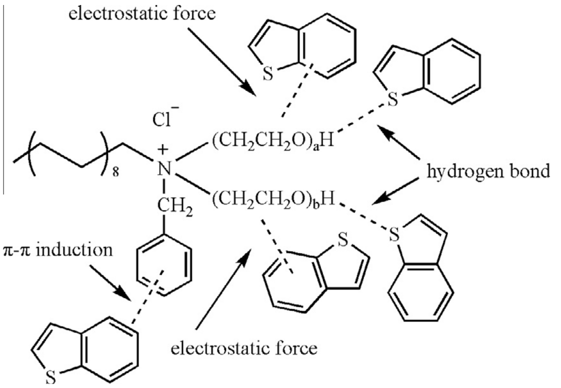
HIGHLIGHTS

- A highly efficient EDS system with polyether-based ILs has been developed.
- The polyether ILs exhibit high affinities for benzothiophenes and phenyl sulfides.
- The extraction equilibrium can be achieved within a few minutes.
- The polyether IL stabilized by NaCl exhibits a remarkable recyclability.
- The polyether IL only has a very low mass loss (6.1%) after 64 times of recycles.

GRAPHICAL ABSTRACT



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ABSTRACT

A highly efficient extractive desulfurization (EDS) system with polyether-based ionic liquids (ILs) as extractants has been developed. The polyether ILs, with two PEG chains and a benzyl group, exhibit very high affinities for sulfur compounds, in particular, for benzothiophenes and phenyl sulfides. These exceptional affinities are due to various interactions between the IL and sulfur compounds, which include electrostatic effects, hydrogen bonding, π–π interactions, and so on. The extraction equilibrium can be achieved within a few minutes near room temperature. The desulfurization rates of the refractory sulfur compounds, viz. benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT), in model gasoline can reach 84.7%, 91.4%, and 81.0%, respectively. For multiple extractions of real gasolines, within four extraction cycles, the desulfurization rate of gasoline $93^{\#}$ was nearly 100%, while the desulfurization rates of gasoline $90^{\#}$ and light hydrocarbon gasoline reached 88.0% and 91.0%, respectively. Furthermore, the polyether IL stabilized by NaCl exhibited remarkable recyclability. The addition of NaCl into the IL minimized the loss of the extractant, making it negligible. After recycling the IL over 64 extraction cycles, the desulfurization rate was reduced by only a small amount and the mass loss of the IL was also very low (6.1%).

1. Introduction

It is well known that sulfur oxides (SO_X) are one of the major sources of air pollution. They are produced during the combustion of fuel containing sulfur compounds. SO_X compounds not only destroy the noble metal catalysts used in automobiles but also lead

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Abbreviations: EDS, extractive desulfurization; IL, ionic liquid; BT, benzothiophene; DBT, dibenzothiophene; 4,6-DMDBT, 4,6-dimethyldibenzothiophene; HDS, hydrodesulfurization; RTIL, room-temperature ionic liquid; TSIL, task-specific ionic liquids; 3-MT, 3-methylthiophene; $DBTO_2$, dibenzothiophene sulfone; BTO_2, benzothiophene sulfone; FPD, flame photometric detector; DR, desulfurization rate.

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to acid rain and ozone depletion. Therefore, to comply with the stringent environmental regulations worldwide, many petroleum refineries are required to reduce the sulfur content in fuel to near-zero levels (<10 ppm) [1–3].

Deep desulfurization has attracted considerable attention and has become a hot research topic in recent years. Many desulfurization technologies have been developed, including extractive desulfurization (EDS) [4], oxidative desulfurization [5–7], ultrasound desulfurization [8,9], biodesulfurization [10,11] and others. Although superior sulfur removal can be achieved with many of these methods, the technology currently used in industry is still based on conventional hydrodesulfurization (HDS) or HDS coupled with pre-EDS. HDS, with its strict operating conditions, not only reduces the octane number of fuel due to the saturation of olefins, but also has limited capacity to efficiently eliminate refractory benzothiophenes such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) due to steric hindrance [12–14].

Among all the developed desulfurization technologies, EDS should be the easiest to implement in industry because of its mild operating conditions, simple operating technology, and cheap equipment. Additionally, EDS has no effect on the octane number of the fuel [15–18]. However, the desulfurization efficiency with simple extraction is relatively low, and it is difficult to achieve deep desulfurization with this process [19]. The conventional flammable/volatile organic extractants such as N,N-dimethylformamide, dimethyl sulfoxide, imidazolidinone, and N-methylpyrrolidone are inefficient and environmentally unfriendly [20,21]. Therefore, it is of great significance to explore new extractants that are highly efficient, environmentally friendly, and economical. Recently, PEG has been investigated as a cheap and green extractant for the EDS of model fuel [22].

From an environmental standpoint, room-temperature ionic liquids (RTILs), as “green” “designer” solvents with many unique properties, such as negligible vapor pressure, high thermal stability, and recyclability, have opened up new ideas for EDS [23,24]. In 2001, Wasserscheid, for the first time, utilized Lewis acidic RTILs as extractants in EDS technology for fuel [25]. Since then, on account of the designability of the ionic liquid (IL) structure, a number of task-specific ionic liquids (TSILs) have been designed and synthesized [26–29]. These pre-designed ILs were endowed with a higher affinity for sulfur compound. Examples of these ILs mostly include imidazolium- and pyridinium-based ILs with different anions, such as [BMIM][MeSO$_4$], [EMIM][DEP], [BPy][NO$_3$], and [MBPy][N(CN)$_2$] [30–33]. Although IL-based EDS has been studied for more than ten years, the process is still not favored for industrial applications due to factors like the high cost of ILs and high mutual solubility of the IL with the fuel. Therefore, rational design of TSILs as extractants should receive more attention for improving the EDS process [34].

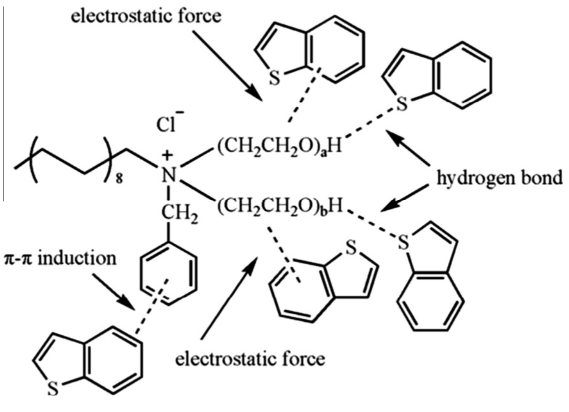

Fig. 1. Proposed mechanism of EDS with the polyether-based IL.

In this paper, we report the development of a highly energy-efficient EDS system using polyether-based ILs as extractants. A series of polyether ILs with two PEG chains, an aromatic ring, and a long-chain alkyl in the structure have been designed and synthesized. As shown in Fig. 1, various interactions operate between the IL and sulfur compounds, which include electrostatic effects, hydrogen bonding, and π–π interactions. The sum total of these weak interactions could lead to very high affinities between the ILs and sulfur compounds like benzothiophenes and phenyl sulfides. The extraction equilibrium can be achieved within a few minutes near room temperature. Moreover, the polyether IL can be stabilized by the addition of a required amount of NaCl, and the loss of the extractant during the extraction process is negligible.

2. Materials and methods

2.1. Materials and instruments

All chemicals purchased were of reagent grade and were used as received. Solvents were dried by known procedures and were freshly distilled before use. A variety of model gasolines were prepared by dissolving different sulfur-containing compounds (4,6-DMDBT, dibenzothiophene (DBT), benzothiophene (BT), thiophene, 3-methylthiophene (3-MT), diphenyl sulfide, methyl phenyl sulfide, ethyl sulfide, and *n*-butyl mercaptan) in *n*-octane. All of the model gasolines had a sulfur content of 500 ppm. Two model fuels were prepared by dissolving dibenzothiophene sulfone (DBTO$_2$) and benzothiophene sulfone (BTO$_2$), respectively, in a 3:1 volume ratio of *n*-octane/toluene both with a sulfur content of 200 ppm. Gasolines 90$^{\#}$ and 93$^{\#}$ with sulfur contents of 464 and 47 ppm, respectively, were purchased from a PetroChina gas station. Light hydrocarbon fuel with a sulfur content of 112 ppm was purchased from Shanxi Petrochemical Co., LTD. Infrared (IR) spectra of the products were recorded using a Nicolet-510P IR spectrometer. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AV 500 MHz spectrometer with tetramethylsilane as the standard. The viscosity of the product was measured using a NDJ-5S rotational viscometer. A Netzsch-TG209 thermal analyzer was used to determine the thermal stability of the product. Gas chromatography (GC) was performed using an Agilent 6890 N instrument equipped with a flame photometric detector (FPD) and a capillary column (OV-1701, 50 m × 0.25 mm × 0.25 mm). The sulfur content of the fuel was measured using a WK-2D microcoulometric detector.

2.2. Synthesis of the polyether-based ILs

The synthesis route of the polyether-based ammonium ILs is outlined in Scheme 1. A certain volume of ethylene oxide was added to *n*-octadecylamine (0.01 mol) in absolute ethyl alcohol in a high-pressure reaction kettle, which was kept at 60 °C for 4–6 h. After the reaction, the solvent and the unreacted ethylene oxide were removed by vacuum distillation to give the *n*-octadecylamine polyether **1**. *n*-Octadecylamine polyether **1** (0.01 mol) and *n*-chlorobutane or benzyl chloride (0.01 mol) were added to a reaction autoclave. The autoclave was filled with N$_2$ gas (5 MPa), and the reaction was performed for 8–10 h at 90 °C under stirring. Subsequently, the reaction mixture was washed with anhydrous diethyl ether, followed by drying in high vacuum to afford the *n*-octadecylamine polyether IL **2** with Cl$^-$ counterions. The polyether IL **2** (0.01 mol) and 10 mL distilled water were added to a round-bottomed flask equipped with a thermometer