Desulfurization of dibenzothiophene by chemical oxidation and solvent extraction with $Me_3NCH_2C_6H_5Cl·2ZnCl_2$ ionic liquid

Fa-tang Li,*[a] Rui-hong Liu,[a] Jin-hua Wen,[a] Di-shun Zhao,[b] Zhi-min Sun[a] and Ying Liu[a]

Received 5th September 2008, Accepted 12th March 2009
First published as an Advance Article on the web 1st April 2009
DOI: 10.1039/b815575e

Desulfurization of dibenzothiophene (DBT) by a combination of both chemical oxidation and solvent extraction was investigated. $Me_3NCH_2C_6H_5Cl·2ZnCl_2$ ionic liquid was prepared from cheap starting materials and used as extractant for oxidative desulfurization of DBT in *n*-octane. DBT in oil phase was extracted into ionic liquid phase and then oxidized to its corresponding sulfone by H_2O_2 and equal volume of acetic acid. The desulfurization yield of DBT in *n*-octane was 94% at 30 min under the conditions of H_2O_2/DBT molar ratio at 6 and *V* (ionic liquid) : *V* (*n*-octane) = 1 : 5, which was remarkably higher than that by mere extraction with ionic liquid (28.9%). The $Me_3NCH_2C_6H_5Cl·2ZnCl_2$ ionic liquid could be recycled six times without a significant decrease in activity. Kinetics of oxidative desulfurization of DBT by H_2O_2 and acetic acid was first-order with an apparent rate constant of 0.0842 min^{-1} and half-time of 8.23 min.

Introduction

Air pollution, caused by diesel exhaust gas (SO*x*), is one of the most serious problems in the world, and much attention has been focused on deep desulfurization of light oils. To protect the environment against contamination, the S-limit will be reduced in USA to a maximum of 15 ppm by 2010 and to 10 ppm in Europe by 2009.[1] Many other countries also have tightened their sulfur content specifications.

The removal of sulfur-containing compounds is carried out industrially *via* hydrodesulfurization (HDS). However, the HDS is limited in treating benzothiophenes (BTs) and dibenzothiophenes (DBTs).[2] Therefore, approaches based on adsorption,[3] extraction,[4] oxidation[5] and biodesulfurization[6] have been explored. Among them, oxidative desulfurization (ODS) is more attractive because BTs and DBTs can be oxidized to their corresponding sulfoxides and sulfones easily, which can be removed by extraction with water[7] or water-soluble polar solvents, such as dimethyl sulfoxide (DMSO),[8] 1-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF), *etc.*[9] Although the ODS processes are effective, one of the prime concerns is that the flammable and volatile organic compounds (VOCs) or water, employed as extractants, are leading to further environmental and safety concerns, such as wastewater emission and fire hazards.

Ionic liquids (ILs) have been extensively employed in gas separation,[10] liquid/liquid extraction,[11] chemical synthesis,[12] catalysis,[13] *etc.*,[14] because of their non-volatility, non-flammability, easy to handle, recyclable, good solubility characteristics, and high thermal stability.[15] Desulfurization of oils by extraction with ILs has been reported from 2001.[16–25] Compared with VOCs or water, ionic liquids have much higher extraction abilities which lead to shorter reaction time. Ionic liquids also have a much higher density, which makes it possible to readily recycle the ionic liquids for multiple extractions without additional environmental concern. Many types of ILs, such as $[BMIm]AlCl_4$,[16,17] $[EMIm]AlCl_4$,[16] $[EMIm]BF_4$,[18] $[BMIm]BF_4$,[18,19] $[BMIm]PF_6$,[18,19] $[BMIm][OcSO_4]$,[20] $[EMIm][EtSO_4]$,[20] $[BMIm]Cu_2Cl_3$,[21] [BMIm]DBP,[22] $[C_8MIm]BF_4$,[23] $[C_4MPy]SCN$,[24] $[EMIm]FeCl_4$,[25] have been employed in the extraction desulfurization of oils because of their high affinity to sulfur-containing compounds. The desulfurization yield of light oils, however, is relative low by only extraction with ILs. To improve efficiency of sulfur removal from light oils, a new effectual approach has been explored, which is chemical oxidation in conjunction with ILs extraction.[26–30] For instance, Gao and coworkers[26] used $[HMIm]BF_4$ as extractant and H_2O_2 as oxidant for sulfur removal of DBT-containing model oil, which could reach 60–93%. Li and coworkers[27,28] developed an extraction and catalytic oxidative desulfurization system composed of IL, H_2O_2 and catalyst. $[BMIm]BF_4$, $[OMIm]BF_4$, $[BMIm]PF_6$, $[OMIm]PF_6$, [BMIm]TA and [OMIm]TA doped with peroxotungsten and peroxomolybdenum complexes or molybdic compounds were selected for desulfurization as catalysts. The desulfurization yield of DBT-containing model oil could reach above 98%. Wei and coworkers[29] found $[BMIm]PF_6$ was a more effective solvent than $[BMIm]BF_4$ for providing an environment that results in a higher rate of chemical oxidation. Zhao *et al.*[30] studied the ODS of DBT by using $[HNMP]BF_4$ as extractant in the presence of H_2O_2 and pointed out that $[HNMP]BF_4$ was also a catalyst, which could decompose H_2O_2 to form hydroxyl radicals that were strong oxidizing agents for DBT.

However, the imidazolium- or pyrrolidonium-based ILs used as extractants previously are relatively expensive and it is impossible to use these ILs in industry. More recently, a series

---

[a] *College of Science, Hebei University of Science and Technology, Shijiazhuang, 050018, China. E-mail: lifatang@126.com; Fax: +86-311-88632009; Tel: +86-311-81668536*
[b] *College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, 050018, China*

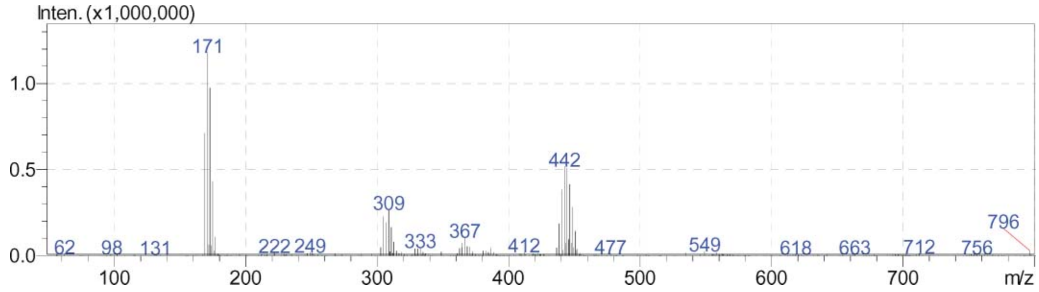


Fig. 1 Negative ion ESI-MS spectrum of BTMAC·2$ZnCl_2$.

of inexpensive ILs have been prepared from cheap starting materials, such as choline chloride·$x$$ZnCl_2$ and trimethylammonium chloride·$x$$AlCl_3$, which have been used in Fischer indole reactions,[31] protection of carbonyls[32] and also desulfurization of fuels.[18] The Lewis acidic ILs containing metal halide anions, such as $AlCl_4^-$,[19] $FeCl_4^-$[25] and $CuCl_2^-$,[21] have showed promising results on the removal of sulfur-containing compounds because of their inherent low fluidity and the π-complexation of metal anions with thiophenes. In this paper, $Me_3NCH_2C_6H_5Cl$·$x$$ZnCl_2$ (BTMAC·$x$$ZnCl_2$, x = 1~3), has been prepared from cheap starting materials of $Me_3NCH_2C_6H_5Cl$ and $ZnCl_2$ and used as extractant in ODS of DBT.

Results and discussion

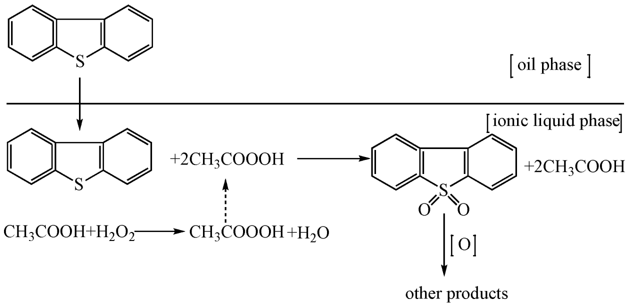
Structures of anions in $ZnCl_2$-based ionic liquid

To identify the Zn^{2+} species of BTMAC·$x$$ZnCl_2$ ionic liquid and verify its stability to air, electrospray ionization tandem mass (ESI-MS) spectral analysis was carried out. ESI-MS spectrum of BTMAC·2$ZnCl_2$ ionic liquid, as typical representative of BTMAC·$x$$ZnCl_2$, is shown in Fig. 1. Intensive peaks are observed at m/z 171, 309 and 442, which correspond to $ZnCl_3^-$, $Zn_2Cl_5^-$ and $Zn_3Cl_7^-$, respectively, using the atomic weights of Zn and Cl.

Wicelinski *et al.*[33] prepared ionic liquids composed of $AlCl_3$ with 1-butylpyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC) and found there were hydroxychloro and oxychloro anionic species (such as $Al_2Cl_6OH^-$, $Al_3Cl_7O_2H^-$) in the ionic liquids because of the strong Lewis acidity of anions. It indicated that the $AlCl_3$-based ionic liquids are moisture sensitive. Whereas there were no obvious oxygen-containing anionic species in Fig. 1, which showed that BTMAC·2$ZnCl_2$ was stable to moisture and air.

The process and mechanism of ODS/extraction by BTMAC·2$ZnCl_2$

There are two steps in the process of the oil–ionic liquid phase system of oxidation of DBT, containing the extractive equilibrium and the oxidative reaction.[34] In the first step, DBT is extracted from oil phase into ionic liquid until the extractive equilibrium is stabled. The second step is oxidation of DBT. In presence of H_2O_2, the acetic acid (AcOH) gives peracetic acid (CH_3COOOH), which is a strong oxidant and its oxidative ability is stronger than that of H_2O_2.[35] DBT in ionic liquid phase is oxidized to its corresponding sulfone ($DBTO_2$) by CH_3COOOH. The decrease of DBT concentration in ionic liquid promotes the extraction process and the sulfur content in the oil phase decreases continuously. On the basis of this and the combined oxidative process developed by Wei and coworkers,[29] the process of extraction and oxidation mechanism of DBT is proposed, as shown in Scheme 1.



Scheme 1 The process of extraction and oxidation mechanism of DBT using H_2O_2 and AcOH as the oxidants in an oil–ionic liquid system.

Extraction desulfurization performance of ILs for DBT in *n*-octane

Table 1 shows the Nernst partition coefficients k_N sulfur of DBT with BTMAC·$x$$ZnCl_2$ ILs. For comparison, some results of k_N with other ILs from literature are also listed.

As can be seen by the Nernst partition coefficients k_N listed in Table 1, all of the BTMAC·$x$$ZnCl_2$ ionic liquids show remarkable ability for sulfur removal. It is found that sulfur removal of model oil can reach above 23.3% after extraction with BTMAC·$x$$ZnCl_2$ ionic liquids, whereas the sulfur removal of DBT with imidazolium-based ILs are all below 20%. The reason for the difference of extraction capabilities is that the desulfurization mechanism with $ZnCl_2$-based ionic liquids is different from that with imidazolium-based ionic liquids. Hernández-Maldonado and Yang *et al.*[37] found there was π-complexation between DBT with Zn^{2+} when performing desulfurization with Zn(II)–X and Y zeolite sorbents. The mechanism for the extraction of sulfur-containing compounds with imidazolium-based IL is likely relevant to the formation of liquid clathrate due to the π–π interaction between the unsaturated bonds of the S-compound and the imidazolium ring of ILs.[22,36] In reference 19, Zhang *et al.* compared the absorption capacities of several ILs, including trimethylammonium chloride salt-aluminium trichloride ($AlCl_3$-TMAC),

Table 1 Nernst partition coefficients k_N for extraction of DBT with ILs

IL	k_N [mg of S (L of IL)$^{-1}$/mg of S (L of oil)$^{-1}$]	IL	k_N [mg of S (L of IL)$^{-1}$/mg of S (L of oil)$^{-1}$]
BTMAC·$ZnCl_2$[a]	1.52	BTMAC·3$ZnCl_2$[a]	1.68
BTMAC·1.5$ZnCl_2$[a]	1.82	[BMIm]BF[b]	0.96
BTMAC·2$ZnCl_2$[a]	2.03	[BMIm]TA[b]	0.79
BTMAC·2.5$ZnCl_2$[a]	1.89	[OMIm]TA[b]	1.02

[a] Reaction conditions: model oil = 10 mL, IL = 2 mL, the mixture was stirred at 30 °C for 10 min. [b] Results from Li and coworkers.[27] Model oil was prepared by dissolving DBT in *n*-octane to give a solution with S-content of 1000 ppm. Reaction conditions: model oil = 5 mL, IL = 1 mL, the mixture was stirred at 30 °C for 15 min.

[BMIm]PF_6, [BMIm]BF_4 and [EMIm]BF_4 for model organosulfur compounds and found that the absorption capacity of $AlCl_3$-TMAC was higher than that of others. So the π-complexation between lone pair electrons on organosulfur compounds and the unoccupied orbital on transition metal ions was higher than the π–π interaction between the unsaturated bonds of the S-compound and the imidazolium ring of IL. Compared to ionic liquids, the organic solvents show lower k_N. For example, Shiraishi *et al.*[8] reported that acetonitrile was considered to be the most suitable solvent for the extraction of the sulfur-containing compounds. As a result, the k_N was 1.32 and 0.19 when acetonitrile was employed as extractant to extract DBT from *n*-octane at 60 °C[38] and commercial light oil at ambient temperature,[8] respectively.

The high sulfur removal ability of BTMAC·*x*$ZnCl_2$ ionic liquids make them good extraction solvents for desulfurization. Although the Nernst partition coefficients are lower than that of DBT in *n*-dodecane with [BMIm]Cl/$AlCl_3$ (4.09),[16] BTMAC·*x*$ZnCl_2$ are also competitive ILs with wide developing prospect because they are cheap and insensitive to moisture and air. It also can be seen that the highest Nernst partition coefficient was 2.03 when BTMAC·2$ZnCl_2$ was used as extractant. That is, BTMAC·2$ZnCl_2$ is the ideal ionic liquid.

Relative Lewis acidity and viscosities of ionic liquids

The Lewis acidic strength of [HSO_3–$(CH_2)_3$–NEt_3]Cl–$ZnCl_2$ ionic liquids could be adjusted by varying the molar fraction of $ZnCl_2$ reported by previous literature.[39] Here the relative acidity of BTMAC·*x*$ZnCl_2$ ionic liquids is compared by FT-IR to investigate the reason why the molar ratio of $ZnCl_2$ to BTMAC affects the extraction performance. As shown in Fig. 2, pure acetonitrile shows two characteristic bands around 2292 and 2253 cm^{-1}, which are assigned to CN stretching vibrations. When acetonitrile is mixed with ionic liquids, a higher wavenumber around 2313 cm^{-1} appears. The band at around 2313 cm^{-1} is indicative of the existence of Lewis acidic sites. It is known that the higher intensity of characteristic band means the stronger Lewis acidity of the corresponding ionic liquid, so the Lewis acidity strength of the ionic liquids increased with the increase of the fraction of $ZnCl_2$. Zhang *et al.*[19] reported that the acidity change did not have a significant effect on the sulfur removal efficiency with ionic liquids and our extraction desulfurization results are in agreement with them. That is, Lewis acidity is not the only factor affecting the sulfur removal.

The viscosities of liquids always have a greater effect on their extraction ability. The viscosities of BTMAC·*x*$ZnCl_2$ ionic liquids are shown in Table 2.

The viscosities of the ionic liquids appear to be governed essentially by H-bonding.[40] When the molar ratio of $ZnCl_2$ to BTMAC increased from 1 to 1.5 or 2, the H-bonding between H^+ on the cation and Cl^- on the anion weakened and the viscosity decreased because of the existence of the large anion[41] of $ZnCl_3^-$, $Zn_2Cl_5^-$ and $Zn_3Cl_7^-$. However, when the molar ratio of $ZnCl_2$ to BTMAC exceeded 1.5 or 2, some $ZnCl_2$ could not fully react with BTMAC and the ionic liquid was not really pure, so the viscosity increased. It can be seen that the extraction performance of ionic liquids depends on both Lewis acidity and viscosity. That is, the extraction ability increases with the increase of Lewis acidity and the decrease of viscosity. By combining the influence of the two factors on the extraction ability of ionic liquid, BTMAC·2$ZnCl_2$ is the ideal ionic liquid.

Effect of H_2O_2/DBT molar ratio and IL/oil volume ratio on sulfur removal of DBT

To investigate the effect of the amount of oxidizing agent and extractant on the sulfur removal properties, the oxidation/extraction of DBT in *n*-octane under different H_2O_2/DBT (O/S) molar ratios and IL/oil volume ratios is carried out at 30 °C. The results are shown in Fig. 3 when BTMAC·2$ZnCl_2$, H_2O_2 and an equal volume of AcOH are employed as extractant and oxidants in the system, respectively. As can be seen, the sulfur removal of model gasoline increases with the increase of IL/oil volume ratio. When the IL/oil volume ratio is low (below 1 : 5), the extraction effect of IL for model gasoline is bad. As the IL/oil volume ratio goes above 1 : 5, *i.e.* 1 : 1, the sulfur removal of model gasoline increases slightly and much IL is wasted. So the most appropriate IL/oil volume ratio is 1 : 5.

In the presence of H_2O_2 and AcOH, DBT was oxidized chemically to $DBTO_2$ *etc.* and the remaining DBT in *n*-octane phase was further extracted into the IL phase. As shown in Fig. 3, the sulfur removal of DBT in oil phase continued to increase at different IL/oil volume ratios when the O/S molar ratio was increased from 2 : 1 to 10 : 1. According to the stoichiometric reaction, 2 mol of hydrogen peroxide are consumed for oxidation of 1 mol of DBT to $DBTO_2$. With the increase of H_2O_2, the oxidant had more opportunity to react with DBT and the desulfurization yield increased. It can be seen that when $V(IL)/V(oil) = 1 : 5$, the sulfur removal of DBT increased from 75.9% at a molar ratio of O/S = 2 to 94% at a molar ratio of O/S = 6. When the O/S molar ratio reached 8, 10 and 12, the sulfur removal of DBT increased slowly to 98, 98.5 and 99.1%, respectively. The results indicated that the optimal O/S molar ratio was 6 because less H_2O_2 was used, it is not economical to use excess amounts of oxidant.

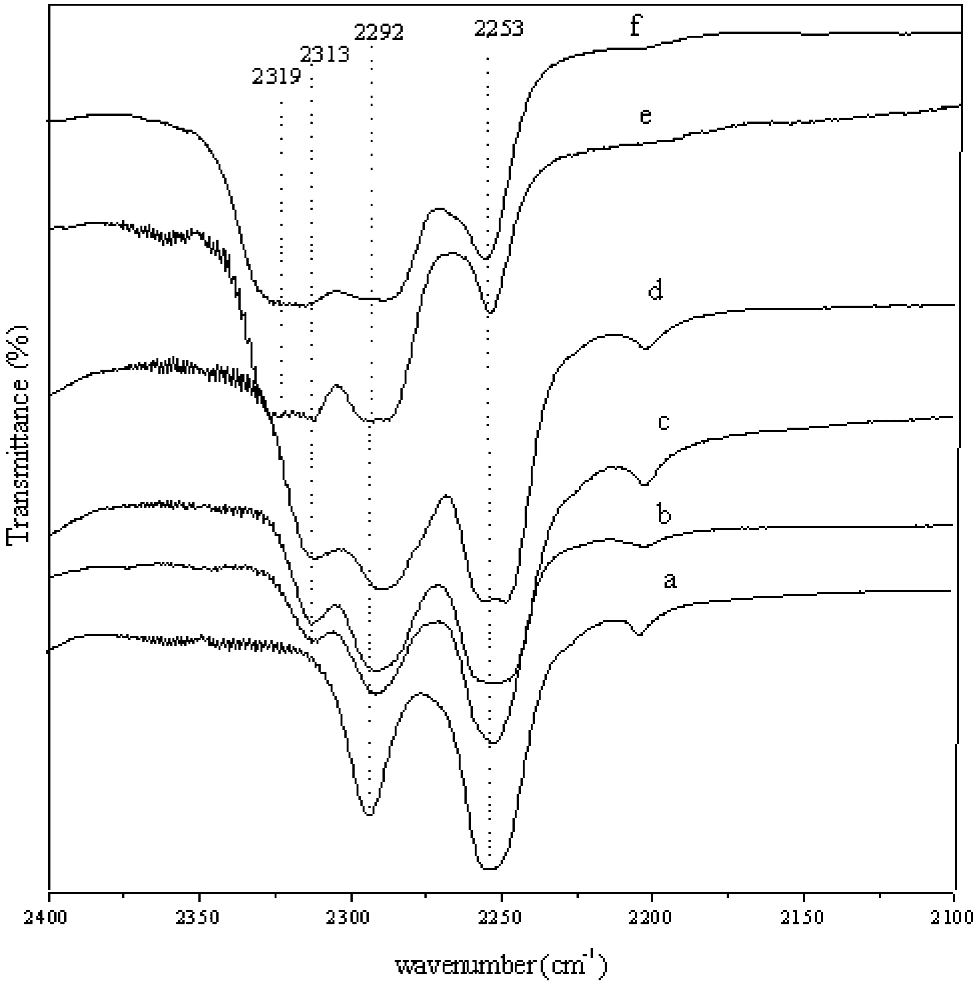


Fig. 2 FT-IR spectra of mixtures of acetonitrile and ionic liquids. (a) Pure acetonitrile, (b) molar ratio of $ZnCl_2$ to BTMAC = 1.0, (c) molar ratio of $ZnCl_2$ to BTMAC = 1.5, (d) molar ratio of $ZnCl_2$ to BTMAC = 2.0, (e) molar ratio of $ZnCl_2$ to BTMAC = 2.5 and (f) molar ratio of $ZnCl_2$ to BTMAC = 3.0.

Table 2 Dynamic viscosities at 30 °C (Pa s) of the BTMAC·xZnCl$_2$ ionic liquids

BTMAC·ZnCl$_2$	BTMAC·1.5ZnCl$_2$	BTMAC·2ZnCl$_2$	BTMAC·2.5ZnCl$_2$	BTMAC·3ZnCl$_2$
3.548	3.067	3.112	3.358	3.649

Kinetics of oxidation of DBT in *n*-octane by H_2O_2 and AcOH

To study kinetics of oxidation of DBT, samples (10 μL) were taken out from *n*-octane phase and measured with a micro coulometer to determine sulfur content every 5 min in the reaction course. The results are shown in Fig. 4.

The oxidation of DBT in tetradecane has been studied by Wei and coworkers[29], who found that the rate of DBT oxidation was first-order when excess H_2O_2 and AcOH were employed as oxidants and [BMIm]BF$_4$ or [BMIm]PF$_6$ was used as extractant. In this experiment, when the oxidation of DBT in *n*-octane by H_2O_2 and AcOH is assumed to be the first-order reaction, the sulfur content of model gasoline will meet eqn (1):[7]

$$\ln(C_0/C_t) = kt \qquad (1)$$

Where C_0 and C_t are the sulfur content of model gasoline at time zero and time t (s), respectively, and k is the first-order rate constant (min^{-1}). Half-life ($t_{1/2}$ (min)) is calculated using eqn (2), which is derived from eqn (1) by replacing C_t with $C_0/2$

$$t_{1/2} = 0.693/k \qquad (2)$$

Fig. 5 illustrates the time-course variation in $\ln(C_0/C_t)$ which was obtained from data shown in Fig. 4. k and $t_{1/2}$ could be calculated. k and $t_{1/2}$ were 0.0842 min^{-1} and 8.23 min, respectively. Here, the results of the experiments strongly supported the first-order reaction of oxidation kinetics of DBT.

Regeneration/recycling of ionic liquid

The recycling of the BTMAC·2ZnCl$_2$ was investigated in ODS of DBT in *n*-octane. After the reaction, the ionic liquid phase was recycled and residual oxidizing agents (H_2O_2 and AcOH) were evaporated from the ionic liquid. Then the system was charged again with fresh H_2O_2 and AcOH for the next run.

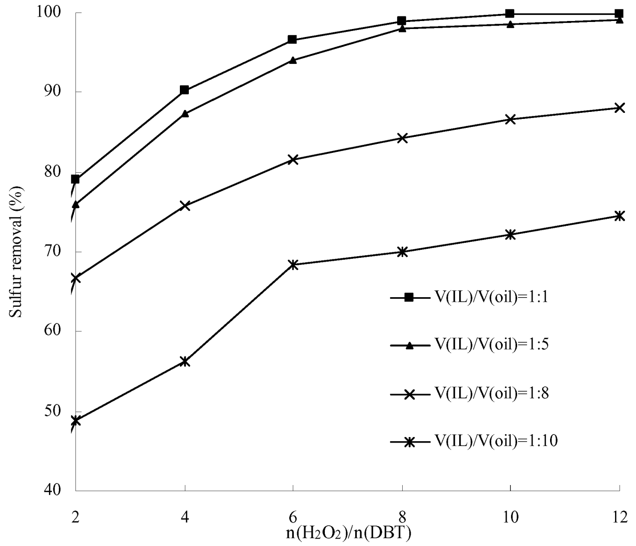


Fig. 3 Effect of H_2O_2/DBT molar ratio and IL/oil volume ratio on sulfur removal of DBT. Reaction conditions: model oil = 10 mL, *t* = 30 min, 30 °C.

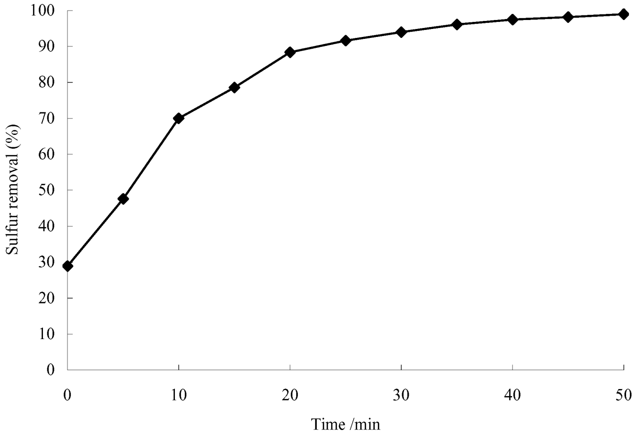


Fig. 4 Time-course variation of sulfur removal of DBT in *n*-octane. Reaction conditions: *T* = 30 °C; model oil = 10 mL, IL = 2 mL; molar ratio of O/S = 6.

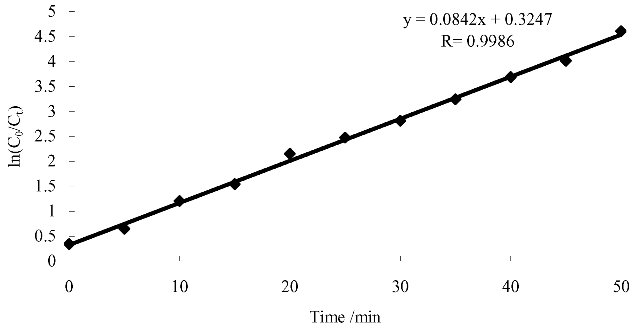


Fig. 5 Time-course variation of $\ln(C_0/C_t)$. Reaction conditions: *T* = 30 °C; model oil = 10 mL, IL = 2 mL; molar ratio of O/S = 6.

After four times, $DBTO_2$ was precipitated in the ionic liquid phase and reclaimed from the ionic liquid by centrifugation. The data shown in Table 3 indicated that the BTMAC·2$ZnCl_2$ ionic liquid could be recycled six times without a significant decrease in activity. When six cycles had finished, the desulfurization yield decreased slightly with the increase of the cycle. The reason was that $DBTO_2$ in the ionic liquid was more and more and the extraction performance of ionic liquid decreased.

Table 3 Recycle of BTMAC·2$ZnCl_2$ in desulfurization of model oil[a]

Cycle	Sulfur removal (%)	Cycle	Sulfur removal (%)
1	94	5	93.8
2	93.7	6	93.0
3	93.2	7	92.1
4	92.5	8	91.2

[a] Reaction onditions: *T* = 30 °C; *t* = 30 min; model oil = 10 mL, IL = 2 mL; molar ratio of O/S = 6.

Conclusion

BTMAC·2$ZnCl_2$ ionic liquid is an excellent extraction solvent because it is not only stable to moisture and air, but also exhibits remarkable extraction desulfurization for DBT in *n*-octane, which may be attributed to the π-complexing interaction of DBT and Zn(II). In the presence of H_2O_2 and AcOH, DBT is extracted from oil phase and oxidized to its corresponding sulfone. The desulfurization yield of DBT can reach 94% at 30 min and 99% at 50 min. The BTMAC·2$ZnCl_2$ ionic liquid can be recycled six times without a significant decrease in activity. The kinetics of oxidative desulfurization of DBT by H_2O_2 and AcOH is first-order with an apparent rate constant of 0.0842 min^{-1} and half-time of 8.23 min. All the experiments were conducted at room temperature and it was easy to handle. The study on extraction/oxidation desulfurization of DBT can guide the desulfurization of light oils.

Experimental

Preparation of ionic liquids and detection of the structure of anions in ionic liquid

Anhydrous $ZnCl_2$ and $Me_3NCH_2C_6H_5Cl$ were used as received. $Me_3NCH_2C_6H_5Cl$ (0.1 mol) was mixed with $ZnCl_2$ (0.1 *x*mol, *x* = 1–3) and heated to *ca.* 120 °C in air with stirring until a clear colorless liquid was obtained.

Structure of anions in ionic liquid was detected *via* ESI-MS, which had been confirmed by Ko *et al.*[25] to be an ideal analytical tool in characterizing the structure of negative ions in IL. ESI-MS spectrum of BTMAC·2$ZnCl_2$ was collected on Shimadzu 2010EV LC-MS.

Evaluation of the Lewis acidity and measurement of viscosity of ionic liquids

FT-IR spectra were obtained on Shimadzu IRPrestige 21 spectrometer. Acetonitrile was used as a base probe molecule to determine the acidity of ionic liquids. The detail process was similar to that outlined in the previous literature.[42] The measurement of viscosity was carried out using an NDJ-8S rotational viscometer.

Oxidative desulfurization of DBT in *n*-octane

0.056 g DBT was dissolved in 10 mL *n*-octane to form the model oil, the sulfur content of which was 1000 μg mL^{-1}. IL (1–10 mL) was then added and mixed with the oil. The sulfur content of oil was detected using a micro coulometer with the process of extraction. After 10 min, the sulfur content of oil did not change which meant that the extraction equilibrium of DBT in oil and ionic liquid phase was reached. 30 wt% H_2O_2 and an equal volume of AcOH were added to the mixture, which was then stirred vigorously. The upper phase (model oil) was periodically withdrawn and analyzed for sulfur content using a micro coulometer.

Recovery/regeneration of used ionic liquid

At the end of each run, the ionic liquid phase was separated by decantation from the oil phase. The oxidizing agents were then evaporated from the ionic liquid phase at 100 °C for 3 h by rotary evaporation. The $DBTO_2$ was not removed from the ionic liquid. The fresh H_2O_2, AcOH and model oil were introduced for the next reaction under the same conditions as described above. By this procedure, the $DBTO_2$ was accumulated in the ionic liquid successively. The solubility of $DBTO_2$ in BTMAC·$2ZnCl_2$ ionic liquid is about 1805 ppm calculated by S-content and $DBTO_2$ is insoluble in *n*-octane. After four times, there was yellow solid, *i.e.* $DBTO_2$ in the ionic liquid phase. Then $DBTO_2$ was reclaimed from the ionic liquid by centrifugation and the ionic liquid was reused.[27,29]

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (under No. 20806021 and 20576026) and the Scientific Research Project Item of Hebei Province Educational Department (under No. 2007440).

References

1 J. M. Campos-Martin, M. C. Capel-Sanchez and J. L. G. Fierro, *Green Chem.*, 2004, **6**, 557–562.
2 M. Houalla, D. Broderick, A. V. Sapre, N. K. Nag, V. H. J. de Beer, B. C. Gates and H. Kwart, *J. Catal.*, 1980, **61**, 523–527.
3 J. G. Park, C. H. Ko, K. B. Yi, J. H. Park, S. S. Han, S. H. Cho and J. N. Kim, *Appl. Catal. B*, 2008, **81**, 244–250.
4 N. H. Ko, J. S. Lee, E. S. Huh, H. Lee, K. D. Jung, H. S. Kim and M. Cheong, *Energy Fuels*, 2008, **22**, 1687–1690.
5 X. Ma, A. Zhou and C. Song, *Catalysis Today*, 2007, **123**, 276–284.
6 M. Soleimani, A. Bassi and A. Margaritis, *Biotechnology Advances*, 2007, **25**, 570–596.
7 D. S. Zhao, F. T. Li, E. P. Zhou and Z. M. Sun, *Chemical Research in Chinese Universities*, 2008, **24**, 96–100.
8 Y. Shiraishi, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.*, 1998, **37**, 203–211.
9 J. T. Sampanthar, H. Xiao, J. Dou, T. Y. Nah, X. Rong and W. P. Kwan, *Appl. Catal. B*, 2006, **63**, 85–93.
10 M. Schilderman, S. Raeissi and C. J. Peters, *Fluid Phase Equilibria*, 2007, **260**, 19–22.
11 Y. P. Tzeng, C. W. Shen and T. Yu, *Journal of Chromatography A*, 2008, **1193**, 1–6.
12 E. K. Goharshadi, Y. Ding and P. Nancarrow, *Journal of Physics and Chemistry of Solids*, 2008, **69**, 2057–2060.
13 B. C. Ranu, S. Banerjee and A. Das, *Tetrahedron Letters*, 2006, **47**, 881–884.
14 D. Wei and A. Ivaska, *Analytica Chimica Acta*, 2008, **607**, 126–135.
15 T. Welton, *Coordination Chemistry Reviews*, 2004, **248**, 2459–2477.
16 A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz and P. Wasserscheid, *Chem. Commun.*, 2001, 2494–2495.
17 R. Schmidt, *Energy Fuels*, 2008, **22**, 1774–1778.
18 S. Zhang and Z. C. Zhang, *Green Chem.*, 2002, **4**, 376–379.
19 S. Zhang, Q. Zhang and Z. C. Zhang, *Ind. Eng. Chem. Res.*, 2004, **43**, 614–622.
20 J. Eßer, P. Wasserscheid and A. Jess, *Green Chem.*, 2004, **6**, 316–322.
21 C. Huang, B. Chen, J. Zhang, Z. Liu and Y. Li, *Energy Fuels*, 2004, **18**, 1862–1864.
22 Y. Nie, C. Li, A. Sun, H. Meng and Z. Wang, *Energy Fuels*, 2006, **20**, 2083–2087.
23 L. Alonso, A. Arce, M. Francisco, O. Rodriguez and A. Soto, *AIChE Journal*, 2007, **53**, 3108–3115.
24 J. D. Holbrey, I. Lopez-Martin, G. Rothenberg, K. R. Seddon, G. Silvero and X. Zheng, *Green Chem.*, 2008, **10**, 87–92.
25 N. H. Ko, J. S. Lee, E. S. Hub, H. Lee, K. D. Jung, H. S. Kim and M. Cheong, *Energy Fuels*, 2008, **22**, 1687–1690.
26 L. Lu, S. Cheng, J. Gao, G. Gao and M. Y. He, *Energy Fuels*, 2007, **21**, 383–384.
27 W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He and J. Xia, *Green Chem.*, 2008, **10**, 641–646.
28 W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He and J. Xia, *Energy Fuels*, 2007, **21**, 2514–2516.
29 W. H. Lo, H. Y. Yang ang and G. T. Wei, *Green Chem.*, 2003, **5**, 639–642.
30 D. Zhao, J. Wang and E. Zhou, *Green Chem.*, 2007, **9**, 1219–1222.
31 R. C. Morales, V. Tambyrajah, P. R. Jenkins, D. L. Davies and A. P. Abbott, *Chem. Commun.*, 2004, 158–159.
32 Z. Duan, Y. Gu and Y. Deng, *Catalysis Communication*, 2006, **7**, 651–656.
33 S. P. Wicelinski, R. J. Gale, K. M. Pamidimukkala and R. A. Laine, *Analytical Chemistry.*, 1988, **60**, 2228–2232.
34 D. Zhao, H. Ren, J. Wang, Y. Yang and Y. Zhao, *Energy Fuels*, 2007, **21**, 2543–2547.
35 S. Mallik, K. M. Parida and S. S. Dash, *Journal of Molecular Catalysis A: Chemical*, 2007, **261**, 172–179.
36 J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, O. Sheppard, C. Hardacre and R. D. Rogers, *Chem. Commun.*, 2003, **4**, 476–477.
37 J. Hernández-Maldonado, F. H. Yang, G. Qi and R. T. Yang, *Appl. Catal. B*, 2005, **56**, 111–126.
38 K. Yazu, Y. Yamamoto, T. Furuya, K. Miki and K. Ukegawa, *Energy Fuels*, 2001, **15**, 1535–1536.
39 S. Liu, C. Xie, S. Yu and F. Liu, *Catalysis Communications.*, 2008, **9**, 2030–2034.
40 P. Bonhte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grtzel, *Inorg. Chem.*, 1996, **35**(5), 1168–1178.
41 A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and W. John, *J. Phys. Chem.*, 1984, **88**(12), 2614–2621.
42 H. Xin, Q. Wu, M. Han, D. Wang and Y. Jin, *Appl. Catal. A*, 2005, **292**, 354–361.