



Full Length Article

Extractive desulfurization of liquid fuel by using a green, neutral and task specific phosphonium ionic liquid with glyceryl moiety: A joint experimental and computational study



Fatemeh Rafiei Moghadam^a, Saeid Azizian^{a,*}, Mehdi Bayat^b, Meysam Yarie^c, Effat Kianpour^a, Mohammad Ali Zolfigol^{c,*}

^a Department of Physical Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65167, Iran

^b Department of Inorganic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65167, Iran

^c Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65167, Iran

HIGHLIGHTS

- Phosphonium ionic liquids (PIL) containing two functional groups were synthesized.
- The prepared PILs show good extraction desulfurization efficiencies from liquid fuel.
- PIL with two alcoholic moieties is recommended for extractive desulfurization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 March 2017

Received in revised form 5 July 2017

Accepted 6 July 2017

Available online 14 July 2017

Keywords:

Desulfurization

Extraction

Ionic liquid

Fuel

Phosphonium

DFT

NBO

EDA

ABSTRACT

A phosphonium ionic liquid with glyceryl moiety was synthesized and used as an efficient extractant in the removal of sulfur compounds from a model liquid fuel. The effects of different parameters such as volume ratio, time, initial concentration, temperature and type of sulfur compound on the desulfurization efficiency were investigated. The reusability and the recyclability of the described ionic liquid in the extractive desulfurization were also studied. For comparison, another ionic liquid with two acidic moieties was synthesized and used in the extractive desulfurization. To understand the mechanism of the extractive desulfurization by the phosphonium ionic liquid, a computational study consisting of structural investigations, interaction energy, NBO, AIM and EDA analysis on the type and nature of the interaction between dibenzothiophene (DBT) and the prepared ionic liquid was also performed. The obtained results of this research support the idea of rational design, synthesis and application of the task specific extractants for the green desulfurization of liquid fuels.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Crude oil contains sulfur, oxygen, nitrogen compounds and some metals in addition to hydrocarbons as the main component. Due to various drawbacks such as catalyst poisoning, corrosive

* Corresponding authors.

E-mail addresses: sdazizian@yahoo.com, sazizian@basu.ac.ir (S. Azizian), mzolfigol@yahoo.com, zolfigol@basu.ac.ir (M.A. Zolfigol).

property, carcinogenicity and environmental problems, these compounds are considered impurities in the crude oil [1]. Sulfur compounds are one of the most important classes of impurities, affecting quality and cost of crude oil and its refined products. Some of the important sulfur compounds in crude oil are sulfides, thiophene, benzothiophene and their derivatives [2]. Sulfur oxides, produced during combustion of fuels, have detrimental effects on the environment [2–4]. Therefore, it is essential to remove sulfur components from liquid fuels effectively. In many countries, the maximum allowable sulfur concentration in fuel is less than 10 ppm [5]. Hydrodesulfurization process (HDS) was introduced in 1930 and has been known as the most important approach in the desulfurization process in the refineries worldwide [2]. The disadvantages of this process are the requirement for high hydrogen content and high temperature (300–450 °C) and pressure (30–100 bar) operating conditions [6–9]. In addition, removal of some aromatic sulfur compounds such as thiophene (TS), benzothiophene (BT), dibenzothiophene (DBT) and their derivatives by the catalytic HDS method is difficult, due to their limited reactivity [10,11]. Therefore, other methods, for instance oxidative desulfurization (ODS), biological desulfurization (BDS), adsorptive desulfurization (ADS) and extractive desulfurization (EDS) are considered for the removal of sulfur compounds from fuels. Among these methods, special attention has been allocated to the extractive desulfurization method because of mild operation conditions (ambient temperature and atmospheric pressure), recyclability of the solvent, maintaining the fuel quality, high speed of the process and easy separation of the refined fuel from the solvent [2,12,13]. The selectivity and removal efficiency of the extraction process are strongly influenced by the type of the extractant. Thus, it is vital to select an appropriate solvent. Ionic liquids, as green solvents, are suitable choices for this purpose [14,15]. The most important features of ionic liquids include [12,15] low vapor pressure, designability and ease of separation from the operating environment [8]. Bossman et al. [16] used a class of imidazolium ionic liquids for extraction of sulfur compounds from liquid fuels for the first time. Afterwards, researches have been trying to find a suitable ionic liquid for the desulfurization of various fuels [9,17]. Although imidazolium ionic liquids perform well in the extractive desulfurization process [8,18], they are expensive [19]. On the other hand, phosphonium ionic liquids are more stable with lower prices [20] and are therefore good candidates for the extractive desulfurization of the liquid fuels. In some research studies, applications of ionic liquids containing long alkyl chains (6–14 carbons) have been reported [5,21]. The presence of long alkyl chains in the structure of the ionic liquids, in spite of their good extraction performance, increases the mutual solubility of the ionic liquids and fuel [20]. In recent studies in our laboratory, phosphonium based ionic liquids, including tributyl (carboxymethyl) phosphonium bromide [TBCMP][Br] (containing an acidic moiety) [20] and tributyl(2-hydroxy ethyl) phosphonium bromide [TBHEP][Br] (containing an alcoholic moiety) [22] have been synthesized and their extractive desulfurization performances have been studied. The obtained results show that the synthesized ionic liquids not only have desirable performances in the extraction desulfurization, but they also have very low mutual solubility with liquid fuel. Hence, to check out more on this class of ionic liquids, two phosphonium ionic liquids, tributyl(2,3-dihydroxy propyl) phosphonium chloride [TBHPP][Cl] (containing two alcoholic functional groups) and tributyl(1,2-dicarboxy ethyl)phosphonium bromide [TBCEP][Br] (containing two acidic functional groups), have been synthesized and their extractive desulfurization performances have been investigated in the present research.

2. Experimental

2.1. Materials

Chemicals including *n*-heptane (>99 wt%), *n*-hexane (>99 wt%) and 1-chloro-2,3-dihydroxy-propane (>98 wt%), purchased from Merck Chemical Co., tri-*n*-butylphosphine (>95 wt%), obtained from Acros Chemical Co., benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) (>98 wt%), supplied by Sigma Aldrich Chemical Co., have been used in order to synthesize the ionic liquid and carry out the extractive desulfurization process in this study.

2.2. Synthesis of the ionic liquids

2.2.1. General procedure for the preparation of tributyl(2,3-dihydroxypropyl)phosphonium chloride

Tributyl(2,3-dihydroxypropyl)phosphonium chloride [TBHPP][Cl] was prepared using the similar reported method for the preparation of phosphonium based ionic liquids by Bellina et al. [23], as follows:

Tri-*n*-butylphosphine (100 mmol, 20.2 g) and 1-chloro-2,3-dihydroxypropane (100 mmol, 11.5 g) were reacted at 120 °C in an oil bath for 72 h under N₂ atmosphere. After completion of the reaction, the mixture was cooled to ambient temperature and washed with *n*-hexane (3 × 100 mL) to afford the desired product (Scheme 1).

2.2.2. General procedure for the preparation of tributyl(1,2-dicarboxyethyl)phosphonium bromide

Bromosuccinic acid (10 mmol, 1.97 g) was added gradually to a round bottom flask containing tri-*n*-butylphosphine (10 mmol, 2.02 g), under nitrogen atmosphere. After the completion of the addition, the mixture was stirred for 48 h at room temperature. The obtained crude product was washed with *n*-hexane and diethyl ether (3 × 10 mL), repetitively, to afford the pure product (Scheme 2). C-NMR, H-NMR and FT-IR spectra of the prepared sample are presented in the [Supporting Information file](#).

2.3. The extractive desulfurization process

In order to carry out the extractive desulfurization process, the model fuel was prepared by dissolving certain amounts of BT, DBT and DMDBT in *n*-heptane. In all the experiments, except in the study of the effect of the sulfur compound, heptane containing DBT has been applied as the model fuel.

In the equilibrium experiments, certain volume ratios of the model fuel and ionic liquid were stirred for 30 min. Having allowed one minute for separation of the two phases from each other, the sampling was done from the top phase (the fuel phase) to measure the residual concentration of the sulfur compound.

In the kinetic experiments, a certain volume ratio of the fuel to the ionic liquid was stirred using a magnetic stirrer. Samples were then taken at different time intervals to determine the residual sulfur content in the model fuel.

Reusability of [TBHPP][Cl] was also tested. After separation of the phases, the used [TBHPP][Cl] was exposed to fresh model fuel and its removal efficiency was measured.

In order to recycle the ionic liquid with water, a determined weight of the used ionic liquid and a specific amount of water (80 wt%) were stirred for 20 min, followed by centrifuging (5 min at 13500 rpm). Afterwards, the solution was heated at 80 °C for 30 min. The obtained recycled ionic liquid was then used in the

Download English Version:

<https://daneshyari.com/en/article/6474086>

Download Persian Version:

<https://daneshyari.com/article/6474086>

[Daneshyari.com](https://daneshyari.com)