



A task-specific phosphonium ionic liquid as an efficient extractant for green desulfurization of liquid fuel: An experimental and computational study



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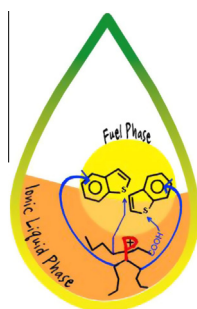
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HIGHLIGHTS

- Successful extractive desulfurization of liquid fuel with [TBCMP][Br].
- [TBCMP][Br] is a task-specific phosphonium ionic liquid (PIL) with acetic acid moiety.
- Desulfurization mechanism by PIL is investigated theoretically for the first time.
- The presence of acid moiety in cation core is vital for effective desulfurization.

GRAPHICAL ABSTRACT



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ABSTRACT

Desulfurization of fuel is essential to be done from the environmental and industrial points of view. Extractive desulfurization (EDS) is one of the most promising methods in order to meet statutory sulfur content. Among of various extractants, ionic liquids (ILs) are more suitable ones due to their desirable and compatible properties having green chemistry disciplines. This work shows that tributyl(carboxymethyl) phosphonium bromide [TBCMP][Br], as a task-specific phosphonium ionic liquid (PIL) including acetic acid moiety, is able to extract benzothiophenic compounds from liquid fuel, successfully. A series of experiments were done to determine the effect of PIL/fuel volume ratio, time, temperature, multiple extraction and initial concentration on EDS performance of [TBCMP][Br]. The efficiency of extraction for sulfur compounds was determined and obeyed the order of dibenzothiophene > benzothiophene > dimethyldibenzothiophene at 69%, 53% and 40%, respectively. For the volume ratio 0.5 in 15 min at room temperature, deep desulfurization can obtain after four extraction times. Finally, the extraction mechanism of PIL, especially the role of acetic acid moiety, was studied experimentally and theoretically for the first time. The computational results show that the alpha hydrogens of methylene groups, connected to phosphonium core and hydrogen of acetic acid moiety, provide hydrogen bonding interaction which indicate [TBCMP][Br] acts as a bi-functional IL for EDS. So, the present work is supposed to create a new and promising insight into the courses of rational designs, syntheses and applications of task-specific ionic liquids for green desulfurization.

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1. Introduction

Sulfur compounds in chemical feed stocks and liquid fuels are one of the most important sources of sulfurous pollutants [1]. Oxyacids of sulfur, producing during the combustion of fuel, lead to many adverse environmental effects so that these have aroused worldwide concerns. In addition, sulfur compounds cause corrosion for parts of internal combustion engines and refineries and also poison and deactivate catalysts used in the crude oil refineries, automobiles and fuel cells [2]. Therefore, removal of sulfur compounds is necessary to be done from the industrial and environmental points of view. Serious regulations were legislated to reduce sulfur contents in fuels to around 10 ppm in many countries from 2010 onward [3].

Although hydrodesulfurization (HDS) process, employed by refineries, is a mature and conventional technology, it is not so effective for benzothiophenic compounds and requires severe conditions with more active catalysts to overcome this problem. This leads to increase the costs [3,4]. Therefore, serious researches were done to upgrade the quality of existing desulfurization technologies such as extraction, oxidation, adsorption, bio-desulfurization and extraction-reduction [5,6] to achieve deep desulfurization. Extractive desulfurization, as a moderate, cheap, fast and effective technology, is a potential method to produce liquid fuel having statutory sulfur content without changing the quality of fuel.

In the recent years, ionic liquids (ILs) have gained more attention because they can be used as a suitable replacements for volatile, flammable and toxic organic solvents in different processes [7,8] including extractive desulfurization (EDS) [6]. Because most of ILs have desirable properties including negligible vapor pressure (which is one of the criteria for green solvents), high thermal and chemical stability, good solvating capacity for a wide range of organic and inorganic compounds and especially design ability [9,10].

After proposing ILs for selective extraction of sulfur compounds from the liquid fuel by Bösmann et al. [11] research efforts have been focused on finding more suitable ILs for EDS [6,12]. These challenges arose from the feasibility of synthesis and availability of a huge number of ILs through the adequate cation–anion combination. The EDS efficiency of ILs is more affected by the interaction between cation of IL and sulfur compounds. Therefore, size and structure of cation play a vital role in extractive performance of IL [10]. ILs containing imidazolium, pyridinium and thiazolium cations have been investigated for EDS [6]. Despite the fact that phosphonium-based ionic liquids (PILs) are well-recognized and they have higher thermal and chemical stability than those ILs mentioned above [13,14]. There are a few works which addressed the use of these types of ILs for EDS [13,15–18]. So exploring the extractive desulfurization of PILs is rewarding. At a glance, it was observed that almost all of the PILs utilized for EDS, contained long alkyl chains [13,16,17]. Although the solubility of organic sulfur compounds in IL and consequently the extraction capacity from fuel increases as the alkyl chains length of IL increases [19], this leads to rise the miscibility and/or mutual-solubility of fuel and IL [20]. As an unwanted effect, this leads to a loss of liquid fuel and increase of process cost. Therefore, PIL containing butyl side chains was selected in this research to decrease the mutual-solubility in this research.

During our researches on the knowledge-based development of task-specific ionic liquids (TSILs) [21], we found that the desirable structural diversity of ILs, having especial properties, could be achieved via design and synthesis of novel cationic cores using suitable anionic counterparts. To follow our recent studies on desulfurization of liquid fuel [22], we decided to join both of these research areas in order to apply a new IL as a green solvent for purification of liquid fuel.

On the basis of our supporting knowledge from literature surveys, the above-mentioned research proposal and our investigations on design, syntheses and applications of TSILs for one decade [21], and various inorganic salts with acidic ability [23], we have prepared tributyl(carboxymethyl)phosphonium bromide (briefly [TBCMP][Br]) with acetic acid moiety according to our previous reported procedure [24]. It is suggested that the interaction between sulfur compounds and ILs occurs in the relatively electron-deficient regions of the ILs [15]. From the chemical structure of [TBCMP][Br] (Fig. 1), it seems that this PIL can provide two electron-deficient regions, as active sites to interact with benzothiophenic compounds having the alpha hydrogens of methylene groups (CH), which are connected to central phosphorus of cationic phosphonium core and COOH functional group of acetic acid moiety. By increasing the number of active sites of the extractant, the extraction capacity may rise, hence we decided to study the EDS performance of [TBCMP][Br], as a dual acidic IL, to remove refractory benzothiophenic compounds i.e. benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) from liquid fuel in the present work. For this purpose, influences of reaction time, volume ratio, initial concentration, sulfur compounds, reaction temperature, multi extraction and reusability were investigated systematically. In addition, the nature of the ILs interaction with aromatic sulfur compounds in fuel is crucial to understand. While the interaction between aromatic sulfur compounds and ILs containing imidazolium, pyridinium cations and metal based ILs has been explored by theoretical studies [25,26]. As far as, we know there is no report on the nature of interaction between aromatic sulfur compounds and PIL. Therefore, some theoretical calculations were performed to reach a better understanding of the interaction between aromatic sulfur compounds and PIL and disclose the mechanism of EDS. Most importantly, the role of carboxylic acid group was experimentally and theoretically investigated by comparing desulfurization performance of [TBCMP][Br] and synthesized tributylethylphosphonium bromide ([TBEP][Br]). To the best of our knowledge, this is the first report about the utilizing of PIL containing acidic site in cationic part for EDS of liquid fuel.

2. Experiment

2.1. Materials

The sources and grade of chemicals utilized to prepare model fuel and synthesize PIL are as follows: *n*-heptane (Merck, >99%), BT, DBT and DMDBT (Sigma–Aldrich, >98%), tributylphosphine (Acros, 98%), bromoacetic acid (Sigma–Aldrich, >99%), *n*-hexane (Merck, 99%) and bromoethane (Merck, 99%). All chemicals were used as received without any further processing and purification.

2.2. Preparation of tributyl(carboxymethyl)phosphonium bromide and Tributylethylphosphonium bromide

Tributyl(carboxymethyl)phosphonium bromide was prepared according to our previous reported procedure [24]. Briefly,

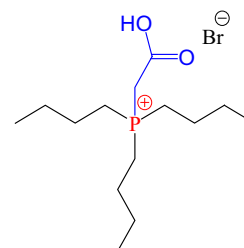


Fig. 1. The chemical structures of [TBCMP][Br].

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