



Review Paper

## Ionic Liquids (A Review): The Green Solvents for Petroleum and Hydrocarbon Industries

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### Abstract

*Ionic liquids can be considered as green solvents due to their very low vapor pressure and wide range of applications with unique physical and chemical properties. 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 options 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. To minimize the negative health and environmental effects from automobile exhaust, many countries recently have mandated a drastic reduction in the sulfur content in transportation fuel. In petroleum industry, low-sulfur fuels are often obtained from hydrocracking processes or hydrotreating processes. Although hydrotreating processes have been highly effective for the reduction of sulfur levels, further improvement of the hydrodesulfurization efficiency is limited to increasing severe operational conditions at escalated cost with high energy and hydrogen consumption and other undesired side reactions. In present paper, the attempts are made to write a critical review on various aspects of ionic liquids with the aim of their applications in petroleum and hydrocarbon industries and the various factors affecting their activity in removal of sulfur from transportation fuels.*

**Keywords:** Ionic Liquids, desulfurization, green technology, industrial application.

### Introduction

Sulfur that is present in transportation fuels leads to sulfur oxide (SO<sub>x</sub>) emissions into the atmosphere and causes many environmental problems. It also inhibits the performance of pollution control equipment on vehicles. Therefore, it is to minimize the negative health and environmental effects from automobile exhaust with reducing the sulfur content in fuels at its lowest. Most of the countries are going to make mandatory to have the fuels as "S-free" (by definition <10 ppm) sooner or later<sup>1</sup>. These efforts aim to limit SO<sub>2</sub> emission from the fuel engines and to protect equipment from corrosion. Moreover, lower sulfur content of fuels would allow the use of other catalysts for the reduction of NO<sub>x</sub> emission, which is also an important issue. Thus, the increased reductions of statutory sulfur content in fossil fuels as gasoline or diesel have forced to intense research into all the possible methods of desulfurization<sup>2</sup>.

Although, in the petroleum industry, low-sulfur fuels are often obtained from hydrocracking processes or hydrotreating processes among which hydrotreating processes have been highly effective for the reduction of sulfur levels<sup>3</sup>. But further improvement in the hydrodesulfurization efficiency is limited to increasingly severe operational conditions at escalated cost. Moreover, when the deep hydrodesulfurization of transportation

fuels is needed, the energy and hydrogen consumption will be evidently increased along with some of the undesired side reactions e.g. saturation of more olefins, will also take place. Such side reactions result in a decrease in the octane number of the gasoline and also may affect other properties of the fuels. Furthermore, hydrotreating allows the elimination of aliphatic and alicyclic sulfur compounds. However, dibenzothiophene (DBT) and especially 4,6-alkyl-substituted DBTs are difficult to convert into H<sub>2</sub>S due to the sterically hindered adsorption of these compounds on the catalyst surface<sup>4</sup>. The expenses (energy consumption, hydrogen pressure, reactor size) to meet future legal specifications with classical hydrotreating processes are therefore high and thus appear difficult to meet the present challenges.

Use of green technology is the demand of time in view of environmental concerns. Ionic liquids which are termed as green solvents can be used for desulfurization of liquid fuel due to their very low vapor pressure and wide range of applications with unique physical and chemical properties. In addition to these applications of ionic liquids, it can be found that these noble solvents are very useful in many other fields with its recycle ability and without any impact on environment which is the most impressive factor in the present era of environmental concern<sup>5</sup>. Selective adsorption of sulfur compounds from gasoline has been regarded as an effective supplement to the

hydrotreating process for deep desulfurization. But the selective extraction of sulfur compounds from diesel/gasoline fuel with using ILs is much attractive due to their removal efficiency and other noble properties.

**Ionic Liquid:** Ionic Liquids (ILs) are usually composed of heterocyclic organic cations and various anions and have unique properties such as non-volatility, non-flammability, and a wide temperature range for liquid phase. The reality is that ionic liquids can be liquid at temperatures as low as  $-96^{\circ}\text{C}$  and some are liquid at over  $400^{\circ}\text{C}$ <sup>6</sup>. Furthermore, room-temperature ionic liquids (RTILs) are frequently colorless, fluid, and easy to handle. In the patent and academic literature, the term "ionic liquids" now refers to liquids composed entirely of ions that are fluid around or below  $100^{\circ}\text{C}$ <sup>7</sup>.

ILs have many advantages, such as, they have no detectable vapor pressure, and therefore contribute no VOCs to the atmosphere. Another reason for using ILs is that at least a million binary ionic liquids, and  $10^{18}$  ternary ionic liquids, are potentially possible having their own beauty in different applications in the eco-friendly way. For comparison, more than about 600 molecular solvents are in use today. This diversity enables the solvent to be designed and tuned to optimize yield, selectivity, substrate solubility, product separation, and even enantioselectivity. ILs can be highly conducting, dissolve enzymes, form versatile biphasic systems for separations, can form both polymers and gels for device applications, are media for a wide range of organic and inorganic reactions.

Research into RTILs is booming. In the past few years significant literature has become available in the area of preparation, characterization and application of ILs for synthesis, catalysis and separation. Different ILs can be synthesized having a wide range of physical and chemical properties that can be fine-tuned by using different cations and anions to meet the requirement of specific applications. ILs are

good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase. They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet noncoordinating solvents. They are immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water. Ionic liquids are nonvolatile, hence they may be used in high-vacuum systems and eliminate many contaminant problems<sup>8</sup>.

## Properties of Ionic Liquids

The ILs investigated most comprises the organic 1-alkyl-3-methylimidazolium ( $[\text{C}_n\text{MIM}]$ ), N-alkylpyridinium, tetraalkylammonium or tetraalkylphosphonium cations. The anions are either organic or inorganic, including: hexafluorophosphate  $[\text{PF}_6]$ ; tetrafluoroborate  $[\text{BF}_4]$ ; trifluoromethylsulfonate  $[\text{CF}_3\text{SO}_3]$ ; bis(trifluoromethyl)sulfonyl amide  $[(\text{CF}_3\text{SO}_2)_2\text{N}]$ ; trifluoroethanoate  $[\text{CF}_3\text{CO}_2]$ ; acetate  $[\text{CH}_3\text{CO}_2]$ ; nitrate, and halide. The physicochemical properties of ILs depend on the nature and size of both their cation and anion constituents. In context of hydrolysis stability, the lower homologues of alkylsulfate anions, namely methanesulfate and ethanesulfate may have sensitive towards hydrolysis. In the presence of water these anions may form the corresponding alcohol and hydrogensulfate at elevated temperatures. But for alkylsulfates with longer alkyl groups the sensitivity towards hydrolysis is much lower. After checking the expected hydrolysis stability of  $[\text{bmim}][n\text{C}_8\text{H}_{17}\text{OSO}_3]$ ,<sup>9</sup> we find that no decrease of pH-value was determined for  $[\text{bmim}][n\text{-C}_8\text{H}_{17}\text{OSO}_3]$  during 8 hours. Table 1 illustrates some physicochemical properties of the RTILs commonly used in analytical chemistry. More detailed information on the properties of ILs can be found in literature<sup>10-14</sup>.

**Table-1**  
Some physicochemical properties of the commonly used ILs in analytical chemistry

Ionic Liquids	Melting Point ( $^{\circ}\text{C}$ )	Density (g/mL)	Viscosity (mPa s)	Water Solubility (g/100 mL)	Conductivity (S/m)
$[\text{C}_4\text{MIM}][\text{PF}_6]$	10, -8	1.36–1.37 ( $25^{\circ}\text{C}$ )	148–450 ( $25^{\circ}\text{C}$ )	1.88	0.14 ( $25^{\circ}\text{C}$ )
$[\text{C}_6\text{MIM}][\text{PF}_6]$	-61	1.29–1.31 ( $25^{\circ}\text{C}$ )	560–586 ( $25^{\circ}\text{C}$ )	0.75	
$[\text{C}_8\text{MIM}][\text{PF}_6]$		1.20–1.23 ( $25^{\circ}\text{C}$ )	682–710 ( $25^{\circ}\text{C}$ )	0.20	
$[\text{CMIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$	22	1.56	44 ( $20^{\circ}\text{C}$ )		0.84 ( $20^{\circ}\text{C}$ )
$[\text{C}_2\text{MIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$	-3	1.50	34 ( $20^{\circ}\text{C}$ )	1.77	0.88 ( $20^{\circ}\text{C}$ )
$[\text{C}_4\text{MIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$	-4	1.42	52 ( $20^{\circ}\text{C}$ )	0.80	0.39 ( $20^{\circ}\text{C}$ )
$[\text{C}_6\text{MIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$		1.33		0.34	
$[\text{C}_8\text{MIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$		1.31		0.21	
$[\text{C}_4\text{MIM}][\text{Cl}]$	65, 41	1.10 (Supercooled liquid at $25^{\circ}\text{C}$ )	Solid	Miscible	Solid
$[\text{C}_2\text{MIM}][\text{BF}_4]$	15	1.15 ( $30^{\circ}\text{C}$ ), 1.28 ( $25^{\circ}\text{C}$ )	37 ( $25^{\circ}\text{C}$ )	Miscible	
$[\text{C}_4\text{MIM}][\text{BF}_4]$	-81	1.17 ( $30^{\circ}\text{C}$ ), 1.21 ( $25^{\circ}\text{C}$ )	233 ( $30^{\circ}\text{C}$ ), 180 ( $25^{\circ}\text{C}$ )	Miscible	0.17 ( $25^{\circ}\text{C}$ )
$[\text{C}_6\text{MIM}][\text{BF}_4]$			314 ( $20^{\circ}\text{C}$ ), 177 ( $30^{\circ}\text{C}$ )	Miscible	
$[\text{C}_4\text{MIM}][\text{CF}_3\text{SO}_3]$	16	1.29 ( $20^{\circ}\text{C}$ )	90 ( $20^{\circ}\text{C}$ )	Miscible	0.37 ( $20^{\circ}\text{C}$ )

## Applications of Ionic Liquids

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. A few applications to mention are like in purification of essential oils by extraction, separation of azeotropic mixtures, in hydrogen purification, in extraction of rare earth metals, in extraction of carboxylic acids, for removal of sulphur from refinery streams, in separation of isomers, for microfluidic separation using enzymatic reaction, in microextraction, for separation of fission products, in extraction and recovery of dyes, for extraction of ethanol etc. In addition to these applications of ionic liquids, it can be found that these noble solvents are very useful in many other fields with its recycle ability and without any impact on environment which is the most impressive factor in the present era of environmental concern<sup>15</sup>.

## Limitations of Ionic Liquids

Some typical ionic liquids consist of halogen containing anions (such as  $[AlCl_4]^-$ ,  $[PF_6]^-$ ,  $[BF_4]^-$ ,  $[CF_3SO_3]^-$  or  $[(CF_3SO_2)_2N]^-$ ) which in some regard limit their ‘greenness’. The presence of halogen atoms may cause serious concerns if the hydrolysis stability of the anion is poor (e.g. for  $[AlCl_4]^-$  and  $[PF_6]^-$ ) or if a thermal treatment of spent ionic liquids is desired. In both cases additional effort is needed to avoid the liberation of toxic and corrosive HF or HCl into the environment. Bearing these aspects in mind, it should be to looked for new, even ‘greener’ ionic liquids for industrial catalytic applications, which should meet the following, technically desired combination of properties: i. melting point or glass point below 40°C, ii. hydrolysis stable in neutral aqueous solution up to 80°C, iii. temperature of thermal decomposition above 250°C, iv. possible disposal by combustion without formation of HF or HCl, v. possible biodegradation of the used anion in ordinary waste water treatment, vi. synthesis from cheap, technically available raw materials e.g. alkali-metal salts. However, many systems do not fulfill all the above mentioned, complex combination of properties<sup>16</sup>.

Again, it is well known that impurities in an ionic liquid can have large effects on the physico-chemical properties of the material under investigation. For example, in the case of  $[bmim][n-C_8H_{17}OSO_3]$  the following potential sources for impurities were identified: i. organic volatiles (e.g. traces of methylimidazole from the synthesis of the chloride salt), ii. halide impurities from incomplete metathesis reaction, iii. other ionic impurities resulting from the  $Na[n-C_8H_{17}OSO_3]$  that was applied in technical grade or from some solubility of  $Na[n-C_8H_{17}OSO_3]$  in the ionic liquid product, iv. water. Therefore, in order to obtain reliable data for physico-chemical properties of  $[bmim][n-C_8H_{17}OSO_3]$  it must be taken maximum care to either

eliminate the impurities completely during synthesis (in case of impurities a–c) or to investigate a material with a clearly defined amount of the impurity (in case of water). Thus, the technical availability and the well-documented toxicology of the ionic liquid are highly essential for their industrial application.

## Discussion

The investigation for desulfurization of model diesel oil obtained by dissolving 500 ppm DBT in *n*-dodecane shows very good results. Based on the initial idea to extract the sulfur compound by chemical interaction, the extraction with Lewis and Brønsted-acidic ILs was studied as shown in table 1.

**Table-2**  
**Desulfurization of model diesel fuel (500 ppm sulfur in ndodecane) by extraction with Lewis- and Brønsted-acidic ionic liquids<sup>a</sup>**

Entry	Ionic Liquid	Sulfur conten/ ppm
a	$[BMIM]Cl/AlCl_3 = 0.35/0.65^b$	275
b	$[EMIM]Cl/AlCl_3 = 0.35/0.65^b$	335
c	$[HN(C_6H_{11})Et_2][CH_3SO_3]/[HNBu_3]$ $[CH_3SO_3] = 1/1$	310

<sup>a</sup>General conditions: room temperature, mass ratio model oil/IL = 5/1, Extraction time: 15 min, initial sulfur content 500 ppm. <sup>b</sup>Mol/mol.

All ILs formed a biphasic system with the model oil at room temperature and showed good properties to extract DBT out of the model oil. The comparison of the extraction with the two different chloroaluminate melts suggests a certain influence of the ionic liquid’s cation. The relatively good extraction property of the Brønsted-acidic methanesulfonate mixture indicates both good extraction power for DBT and no leaching of the ionic liquid into the model oil. The solubility of hydrocarbons in ILs compared to S-compounds is very low<sup>17</sup>.

Encouraged by these results, different cation/anion combinations of neutral ILs in the extraction of DBT were tested. Selected results of an anion variation with ILs of the general type  $[BMIM][anion]$  are given in table 2. The data indicate that the desulfurization is hardly affected by the chemical nature of the anion. Only the IL with the somewhat bigger octylsulfate ion showed significantly better extraction properties. From these results it can be concluded that the size of the ions is rather important for the extraction effect. This assumption was further supported by extraction with different tetrafluoroborate salts (table 3). This may be due to the steric factors in the IL.

Figure 1 shows that a lower mass ratio of model oil to ionic liquid results in lower sulfur contents. However, sulfur contents below 50 ppm can be reached for all mass ratios if the number of extraction steps is high enough. The almost linear relationship of  $\log(S\text{-content})$  vs. the number of extraction steps indicates that the extraction can be formally described by a partition coefficient according to Nernst’s law<sup>18</sup>.

**Table-3**

Comparison of different anions in the desulfurization process of a model diesel oil (500 ppm sulfur in *n*-dodecane) by extraction with neutral ionic liquids of the general type [BMIM][anion]<sup>a</sup>

Entry	Anion	Sulfur content/ppm
a	[PF <sub>6</sub> ] <sup>2</sup>	440
b	[CF <sub>3</sub> SO <sub>3</sub> ] <sup>2</sup>	430
c	[BF <sub>4</sub> ] <sup>2</sup>	420
d	Cl <sub>2</sub>	410
e	[MeSO <sub>4</sub> ] <sup>2</sup>	410
f	[MeSO <sub>3</sub> ] <sup>2</sup>	410
g	[O <sub>c</sub> SO <sub>4</sub> ] <sup>2</sup>	350

<sup>a</sup>General conditions: Temperature = 60 °C (except entry d: 80 °C), mass ratio model oil/ IL = 5/1, reaction time 15 min, initial sulfur content: 500 ppm.

**Table-4**

Comparison of different cations in the extraction of DBT from *n*-dodecane with different tetrafluoroborate ionic liquids<sup>a</sup>

Cation	Sulfur content/ppm
[EMIM]	450
[BMIM]	420
[OMIM]	380

<sup>a</sup>General conditions: Temperature = 50 °C, mass ratio model oil/IL = 5/1, reaction time 15 min, initial sulfur concentration 500 ppm; [OMIM] = 1-methyl-3-*n*-octylimidazolium.

Nevertheless, the results of experiments with pre-desulfurized diesel are also promising. As shown in table 4, the Lewis-acidic ionic liquid [BMIM]Cl/AlCl<sub>3</sub>: 0.35/0.65 showed much higher

efficiency in the sulfur extraction from real diesel in comparison to the methanesulfonate and octylsulfate melts<sup>19</sup>.

**Table-5**

Multistage desulfurization of pre-desulfurized (real) diesel oil<sup>a</sup>

Stage	[BMIM]Cl/ AlCl <sub>3</sub>	[HN(C <sub>6</sub> H <sub>11</sub> )Et <sub>2</sub> ][ CH <sub>3</sub> SO <sub>3</sub> ]/ [HNBu <sub>3</sub> ][CH <sub>3</sub> SO <sub>3</sub> ] = 1/1	[BMIM][octyl sulfate]
1	375	375	375
2	220	330	320
3	160	300	280
4	130	270	260
5	75	240	235

<sup>a</sup>General Conditions: Temperature = 60 °C, mass ratio diesel oil/IL = 5/1, reaction time: 15 min.

This indicates that Lewis acid–base interactions enhance the extraction power of the IL here. Nevertheless, the extraction power of the neutral methanesulfonate and octylsulfate melts is still remarkable. However, more extraction steps are necessary in case of ‘real’ diesel oil to reach future technical sulfur content specifications (< 50 ppm). The use of AlCl<sub>3</sub>-free ILs is particularly promising as the use of AlCl<sub>3</sub> in desulfurization is probably unlikely to be accepted by refiners.

The investigation for desulfurization of model gasoline oil obtained by dissolving 680 ppm DBT and 20% toluene in heptane.

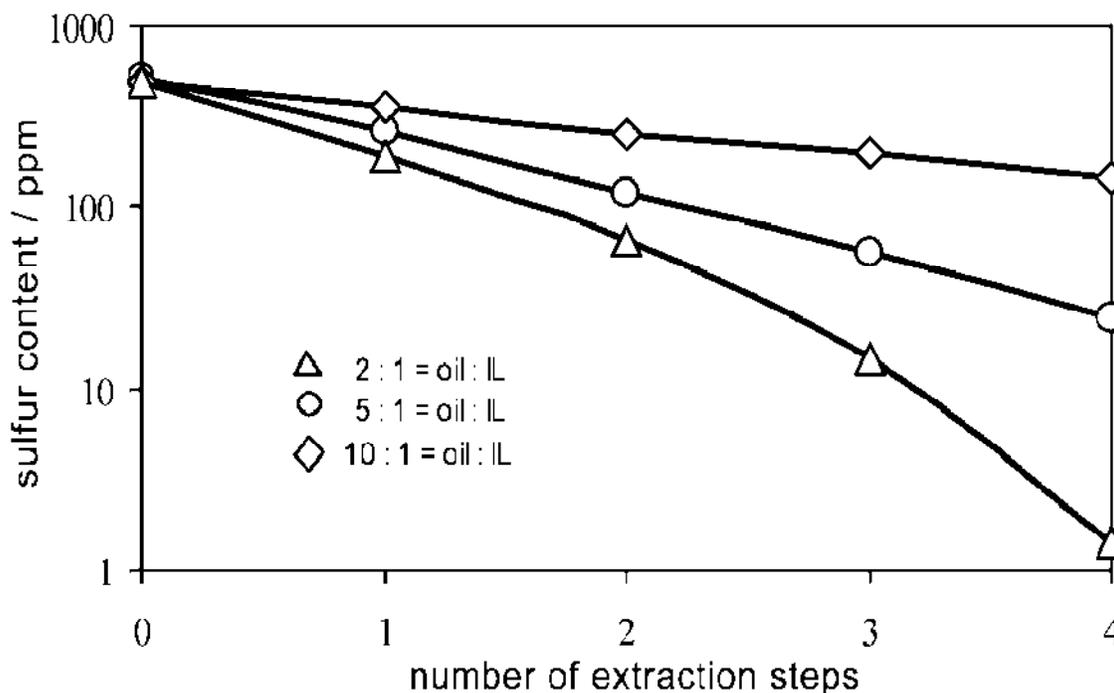


Figure-1  
Removal of Sulfur Vs Number of Extraction Steps

**Table-6**  
**Desulfurization of Model Oil by Extraction with Different Ionic Liquids**

Ionic Liquid	Oil to be treated	Sulfur content in oil to be treated (ppmw)	Sulfur removal (%)
BMIMCu <sub>2</sub> Cl <sub>3</sub>	model oil	680	23.4
BMIMAICl <sub>4</sub> <sup>a</sup>	model oil	500	16.0
BMIMBF <sub>4</sub> <sup>b</sup>	model oil	764	11.0

<sup>a</sup>General conditions: Temperature = 80 °C, and model oil was prepared by adding dibenzothiophene to n-dodecane. <sup>b</sup>General conditions: room temperature, and the model oil was prepared by adding dibenzothiophene and piperidine to n-dodecane.

BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid shows remarkable ability for sulfur removal. After extraction with BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid, more than 23% of the sulfur compounds have been removed from model oil, whereas the sulfur removal for BMIMBF<sub>4</sub> ionic liquids is only 11.0%. Although BMIMAICl<sub>4</sub> ionic liquid exhibits a sulfur removal of 16.0%, because of the strong Lewis acidity of Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> anion traces in ionic liquids, the olefin in commercial gasoline will polymerize to heavy compounds and furthermore crack into light compounds such as C<sub>4</sub> and C<sub>5</sub>, which will result in a loss of gasoline with BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid, no polymerization of the olefins has been observed<sup>20</sup>.

The desulfurization results of gasoline with different sulfur contents, using BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid, are listed in table 7.

**Table-7**  
**Desulfurization of Gasoline by Extraction with Ionic Liquids**

Ionic Liquid	Oil to be treated	Sulfur content in oil to be treated (ppmw)	Sulfur removal (%)
BMIMCu <sub>2</sub> Cl <sub>3</sub>	gasoline	950	16.2
BMIMCu <sub>2</sub> Cl <sub>3</sub>	gasoline	680	21.6
BMIMCu <sub>2</sub> Cl <sub>3</sub>	gasoline	410	29.1
BMIMCu <sub>2</sub> Cl <sub>3</sub>	gasoline	196	37.4

A comparison of these results to those in table 5 shows that sulfur removal by BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid from gasoline is lower than that from model oil. More-complex compounds such as olefins, nitrogen-containing compounds, and aromatic compounds existed in the gasoline, compared to the model oil, which indicates that these compounds can decrease the sulfur removal ability of BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid<sup>21-24</sup>.

More interestingly, the data in table 6 show that the sulfur removal by BMIMCu<sub>2</sub>Cl<sub>3</sub> ionic liquid increases as the sulfur content in the gasoline decreases.

## Conclusion

In conclusion, Ionic liquids can be used as novel extractive solvents and also the presented results shows a new approach

for the deep desulfurization of model liquid fuels, especially with regards to those sulfur compounds that are very difficult to remove by common hydrodesulfurization technique. Traces of such sulfur compounds could easily be removed. Imidazolium based ionic liquid showed remarkable efficiency to remove sulfur compounds from model liquid fuel sample, however this compounds are air and moisture sensitive Ionic liquids containing chloride as anion are a good alternative as desulfurization agent because its shows high capacity to remove sulfur compounds and due to their stability to air, temperature and moisture, this halogen free ILs can be easily regenerated and recycled. The structure of cation and anions in ionic liquids, the extraction time, the operation temperature, and the dosage of ionic liquid are all important parameters affecting the extracting ability of sulfur. The application of very mild process conditions (low pressure and temperature) is an additional advantage of this new approach in comparison to traditional hydrodesulfurization. Keeping in view of the noble properties of Ionic Liquid and its detailed knowledge, the applications of Ionic Liquids can be explored in many other areas.

**Future Scope:** As mentioned in the conclusion, the unusual properties of Ionic Liquids like non-flammability may open the possible uses of room temperature ionic liquids (RTILs) in many research areas such as electrical devices to avoid the explosion or ignition.

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