A Carbonium Pseudo Ionic Liquid with Excellent Extractive Desulfurization Performance

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Lewis hard acid $AlCl_3$ was softened by some butyl halides forming highly polarized liquids. These liquids are similar to the ionic liquids (ILs) with metallic complex anion and varying composition, and thus termed here as carbonium pseudo ILs (CPILs). The CPILs, that is, t-C_4H_9Cl-$AlCl_3$*,* n-C_4H_9Cl-$AlCl_3$*, and* t-C_4H_9Br-$AlCl_3$*, show very strong desulfurization activity for various thiophenic compounds like 3-methylthiophene, benzothiophene, and dibenzothiophene. The above thiophenic compounds can be removed completely from model oils within 20 min by a very small amount of CPILs reactive extractant. The extractive mechanism is deemed as an acid–base complexation along with alkylation of the thiophenic compounds, and the Lewis acidity comes from both carbonium ion (borderline acid) and the dissolved $AlCl_3$ (hard acid). The* t-C_4H_9Cl-$AlCl_3$ *shows good selectivity for three thiophenic compounds even in toluene-containing system. Further, some CPILs show satisfactory desulfurization performance for the model gasoline that mimics the composition of real one.*

Keywords: carbonium pseudo ionic liquid, softening hard acid, Lewis acid, complexation, extractive desulfurization

Introduction

Aromatic sulfur (S-) compounds in the real gasoline and diesel, that is, thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), and their alkyl substituted derivatives,[1] result in a great many environmental problems such as acidic rain. The desulfurization methods with respect to the real oil are studied extensively with scientific development and official requirement. Currently, hydrodesulfurization (HDS) is the main process, being deemed as one of industrial application methods. However, the HDS encounters a very big challenge due to the harsh conditions. Thus, some alternative methods have been also explored for a long time, including adsorption desulfurization, extraction desulfurization (EDS), and oxidation desulfurization. Among them, Lewis acid–base desulfurization attracts a lot of researchers. Ionic liquids (ILs) as novel extractants show quite excellent desulfurization ability. A Lewis acid IL ([Bmim]Cl-$AlCl_3$) is used to extract DBT in model oil for the first time, other Lewis acid ILs (TMAC-$AlCl_3$, [Bmim]Cl-$FeCl_3$, and [Bmim]Cl-CuCl) are then investigated for sulfur removal,[2–5] and, the EDS of [Emim]BF_4, [Bmim]PF_6, [Bmim]BF_4, [Opy]BF_4, [Bmim]DBP, [Emim]DEP, and [Emim]$N(CN)_2$ are reported, too.[6–10] Moreover, the mechanism of ILs desulfurization starts to be explained by molecular dynamics simulation and quantum chemical study.[11,12] In fact, the thiophenic compounds are removed by the ILs through a soft acid-soft base interaction. However, the ILs that show weak Lewis acidity will interact competitively with other soft base (benzene or toluene), which results in the inferior selectivity for thiophenic compounds. To improve desulfurization efficiency and selectivity, an appropriate acid–base interaction is very crucial for sulfur removal process. For example, π-complexation of Cu(I)-Y and Ag(I)-Y zeolites is stronger for the thiophenic compounds than for other aromatics (benzene).[13] Meanwhile, tetranitrofluorenone shows a high selectivity for DBT since it is a strong and soft acid and thus interact favorably with stronger base DBT instead of 1-methylnaphthalene.[14] In contrast, the favorable S-M direct interaction between Ce^{4+} and S atom on thiophene also arises from the

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Additional Supporting Information may be found in the online version of this article.

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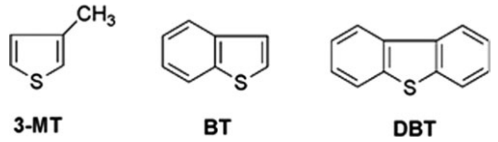


Figure 1. The three S-compounds in model oil.

weak combination between hard acid Ce^{4+} and soft base benzene.[15] Studies carried out previously indicate that strong and hard Lewis acid $AlCl_3$ manages to remove 3-methylthiophene (3-MT) and BT by acid–base complexation, but it fails to remove DBT, for detail see Supporting Information (Table S1).[16] To remove effectively more S-compounds, the hard acid $AlCl_3$ needs to be softened to form a new Lewis acid system. According to organic chemistry theory, alkyl halide and inorganic Lewis acid are apt to combine with each other and create carbonium ion intermediate. It is reported that tert-butyl carbonium ion ($[Tebu]^+$) can stably exist in the presence of strong Lewis acid such as SbF_5.[17] The carbonium ion formed is still a strong Lewis acid due to its electron-deficient property, and, the $[Tebu]^+$ is a softer Lewis acid than $AlCl_3$, as Pearson pointed out that $[Tebu]^+$ belongs to a borderline acid.[18] Presumably, the mixture of alkyl halide and $AlCl_3$ may remove efficiently aromatic S-compounds by the acid–base complexation. In model oil, three thiophenic compounds (3-MT, BT, and DBT) used are seen in Figure 1, in which 3-MT and BT are deemed as the model S-compounds of the gasoline, and DBT simulates those of the diesel.

The objective of this work is to soften the hard acid to form some new Lewis acid systems containing carbonium ion, use them to remove aromatic S-compounds and discuss the desulfurization mechanism involved. It is showed that $AlCl_3$ can be softened by a series of alkyl halide, viz t-C_4H_9Cl, n-C_4H_9Cl, and t-C_4H_9Br. Meanwhile, some highly polarized liquids are formed during the softening process, and their appearance and composition is similar to traditional ILs, being termed vividly as carbonium pseudo ILs (CPILs). Further, the desulfurization experiments show that the t-C_4H_9Cl-$AlCl_3$ and n-C_4H_9Cl-$AlCl_3$ are able to remove completely 3-MT, BT, and DBT in model oil within 20 min. The desulfurization mechanism is then discussed deeply, proposing that the extractive desulfurization process is a Lewis acid–base (electron donor–acceptor) complexation along with the alkylation of thiophenic compounds. As expected, the desulfurization performance of t-C_4H_9Cl-$AlCl_3$ and n-C_4H_9Cl-$AlCl_3$ for 3-MT and BT in toluene-rich (25 wt % toluene) system is still amazing. However, the S-content of DBT in toluene-containing system shows the different tendency for the two CPILs mentioned above. Satisfactorily, the desulfurization performances of three CPILs are all good in model gasoline (MG) containing the complex composition.

Experimental Section

Chemical materials

3-MT (ACROS, >99%), BT (ACROS, >99%), and DBT (ACROS, >99%) were purchased from J&K Scientific, and their chemical structure were shown in Figure 1. *Tert*-butyl chloride (AR), nomal-butyl chloride (AR) and n-octane (AR) were bought from Tianjin Guangfu Fine Chemical Industry Institute. *Tert*-butyl bromide (CP) was the product of Beijing Jinlong Chemical, and normal-butyl bromide (AR) was the reagent of Beijing Yili Fine Chemical. Aluminium chloride anhydrous ($AlCl_3$, >99%) and ferric chloride anhydrous ($FeCl_3$, >99%) were made by Shantou Xilong Chemical. Di-n-butyl sulfide (>98%) and 1-hexene (>98%) are from Alfa Aesar, whereas thiophene (>99%) and cyclohexene (>98%) are the agents of Sinopharm Chemical Reagent. Benzene (AR), toluene (AR), and cyclohexane (AR) came from Beijing Chemical Industry. Cumene (AR) is bought from Aladdin Chemistry.

Extractive desulfurization process

The model oils used here are a binary solution of n-octane and an organic S-compound namely 3-MT, BT, or DBT with their S-content all being 1000 μg/g. A certain amount of alkyl halides were added first into 20 g model oil, the Lewis acids were then added directly, too. All the experiments were under magnetic stirring, and samples (0.2 ml for each) at different time were taken out for the analysis of S-content after filtering the impurity by microfiltration membrane (0.22 μm). The whole desulfurization experiment was controlled within 20 min. To study the products extracted in bottom phase, oil layer was removed by decantation while dilute HCl solution and CH_2Cl_2 were added into the system to destroy the t-C_4H_9Cl-$AlCl_3$ and dissolve the products. After the separating operation, the products were recovered by evaporating CH_2Cl_2 and other low boiling point substances completely, and their composition could be then characterized by ^{1}H-nuclear magnetic resonance (NMR) and gas chromatography mass spectrometry (GC-MS). The complex composed of the t-C_4H_9Cl-$AlCl_3$ and S-compounds was dissolved in CH_2Cl_2 after removing the oil phase, and then analyzed by UV spectrum. The toluene-containing model oil (25 wt % toluene; S-content 1000 μg/g) was prepared to study the influence of other aromatics on desulfurization performance of the C_4H_9Cl-$AlCl_3$. Moreover, the MG containing various components similar to real oil was prepared, in which the desulfurization activity of three CPILs is investigated, too.

Analysis methods

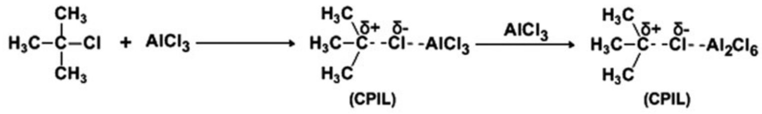
The S-content with regard to 3-MT, BT, DBT and their butyl substituted derivatives in model oils was analyzed by high performance liquid chromatography (HPLC) using external standard method (Shimadzu 10A-VP, equipped with UV–vis detector and a C-18 column; wavelength 242 nm for 3-MT, 251 nm for BT, and 310 nm for DBT; methanol:water = 8:2 for 3-MT and BT, methanol:water = 9:1 for DBT; flow rate= 1 ml/min) with its minimum detectable S-content being about 0.2 μg/g for 3-MT and BT, 0.3 μg/g for DBT, and the maximum relative error of S-content determined by the HPLC is within 2% (100–1000 μg/g), 4% (10–100 μg/g), 10% (1–10 μg/g), and 30% (<1 μg/g). The total S-content of BT-toluene system and MG is determined by sulfur and nitro analyzer (KY-3000SN, Keyuan Electronic Instrument, China) with its minimum detectable S-content being about 0.2 μg/ml. Some complexes, that is, the mixture of thiophenic compounds and t-C_4H_9Cl-$AlCl_3$, were dissolved in CH_2Cl_2 following identification by UV spectrum (Beijing Labtech). The S-compounds extracted by the t-C_4H_9Cl-$AlCl_3$ were characterized by GC-MS (HP 6890-Quattro II; HP-35 MS column, 25 m × 0.25 mm × 0.25 μm; temperature program: 50°C for 1 min–temperature rising 10°C/min—280°C for 10 min) and ^{1}H-NMR spectrum using AV400 NMR spectrometer (Bruker) in dimethylsuloxide (DMSO)-d6 solvent.

Results and Discussion

Extractive desulfurization of the CPILs

Two alkyl halides, namely t-butyl chloride and n-butyl chloride, were used to soften hard acid $AlCl_3$ to explore their

(a). The formation mechanism of the t-C_4H_9Cl-$AlCl_3$



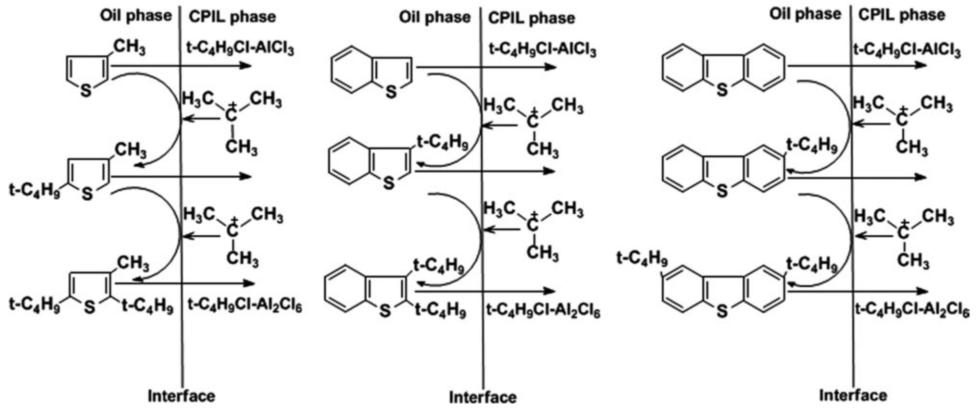
(b). The formation mechanism of the traditional Lewis acid ILs[3-5]

$$(CH_3)_3\overset{+}{N}HCl + AlCl_3 \longrightarrow (CH_3)_3\overset{+}{N}HAlCl_4^- \xrightarrow{AlCl_3} (CH_3)_3\overset{+}{N}HAl_2Cl_7^-$$

$$Bmim^+Cl^- + FeCl_3 \longrightarrow Bmim^+FeCl_4^- \xrightarrow{FeCl_3} Bmim^+Fe_2Cl_7^-$$

$$Bmim^+Cl^- + CuCl \longrightarrow Bmim^+CuCl_2^- \xrightarrow{CuCl} Bmim^+Cu_2Cl_3^-$$

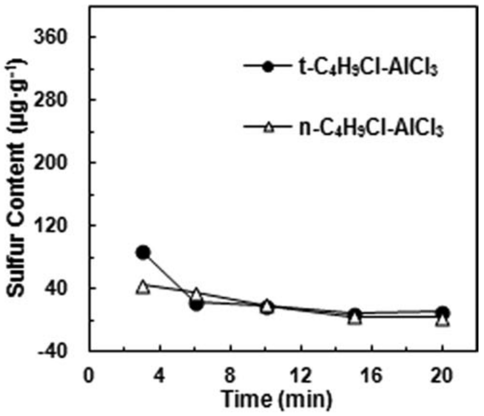
(c). The interaction mechanism between the CPIL and aromatic S-Compounds[20-22]



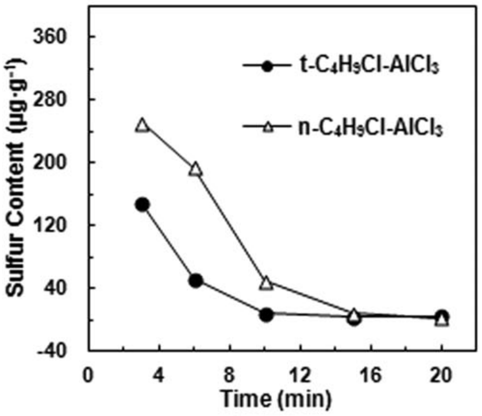
Scheme 1. The formation and complexing extraction mechanism of the CPIL.

desulfurization activity. Fivefold (mole ratio for sulfur) butyl chloride and fivefold $AlCl_3$ were added into 20 g model oil for stirring 20 min at 303 K, S-content of different samples (0.2 ml for each) was analyzed by HPLC. In the extraction process, two phases are formed gradually coupled with the stirring proceeding, it can be known that the upper is the oil phase, and bottom phase is the mixture of butyl chloride and $AlCl_3$. The mixture formed such as *t*-C_4H_9Cl-$AlCl_3$ is a viscous and highly polarized liquid, and its composition is like conventional Lewis acid ILs with metallic complex anion and varying composition (TMAC-$AlCl_3$, BmimCl-$FeCl_3$ and BmimCl-CuCl) presented in Schemes 1a, b.[3–5] Thus, the liquid mixture *t*-C_4H_9Cl-$AlCl_3$ can be named as CPIL considering the partially electropositive carbon atom on the *t*-butyl. Further, the bottom phase color changes gradually with the extraction process, more specifically, golden yellow for 3-MT, bright red for BT and dark red for DBT, which implies the desulfurization process is the acid–base complexing extraction.

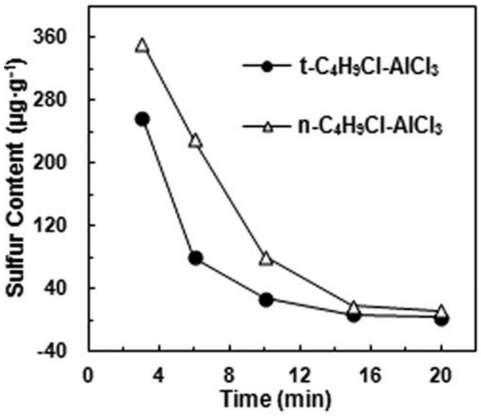
In this process, however, some new small peaks in oil phase are detected by HPLC besides those of initial S-components, which may be explained by the fact that thiophenic compounds are alkylated due to inevitable Friedel–Crafts alkylation reaction. To determine the S-content of butyl substituted S-components (3-MTs, BTs, and DBTs), their peak area responses to the S-contents have been analyzed in terms of the HPLC peak area, for detail see Supporting Information. Thereby, the S-content described in this article means the total S-content in specific model oil. Figure 2 presents the relationship between S-content of three thiophenic compounds and time with respect to *t*-C_4H_9Cl-$AlCl_3$ and *n*-C_4H_9Cl-$AlCl_3$. It is seen surprisingly that the S-content of three aromatic S-compounds dramatically decreases with time, and S-components can be hardly detected in oil layer after 15 min. Considering negligible interaction between sole $AlCl_3$ and DBT,[16] the experimental results indicate that the hard acid $AlCl_3$ has been softened by butyl chloride, and the new Lewis acid system formed (*t*-C_4H_9Cl-$AlCl_3$ and *n*-C_4H_9Cl-$AlCl_3$) have very good desulfurization activity. Meanwhile, the high efficiency of sulfur removal for the three S-compounds is very amazing under such a small amount of extractants compared with other traditional ILs. As listed in Table 1, the desulfurization yield of *t*-C_4H_9Cl-$AlCl_3$ is 99.2% for 3-MT, 99.6% for BT, and 99.4% for DBT at 15 min, respectively, which is much more than that of the traditional Lewis acid ILs. It could be assumed that the *t*-C_4H_9Cl-$AlCl_3$ is a novel extractant for the complexing desulfurization. Moreover, the desulfurization rate of the two CPILs for three thiophenic compounds follows the order of 3-MT > BT > DBT as presented in Figure 2, which implies the new Lewis acid system formed may still belong to hard acid. It can be also seen that *t*-butyl chloride shows stronger desulfurization activity than *n*-butyl chloride in the presence of $AlCl_3$, especially for BT and DBT as shown in Figures 2b, c. The difference between *t*-C_4H_9Cl-$AlCl_3$ and *n*-C_4H_9Cl-$AlCl_3$ is attributed mainly to the stability of their carbonium ions, in which quaternary carbonium ion is much more stable than primary one. So, *tert*-butyl carbonium ion ([Tebu$^+$]) is more easily formed than nomal-butyl carbonium ion ([Nobu]$^+$), and thus *t*-C_4H_9Cl-$AlCl_3$ shows more electropositive on the central carbon atom than *n*-C_4H_9Cl-$AlCl_3$, that is, stronger Lewis acidity, resulting in a better acid–base complexation in model oil.



a. 3-MT



b. BT



c. DBT

Figure 2. The relationship between S-content of different S-compounds and time.

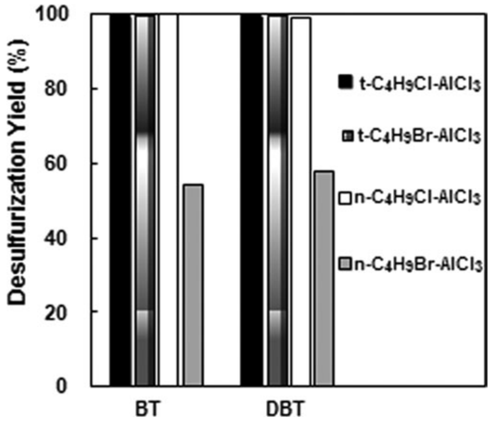


Figure 3. The desulfurization yield comparison among four CPILs.

To know more about desulfurization performance of the novel CPILs, t-C_4H_9Br-$AlCl_3$ and n-C_4H_9Br-$AlCl_3$ are selected to explore their desulfurization activity for BT and DBT, the adding quantities of butyl bromide and $AlCl_3$ are both fivefold mole ratio for sulfur, and the experiment conditions are same to those of the previous system, that is, the temperature is 303 K and the extraction time is controlled in 20 min. As presented in Figure 3, n-C_4H_9Br-$AlCl_3$ shows the lowest extractive efficiency for BT and DBT at 20 min. There are two reasons, one is still the weaker stability of $[\text{Notu}]^+$ than that of $[\text{Tebu}]^+$, the other is that Br atom combines more difficultly with $AlCl_3$ than Cl atom due to its larger atom radius, which causes smaller amount of the carbonium ions. It can be also seen that t-C_4H_9Br-$AlCl_3$ has no significant difference from t-C_4H_9Cl-$AlCl_3$ in terms of the sulfur removal, which may be attributed to the fact that the strong activity of $[\text{Tebu}]^+$ covered up the negative effect of Br atom.

Figure 4 presents the comparison of t-C_4H_9Cl-$FeCl_3$ and t-C_4H_9Cl-$AlCl_3$ in terms of desulfurization activity at 303 K. In this system, the amounts of inorganic Lewis acid and t-butyl chloride are both fivefold mole ratio for sulfur, and the time is 20 min. Compared with t-C_4H_9Cl-$AlCl_3$, the desulfurization performance of t-C_4H_9Cl-$FeCl_3$ is good for 3-MT but negligible for BT and DBT. It can be explained that $FeCl_3$ has weaker Lewis acidity than $AlCl_3$, which results in unstable combination between $FeCl_3$ and t-butyl chloride, thereby the formation of $[\text{Tebu}]^+$ is more difficult. Considering the fact that sole $FeCl_3$ shows weak complexation with BT and DBT, the insufficient $[\text{Tebu}]^+$ leads directly to negligible desulfurization performance. However, the t-C_4H_9Cl-

Table 1. Comparison of Sulfur Removal Rate Between the CPIL and Traditional ILs

Extractants	S-Compounds	S-Content (μg/g)	Extractant/Oil (g/g)	Extraction Time (min)	Desulfurization Yield (%)
t-C_4H_9Cl-$AlCl_3$	3-MT	1000	0.176/5	15	99.2
BmimCl-CuCl*	T	680	1/5	30	23.4
t-C_4H_9Cl-$AlCl_3$	BT	1000	0.176/5	15	99.6
$OpyBF_4$[†]	BT	160	1/5	15	28.1
t-C_4H_9Cl-$AlCl_3$	DBT	1000	0.176/5	15	99.4
BmimCl-$AlCl_3$[‡]	DBT	500	1/5	15	45.0
$BmimBF_4$[§]	DBT	747	1/5	30	12.0

*Ref. 5.
[†] Ref. 8.
[‡] Ref. 2.
[§] Ref. 3.

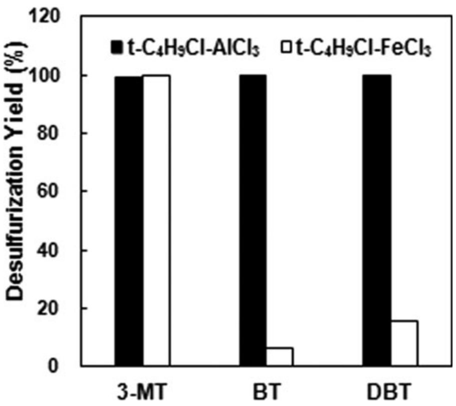


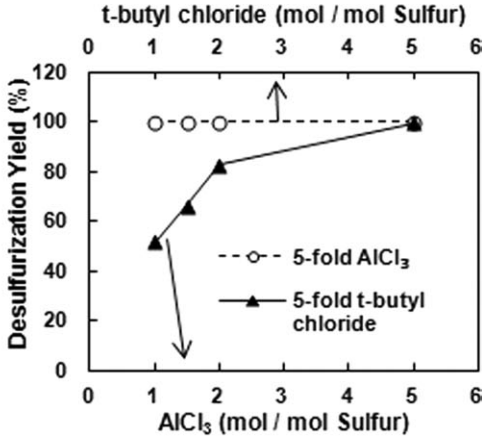
Figure 4. The desulfurization yield comparison between *t*-C_4H_9Cl-$AlCl_3$ and *t*-C_4H_9Cl-$FeCl_3$.

$FeCl_3$ can also remove 3-MT rapidly, which may be ascribed to the fact that the sole $FeCl_3$ can effectively remove 3-MT as listed in Supporting Information Table S1.[16]

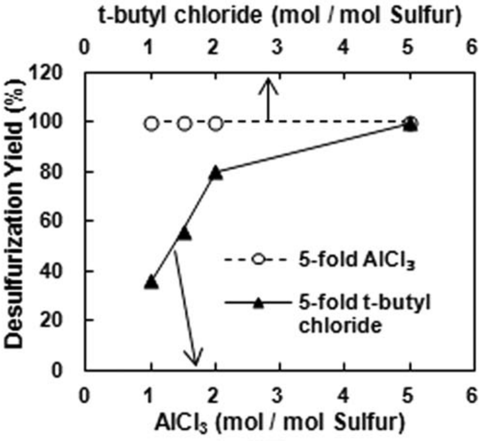
Other factors influencing the desulfurization of t-C_4H_9Cl-$AlCl_3$

As stated previously, S-compounds can be efficiently removed by the CPILs, thus one of them *t*-C_4H_9Cl-$AlCl_3$ is chosen for further study. Two factors, that is, different mole ratio ($AlCl_3$:*t*-C_4H_9Cl) and temperature, are discussed in detail. First, varying amounts of *t*-butyl chloride or $AlCl_3$ in terms of mole ratio to sulfur were directly added into the model oils for stirring 20 min at 303 K, and the results are presented in Figure 5. As shown from the figure, under fixed fivefold *t*-C_4H_9Cl the S-contents decrease with the increasing amount of $AlCl_3$ as indicated by the solid lines, while under fixed fivefold $AlCl_3$ the S-contents decrease insignificantly with increasing amounts of *t*-C_4H_9Cl, especially for 3-MT and BT, as noted from the dotted lines. It is noted that different mole ratio ($AlCl_3$:*t*-C_4H_9Cl) shows significant difference with respect to desulfurization yield under identical total mole amount of $AlCl_3$ and *t*-C_4H_9Cl. For example, the desulfurization yield at fivefold $AlCl_3$ and onefold *t*-C_4H_9Cl is 99.8% for 3-MT, 99.8% for BT, and 80.9% for DBT, but the counterpart data at onefold $AlCl_3$ and fivefold *t*-C_4H_9Cl reduces to 51.5, 35.8, and 30.1%, respectively. Obviously, the system containing excess $AlCl_3$ has better desulfurization performance than excess *t*-C_4H_9Cl system. The results are rational, since optimum desulfurization performance of some traditional ILs, such as [Bmim]Cl-$AlCl_3$, TMAC-$AlCl_3$, [Bmim]Cl-$FeCl_3$, and [Bmim]Cl-CuCl, are all in the presence of excess inorganic Lewis acids.[2–5] In contrast, *t*-C_4H_9Cl is a Lewis base, thereby excess *t*-C_4H_9Cl in the system will have competitive complexation with Lewis acids, which results in reducing Lewis acidity of the CPIL formed and accordingly decreasing the desulfurization activity.

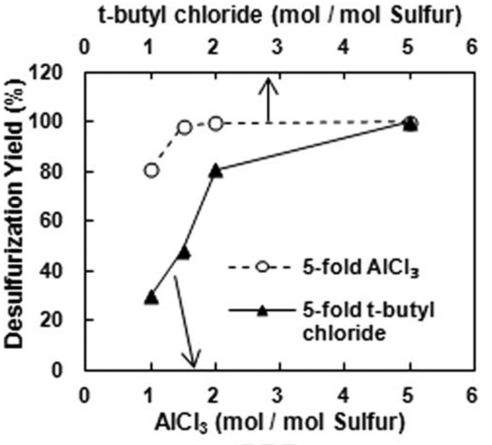
For an EDS process, the temperature may play a major role in desulfurization yield. Thus, the results of 353 and 303 K for the extraction experiments are compared each other at 20 min, and the other conditions are completely consistent with what has been described previously. From Figure 6, it can be seen that the desulfurization yield at 353 K for the three thiophenic compounds decreases, which indicates that the extractive desulfurization of the *t*-C_4H_9Cl-$AlCl_3$ is unstable at high temperature. It may be explained that the acid–base complexation is an exothermic reaction, so higher temperature is unfavorable to the complexing extraction,[19] and the increasing temperature may accelerate electrophilic substitution reaction on aromatic ring, resulting in lower amount of $[Tebu]^+$. Further, it can be seen that BT shows the best stability for high temperature, which may be ascribed to the fact that BT lies between 3-MT and DBT in terms of alkaline hardness, thereby the moderate hardness base BT shows most stable interaction with borderline acid $[Tebu]^+$ under high temperature.



a. 3-MT



b. BT



c. DBT

Figure 5. The desulfurization yield of different mole ratio between *t*-C_4H_9Cl and $AlCl_3$.

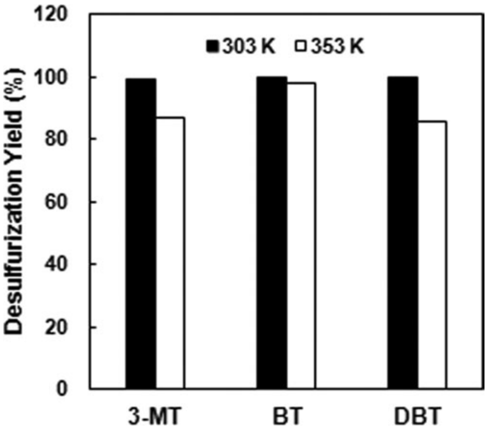


Figure 6. The influence of temperature on extractive desulfurization in terms of t-C_4H_9Cl-$AlCl_3$.

The alkylation reaction during extractive desulfurization process

For the extractive desulfurization system in this article, some alkylated thiophenic compounds (3-MTs, BTs and DBTs) in oil phase are detected by HPLC due to the electrophilic substitution reaction, which implies that the products extracted by the t-C_4H_9Cl-$AlCl_3$ may be also the alkylated S-compounds. To identify the assumption, dilute HCl solution and CH_2Cl_2 were selected to destroy the CPIL and dissolve the S-compounds released from the CPIL after removing n-octane layer. After that, the products can be recovered when the CH_2Cl_2 and other low boiling point substances were evaporated completely. Then, the S-compounds can be analyzed by ^{1}H-NMR and GC-MS. In Figure 7, the ^{1}H-NMR spectrum of 3-MTs shows some aromatic protons ranged from 6.5 to 7.1 ppm and t-butyl proton that appears at about 1.3 ppm, which can be regarded as the formation of 3-MTs, and the chemical shifts of aromatic and t-butyl protons of both BTs and DBTs are also found by ^{1}H-NMR spectrum. For GC-MS result listed in Table 2, the 3-MTs system has the molecular ion at m/z 154 and 210, the BTs shows molecular ion at m/z 190 and 246, and the molecular ion at m/z 240 and 296 for the DBTs is found. Therefore, the results from the ^{1}H-NMR and GC-MS indicate that the S-compounds in the CPIL phase are butyl substituted thiophenic compounds.[20–22] According to the analysis results stated above, the distribution of the S-compounds for the products extracted can be shown in Figure 8, and the structure of alkylated thiophenic compounds can be obtained as presented in Figure 9. According to the chromatography theory, however, tri-butyl BT is also detected by HPLC instead of the GC-MS, which might be ascribed to its high boiling point and low content.

Table 2. GC-MS Result for Alkylated Thiophenic Compounds

S-Compounds	m/z
3-MTs	154
	210
BTs	190
	246
DBTs	240
	296

For the three thiophenic compounds, their alkylation conversion follows the order of BT > 3-MT > DBT as presented in Table 3. It can be explained by their different bond orders on unsaturated double-bond. The bond order represents the electron density on unsaturated bond, and the larger the bond order is the more the electron density is.[21] Table 3 also lists the largest bond order for the three S-compounds,[23,24] it can be seen that the bond order follows the same order to the alkylation conversion, that is, alkylation activity arises with the increasing bond order.

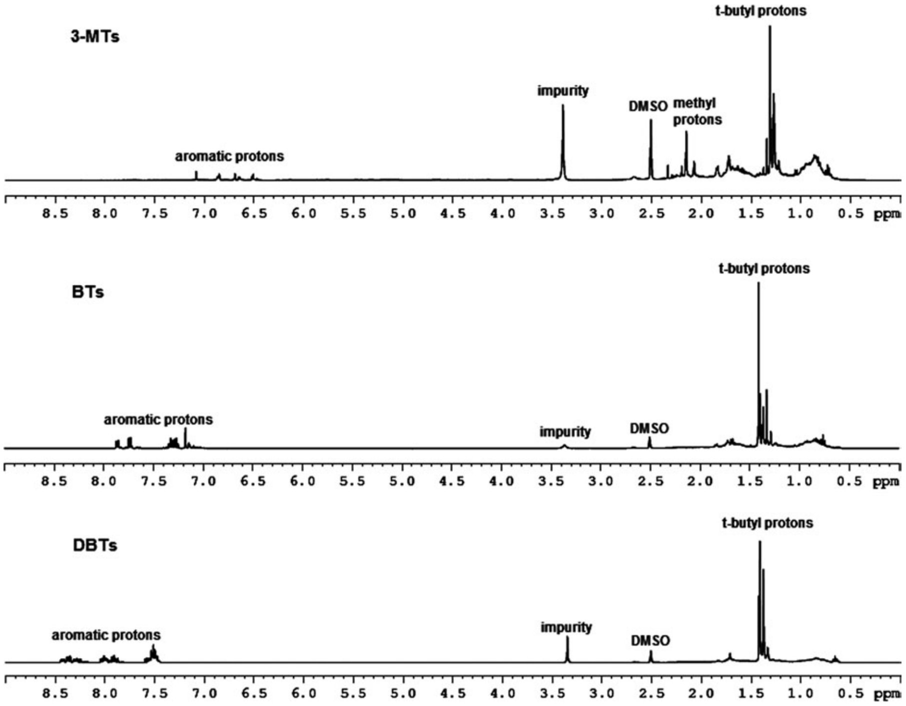


Figure 7. The ^{1}H-NMR spectrum for alkylated thiophenic compounds.

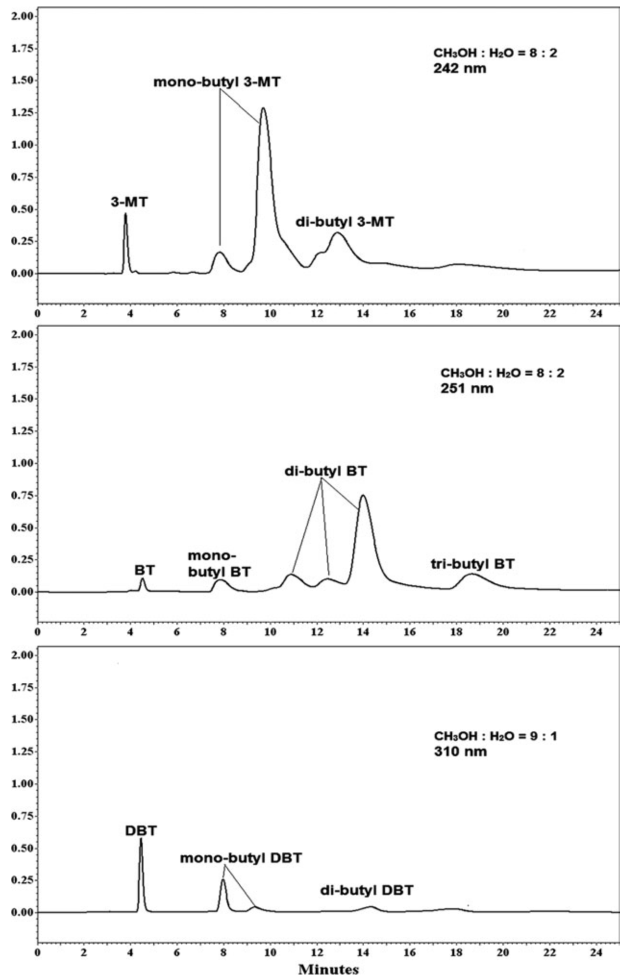


Figure 8. The distribution of thiopheinc compounds in HPLC spectrum.

Table 3. The Relationship Between S-Compounds Alkylation Conversion (%) and Largest Bond Order

S-Compounds	Alkylation Conversion (%)	Largest Bond Order
3-MT	94.69	1.699
BT	98.57	1.769
DBT	85.75	1.448

To explore the effect of alkylation reaction on extractive process, BT and DBT were selected to prepare their pre-alkylated model oil. 30 g BT-octane was mixed with fivefold *t*-butyl chloride and 10-fold $FeCl_3$ for 30 min at 303 K, whereas DBT-octane was mixed with fivefold *t*-butyl chloride and 10-fold $FeCl_3$ for 30 min at 303 K. After that, 30 ml CH_3OH-H_2O (volume ratio 1:1) solution was added to the system stirring for 20 min, so as to ensure all the alkylated S-compounds go back to the oil phase, thereby the pre-alkylated model oil can be obtained. In those two pre-alkylated model oil (total S-content 1000 μg/g), the S-content of BTs and DBTs is about 962.02 and 721.63 μg/g, respectively. Thereby, 20 g pre-alkylated oil can be used to investigate the influence of alkylation reaction on the desulfurization process by the comparison with sole BT or DBT model oil under the same conditions. Figure 10 presents the desulfurization yield of the model oil containing sole BT or DBT and pre-alkylated oil by the extraction of *t*-C_4H_9Cl-$AlCl_3$ (fivefold *t*-butyl chloride and equivalent $AlCl_3$). It is clear that alkylated S-compounds show no significant difference from sole thiophenic compounds in terms of desulfurization rate, especially 15 min later. The results suggest that alkylation reaction cannot enhance the desulfurization process, so the sulfur removal is attributed dominantly to acid–base complexation.

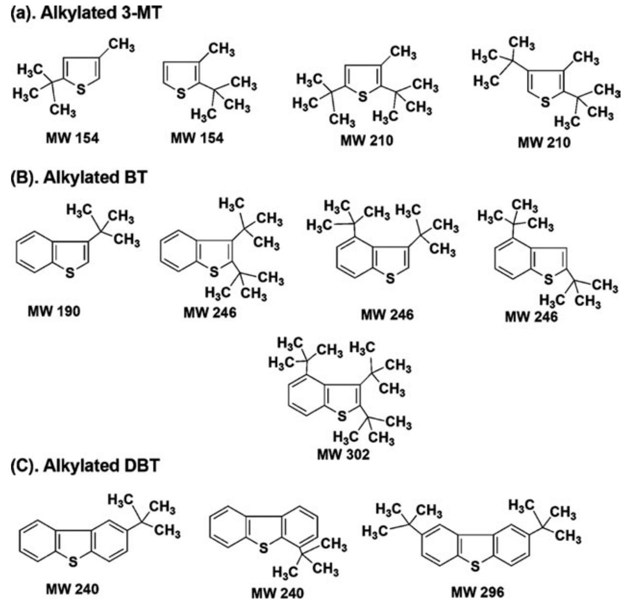


Figure 9. The chemical structure of the alkylated thiophenic compounds.

Complexing extraction mechanism of t-C_4H_9Cl-$AlCl_3$

As stated above, *t*-C_4H_9Cl-$AlCl_3$ can remove the aromatic S-compounds rapidly, and the S-compounds extracted by the *t*-C_4H_9Cl-$AlCl_3$ consist mainly of alkylated thiophenic compounds. Meanwhile, the colors of the bottom phase are different with respect to the three kinds of S-compounds. In detail, the mixture of 3-MTs and *t*-C_4H_9Cl-$AlCl_3$ shows golden yellow color, the color of BTs and *t*-C_4H_9Cl-$AlCl_3$ is bright red, and the color of DBTs and *t*-C_4H_9Cl-$AlCl_3$ is dark red. The different color implies that the extraction is the acid–base (electron donor–acceptor) complexation. To demonstrate the view, the mixtures of the S-compounds and *t*-C_4H_9Cl-$AlCl_3$ are dissolved in CH_2Cl_2 and analyzed by UV spectrum, while their spectrums are compared with the S-compounds (3-MTs, BTs, and DBTs) extracted by the CPIL. As shown in Figure 11, the mixtures have much wider absorption range than the alkylated S-compounds, that is, red shift phenomenon emerges. Meanwhile, some new peaks appear in the UV spectrum. Specifically, 3-MTs system has the absorption peak at 298, 380, and 455 nm, BTs system shows new peaks at 320, 389, and 490 nm, and the new peaks of DBTs mixture are at 361 and 458 nm. The results indicate that the mixtures formed by *t*-C_4H_9Cl-$AlCl_3$ and S-compounds are the electron donor–acceptor complexes.[14]

According to the hard and soft acids and bases (HSAB) theory, hard acids and bases are relatively small, compact, and nonpolarizable; soft acids and bases are larger and more polarizable. The acid–base complexation are more favorable for hard–hard and soft–soft interactions than for the hard and soft ones.[25] Hard Lewis acids have large and concentrated

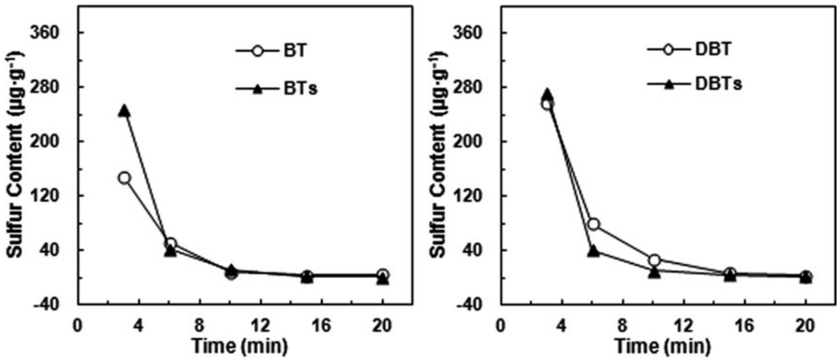


Figure 10. The comparison of desulfurization activity between thiophenic compounds and their butyl substitutes.

positive charge (e.g., Al^{3+} and Ce^{4+}), the soft acids show low and dispersed positive charge (e.g., Ag^{+} and $Bmim^{+}$), while the borderline acids lie between the hard and soft acids. In contrast, the hard Lewis bases, such as H_2O, have non-bonding and concentrated electrons, while the soft bases, such as benzene, possess the well-dispersed electrons, for example, conjugated π electrons. In this complexation, the S-compounds are the bases, and the t-C_4H_9Cl-$AlCl_3$ is the Lewis acid, and the thiophenic compounds are both hard and soft alkalines, the non-bonding σ lone-pair electron on S atom is hard region, and conjugated π lone-pair electron belongs to soft part as shown in Scheme 2a.[16,21] Based on the fundamental chemistry theory, moreover, $[Tebu]^{+}$ belongs to sp^2 hybridization, having the planar conformation with four carbon atoms. Thereby, the central carbon with positive charge can be deemed as the hard acid region, while the plane formed by other three carbon atoms may represent soft acid part due to the electron-donating effect of three methyl presented in Scheme 2b. Obviously, $[Tebu]^{+}$ can be considered as both hard and soft acid, and thus interact with those S-compounds by both hard acid-hard base and soft acid-soft base interaction.

In this system, $AlCl_3$ is excess vs. t-butyl chloride in the t-C_4H_9Cl-$AlCl_3$ phase (bottom phase) though initial mole quantities are equal for both, because a part of t-butyl chloride will be consumed by the alkylation reaction. Some traditional ILs containing excess inorganic Lewis acid have been reported, for example, TMAC-Al_2Cl_6, BmimCl-Fe_2Cl_6, and BmimCl-Cu_2Cl_2, in which the excess Lewis acid will be dissolved in the ILs as presented in Scheme 1b.[3–5] It can be assumed that the CPIL containing excess $AlCl_3$ may also form t-C_4H_9Cl-Al_2Cl_6 as shown in Scheme 1a, because the

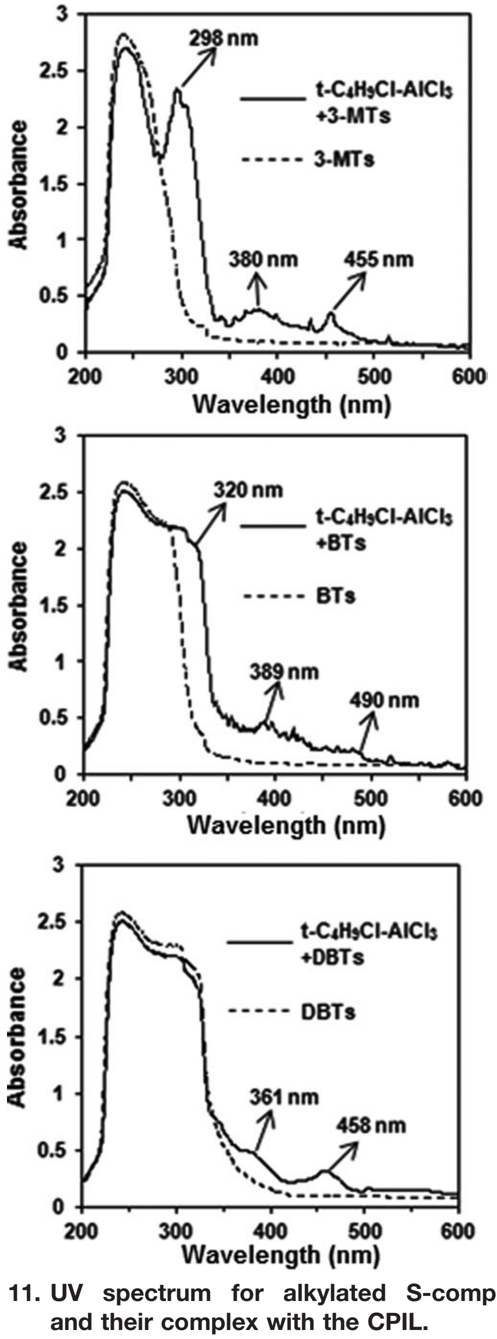
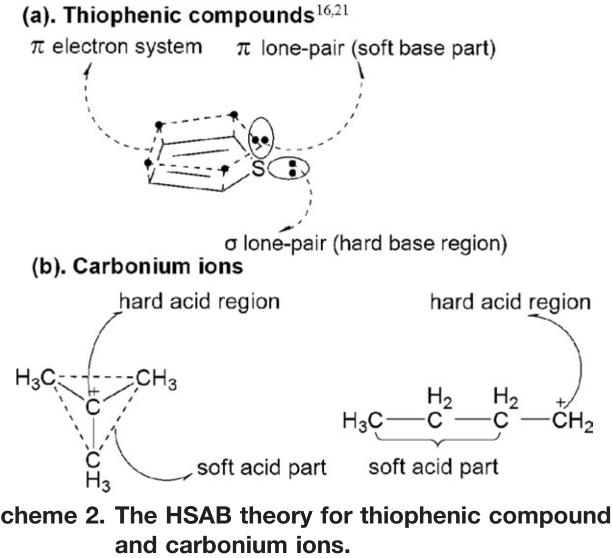
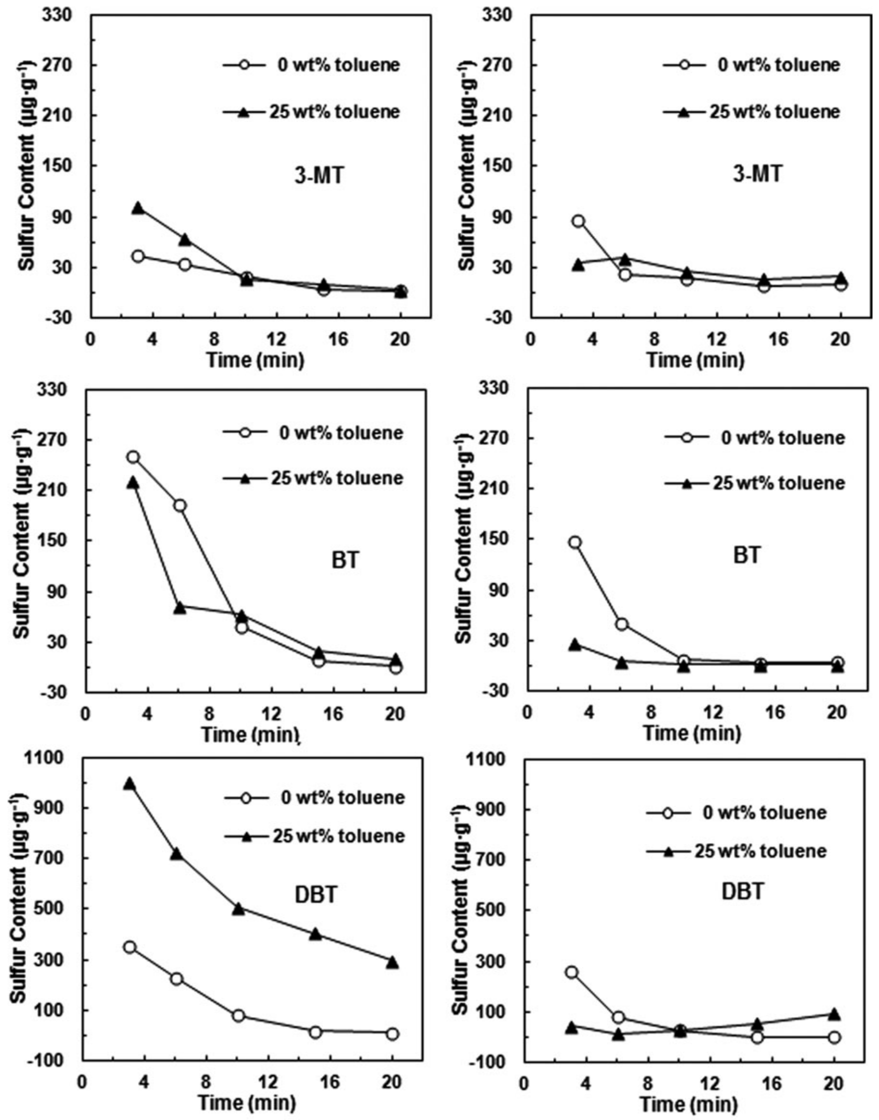


Figure 11. UV spectrum for alkylated S-compounds and their complex with the CPIL.



Scheme 2. The HSAB theory for thiophenic compounds and carbonium ions.



a. n-C_4H_9Cl-$AlCl_3$ b. t-C_4H_9Cl-$AlCl_3$

Figure 12. The desulfurization comparison between 25 and 0 wt % toluene system.

bottom phase is the liquid rather than the solid. Dissolved excess $AlCl_3$ is dispersed in liquid phase, and accordingly has stronger activity than the solid $AlCl_3$. As presented in Figure 5, onefold *t*-C_4H_9Cl and fivefold $AlCl_3$ still lead to high desulfurization yield for the three S-compounds, the result suggests the desulfurization performance of dispersed $AlCl_3$, because the amount of $[Tebu]^+$ is actually less than onefold. Consequently, the active Lewis acids that can remove S-compounds consist of two parts, one is the carbonium ion, the other is the dissolved $AlCl_3$, and the cooperation from the two Lewis acids brings in amazing desulfurization performance.

It can be concluded that sulfur removal process is acid–base complexing extraction accompanying with the formation of the alkylated thiophenic compounds. Taking the 3-MT system as an example, initial 3-MT is first attracted by the CPIL, only a few are then extracted and the most of the 3-MT are alkylated in the interface as shown in Scheme 1c. After that, a part of mono-butyl 3-MT are extracted by the CPIL, and the remaining mono-butyl 3-MT are alkylated again. The S-compounds can be extracted thoroughly when the di-butyl 3-MT drop into the CPIL. In a word, the sulfur removal mechanism is acid–base complexation containing both hard–hard and soft–soft interaction rather than alkylation reaction of the thiophenic compounds, because alkylated S-compounds are still oil soluble.

The influence of adding toluene on the extractive desulfurization

In the real oils, some aromatics, such as benzene and toluene, may hamper the extractive desulfurization of traditional ILs due to the competitive soft–soft interaction between the aromatics and the ILs. In this article, toluene was deemed as a model aromatic compound to investigate its negative effect on the extractive desulfurization of two CPILs (*t*-C_4H_9Cl-$AlCl_3$ and *n*-C_4H_9Cl-$AlCl_3$). On one hand, the toluene may be extracted competitively by the CPILs, and on the other hand it might consume $[Tebu]^+$ and $[Nobu]^+$ due to the formation of butyl substituted toluene. Therefore, the selectivity of these two CPILs can be known by the extractive experiment in toluene-rich model oil.

The aromatic-containing model oil that contains 25 wt % toluene and 1000 μg/g sulfur are prepared and mixed with fivefold butyl chloride and fivefold $AlCl_3$ at 303 K. The

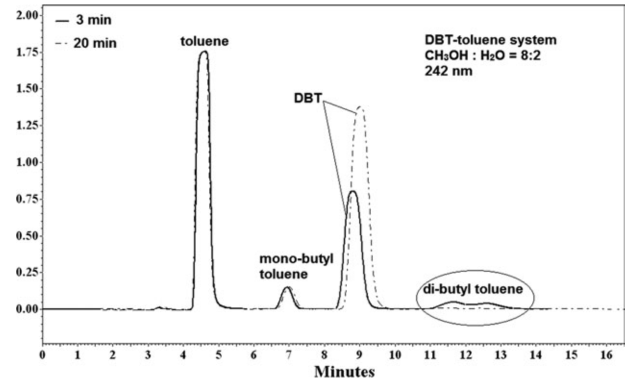


Figure 13. The HPLC picture for DBT-toluene system with different extraction time.

S-content of 3-MT and DBT in the new model oil is analyzed by the HPLC. Meanwhile, the S-content of BT in toluene-containing system is determined by sulfur and nitro analyzer (KY-3000SN) due to the peak overlaps between BT and toluene in the HPLC. The desulfurization performance of toluene-containing system is compared with that of toluene-free system, and the results are shown in Figure 12. In Figure 12a, it can be seen that toluene does not result in decreasing significantly desulfurization activity of the n-C_4H_9Cl-$AlCl_3$ for 3-MT and BT, however, extractive desulfurization of the DBT-toluene system encounters strong competition. The results can be explained by base hardness of DBT similar to that of toluene and relatively weak acidity of $[\text{Nobu}]^+$. For the desulfurization performance of the t-C_4H_9Cl-$AlCl_3$ presented in Figure 12b, similarly, the 3-MT or BT also has strong complexing activity in the toluene-containing system, and the DBT-toluene system shows different trend from n-C_4H_9Cl-$AlCl_3$. It can be seen that the S-content of DBT-toluene decreases first, increases then with the time expanding. The interesting phenomenon might be explained by the following reasons, first the strong Lewis acidity and appropriate hardness of $[\text{Tebu}]^+$ brings in good desulfurization activity in short time. But, the amount of $[\text{Tebu}]^+$ would be gradually reduced by the alkylation of toluene for a relatively long time, which results in decreasing desulfurization yield of the CPIL due to the weak interaction between sole $AlCl_3$ and DBT. As shown in Figure 13, moreover, the peaks (retention time 11–13.5 min) should be di-butyl toluene when the extraction time is 3 min (solid line) but they are disappeared at 20 min (dotted line), which implies that the di-butyl toluene is extracted competitively by the CPIL. Above all, for the t-C_4H_9Cl-$AlCl_3$, the alkylation of toluene and the competitive extraction of di-butyl toluene result in the fact that DBT return to oil phase from the CPIL phase.

Table 4. The Composition in the Model Gasoline

Components	Name	S-Content (μg/g)	Content (wt %)
S-compounds	Di-*n*-butyl sulfide	208	0.095
	Thiophene	440	0.1155
	3-MT	150	0.046
	BT	202	0.0845
	Total sulfur	1000	
Paraffins	*n*-Octane	–	30
Naphthenes	Cyclohexane	–	29.66
Aromatics	Benzene	–	2.5
	Toluene	–	12.5
	Cumene	–	10
Olefins	1-Hexene	–	5
	Cyclohexene	–	10

Note: The density of the model gasoline is 0.788 g/ml.

Table 5. The Total S-Content in the Model Gasoline Treated by the Three CPILs

CPILs	t-C_4H_9Cl-$AlCl_3$	n-C_4H_9Cl-$AlCl_3$	t-C_4H_9Br-$AlCl_3$
S-Content (μg/g)	7.36	3.81	1.27

The desulfurization investigation of the model gasoline

According to the results of adding toluene system, it can be assumed that the CPILs could show good desulfurization performance for the real gasoline. To approach real condition, the MG was prepared here to study the sulfur removal. In the MG, four kinds of the S-compounds (di-*n*-sulfide, thiophene, 3-MT, and BT) were selected, and the total S-content was 1000 μg/g. Meanwhile, other components in the real gasoline, such as paraffins, naphthenes, aromatics, and olefins, were also added to the MG, for detail see Table 4, and the three CPILs, namely t-C_4H_9Cl-$AlCl_3$, n-C_4H_9Cl-$AlCl_3$, and t-C_4H_9Br-$AlCl_3$, were used to investigate their extractive desulfurization activity in the MG. All the experiments were carried out under the same condition (fivefold butyl halide, fivefold $AlCl_3$, 303 K) with previous experiments, the time was 20 min. When the extraction ended, the total S-content for the three systems was determined by sulfur and nitro analyzer (KY-3000SN).

Table 5 shows the results of the extractive desulfurization in the MG. It can be seen that the three CPILs have very amazing desulfurization performance, and the remaining S-contents are all less than 8 μg/g. The results indicate that the CPILs have very good desulfurization activity and amazing selectivity even in the MG, which implies that these novel CPILs may be used in the real gasoline. The CPILs, therefore, as a novel kind of S-removal reagent, may be viable for commercial application due to their lower material cost, higher desulfurization activity and selectivity in comparison with traditional ILs, although they are sensitive to the moisture and hard to be reused.

Conclusion

Three butyl halides, namely *t*-butyl chloride, *n*-butyl chloride, and *t*-butyl bromide, can soften the hard acid $AlCl_3$. Meanwhile, the CPILs formed show very good extractive desulfurization efficiency in model oil, removing completely S-compounds within 20 min, and the desulfurization performance of t-C_4H_9Cl-$AlCl_3$ is better and faster than many traditional ILs reported. The extraction process accompanies with the alkylation reaction of the thiophenic compounds, and the S-compounds extracted consist mainly of some butyl substituted thiophenic compounds. Further, the extraordinary desulfurization performance is ascribed dominantly to the acid–base complexation instead of the alkylation reaction, and the active Lewis acid is composed of the carbonium ion and the dissolved $AlCl_3$. In toluene-containing system, t-C_4H_9Cl-$AlCl_3$ still keep the strong desulfurization activity for 3-MT and BT, however, DBT extracted will be released from CPIL phase to oil phase with consumption of $[\text{Tebu}]^+$. Satisfactorily, three CPILs are able to remove thoroughly the S-compounds in MG, which indicates that the CPILs can also have very good selectivity even in the system close to the real one.

Acknowledgments

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