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Deep Desulfurization of Fuel Diesels Using Alkyl Sulfate and Nitrate Containing Imidazolium as Ionic Liquids

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Abstract

1-ethyl-3-methylimidazolium ethyl sulfate [Etmim][$EtSO_4$],1, 3-dimethylimidazolium methyl sulfate [Mmim][$MeSO_4$] and 1-octyl-3-methylimidazolium nitrate [Omim][NO_3] ionic liquids have been used in thermal oxidative desulfurization of model fuel oils consisting of 500 ppm solutions of benzothiophene (BT) and dibenzothiophene (DBT) in dodecane. The efficiency of sulfur removal from BT and DBT solutions by these ILs as well as the effect of anion and cation chain length have also been investigated. The ILs studied performed pretty efficiently in removal of sulfur containing compounds and sulfur contents have been reduced to 18-27% following the order below: [Mmim][$MeSO_4$] > [Etmim][$EtSO_4$] > [Omim][NO_3]. To further study the performance of the ILs studied, multiple extractions of BT and DBT solutions were also carried out to reduce sulfur content to 81% and 68% for DBT and BT solutions, respectively, after 5 extraction cycles. These environmentally friendly ILs could also be quantitatively regenerated and were shown to be as efficient in sulfur removal after 5 regeneration cycles.

Keywords: *Desulfurization, Ionic liquids, Extraction, Benzothiophene, Dibenzothiophene.*

Introduction

Over the last three decades, sulfur removal from diesel fuel has attracted much attention due to major air pollution and acid rain resulting from sulfur compounds, which are present in such fuels. In the oil refinery industry, hydrodesulfurization (HDS) has long been the method of choice for removal of acyclic and cyclic sulfur compounds from diesel fuel. This process, which employs mixed catalysts such as Co-Mo, converts sulfur containing compounds to H_2S [1]. A major drawback

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associated with HDS method, which leads to very low sulfur contents, is the high expense of the process due to harsh reaction conditions including high hydrogen pressure, reaction temperature and the necessity of application of a very highly active catalyst.

In addition, some sulfur containing compounds in fuels such as benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dialkyl substituted DBTs are difficult to convert into H_2S on the Co-Mo or Ni-Mo catalyst surfaces because of the steric hindrance associated with them [2,3]. Thus, alternative methods for deep desulfurization of diesel oil are becoming attractive. Organic compounds with steric hindrance such as BT, DBT and their derivatives can be selectively oxidized to their corresponding sulfoxides and sulfones, which are then removed by adsorption on the catalyst surface through a competitive technology known as oxidative desulfurization (ODS) process [4]. Taking advantage of the polar nature of these oxidation products, the oxidation process is then followed by extraction with polar solvents such as dimethyl sulfoxide in the second step [5].

In order to improve the efficiency of HDS and ODS technologies, research has been focused on better reactor design and new catalysts based on noble metals have been developed for this purpose. These modifications yield diesel fuels of low sulfur contents (<100 ppm) and are therefore applicable for deep desulfurization [6]. Although ODS is an effective method in this regard, large quantities of flammable and volatile organic compounds (VOCs) are required in the process.

On the other hand, there are other more competitive deep desulfurization techniques such as extraction desulfurization process (EDS). The latter process does not involve hydrogen consumption, catalyst, high temperature or pressure and requires mild and simple operation conditions [6,7]. In addition, sulfur compounds are not chemically altered during this process and can thus be reused as raw materials. Though still not an industrially established process for deep desulfurization, the attractive features of EDS make it worthwhile to consider alternative solvents to use in this process. Examples for solvents employed in EDS process, all of which have proved to perform undesirably, include polyalkylene glycol, imidazolidinone, pyrimidinone and DMSO [8].

Room Temperature Ionic Liquids (RTILs) can be thought of as alternative solvents for conventional EDS solvents since they are non-volatile, non-explosive, recyclable, easy to handle, thermally and hydrothermally stable, non-moisture sensitive, and most importantly polar in nature, which makes them good candidates for extraction of polar, oxidized sulfur containing compounds [8]. In fact, many imidazolium based ILs containing BF_4, PF_6, and Cl anions have been investigated in

EDS [9]. Some ILs previously used in EDS are given in Table 1.

Table 1. Some ILs used in EDS and their sulfur removal efficiency.

IL	Viscosity (cP)	% S Removal	Reference
$[omim][BF_4]$	341.0 @ 25 ºC	40	10
$[bmim][OcSO_4]$	262.3 @ 40 ºC	30	11
$[bmim][MeSO_4]$	122 @ 25 ºC	18	11
[bmim][Cl]	3950@ 30 ºC	18	11
$[bmim][PF_6]$	273.0 @ 25 ºC	14	9
$[bmim][BF_4]$	106.8 @ 25 ºC	8	9

However, some of these ILs exhibit some undesirable characteristics including release of corrosive hydrofluoric acid (HF) caused by decomposition of fluorinated anions (BF_4 and PF_6) and the non-moisture stability and high viscosities of all these ILs make their handling difficult. Furthermore, the efficiency of sulfur removal using ILs is generally rather low, in the range of 10-30% because of the similar polarities of competing alkenes, aromatic and sulfur compounds present in the fuels [8].

We herein report application of other non-fluorinated, low viscosity ILs, 1-octyl-3-methylimidazolium nitrate $[Omim][NO_3]$, 1-ethyl-3-methylimidazolium ethyl sulfate $[Etmim][EtSO_4]$, and 1,3-dimethylimidazolium methyl sulfate $[Mmim][MeSO_4]$, prepared from relatively cheap starting materials, in the oxidative desulfurization of BT and DBT solutions in dodecane as model fuel oils. The desirable characteristics of these ILs such as their negligible miscibility with fuels, high affinity for sulfur containing compounds, and ease of regeneration make them potential alternative solvents in EDS process.

Experimental

Benzothiophene (BT), dibenzothiophene (DBT), hydrogen peroxide (20% aqueous solution), acetic acid, and 1-methylimidazole were purchased from Merck Chemical Co. Diethyl sulfate, dodecane, and toluene were supplied by Fluka Chemical Co. 1-chlorooctane and $AgNO_3$ were obtained from Aldrich Chemical Co. Except for 1-methylimidazole; all reagents were used without further purification. 1-methylimidazole was purified by refluxing over KOH pellets at reduced pressure. BT and DBT solutions of 500 ppm concentrations were prepared by dissolving the appropriate amounts of the solutes in a known volume of dodecane solvent in a volumetric flask and diluting up to the mark. Ionic liquids prepared in this work were known compounds and their structures were confirmed by comparing their ^{1}HNMR spectral data with those of authentic samples. ^{1}HNMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer.

Determination of sulfur content

Sulfur analyses were carried out using “Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry (ASTM D-2622)”. In this method, the sample is placed in the X-ray beam, and the peak intensity of the sulfur Ka line at 0.5373 nm is measured. The background intensity, measured at a recommended wavelength of 0.5190 nm (0.5437 nm for a Rh target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in mg/kg or mass %.

Synthesis of 1-octyl-3-methylimidazolium chloride [Omim][Cl]

A mixture containing 10.9 g (67 mmol) of 1-chlorooctane and 5 g of 1-methylimidazole (61 mmol) is refluxed in an inert atmosphere at 100 ºC for 29 hours. The resulting oil is then washed with ethyl acetate (3x10 mL) to remove trace quantities of starting materials. Removing the solvent at reduced pressure and heating the product at 70 ºC for 7 hours to remove residual moisture affords 12.63 g (91%) of the pure product (mp=12 ºC) [12].

^{1}HNMR (300 MHz,$CDCl_3$, 25 °C) δ (ppm) = 0.75 (3H, t, $NCH_2(CH_2)_6\underline{CH_3}$), 1.2 (10H, m, $NCH_2CH_2\underline{(CH_2)_5}CH_3$), 1.80 (2H, m, $NCH_2\underline{CH_2}(CH_2)_5CH_3$), 4.03 (3H, S, NCH_3), 4.20 (2H, t, $N\underline{CH_2}(CH_2)_6CH_3$), 7.41 (1H, d, H-4), 7.65 (1H, d, H-5), 10.46 (1H, S, H-2).

1-octyl-3-methylimidazolium nitrate [Omim][NO_3]

To 5 g of 1-octyl-3-methylimidazolium chloride (22 mmol) dissolved in 5 mL of deionized water is added 3.68 g of silver nitrate (22 mmol) in 4 ml of deionized water in a round-bottomed flask equipped with a magnetic stirrer in an inert atmosphere. Upon addition of silver nitrate, white AgCl precipitate forms. The suspension is then stirred for 20 minutes at room temperature, followed by filtration of AgCl. The filtrate did not become cloudy on addition of $AgNO_3$ solution thus confirming no unreacted starting material. Removing the solvent at reduced pressure and heating the product at 70 ºC for 7 hours to remove residual moisture affords 4.60 g (82.5%) of the product [13].

^{1}HNMR (80 MHz, $CDCl_3$, 25 °C): δ (ppm) = 0.54 (3H, t, $NCH_2(CH_2)_6\underline{CH_3}$), 0.97 (10H, m, $NCH_2CH_2\underline{(CH_2)_5}CH_3$), 1.59 (2H, m, $NCH_2\underline{CH_2}(CH_2)_5CH_3$), 3.72 (3H, S, NCH_3), 3.95 (2H, t, $N\underline{CH_2}(CH_2)_6CH_3$), 7.29 (1H, d, H-4), 7.35 (1H, d, H-5), 9.42 (1H, S, H- 2).

1-ethyl-3-methylimidazolium ethyl sulfate [Etmim][$EtSO_4$]

To 5 g of 1-methylimidazole (61 mmol) dissolved in toluene (20 mL) in a round-bottomed flask equipped with an addition funnel, a magnetic stirrer and a thermometer is added 9.39 g of diethyl sulfate (61 mmol) drop wise in an inert atmosphere over a period of an hour such that the temperature of the resulting mixture does not exceed 10 ºC during the addition. At the end of this period, the reaction temperature is increased to the ambient temperature and stirring is continued at this temperature for 2 hours. The mixture is biphasic and the bottom phase containing the ionic liquid is separated from the top phase and washed with 5 mL of toluene (3 times) to remove unreacted starting material. Removing the solvent at reduced pressure and heating the product at 70 ºC for 7 hours to remove residual moisture gives 13.0 g (90.4%) of the product (mp= -30 ºC) [14].

^{1}HNMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.25 (3H, t, $NCH_2\underline{CH_3}$), 1.53 (3H, t, $\underline{CH_3}CH_2O$), 4.10 (3H, S, NCH_3), 4.25 (2H, q, $O\underline{CH_2}CH_3$), 4.30 (2H, q, $N\underline{CH_2}CH_3$), 7.50 (2H, m, H- 4, H-5), 9.49 (1H, S, H- 2)

1,3-dimethylimidazolium methyl sulfate [Mmim][MeSO$_4$]

To 5 g of 1-methylimidazole (61 mmol) in toluene (20 mL) in a round-bottomed flask equipped with an addition funnel, a magnetic stirrer and a thermometer is added 7.67 g of dimethyl sulfate (61 mmol) drop wise in an inert atmosphere over a period of an hour such that the temperature of the resulting mixture does not exceed 10 ºC during the addition. At the end of this period, the reaction temperature is increased to the ambient temperature and stirring is continued at this temperature for 2 hours. The mixture is biphasic and the bottom phase containing the ionic liquid is separated from the top phase and washed with 5 mL of toluene (3 times) to remove unreacted starting material. Removing the solvent at reduced pressure and heating the product at 70 ºC for 7 hours to remove residual moisture affords 9.62 g (75.9%) of the product [14].

^{1}HNMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.0 (3H, t, $NCH_2CH_2CH_2\underline{CH_3}$), 1.33 (4H, m, $NCH_2\underline{CH_2}\underline{CH_2}CH_3$), 4.64 (2H, m, $N\underline{CH_2}CH_2CH_2CH_3$), 8.49 (2H, m, H- 4), 8.52 (1H, d, H-5), 8.56 (1H, S, H- 2).

General procedure for extraction/ desulfurization of model diesel fuel

In a typical experiment, the selected IL, solution of DBT or BT in dodecane, H_2O_2, and acetic acid were mixed in a glass reactor equipped with an external heating Jacket and a mechanical stirrer such that the weight ratio of IL to BT or DBT solution was 1:1 and the molar ratios of elemental sulfur to H_2O_2 and acetic acid were 1:100 and 1:50, respectively. The two-phase mixtures were vigorously stirred (300 rpm) at 60 ºC for 15 minutes. At the end of this period, the mixture was allowed to cool and the phases were separated. The fuel containing upper dodecane phase was then removed and analyzed for its sulfur content [15].

The ILs saturated with sulfur containing compounds were recovered by either direct distillation of the dissolved species to leave the IL as the residue in the case of water insoluble IL, 1-octyl-3-methylimidazolium nitrate [Omim][NO_3], or by dissolution of the sulfur containing IL in water followed by solvent removal at reduced pressure in the case of water soluble ILs, 1-ethyl-3-methylimidazolium ethyl sulfate [Etmim][$EtSO_4$] and 1,3-dimethylimidazolium methyl sulfate [Mmim][$MeSO_4$].

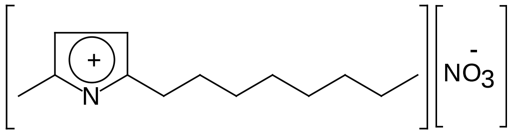
In the latter case, 5 g of the used ILs were dissolved in 10 mL of distilled water followed by extraction of the dissolved sulfur containing compounds in diethyl ether (3×5 mL). Distillation of water at reduced pressure then yielded the pure IL. ^{1}H NMR spectroscopy was used to confirm the purity of the ILs thus recovered [9].

Results and discussion

Considering the difficulty associated with removal of sterically hindered sulfur containing compounds such as benzothiophene (BT) and dibenzothiophene (DBT) using HDS method, alternative methods such as ODS and EDS have to be considered for removal of such compounds. Although the extraction of sterically hindered sulfur containing compounds is facilitated by their oxidation and conversion into polar compounds in ODS process, EDS is the more favorable process of the latter two methods since it does not involve harsh operation conditions. Nevertheless, the application of environmentally undesirable solvents used in this process such as DMSO and polyalkylene glycol is the drawback, which calls for substitution of these solvents with less hazardous, more environmentally friendly solvents such as room temperature ionic liquids.

Much work has already been carried out on selective removal of sulfur compounds from model diesel fuels using ionic liquids [8]. The objective of this work, however, was to evaluate the efficiency of easy to prepare ionic liquids in sulfur removal from model diesel fuels consisting of benzothiophene (BT) and dibenzothiophene (DBT) solutions in dodecane and compare the results with those reported in the literature.

In the present work, 500 ppm solutions of BT and DBT in dodecane solvent were mixed with selected ionic liquids, an oxidizing agent (H_2O_2), and acetic acid as an oxidation catalyst. The resulting mixtures were then subjected to thermal treatment at 60 ºC for 15 minutes. The sulfur contents of the solutions were determined prior to and following oxidative desulfurization treatments with ionic liquids. The structures of the ILs in this work for extractive desulfurization of model diesel oils are shown in Scheme 1.



1-octyl-3-methylimidazolium nitrate

1-ethyl-3-methylimidazolium ethyl sulfate

1, 3-dimethylimidazolium methyl sulfate

Scheme 1. Structures of ILs used in this work.

The results obtained in the oxidative desulfurization of model diesel fuels using imidazolium based ILs containing selected anions are shown in Table 2 (Entries 1-6). For the sake of comparison, results from desulfurization studies using other ILs have also been included (Entries 7-8).

Table 2. Desulfurization of model diesel oil using ILs.

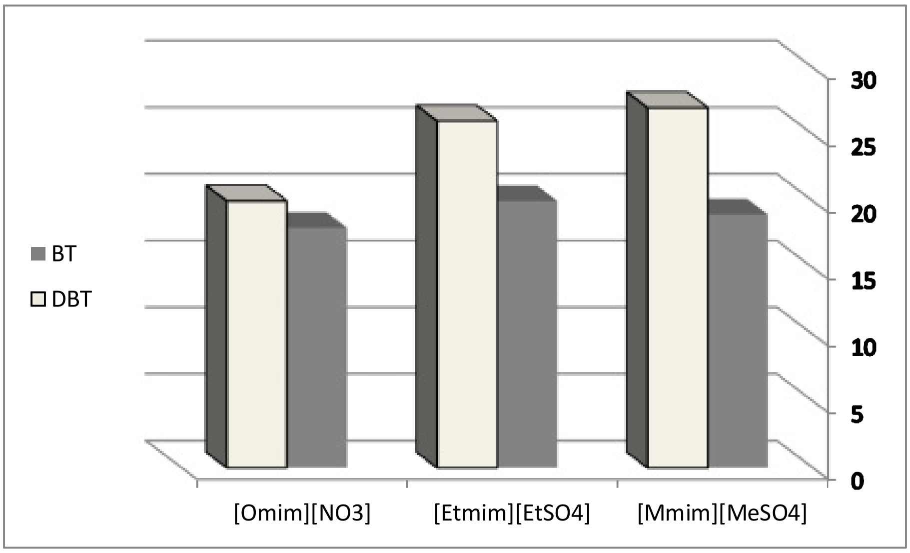
No	S Compound*	IL	S Content/ppm	t/min	T/ºC	% S removed	Ref.
1	BT	$[Mmim][MeSO_4]$	405	15	60	19	a
2	DBT	$[Mmim][MeSO_4]$	365	15	60	27	a
3	BT	$[Etmim][EtSO_4]$	400	15	60	20	a
4	DBT	$[Etmim][EtSO_4]$	370	15	60	26	a
5	BT	$[Omim][NO_3]$	410	45	70	18	a
6	DBT	$[Omim][NO_3]$	400	45	70	20	a
7	DBT	$[bmim][MeSO_4]$	410	15	60	18	[11]
8	DBT	$[bmim][OcSO_4]$	350	15	60	30	[11]

* Mass ratio model diesel oil:IL=1:1, Initial sulfur content=500 ppm

a) The present work

As observed in Table 2, the ILs studied reduced sulfur content of model diesel fuels from 500 to 365-400 ppm (18-27%) in a single extraction. Percent sulfur reductions for the three ILs are also shown in Scheme 2 for BT and DBT solutions. As clearly observed in Scheme 2 and Table 2, under identical experimental conditions, the efficiency of sulfur reduction by all ILs studied is about 10-23% greater for DBT compared with BT (entries 1-2 and 3-4). This is unexpected because the relatively accessible sulfur in BT would seem to be more easily oxidized than that in the sterically hindered DBT molecule. This can be explained in terms of S-C bond stabilization in BT molecule.

In the case of DBT, the inducing effect of the aromatic rings increases the electron charge density of S, that is, the oxidization reaction by H_2O_2 can be more readily accomplished [13]. Furthermore, [Etmim][$EtSO_4$] and [Mmim][$MeSO_4$] ILs perform reasonably better in sulfur removal from model fuels compared with [Omim][NO_3] (entries 5-6). In fact, extractions using the former two ionic liquids result in removal of around 30% of the sulfur initially present in the model diesel fuels whereas the amount of sulfur removed by [Omim][NO_3] is about 20%. The comparably lower sulfur removal by [Omim][NO_3] can be attributed to the strong ionic interaction resulting from increased charge density on NO_3 anion, which decreases the affinity between the ionic liquid and the oxidized sulfur compounds caused by the π-π interaction.



Scheme 2. Desulfurization efficiency of different ILs.

The other factor that seems to be playing a part in the sulfur removal efficiency of ILs used in this work is the alkyl chain length of the ions. The lower the alkyl chain length of the cation, the higher the amount of sulfur removed (entries 2 and 7). Alkyl chain length of the anion also has an identical effect on sulfur removal efficiency; that is ILs containing shorter alkyl chains in their anion remove sulfur more efficiently (entries 2 and 8).

Finally, the order of extraction efficiency by the ILs studied is as follows:

[Mmim][$MeSO_4$] > [Etmim][$EtSO_4$] > [Omim][NO_3].

In other words, [Mmim][$MeSO_4$] has the highest extractive performance in the ILs tested.

Thus, the ILs used perform well in sulfur removal while not possessing undesirable characteristics such as causing corrosion or high viscosity. To investigate the performance of the ILs studied in sulfur removal, multiple extractions of BT and DBT solutions were carried out under identical conditions. The results for repeated extractions of 500 ppm DBT and BT solutions are given in Tables 3 and 4, respectively.

Table 3. Repeated extractions of 500 ppm DBT solution using ILs.

Extraction No. **IL**	**[Mmim][$MeSO_4$] S Content/ppm**	**[Etmim][$EtSO_4$] S Content/ppm**	**[Omim][NO_3] S Content/ppm**
1	365	370	400
2	263	270	316
3	184	192	243
4	131	138	190
5	97	104	154

Table 4. Repeated extractions of 500 ppm BT solution using ILs.

Extraction No. **IL**	**[Mmim][$MeSO_4$] S Content/ppm**	**[Etmim][$EtSO_4$] S Content/ppm**	**[Omim][NO_3] S Content/ppm**
1	405	400	410
2	332	318	334
3	276	241	266
4	226	195	212
5	183	160	176

As one can observe, the sulfur content in these model fuel solutions in both cases drastically reduces to a minimum of 97 (81%) and 160 ppm (68%) for DBT and BT solutions, respectively, after 5 extraction cycles. The sulfur extraction performance of regenerated ILs was also evaluated by using them in extraction experiments following their regeneration. The results obtained for 5 regeneration cycles are shown in Tables 5 and 6 for DBT and BT solutions, respectively.

Table 5. Evaluation of sulfur extraction performance of regenerated ILs using 500 ppm DBT. Solution

Extraction No. **IL**	**[Mmim][$MeSO_4$] S Content/ppm**	**[Etmim][$EtSO_4$] S Content/ppm**	**[Omim][NO_3] S Content/ppm**
1	365	370	400
2	365	370	400
3	380	370	425
4	365	380	420
5	385	380	405

Table 6. Evaluation of sulfur extraction performance of regenerated ILs using 500 ppm BT solution.

Regeneration No. / IL	[Mmim][MeSO$_4$] S Content/ppm	[Etmim][EtSO$_4$] S Content/ppm	[Omim][NO$_3$] S Content/ppm
1	405	400	410
2	420	410	430
3	405	415	435
4	415	400	430
5	415	420	405

As observed, the sulfur extraction performance of regenerated ILs does not appreciably decrease after 5 regeneration cycles.

Conclusion

Selected ILs have shown to be good extraction media in oxidative desulfurization of model diesel fuels consisting of benzothiophene and dibenzothiophene solutions in dodecane. Of the three ILs investigated, [Mmim][EtSO$_4$] is the most efficient extraction solvent for both model diesel fuels tested. The ILs tested were quite capable of repeated extractions to lower the sulfur contents of model fuel to appreciably low values. These ILs also proved to be recyclable and did not lose their sulfur extracting capability on multiple regenerations.

All ILs studied were shown to reduce sulfur content of DBT model fuel solutions more efficiently than BT. Also, [Etmim][EtSO$_4$] and [Mmim][MeSO$_4$] ILs perform better than [Omim][NO$_3$]. In addition, the alkyl chain length of anions and cations of ionic liquids used are inversely proportional with their sulfur removal efficiency.

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