Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel

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Abstract In the present paper the experimental data of extractive desulfurization of liquid fuel using 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF4 have been presented. The data of FTIR, 1H NMR and 13C NMR have been discussed for the molecular confirmation of synthesized [BMIM]BF4. Further, the thermal properties, conductivity, solubility, and viscosity analysis of the [BMIM]BF4 were carried out. The effects of reaction time, reaction temperature, sulfur compounds, and recycling of ionic liquid without regeneration on dibenzothiophene removal of liquid fuel were presented. In extractive desulfurization process, the removal of dibenzothiophene in n-dodecane was 73.02% for mass ratio of 1:1 in 30 min at 30 °C under the mild reaction conditions. The ionic liquids could be reused four times without a significant decrease in activity. Also, the desulfurizations of real fuels, multistage extraction were presented. The data and results provided in the present paper explore the significant insights of imidazole ILs for extractive desulfurization of liquid fuels.

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1. Introduction

Sulfur compounds present in liquid fuels may possibly be changed into SOX in fuel engine which pollute the air and causes acid rain, the combustion efficiency of fuels may be reduced by sulfur compounds (S-compounds) which destroy the active catalyst, and promote the emissions of pollutants. Hence, to reduce the content of sulfur as much as possible is a substantial task to produce clean sulfur free fuels (Yu et al., 2011).
In Industry, the hydrodesulfurization (HDS) process is comprehensively used for extractive desulfurization of liquid fuels (Isao and Choi, 2004; Tropsoe et al., 1997; Ma et al., 1994), where S-compounds react with H_{2} and converted into H_{2}S and hydrocarbons (Ferrari et al., 2001; Dumeignil et al., 2006; Pawelec et al., 2001). HDS process is able to remove aliphatic thiols, sulfides, and disulfides effectively, whereas it is not as much efficient for some thiophenic S-compounds like dibenzothiophene (DBT) and its derivatives (Girgis and Gates, 1991). For environmental protection purpose, many countries have mandated reduction of S-level in fuels down to 10 ppm by 2012, and with more stringent regulatory constraint, no sulfur fuels in the next few years are expected (Lu et al., 2006; Nie et al., 2007; Kabe et al., 1992; Huang et al., 2004).

In recent years, several technologies such as extractive desulfurization (EDS), selective adsorption, catalytic oxidation, and biodesulfurization were applied. Among these, EDS is an eye-catching technology, which may be carried out at ambient temperature, pressure, and without H_{2} as a catalyst. A good extractant must have good extractive ability for sulfur compounds, free of contamination to the fuels, non-toxicity, environmental benignity, and stability for repetitive use (Dharaskar et al., 2013). Conventional solvents have their own boundaries of environmental issue, reuse capability, etc. which may be overcome by ionic liquids (ILs) (Jiang et al., 2008). Over the past decade, ILs have fascinated much interest and have been regarded as an environmentally benign solvent. ILs have been studied for many possible applications for green chemical processes, such as an ion conductive matrix, reaction solvent (Li, 2004; Dharaskar et al., 2013). Based on the excellent performance, many research studies have been done about the effectiveness of ILs in some extraction processes, such as desulfurization and denitrogenation. [BMIM]BF_{4} with a mass ratio of 1:1 between tetrafluoroborate anion and imidazole cation has not been investigated in detail for EDS of liquid fuels.

A new class of green solvents, known as ILs have been extensively employed in green chemistry instead of organic solvents because of their low melting point, wide liquid range, negligible vapor pressure and good solubility characteristics etc., (Al-Shahrani et al., 2007) which can competently avoid further environmental concerns.

ILs are usually composed of heterocyclic organic cations and various anions. ILs can be liquid at low temperatures of −96 °C and some are at over 400 °C (Dharaskar et al., 2013; Li, 2004; Earle and Seddon, 2000; Zhou and Antonietti, 2003). ILs can be easily synthesized for any specific application either by careful selection of cation or anion or both, or by attaching new functional groups, such as imide, nitrile, amine, sulfonic acid, ether, alcohol, carboxylic, and thiol, to the structure to impart the desired properties (Muhammad et al., 2011). In the present work, imidazolium based [BMIM]BF_{4} was synthesized, characterized and used for extractive desulfurization of liquid fuel. The data of FTIR, 1H NMR, 13C NMR, thermal properties, conductivity, solubility, and viscosity have been presented. [BMIM]BF_{4} was selected as a representative of imidazolium IL to systematically investigate the effect of time, temperature, sulfur compounds, recycling of spent IL without regeneration, desulfurization of real fuels, and multistage extractions for extractive desulfurization of liquid fuels.

2. Experimental section

2.1. Chemical and materials

IL used in the experimental was synthesized using analytical grade chemicals. The details of the chemicals used are as follows: 1-methylimidazole (CAS 616-47-7, Acros, 99%), 1-bromobutane (CAS 109-69-3, Acros, min 99%), NaBF_{4} (CAS 237-340-6, Sigma Aldrich, 98%), Acetone (CAS 20003-L25, SDFCL, 99.5%), Ethyl Acetate (CAS 20108-L25, SDFCL, 99.5%), dibenzothiophene (DBT) (CAS 132-65-0, Acros, 98%), n-dodecane (CAS 94094-93-6, Acros, 99%), Benzothiophene (BT) (CAS 95-15-8, Sigma–Aldrich, 99%), Thiophene (T) (CAS 110-02-1, Sigma Aldrich, 99%), 3-methylthiophene (3-MT) (CAS 616-44-4, Sigma–Aldrich, 98%). All chemicals were used without any further purification. Real fuels were purchased from Local Petroleum Pump House, Nagpur, Maharashtra (India).

2.2. Synthesis of IL

2.2.1. Synthesis of [BMIM]Br

10.8 g (0.8 mol) of bromobutane and 8.2 g (0.1 mol) of 1-methylimidazole were mixed in three round bottomed flasks fitted with a reflux condenser for 48 h at 70 °C with stirring until formation of two phases. The top layer contains unreacted material which was decanted and 30 ml organic solvent (ethyl acetate) was added with comprehensive mixing. Decanted ethyl acetate was followed by adding fresh ethyl acetate twice. Then, the reaction mixture was washed with ethyl acetate to eliminate unreacted material. After the third decanting of ethyl acetate, remaining solvent was removed by heating at 70 °C. The obtained pale yellow liquid was vacuum distilled and the intermediate product was placed for vacuum drying at 80 °C in a vacuum drying oven (Tshibangu et al., 2011).

2.2.2. Synthesis of [BMIM]BF_{4}

6.57 g (0.03 mol) [BMIM]Br and 3.29 g (0.03 mol) NaBF_{4} were added to the single mouth flask with a definite amount of acetone as solvent, for 10 h at 40 °C under vigorous stirring. The reaction mixture was filtered, and vacuum distilled. Dichloromethane was added to the residue of [BMIM]Br and NaBF_{4}, and white solids precipitated were obtained. Then, the solid precipitate was separated by filtration. Finally, the product was vacuum dried in an oven at 80 °C for 2 h to remove the traces of dichloromethane (Da-peng et al., 2010). The typical synthesis route of [BMIM]BF_{4} is shown in Fig. 1.

2.3. Model liquid fuel preparation

A model liquid fuel with 500 ppmw (parts per million by weight) sulfur (DBT as sulfur source) was prepared in n-dodecane. Similarly, the model liquid fuels were prepared by dissolving BT, T, and 3-MT individually in n-dodecane respectively. Actual diesel and gasoline with total S-content of 385.13 and 180.79 ppmw respectively were used.
2.4. Extractive deep-desulfurization

100 ml two necked flasks were used for the extractive desulfurization experiments where 10 ml model liquid fuel and defined amount of IL with various mass ratios (model fuel to IL as 5:1, 3:1, and 1:1) were mixed by vigorous stirring for time range between 5 and 30 min at 30 °C in a water bath. The upper phase (model liquid fuel) was separated after completion of the reaction and settling of the reaction mixture. The upper phase (fuel phase) was analyzed for the sulfur content. The extraction efficiency is presented in terms of the sulfur removal based on the initial and final sulfur content in the fuel.

2.5. Instrumentation

A structure of the [BMIM]BF₄ was analyzed by Fourier transform infrared (FTIR) Shimadzu IR-Affinity 1 Spectrometer (Japan), using the method of KBr pellet. The [BMIM]BF₄ was characterized by 1H NMR and 13C NMR using CDCl3 as solvent on a Varian, USA Mercury Plus 300 MHz for 1H NMR and 76 MHz for 13C NMR spectrometer for the determination of molecular structures and conformations. Thermal stability of [BMIM]BF₄ was determined with SII Co. Exstar TG/DTA (Japan) Thermo-gravimetric analyzer in order to know their upper temperature limit. The sample (10–20 mg) was placed in an aluminum pan and heated above a temperature range of 30–500 °C at a heating rate of 20 °C min⁻¹. The total time given to analyze the thermal stability was 23.5 min over a temperature range from 5 to 300 °C.

Conductivity of [BMIM]BF₄ was measured by PICO + (Lab India) p⁺/conductivity meter. Viscosity of [BMIM]BF₄ was measured using ARG2 Rheometer (TA instruments USA). Solubility of ILs and various solvents are placed into a 50 ml round bottom flask, magnetically stirred and allowed to settle. After phase equilibrium and splitting, the top layer was analyzed by high performance liquid chromatography (HPLC) (Agilent Technologies, 1200 series equipped with a UV–Vis detector and flame ionization detector), and the bottom flask, magnetically stirred and allowed to settle. The upper phase (fuel phase) was analyzed for the sulfur content. The extraction efficiency is presented in terms of the sulfur removal based on the initial and final sulfur content in the fuel.

2.6. Characterization of [BMIM]BF₄

FTIR, 1H NMR, and 13C NMR analyses were carried out for characterization of IL.

2.6.1. FTIR analysis

The FTIR spectra of [BMIM]BF₄ are shown in Fig. 2. The peaks of wave number of 2941 and 2877 cm⁻¹ are the aliphatic asymmetric and symmetric (C–H) stretching vibrations and in-plane bending vibrations at 1193 and 1112.93 cm⁻¹ are due to methyl groups. A broad peak in the range of 3124.68–3200.97 cm⁻¹ is due to quaternary amine salt formation with tetrafluoroborate. Peaks at wave number 1655 and 1465.9 cm⁻¹ are due to C=C and C≡N stretches. Peak at wave number 748.38 and 623.01 cm⁻¹ is due to C–N stretching vibration. Based on FTIR analysis, It was confirmed that a synthesized IL was [BMIM]BF₄.

2.6.2. 1H NMR and 13C NMR analysis

For all NMR analysis, approximately 30 mg of the IL was added into a 5 mm NMR tube. A stem coaxial capillary tube loaded with 0.5 ml of solute was inserted into the 5 mm NMR tube. 1H NMR data (Fig. 3) in ppm (δ) from the internal standard (TMS, 0.0 ppm), chemical shift (multiplicity, integration), and the 13C NMR data (Fig. 4) in ppm (δ) were reported. The results of 1H NMR and 13C NMR analysis of [BMIM]BF₄ are given as follows:

1H NMR (300 MHz, CDCl₃): δ (ppm) 8.857 (2, 1H, t), 7.417 (3, 1H, t), 7.257 (3, 1H, t), 4.191 (6, 2H, t), 1.864 (7, 2H, m), 1.358 (8, 2H, m), 0.959 (9, 3H, t), 3.962 (10, 3H, s).

13C NMR (76 MHz, CDCl₃): δ (ppm) 153.99 (C2), 123.80 (C3, C4), 126.5 (C5, d), 49.57 (C6, d), 31.86 (C7), 19.25 (C8), 13.27 (C9), 36.04 (C10) (see Scheme 1).

3. Results and discussion

The thermal properties, conductivity, solubility and viscosity analysis of IL were also presented. The production of pure IL is very important since impurities have a strong influence on their physical properties and stability.

3.1. Thermal analysis

In [BMIM]BF₄, the onset of thermal decomposition started at 318.2 °C with weight loss of 44.4% and decomposition ends around 445.3 °C with weight loss of 65.7% as shown in Fig. 5. This shows a high thermal stability of the synthesized [BMIM]BF₄.
3.1.1. Conductivity analysis

IL conductivity mainly depends on mobility of its cation because the diffusion coefficients of ILs cations are higher than anions. ILs based on imidazolium cations have the highest ionic conductivity. ILs showing the highest conductivities, e.g., 1-ethyl-3-methylimidazolium thiocyanate and dicyanamide exhibit the lowest electrochemical stabilities.

When conductivity and thermal stability are both required in a separation or extraction process, imidazolium based ILs with stable anions e.g., tetrafluoroborate or trifluoromethylsulfonate are applied (Faridbod et al., 2011). [BMIM]BF₄ shows conductivity value of 1180 (µS cm⁻¹) which is comparatively small. After exchanging of anion, the conductivity of IL could be increased. So, IL has great

Figure 2  FT-IR spectra of [BMIM]BF₄.

Figure 3  ¹H NMR spectra of [BMIM]BF₄.
advantages as compared to conventional organic solvents (Liu et al., 2008).

3.1.2. Viscosity analysis

Viscosity of IL varies inversely with respect to shear rate. The larger cation structure of ILs has more viscosity due to an increase in intermolecular van der waals interactions. Longer alkyl chains of the cation make the liquid more viscous. Table 1 represents that as shear rate increases from 0 to 250 (s$^{-1}$), viscosity of [BMIM]BF$_4$ decreases from 0.1725 to 0.1686 (Pa.s) respectively. Also it was observed that most favorable viscosity found to be at a shear rate of 250 (s$^{-1}$). Similar trends were observed in the literature (Ziyada et al., 2011; Chen et al., 2012).

Similarly, viscosity of IL decreases with respect to shear time at constant temperature (298.2 K) as shown in Table 1, it was observed that the best possible value of viscosity was obtained at 670.55 (s). Similar trends were reported in the literature (Chen et al., 2012).

3.1.3. Solubility analysis

The solubility of IL with six conventional solvents was studied. ILs may be dissolved in some conventional organic solvents such as methanol, acetonitrile, ethanol, acetone and water, but not in all the organic solvents (e.g., IL not dissolved in ethyl acetate). The IL solubility might be changed by changing the anions. Novel two-phase system can be created and used for various applications such as synthesis and extraction (Sun and Zhao, 2006). For the application of IL extractant the solubility mechanism of IL is needed. The imidazolium based IL solubility in liquid fuel may give rise to extractant loss and liquid fuel contamination. This results suggest that the solubility of imidazolium based IL in liquid fuel has to be optimized for future applications.

3.2. Effect of reaction time on sulfur removal

The extractions of model fuel (DBT in $n$-dodecane) with [BMIM]BF$_4$ were carried out for 5, 10, 20, and 30 min at 30 °C with mass ratios of 5:1, 3:1, and 1:1 (Mass ratio of model liquid fuel to IL) as shown in Fig. 6. The desulfurization pro-
cess went quite quickly and sulfur concentration in model fuel decreased with an increase in extraction time and was reduced from 500 to 238.72 ppmw (S-removal 52.2%), 193.85 ppmw (S-removal 61.2%), and 154.20 ppmw (S-removal 69.1%) with mass ratios of 5:1, 3:1, and 1:1 respectively in 20 min. How-

ever, S-concentration decreased continuously with an increase in extraction time and reduced from 500 to 230.65 ppmw (S-re-

moval 53.9%), 169.55 ppmw (S-removal 66%), and 134.9 ppmw (S-removal 73%) with mass ratios of 5:1, 3:1, and 1:1 respectively in 30 min.

At the initial stage of the reaction, sulfur content in the model fuel was very high hence the extraction rate became high with high S-removal rate. As the reaction proceeds extraction rate becomes low with S-removal rate no longer distinctly in-

creases. The results, in Fig. 6, show that contact time of 30 min between the model liquid fuel and IL phase is more than enough to achieve the equilibrium. So the optimum time required for the desulfurization of model fuel was 30 min. The result indicated that the reaction is fast enough to reach

equilibrium.

Imidazolium ILs are more capable of efficiently extracting DBT than other S-containing compounds (Asumana et al., 2010; Yu et al., 2011). This observation was also reported in other IL extraction process for imidazolium based ILs which was attributed for higher polarizable π-electron density of DBT which tends to insert the molecular structure of ILs (Nie et al., 2006). DBT extraction with imidazolium based [BMIM]BF4 is recognized to the π–π interaction between the aromatic ring of imidazolium and the thiophenic ring of DBT. The better DBT removal ability of [BMIM]BF4 is likely to enhance π–π interactions, since, the cation (–C≡N) group in the [BMIM]BF4 anions may interact with the thiophenic ring of DBT (MuMurry, 1992).

3.3. Effect of reaction temperature on sulfur removal

Reaction temperature plays a vital role in the extractive desul-

furization process, Fig. 7 shows the effect of the reaction tem-

perature (20, 25, 35, 45, and 55 °C) on the removal of sulfur.

As shown in Fig. 7, with the increasing reaction temperature from 20 to 35 °C, the removal efficiency of sulfur increases ini-

tially and then decreases. This effect may be attributed that when the reaction temperature was less than 45 °C, as temper-

ature increases the viscosity of IL reduced and then the flexibil-

ity of IL was also improved which forms a viscous flow layer. Thus, DBT removal efficiency in the model fuel by IL in-

creased. When temperature exceeds 35 °C, the flexibility of IL is not noticeably improved. Moreover, S-removal rate will no longer increase and even to some extent decline (Cun et al., 2011).

Therefore, [BMIM]BF4 was best suitable to remove DBT reflected at 35 °C which was taken as the optimal reaction tem-

perature. The S-content of the model fuel decreased from 500 to 254.64 ppmw (49% S-removal), 194.8 ppmw (61% S-re-

moval), and 122 ppmw (75% S-removal) with mass ratios of 5:1, 3:1, and 1:1 respectively as shown in Fig. 7. A significant drop in S-removal was observed when reaction temperature reached 55 °C, and the S-removal was only 21.9%, 40%, and 49.3% with mass ratios of 5:1, 3:1, and 1:1 respectively. Insensitivity to temperature was also observed in other extraction systems such as [BPy]BF4 (Wang et al., 2007), [C(CH2)4SO3H-MIM]Tos (Liu et al., 2008), [BMIM]BF6 and [BMIM]PF6 (MuMurry, 1992). Subsequently, sulfur extraction may be

| Table 1 | Effect of shear rate and shear time on viscosity of [BMIM]BF4. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Shear stress (Pa) | Shear rate (s⁻¹) | Viscosity (Pa.s) | Time (s) | Temperature (K) | Normal stress (Pa) |
| 1.735            | 0.1735          | 10.00           | 0.1735 | 298.2          | 40.482          | 298.2          | 114.8          |
| 2.180            | 0.1731          | 12.59           | 0.1731 | 298.2          | 85.582          | 298.2          | 113.0          |
| 2.734            | 0.1725          | 15.85           | 0.1725 | 298.2          | 130.53          | 298.2          | 108.5          |
| 3.431            | 0.1720          | 19.95           | 0.1720 | 298.2          | 175.50          | 298.2          | 111.5          |
| 4.310            | 0.1716          | 25.12           | 0.1716 | 298.2          | 220.55          | 298.2          | 113.9          |
| 5.392            | 0.1705          | 31.62           | 0.1705 | 298.2          | 265.53          | 298.2          | 110.3          |
| 6.775            | 0.1702          | 39.81           | 0.1702 | 298.2          | 310.52          | 298.2          | 110.2          |
| 8.517            | 0.1699          | 50.12           | 0.1699 | 298.2          | 355.51          | 298.2          | 109.5          |
| 10.71            | 0.1697          | 63.10           | 0.1697 | 298.2          | 400.52          | 298.2          | 107.0          |
| 13.46            | 0.1694          | 79.43           | 0.1694 | 298.2          | 445.49          | 298.2          | 108.2          |
| 16.92            | 0.1692          | 100.0           | 0.1692 | 298.2          | 490.50          | 298.2          | 109.0          |
| 21.27            | 0.1690          | 125.9           | 0.1690 | 298.2          | 535.52          | 298.2          | 108.6          |
| 26.75            | 0.1688          | 158.5           | 0.1688 | 298.2          | 580.56          | 298.2          | 107.6          |
| 33.67            | 0.1687          | 199.5           | 0.1687 | 298.2          | 625.52          | 298.2          | 106.7          |
| 42.14            | 0.1686          | 250.0           | 0.1686 | 298.2          | 670.55          | 298.2          | 99.96          |
is the formation of liquid clathrates and is obtained as without regeneration was re-
exhibits the best sulfur extraction ability for S-re-
displays high S-removal capability from diesel
as shown in Table 3. These results also represented the same reac-
with synthesized ILs. However, the removal of BT, T, and 3-
reached 79% in 30 min in comparison with mass ratios of model fuel to IL as 5:1, 3:1, and 1:1 respectively with spent IL. Reduction of S-removal might be recognized by DBT which is dissolved in IL and decreased the extraction performance of IL. These results indicated that after the IL was recycled four times, the rate of S-removal decreases slightly (Chen et al., 2012).

3.6. Desulfurization of real fuels using [BMIM]BF₄

Real fuel extraction such as diesel and gasoline is much more difficult due to its typical content of various S-compounds and other impurities. The results of extractive desulfurization of diesel and gasoline with imidazolium ILs are also promising. [BMIM]BF₄ displays high S-removal capability from diesel and gasoline in single stage extraction in 30 min at 30 °C with mass ratios of 5:1, 3:1, and 1:1 as shown in Table 5. [BMIM]BF₄ exhibits the best sulfur extraction ability for S-removal in diesel which was reduced from initial sulfur of 385.13 to 278.31 ppmw (27.7% S-removal), 230.58 ppmw (40.1% S-removal), and 170.27 ppmw (55.8% S-removal) with mass ratios of 5:1, 3:1, and 1:1 in single stage extraction respectively. However, in gasoline it was reduced from initial sulfur of 180.79 to 99.78 ppmw (44.8% S-removal), 73.78 ppmw (59.2% S-removal), and 54.07 ppmw (70% S-removal) with mass ratios of 5:1, 3:1, and 1:1 in single stage extraction respectively. Diesel and gasoline contain more heteronuclear compounds than the model fuel, such as nitrogen and sulfur containing compounds (alkylthiophene and benzothiophene) which decrease the ability of imidazolium [BMIM]BF₄ for S-removal. Because of the steric effect of the alkyl group in the aromatic rings, methyl-thiophene, methyl-benzothiophene, methyl-dibenzothiophene, etc., S-containing compounds in diesel and gasoline are extracted less than DBT in the model fuel by ILs (Wang et al., 2007).

3.7. Multistage extraction

Although a high S-removal by [BMIM]BF₄ is obtained as shown in Table 5, the final S-content in fuels cannot meet the definite requirement of low sulfur fuels (e.g., <10–50 ppm). Consequently, multistage extractions are performed, and the results are shown in Tables 6 and 7 respectively. The S-content in diesel drops significantly from 385.13 to 190.99 ppmw (50.4% of S-removal) after 4 cycles and the S-content in gasoline reduced from 180.79 to 49.90 ppmw (44.8% S-removal) after 4 cycles and the S-content in gasoline drops significantly from 180.79 to 99.78 ppmw (44.8% S-removal), 73.78 ppmw (59.2% S-removal), and 54.07 ppmw (70% S-removal) with mass ratios of 5:1, 3:1, and 1:1 in single stage extraction respectively. Diesel and gasoline contain more heteronuclear compounds than the model fuel, such as nitrogen and sulfur containing compounds (alkylthiophene and benzothiophene) which decrease the ability of imidazolium [BMIM]BF₄ for S-removal. Because of the steric effect of the alkyl group in the aromatic rings, methyl-thiophene, methyl-benzothiophene, methyl-dibenzothiophene, etc., S-containing compounds in diesel and gasoline are extracted less than DBT in the model fuel by ILs (Wang et al., 2007).

3.5. Recycling of [BMIM]BF₄ without regeneration

In practical processes, considering the high cost of ILs regeneration process is needed. The S-extraction performance of the [BMIM]BF₄ without regeneration was investigated and the results are shown in Table 4, which shows the desulfurization efficiency of [BMIM]BF₄ without regeneration was reused up to four cycles. It was seen that the spent IL was able to remove DBT from liquid fuel even without regeneration, nevertheless, at a lower efficiency of 30% from 53.9%, 31.2% from 66%, and 38.8% from 73% with mass ratios of model fuel to IL as 5:1, 3:1, and 1:1 respectively with spent IL. Reduction of S-removal might be recognized by DBT which is dissolved in IL and decreased the extraction performance of IL. These results indicated that after the IL was recycled four times, the rate of S-removal decreases slightly (Chen et al., 2012).

Table 2 represents the molecular structures and properties of S-compounds normally found in real fuels such as diesel and gasoline on extraction with pure hydrocarbons. It might be seen that results for thiols, sulfides, and related compounds are quite low (Liu et al., 2008). However, the results for DBT, T, BT, and 3-MT are excellent. Table 2, shows that the most likely mechanism for the extraction of S-compounds with [BMIM]BF₄ is the formation of liquid clathrates and π–π interactions between aromatic structures of the extraction target and the imidazolium ring system (Liu et al., 2008).

In real fuels, many nitrogen, oxygen, and aromatic compounds have existed, which decreased the extraction performance of the IL for S-containing compounds. In real diesel, there were different kinds of alkyl substituted DBTs that are present such as BT, T, and 3-MT. The removal of DBT reached 66% in 30 min. However, the removal of BT, T, and 3-MT was only 63.9%, 53.8%, and 47.9% within 30 min respectively as shown in Table 2 compared with DBT, the electron density on the sulfur atom on BT, T, and 3-MT is lower, which leads to the lower reactivity of S-compounds (Huang et al., 2010). However, the reactivity of the DBT decreased with increasing methyl substituents at the derivative substitute positions, the reactivity sequencing was DBT > BT > T > 3-MT (Ge et al., 2011).

From Table 3, it has been also observed that the removal of DBT using commercial imidazolium ILs was much promising for S-removal and shows the highest removal efficiency of sulfur with a fixed mass ratio of model liquid fuel to ILs as 5:1 in 30 min at 30 °C. The results suggested that using commercial imidazolium based ILs S-removal reached 79% in 30 min in comparison with synthesized ILs. However, the removal of BT, T, and 3-MT was 73.7%, 62.2%, and 56.1% within same time respectively as shown in Table 3. These results also represented the same reactivity sequencing which was DBT > BT > T > 3-MT.

Figure 7 Removal of sulfur from model fuel (DBT in n-dodecane) using [BMIM]BF₄ at different extraction temperature (°C). (Temperature = 20 – 55 °C, Extraction time = 30 min, Initial sulfur concentration = 500 ppmw).
4. Conclusion

Imidazolium ILs can be used for extractive desulfurization of liquid fuels, mainly with regard to those S-compounds that are very complicated to eliminate by common HDS process. [BMIM]BF₄ is the most efficient in the removal of DBT containing liquid fuels and it can reach to 73.02% for single stage extraction at 30 °C in 30 min with a mass ratio of 1:1, which is the noteworthy progress of EDS over HDS process. The data and results of presented work could provide significant insights.
of imidazolium ILs. Thus, the EDS method could be developed into a simple, mild, and environmentally benign method for deep desulfurization.

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