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Deep removal of sulfur from model liquid fuels using 1-Butyl-3-Methylimidazolium Chloride

Swapnil A. Dharaskar^a, Kailas L. Wasewar^{a*}, Mahesh. N. Varma^a, Diwakar. Z Shende^a, Chang Kyoo Yoo^b

^aAdvance Separation Processes and Analytical Laboratory (ASPAL), Department of Chemical Engineering,
Visvesvaraya National Institute of Technology (VNIT),
Nagpur (M.S) India. 440010.

^bEnvironmental Management & Systems Engineering Lab (EMSEL), Dept. of Environmental Science and Engineering,
College of Engineering, Kyung Hee University, Seocheon-dong 1, Giheung-gu, Yongin-Si, Gyeonggi-Do, 446-701, Korea

Abstract

Ionic liquids (ILs) as one kind of green solvents was studied and applied more and more with the development of green technology because of their unique physical and chemical properties. The removal of sulfur from liquid fuel using ionic liquids has been studied. The desulfurization efficiency of 1-butyl-3-methylimidazolium chloride [Bmim]Cl has been tested. The effects of ionic liquid loading, extraction temperature and extraction time on the removal of dibenzothiophene from different model liquid fuels n-dodecane, n-octane, n-hexane, and n-heptane were investigated. The highest extraction with 77.15% sulfur removal efficiency in a single stage extraction process was observed. Also the [Bmim]Cl can be reused in extraction without regeneration with considerable extraction efficiency.

Keywords: Liquid fuel, Sulfur removal, Ionic liquid, Green technology

Nomenclature

ILs	Ionic Liquids
DBT	Dibenzothiophene
[Bmim]Cl	1-butyl-3-methylimidazolium chloride
MF-1	Model Fuel (n –dodecane +DBT)
MF-1	Model Fuel (n –hexane +DBT)
MF-1	Model Fuel (n –heptanes +DBT)
MF-1	Model Fuel (n –octane +DBT)

1. Introduction

In the recent years, deep desulfurization (removal of sulfur at very low level < 200 ppm) of liquid fuel has been getting much attention due to stringent regulations. Sulfur removal from liquid fuels has increasing technical challenge as oil refineries face strong environmental pressures and strict regulatory requirements [1]. Sulfur present in liquid fuels leads to sulfur oxides (SO_x) emissions into the air and inhibits the performance of pollution control equipment of vehicles. Therefore to minimize the negative health and environmental effects from automobile exhaust many countries recently have mandated a reduction in the sulfur content in motor fuel. In 2016, the maximum sulfur content is limited to 10-50 ppm, compared to earlier permitted value of 500 ppm in most countries.

*Corresponding author. Tel.: 0712-2801561; fax.: 0712-2801564
E-mail address: k_wasewar@rediffmail.com, klwasewar@che.vnit.ac.in.

The European Union has stringent fuel quality rules that require maximum diesel sulfur content of 50 ppm in 2005 (350 ppm in 2000), and maximum petrol (gasoline) sulfur content of 50 ppm in 2005 (150 ppm in 2000) [2]. In India as per the Central Pollution Control Board (CPCB) norms the current value of total sulfur content in liquid fuels is upto 350 ppm which has to be lower down to possible extent. Consequently, the deep desulfurization of liquid fuels has attracted attention of the research community worldwide [3].

To obtain low sulfur fuels, hydro-cracking processes or hydro-treating processes are often used in petroleum and hydrocarbon industry. Also catalytic processes for desulfurization through hydro processing are used. While the performance of conventional hydro-processing catalysts have been highly effective for the reduction of sulfur levels, further removal of residual sulfur from the processed fuels is seen to largely increase the cost of hydro-processing. Hence these are highly energy intensive and consumes large amount of hydrogen [4]. There are many other processes for deep-desulfurization of liquid fuel such as extraction, selective adsorption, absorption, azeotropic distillation, hydrodesulfurization, catalytic hydrodesulfurization etc. The deep desulfurization of sulfur compounds from diesel/gasoline fuel with using Ionic liquids is much attractive due to their removal efficiency and other noble properties [5-6].

Ionic liquids, termed as green solvents can be used for desulfurization of liquid fuel due to their unique physical and chemical properties. The potential of ionic liquids for new chemical technologies is beginning to be recognized as they have different application in many areas like as solvent for synthesis, catalysis or extraction, as an enzyme-‘friendly’ co-solvent, in batteries, as lubricant additives, in polymerization, in synthesis of nanoparticles, in analytical chemistry, etc. The potential of ionic liquids have been recognized worldwide. Scientists and engineers have been working in the advancement of preparation and applications of ionic liquid so that it can provide a range of options to industrialists looking to minimize the environmental impact of their chemical processes and processing cost. In petroleum and hydrocarbon industries, various solvents have been used such as ethers, amines, alcohols and other volatile organic compounds for the processes like extraction, absorption, azeotropic distillation etc. These solvents have their own limitations as environmental issue, recycle ability etc. These limitations can be overcome by the use of ionic liquids. So ionic liquids have been studied for possible application related to green chemical processes [7-15]

Ionic liquids are liquids that are comprised entirely by ions. One of the most important advantages of ionic liquids can be tuned or controlled by tailoring their cationic and anionic structures to optimize their physicochemical properties [16-19]. As a kind of extraction solvent, ionic liquid does not remain in the organic phase, which can be greatly convenient for separation [20]. In present paper, the desulfurization efficiency of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) has been tested. Also the effect of ionic liquid loading, extraction temperature, and extraction time on the removal of sulfur from different model fuels was investigated. Also the used [Bmim]Cl was reused in extraction without regeneration with considerable extraction efficiency.

2. Experimental

2.1. Materials and Reagents

All Solvents and chemicals in the experiment were commercially available and used without further purification. 1-methylimidazole ($C_4H_6N_2$) (Acros, min 99+% CAS 616-47-7), 1-chlorobutane or n-butyl chloride C_4H_9Cl (Loba, min 99%, CAS 109-69-3), n-dodecane ($C_{12}H_{26}$) (Acros organics, 99% CAS 112-40-3, USA), dibenzothiophene ($C_{12}H_8S$) (Acros organics, 98% CAS 132-65-0, USA), n-Hexane (SDFCL, min 95%, Product Code:88485.L.25), n- Heptane (C_7H_{16}) (Acros organics, min 99+% CAS 142-82-5), n-Octane (C_8H_{18}) (Acros organics, min 99+% CAS 142-82-5), Acetone (C_3H_6O) (SDFCL, min 99.5%, Product Code: 20003-L25), Ethyl Acetate ($C_4H_8O_2$) (SDFCL, min 99.5%, Product Code: 20108-L25).

2.2. Preparation of [Bmim]Cl

1-butyl-3-methylimidazolium chloride was prepared by the reaction of equimolar amounts of 1-methylimidazole and 1-chlorobutane by heating at 60°C using rota mantle and solution is heated under reflux for 48hr and then cooled to room temperature. Then the product was washed twice with ethyl acetate, the remaining ethyl acetate has removed by heating at 60°C under vacuum drying oven, and the product was freeze-dried for 24hr to obtain a slightly yellow crystalline product.[23]

2.3. Characterization of [Bmim]Cl

The production of pure ionic liquids is very important since impurities have a strong influence on their physical properties and stability. So, special attention was given to characterization of the ionic liquids. The 1-butyl-3-methylimidazolium chloride was analyzed by Varian, USA Mercury Plus 300 MHz NMR spectrometer ($^1\text{H-NMR}$), Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu IR-prestige 21 spectrometer. Their thermal stability was determined with SII Co.TG/DTA Thermo-gravimetric analyzer in order to know their upper temperature limit and also melting point was measured with SIICO AS-3 DSC-7020 differential scanning calorimetry.

The yield of [bmim]Cl was 77%. Typical $^1\text{H-NMR}$ for [Bmim]Cl is obtained as $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ : 0.97 (t, 3H, $J = 7.3$ Hz, CH_3) 1.37 (m, 2H, $J = 7.4$ Hz, CH_2), 1.90 (m, 2H, $J = 7.4$ Hz, CH_2), 4.13 (s, 3H, NCH_3), 4.33 (t, 2H, $J = 7.3$ Hz, NCH_2), 7.33 (t, 1H, $J = 1.8$ Hz, C(2)H), 7.44 (t, 1H, $J = 1.8$ Hz, C(3)H) and 10.9 (s, 1H, C(1)H) [21,23].

Structure of the 1-butyl-3-methylimidazolium chloride [Bmim]Cl were analyzed by Fourier Transform Infra Red Shimadzu IR-Affinity-1 spectrometer, using the method of KBr pellet. The results are shown in Fig. 1.

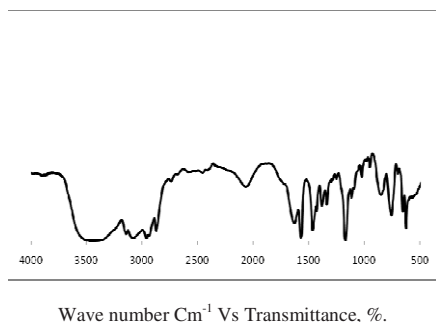


Fig. 1. The IR Spectrum and main IR Peaks of [Bmim]Cl.

The peaks of wave number of 3470 Cm^{-1} and 3350 Cm^{-1} are the stretching vibration peaks of n-butyl hydrogen. At wave number 1570.6 Cm^{-1} and 1485.90 Cm^{-1} there are the imidazole ring skeletons vibration absorption peaks. At wave number 1186 Cm^{-1} there is the methyl hydrogen's deformation absorption peak. The skeleton vibration of C-C is at 1570.6 Cm^{-1} . 1186 Cm^{-1} , 623.01 Cm^{-1} is the inner and outer bending vibration of C-H respectively. From these curve we can get the preliminary conclusion that what we synthesizes was the aimed product 1-butyl-3-methylimidazolium chloride [Bmim]Cl [22].

To determine the thermal stability of the [Bmim]Cl, TGA and DTG Curve of the 1-butyl-3-methylimidazolium chloride [Bmim]Cl were shown in Fig.2.

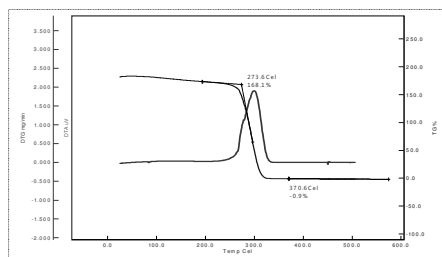


Fig. 2. Thermo-gravimetric analyzer (TGA) analysis of [Bmim]Cl.

The sample (10-20 mg) was placed in an aluminium pan and heated over a temperature range of $30\text{--}500\text{ }^\circ\text{C}$ or $30\text{--}600\text{ }^\circ\text{C}$ at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$. The thermal stability was determined over temperature range from $30\text{--}500\text{ }^\circ\text{C}$. The onset of thermal decomposition started at $270\text{ }^\circ\text{C}$ with the weight loss in TG% and decomposition ends around $370.6\text{ }^\circ\text{C}$ with some weight loss in TG %. No further decomposition was observed. This gives a high thermal stability for the ionic liquid under study.

Imidazolium salts have high thermal stability beginning to decompose around $400\text{ }^\circ\text{C}$. Recent reports have shown that the presence of a halide anion reduced the thermal stability of an imidazolium ionic liquid with onset occurring at least at a room temperature of about $100\text{ }^\circ\text{C}$ below other imidazolium salts. The derivative thermogravimetric analyses (DTG), of the ionic liquid indicate the presence of single decomposition peak as observed in TGA [23].

The melting point of synthesised 1-butyl-3-methylimidazolium chloride is the important indicator of an ionic liquid

analyzed by differential scanning calorimetry (DSC). The samples for DSC analysis were 10-20 mg; the heating and cooling rate was 20 °C min⁻¹ over a temperature range of 30-120 °C and the carrier gas was nitrogen. The samples were placed in an aluminium pan, and an empty aluminium pan was used as a reference. The melting point was measured from the highest position at the peak of the heating cycle. The melting point determine with DSC showed only one transition, indicating that the product was pure. The melting point of [Bmim]Cl measured with DSC was 65.1⁰C and the results are shown in Fig.3. The DSC trace showed only one transition, indicating that product was pure [21].

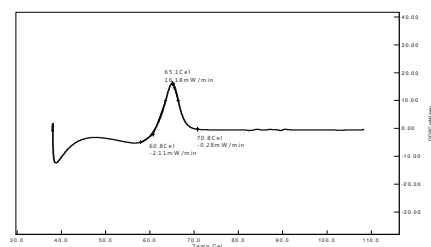


Fig. 3. Differential Scanning Calorimetric (DSC) analysis of [Bmim]Cl.

2.4. Preparation of model fuels

Model fuel was prepared by dissolving dibenzothiophene (DBT) in n-dodecane, n-octane, n-hexane, and n-heptane and named as MF-1, MF-2, MF-3, and MF-4 respectively (Table 1).

Table 1. Composition of model fuels (MFs).

System	Sulfur Compound	Sulfur Content [ppm]	Hydrocarbon solvent
MF-1	Dibenzothiophene	50 - 1000	n-Dodecane
MF-2	Dibenzothiophene	50 - 1000	n-Hexane
MF-3	Dibenzothiophene	50 - 1000	n-Heptane
MF-4	Dibenzothiophene	50 - 1000	n-Octane

2.5. Desulfurization experiment

All the desulfurization experiments were conducted in a 100 ml conical flask. Extraction experiment was carried out by mixing 5ml of model fuel and some amount of Ionic Liquids (IL). The mass ratios of the model fuel were 5:1. The biphasic mixture was stirred for 30 min in water bath. Then upper phase (model fuel) was withdrawn and the sulfur content was determined with an uncertainty of ± 1 ppm by using Thermo Scientific ECS 3000 Total Sulfur analyzer with Micro coulometer detector. The carrier gas was Argon or Helium (99.998%) technical grade with a gas pressure 1-3 bar (14-45 psig) at ambient temperature (15 – 35 °C). The injection volume was 2 μ l and furnace temperature was 1250 °C maximum for lower sulfur content mixtures. The % sulfur removed was calculated as:

$$\% \text{ Sulfur removal} = \{ [\text{DBT}]_{\text{initial}} - [\text{DBT}]_{\text{final}} \} \times 100 / [\text{DBT}]_{\text{initial}}$$

3. Results and Discussion

The experiments were conducted for deep-desulfurization of various model fuels using [Bmim]Cl ionic liquid. The progress of desulfurization was studied at 30°C and shown in Table 2.

Table 2. Effect of time on desulfurization of MF-1 with [Bmim]Cl.

Time (min)	Sulfur removal %
5	60.94
10	62.48
20	63.98
30	66
60	75.98
90	77.15
120	77.15

(Initial Sulfur Concentration = 1000ppm,
Temperature=30°C, Mass ratio of model fuels to Ionic liquid = 5/1).

The desulfurization process went quiet quickly and sulfur concentration reduced from 1000 ppm to 340 ppm (66% removal) within 30 minutes. The sulfur concentration in model fuel decreased continuously with increased in extraction time and was reached to 228.49 ppm (77.15% removal) at 90 minutes. Further extraction time did not lead to increase in desulfurization efficiency. So the optimum time required for the desulfurization of model fuel is 90 minutes. In addition it is worth noting that the sulfur content in model fuel after 90 min does not significantly differ from the final sulfur content. Such a short equilibrium time is very necessary in industrial application to generate high production yield.

Considering high cost of ionic liquids it is preferable to use low quantity of ionic liquids in fuel desulfurization. Hence this work observed the effect of ionic liquids to model fuel mass ratio on sulfur removal.

The experiments at different temperatures (30 – 80°C) were carried out to study the effect of temperature on desulfurization (Table 3).

Table 3. Effect of temperature on desulfurization of MF-1 with [Bmim] Cl.

Temperature (°C)	Sulfur removal %
30	77.15
40	66.25
50	64.13
60	60.67
70	54.71
80	49.31

(Temperature=30 - 80°C, Mass ratio of model fuels to Ionic liquid = 5/1,
Initial Sulfur Concentration = 1000ppm, Extraction Time = 90 min).

The best ability of [Bmim]Cl to extract dibenzothiophene (DBT) from n-dodecane was reflected at 30°C. The sulfur content of the model fuel decreased from 1000 to 228.49 ppm (77.15 % removal) as temperature increased. There was remarkable drop in sulfur removal when the temperature reached to 80°C, and the desulfurization was only 49.31%, which may be because the stability of ionic liquid is lower with increasing temperature. Hence, 30°C is an appropriate temperature in the desulfurization process. The extraction experiments for removal of sulfur from different model fuels using [Bmim]Cl was studied (Table 4).

Table 4. Desulfurization of model fuels with [Bmim]Cl.

Initial Sulfur Content [ppm]	Sulfur removal (%)			
	MF-1	MF-2	MF-3	MF-4
1000	77.15	76.77	68.98	72.98
500	77.02	72.92	66.88	71.41
300	77.12	71.78	67.26	70.27
200	77.21	71.43	67.94	70.45
100	75.28	69.44	66.39	70.38
50	66.7	65.1	64.38	69.6

(Temperature=30°C, Mass ratio of model fuels to Ionic liquid = 5/1, Extraction Time = 90 min).

[Bmim]Cl exhibited the excellent sulfur extraction behaviour for different model fuels and able to reduce the sulfur

content. The sulfur removal of model fuels with initial sulfur content of 1000ppm to 77.15%, 76.77%, 68.98%, and 72.98% were observed for MF-1, MF-2, MF-3, and MF-4 respectively. Similarly, the sulfur removal of model fuels with initial sulfur content of 500ppm to 77.02%, 72.92%, 66.88%, and 71.41% were observed for MF-1, MF-2, MF-3, and MF-4 respectively. In MF-3 the % of sulfur removal of the model fuel which shows that the solubility of n-heptane in [Bmim]Cl is very minimal while the solubility of other model fuels were observed. This clearly shows the sulfur removal ability of [Bmim]Cl from model fuels is extremely high and also demonstrates that [Bmim]Cl can be used as extractant to achieved the highest % sulfur removal and also suggest that the solubility of this imidazolium based ionic liquids in model fuels has to be optimized for future application.

In order to examine the reusability of the ionic liquid, the used 1-butyl-3-methylimidazolium chloride was further used for desulfurization.

Table 5. Desulfurization efficiency of [Bmim]Cl which was reused for three times in different model fuels.

System	Ionic Liquid	No. of Stages	Initial Sulfur Content (ppm)	Sulfur removal %
MF-1	[Bmim]Cl	I	1000	77.15
		II		58.16
		III		44.31
MF-2	[Bmim]Cl	I	1000	76.77
		II		52.21
		III		46.06
MF-3	[Bmim]Cl	I	1000	68.98
		II		48.90
		III		36
MF-4	[Bmim]Cl	I	1000	72.98
		II		54.04
		III		30.61

(Temperature=30°C, Mass ratio model fuels/Ionic liquid = 5/1, Extraction Time = 90 min).

Table 5 Shows the desulfurization efficiency of [bmim]Cl in model fuels which was reused for three times without regeneration. The used ionic liquid was able to extract dibenzothiophene from model fuels even without regeneration, however, at a lower efficiency.

4. Conclusion

1-butyl-3-methylimidazolium chloride [Bmim]Cl can be used as novel extractive solvents for the deep desulfurization of liquid fuels, especially with regards to those sulfur compounds that are very difficult to remove by common hydrodesulfurization technique. [Bmim]Cl showed remarkable efficiency to remove sulfur compounds from different model liquid fuel. The desulfurization of [Bmim]Cl was the most effective in the removal of dibenzothiophene containing model liquid fuels and it can reach to 77.15 % for single stage extraction at 30°C in 90 min, which is the remarkable advantage of this process over hydrodesulfurization process. Also the used [Bmim]Cl can be reused in extraction without regeneration with considerable extraction efficiency.

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