IONIC LIQUID FOR DESULFURIZATION OF LIGHT FUELS

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ABSTRACT

The ionic liquid for desulfurization of light fuels is 1-methyl-3-pentyl 1H-imidazolium periodate, having the structural formula:

\[ \text{structure image} \]

The compound is prepared by mixing 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate with sodium periodate in dichloromethane and water, stirring the mixture for 24 hours, and extracting the compound from the product with dichloromethane. The ionic liquid may be used for the desulfurization of light fuels by bringing the ionic liquid into contact with the crude light petroleum oil at a temperature of about 50° C. with stirring for a period of time sufficient to oxidize the sulfur containing impurities to water soluble sulfones, washing the mixture with water to remove the ionic liquids and water soluble sulfones, and drying the desulfurized light fuel product.
Fig. 1
Fig. 3

\[ ^{13}C \text{NMR, CDCl}_3, 125 \text{ MHz} \]

- 77.41 ppm
- 77.16 ppm
- 76.80 ppm
- 49.59 ppm
- 36.29 ppm
- 29.53 ppm
- 27.17 ppm
- 21.59 ppm
- 13.40 ppm

SA-IL-13C(SR)
Fig. 5

NaBF₄, CH₂Cl₂
RT, 24 h
Fig. 9

NaI\textsubscript{O}+ \textsubscript{4} \textsubscript{CH}_2\textsubscript{Cl}_2 \text{ RT, 24 h}
IONIC LIQUID FOR DESULFURIZATION OF LIGHT FUELS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention
[0002] The present invention relates to the desulfurization of light fuels and petroleum products, and particularly to ionic liquids for the desulfurization of light fuels.

[0003] 2. Description of the Related Art
[0004] The desulfurization of fuel constitutes a major target of oil refineries due to growing public concern of environmental pollution from emissions from the combustion of fuels. The sulfur compounds present in light fuel are converted to sulfur dioxides, which are considered to be a major source of acid rain and air pollution. To control the SO_x emissions, severe regulations are being imposed on oil refineries to reduce the sulfur content to an acceptably low limit.

[0005] The catalytic hydrodesulfurization method, which is typically employed in the refineries, requires both high temperature and high pressures of hydrogen gas. Thus, this method entails high risk for personnel operating the refinery. Thus, alternative methods are being sought to avoid the use of high pressure and high temperature hydrogen gas. Oxidative desulfurization is particularly attractive, due to its relatively low risk and environmental impact.

[0006] Recently, ionic liquids have received considerable interest due to their environmentally friendly properties, such as low volatility and thermal stability. Several methods have been developed that use hydrogen peroxide in combination with ionic liquids, and combine solvent extraction with oxidation of dibenzothiophene (DBT), which is the major sulfur compound in light oil. However, these techniques require the use of an external oxidant and presently lack efficiency for complete removal of DBT.

[0007] Thus, an ionic liquid for desulfurization of light fuels solving the aforementioned problems is desired.

SUMMARY OF THE INVENTION

[0008] The ionic liquid for desulfurization of light fuels is 1-methyl-3-pentyl 1H-imidazolium periodate, having the structural formula:

\[
\begin{array}{c}
\text{N} \\
\text{I}_4 \text{O} \\
\end{array}
\]

The compound is prepared by mixing 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate with sodium periodate in dichloromethane and water, stirring the mixture for 24 hours, and extracting the compound from the product with dichloromethane. The ionic liquid may be used for the desulfurization of light fuels by bringing the ionic liquid into contact with the crude light petroleum oil at a temperature of about 50°C with stirring for a period of time sufficient to oxidize the sulfur containing impurities to water soluble sulfones, washing the mixture with water to remove the ionic liquids and water soluble sulfones, and drying the desulfurized light fuel product.

[0009] These and other features of the present invention will become readily apparent upon further review of the following specification and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is a chemical equation showing a reaction scheme for the synthesis of 1-methyl-3-pentyl 1H-imidazolium bromide.

[0011] FIG. 2 is the H^1 NMR spectrum of 1-methyl-3-pentyl 1H-imidazolium bromide synthesized according to the scheme of FIG. 1.

[0012] FIG. 3 is the C^13 NMR spectrum of 1-methyl-3-pentyl 1H-imidazolium bromide synthesized according to the scheme of FIG. 1.

[0013] FIG. 4 is the FT-IR spectrum of 1-methyl-3-pentyl 1H-imidazolium bromide synthesized according to the scheme of FIG. 1.

[0014] FIG. 5 is a chemical equation showing the reaction scheme for the synthesis of 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate.

[0015] FIG. 6 is the H^1 NMR spectrum of 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate prepared according to the scheme of FIG. 5.

[0016] FIG. 7 is the C^13 NMR spectrum of 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate prepared according to the scheme of FIG. 5.

[0017] FIG. 8 is the FT-IR spectrum of 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate prepared according to the scheme of FIG. 5.

[0018] FIG. 9 is a chemical equation showing the reaction scheme for the synthesis of 1-methyl-3-pentyl 1H-imidazolium periodate, which is the ionic liquid for the desulfurization of light fuels according to the present invention.

[0019] FIG. 10 is the H^1 NMR spectrum of 1-methyl-3-pentyl 1H-imidazolium periodate prepared according to the scheme of FIG. 9.

[0020] FIG. 11 is the C^13 NMR spectrum of 1-methyl-3-pentyl 1H-imidazolium periodate prepared according to the scheme of FIG. 9.

[0021] FIG. 12 is the FT-IR spectrum of 1-methyl-3-pentyl 1H-imidazolium periodate prepared according to the scheme of FIG. 9.

[0022] FIG. 13 is a chemical equation showing the oxidation reaction of 1-methyl-3-pentyl 1H-imidazolium periodate prepared according to the scheme of FIG. 9 with dibenzothiophene.

[0023] FIG. 14 is the H^1 NMR spectrum of the sulfone product of the reaction of FIG. 13.

[0024] FIG. 15 is the C^13 NMR spectrum of the sulfone product of the reaction of FIG. 13.

[0025] FIG. 16 is the FT-IR spectrum of the sulfone product of the reaction of FIG. 13.

[0026] Similar reference characters denote corresponding features consistently throughout the attached drawings.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] The ionic liquid for desulfurization of light fuels is 1-methyl-3-pentyl 1H-imidazolium periodate, having the structural formula:

\[
\begin{array}{c}
\text{N} \\
\text{I}_4 \text{O} \\
\end{array}
\]
The circle inside the 5-member ring indicates that the ring is aromatic, i.e., it has two double bonds, and the ‘+’ sign inside the circle indicates that the ring is cationic, the charge being distributed in the ring by conjugation of the double bonds. The same convention is used in the structural formulas for 1-methyl-3-pentyl 1H-imidazolium bromide, 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate, and in the drawings. The compound is prepared by mixing 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate with sodium periodate in dichloromethane and water, stirring the mixture for 24 hours, and extracting the compound from the product with dichloromethane. The ionic liquid may be used for the desulfurization of light fuels by bringing the ionic liquid into contact with the crude light petroleum oil at a temperature of about 50°C with stirring for a period of time sufficient to oxidize the sulfur-containing impurities to water-soluble sulfones, washing the mixture with water to remove the ionic liquids and water-soluble sulfones, and drying the desulfurized light fuel product.

In order to investigate the usefulness of 1-methyl-3-pentyl imidazolium-based ionic liquids for the desulfurization of light petroleum fuels, the inventors synthesized a bromide, a tetrafluoroborate, and a periodate ionic liquid, tested the ability of the periodate compound to oxidize dibenzothiophene (which is the major sulfur contaminant in the refining of light fuels), and performed a comparative experiment of the ability of the ionic liquids to remove sulfur-containing impurities from crude petroleum light fuel samples. The experiments are reported in the following Examples.

**Example 1**

As shown in FIG. 1, a first 1-methyl-3-pentyl imidazolium ionic liquid is made by mixing 2.2 mmol of 1-bromopentane and 2 mmol of N-methyl imidazole to form a mixture. Mixing preferably occurs for about 10 seconds. This mixture is then irradiated with microwave radiation in a conventional microwave oven. The microwave radiation has a power of about 240 W, and the mixture is irradiated for about 30 seconds. Following irradiation, the mixture is removed from the oven, shaken well, and then re-irradiated for another 30 seconds to form a clear, viscous, single-phase solution. The single-phase solution is then cooled, washed twice with 2 mL of ether to remove unreacted starting components, and then dried under vacuum at a temperature of about 70°C, yielding about 80% pure 1-methyl-3-pentyl 1H-imidazolium bromide ionic liquid having the structure:

![Structure](image)

**Example 2**

From the 1-methyl-3-pentyl 1H-imidazolium bromide ionic liquid, a second 1-methyl-3-pentyl imidazolium ionic liquid is further developed, as illustrated in FIG. 5. The 1-methyl-3-pentyl 1H-imidazolium bromide ionic liquid, prepared as described above, is stirred with 3 mmol of NaBO_3 in a mixture of dichloromethane (DCM) and water having a molar ratio of 7:3 for 24 hours at room temperature. The resulting second ionic liquid is extracted with DCM and dried under vacuum to provide 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate ionic liquid having the structure:

![Structure](image)

**Example 3**

The 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate ionic liquid prepared as described above may be used to make a third 1-methyl-3-pentyl imidazolium ionic liquid, as shown in FIG. 9. The 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate ionic liquid is put in a round bottom flask and stirred with 3 mmol of NaOCl (sodium periodate) in a mixture of dichloromethane (DCM) and water having a molar ratio of 7:3 for 24 hours at room temperature. The resulting third ionic liquid is extracted with DCM and dried under vacuum to provide a 1-methyl-3-pentyl 1H-imidazolium iodate ionic liquid having the structure:

![Structure](image)
3-pentyl 1H-imidazolium iodate ionic liquid, and the FT-IR spectrum of the 1-methyl-3-pentyl 1H-imidazolium iodate ionic liquid. Spectral peaks for the $^1$H NMR spectrum of FIG. 10 are summarized as: (CDCl$_3$, 500 MHz) δ 0.78 (t, J=6.7 Hz, 3H), 1.22 (br s, 4H), 1.77-1.80 (m, 2H), 3.87 (s, 3H), 4.09 (t, J=7.2 Hz, 2H), 7.34-7.36 (m, 2H), 8.71 (s, 1H). Spectral peaks for the $^{13}$C NMR spectrum of FIG. 11 are summarized as: (CDCl$_3$, 125 MHz): δ 135.6, 123.69, 122.5, 49.9, 36.3, 29.5, 27.9, 21.7, 13.5. The spectral peaks for the FT-IR spectrum of FIG. 12 are summarized as: 3572, 3533, 3514, 3498, 3477, 3151, 3113, 3007, 2958, 2933, 2864, 1629, 1573, 1462, 1381, 1232, 1168, 1062 cm$^{-1}$.

Example 4

[0035] In order to test the efficacy of the ionic liquids at desulfurization of light fuels, a solution of dibenzo thiophene in petroleum ether (0.25 mg in a 2 mL solution) was placed in a round bottom flask. The 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid, prepared as described above, was added to the mixture and stirred vigorously for about 6 hours at a temperature of about 50°C in open atmosphere. The reaction was monitored by thin layer chromatography (TLC). After the reaction was over, the reaction mixture was washed four times in 5 mL of water. The unreacted ionic liquid and sulfone of dibenzothiophene were washed out with the water. The resultant petroleum ether was dried and collected in a round bottom flask. The reaction is illustrated in FIG. 13, where the 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid is represented as [pmIm]IO$_4$.

[0036] FIGS. 14, 15 and 16 illustrate, respectively, the $^1$H NMR spectrum of the isolated sulfone, the $^{13}$C NMR spectrum of the isolated sulfone, and the FT-IR spectrum of the isolated sulfone. Spectral peaks for the $^1$H NMR spectrum of FIG. 14 are summarized as: (CDCl$_3$, 500 MHz) δ 7.54 (t, J=7.5 Hz, 2H), 7.65 (t, J=7.5 Hz, 2H), 7.80-7.84 (m, 4H). Spectral peaks for the $^{13}$C NMR spectrum of FIG. 15 are summarized as: (CDCl$_3$, 125 MHz): δ 138.0, 134.0, 131.8, 130.5, 122.3, 121.7, 77, 77.2, 76.9. The spectral peaks for the FT-IR spectrum of FIG. 16 are summarized as: 3421, 3082, 2958, 1817, 1591, 1575, 1479, 1452, 1455, 1288, 1165, 1157, 1118, 1074, 1047, 943, 869, 756, 734, 711, 613, 580, 567, 538 cm$^{-1}$.

Example 5

[0037] Crude petroleum contains dibenzo thiophene, benzo thiophene and thiophene as major sulfur-containing materials. Thus, removal of these thiophenes is an important step towards desulfurization of fuel oils. To standardize the reaction conditions for oxidation, the three ionic liquids described above were each tested as oxidizing agents. The results are summarized in the Table 1 below. Table 1, the 1-methyl-3-pentyl 1H-imidazolium bromide ionic liquid is represented as [pmIm]Br, the 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate ionic liquid is represented as [pmIm]BF$_4$, and the 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid is represented as [pmIm]IO$_4$. The first two ionic liquids, prepared as described above, are found to be not effective enough for oxidation of dibenzo thiophene. The 1-methyl-3-pentyl 1H-imidazolium periodate was found to exhibit the best results in terms of conversion and yield when the reaction was carried out at 50°C for 6 hours. In Table 1 below, room temperature is abbreviated as RT.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Time (hours)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[pmIm]Br</td>
<td>5</td>
<td>RT</td>
<td>—</td>
</tr>
<tr>
<td>[pmIm]BF$_4$</td>
<td>6</td>
<td>RT</td>
<td>—</td>
</tr>
<tr>
<td>[pmIm]IO$_4$</td>
<td>5</td>
<td>RT</td>
<td>21</td>
</tr>
<tr>
<td>[pmIm]IO$_4$</td>
<td>3</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>[pmIm]IO$_4$</td>
<td>6</td>
<td>50</td>
<td>98</td>
</tr>
</tbody>
</table>

[0038] The fuel sample was found almost completely DBT free and the corresponding sulfone of DBT was isolated from the aqueous part by solvent extraction and characterized by NMR spectroscopy. The 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid was effective in removing all three organosulfur compounds. The 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid contains the active oxidizing species periodate, whereas the other two ionic liquids do not bear such a moiety, which explains why the 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid is an oxidizing agent and the other two are not. The thiophene and benzo thiophenes are removed nearly quantitatively (>95%), as indicated by thin layer chromatography (TLC). However, 81% and 93% are isolated yields of the corresponding sulfones. Typically, the isolated yields are lower than actual conversion yields due to some loss of product during the process.

[0039] The percent yield of isolated sulfone is calculated using the mass of sulfone. The mass of sulfones were divided by the molar mass of sulfone to yield the number of moles of sulfone. The moles of sulfone are the actual yield. The moles of benzo thiophenes are known, which is the theoretical yield. The percent yield of any reaction is calculated using moles of reactants and moles of products is:

Percent Yield = \( \frac{\text{moles of actual yield}}{\text{moles of theoretical yield}} \times 100 \).

[0040] By substituting the number of moles of sulfones isolated and the moles of benzo thiophenes, the percent of sulfur isolated from the model gasoline may be calculated in the form of sulfones as:

Percent Sulfur Isolated = \( \frac{\text{moles of sulfones isolated}}{\text{moles of benzo thiophenes used}} \times 100 \).

The 1-methyl-3-pentyl 1H-imidazolium periodate ionic liquid is found to be effective at removing about 90% of the sulfur from the model gasoline.

[0041] It is to be understood that the present invention is not limited to the embodiments described above, but encompasses any and all embodiments within the scope of the following claims.

We claim:

1. An ionic liquid for desulfurization of light fuels, comprising 1-methyl-3-pentyl 1H-imidazolium periodate, having the structural formula:
2. A method of desulfurizing light fuels, comprising the steps of:
   bringing the ionic liquid into contact with crude light petroleum oil at a temperature of about 50°C with stirring for a period of time sufficient to oxidize any sulfur-containing impurities in the crude light petroleum oil to water soluble sulfones;
   washing the mixture with water to remove the ionic liquids and water soluble sulfones; and
   drying the desulfurized light petroleum oil product.
3. The method of desulfurizing light fuels according to claim 2, wherein said period of time sufficient to oxidize any sulfur-containing impurities comprises about six hours.
4. A method of making 1-methyl-3-pentyl 1H-imidazolium periodate, comprising the steps of:
   mixing 1-methyl-3-pentyl 1H-imidazolium tetrafluoroborate with sodium periodate in dichloromethane and water;
   stirring the mixture for 24 hours; and
   extracting the 1-methyl-3-pentyl 1H-imidazolium periodate from the mixture with dichloromethane.