Deep extractive and oxidative desulfurization of dibenzothiophene with $C_5H_9NO \cdot SnCl_2$ coordinated ionic liquid

Fa-tang Li [a,*], Cheng-guang Kou [a], Zhi-min Sun [a], Ying-juan Hao [a], Rui-hong Liu [a], Di-shun Zhao [b]

[a] College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China
[b] College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China

ABSTRACT

A new $C_5H_9NO \cdot SnCl_2$ coordinated ionic liquid (IL) was prepared by reacting N-methyl-pyrrolidone with anhydrous $SnCl_2$. Desulfurization of dibenzothiophene (DBT) via extraction and oxidation with $C_5H_9NO \cdot SnCl_2$ IL as extractant, H_2O_2 and equal mol of CH_3COOH as oxidants was investigated. The Nernst partition coefficients k_N of $C_5H_9NO \cdot SnCl_2$ IL for the DBT in n-octane was above 5.0, showing its excellent extraction ability. During the oxidative desulfurization process, the optimal molar ratio of H_2O_2/DBT was six. Sulfur removal of DBT in n-octane was 94.8% in 30 min at 30 °C under the conditions of H_2O_2/DBT molar ratio of six and V (IL):V (oil) = 1:3. Moreover, the sulfur removal increased with increasing temperature because of the high reaction rate constant, low viscosity, and high solubility of dibenzothiophene-sulfone in the IL. The kinetics of oxidative desulfurization of DBT was also investigated, and the apparent activation energy was found to be 32.5 kJ/mol. The IL could be recycled six times without a significant decrease in activity.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Deep desulfurization of fuel oils has attracted increasing attention worldwide because sulfur compounds present in oils lead to SOx emission, which pollutes the air and forms acid rains [1]. With more and more stringent sulfur content regulations, achieving "S-free" fuels (S content < 10 ppm) has become a trend [2]. Conventional catalytic hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides, and disulfides. However, aromatic sulfur compounds, such as dibenzothiophene (DBT) and its derivatives, present in the highest proportion in diesel fuels are hardly desulfurized by HDS because of their steric hindrance [3,4]. Severe operating conditions, i.e., very low space velocities, high temperatures, high hydrogen pressures, and the use of highly active catalysts, are inevitably required to produce ultra-clean fuel oils [4–6]. Therefore, alternative deep desulfurization techniques, such as biodesulfurization [7], adsorption [8,9], extraction by ionic liquids (ILs) [1,4,10–12], oxidation [2–6,13–20], and photooxidation [21–23], have been explored. Among these techniques, the extractive desulfurization by ILs has been extensively studied because of its facile operation and the high extraction ability of some ILs for sulfur compounds. For example, we [12] have used $1.6Et_3NHCl \cdot FeCl_3$ IL

as the extractant for thiophene, and the sulfur removal reached 87.6% after a single extraction. The IL can be regenerated via distillation because the boiling points of thiophene and gasoline are lower than that of the ILs. Ko et al. [4] found that 5000 ppm of DBT (as model for diesel oil) in n-heptane could be completely extracted by [BMIm]Cl·2FeCl$_3$ IL. However, in case of diesel oils, regenerating the ILs from diesel oils via simple distillation is impossible because of the high boiling points of DBT and diesel oil (about 332 °C for DBT). Although ILs can be regenerated and re-extracted using organic solvents, the subsequent flammable and volatile organic solvents containing sulfur compounds need to be treated. Thus, extraction is probably only applicable for the desulfurization of gasoline in which the S-species have a relatively low boiling point [24].

As to the desulfurization for diesel oils, oxidative desulfurization combined with extraction has been regarded as a promising process because benzothiophenes (BTs) and DBTs can be easily oxidized to their corresponding sulfoxides and sulfones, which can be removed via extraction with various ILs, including imidazolium- [2,6,16–19] and pyridinium- based ILs [20,25]. As the reaction proceeds, the sulfoxides and sulfones precipitate from the ILs, regenerating the ILs.

However, most reported ILs pertains to imidazolium cation with counteranions, such as tetrafluoroborate or hexafluorophosphate. Swatlowski et al. [26] reported that ILs with fluorous anions could harm the environment. Moreover, imidazolium- or pyrrolidonium-based ILs are relatively expensive and are

---

* Corresponding author. Tel.: +86 311 81669971; fax: +86 311 81668512.
E-mail address: lifatang@126.com (F.-t. Li).

difficult to use in industries. Recently, some inexpensive quaternary ammonium-based ILs have been prepared from quaternary ammonium salts and metal halide anions, including $xEt_3NHCl\cdot FeCl_3$ [12], $Me_3NCH_2C_6H_5Cl\cdot xZnCl_2$ [13], and $[(C_8H_{17})_3CH_3N]Cl/SnCl_2$ [27]. The π-complexation between sulfur compounds and metals is the extraction desulfurization mechanism for metal halide-based ILs [10,12,28–30], which is different from that of the commonly used imidazolium-based IL. Moreover, π-complexation is likely relevant to the formation of liquid clathrate because of the π–π interaction between the unsaturated bonds of the S-compound and imidazolium or pyrrolidonium ring of ILs [20,31]. Furthermore, Lemaire et al. used 4,5-dicyano-2,7-dinitrofluorenone, which is a kind of salt, for adsorption desulfurization and found that the surface charge-transfer complexes between the large-ring thiophenes (electron donors) present in liquid fuels and the substituted fluorenone groups (electron acceptors) are formed [32,33].

Based on the similarity-intermiscibility theory and on the imidazolium ring extraction mechanism, N-methyl-pyrrolidone (NMP, C_5H_9NO), which is another kind of ammonium salt, containing a five-membered ring was found to have a surprising extraction ability for sulfur-containing compounds. However, the use of NMP in practice is impossible because the solubility of diesel in NMP is above 8%. Herein, a new coordinated ionic liquid was prepared by reacting NMP with $SnCl_2$, which showed excellent extraction performance and stability for diesel oil. The prepared ionic liquid was also used as the extractant in the oxidative desulfurization of DBT and diesel oil.

2. Experimental

2.1. Materials

NMP (AR grade), anhydrous $SnCl_2$ (99%), DBT (99%), n-octane (AR grade), H_2O_2 (aqueous solution, 30 wt%), CH_3COOH (AR grade), and $DBTO_2$ (97%) were purchased from Aladdin, China, and were used as received without further purification. Actual diesel oil (492 μg mL^{-1} S) was purchased from a fuel station.

2.2. Preparation and characterization of ionic liquids

NMP (0.1 mol) was mixed with $SnCl_2$ (0.1x mol, x = 0.6–1.5), heated to ca. 80 °C in air, and was stirred until a clear liquid was obtained, which can be called coordinated ionic liquid. The viscosity of the ionic liquids was measured using the NDJ-8S rotational viscometer. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu IR-Prestige 21 spectrometer. Thermogravimetry (TG) experiments on NMP and $C_5H_9NO\cdot SnCl_2$ IL were carried out using a Mettler–Toledo TGA/SDTA851^e thermal analyzer at a heating rate of 0.5 °C/min to observe the thermal stability of IL.

2.3. Extractive/oxidative desulfurization of DBT in n-octane

The model oil (500 μg mL^{-1} S) was prepared by dissolving 2.9018 g DBT in 1 L n-octane. The desulfurization experiments were conducted in a 50 mL flask. In a typical run, the mixture containing 15 mL of model or actual oil and 5 mL of different $C_5H_9NO\cdot xSnCl_2$ (x = 0.6–1.5) ILs was stirred vigorously for 10 min until the extraction equilibrium was reached. Then 30 wt% H_2O_2 and the equal mol of CH_3COOH were added to the mixture to oxidize the DBT. The upper oil phase was periodically withdrawn, and then it was analyzed for sulfur content using a micro coulometer.

2.4. Regeneration/recovery of used ionic liquid

At the end of each run, the upper-layer oil was separated via decantation from the $C_5H_9NO\cdot SnCl_2$ IL solution. The IL was distilled
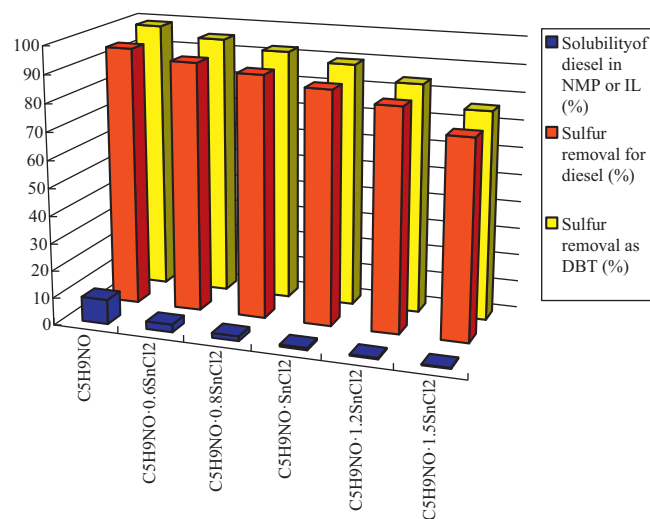

Fig. 1. Sulfur removal of DBT and diesel with $C_5H_9NO\cdot xSnCl_2$ and solubility of diesel in $C_5H_9NO\cdot xSnCl_2$. Reaction conditions: model or actual oil = 10 mL, solvent = 10 mL, t = 10 min, 30 °C.

via rotary evaporation at 100 °C for 2 h until the oxidants were completely removed. Then, the fresh H_2O_2, CH_3COOH, and model oil were introduced to the next reaction under the same conditions as described above. After five runs, the IL phase was cooled to 5 °C in a refrigerator for 2 h. The $DBTO_2$ precipitate was reclaimed from the IL via centrifugation or filtration, and the IL was reused.

2.5. Solubility of oil in the IL

The solubility of oil in the IL was measured according to [34] using the gravimetric method. The results show that there was no model oil dissolved in the IL. The actual diesel oil solubility in various ILs is shown in Fig. 1.

3. Results and discussion

3.1. Extractive desulfurization performance of $C_5H_9NO\cdot xSnCl_2$ and solubility of diesel in $C_5H_9NO\cdot xSnCl_2$

Fig. 1 shows the sulfur removal of DBT and diesel oil, as well as the solubility of diesel in $C_5H_9NO\cdot xSnCl_2$. The NMP exhibits a notable sulfur removal of 98.8% for DBT because of the similarity-intermiscibility theory based on the fact that both NMP and DBT contain a five-membered ring. The removal of sulfur from the actual diesel oil was more difficult than that from the model oil because many nitrogen, oxygen, and aromatic compounds existed in the actual oil, which decreased the extraction performance of the ILs, as shown in Fig. 1 [12]. However, the high solubility of 8.94% of the actual diesel oil in NMP made the use of NMP in industries impossible.

$FeCl_3$, $ZnCl_2$, CuCl, $SnCl_4$, and $NiCl_2$ have been used to modify NMP and decrease the solubility, but a clear solution could not be obtained, except $SnCl_2$. The solubility of diesel decreased when $SnCl_2$ was added into the NMP. When $SnCl_2$ was mixed with NMP, π-complexation formed between the lone pair of electrons on the O atom of NMP and on the empty 5p orbital on Sn^{2+} ion with an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^0$, which decreased the dissolubility of fuel oil in NMP. The obtained solution can be called the coordinated ionic liquid [35]. Scheme 1 shows the possible formation process and structure of the IL. The conductivity of ILs $C_5H_9NO\cdot 0.6SnCl_2$, $C_5H_9NO\cdot 0.8SnCl_2$, $C_5H_9NO\cdot SnCl_2$,
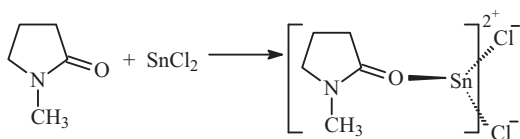
Scheme 1. The possible formation process and structure of $C_5H_9NO \cdot xSnCl_2$ IL.

$C_5H_9NO \cdot 1.2SnCl_2$, $C_5H_9NO \cdot 1.5SnCl_2$, and pure C_5H_9NO is 1188, 676, 424, 309, 166, and 5.5 μs/cm, showing the existence of ions.

To observe the coordination bond between O atom and Sn^{2+} ion, FT-IR spectra of C_5H_9NO and $C_5H_9NO \cdot SnCl_2$ are shown in Fig. 2. The formation of oxygen-to-metal coordination bond should result in a shift of the band for C=O to lower frequencies [36]. It is clearly that the band at 1686.82 cm^{-1} for C=O in C_5H_9NO was shifted to 1617.38 cm^{-1} in $C_5H_9NO \cdot SnCl_2$, showing the formation of coordination bond between NMP molecule and the Sn^{2+} ion. The bands at 2360.01 cm^{-1} and 418.57 cm^{-1} in $C_5H_9NO \cdot SnCl_2$ can be attributed to the propagation of the IR beam through air and Sn–Cl bond, respectively.

It is seen that the extraction ability of ILs for DBT and diesel oil decreased with increasing SnCl$_2$ despite the ability of DBT and Sn^{2+} to form charge-transfer complex. Aside from the decreased solvation of NMP, the viscosities of liquids have always been known to have great effects on their extraction ability. Fig. 3 shows the viscosities of $C_5H_9NO \cdot xSnCl_2$ ionic liquids. The viscosity greatly increased with increasing SnCl$_2$ in the ILs, which also reduced the extraction ability. When the molar ratio of SnCl$_2$ to NMP was below 1, the viscosity was below 500 mPa S^{-1}, which facilitated the fast mass transfer of S-compounds from the oils to the ILs [11]. Considering both the sulfur removal ability and the solubility of diesel oil, $C_5H_9NO \cdot SnCl_2$ was found to be the ideal ionic liquid.

3.2. The extractive/oxidative desulfurization process and mechanism for DBT

During the oxidative desulfurization (ODS) process of fuel oils, the H$_2$O$_2$ in the presence of organic acids, including HCOOH [37], CH$_3$COOH [13], CCl$_x$COOH ($x = 1$–3) [38], and CF$_3$COOH [39], have been used as oxidants because these organic acids react with H$_2$O$_2$
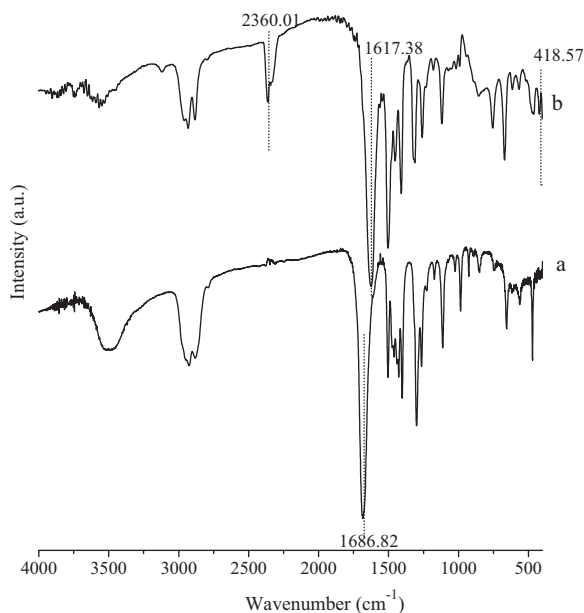

Fig. 2. FT-IR spectra of C_5H_9NO and ionic liquid. (a) pure C_5H_9NO, (b) $C_5H_9NO \cdot SnCl_2$ ionic liquid.
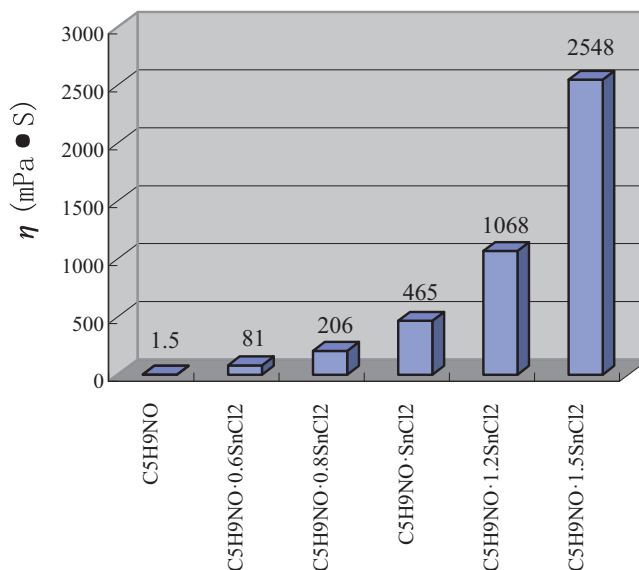

Fig. 3. Dynamic viscosities of the $C_5H_9NO \cdot xSnCl_2$ ILs at 30 °C.

to in situ produce peracids, which can efficiently convert organic sulfur to sulfones without forming a substantial amount of residual product [40]. Among these acids, HCOOH and CH$_3$COOH are inexpensive reagents. CH$_3$COOH has lesser toxicity than HCOOH. Thus, in the current study, H$_2$O$_2$/CH$_3$COOH were used as oxidants for the ODS.

During the extractive/ODS process, DBT was extracted from the oil phase into the IL phase and was oxidized to its corresponding sulfone (DBTO$_2$) using the peracetic acid (CH$_3$COOOH) obtained from H$_2$O$_2$ and CH$_3$COOH. The decrease in DBT concentration in the IL promoted the extraction process, and the sulfur content in oil phase decreased continuously. Scheme 2 shows the extractive/ODS process of DBT.

3.3. Influence of H$_2$O$_2$/DBT (O/S) molar ratio and IL/oil volume ratio on the sulfur removal of DBT

The extraction/oxidation of DBT in *n*-octane under different H$_2$O$_2$/DBT (O/S) molar ratios and IL/oil volume ratios was conducted at 30 °C to investigate the effects of the amount of oxidants and extractants on the sulfur removal of DBT. Fig. 4 shows the results when $C_5H_9NO \cdot SnCl_2$ was used as the extractant, and H$_2$O$_2$ and equal mol of CH$_3$COOH were used as oxidants.

When no oxidants were added, extraction equilibrium was almost reached only after ~5 min, and the complete equilibrium
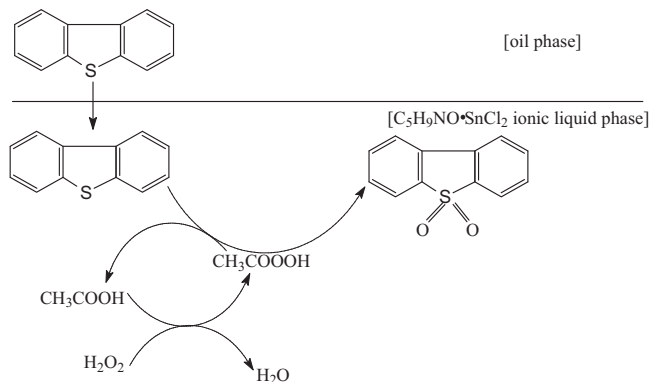
Scheme 2. The extractive/ODS process of DBT using H$_2$O$_2$ and CH$_3$COOH as oxidants in an oil–ionic liquid system.

Table 1
Nernst partition coefficeents k_N under different V(IL)/V(oil) for extraction of DBT.

IL	Model oil	T (°C)	k_N (mg of S (L of IL)$^{-1}$/mg of S (L of oil)$^{-1}$)				Ref.
			V(IL)/V(oil)				
			1:1	1:2	1:3	1:5	
$C_5H_9NO·SnCl_2$	n-octane	30	5.76	5.72	5.67	5.30	This work
[BMIM]Cl/AlCl$_3$	n-dodecane	Room temperature				4.09	[10]
[BMI][N(CN)$_2$]	n-hexane	25	2.28		2.30	2.01	[11]
[C$_8$^{3}MPy][BF$_4$]	n-dodecane	Room temperature	3.11				[34]
[C$_6$^{3}MPy][BF$_4$]	n-dodecane	Room temperature	2.89				[34]
[C$_4$^{3}MPy][BF$_4$]	n-dodecane	Room temperature	2.08				[34]
[OMIM]Me$_2$PO$_4$	n-dodecane	25	1.34				[41]
[BEIM]DBP	n-dodecane	25	1.72				[18]
[OMIM]BF$_4$	n-octane	70				1.35	[2]

Reaction conditions: model oil = 15 mL, t = 10 min, 30 °C.

was attained after 10 min. Table 1 shows the k_N in 10 min under different V (IL)/V (oil). For comparison, some k_N with other ILs from literature are also listed.

As shown in the k_N listed in Table 1, $C_5H_9NO·SnCl_2$ IL showed a remarkable ability for sulfur removal, indicating that it is an excellent extractant for DBT. Furthermore, k_N were not too sensitive to the IL/oil volume ratio.

When oxidants were added into the system after the extraction equilibrium, the sulfur removal of DBT increased at different IL/oil volume ratios with increasing O/S molar ratio from 2:1 to 10:1 as shown in Fig. 4. According to the stoichiometric reaction, 2 mol of CH$_3$COOOH (derived from 2 mol of H$_2$O$_2$ and CH$_3$COOH) were consumed for the oxidation of 1 mol of DBT, which corresponds to DBTO$_2$. With the increase in H$_2$O$_2$ and CH$_3$COOH, the oxidants had more opportunities to react with DBT, and thus the sulfur removal increased. The sulfur removal of DBT slowly increased when the O/S molar ratio was above 6. For example, when V (IL)/V (oil) = 1:3, the sulfur removal of DBT was only 65.4% via extraction, and was up to 78.6% at the molar ratio of O/S = 2. The sulfur removal of DBT was up to 88.5% and 95.0% when the O/S was increased to 4 and 6, respectively. Moreover, the sulfur removal of DBT increased slowly to 95.8% and 96.5% when the O/S molar ratio was further increased to 8 and 10, respectively. The results indicate that the O/S molar ratio of 6 is optimal because less H$_2$O$_2$ was used, and that the utilization of excessive amounts of oxidants is not economical [13].
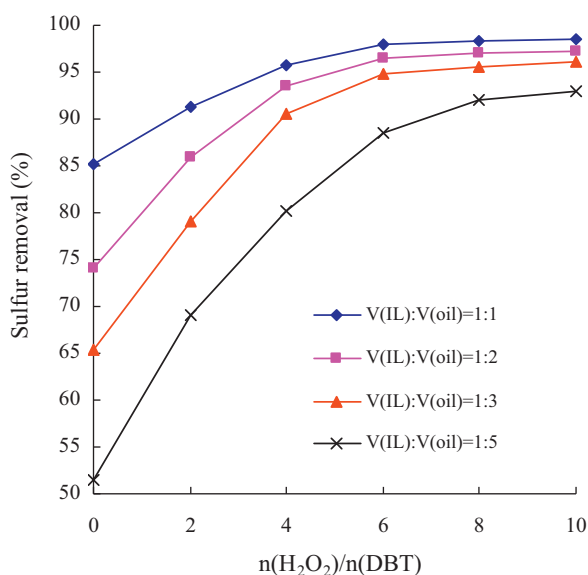
Furthermore, the sulfur removal of DBT increased with increasing IL/oil volume ratio. When the IL/oil volume ratio was below 1:3, the extraction effect of IL for DBT was low. When the IL/oil volume ratio was 1:2 or 1:1, the sulfur removal of DBT slightly increased, and many ILs were used. Thus, the IL/oil volume ratio of 1:3 is the most appropriate ratio.

3.4. Effects of temperature and time on the sulfur removal of DBT

Fig. 5 shows the sulfur removal of DBT versus reaction time at various temperatures using $C_5H_9NO·SnCl_2$ as the extractant. The sulfur removal at time zero reflected the ability of $C_5H_9NO·SnCl_2$ to extract DBT from n-octane at various temperatures, in which the sulfur removal increased with increasing temperature because the viscosity of IL reduced with increasing temperature (465, 231, 106 mPa S at 30, 40, 50 °C, respectively). The sulfur removal of DBT reached 97.3% at 30 °C and 99.3% at 40 °C in 40 min. When the temperature was increased to 50 °C, DBT was completely removed from the n-octane in 35 min. Aside from reaction rate constant and viscosity, the factors that influence the removal rate of DBT were also related to the solubility of the product (DBTO$_2$) in the IL. Under oxidative desulfurization process, sulfur compounds can be oxidized to sulfoxides or sulfones. These are highly polar compounds, which have high solubility in polar extractants, including water, acetonitrile, or ILs [13]. In this study, the solubility of pure DBTO$_2$ reagent in IL at various temperatures was tested, and the results are shown in Fig. 6. It is obvious that the solubility of DBTO$_2$ in the IL increased sharply with increasing temperature.

Fig. 4. Effect of H$_2$O$_2$/DBT molar ratio and IL/oil volume ratio on sulfur removal of DBT. Reaction conditions: model oil = 15 mL, t = 30 min, 30 °C.
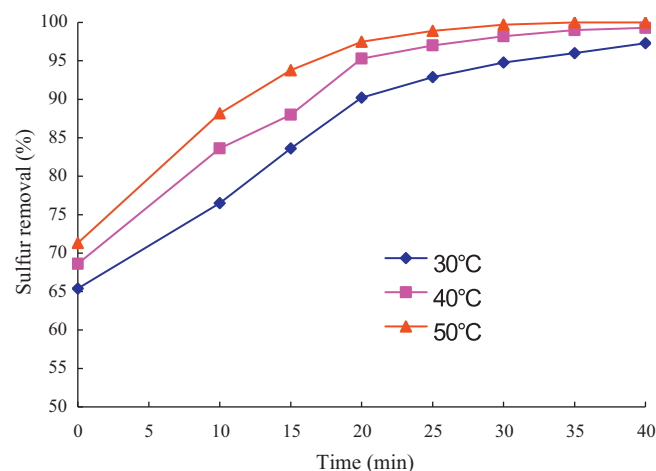

Fig. 5. Time-course variation of sulfur removal of DBT in n-octane at various temperatures. Reaction conditions: model oil = 15 mL, IL = 5 mL; molar ratio of O/S = 6.
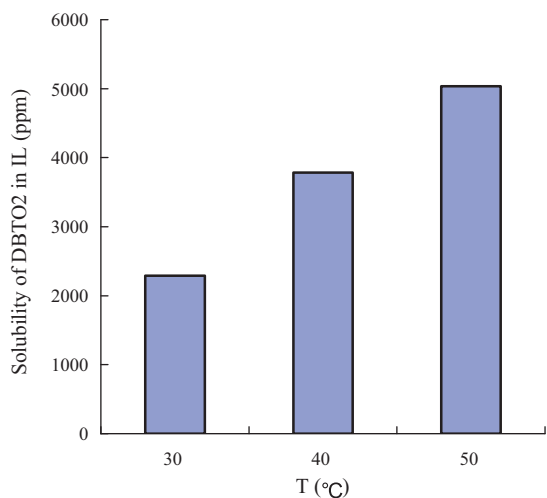
Fig. 6. Solubility of $DBTO_2$ calculated by S-content in IL at various temperatures.

The oxidation kinetics of DBT at various temperatures was also investigated. Scheme 1 shows that the oxidation reaction equation of DBT in the presence of oxidant CH_3COOOH can be described as follows:

$$-\frac{dC_{DBT}}{dt} = k'C_{CH_3COOOH}^m C_{DBT}^n \qquad (1)$$

The term dependent on CH_3COOOH concentration could be treated as a constant because the CH_3COOOH was taken in excess amount and the change in concentration of CH_3COOOH is negligible compared to the change in DBT concentration [42]. Thus, Eq. (1) may be expressed as:

$$-\frac{dC_{DBT}}{dt} = kC_{DBT}^n \qquad (2)$$

where $k = k'C_{CH_3COOOH}^m$, which may be termed as the apparent rate constant.

The oxidation of DBT in n-octane using H_2O_2 and CH_3COOH was assumed as the first-order reaction. Eq. (2) has been integrated for $n = 1$, with limit $t = 0$, $C_{DBT} = C_1$ (extractive sulfur removal of DBT at time zero), $t = t$, $C_{DBT} = C_t$, and $C_0 = 500$ ppm.

$$\ln\frac{C_0}{C_t} = kt + \ln\frac{C_0}{C_1} \qquad (3)$$

The plot of $\ln(C_0/C_t)$ versus time is linear, as shown in Fig. 7. The kinetics equation, rate constant k, and correlation coefficient R are listed in Table 2.
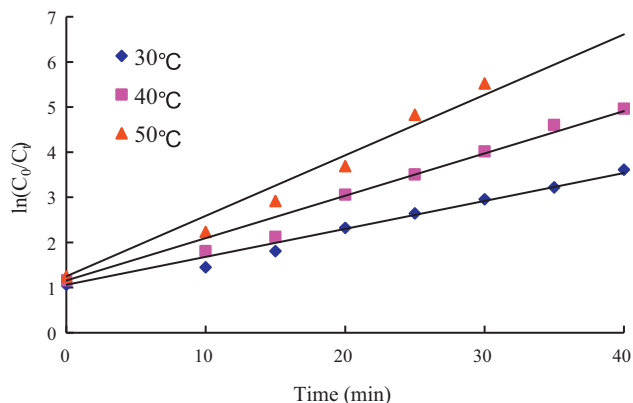

Fig. 7. Time-course variation of $\ln(C_0/C_t)$ under different temperature. Reaction conditions: model oil = 15 mL, IL = 5 mL; molar ratio of O/S = 6.

Table 2
Kinetics equation, rate constant k, and correlation coefficient R at various temperatures.

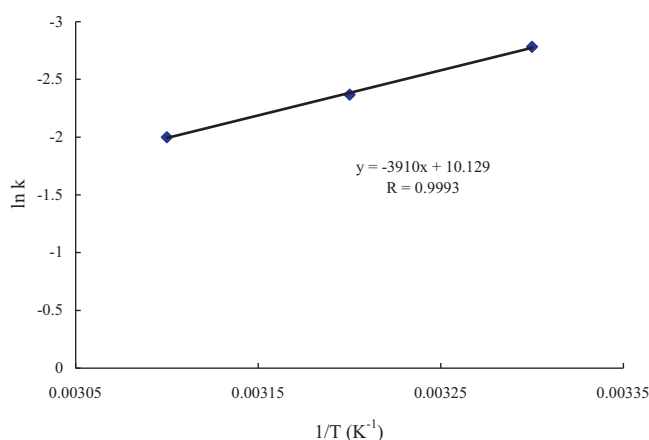| T (°C)	Kinetics equation	Rate constant k (min^{-1})	Correlation coefficient R
30	$\ln(C_0/C_t) = 0.0619t + 1.0613$	0.0619	0.9913
40	$\ln(C_0/C_t) = 0.0938t + 1.1584$	0.0938	0.9880
50	$\ln(C_0/C_t) = 0.1340t + 1.2483$	0.1340	0.9837

Fig. 8. Arrheniul plot for the determination of activation energy.

Based on the reaction rate constants at various temperatures listed in Table 2, the apparent activation energy was estimated from the plot of $\ln k$ versus $1/T$, which was derived from the Arrhenius equation. The apparent activation energy obtained from the desulfurization reaction was 32.5 kJ/mol, as shown in Fig. 8. Sachdeva et al. [43] obtained the apparent activation energy for the commercial diesel desulfurization of 30.6 kJ/mol using phosphotungstic acid as the phase transfer catalyst (PTA) and H_2O_2 as the oxidant. Qiu et al. [44] reported that the apparent activation energy values for the DBT desulfurization were 26.8 kJ/mol and 31.4 kJ/mol for the hexadecyltrimethyl ammonium chloride and dodecyltrimethylammonium chloride, respectively, which were used as the PTA. PTA was not used in the current study. The apparent activation energy value was similar with the reported reference because of the use of the stronger oxidant H_2O_2/CH_3COOH.

3.5. Effect of regeneration/recycling of ionic liquid

The possibility of recycling the $C_5H_9NO \cdot SnCl_2$ IL was examined. At the end of each run, the IL phase was recycled, and residual oxidants (H_2O_2 and CH_3COOH) were evaporated from the IL. The system was then recharged with fresh H_2O_2 and CH_3COOH for the next run. After five runs, the IL phase was cooled to 5 °C to remove the $DBTO_2$ precipitate, and then the IL was used for the next run. The data shown in Table 3 indicate that there was little decrease in activity after the five reactions using $C_5H_9NO \cdot SnCl_2$ IL. When the product was removed from the IL, the sulfur removal was further improved (sixth run). To determine the thermal stability of the IL, TG curve of $C_5H_9NO \cdot SnCl_2$ was shown in Fig. 9, as well as curve

Table 3
Recycle of $C_5H_9NO \cdot SnCl_2$ IL in sulfur removal of DBT.

Cycle	Sulfur removal (%)	Cycle	Sulfur removal (%)
1	94.8	4	92.1
2	94.2	5	90.6
3	93.3	6	93.8

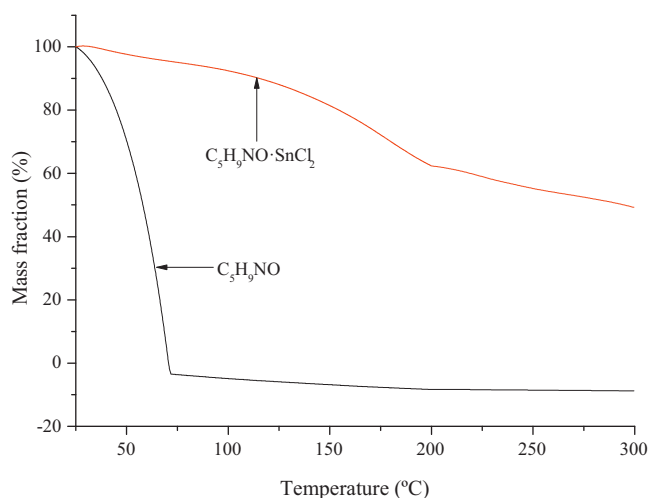Conditions: $t = 30$ min; model oil = 15 mL, IL = 5 mL; molar ratio of O/S = 6; 30 °C.

Fig. 9. TG curves of C_5H_9NO and $C_5H_9NO \cdot SnCl_2$ IL.

of pure C_5H_9NO as comparison. The quality of IL reduced by 7.5% at 100 °C, whereas pure C_5H_9NO was evaporated entirely at about 70 °C, in spite of its high boiling point at 202 °C because of the slow heating rate. Hence, the addition of $SnCl_2$ improved thermal stability of C_5H_9NO greatly and it was practicable to remove oxidants from IL under 100 °C distillation. The FT-IR test verified that there was no structure difference between regenerated and fresh IL.

3.6. Desulfurization of actual diesel oil

The desulfurization of actual diesel oil was investigated using the IL/oil volume ratio of 1:3 at 30 °C. The sulfur removal of the actual diesel oil was 87.6% in 30 min, which was much lower than that of DBT with 94.8%. This phenomenon was influenced by two factors. First, many nitrogen, oxygen, and aromatic compounds existed in the actual oil, which decreased the extraction performance of the IL for sulfur-containing compounds. Second, there were different kinds of alkyl substituted DBTs in the actual diesel, such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). Previous reports suggested that methyl substituted DBTs are more reactive than DBT during oxidation reactions [35,45]. However, Te et al. [46] reported that the reactivity of the dibenzothiophenes decreased with increasing methyl substitutes at the 4 and 6 positions, that is, the reactivity ordering was DBT > 4-MDBT > 4,6-DMDBT. Li et al. [47] also pointed out that the methyl groups of 4,6-DMDBT was an obstacle for the approach of the sulfur atom in the catalytic active species in the IL. DBT had the highest oxidative reactivity compared to benzothiophene and 4,6-DMDBT. These less reactive compounds significantly retarded the oxidation reaction of the actual diesel fuel.

4. Conclusions

A new $C_5H_9NO \cdot SnCl_2$ coordinated ionic liquid was initially prepared for the extractive/oxidative desulfurization of DBT and actual diesel oil. The C_5H_9NO showed surprising extraction ability for DBT and diesel oil because of their mutual five-membered rings. However, the high solubility of diesel in C_5H_9NO made its use in practice impossible. When $SnCl_2$ was added to modify C_5H_9NO and form the coordinated ionic liquid, the solubility decreased sharply from 8.94% to below 1%. The oxidative desulfurization of DBT using $C_5H_9NO \cdot SnCl_2$ as the extractant was also investigated. In the presence of H_2O_2 and CH_3COOH, the sulfur removal of DBT and diesel reached 94.8% and 87.6% in 30 min, respectively. The

$C_5H_9NO \cdot SnCl_2$ ionic liquid could be recycled six times without a significant decrease in activity. The $C_5H_9NO \cdot SnCl_2$ ionic liquid is an inexpensive, easily synthesized, and an excellent extractant for sulfur-containing compounds. We hope the current study can promote and provide reference for the extractive/oxidative desulfurization of light oils in further theoretical research and industry application.

References

[1] L.Z. Zhai, Q. Zhong, C. He, J. Wang, Hydroxyl ammonium ionic liquids synthesized by water-bath microwave: synthesis and desulfurization, J. Hazard. Mater. 161 (2009) 1360–1368.
[2] W.S. Zhu, H.M. Li, X. Jiang, Y.S. Yan, J.D. Lu, L.M. He, J.X. Xia, Commercially available molybdic compound-catalyzed ultra-deep desulfurization of fuels in ionic liquids, Green Chem. 10 (2008) 641–646.
[3] H.Y. Lu, J.B. Gao, Z.X. Jiang, F. Jing, Y.X. Yang, G. Wang, C. Li, Ultra-deep desulfurization of diesel by selective oxidation with $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ catalyst assembled in emulsion droplets, J. Catal. 239 (2006) 369–375.
[4] N.H. Ko, J.S. Lee, E.S. Huh, H. Lee, K.D. Jung, H.S. Kim, M. Cheong, Extractive desulfurization using Fe-containing ionic liquids, Energy Fuels 22 (2008) 1687–1690.
[5] J.M. Campos-Martin, M.C. Capel-Sanchez, P. Perez-Presas, J.L.G. Fierro, Oxidative processes of desulfurization of liquid fuels, J. Chem. Technol. Biotechnol. 85 (2010) 879–890.
[6] L.N. He, H.M. Li, W.S. Zhu, J.X. Guo, X. Jiang, J.D. Lu, Y.S. Yan, Deep oxidative desulfurization of fuels using peroxophosphomolybdate catalysts in ionic liquids, Ind. Eng. Chem. Res. 47 (2008) 6890–6895.
[7] K. Kirimura, T. Furuya, Y. Nishii, Y. Ishii, K. Kino, S. Usami, Biodesulfurization of dibenzothiophene and its derivatives through the selective cleavage of carbon–sulfur bonds by a moderately thermophilic bacterim *Bacillus subtilis* WU-S2B, J. Biosci. Bioeng. 91 (2001) 262–266.
[8] J.M. Kwon, J.H. Moon, Y.S. Bae, D.G. Lee, H.C. Sohn, C.H. Lee, Adsorptive desulfurization and denitrogenation of refinery fuels using mesoporous silica adsorbents, ChemSusChem 1 (2008) 307–309.
[9] A. Srivastav, V.C. Srivastava, Adsorptive desulfurization by activated alumina, J. Hazard. Mater. 170 (2009) 1133–1140.
[10] A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid, Deep desulfurization of diesel fuel by extraction with ionic liquids, Chem. Commun. 249 (2001) 4–2495.
[11] C. Asumana, G. Yu, X. Li, J. Zhao, G. Liu, X. Chen, Extractive desulfurization of fuel oils with low-viscosity dicyanamide-based ionic liquids, Green Chem. 12 (2010) 2030–2037.
[12] F.T. Li, Y. Liu, Z.M. Sun, L.J. Chen, D.S. Zhao, R.H. Liu, C.G. Kou, Deep extractive desulfurization of gasoline with xEt$_3$NHCl·FeCl$_3$ ionic liquids, Energy Fuels 24 (2010) 4285–4289.
[13] F.T. Li, R.H. Liu, J.H. Wen, D.S. Zhao, Z.M. Sun, Y. Liu, Desulfurization of dibenzothiophene by chemical oxidation and solvent extraction with $Me_3NCH_2C_6H_5Cl \cdot 2ZnCl_2$ ionic liquid, Green Chem. 11 (2009) 883–888.
[14] S. Dhir, R. Uppaluri, M.K. Purkait, Oxidative desulfurization: kinetic modeling, J. Hazard. Mater. 161 (2009) 1360–1368.
[15] B. Wang, J.P. Zhu, H.Z. Ma, Desulfurization from thiophene by SO_4^{2-}/ZrO_2 catalytic oxidation at room temperature and atmospheric pressure, J. Hazard. Mater. 164 (2009) 256–264.
[16] W.S. Zhu, H.M. Li, Q.Q. Gu, P.W. Wu, G.P. Zhu,.S. Yan, Y. Chen, Kinetics and mechanism for oxidative desulfurization of fuels catalyzed by peroxo-molybdenum amino acid complexes in water-immiscible ionic liquids, J. Mol. Catal. A: Chem. 336 (2011) 16–22.
[17] J. Zhang, A.J. Wang, X. Li, X.H. Ma, Oxidative desulfurization of dibenzothiophene and diesel over [Bmim]$_3$PMo$_{12}$O$_{40}$, J. Catal. 279 (2011) 269–275.
[18] X.C. Jiang, Y. Nie, C.X. Li, Z.H. Wang, Imidazolium-based alkylphosphate ionic liquids—a potential solvent for extractive desulfurization of fuel, Fuel 87 (2008) 79–84.
[19] L. Liang, S.F. Cheng, J.B. Gao, G.H. Gao, M.Y. He, Deep oxidative desulfurization of fuels catalyzed by ionic liquid in the presence of H_2O_2, Energy Fuels 21 (2007) 383–384.
[20] D.S. Zhao, J.L. Wang, E.P. Zhou, Oxidative desulfurization of diesel fuel using a Brønsted acid room temperature ionic liquid in the presence of H_2O_2, Green Chem. 9 (2007) 1219–1222.
[21] Y. Shiraishi, Y. Taki, T. Hirai, I. Komasawa, Visible light-induced desulfurization technique for light oil, Chem. Commun. 260 (1998) 1–2602.

[22] F.T. Li, D.S. Zhao, H.X. Li, R.H. Liu, Photochemical oxidation of thiophene by O_2 in an oil/acetonitrile two-phase extraction system, Ann. N.Y. Acad. Sci. 1140 (2008) 383–388.

[23] F.T. Li, D.S. Zhao, R.H. Liu, Z.J. Jin, Z.M. Sun, The photooxidative desulfurization of thiophene with tetrabutylammonium bromide as a phase transfer catalyst, Petrol. Sci. Technol. 28 (2010) 1140–1146.

[24] A. Seeberger, A. Jess, Desulfurization of diesel oil by selective oxidation and extraction of sulfur compounds by ionic liquids—a contribution to a competitive process design, Green Chem. 12 (2010) 602–608.

[25] A.R. Hansmeier, G.W. Meindersma, A.B. de Haan, Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids, Green Chem. 13 (2011) 1907–1913.

[26] R.P. Swatloski, J.D. Holbrey, R.D. Rogers, Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate, Green Chem. 5 (2003) 361–363.

[27] Y.Q. Jiang, W.S. Zhu, H.M. Li, S. Yin, H. Liu, Q.J. Xie, Oxidative desulfurization of fuels catalyzed by fenton-like ionic liquids at room temperature, ChemSusChem 4 (2011) 399–403.

[28] R.T. Yang, A.J. Hernandez-Maldonado, F.H. Yang, Desulfurization of transportation fuels with zeolites under ambient conditions, Science 301 (2003) 79–81.

[29] S.G. Zhang, Q.L. Zhang, Z.C. Zhang, Extractive desulfurization and denitrogenation of fuels using ionic liquids, Ind. Eng. Chem. Res. 43 (2004) 614–622.

[30] C.P. Huang, B.H. Chen, J. Zhang, Z.C. Liu, Y.X. Li, Desulfurization of gasoline by extraction with new ionic liquids, Energy Fuels 18 (2004) 1862–1864.

[31] Y. Nie, C. Li, A. Sun, H. Meng, Z. Wang, Extractive desulfurization of gasoline using imidazolium-based phosphoric ionic liquids, Energy Fuels 20 (2006) 2083–2087.

[32] M. Sevignon, M. Macaud, A. Favre-Reguillon, J. Schulz, M. Rocault, R. Faure, M. Vrinat, M. Lemaire, Ultra-deep desulfurization of transportation fuels via charge-transfer complexes under ambient conditions, Green Chem. 7 (2005) 413–420.

[33] A. Samokhvalov, B.J. Tatarchuk, Review of experimental characterization of active sites and determination of molecular mechanisms of adsorption, desorption and regeneration of the deep and ultradeep desulfurization sorbents for liquid fuels, Catal. Rev. 52 (2010) 381–410.

[34] H.S. Gao, Y.G. Li, Y. Wu, M.F. Luo, Q. Li, J.M. Xing, H.Z. Liu, Extractive desulfurization of fuel using 3-methylpyridinium-based ionic liquids, Energy Fuels 23 (2009) 26902694.

[35] D.S. Zhao, Z.M. Sun, F.T. Li, R. Liu, H.D. Shan, Oxidative desulfurization of thiophene catalyzed by $(C_4H_9)_4NBr \cdot 2C_6H_{11}NO$ coordinated ionic liquid, Energy Fuels 22 (2008) 3065–3069.

[36] R.B. Penland, S. Mizushima, C. Curran, J.V. Quagliano, Infrared absorption spectra of inorganic coördination complexes. X. Studies of some metal–urea complexes, J. Am. Chem. Soc. 79 (1957) 1575–1578.

[37] S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai, T. Kabe, Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction, Energy Fuels 14 (2000) 1232–1239.

[38] T. Aida, I. Funakoshi, Method of recovering organic sulfur compound from liquid oil, EP 0565324 (A1) (1993) 10–13.

[39] A. Treiber, P.M. Dansette, H. El Amri, J.P. Girault, D. Ginderow, J.P. Mornon, D. Mansuy, Chemical and biological oxidation of thiophene: preparation and complete characterization of thiophene S-oxide dimers and evidence for thiophene S-oxide as an intermediate in thiophene metabolism in vivo and in vitro, J. Am. Chem. Soc. 119 (1997) 1565–1571.

[40] P.S. Kulkarni, C.A.M. Afonso, Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges, Green Chem. 12 (2010) 1139–1149.

[41] E. Kuhlmann, M. Haumann, A. Jess, A. Seeberger, P. Wasserscheid, Ionic liquids in refinery desulfurization: comparison between biphasic and supported ionic liquid phase suspension processes, ChemSusChem 2 (2009) 969–977.

[42] N. Jose, S. Sengupta, J.K. Basu, Optimization of oxidative desulfurization of thiophene using Cu/titanium silicate-1 by box-behnken design, Fuel 90 (2011) 626–632.

[43] T.O. Sachdeva, K.K. Pant, Deep desulfurization of diesel via peroxide oxidation using phosphotungstic acid as phase transfer catalyst, Fuel Process. Technol. 91 (2010) 1133–1138.

[44] J. Qiu, G. Wang, D. Zeng, Y. Tang, M. Wang, Y. Li, Oxidative desulfurization of diesel fuel using amphiphilic quaternary ammonium phosphomolybdate catalysts, Fuel Process. Technol. 90 (2009) 1538–1542.

[45] F.M. Collins, A.R. Lucy, C. Sharp, Oxidative desulphurisation of oils via hydrogen peroxide and heteropolyanion catalysis, J. Mol. Catal. A: Chem. 117 (1997) 397–403.

[46] M. Te, C. Fairbridge, Z. Ring, Oxidation reactivities of dibenzothiophenes in polyoxometalate/H_2O_2 and formic acid/H_2O_2 systems, Appl. Catal. A: Gen. 219 (2001) 267–280.

[47] J.T. Zhang, W.S. Zhu, H.M. Li, W. Jiang, Y.Q. Jiang, W.L. Huang, Y.S. Yan, Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids, Green Chem. 11 (2009) 1801–1807.