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Deep desulfurization of diesel fuel by extraction with ionic liquids

A. Bösmann, L. Datsevich, A. Jess,* A. Lauter, C. Schmitz and P. Wasserscheid

Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Sammelbau Chemie, Worringer Weg 1, D-52074 Aachen, Germany, E-mail: jess@itmc.rwth-aachen.de

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A new approach for the deep desulfurization of diesel fuels by extraction with ionic liquids is described.

In recent years deep desulfurization of diesel fuel has attracted much attention due to the gradual reduction of the statutory sulfur content in most western countries. In 2005 the max. S-content will be limited down to 10–50 ppm compared to today's value of 500 ppm S. These efforts aim to limit SO_2 emission from diesel engines and to protect equipment from corrosion. Moreover, lower sulfur content of diesel fuels would allow the use of other catalysts for the reduction of NO_x emissions.

In industry, desulfurization of diesel is actually carried out by hydrotreating. Generally, this allows the elimination of aliphatic and alicyclic sulfur compounds.[1] However, dibenzothiophene (DBT) and especially 4,6-alkyl-substituted DBTs are difficult to convert into H_2S due to the sterically hindered adsorption of these compounds on the catalyst surface.[2–4] The expenses (hydrogen pressure, reactor size) to meet future legal specifications with classical hydrotreating processes are therefore high. Thus, alternative ways for the production of low or even ultra-low sulfur contents in diesel oil are attractive.

In the present paper, the use of ionic liquids (ILs) for the selective extraction of sulfur compounds from diesel fuel is described for the first time. ILs are low melting (< 100 °C) salts which represent a new class of non-molecular, ionic solvents.[5,6] Up to now, ILs have been mainly studied with respect to biphasic homogeneous catalysed processes. The range of known and available ILs has been expanded so that many different candidates are accessible today.[7,8]

In a first set of experiments, the desulfurization of a model diesel oil obtained by dissolving 500 ppm DBT in *n*-dodecane was investigated. Based on the initial idea to extract the sulfur compound by chemical interaction, the extraction with Lewis- and Brønsted-acidic ILs was studied. As Lewis-acidic ILs, acidic mixtures of 1-*n*-butyl-3-methylimidazolium ([BMIM]) chloride and 1-ethyl-3-methylimidazolium ([EMIM]) chloride[8] with $AlCl_3$ (molar ratio [cation]Cl/$AlCl_3$ = 0.35/0.65) were investigated. A 1 : 1 (mol/mol) mixture of two trialkylammonium methanesulfonate salts was tested as Brønsted-acidic ILs. All ILs formed a biphasic system with the model oil at room temperature. Application of the methanesulfonate melt had the additional advantage of having an easy analytical control of IL leaching into the (for this specific experiment S-free) oil, although this was never observed.

For the extraction experiments, the IL was added to an excess of model oil in a mass ratio of 1/5. The obtained biphasic mixture was then stirred at room temperature. Samples were taken every 5 min. However, it was found that the extraction process proceeded quickly. Consequently, the final sulfur concentration was reached after 5 min and longer stirring did not result in lower sulfur contents. All sulfur contents presented were determined with an Antek Pyroreactor 771, which was equipped with an Antek UV-sulfur-detector 714. Repeated measurements indicated an average error of this method of ± 5 ppm.

The results of a single extraction step with selected Lewis- and Brønsted-acidic ILs are presented in Table 1. All ILs under investigaton showed good properties to extract DBT out of the model oil. The comparison of the extraction experiments with the two different chloroaluminate melts suggests a certain influence of the ionic liquid's cation (compare entries a and b in Table 1). The relatively good extraction properties of the Brønsted-acidic methanesulfonate mixture indicates both good extraction power for DBT and no (or at least not measurable) leaching of the ionic liquid into the model oil. The solubility of hydrocarbons in ILs compared to S-compounds is very low.

Table 1 Desulfurization of model diesel fuel (500 ppm sulfur in *n*-dodecane) by extraction with Lewis- and Brønsted-acidic ionic liquids[a]

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

[a] *General conditions*: room temperature, mass ratio model oil/IL = 5/1, extraction time: 15 min, initial sulfur content 500 ppm. [b] Mol/mol.

In order to understand in more detail the observed DBT extraction, the extraction with the neutral methanesulfonate mixture $[N(C_6H_{11})Et_2Me][CH_3SO_3]/[NBu_3Me][CH_3SO_3]$ = 1/1 (C_6H_{11} = cyclohexyl) under otherwise identical conditions was investigated. The latter was obtained in a simple manner by mixing equimolar amounts of $N(C_6H_{11})Et_2$ and NBu_3 with a stoichiometric amount of methanesulfonic acid methylester. Surprisingly, the sulfur content of the model oil was found to be as low as 300 ppm after a single extraction step. This demonstrates—at least for the methanesulfonate melts under investigation—that the ionic liquid's extraction power for DBT is not uniquely based on chemical interactions involving the acid proton.

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

Table 2 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][a]

Entry	Anion	Sulfur content/ppm
a	$[PF_6]^-$	440
b	$[CF_3SO_3]^-$	430
c	$[BF_4]^-$	420
d	Cl^-	410
e	$[MeSO_4]^-$	410
f	$[MeSO_3]^-$	410
g	$[OcSO_4]^-$	350

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

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Table 3 Comparison of different cations in the extraction of DBT from *n*-dodecane with different tetrafluoroborate ionic liquids[a]

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

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

Table 4 Multistage desulfurization of predesulfurized (real) diesel oil[a]

Stage	[BMIM]Cl/$AlCl_3$	$[HN(C_6H_{11})Et_2]$-$[CH_3SO_3]$/$[HNBu_3]$-$[CH_3SO_3]$ = 1/1	[BMIM]-[octylsulfate]
1	375	375	375
2	220	330	320
3	160	300	280
4	130	270	260
5	75	240	235

[a] 60 °C, mass ratio diesel oil/IL = 5/1, reaction time: 15 min.

assumption was further supported by extraction experiments with different tetrafluoroborate salts (Table 3).

In this context, it is important to note that the comparison of different ILs in Tables 2 and 3 is based on equal mass ratio model oil/IL. A comparison on the base of equal molar levels would show an even more pronounced effect of the cation's/anion's size on the extraction power of the ILs. A possible explanation for this behaviour may be that the physical solubility of DBT in the IL is dependent on steric factors in the IL.

In order to check the feasibility of our concept for a deep desulfurization process, we tried to reach very low sulfur levels by application of a multistage extraction process (mixer–settler-system). For these experiments the best IL candidate [BMIM]Cl/$AlCl_3$: 0.35/0.65 was chosen as extraction medium. The desulfurized model oil from the first extraction step was again treated with fresh ionic liquid. This process was repeated up to four times. The results with different mass ratios model oil/IL are presented in Fig. 1.

As expected, Fig. 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-content) *vs*. the number of extraction steps indicates that the extraction can be formally described by a partition coefficient according to Nernst's law. This is confirmed by re-extraction experiments (mixture of IL with extracted S-compound and S-free *n*-dodecane): The same distribution of sulfur (ratio of concentration in IL to concentration in *n*-dodecane) is obtained, which was tested by the re-extraction of DBT from the loaded ionic liquid $[HN(C_6H_{11})Et_2][CH_3SO_3]/[HNBu_3][CH_3SO_3]$ = 1/1 with in this case S-free *n*-dodecane. In this context NMR measurements of the used ILs confirm also that the extracted DBT remains unreacted. Thus regeneration of the ILs should be generally achievable, although more systematic experiments are needed.

In a technical extraction process, the IL, which has been loaded with organic sulfur components in the extraction column (or mixer–settler-system), would be continuously regenerated in a second column, and then pumped back into the extraction unit. Thus the potential to regenerate the IL is an important aspect. Interesting re-extraction media are probably light alkanes (C_2–C_5) or supercritical CO_2, as these solvents can be easily recovered and separated from the higher boiling sulfur compounds by evaporation. The organic sulfur would than be converted into elemental sulfur by the common Claus-process.

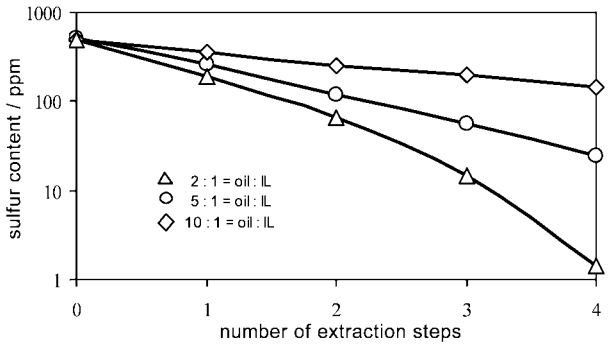

Fig. 1 Multistage desulfurization of model diesel oil (500 ppm sulfur in *n*dodecane) by the IL [BMIM]Cl/$AlCl_3$ (0.35/0.65; different mass ratios oil/IL) at room temperature.

Subsequently, the new desulfurization concept was tested by additional experiments with a 'real' predesulfurised diesel oil (without additives, sulfur content: 375 ppm). As expected, the extraction of real diesel oil is much more complicated due to its complex chemical composition including many different sulfur compounds and other impurities like organic nitrogen and oxygen compounds.

Nevertheless, the results of experiments with predesulfurized diesel are also promising. As shown in Table 4, the Lewis-acidic ionic liquid [BMIM]Cl/$AlCl_3$: 0.35/0.65 showed much higher efficiency in the sulfur extraction from real diesel in comparison to the methanesulfonate and octylsulfate melts.

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 $AlCl_3$-free ILs is particularly promising as the use of $AlCl_3$ in desulfurization is probably unlikely to be accepted by refiners.

In conclusion, the presented results show a new approach for the deep desulfurization of diesel oil, especially with regard to those sulfur compounds that are very difficult to remove by common hydrodesulfurization techniques. Traces of such sulfur compounds could easily be removed. The new method is based on the extraction of the sulfur compounds with ILs. The application of very mild process conditions (low pressure and temperature) is an additional advantage of this new approach in comparison to traditional HDS.

Generally the extraction of polarizeable compounds by ionic liquids may be a possibility to isolate valued products which reside in complex mixtures of a multitude of different organic substances as is likely to occur in aromas and scents.

Present work is directed towards a deeper understanding of the extraction properties of ILs, and to identify inexpensive, unchlorinated IL systems with enhanced extraction power.

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8 Many ionic liquids are commercially available nowadays. For example, [BMIM]Cl and [EMIM]Cl can be purchased from Solvent Innovation GmbH, Cologne, Germany (www.solvent-innovation.de).