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Fuel oil desulfurization with dual functionalized imidazolium based ionic liquids

Hussain Shakeel Butt[1], Kallidanthiyil Chellappan Lethesh*,[1], Anne Fiksdahl*

Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway

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ABSTRACT

A series of 36 dual functionalized *N*-(poly)ethylen glycol *N*-allyl-/N-benzyl imidazolium and benzimidazolium ILs were synthesized for extractive desulfurization studies (EDS). The novel ILs were readily prepared from imidazole by a three-step dialkylation and anion exchange procedure and characterised (^{1}H, ^{13}C, ^{19}F NMR; IR; HRMS positive/negative mode). The desulfurization studies were performed on a model oil with dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in *n*-dodecane. The *N*-allyl benzimidazolium based ILs exhibited higher extraction efficiency than corresponding imidazolium-based ILs (69 vs 59% DBT; 52 vs 29% 4,6-DMDBT). The EDS efficiency of the prepared ILs varied with the *N*-ethylen glycol chains length and by *N*-allyl or *N*-benzyl substitution on the imidazolium ILs. The results indicated that desulfurization efficiency is mainly affected by variation of the IL cation, as the IL anions (NTf_2; $N(CN)_2^-$, SCN^-, BF_4^-) only had minor impact on the extraction capacity of sulfur compounds.

^{1}H NMR studies of IL-DBT solutions illustrated different EDS mechanisms, and specific interactions could explain the higher desulfurization capacity of dual functionalized benzimidazolium than the corresponding imidazolium ILs. ^{1}H NMR confirmed that stronger π-π interactions between the planar aromatic electron system of benzimidazolium ILs and aromatic dibenzothiophenes play a major role for the high EDS extraction efficiency.

1. Introduction

The presence of sulfur compounds in fossil fuels (gasoline, diesel and kerosene) is a major challenge for petroleum refineries. One of the main contributors to air pollution is the formation of sulfur oxides (SO_X) and nitrogen oxides (NO_X) gases, derived from their respective sulfurated- and nitrogenated compounds upon combustion in automobiles. The SO_X and NO_X compounds can lead to health problems and environmental issues such as acid rain. Hence, regulatory authorities impose stringent regulations on the maximum level of sulfur content in transport fuels [1–4].

The most common industrial method for removal of sulfur compounds from transport fuel is hydrodesulfurization (HDS), where desulfurization is achieved by catalytic conversion of sulfur compounds to H_2S, using expensive catalysts in a trickle bed reactor. The H_2S is converted to elemental sulfur by the Claus process [5,6]. HDS is successful for removal of sulfides, disulfides and thiols, but suffers from various drawbacks, including harsh operating conditions, such as high temperature (300–400 °C) and high pressure (20–100 atm of H_2). Most importantly, HDS is not effective for removal of heterocyclic sulfur compounds, as the harsh conditions and expensive catalysts required for hydrodesulfurization of heterocyclic thiophene, dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) compounds severely affect the economic feasibility of the HDS process [7].

Although other processes for desulfurization of fuel oils, such as oxidative desulfurization (ODS), biodesulfurization (BDS) and extractive desulfurization (EDS), have been explored, these methods suffer from several disadvantages. ODS has resulted in high desulfurization efficiency, but long extraction time, high cost and regeneration of the catalyst are still to be addressed [8,9], while the lack of an efficient biocatalyst has prevented the commercialization of the BDS method [10,11]. The EDS process requires high solvent-to-fuel-oil ratio, and the lack of environmentally friendly extracting solvent systems has limited the development of the EDS method [12–14]. Although organic solvents are suitable extraction media in EDS, the high volatility, the poor selectivity towards sulfur compounds as well as their high toxicity, are severe drawbacks [15]. Hence, development of efficient extraction solvents which are more environmentally friendly (non-volatile, non-toxic and readily biodegradable) is needed.

Ionic liquids (ILs) have recently been employed in EDS

* Corresponding authors.
E-mail address: anne.fiksdahl@ntnu.no (A. Fiksdahl).
[1] Both authors contributed equally.

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desulfurization [1,16–21]. ILs are organic salt with melting point below 100 °C. Owing to their negligible vapour pressure, high thermal stability, recyclability and high affinity towards sulfur, ILs represent a group of promising extracting solvents than conventional organic solvents in EDS [1,20] and other extraction processes [22–25]. Promising EDS results are reported for nitrate based imidazolium ILs (e.g. [C_8mim][NO_3]) [26]. However, nitrate ILs are unsuitable, due to their explosive and toxic nature [26,27]. High desulfurization efficiency of DBT from fuel oil was also obtained by imidazolium ILs with chloride and [$FeCl_3$] anions [28], but IL metal halide anions increase the toxicity against marine organisms [29]. Ultrasound assisted desulfurization of fuel oil with trihexyl(tetradecyl)phosphonium tetrafluoroborate ([THTDP][BF_4]) afforded 93% sulfur removal efficiency in a single step [30]. Nonetheless, fluoride containing anions, such as BF_4, have ecotoxicological issues due to the tendency to form hydrogen fluoride in the presence of moisture [31].

Considering environmental problems upon waste disposal, in order to implement EDS in industrial scale, non-toxic and biodegradable ILs with high sulfur desulfurization efficiency is required. Relatively non-toxic and biodegradable ILs for EDS are obtained by introducing an ester moiety [20], but the extraction efficiency was not very high (< 80%). Another approach to reduce the toxicity and increase the biodegradability of ILs has been to attach *N*-polyethylene glycol (PEG) groups to the IL cationic core. High desulfurization efficiency was obtained with three PEG units [32,33].

Hence, promising parameters for design of efficient and environmentally friendly IL solvents for extractive desulfurization (EDS) made us select imidazolium based ILs, due to low toxicity, biodegradability [34] and the possibility of attaching two functional groups. The ability of the imidazolium moiety to form π-π interactions with aromatic sulfur compounds is important, as such factors are known to play an important role in desulfurization [35]. Fused planar benzimidazolium-based ILs with enhanced π-electron delocalization, were also included in the study, as increased π-π interactions between benzimidazolium ILs and sulfur compounds may be expected to increase desulfurization efficiency. The target dual functionalized imidazolium ILs were carrying *N*-benzyl or *N*-allyl groups, to observe whether such groups may partially contribute to π-π interactions. The effect of *N*-polyethylene glycol (PEG) groups was also studied, as the electronegative ether oxygen atoms may increase the electrostatic n-π interactions between ILs and sulfur compounds [19].

Based on this strategy, the present study focused on preparation of new dual functionalized (benz)imidazolium based ILs, with *N*-(poly) ethylene glycol and *N*-allyl or *N*-benzyl groups, for extractive desulfurization (EDS) of aromatic DBT and 4,6-DMDBTsulfur compounds.

2. Experimental

2.1. General methods

All commercially available chemicals were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400 MHz spectrometer or a Bruker Advance III 600 MHz spectrometer. Chemical shifts (δ) are given in parts per million (ppm) and the shifts are assigned with respect to tetramethylsilane (TMS). Coupling constants are given in Hertz. The multiplicities are assigned as singlet (s), doublet (d), triplet (t), multiplet (m) or a combination of these. IL water content were measured with a Coulometric Karl Fischer titrator (Mettler Toledo, DL39). Infrared spectroscopy (IR) was performed with a Nicolet 20SXC FTIR spectrometer using EZ OMNIC software and a Bruker Alpha FTIR spectrometer using OPUS V7 software. Accurate mass determination (HRMS) in positive and negative mode was performed on a "Synapt G2-S" Q-TOF instrument from Water TM. Samples were ionized using ASAP probe (APCI) or ESI probe. No chromatographic separation was used before the mass analysis. Calculated exact mass and spectra processing was done by Waters TM Software Masslynx V4.1 SCN871. High Performance Liquid Chromatography (HPLC) was performed using Agilent 1260 TCC with autosampler and a 1260 Diode Array Detector (DAD). A Zorbax Eclipse XDB-C18 4.6 × 150 mm reverse phase column was used.

2.2. Extractive desulfurization procedure

A model oil (MO) with sulfur compounds was prepared by dissolving dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in *n*-dodecane (500 ppm concentration of each compound). Solutions of fixed IL:MO ratio (1:1, 2:1, 3:1, 4:1, 5:1) were vigorously stirred in a glass vial(5 mL) using a reaction block (STEM, Thermo scientific, PS80067A) at the desired temperature. The temperature uncertainty was (± 0.1 °C) for each experiment. The extraction experiments were conducted at different temperatures by varied extraction time. After completion, the biphasic mixture was allowed to settle for 15 min to generate a two-phase solution. The model oil top layer was removed with a syringe and subjected to sulfur quantification by HPLC by an external standard method based on the relevant DBT and 4,6-DMDBT compounds. A methanol / isopropanol / water eluent system (90:2:8 V/V) was used as mobile phase (flow rate1 mL/min). The model oil was analysed by HPLC before and after extraction, and the desulfurization efficiency (R) was calculated from Eq. (1), based on the respective DBT and 4,6-DMDBT peak areas (retention times; $t_{R\text{-}DBT}$: 3.19 min and $t_{R\text{-}4,6\text{-}DMDBT}$: 5.39 min; detector wave length 310 nm).

$$R = \frac{Ci - Cf}{Ci} \times 100 \quad (1)$$

R: percentage sulfur removal; C_i: initial/C_f : final concentrations of sulfur in model oil (MO).

3. Results and discussion

3.1. Synthesis of ionic liquids

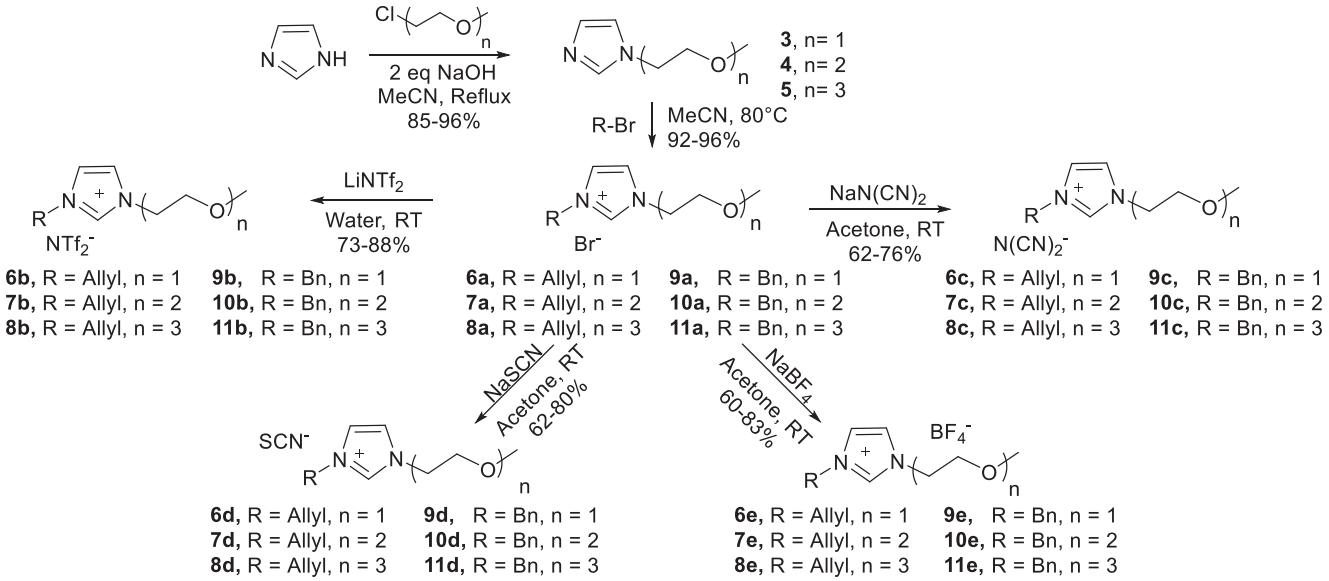
A series of 24 dual functionalized imidazolium ILs (**6b-11e**) with *N*-(poly)ethylene glycol (n = 1–3) and *N*-allyl or benzyl groups were synthesized in a three-step procedure from imidazole and appropriate organohalides followed by final anion exchange (Scheme 1) [36–40]. The initial *N*-oxyethylene imidazoles **3–5** (85–96% yield) were prepared by *N*-alkylation of imidazole in acetonitrile at 80 °C with sodium hydroxide and the respective 1-Cl-2-alkoxyethanes [41]. The allyl and benzyl groups were introduced by a quaternization reaction of the *N*-oxyethylene imidazoles (**3–5**) with allyl bromide and benzyl bromide, affording imidazolium bromides (92–96%; **6a, 7a, 8a, 9a, 10a** and **11a**). The target IL products (**6b-11b, 6c-11c, 6d-11d, 6e-11e**) were obtained (60–88%) by anion exchange of the bromide salts (**6a-11a**) with the desired NTf_2^-, $N(CN)_2^-$, SCN^-or BF_4^- counter-anions by treatment with the respective metal salts ($LiNTf_2$, $NaN(CN)_2$, NaSCN, $NaBF_4$) in acetone or water.

Furthermore,12 dual functionalized *N*-allyl-benzimidazolium ILs (**15b-17e**) with varying *N*-PEG ether chain length (n = 1–3) and NTf_2^-, $N(CN)_2^-$, SCN^- or BF_4^- counter-anions, were synthesized by a similar procedure (Scheme 2). All the novel synthesized dual functionalized ILs **6–11** and **15–17** were characterised by ^{1}H, ^{13}C, ^{19}F NMR and IR. HRMS analyses in positive and negative mode confirmed the respective cation and anion IL structures.

3.2. Desulfurization of model oil with dual functionalized imidazolium based ILs

3.2.1. Effect of the anion

Desulfurization studies with *N*-allyl-*N*-ethylene glycol-imidazolium ILs **6b-8e** (Table 1a) showed that the DBT removal efficiency (up to 59%, entry 10) decreased in the following order of anion: $N(CN)_2$ > NTf_2 > SCN > BF_4, as shown for ILs **8c** > **8b** > **8d** >



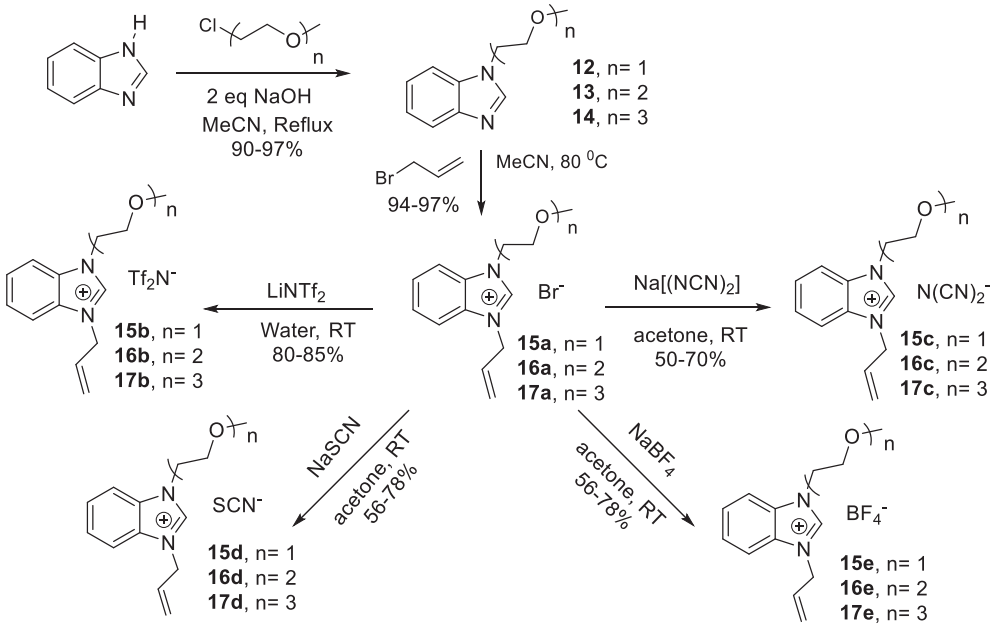
Scheme 1. . Synthesis of dual functionalized imidazolium based ILs (**6b-11e**) with varied *N*-ethylene glycol chain length (n = 1–3) and *N*-allyl or *N*-benzyl groups.

8e (59% – 50% – 44% – 40%). Earlier studies report that the NTf_2 anion based ILs were more efficient compared to other anions [1]; and oppositely, that NTf_2 anion of butylpyridinium and imidazolium ILs were less efficient than $N(CN)_2$based ILs [42]. The extraction ability of 4,6-DMDBTwas significantly lower than DBT, in accordance with previous studies [43], as demonstrated for e.g. IL **6c** (40% of DBT vs 14% 4,6-DMDBT, entry 2). The low extraction efficiency of the sterically hindered di-methylated 4,6-DMDBT may be due to the restricted interaction between the IL and the less accessible sulfur [44]. In contrast to the highest DBT extraction efficiency obtained with $N(CN)_2$ based ILs (entries 2, 6, 10), the NTf_2based ILs were most efficient for removal of 4,6-DMDBT (entries 1, 5, 9), and the order of 4,6-DMDBT removal was NTf_2 > $N(CN)_2$ > SCN > BF_4. The different extraction efficiency may be explained by hydrophobic nature of NTf_2 anion based ILs [7] which may interact stronger with the hydrophobic 4,6-DMDBT than DBT.

From these results it is evident that the IL anion has only small impact on the removal of sulfur compounds. Hence, it seems that desulfurization efficiency is mainly affected by the IL cation.

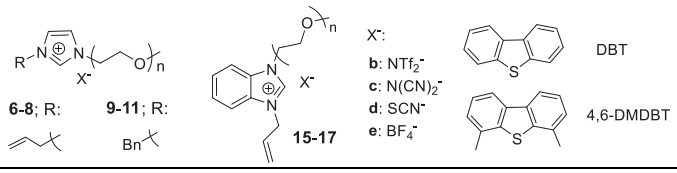
3.2.2. *Effect of the cation*

Investigations of the contribution of the imidazolium IL **6b-8e** cation on EDS efficiency showed that longer ether chain length increased the extraction efficiency (Table 1a),according to studies on pyridinium based protic ILs [45].This effect is illustrated by the most efficient N $(CN)_2$ based *N*-allyl-*N*-glycolethyl-imidazolium ILs **6c**, **7c** and **8c** with increasing *N*-ether chain length (n = 1–2-3; 45–53–59%; entries 2, 6, 10). These observations have been explained by the fact that increased *N*-alkoxy ether chain length decreases IL viscosity, thereby increasing the mass-transport [37]. Consequently, longer IL *N*-alkoxy chains enhances the sulfur extraction efficiency, in accordance with reports on polyether-based ammonium ILs [46].The electrostatic interactions (n-π) between the IL *N*-ether oxygen atoms and the aromatic sulfur compounds in fuel oil would also contribute to the desulfurization



Scheme 2. . Synthesis of *N*-allyl-benzimidazolium based dual functionalized ILs (**15b-17e**) with varied *N*-ethylene glycol chain length (n = 1–3).

Table 1
Desulfurization studies of model oil (MO) with a) *N*-allyl-*N*-PEG-imidazolium ILs **6b-8e**, b) *N*-benzyl-*N*-PEG-imidazolium ILs **9b-11e** and c) *N*-allyl-*N*-PEG-benzimidazolium ILs **15b-17e** (n = 1–3).[a]



Entry	n:	a) **6b-8e** Extraction efficiency (%)			b) **9b-11e** Extraction efficiency (%)			c) **15b-17e** Extraction efficiency (%)		
		IL	DBT	4,6-DMDBT	IL	DBT	4,6-DMDBT	IL	DBT	4,6-DMDBT
1		**6b**	40	19	**9b**	48	26	**15b**	69	51
2	1	**6c**	45	14	**9c**	44	15	**15c**	b)	b)
3		**6d**	40	12	**9d**	12	5	**15d**	b)	b)
4		**6e**	27	8	**9e**	36	18	**15e**	b)	b)
5		**7b**	49	28	**10b**	50	29	**16b**	68	52
6	2	**7c**	53	19	**10c**	50	26	**16c**	60	39
7		**7d**	40	13	**10d**	44	22	**16d**	46	18
8		**7e**	39	14	**10e**	40	20	**16e**	57	32
9		**8b**	50	26	**11b**	55	29	**17b**	56	52
10	3	**8c**	59	24	**11c**	56	24	**17c**	46	41
11		**8d**	44	14	**11d**	40	19	**17d**	35	30
12		**8e**	40	12	**11e**	47	19	**17e**	37	32

[a] Desulfurization conditions; model oil (MO): DBT and 4,6-DMDBT (500 ppm of each) in *n*-dodecane; 25 °C, extraction time: 2 h, IL:MO mass ratio 1:1.
[b] nd: not determined because IL was solid at room temperature.

performance, in accordance with observations in earlier studies [32,47].Higher extraction efficiency of 4,6-DMDBT by increased *N*-ether chain length was only seen for $N(CN)_2$ILs (**6c**, **7c** and **8c**) (n = 1-2-3; 14 – 19 – 24%). In general, the cationic *N*-ether chain length had mixed influence of extraction of 4,6-DMDBT.

3.3. Desulfurization studies with benzyl-imidazolium and benzimidazolium ILs

π-π Interactions between aromatic sulfur compounds and aromatic ILs play a major role for the EDS extraction efficiency. As such interactions between heterocyclic compounds can be increased by introduction of aromatic structure moieties in imidazolium ILs [48], the *N*-benzyl-imidazolium ILs **9–11** and the benzimidazolium ILs **15–17** with *N*-ether chain length (n = 1-2-3) were synthesized (Schemes 1 and 2) in order to study the effect of π-π interactions on desulfurization efficiency (Table 1b,c).

The EDS efficiency of *N*-benzyl-imidazolium ILs **9–11** was mainly comparable to the results for the *N*-allyl-based ILs (**6–8,** Table 1a), and they also followed the same trends as discussed above. Thus, the highest DBT desulfurization efficiency (up to 56%) was obtained for *N*-benzyl-imidazolium IL*s* with NTf_2 and $N(CN)_2$ anions (Table 1b, entries 1,5,6,9,10). The highest efficiency for extraction of DBT was obtained with *N*-benzyl-*N*-triethylene glycol ether ILs **11c** with $N(CN)_2$ anion (56%), similar to *N*-allyl IL **8c** (59%) above (entry 10).

The high viscosity of the [SCN] based *N*-monoether IL **9d** (entry 3) dropped by increased ether chain (n = 2), and the lower viscosity explains the significant increased capacity for removal of 4,6-DMDBT (5% to 22%) and DBT (12% to 44%) with *N*-diether IL **10d** (entry 7).The slightly higher EDS efficiency for removal of 4,6-DMDBT with *N*-benzyl-imidazolium ILs (**9–11**, Table 1b) than the corresponding *N*-allylic ILs (**6–8,** Table 1a) might be explained by increased hydrophobicity of *N*-benzyl IL*s*. As more efficient IL dispersion in the oil phase is facilitated, π-π interactions between the ILs and the more hydrophobic 4,6-DMDBT (compared to DBT) becomes stronger. In addition, the aromatic *N*-benzyl group would contribute by π-π interactions, as reported by Yu *et al.* by benzyl-based IL [49].

Earlier studies suggest that benzofused aromatic IL cations afford increased π-π interactions with heterocyclic compounds due to the larger planar aromatic π electron systems [48]. The present EDS study confirmed that dual functionalized benzimidazolium based IL*s* **15–17** had higher desulfurization capacity than corresponding imidazolium IL*s* **6–11**. The NTf_2 and $N(CN)_2$based benzimidazolium ILs (Table 1c, entries 1,5,6,9,10) were the most efficient EDS solvents, similar to corresponding imidazolium based IL*s* above (Table 1a). Compounds **15c-15e** are solids at room temperature and were not used for desulfurization studies. It is evident that the anion has significant impact on viscosity of IL*s* with *N*-diether groups, and thereby on EDS efficiency, as shown for the low-viscous $N(CN)_2$ based IL **16c** (DBT 60% and 4,6-DMDBT 39%, entry 6) dropping to 46% and 18%, respectively, with the high-viscosity SCN based IL **16d** (entry 7).

However, increased number of benzimidazolium *N*-ether groups seems to have a negative effect on DBT desulfurization efficiency, as seen for **16b-e** (n = 2, 46–68%, entries 5–8)) *versus* **17b-e** (n = 3, 35–56%, entries 9–12). In contrast, extraction of 4,6-DMDBT was not significantly affected by increased ether chain length (entries 5–12), which might be due to steric hindrance of the sulfur atom by the methyl groups.

The considerably higher desulfurization efficiency obtained with benzimidazolium-based ILs (**15–17**) than the corresponding *N*-benzyl imidazolium-based ILs (**9–11**) might be due to the enhanced delocalized aromatic π-electron system, which increases intermolecular π-π interactions. The more flexible phenyl moiety of the benzyl group may rotate freely around CH_2 and would not be in the same plane as the imidazolium core. Hence, the benzyl group would only partially contribute with π-π interactions in EDS. In contrast, in the condensed heterocyclic benzimidazole, the phenyl ring and an imidazolium core are forced into a planar fused aromatic system, which gives stronger π-π interactions between the ILs and the aromatic dibenzothiophene compounds. These effects were further studied by ^{1}H NMR (see below).

The most efficient ILs in this study for extractive desulfurization of DBT and 4,6-DMDBT was obtained in a single extraction step with *N*-allyl-benzimidazolium *N*-mono-ether **15b** and *N*-di-ether **16b** NTf_2 ILs. EDS performance for extraction of DBT (68–69%) with imidazolium ILs

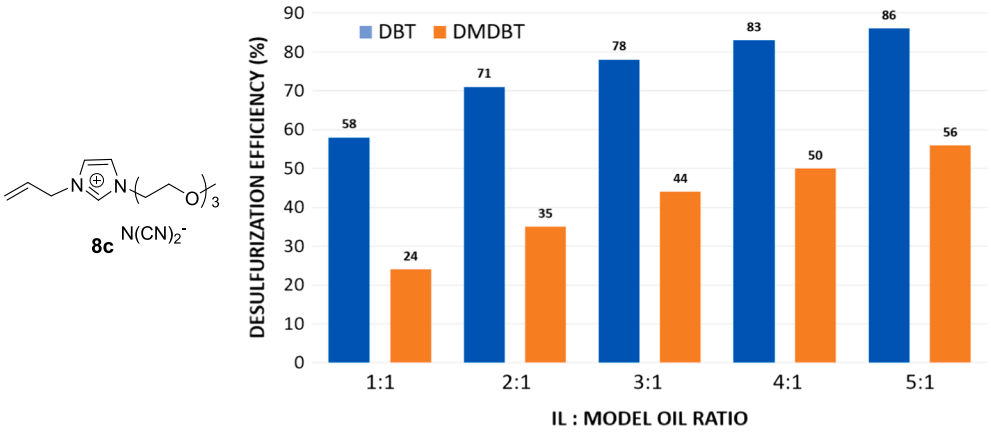


Fig. 1. The effect of IL:MO mass ratio on DBT and 4,6-DMDBT desulfurization efficiency with IL **8c**. (Experimental conditions: Temperature: 25 °C, extraction time: 2 h).

15b and **16b** were comparable to previous reports for *N*-ether and *N*-ester functionalized imidazolium ILs (73–80% of DBT) [1,20], while ILs **15b** and **16b** had extraordinary extraction capacity for the sterically hindered 4,6-DMDBT (52%), which was much higher than previous IL reports (< 20%) [1,20].

3.4. Optimization of desulfurization conditions

EDS studies of ILs **6–8** (Table 1a) showed that highest DBT and 4,6-DMDBT efficiencies were obtained with *N*-triethylene glycol ether ILs **8b** and **8c** with NTf_2 and $N(CN)_2$ anions. Taking the toxicity of the NTf_2 anion into account, further optimization studies focussed on the N $(CN)_2$based IL (**8c**). The parameters such as (a) IL:MO mass ratio, (b) extraction time and (c) extraction temperature were studied.

3.4.1. Effect of IL:MO mass ratio

The IL:MO mass ratio is an important parameter in determining the potential of ILs in EDS. In order to compensate the high cost of ILs, a low IL:MO mass ratio is preferred. The effect of the IL:MO mass ratio on the extraction capacity of DBT and 4,6-DMDBT with IL **8c** was studied (Fig. 1) and showed that an increase in the extraction efficiency of DBT and 4,6-DMDBT was obtained by increased ILs: MO mass ratio (IL:MO 1:1 < 2:1 < 3:1 < 4:1 / 5:1; DBT 59-71-79-83-85% and 4,6-DMDBT 24-35-44-50-56%). Larger relative increase in efficiency was seen for 4,6-DMDBT (40%) than for DBT (20%) by going from IL:MO 1:1 to 2:1, probably caused by increased IL hydrophobic interactions with the 4,6-DMDBT methyl groups. By higher IL:MO mass ratios, smaller efficiency improvements were seen, in agreement with earlier reports [13,50,51]. In order to keep the EDS economically viable, 2:1 IL:MO mass ratio (EDS efficiency: DBT71% /2,6-DMDBT 35%) was chosen for further optimization studies.

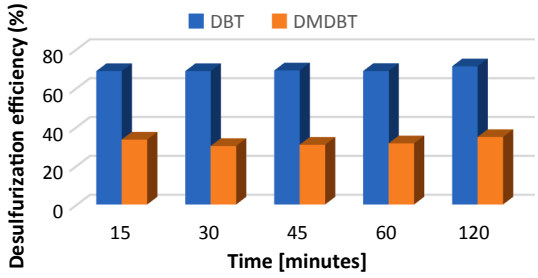


Fig. 2. The effect of extraction time on DBT and 4,6-DMDBT desulfurization efficiency with IL **8c.** (Experimental conditions: Temperature: 25 °C, IL: MO mass ratio: 2:1).

3.4.2. Effect of extraction time

The effect of extraction time for removal of DBT and 4,6-DMDBT with IL **8c** (Fig. 2) was studied. Based on introductory experiments, increased extraction time (from 15 to 60 min) was studied and was shown to have no effect on the DBT extraction efficiency, which remained at 69%. Hence, the thermodynamic equilibrium between the IL and DBT seems to be attained within 15 min. The fast extractions may be caused by several kind of interactions of the imidazolium IL dual functional groups with the aromatic sulfur compounds, such as π-π interactions and n-π interactions of dibenzothiophenes and ether oxygens. Even if the extracted amount of 4,6-DMDBT increased more (33%) after 15 min, the sulfur removal capacity seems to be stabilized within 15 min, which may be used as a suitable extraction time.

3.4.3. Effect of temperature

The effect of the temperature on desulfurization efficiency of DBT and 4,6-DMDBT was studied (Fig. 3) and showed that increased temperature (25-40-60-90 °C) had no significant influence on the extraction capacity of DBT (69–63%) or 4,6-DMDBT (28–27%). This might be because the temperature has minor influence on the interaction between the ILs and sulphur components in the model oil. In other words, poor partitioning of sulphur components takes place in ILs phase after the optimum temperature of 25 °C. Similar results have been reported [52]. The results indicate that the maximum extraction efficiency was reached at 25 °C, which represents the optimum temperature.

3.4.4. Recyclability of ILs

In addition to high extraction efficiency, the IL recyclability is an important aspect of potential extraction media. To be economical and environmentally friendly, the IL desulfurization capacity should be consistent through several cycles. To explore this property, the recyclability of the IL **8c** was conducted at optimized extraction conditions

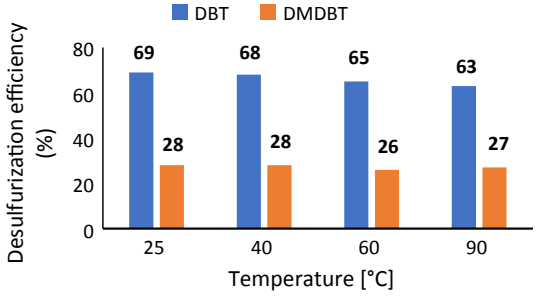


Fig. 3. The effect of temperature on DBT and 4,6-DMDBT desulfurization efficiency with IL **8c**. (Experimental conditions: Extraction time: 15 min, IL:MO mass ratio: 2:1).

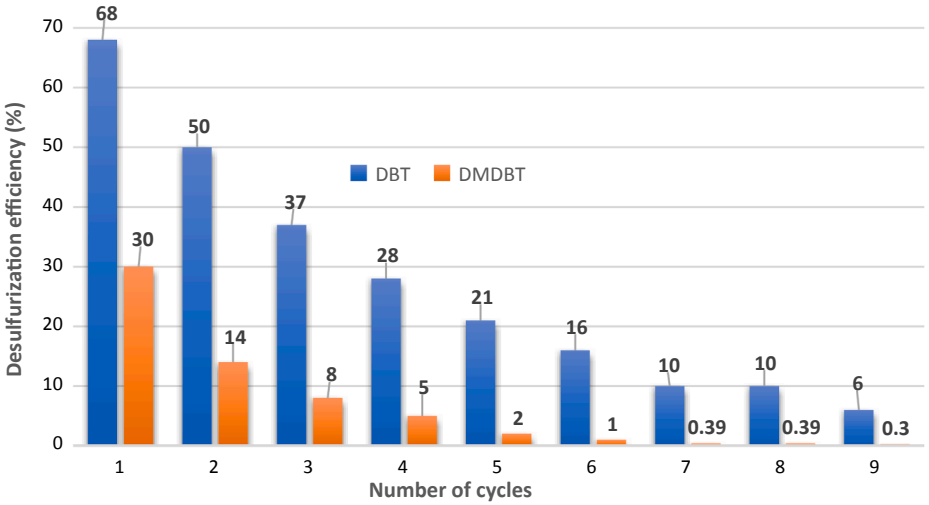


Fig. 4. Recyclability studies of IL **8c** by repeated EDS (Experimental conditions; DBT and 4,6-DMDBT; 500 ppm of each, in *n*-dodecane; temperature: 25 °C; IL: extraction time: 15 min; IL:MO mass ratio: 2:1).

(Fig. 4). The recyclability study showed a significant reduction (68% – 50% – 21%) of IL extraction capacity of DBT from the first extraction to the second and the fifth cycle, respectively, and the efficiency was drastically reduced (to 6%) in the final ninth extraction. The large efficiency drop by recycling, may be due to rapid saturation of IL active sites, hence preventing remaining DBT molecules from IL interacting, in accordance with previous studies [53,54]. Another possible explanation is the clathrates formation in ILs. It has been reported that the ILs with long alkyl or ether groups has the potential to form clathrates [55–57], which can accommodate guest molecules. After the first few extraction cycles, the clathrates formed in the ILs were completely occupied by the sulphur molecules and blocked the trapping of DBT/DMDBT, which resulted in drastic reduction of the extraction efficiency of the ILs. The extraction efficiency of 4,6-DMDBT dropped even more by IL recycling, and the extraction was negligible at the ninth cycle.

3.5. ^{1}H NMR study

In order to get a better understanding of the IL extraction mechanism, comparative ^{1}H NMR studies were performed on solutions of DBT with *N*-allyl imidazolium **8c** or *N*-allylbenzimidazolium **15b** ILs (Figs. 5 and 6).^{1}H NMR would readily demonstrate specific DBT-IL interactions appearing by EDS.

To identify selective effects contributing to extraction of aromatic thio-compounds, mixtures of IL **8c** and DBT (mass ratios 1:1 and 1:3) were analysed by ^{1}H NMR and compared with ^{1}H NMR of pure IL and DBT (Fig. 5),

All the IL **8c** protons (H*a*-H*j*, Fig. 5d), and in particular imidazolium protons H*b* and H*c*, experienced an upfield shift by increased concentration of DBT (Figure c,b). The shielding effect on IL allyl protons (H*d-f*) decreased as the spatial distance between the protons and the imidazolium unit increased (H*f* > H*d* > H*e*). Similar upfield shifts

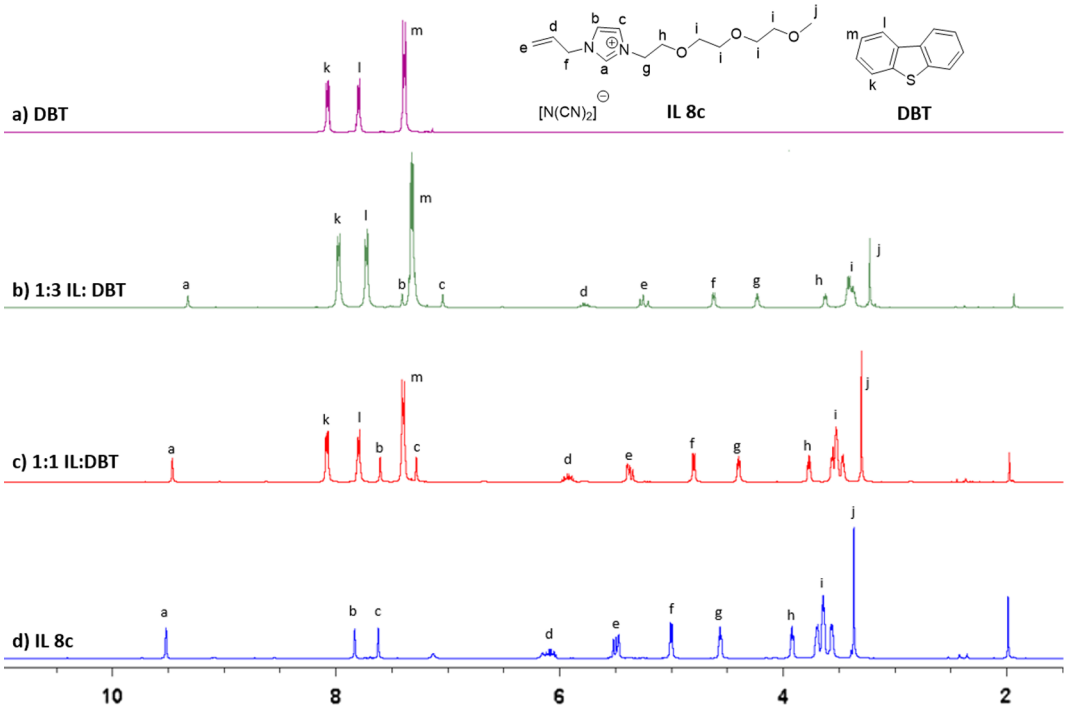


Fig. 5. ^{1}H NMR studies of DBT and IL **8c** interactions. (a) DBT. IL: DBT ratios: (b) 1:3; (c) 1:1. (d) IL **8c**.

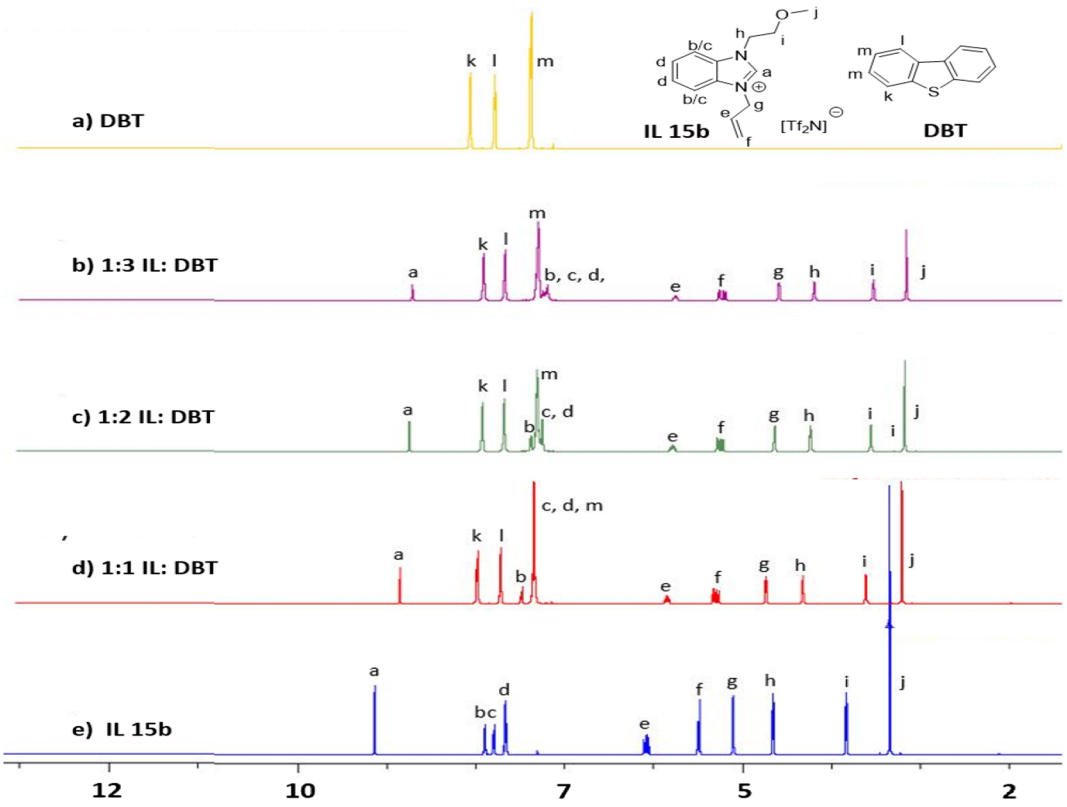
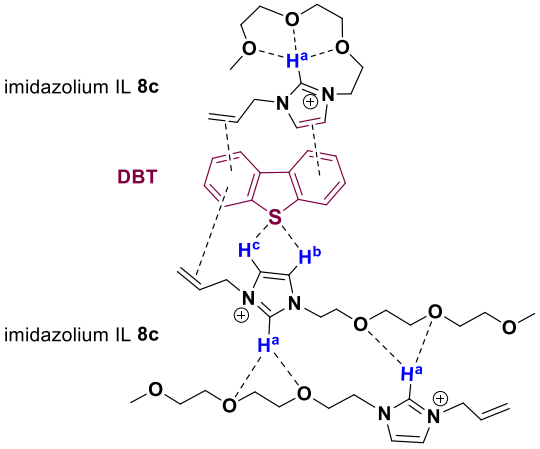


Fig. 6. . ^{1}H NMR studies of DBT and IL **15b**interactions. (a) DBT. IL: DBT ratios: (b) 1:3 ; (c) 1:2 ; (d) 1:1. (e) IL **15b.**



Scheme 3. . Proposed interactions between DBT and *N*-triethylene glycol ether imidazolium IL **8c**.

were observed for all polyether protons (H*g*, H*h*, H*i* and H*j*), indicating that the IL *N*-allyl and *N*-ether groups contribute almost equally to the interactions between aromatic dibenzothiophene compounds and these ILs. The acidic H*a* proton of imidazolium **8c** experienced only a minor shielding effect, presumably due to inter/intra-molecular hydrogen bonding with ether oxygen atoms, which prohibits the acidic H*a* proton from interaction with the DBT sulfur atom (Scheme 3). Thus, the sulfur atom interacts only with the H*b* and H*c* alkene imidazolium protons [55], as seen by NMR. In contrast, ^{1}H NMR studies of aromatic sulfur compounds and corresponding ILs with alkyl groups showed the opposite effect [58], as the acidic H*a* imidazolium proton experienced a significant shielding effect by increased concentration of DBT, indicating H*a* proton interaction with the DBT sulfur atom in the absence of competing ether groups.

Considerably higher EDS efficiency was obtained with benzimidazolium-based ILs (**15–17**, Table 1c) than imidazolium-based ILs (**6–11**, Table 1a,b). To identify selective effects explaining the different extraction efficiency of the two groups of ILs, ^{1}H NMR studies (Fig. 6) were also performed on solutions of IL **15b** and DBT, by similar conditions as for IL **8c** above (Fig. 5). ^{1}H NMR showed that all protons experienced significant upfield shifts upon EDS, demonstrating that all aromatic **15b** IL protons (H*a-d*) are almost equally deshielded by strong π-π interactions between the planar fused aromatic benzimidazolium ILs and the aromatic DBT compounds.

However, a striking difference is that the acidic H*a* proton of *N*-monoether benzimidazolium ILs (**15b**) is strongly affected by addition of DBT, in contrast to the *N*-triether-imidazolium IL (**8c**, Fig. 5), where proton H*a* remains unchanged by addition of DBT, explained by favoured inter/intramolecular H*a* hydrogen bonds with the oxygens of the longer *N*-triether system of IL **8c** (Scheme 3). Consequently, the limited interaction of DBT with proton H*a* leads to reduced EDS capacity of IL **8c**. This effect shows that IL H*a*-proton/DBT-sulfur hydrogen bonds plays a vital role in efficient desulfurization of DBTs. These ^{1}H NMR observations also explain the significantly reduced DBT extraction efficiency (from 69% to 56%) for benzimidazolium IL **15b** to **17b** with increased *N*-ether chain length (n = 1 to 3, Table 1c, entries 1,9).

However, the 4,6-DMDBT extraction efficiency was not much affected by increased *N*-ether chain length of (benz)imidazolium ILs (e.g. n = 2 to 3, Table 1a,b,c; entries 5 and 9), due to the steric hindrance of the sulfur atom by the methyl groups. This limits 4,6-DMDBT from interacting with the H*a* proton, which also explains the general less efficient extraction of 4,6-DMDBT than of DBT with (benz)imidazolium ILs.

In summary, the ^{1}H NMR observations explain both the higher extraction capacity of benzimidazolium ILs than imidazolium-based ILs and the more efficient desulfurization of DBT than of 4,6-DMDBT, as well as the complex effects of long *N*-ether chains on (benz)imidazolium ILs (Scheme 3).

4. Conclusion

EDS desulfurization studies of model oil (MO: DBT/4,6-DMDBT in *n*-dodecane) were performed on a series of 36 novel dual functionalized imidazolium and benzimidazolium based ILs with *N*-ethylene glycol (poly)ether and *N*-allyl or *N*-benzyl groups. The new ILs were readily prepared from imidazole by a three-step dialkylation and anion exchange procedure.

To the best of our knowledge, there are no known EDS studies with benzimidazolium ILs, which outperformed imidazolium ILs in the present study, as higher efficiencies for both DBT and 4,6-DMDBT extraction were obtained for benzimidazolium-based ILs than imidazolium based ILs. Most efficient EDS was obtained with the dual functionalized *N*-allyl-*N*-mono-/diether benzimidazolium NTs_2 ILs **15b** and **16b** (up to 69% DBT), which is close to the reported values for *N*-(poly)ether and *N*-alkylester dual functionalized imidazolium ILs (73–80% DBT) [1,20].The benzimidazolium NTs_2 ILs **15b** and **16b** had extraordinary extraction capacity for the sterically hindered 4,6-DMDBT sulfur compound (52%), being much higher than previous IL reports (< 20%) [1,20]. The *N*-allyl-and *N*-benzyl-*N*-triether imidazolium $N(CN)_2$ ILs **8c** and **11c** had some lower EDS capacity (up to 59% DBT). Optimization of extraction conditions with imidazolium IL **8c** showed that potentially 20–40% higher EDS efficiency could be obtained by increased IL:MO mass ratio (from 1:1 to 2:1). Depending on the IL price, this may represent a more economically viable EDS process. EDS capacity seemed to be stabilized within 15 min. at 25 °C. Therefore, these extraction conditions (25 °C, 15 min. extraction time, IL:MO mass ratio: 2:1) may be suggested for further studies.

The higher EDS capacity of dual functionalized benzimidazolium ILs than imidazolium ILs may be caused by the larger aromatic π electron system of the benzofused IL cation, which would increase intermolecular π-π interactions with heterocyclic compounds. ^{1}H NMR studies of IL-DBT solutions illustrated such EDS mechanism by specific IL-DBT interactions. ^{1}H NMR showed that all aromatic benzimidazolium **15b** protons were stronger affected by addition of DBT compounds than the corresponding imidazolium protons **8c**. This confirms that strong intermolecular π-π interactions between the planar aromatic electron system of benzimidazolium ILs and aromatic DBT play a major role for the higher EDS extraction efficiency. Additionally, the strong intermolecular hydrogen bonds between the acidic benzimidazolium **15b** H2-proton and DBT, as observed by ^{1}H NMR, was not seen for the imidazolium IL, as strong competing inter/intramolecular hydrogen bonds were formed between the imidazolium **8c** H2-proton and the ether-oxygen(s). Thus, only weak intermolecular H2 hydrogen bonds to DBT contribute to imidazolium ILs desulfurization. As shown by ^{1}H NMR, IL **8c** desulfurization is mainly based on strong π-π interactions between DBT and the imidazolium H3/H4 alkene protons. ^{1}H NMR studies of IL-DBT solutions readily demonstrated the intermolecular interactions which may give rise to higher extraction capacity of benzimidazolium than the corresponding imidazolium ILs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.116959.

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