Extractive desulfurization of fuel oils with low-viscosity dicyanamide-based ionic liquids†

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Four low-viscosity ionic liquids (ILs) based on the dicyanamide anion ($[N(CN)_2]^-$), *i.e.*, 1-butyl-3-methylimdazolium ($[BMI][N(CN)_2]$), 1-ethyl-3-methylimdazolium ($[EMI][N(CN)_2]$), ethylated tetrahydrothiophenium ($[S2][N(CN)_2]$) and ethyldimethylsulfonium ($[EtMe_2S][N(CN)_2]$), have been investigated to determine their extraction capability for thiophene (TS) and dibenzothiophene (DBT) from model fuel oils. Aromatic imidazolium is more efficient than cyclic thiophenium and tetrahedral trialkylsulfonium; specifically, the S-extraction ability follows the order $[BMI][N(CN)_2] > [EMI][N(CN)_2] > [S2][N(CN)_2] > [EtMe_2S][N(CN)_2]$, with DBT being more efficiently extracted than TS. The S-extraction of $[BMI][N(CN)_2]$ has been investigated as a representative with respect to the influence of extraction temperature, IL : oil mass ratio, initial S-content, multiple extractions and reusability, along with its mutual solubility in oil. The percentage of S-removal from gasoline and diesel fuel were 48.5 and 68.7%, respectively, in a single extraction at 25 °C, 1 : 1(w/w) IL : oil, 5 min; the S-content in gasoline decreased from 599 ppm to 4 ppm after 5 extraction cycles and in diesel fuel decreased from 606 ppm to an undetectable value after 4 cycles. The mutual solubility is not pronounced and the extraction efficiency is not conspicuously changed after 6 regeneration cycles. It is worth noting that a short extraction time of < 5 min is observed for all the ILs at room temperature, which is understood by their low viscosities and effective mass transfer. This work may offer a new option for the deep desulfurization of fuel oils.

Introduction

With the rapid increase in automobiles, environmental pollution caused by SO_x during fuel combustion (gasoline, diesel fuel, *etc.*) has attracted widespread attention. In this regard, new legislation to lower the sulfur limits in fuel oils are continuously being introduced by governments. For example, in 1998 the European Directive on Transportation Fuels placed a limit on the S-content in gasoline and diesel fuel at 150 and 350 ppm, respectively, with a sterner limit in 2003, where the S-content in all transportation fuels was reduced to 50 ppm, and now to less than 10 ppm.[1,2] In developed countries such as the United States of America, Japan, Germany and Sweden, there has been an increase in taxes on transportation fuel exceeding 10 ppm S-content.[1] As the decreasing S-content in fuel oils becomes a pressing subject in the petroleum refining industry due to legislation and growing environmental awareness, it is anticipated that the future trend will be to produce sulfur-free (<10 ppm) transportation fuel oils.[3] However, there is increasing S-content in crude oil today, leaving current refineries with mounting challenges. A standard process for removing S-compounds in fuel oils is hydrodesulfurization (HDS),[4–7] a process in which the S-compounds react with hydrogen and are converted into hydrogen sulfide (H_2S) and other corresponding hydrocarbons,[8–11] with the aid of specific catalysts at high temperature (>300 °C) and high pressure (3~10 MPa). H_2S is subsequently separated from oils and catalytically oxidized into elemental sulfur by the classic Claus process. HDS is capable of effectively removing aliphatic thiols, sulfides and disulfides. However, it is less effective for removing certain condensed heterocyclic S-compounds such as thiophene, benzothiophene, dibenzothiophene or their derivatives, because of the sterically-hindered adsorption of these compounds on the surface of the catalyst.[12] Besides, harsh conditions, such as high temperature, high pressure of hydrogen gas or a more active catalyst, are required to obtain oils with low levels of sulfur, which evidently poses high operational or investment costs.[13–16]

Therefore, to improve or complement HDS technology, some alternative deep-desulfurization methods, such as extractive,[14,16–35] oxidative,[36–49] adsorptive[50–54] and bio-desulfurizations,[55–58] have been investigated to more effectively remove condensed heterocyclic S-compounds. Among them, extractive desulfurization (EDS) seems more competitive because it does not involve hydrogen consumption, catalyst, high temperature or high pressure, and with mild and simple operating conditions.[59,60] Furthermore, it does not alter the chemical structure of the compounds in fuel oils, and the extracted S-compounds can be re-used as raw materials. Earlier, a few molecular solvents,[33,61] such as polyalkylene glycol, imidazolidinone, pyrimidinone and dimethylsulfoxide, were tested

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Table 1 Some ILs used in EDS and their viscosities

IL	Abbreviation	T/K	Viscosity/cP	Ref.
1-Ethyl-3-methylimidazolium diethyl phosphate	$[C_2mim][PO_2(C_2O)_2]$	294.15	460	17,19,21
1-Butylpyridinium tetrafluoroborate	$[C_4py][BF_4]$	298.15	145.23	31,32
1-Hexylpyridinium tetrafluoroborate	$[C_6Py][BF_4]$	293.15	240.9	31
1-Octylpyridinium tetrafluoroborate	$[C_8py][BF_4]$	293.15	319.66	24,31
1-Butyl-3-methylimidazolium chloride	$[C_4mim][Cl]$	303	3950	23
1-Butyl-3-methylimidazolium tetrafluoroborate	$[C_4mim][BF_4]$	298.15	106.820	82
1-Butyl-3-methylimidazolium hexafluorophosphate	$[C_4mim][PF_6]$	298.15	273	82
1-Octyl-3-methylimidazolium hexafluorophosphate	$[C_8mim][PF_6]$	298.15	710	82
1-Octyl-3-methylimidazolium tetrafluoroborate	$[C_8mim][BF_4]$	298.15	341	25,27,82
1-Octyl-3-methylimidazolium chloride	$[C_8mim][Cl]$	298.15	20883	23

Table 2 Properties of the ILs used in this study

IL	Appearance	MW/g mol^{-1}	Viscosity/cP	Density/g cm^{-3}	T_d/°C
$[EMI][N(CN)_2]$	Yellow	177.21	16.1@25 °C	1.06	275
$[BMI][N(CN)_2]$	Transparent	205.26	29.3@ 25 °C	1.06	220
$[EtMe_2S][N(CN)_2]$	Colorless	157.24	25.3@20 °C	n/a	182
$[S2][N(CN)_2]$	Colorless	183.08	34.2@20 °C	1.135	189

in EDS but performed undesirably, and their mutual solubility led to cross-contamination. Direct EDS has not really been used in industry, and this process places emphasis on finding an effective extractant. Many ionic liquids (ILs) reported *inter alia* have some desirable physical and chemical properties, such as non-volatility, thermal/chemical stability, wide liquidus range, non-flammability, recyclability and non-toxicity, which are otherwise lacking in traditional molecular solvents.[62–66] Some ILs have recently been investigated in EDS, but were rather limited to some common anions (*e.g.*, $[BF_4]^-$, $[PF_6]^-$, $[AlCl_4]^-$ and $[EtSO_4]^-$) coupled with the conventional aromatic cations of imidazolium and pyridinium.[16–35] These ILs presented some favorable characteristics, such as negligible miscibility with fuel oils, high affinity for S-containing compounds, easy regeneration and good re-usability;[16,19,26,29,30,67–69] however, they had some undesirable features, *e.g.*, the production of corrosive hydrogen fluoride (HF) from the decomposition of fluorinated anions, non-stability to moisture and air, as well as high viscosities (as shown in Table 1). Their high viscosity would negatively pose handling problems in practical industrial applications, such as transportation, dispersion and dissolution, as well as the hindrance of mass transfer in liquid–liquid extraction systems and prolonged equilibrium times (which could be solved by a twin-obsession: increasing temperature and escalating the energy cost). In fact, current studies are mainly generally concerned with the capacity of S-removal by ILs but pay less attention to the equilibrium time.

Recently, new low-viscosity ILs based on the dicyanamide anion ($[N(CN)_2]^-$) have been synthesized and characterized,[70–72] and they have been used in electrodeposition, solar cells, membrane separation, nanomaterials and the synthesis of organometallic compounds.[73–81] In this work, four different kinds of $[N(CN)_2]^-$-based ILs, *i.e.*, aromatic 1-butyl-3-methylimdazolium ($[BMI][N(CN)_2]$) and 1-ethyl-3-methylimdazolium ($[EMI][N(CN)_2]$), cyclic ethylatedtetrahydrothiophenium ($[S2][N(CN)_2]$), and tetrahedral ethyldimethylsulfonium ($[EtMe_2S][N(CN)_2]$), were investigated to extract TS and DBT from model fuel oils. Their structures are shown in Fig. 1. They are stable to moisture and air, have a low viscosity (as shown in Table 2) and their anion is fluorine-free. The mutual solubility, along with the influence of extraction temperature, IL : oil mass ratio, initial S-content, multiple extractions and reusability, on S-extraction was investigated using the IL with the optimal performance, $[BMI][N(CN)_2]$.

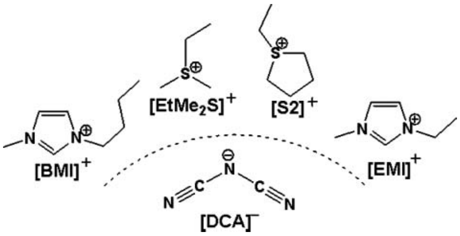

Fig. 1 Structures of the ILs used in this study.

Results and discussion

EDS performance of different ILs

A series of parallel experiments were conducted for each IL in two model oils to determine extraction equilibrium time. As shown in Fig. 2, all the ILs are highly capable of extracting TS and DBT from the model oils. The S-content in the oils decreased from ~500 ppm to 150~350 ppm in a single extraction operation, with an S-extraction efficiency of 30~70%. Here, the term "S-extraction efficiency" is defined by the following equation:

$$\text{S-extraction efficiency} = \frac{S_o - S_f}{S_o} \times 100\%$$

where S_0 is the initial S-content in the oil (ppm, before contact with IL) and S_f is the final S-content in the oil (ppm, after contact with the IL). An interesting observation is that the

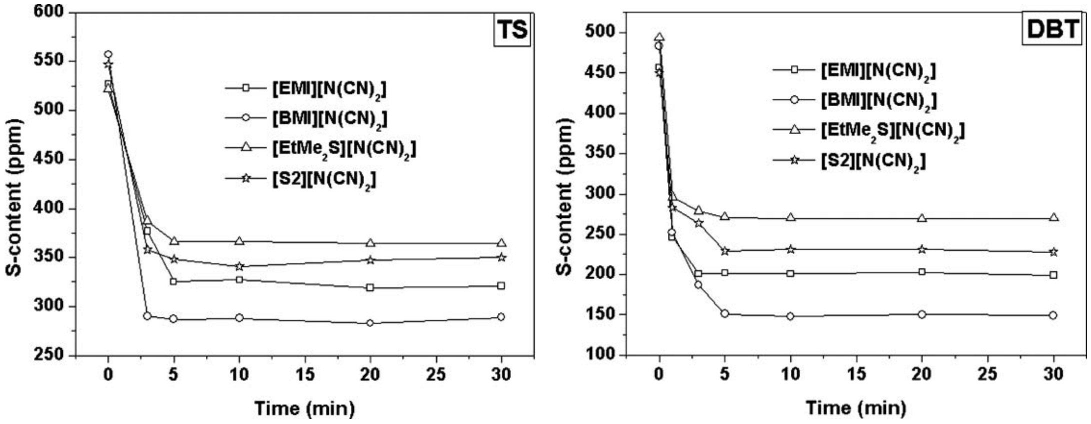

Fig. 2 S-content *vs.* extraction time in extracting TS from model gasoline and DBT from model diesel fuel by $[N(CN)_2]^-$-based ILs (temperature: 25 °C, 1 : 1 (w/w) IL : oil).

extraction equilibrium is almost reached after only ~3 min, with complete equilibrium being attained after 5 min in both model oils. Such a short equilibrium time is very necessary to generate a high production yield in industrial applications. The short extraction time in this study can be attributed to the low IL viscosities, which facilitate their better dispersion in the oils and the faster mass transfer of S-compounds from the oils to the ILs.

A clearer illustration for the S-removal performance of the ILs is given in Fig. 3 (where the extraction time is 20 min, which is more than sufficient to establish equilibrium). The ILs are more capable of effectively extracting DBT than TS, where the S-extraction efficiency for DBT is ~20% higher than that for TS. Similarly, the Nernst partition coefficients for DBT between the ILs and oil are higher than those for TS. The higher selectivity of DBT is also observed in other IL extraction systems, such as pyridinium- and imidazolium-based ILs,[17,19–22,31] and has been attributed to high polarity; molecules with a highly polarizable π-electron density tend to insert into the molecular structure of ILs. $[BMI][N(CN)_2]$ exhibits the highest S-extraction efficiency for both TS and DBT. The S-extraction ability follows the order $[BMI][N(CN)_2] > [EMI][N(CN)_2] > [S2][N(CN)_2] > [EtMe_2S][N(CN)_2]$; specifically, their S removal rate for TS/DBT after 20 min of contact are 49.2/68.9, 39.5/55.6, 36.6/51.2 and 30.3/45.5%, respectively. As a result of its optimal performance, $[BMI][N(CN)_2]$ was selected to undergo multiple experiments to determine the influence of the IL : oil mass ratio, extraction temperature, initial S-content, multiple extractions and regeneration on EDS performance, as well as its solubility in oils.

The S-extraction efficiency of other ILs is summarized in Tables 3 and 4, where comparison is made with other ILs relative to the extraction of both TS and DBT. Aromatic $[BMI][N(CN)_2]$ and $[EMI][N(CN)_2]$ displayed a better performance than $[S2][N(CN)_2]$ and $[EtMe_2S][N(CN)_2]$. Notably $[BMI][N(CN)_2]$ displayed the highest extractive performance. The Nernst partition coefficients depend, to some extent, on the IL : oil mass ratio, which suggests that this extraction in these ILs is not a completely ideal physically-determined extraction. Spectral analysis[25] and computer simulations[85] have preliminarily indicated that there is a strong π–π electronic or Lewis acid–base interaction between ILs and S-compounds.

$[BMI][N(CN)_2]$: oil mass ratio

Considering the high cost of ILs, it is preferable to use less ILs in any operation, including the desulfurization of fuel oil. Hence, this study investigated the effect of the IL : oil ratio on

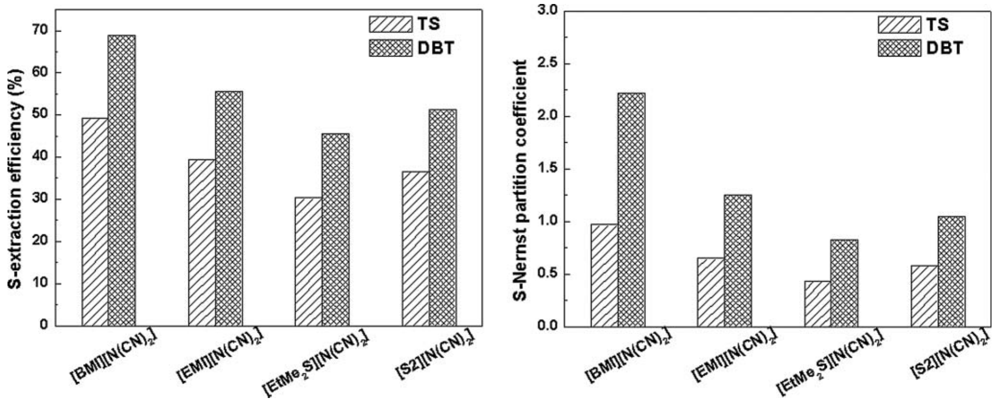

Fig. 3 The S-extraction efficiency of the ILs for TS from model gasoline and DBT from model diesel fuel (temperature: 25 °C; 1 : 1 (w/w) IL : oil, extraction time: 20 min) along with the S-Nernst partition coefficients in $mg_S\ kg_{IL}^{-1}/mg_S\ kg_{oil}^{-1}$.

Table 3 TS removal from model oils by IL extraction

IL	Model oil	T/K	Nernst partition coefficient/mg_S kg_{IL}^{-1}/mg_S kg_{oil}^{-1} IL : model oil 1 : 1	 1 : 3	 1 : 5	Ref.
[BMI][N(CN)$_2$]	n-Hexane, toluene	298	0.91	0.76	0.87	This work
[EMI][N(CN)$_2$]	n-Hexane, toluene	298	0.65			
[EtMe$_2$S][N(CN)$_2$]	n-Hexane, toluene	298	0.43			
[S2][N(CN)$_2$]	n-Hexane, toluene	298	0.6			
[EPy][NO$_3$]	n-Heptane, xylol	Room temperature	0.37	0.48		32
[EPy][AC]	n-Heptane, xylol	Room temperature	0.30	0.32		
[EPy][BF$_4$]	n-Heptane, xylol	Room temperature	0.22			
		323	0.28	0.29		
[BPy][BF$_4$]	n-Heptane, xylol	Room temperature	0.83	0.61		
[BPy][NO$_3$]	n-Heptane, xylol	Room temperature	0.43	0.31		
[BPy][AC]	n-Heptane, xylol	Room temperature	0.47	0.34		
[(CH$_2$)$_4$SO$_3$HMIm][Tos]	i-Octane	Room temperature	0.61			84
[HPy][BF$_4$]	n-Dodecane	Room temperature	0.70			31
[OPy][BF$_4$]	n-Dodecane	Room temperature	0.79			
[C$_4$^{3}MPy][BF$_4$]	n-Dodecane	Room temperature	0.85			83
[C$_6$^{3}MPy][BF$_4$]	n-Dodecane	Room temperature	1.00			
[C$_8$^{3}MPy][BF$_4$]	n-Dodecane	Room temperature	1.07			

Table 4 DBT removal from model oils by IL extraction

IL	Model oil	T/K	K_N/mg_S kg_{IL}^{-1}/mg_S kg_{oil}^{-1} IL : model oil 1 : 1	 1 : 3	 1 : 5	Ref.
[BMI][N(CN)$_2$]	n-Hexane	298	2.28	2.30	2.01	This work
[EMI][N(CN)$_2$]	n-Hexane	298	1.3			
[EtMe$_2$S][N(CN)$_2$]	n-Hexane	298	0.84			
[S2][N(CN)$_2$]	n-Hexane	298	1.08			
[(CH$_2$)$_4$SO$_3$HMIm][Tos]	n-Tetradecane	Room temperature	1.08		—	84
[BMI][PF$_6$]	n-Dodecane	333	—	—	0.68	29
[BMI][CF$_3$SO$_3$]	n-Dodecane	333	—	—	0.81	
[BMI][BF$_4$]	n-Dodecane	333	—	—	0.95	
[EMI][BF$_4$]	n-Dodecane	323	—	—	0.55	
[BPy][BF$_4$]	n-Dodecane	Room temperature	0.77	—	—	31
[HPy][BF$_4$]	n-Dodecane	Room temperature	1.42	—	—	
[OPy][BF$_4$]	n-Dodecane	Room temperature	1.79	—	—	
[BMI][BF$_4$]	n-Dodecane	Room temperature	0.7	—	—	14
[BMI][OcSO$_4$]	n-Dodecane	Room temperature	1.9	—	—	
[EMI][EtSO$_4$]	n-Dodecane	Room temperature	0.8	—	—	
[MMI][Me$_2$PO$_4$]	n-Dodecane	Room temperature	0.7	—	—	
[BMI][PF$_6$]	n-Dodecane	333	0.9	—	—	
[C$_4$^{3}MPy][BF$_4$]	n-Dodecane	Room temperature	2.08	—	—	83

S-extraction. The extraction ratios tested were 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5 (w/w) IL : oil. Each extraction process took place at 25 °C under atmospheric pressure for 20 min; the results are shown in Fig. 4. The mass ratio of IL : oil offers an important effect on the S-extraction efficiency of [BMI][N(CN)$_2$] both for TS and DBT. The S-extraction efficiency decreases with decreasing IL : oil mass ratio, *e.g.*, in the model gasoline at 2 : 1 (w/w) IL : oil, a 62.6% S-removal efficiency was realized, while 78.9% S-removal was realized in the model diesel. Yet still, even at 1 : 1 (w/w) IL : oil, there is a high S-removal efficiency of 47.5 and 69.5% for the respective S-compounds. Chu *et al.*[24] used a series of [BF$_4$]$^-$-based ILs to investigate the influence of mass ratio at a 20 min extraction time, but a lower S-extraction of less than 40% resulted from a 1 : 1 (w/w) IL : oil ratio. On other hand, the Nernst partition coefficients are not too sensitive to the mass ratio of IL : oil.

Extraction temperature

Five sets of parallel experiments at varying temperatures (20, 25, 35, 45 and 55 °C) were performed to investigate the effects of extraction temperature on S-extraction. The results are shown in Fig. 5, which clearly shows that [BMI][N(CN)$_2$] displays the highest efficiency at 20 °C. The temperature has an inverse

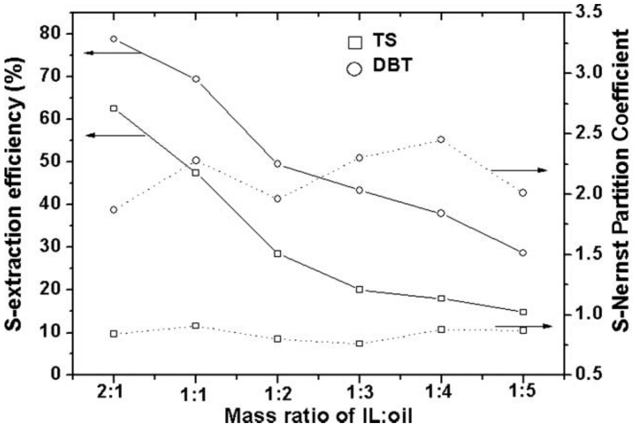

Fig. 4 The S-extraction efficiency of [BMI][N(CN)$_2$] for TS and DBT from model oils at different mass ratios of IL : oil (initial S-contents: 562 ppm in gasoline and 606 ppm in diesel fuel; temperature: 25 °C; extraction time: 20 min) along with the S-Nernst partition coefficients in mg$_S$ kg$_{IL}^{-1}$/mg$_S$ kg$_{oil}^{-1}$.

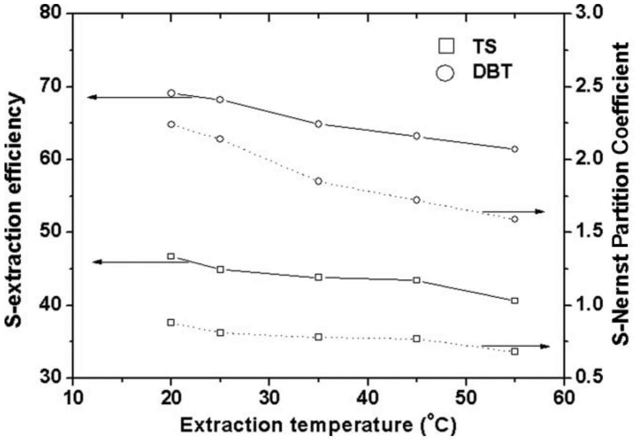

Fig. 5 The S-extraction efficiency of [BMI][N(CN)$_2$] for TS and DBT from model oils at different extraction temperatures (initial S-contents: 488 ppm in gasoline and 459 ppm in diesel fuel; mass ratio of IL : oil = 1 : 1; extraction time: 20 min) along with the S-Nernst partition coefficients in mg$_S$ kg$_{IL}^{-1}$/mg$_S$ kg$_{oil}^{-1}$.

relationship on the EDS performance of [BMI][N(CN)$_2$] for TS and DBT, *i.e.*, an increase in temperature leads to a decrease in S-extraction efficiency. The S-extraction efficiency is not too sensitive to extraction temperature, *e.g.*, the S-extraction efficiency for TS slightly decreases from 46.7% at 20 °C to 40.6% at 55 °C, a difference of only 6%; for DBT, the extraction difference is 7.7%. Such insensitivity to temperature can be understood due to the low viscosity of the ILs used in this study. Therefore, S-extraction can be performed at or below room temperature, which is favorable for less energy consumption. Similarly, the Nernst partition coefficients are also not sensitive to temperature.

Initial S-content in oil

We varied the initial S-content in both the model gasoline and model diesel fuel approximately as follows: 200, 500, 800, 1500 and 2000 ppm. Each extraction was performed at 25 °C, atmospheric pressure, for 20 min and with 1 : 1 (w/w) IL : oil. The result (Fig. 6) shows decreasing sulfur removal with increasing initial S content. Furthermore, the S-extraction efficiency is only slightly reduced, especially in the case of DBT, where the S-extraction efficiency is reduced from 70.9% (~200 ppm S-content) to 67.9% (~2000 ppm S-content). This insensitivity to S-extraction is valuable to industrially deal with oils with a wide range of S-contents; on the other hand, the initial S-content gives a slight effect on the Nernst partition coefficients. For other ILs, such as the CuCl-based ILs, the effect of the initial S-content on real gasoline was obvious; a difference of 21.2% S-extraction efficiency was reported from the 950–196 ppm S-content range.[16] Another paper has reported a rather opposite result for some BF$_4^-$-based ILs.[26] This implies that different desulfurization mechanisms exist for different ILs.

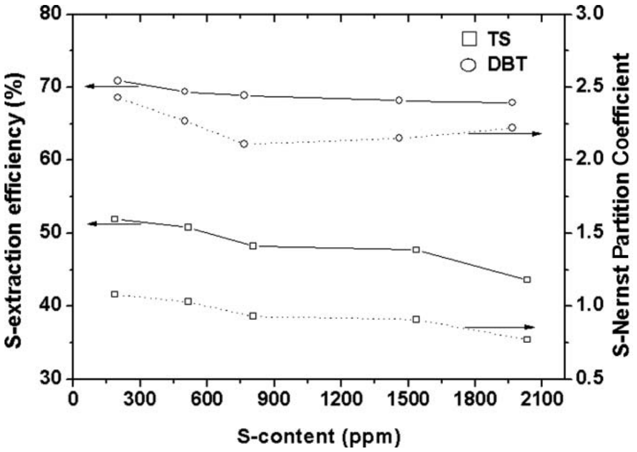

Fig. 6 The S-extraction efficiency of [BMI][N(CN)$_2$] for TS and DBT from model oils with different initial S-contents in the oils (temperature: 25 °C; mass ratio of IL : oil = 1 : 1; extraction time: 20 min) along with the S-Nernst partition coefficients in mg$_S$ kg$_{IL}^{-1}$/mg$_S$ kg$_{oil}^{-1}$.

Multiple extractions

In order to determine the best possible performance of [BMI][N(CN)$_2$], multiple extractions were performed at 25 °C, atmospheric pressure, 20 min extraction time and 1 : 1 (w/w) IL : oil. The results for TS and DBT are presented in Fig. 7 and

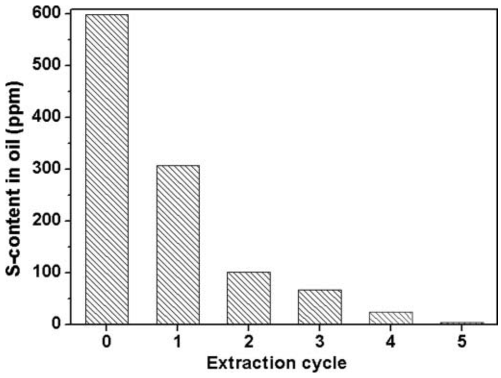

Fig. 7 The multiple extraction performance of [BMI][N(CN)$_2$] for model gasoline (temperature: 25 °C; 1 : 1(w/w) IL : oil; extraction time: 20 min).

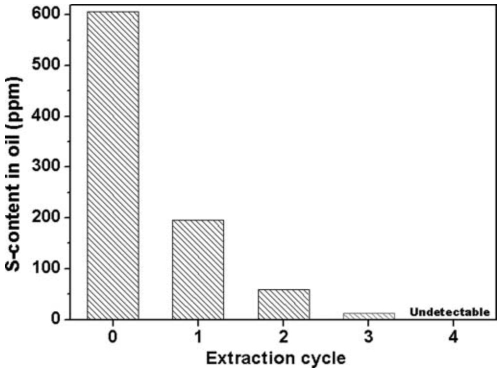

Fig. 8 The multiple extraction performance of [BMI][N(CN)$_2$] for model diesel fuel (temperature: 25 °C; 1 : 1(w/w) IL : oil; extraction time: 20 min).

Fig. 8, respectively. For TS in gasoline, after 5 cycles, the S-content in the gasoline remarkably dropped from 599 to 4 ppm (less than the current S-limit in fuel oils), an upsurge of almost 100% S-removal; for DBT in diesel fuel, after only 4 cycles, the initial S-content of 606 ppm was reduced to an undetectable value, and it is worth noting that the S-content was only 12 ppm after 3 cycles. Therefore, desulfurization by multiple extractions is an effective way to significantly reduce the S-content of fuel oils to a negligible amount.

Extractive performance after regeneration

Regeneration of the used [BMI][N(CN)$_2$] was performed by dilution with water because it is hydrophilic, while all the S-components are hydrophobic. This dilution process was followed by simple distillation. After regeneration, its original structure was unchanged. The S-extraction performance of the regenerated IL was investigated and the results are shown in Fig. 9, indicating an inconspicuous decrease in the S-extraction efficiency after 6 regeneration cycles, *e.g.*, the S-extraction efficiency decreases from 47.9 to 45.2% for TS and from 68.8 to 65.3% for DBT. This is a clear indication that [BMI][N(CN)$_2$] is favorable for industrial applications because of its cost-effective regeneration, good reusability and simple operating conditions.

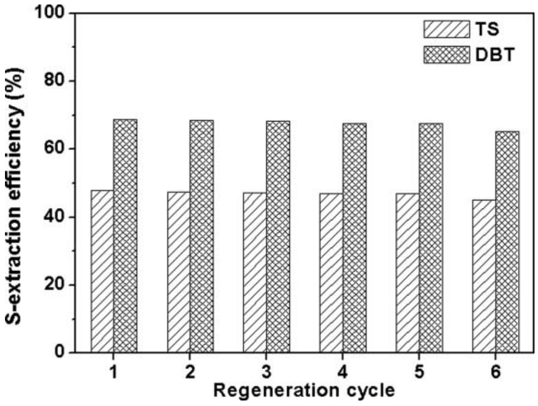

Fig. 9 The S-extraction efficiency *vs.* regeneration cycle for [BMI][N(CN)$_2$] (temperature: 25 °C; mass ratio of IL : oil = 1 : 1; extraction time: 20 min).

Mutual solubility

In selecting an extractant, it is important to consider its mutual solubility with fuel oils because the noticeable solubility of a nitrogen-bearing extractant, such as imidazolium-based ILs, in fuel oils may give rise to the loss of extractants and at the same time to contamination of the fuel oil. In the same token, a noticeable solubility of oils in extractants can also result in the loss of fuel oil and increased process costs. From our analysis, the solubility of [BMI][N(CN)$_2$] in the model oils is negligible; the miscibility of some other ILs in fuel oils such as dialkylphosphate and imidazolium ILs have been reported.[17,20,21] Fig. 10 shows the solubility result of the model oils with different toluene contents, which indicates that although the solubility of hexane in [BMI][N(CN)$_2$] is very minimal (only 0.9 wt% when the mass fraction of toluene in oil is 0%), the solubility of a mixture of hexane and toluene in [BMI][N(CN)$_2$] is observed (6.7 wt% which corresponds to a 20% mass fraction of toluene in oil). This suggests that the solubility of this low-viscosity IL in oils has to be optimized for future applications.

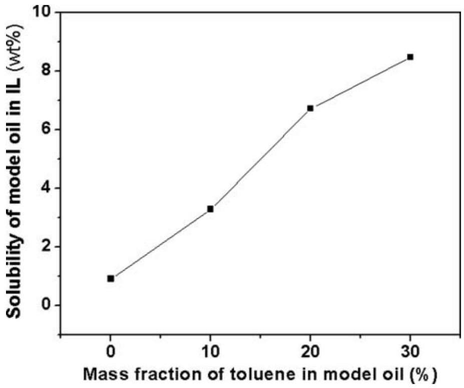

Fig. 10 The solubility of the model oil (hexane and toluene) in [BMI][N(CN)$_2$].

Conclusions

In this study, the extractive desulfurization performance of four low viscosity ILs based on the dicyanamide anion were studied. Interestingly, they presented much shorter extraction equilibrium times than other previously reported ILs, *i.e.*, less than 5 min for all the ILs at room temperature, which is important for generating a high production yield at the industrial level. Compared with cyclic thiophenium [S2][N(CN)$_2$] and tetrahedral trialkylsulfonium [EtMe$_2$S][N(CN)$_2$], the aromatic imidazoliums [BMI][N(CN)$_2$] and [EMI][N(CN)$_2$] were more efficient. For [BMI][N(CN)$_2$], the S-removal from gasoline and diesel fuel were 48.5 and 68.7%, respectively, in a single extraction at 25 °C, 1 : 1 (w/w) IL : oil, 5 min; negligible S-content could be obtained after 3–5 extraction cycles. The insensitivity of the extraction efficiency to temperature and initial S-content, along with easy regeneration and good reusability, are also useful in industrial applications. This work may provide a new option for the deep desulfurization of fuel oils.

Experimental

Preparation and characterization of ILs

The ILs used in this study were synthesized by a two-step synthetic route based on previous literature.[70–73] They were identified by FT-IR (NEXUS8700, Thermo Electron) and ^{1}H NMR (AV600, Bruker) spectra. The spectra and data analyses are contained in the ESI.†

Extractive desulfurization

Composition of model oils. The model gasoline was composed of hexane (~85 wt%), toluene (~15 wt%) and droplets of TS. The model diesel oil was composed of hexane and DBT. In both cases, the initial S-concentration was around 500 ppmw (elemental S/oil).

Extractive desulfurization. In the general procedure, the IL and model oil were placed in a 50 ml round-bottomed flask and then magnetically stirred at a given temperature. After a fixed time, the mixture took ~5 min for phase splitting and settling, followed by a subsequent analysis of the upper oil phase by a liquid chromatograph.

S-content analysis. A high performance liquid chromatograph (HPLC) was used to analyze the S-content in the model oils before and after each desulfurization. The analysis was performed on an LC-100 (WUFENG, Shanghai) liquid chromatograph equipped with a reversed phase UltimateTM XB-C18 column (4.6 mm × 150 mm; 3.6 µm) and a UV detector. The external standard method was used to determine the S-content of samples at 230 nm for TS and 280 nm for DBT. The mobile phase for the quantification of TS was 65% methanol in water (v/v, %) with a flow rate of 0.9 ml min^{-1}, and for DBT the mobile phase was 90% methanol in water (v/v, %) with a flow rate of 1.0 ml min^{-1}. The S-content in the model oils was measured in triplicate for each sample to ensure precision and accuracy.

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