



Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature

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The ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate were found to be effective for the selective removal of sulfur-containing compounds from transportation fuels such as gasoline at room temperature. S-containing compounds with a C₅ aromatic ring are favorably absorbed over C₆ aromatics, while S-containing non-aromatic compounds are poorly absorbed. The ionic liquids are regenerated from absorbed S-containing compounds by distillation or by dissolution in water. These ionic liquids are air- and moisture-stable at low temperature and non-corrosive. Therefore, the ionic liquids can be used in multiple cycles for the removal of S-containing compounds from fuels. The absorption capacity of the ionic liquids for S-containing compounds is sensitive to the structure of both the anion and cation of the ionic liquids, which is manifested by the significant inhibiting effect of methyl group substitution on the aromatic ring.

Introduction

Sulfur removal from transportation fuels has become an increasing technical challenge as oil refineries face growing environmental pressures and strict regulatory requirements. In the United States, the Environment Protection Agency requires that the average concentration of sulfur in gasoline be lowered more than 90%, to 30 parts per million, phased in from by 2004 through 2006.¹ The new on-road diesel regulation specifies a per-gallon sulfur cap of 15 ppm effective mid-2006.² 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).³

The refinery industry utilizes catalytic processes for desulfurization of transportation fuels through hydroprocessing. While the performance of conventional hydroprocessing catalysts have been highly effective for the reduction of sulfur levels, further removal of residual sulfur from the processed fuels is expected to significantly increase the cost of hydroprocessing. These processes are highly energy intensive and consume large amounts of hydrogen. For example, a study based on a typical Co–Mo catalyst shows that either about four times more active catalyst or an increase of 38 °C in reaction temperature is needed to meet the required sulfur reduction of diesel products from 500 to 50 ppm.⁴ Therefore, alternative technologies are of particular interest in providing potential solutions for sulfur-free clean fuels.

Ionic liquids have been examined for possible applications related to green chemical processes, such as liquid/liquid extractions, gas separations, electrochemistry and catalysis.^{5–13} These liquids are easy to handle because of non-volatility, non-flammability, and high thermal stability. Many ionic liquids, except those containing AlCl₄[–], are moisture tolerant.

Even though AlCl₃ based ionic liquids are effective for the removal of S-containing compounds,¹⁴ they often form dark precipitates by contacting compounds that contain thiols and cause darkened color in processed fuels.¹⁵ Thus the application of this type of ionic liquid is limited to the absorption of certain aromatic compounds such as dibenzothiophene.

In the present work, the ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM⁺BF₄[–]), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺PF₆[–]) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM⁺BF₄[–]), are studied for the absorption of various model components in typical gasoline and diesel fuels. They were also investigated for sulfur removal from real transportation fuels. Unlike AlCl₃ based ionic liquids, these ionic liquids are insensitive to the presence of water. EMIM⁺BF₄[–] is water miscible and BMIM⁺PF₆[–] is water immiscible.¹⁶ Fig. 1 shows the structures of these three ionic liquids.

The melting points of EMIM⁺BF₄[–] and BMIM⁺PF₆[–] are both close to 5 °C. BMIM⁺BF₄[–] has a melting point about –80 °C. As liquids at room temperature, these compounds are thermally stable up to about 300 °C.⁸ For example, Holbrey and Seddon's thermogravimetric study showed that BMIM⁺BF₄[–]

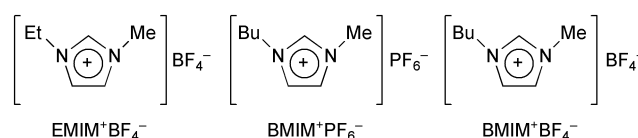


Fig. 1 Structures of ionic liquids.

Green Context

The removal of sulfur-containing impurities from fuels is becoming increasingly challenging as tolerated levels are reduced by legislation. An interesting alternative to hydrodesulfurisation is presented in this article, where the use of ionic liquids as selective adsorbents of S-containing aromatics is described. Considerable structural sensitivity towards absorption is found, but the commonly occurring thiophenes and related compounds are very favourably adsorbed. Recovery and regeneration of the ionic liquid involves simple heating to recover the S-compounds intact.

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had a small weight loss of 3.5 wt% between 280 and 320 °C when heated at 10 °C min⁻¹ under nitrogen and no further degradation was observed until 360 °C.¹⁷

Results and discussion

Absorption capacity of the ionic liquids for model compounds

The absorption capacities of EMIM⁺BF₄⁻, BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻ for eight model compounds are shown in Fig. 2. The three ionic liquids showed little absorption for paraffins and olefins, but absorbed a small amount of aromatics and a relatively larger amount of thiophene and methylthiophene. In the used ionic liquids, the molar ratio of thiophene to ionic liquid was found by NMR analysis to be 0.86:1, 3.5:1 and 2.2:1 for EMIM⁺BF₄⁻, BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻, respectively. These values are consistent with the measured weight loss from the organic phase. No ionic liquid was detected in the organic phase after absorption measurement.

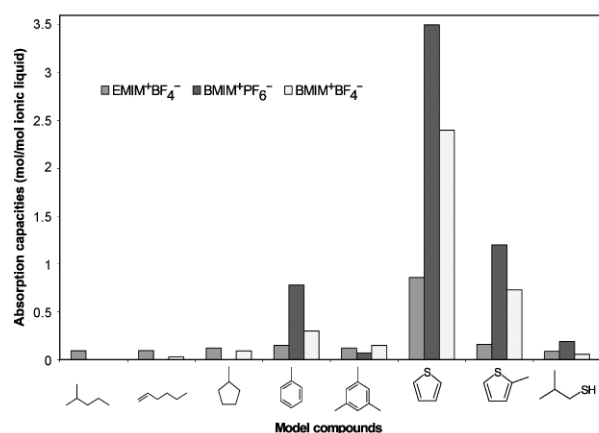


Fig. 2 Absorption capacities of EMIM⁺BF₄⁻, BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻.

The preferred absorption for thiophene, 2-methylthiophene and aromatics by the ionic liquids likely resulted from the interaction of the aromatic ring with the cation of the ionic liquids. It is important to note, however, that the methyl group on the aromatic compounds markedly reduced its absorption capacity. For example, the absorption capacity of BMIM⁺PF₆⁻ for trimethylbenzene is only about 10% of that for toluene. The absorption capacities of BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻ for 2-methylthiophene are about 1/3 of those for thiophene. Methylcyclopentane, a cycloparaffin without aromatic (π) charge density, and isobutylmercaptan, which contains sulfur but lacks aromaticity, were only weakly absorbed.

For most aromatic compounds BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻ have higher absorption capacities than does EMIM⁺BF₄⁻. The results suggest that the structure and the size of both cation and anion of an ionic liquid affect absorption. The local structure of the ionic liquids appears to have a significant

effect on their interaction with the aromatic compounds. As shown in Fig. 2, the absorption capacity follows the general order: thiophene \gg methylthiophene > toluene \gg trimethylbenzene > isobutylthiol, hexene, 2-methylpentane, methylcyclopentane. It appears that absorption is favored for molecules with a higher density of aromatic π electrons. Clearly, those aromatics with a five-membered ring had stronger interaction with the ionic liquids. Sulfur in non-aromatic molecules such as isobutylthiol had weak interaction with the ionic liquids. The specific local structures of the ionic liquids and the chemistry involved in their interaction with the model compounds are under further study.

Absorption of a mixture of thiophene and toluene

When applied to a mixture of thiophene and toluene (weight ratio approximately 1:1), BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻ showed strong preferential absorption for thiophene over toluene. The results of NMR analysis are shown in Table 1. As

Table 1 Competitive absorption of thiophene and toluene in BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻

	Composition (mole ratio)	
	Toluene:thiophene:BMIM ⁺ PF ₆ ⁻	Toluene:thiophene:BMIM ⁺ BF ₄ ⁻
Whole mixture	6.0:7.2:1	5.5:6.2:1
Absorbed	0.65:1.07:1	0.23:0.48:1

compared with a single model compound, the amount of absorbed thiophene from a model mixture was reduced in both BMIM⁺PF₆⁻ and BMIM⁺BF₄⁻ in the presence of toluene. For the model mixture, BMIM⁺PF₆⁻ again showed higher thiophene absorption than did BMIM⁺BF₄⁻, with a combined (toluene + thiophene) molar ratio of 1.72:1. The preferential adsorption of thiophene in both ionic liquids indicates interaction with the ionic liquids favors molecules with higher (π) aromatic electronic density.

Removal of sulfur compounds from gasoline samples

Gasoline samples with low and high sulfur level were also treated with these ionic liquids. The concentrations of total sulfur and aromatics in the untreated and treated gasoline are shown in Table 2. Since there is a huge difference in aromatics vs. sulfur concentrations in the gasoline samples, comparison was made on the percentage loss of these two components from the gasoline samples following treatment with the ionic liquid. About 10–30 wt% of sulfur was preferentially removed from these samples with little change in the content of the aromatics. Removing sulfur without removing aromatics is desired, as aromatics are important for maintaining octane number in gasoline.

Table 2 Sulfur removal from gasolines

Sample		EMIM ⁺ BF ₄ ⁻		BMIM ⁺ PF ₆ ⁻	
		S/ppm	Aromatics ^a (wt%)	S/ppm	Aromatics ^a (wt%)
Low sulfur gasoline	Before treatment	240	33.2	240	33.2
	After treatment	200	33.5	170	33.1
High sulfur gasoline	Before treatment	820	32.6	820	32.6
	After treatment	730	33.0	710	31.7

^a Toluene, ethylbenzene and xylene.

It is evident that the ionic liquids showed remarkable selectivity for the removal of sulfur compounds over aromatics, particularly from the low sulfur gasoline sample. It should be noted that the absorptive removal of sulfur containing compounds from the gasoline sample represents mainly the removal of aromatic S-containing molecules, even though various saturated sulfur compounds are also present.

Regeneration of ionic liquids and recovery of absorbed S-containing compounds

For a thiophene saturated EMIM⁺BF₄[−] phase, the absorbed thiophene was released into a separated phase upon addition of water, as EMIM⁺BF₄[−] is soluble in water. Water was then vaporized from the ionic liquid phase under a nitrogen flow at 110 °C for about 3 h. The EMIM⁺BF₄[−] ionic liquid was nearly quantitatively recovered.

As BMIM⁺PF₆[−] has little miscibility with water and may decompose at high temperature (above 80 °C) when water is present, its regeneration was carried out by direct distillation after saturated absorption of thiophene. The ionic liquid was fully regenerated after heating at 110 °C for 3 h under nitrogen. The absorbed thiophene recovered from distillation corresponds to the amount absorbed. NMR analyses indicated that the ionic liquids, EMIM⁺BF₄[−] and BMIM⁺PF₆[−], maintained their original structures after the regeneration.

Conclusions

The ionic liquids, EMIM⁺BF₄[−], BMIM⁺PF₆[−] and BMIM⁺BF₄[−] showed remarkable selectivity for the absorption of aromatic S-containing molecules from gasoline. These ionic liquids are moisture insensitive at low temperature, thermally stable under the distillation conditions, and readily regenerated for reuse. The absorbed aromatic S-containing compounds were quantitatively recovered during the regeneration. The preferential absorption of thiophene and methylthiophene over toluene suggests that compounds with higher aromatic π electron density in C₅ rings are favorably absorbed. A methyl group on the aromatic rings was found to reduce the absorption capacity, possibly due to a steric effect. The cation and anion structure and size in the ionic liquids are important parameters affecting the absorption capacity for aromatic compounds.

Experimental

Preparation of ionic liquids

Preparation of EMIM⁺BF₄[−]. Equimolar quantities of 1-ethyl-3-methyl-1*H*-imidazolium chloride (from Aldrich) and lithium tetrafluoroborate (from Aldrich) were each dissolved in acetonitrile. These two solutions were gradually mixed together with active stirring. The precipitate, lithium chloride, was separated from the liquid by filtration. The liquid phase was distilled in a three-necked flask at 100 °C to remove acetonitrile from the ionic liquid.

Preparations of BMIM⁺PF₆[−] and BMIM⁺BF₄[−]. BMIM⁺PF₆[−] and BMIM⁺BF₄[−] were prepared following a similar procedure as described above. For BMIM⁺PF₆[−], 1-butyl-3-methylimidazolium chloride and LiPF₆ (Aldrich) were used as starting materials. 1-Butyl-3-methylimidazolium chloride was obtained by refluxing equal molar amounts of

1-methylimidazole and 1-chlorobutane in a flask when heating and stirring at about 70 °C for 48 h.¹⁸ Another sample of BMIM⁺PF₆[−] was obtained from the laboratory of Professor Robin D. Rogers at the University of Alabama. It was prepared by the reaction of 1-butyl-3-methylimidazolium chloride and HPF₆.¹⁶ The preparation of BMIM⁺BF₄[−] started from 1-butyl-3-methylimidazolium chloride and LiBF₄.

A Varian Inova-500 MHz NMR spectrometer and a JEOL GSX-270 MHz NMR spectrometer were used to verify the structures of the ionic liquids. NMR analyses (¹³C quantitative and approached proton test) were also conducted to obtain the sulfur content in the ionic liquid phase after absorption.

Measurement of absorption capacity and efficiency

Eight model compounds, 2-methylpentane, 1-hexene, methylcyclopentane, toluene, trimethylbenzene, thiophene, 2-methylthiophene and isobutyl mercaptan were selected to represent typical molecules in gasoline. The absorption capacity of an ionic liquid for a specific compound was measured at room temperature by adding 1 g of the ionic liquid and 2 g of a model compound to a glass vial. After shaking for a few minutes, two phases were formed and excess model compound in the upper phase was carefully removed. The ionic liquid phase was weighed to obtain the amount of the model compound absorbed.

The absorption selectivity of BMIM⁺BF₄[−] for thiophene from a mixture with toluene was measured by adding 1 g of the ionic liquid to a mixture of 2.12 g of thiophene and 2 g of toluene. After 15 min stirring, the weight loss of the mixture was measured. Concentrations of toluene and thiophene in the ionic liquid phase were measured by NMR spectroscopy after absorption. A similar procedure was applied to BMIM⁺PF₆[−] but with a mixture of 2.04 g of thiophene and 2 g of toluene.

The sulfur removal efficiencies of EMIM⁺BF₄[−] and BMIM⁺PF₆[−] for two gasoline samples were measured. In each case, 2 g of gasoline and 1 g of ionic liquid was mixed in a glass vial and shaken for 15 min. After settling, the upper fuel phase was removed and analyzed. Quantitative elemental analysis of sulfur was conducted on a Bruker S4 Explorer wavelength dispersive X-ray fluorescence spectrometer. Aromatics analysis was carried out on HP 6890 GC/MS using an OV-1 column (30 m \times 0.32 mm id \times 5 μ m) for gasolines.

Recovery of used ionic liquids

The ionic liquids saturated with sulfur containing compounds were readily regenerated by either direct distillation or by successive dissolution in water followed by vaporization of water.

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