Synthesis of Surface-Active Heteropolyacid-Based Ionic Liquids and Their Catalytic Performance for Desulfurization of Fuel Oils
Qin Wu,* Quan Shi, Jiqing Shang, Min Wang, Hansheng Li,* Daxin Shi, Yun Zhao, and Qingze Jiao

ABSTRACT: Surface-active heteropolyacid-based ionic liquids with varying alkyl carbon chains were synthesized, which were subsequently analyzed. The desulfurization of fuels was investigated utilizing various surface-active heteropolyacid-based ionic liquids, and acetonitrile was used as the extractant for the coupling of ODS and EDS. The influences of the alkyl group, surface activity, and hydrophobicity of ionic liquids on sulfur removal were studied. The results suggested that the ionic liquids were stable. Among these ionic liquids, [C$_4$ImBS]$_3$[PW$_{12}$O$_{40}$] exhibited the best catalytic performance. Using [C$_4$ImBS]$_3$[PW$_{12}$O$_{40}$] as the catalyst, the influences of the catalyst amount, aqueous hydrogen peroxide amount, and reaction temperature on the sulfur removal were explored. Under the optimum conditions, the sulfur removal could achieve 100% efficiency. The recycle experiments also proved that the ionic liquid could be reused.

1. INTRODUCTION
The volume of automobiles has increased markedly, leading to a consequent increase in fuel consumption. Sulfur compounds in transportation fuels are notorious for their negative impact on the environment. SO$_2$ emissions from automobile exhaust not only pollute air greatly but also poison the noble metal catalysts irreversibly in automobile exhaust systems. As oil refineries are facing growing environmental pressures and stricter regulatory requirements, sulfur removal from transportation fuels has become an increasing technical challenge.

Hydrodesulfurization (HDS) is a method to remove disulfides, sulfides, and thiols. However, owing to some refractory sulfur compounds such as dibenzothiophene (DBT), it is difficult to achieve a low sulfur content. Research for alternative methods for ultralow-sulfur content fuel oils, such as adsorption, extraction, and oxidation, has attracted intensive attention. Extractive desulfurization (EDS) is a good method that can be carried out under wild reaction conditions and without hydrogen and catalysts. Ethanol, DMF, DMSO, and acetonitrile are common extractants. In addition, EDS can extract DBT and BT S-components. However, EDS has the disadvantage of low desulfurization. Hence, oxidative desulfurization (ODS) was put forward. Compared with HDS, ODS exhibited several advantages such as mild reaction conditions, high selectivity, and the potential for desulfurization of sterically hindered sulfur compounds selectively oxidized to sulfoxides and sulfones. The coupling of ODS and EDS is considered to be a promising technology among various processes in this process area. Nevertheless, low desulfurization efficiency still appears to be an issue, as the coupling of ODS and EDS has the mass transfer resistance of a phase interface.

Ionic liquids (ILs), including functionalized ones, are considered as environment-friendly catalysts and solvents possessing important attributes, such as nonvolatile, high thermal stability, structural designability, high catalytic activity, and great recoverability and separability from reactants. A lot of organic reactions have achieved excellent performance using IL catalysts. Surface-active ILs can improve the mass transfer at the phase interface. A new method for the coupling of ODS and EDS catalyzed by surface-active heteropolyacid-based ILs is proposed in this work.

In this work, surface-active heteropolyacid-based ILs with different alkyl carbon chains (ILs-AC) were synthesized. The structure and thermal stability and surface activity of the ILs-AC were characterized. The catalytic performances of ILs-AC for the desulfurization of fuels were performed by the coupling of ODS and EDS. The relationship between the alkyl carbon chain length and catalytic activity was studied. The influences of different conditions on the sulfur removal in the optimized catalyst were analyzed.
2. RESULTS AND DISCUSSION

2.1. Characterization of the ILs. 2.1.1. IR Analysis of the Intermediate [RIm] and Heteropolyacid-Based ILs. The IR spectra of the C6Im, C6ImBs, and [C6ImBs]3[PW12O40] are shown in Figure 1. For the C6Im, C6ImBs, and [C6ImBs]3[PW12O40], the bands at 3106, 1563, and 1465 were assigned to the ring stretching vibrations of imidazole and the bands at 2930 and 2859 cm\(^{-1}\) were assigned to the asymmetrical stretching vibrations of methyl and methylene groups. For the C6ImBs, the bands at 1185 and 1060 cm\(^{-1}\) were corresponded to the \(\text{O}==\text{S}==\text{O}\) and \(\text{C}==\text{S}==\text{O}\) stretching vibrations, respectively. Hence, the sulfonic acid group existed. For the [C6ImBs]3[PW12O40] IL, the band at 1079 cm\(^{-1}\) was assigned to the P–O asymmetrical stretching vibrations. Moreover, the peaks at 977, 895, and 807 cm\(^{-1}\) should be assigned to the asymmetrical stretching vibrations of W–O–W and W–O–W, respectively. Hence, the heteropolyacid anion existed. Other [CnImBS][PW12O40] and [RImM]3[PW12O40] ILs had similar results (Supporting Information; Figure S2). Thus, the IR spectra correspond to the structures for the ILs-AC shown in Scheme 1.

2.1.2. NMR Analysis of the Heteropolyacid-Based ILs. The NMR spectral data of the ILs are shown in the Supporting Information (Supporting Information; Figure S3). As can be seen in Figure S3, the NMR spectra of the ILs matched those of the designed structures very well (Scheme 1), which demonstrated that the IL-AC catalysts were successfully synthesized. Moreover, it was demonstrated that the synthesized ILs were highly purified.

2.1.3. ESI-MS Analysis of the Heteropolyacid-Based ILs. The electrospray ionization mass spectroscopy (ESI-MS) spectra of the [C6ImBs]3PW12O40 are shown in Figure 2. As shown in Figure 2a, a large peak was found at \(m/z\) 289.2, which is the positive ion of [C6ImBs]3PW12O40. The peak at \(m/z\) 958.8 illustrated the PW12O40\(^{3−}\) presence in Figure 2b. Similar results were observed in other cases of heteropolyacid-based ILs. All the negative ion modes exhibited the PW12O40\(^{3−}\) peak at \(m/z\) 958. The large peaks of the positive ion of ILs in the positive ion mode were found at \(m/z\) 219.1, 247.0, 261.2, 289.2, 317.3, 345.3, 373.4, 401.4, 429.4, 457.4, 139.2, 195.2, and 251.3, respectively (Supporting Information; Figure S4). The ESI-MS results also suggested that the ILs-AC with...
desired structures shown in Scheme 1 was successfully prepared.

2.2. TG-DTA Analysis of the Heteropolyacid-Based ILs. The thermal decomposition temperatures of heteropolyacid-based ILs were determined by thermogravimetry–differential thermal analysis (TG-DTA) analysis (see Table 1). It was found that they have high stability no more than 280 °C.

2.3. Solubility Analysis of the [RImBs]3[PW12O40] ILs. The solubility of the ILs-AC in water was studied at 30 °C (see Figure 3). As can be seen in Figure 3, when the number of alkyl carbon increased, the solubility of ILs in water gradually decreased. The results indicated that the hydrophobicity of IL-AC catalysts enhanced as the number of alkyl carbon increased.

2.4. Surface Activity Analysis of the ILs. The measured conductivity for [C6ImBs]3[PW12O40] solution of various concentrations is shown in Figure 4. The specific conductivity (κ) increased linearly when the [C6ImBs]3[PW12O40] concentration got higher. The steep change in the slope at a certain concentration is due to the formation of micelles, which is the inflection point.21 The inflection point corresponds to the critical micelle concentrations (cmc) of the ILs-AC, which are shown in Table 2 for the [RImBs]3[PW12O40] IL-AC (Supporting Information; Figure S5). As shown in Table 2, under the conditions of the same hydrophilic group, the cmc values of [RImBs]3[PW12O40] decreased greatly with the increase of alkyl chains. It could be concluded that the synthesized [RImBs]3[PW12O40] owns surface activity, and the surface activities enhanced gradually with the increase of alkyl chains.

Table 1. Thermal Decomposition Temperature of Different ILs

| ILs          | thermal decomposition temperature (°C) | ILs          | thermal decomposition temperature (°C) |
|--------------|----------------------------------------|--------------|----------------------------------------|
| [C1ImBs]3[PW12O40] | 286                                    | [C1ImBs]3[PW12O40] | 322                                    |
| [C1ImBs]3[PW12O40] | 296                                    | [C1ImBs]3[PW12O40] | 316                                    |
| [C3ImBs]3[PW12O40] | 302                                    | [C1ImBs]3[PW12O40] | 322                                    |
| [C4ImBs]3[PW12O40] | 314                                    | [C1ImMs]3[PW12O40] | 424                                    |
| [C5ImBs]3[PW12O40] | 319                                    | [C1ImMs]3[PW12O40] | 405                                    |
| [C7ImBs]3[PW12O40] | 315                                    | [C1ImMs]3[PW12O40] | 391                                    |
| [C12ImMs]3[PW12O40] | 320                                    |              |                                        |
2.5. ODS of Fuel Oils Catalyzed by Heteropolyacid-Based ILs.

2.5.1. Effect of Different Desulfurization Systems on the Sulfur Removal.

The influence of different desulfurization systems on DBT removal was studied (see Table 3). As shown in Table 3, when only acetonitrile extraction was used for desulfurization, the sulfur removal was 57.41%, whereas the combination of the acetonitrile extraction and H₂O₂ oxidant achieved a sulfur removal of 63.59%. The sulfur removal was only 35.28% by direct catalytic oxidation. When using an IL as a catalyst, H₂O₂ as an oxidant, and acetonitrile as an extraction solvent, the sulfur removal showed great improvement, with the desulfurization efficiency reaching as high as 99.01% for [C₁ImBs]₃[PW₁₂O₄₀] and 100% for [C₄ImBs]₃[PW₁₂O₄₀]. Acetonitrile has a good ability to extract DBT; therefore, some DBT in the model oil was extracted to the acetonitrile phase. H₂O₂ is miscible in acetonitrile and more importantly has an oxidation effect on DBT, which explains that the sulfur removal is higher than that of DBT with acetonitrile as an extraction solvent only. For the direct catalytic oxidation desulfurization, ILs do not dissolve well with DBT and H₂O₂ reactants, which leads to low desulfurization efficiency. For the coupling of catalytic oxidation desulfurization and extraction, H₂O₂ and the [C₁ImBs]₃[PW₁₂O₄₀] catalyst dissolve in the acetonitrile phase, and a two-phase reaction system is formed, in which the upper layer is the oil phase and the lower layer is the polar phase containing the oxidant, catalyst, and extractant. DBT was extracted to the acetonitrile phase. The reaction rate was accelerated by the coupling of catalytic desulfurization and catalytic oxidation. Moreover, [C₁ImBs]₃[PW₁₂O₄₀] has surface activity. The acetonitrile extraction and IL micellization at the phase interface accelerated the reaction rate of ODS (see Figure 6). Therefore, the desulfurization efficiency of [C₁ImBs]₃[PW₁₂O₄₀] is higher than that of [C₄ImBs]₃[PW₁₂O₄₀]. The coupling of catalytic oxidation desulfurization and extraction showed the best desulfurization efficiency.

2.5.2. Effect of the Alkyl Carbon Number in the ILs-AC on the Sulfur Removal.

The effect of the alkyl carbon number in the ILs-AC on the sulfur removal was investigated (see Figure 5). The profiles in Figure 5 showed that the sulfur removal distinctly increased with the increase in the alkyl carbon number when it was smaller than 4. However, when the number increased from 4 to 16, the sulfur removal declined rapidly. The results illustrated that the alkyl carbon number in the ILs-AC had a remarkable effect on its catalytic performance. Among the IL-AC catalysts, [C₄ImBs]₃[PW₁₂O₄₀] exhibited the best desulfurization efficiency. The sulfur removal could reach 100% at a reaction time of 60 min. The sulfur removal was related to the extractive ability of acetonitrile and surface activity of ILs, which is the coupling of phase transfer catalysis and micellar catalysis. Figure 6 displays the reaction process and mechanism of ODS by the coupling of [C₄ImBs]₃[PW₁₂O₄₀] as a catalyst and surfactant and acetonitrile as an extraction solvent. Some DBT in the

![Figure 3. Solubility of IL-AC catalysts in water at 30 °C.](image)

![Figure 4. Plot of specific conductivity (κ) against [C₄ImBs]₃[PW₁₂O₄₀] concentration.](image)

![Table 2. cmc Values of ILs at 25 °C](table)

| ILs              | cmc (mmol/L) | ILs              | cmc (mmol/L) |
|------------------|--------------|------------------|--------------|
| [C₃ImBs]₃[PW₁₂O₄₀] | 15.841       | [C₁₂ImBs]₃[PW₁₂O₄₀] | 0.152       |
| [C₄ImBs]₃[PW₁₂O₄₀] | 9.232        | [C₁₄ImBs]₃[PW₁₂O₄₀] | 0.0875      |
| [C₆ImBs]₃[PW₁₂O₄₀] | 8.284        | [C₁₆ImBs]₃[PW₁₂O₄₀] | 0.0715      |
| [C₈ImBs]₃[PW₁₂O₄₀] | 0.949        | [C₂₀ImBs]₃[PW₁₂O₄₀] | 0.0553      |
| [C₁₀ImBs]₃[PW₁₂O₄₀] | 0.289       |                  |              |

Table 3. Effect of Desulfurization Systems on DBT Removal

| entry | Catalyst | sulfur removal |
|-------|----------|----------------|
|       |          | extraction | extraction + H₂O₂ | catalyst + H₂O₂ | catalyst + H₂O₂ + extraction |
| 1     |          | 57.41%     |                  |                |                              |
| 2     |          | 63.59%     |                  |                |                              |
| 3     | [C₄ImBs]₃[PW₁₂O₄₀] | 35.28%     |                  | 100%            |                              |
| 4     | [C₁ImBs]₃[PW₁₂O₄₀] | 99.01%     |                  |                |                              |

*Reaction conditions: V(CH₃CN)/V(DBT-oil) = 1:1, n(H₂O₂)/n(DBT)/n(IL) = 6:1:0.02, 60 °C, and 60 min.*
model oil could be extracted to the polar phase with acetonitrile. The H₂O₂ dissolved in the acetonitrile had an oxidation effect on DBT in the polar phase catalyzed by ILs. In addition, the lipophilicity of the alkyl group of ILs increased with the alkyl carbon number increasing. The [PW₁₂O₄₀]⁻ anion is hydrophilic. Thus, the alkyl group in the ILs determined if an emulsion or microemulsion, a pseudo-homogeneous catalysis system, could be formed by a catalyst and reactants, which are DBT in the oil phase and H₂O₂ in the polar phase. When the carbon chain length is short, the lipophilicity of the alkyl group of ILs is weak. However, with the lengthening of the carbon chain, the lipophilicity of the alkyl group of ILs becomes stronger and the formation of an emulsion or microemulsion reaction system becomes more difficult. Moreover, with the increase in the carbon number, the phase interface and steric hindrance increased. Therefore, the mass transfer of DBT from the oil phase to the polar phase could be the rate-determining step in ODS. The catalytic activity was decreased as the result of steric hindrance on reaction when the number increased from 4 to 16. As a result, at a moderate carbon chain length, the emulsion or microemulsion reaction system formation and the mass transfer of DBT were easier and better desulfurization performance was exhibited.

2.5.3. Effect of ILs with a Sulfonic Acid Group on the Sulfur Removal.

The effect of ILs with a sulfonic acid group on the removal of DBT was studied. As shown in Figure 7, with the increase in the alkyl carbon number of [RImM][PW₁₂O₄₀] from 4 to 12, the sulfur removal decreased, which is the same as that of [C₄ImBS][PW₁₂O₄₀] in the Section 2.5.2. The catalytic activity of ILs with −SO₃H showed improvement compared to that without −SO₃H. The results proved that the sulfonic acid group in ILs contributes to desulfurization. The decomposition of hydrogen peroxide produced a hydroxyl radical, which was catalyzed by the sulfonic acid group of ILs. Then, the active hydroxyl radical enhanced the oxidation desulfurization efficiency. Therefore, dual active sites simultaneously enhanced catalytic activity.

2.5.4. Effect of V(CH₃CN)/V(H₂O) on the Sulfur Removal.

In order to study the influence of V(CH₃CN)/V(H₂O) on the DBT removal, a variety of experiments were performed. As shown in Figure 8, with the decrease in acetonitrile and the increase in H₂O, the sulfur removal decreases distinctly, which is believed to be caused by the addition of H₂O, reducing the extraction ability of acetonitrile for DBT in the model oil.

2.5.5. Effect of the Hydrogen Peroxide Amount on the Sulfur Removal.

Plenty of experiments were conducted using the preferable catalyst [C₄ImBS][PW₁₂O₄₀] with different amounts of H₂O₂ (Figure 9). The sulfur removal rapidly increased with the increase in H₂O₂ when the n(H₂O₂)/n(DBT) was less than 6. However, the sulfur removal decreased when the value of n(H₂O₂)/n(DBT) increased from 6 to 10. The optimum n(H₂O₂)/n(DBT) was 6, at which the sulfur removal could reach 100% when the reaction time was 60 min. With increasing the value of n(H₂O₂)/n(DBT), the concentration of H₂O₂ increased, resulting in a higher rate of reaction and thus higher sulfur removal. However, the raw material, hydrogen peroxide (30%), contained a significant amount of water. As the value of n(H₂O₂)/n(DBT) increased further, the H₂O from H₂O₂ caused further dilution of acetonitrile, leading to a decrease in the extraction ability of acetonitrile for DBT. Therefore, when the mole ratio of H₂O₂...
to DBT was more than 6, the sulfur removal decreased. Therefore, the optimal value of $n(\text{H}_2\text{O}_2)/n(\text{DBT})$ is 6.

2.5.6. Effect of the Catalyst Amount on the Sulfur Removal. The influence of the catalyst amount on the sulfur removal was analyzed using the best catalyst $[\text{C}_4\text{ImBS}]_3[P\text{W}_{12}\text{O}_{40}]$ (see Figure 10). As shown in Figure 10, the reaction rate was accelerated and the removal of sulfur became higher with the increase in the catalyst amount when the value of $n(\text{ILs})/n(\text{DBT})$ was less than 0.02. It exhibited that the increase in the catalyst amount enhanced the acidity in the reaction system. However, the reaction rate was higher than the diffusion rate of DBT when the catalyst dosage was more than 0.02. Therefore, the diffusion rate of DBT became the control step of the reaction and the sulfur removal is basically unchanged. Hence, the optimal catalyst dosage is $n(\text{ILs})/n(\text{DBT}) = 0.02$.

2.5.7. Effect of the Reaction Temperature on the Sulfur Removal. Figure 11 displays the effect of the reaction temperature on the catalytic performance. The sulfur removal efficiency was increased at first and then decreased when the temperature increased. The maximum of sulfur removal efficiency was obtained at 60 °C. With the temperature elevated, the rate of effective collision happened between the IL catalyst and reactants became faster. Therefore, the reaction rate of oxidation of DBT was accelerated and the sulfur removal was improved. However, the thermal decomposition of hydrogen peroxide reduces the concentration of H$_2$O$_2$ above 60 °C, and the sulfur removal starts to decrease. Therefore, 60 °C is optimal.

2.6. Reuse of IL Catalysts. The recycle experiments were performed. After each round of recycle reaction, the acetonitrile phase containing the IL catalyst was simply separated and recycled from the oil phase by decantation. The H$_2$O$_2$ and model oil are added to continue the desulfurization reaction. The amount of H$_2$O$_2$ added is the amount consumed in the previous run. As can be seen in Table 4, the sulfur removal did not change obviously in the second run and decreased slightly in the third run because of an increase in H$_2$O in the acetonitrile phase affecting the desulfurization reaction. It was shown that the
Table 4. Reuse of ILs

| catalyst                      | sulfur removal (%) |
|-------------------------------|-------------------|
| [C4ImBs]3[PW12O40] 1st       | 100               |
| [C4ImBs]3[PW12O40] 2nd       | 100               |
| [C4ImBs]3[PW12O40] 3rd       | 91                |

“Reaction conditions: V(CH3CN)/V(DBT-oil) = 1:1, n(H2O2)/n(DBT)/n([C4ImBs]3[PW12O40]) = 6:1:0.02, 60 °C, and 120 min.

sulfur removal decreases distinctly with the decrease in acetonitrile and the increase in H2O in the Section 2.5.4. These results indicated that the [C4ImBs]3[PW12O40] as the catalyst for the ODS is recyclable.

3. CONCLUSIONS

Surface-active heteropolyacid-based IL-AC catalysts were synthesized and further characterized and their solubility was analyzed. Surface activity analysis was determined through cmc. Their catalytic performances for the desulfurization of fuels by the coupling of ODS and EDS were studied. It was found that the highly purified IL-AC catalysts were obtained. These ILs had high stability. The hydrophobicity and surface activities of ILs were enhanced with lengthening the carbon chain. Moreover, these acidic IL-AC catalysts exhibited excellent catalytic activity for sulfur removal by the coupling of ODS and EDS. The alkyl carbon chain, surface activity, −SO3H, and heteropolyacid impacted on the sulfur removal. The [C4ImBs]3[PW12O40] exhibited the best desulfurization efficiency. Optimum reaction conditions were achieved. The surface-active heteropolyacid-based ILs could have a potential application in sulfur removal of fuel oils.

4. EXPERIMENT SECTION

4.1. Materials. Imidazole (99%) and methylimidazole were purchased from Linhai Kaile Chemical Factory. Sodium hydroxide, phosphotungstic acid, and bromomethane were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Bromopropane and 1-bromohexane were purchased from the Tianjin Institute of Guangfu Fine Chemical Industry. 1-Bromobutane, 1-bromoacetone, 1-bromodecane, 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane, 1-bromooctadecane, and hydrogen peroxide (30%) were purchased from Wuhan Fengfan Chemical Co, Ltd. Bromobutane, 1-bromooctane, 1-bromodecane, 1-bromododecane, and 1-bromohexane were purchased from the Linhai Kaile Chemical Factory. Sodium hydroxide, phosphotungstic acid, and bromomethane were purchased from Wuhan Fengfan Chemical Co, Ltd. Toluene, acetone, dichloromethane, and acetonitrile were purchased from Wuhan Fengfan Chemical Co, Ltd. 1,4-Butanone, 1-bromotetradecane, 1-bromohexadecane, 1-bromooctadecane, and hydrogen peroxide (30%) were purchased from Wuhan Fengfan Chemical Co, Ltd.

4.2. Preparation of the Surface-Active Heteropolyacid-Based ILs-AC. The preparation procedure of the surface-active heteropolyacid-based ILs-AC is shown in Scheme 1.

4.2.1. Synthesis of Alkylimidazole. Sodium hydroxide and imidazole were added in turn, and sodium imidazole was prepared after stirring the mixture at 95 °C for 4 h. Then, an equivalent molar RBr was added into sodium imidazole, which is in the tetrahydrofuran solution. Alkylimidazole (RIm) was prepared after stirring the mixture at 65 °C for two days. The RIm was distilled at 45 °C to remove tetrahydrofuran and further extracted repeatedly with dichloromethane and water. Finally, the RIm was dried in vacuum at 60 °C for 12 h.

4.2.2. Synthesis of Heteropolyacid-Based ILs ([RImM]3[PW12O40]). A equivalent molar 1,4-butane sultone was added to the RIm dropwise at 0 °C, and then, they were stirred at 50 °C for 2 days. The obtained zwitterions BsImR, which were white precipitates, were collected after washing with ethyl acetate and ether three times to remove the unreacted reagent and further drying for 12 h in vacuum. All the white precipitates were freely water soluble and undissolved in some organic solvents, such as acetone and toluene.

A equivalent molar aqueous solution of phosphotungstic acid was added to the BsImR dropwise at room temperature, and the mixture was stirred continually at room temperature for 1 day, yielding the [RImBs]3[PW12O40] ILs-AC. The ILs-AC was distilled under vacuum to remove water. Then, the [RImBs]3[PW12O40] IL-AC catalysts were obtained after washing with ethyl acetate and ether several times and drying at 50 °C under vacuum.

4.2.3. Preparation of Heteropolyacid-Based ILs ([RlmM]3[PW12O40]). A equivalent molar aqueous solution of phosphotungstic acid was added to the 1-alkyl-3-methylimidazolium bromide dropwise at room temperature, and the mixture was continued to stir at room temperature for 1 day, yielding the [RlmM]3[PW12O40] ILs-AC. The ILs-AC were distilled under vacuum to remove water. Then, the [RlmM]3[PW12O40] IL-AC catalysts were obtained after washing with ethyl acetate and ether several times and drying at 60 °C under vacuum.

4.3. Characterization of the ILs and Their Intermediates. Fourier transform infrared (FT-IR) spectra were obtained on a PerkinElmer spectrometer. 1H NMR spectra were recorded on a Varian mercury-plus 400 MHz nuclear magnetic resonance spectrometer. ESI-MS spectra were measured on a Varian 500MS instrument. The thermal decomposition temperature was obtained using a Beijing WCT-1D thermogravimetric analyzer from room temperature to 800 °C (10 °C min−1). The thermal decomposition temperature is the temperature corresponding to the intersection point between the maximum slope of the weight loss curve and the extended baseline. The electrical conductivities were measured in a Mettler Toledo FE30 conductivity meter.

4.4. Solubility Determination of the ILs. The solubility measurement of ILs in solvents was carried out according to the method reported in the literature. At 30 °C, an excessive amount of ILs was added to water. The solution was stirred using a magnetic stirrer for 40 min and was retained quietly for 60 min. The upper layer solution was moved to another flask and weighed. The solubility of ILs was determined by the static equilibrium method. The operation was repeated three times. The solubility calculation of ILs is as follows

\[ X = \frac{m_2 - m_0}{m_1 - m_0} \]

where \( m_0 \) is the weight of the empty flask, \( m_1 \) is the mass of the flask containing the saturated solution, and \( m_2 \) is the mass of the flask containing the solute.

4.5. Determination of the cmc. The cmc of ILs was tested by the conductivity method on an FE30 conductivity meter (Mettler Toledo, Switzerland). The IL aqueous solution was prepared and determined at 25 °C. The operation was conducted repeatedly three times.

4.6. ODS of Fuels. The model oil with sulfur contents of 1000 mg/L was prepared by dissolving DBT in n-octane.

The ODS reaction was performed in a three-neck flask. The 30% H2O2 and acetonitrile were added to the flask. When the air and n-octane were added, the reaction reached a certain reaction temperature, the model oil and IL...
catalyst were added to the flask. The reaction was proceeded for 2–6 h with continuous stirring and heating at the desired temperature. After the reaction, two phases were formed after cooling the mixture down to room temperature. The upper phase (model oil) was analyzed using an Agilent 1100 HPLC equipped with a C18 column (5 µm, 4.6 × 150 mm) and a 310 nm ultraviolet detector. The mobile phase was a methanol/water mixture (90:10 v/v) at a flowrate of 1 mL/min (Supporting Information; Figure S1).

■ ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04398.

Calibration curves of DBT in HPLC, FT-IR spectra of [C3ImB]=3[PW12O40], NMR spectral data of the ILs, ESI-MS of the ILs, plots of specific conductivity (κ) against [C3ImB]=3[PW12O40] concentration, and determination of the decomposition temperature (PDF).

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Notes

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■ REFERENCES

(1) Yang, R. T.; Hernandez-Maldonado, A. J.; Yang, F. H. Desulfurization of transportation fuels with zeolites under ambient conditions. Science 2003, 301, 79–81.
(2) Hirai, T.; Ogawa, K.; Komasawa, I. Desulfurization Process for Dibenzothiophenes from Light Oil by Photochemical Reaction and Liquid− Liquid Extraction. Ind. Eng. Chem. Res. 1996, 35, 586–589.
(3) Babich, I.; Moulijn, J. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. Fuel 2003, 82, 607–631.
(4) Yazu, K.; Yamamoto, Y.; Furuya, T.; Miki, K.; Ukegawa, K. Oxidation of dibenzothiophenes in an organic biphase system and its application to oxidative desulfurization of light oil. Energy Fuels 2001, 15, 1535–1536.
(5) Song, C. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. Catal. Today 2003, 86, 211–263.
(6) Shih, S. S.; Keville, K. M.; Lissy, D. N. Gasoline upgrading process. U.S. Patent 5,348,641 A, 1992-05-08, 1994.
(7) Bösmann, A.; Datsevich, I.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. Deep desulfurization of diesel fuel by extraction with ionic liquids. Chem. Commun. 2001, 23, 2494–2495.
(8) Funakoshi, I.; Aida, T. Process for recovering organic sulfur compounds from fuel oil. U.S. Patent 5,753,102 A, 1995-10-03, 1999.
(9) Forte, P. Process for the removal of sulfur from petroleum fractions. U.S. Patent 5,824,714 A, 1995-03-20, 1996.
(10) Horii, Y.; Onuki, H.; Doi, S.; Mori, T.; Takatori, T.; Sato, H.; Ookuro, T.; Sugawara, T. Desulfurization and denitration of light oil by extraction. U.S. Patent 5,852,714 A, 1995-06-02, 1996.
(11) Nie, Y.; Li, C.; Sun, A.; Meng, H.; Wang, Z. Extractive Desulfurization of Gasoline Using Imidazolium-Based Phosphoric Ionic Liquids. Energy Fuels 2006, 20, 2083–2087.
(12) Chaturvedi, D. Recent Developments on Task Specific Ionic Liquids. Curr. Org. Chem. 2011, 15, 1236–1248.
(13) Hallett, J. P.; Welton, T. Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. Chem. Rev. 2011, 111, 3508–3576.
(14) Cocalia, V. A.; Visser, A. E.; Rogers, R. D.; Hobbrey, J. D. Solubility and solvation in ionic liquids. In Ionic Liquids in Synthesis; Wasserscheid, P., Welton, T., Eds.; John Wiley & Sons: New Jersey, 2006; pp 89–101.
(15) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. Chem. Rev. 1999, 99, 2071–2084.
(16) Seddon, K. R. Ionic liquids for clean technology. J. Chem. Technol. Biotechnol. 1997, 68, 351–356.
(17) Xin, H.; Wu, Q.; Han, M.; Wang, D.; Jin, Y. Alkylation of benzene with 1-dodecene in ionic liquids [Rnimi]+ Al2Cl6X− (R= butyl, octyl and dodecyl; X= chlorine, bromine and iodine). Appl. Catal., A 2005, 292, 354–361.
(18) Xing, H.; Wang, T.; Zhou, Z.; Dai, Y. Novel bronsted-acid ionic liquids for esterifications. Ind. Eng. Chem. Res. 2005, 44, 4147–4150.
(19) Qiao, K.; Yokoyama, C. Nitration of aromatic compounds with nitric acid catalyzed by ionic liquids. Chem. Lett. 2004, 33, 808–809.
(20) Zeifman, A. A.; Stroylov, V. S.; Tito, I. Y.; Novikov, F. N.; Stroganov, O. V.; Svitanok, I. V.; Chlov, G. G. Modeling of the Diels−Alder reaction enantioselectivity by quantum mechanics and molecular mechanics. Mendeleev Commun. 2015, 25, 269–270.
(21) Inoue, T.; Ebina, H.; Dong, B.; Zheng, L. Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. *J. Colloid Interface Sci.* 2007, *314*, 236–241.

(22) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H. Novel Bronsted acidic ionic liquids and their use as dual solvent–catalysts. *J. Am. Chem. Soc.* 2002, *124*, 5962–5963.

(23) Wu, Q.; Li, W.; Wang, M.; Hao, Y.; Chu, T.; Shang, J.; Li, H.; Zhao, Y.; Jiao, Q. Synthesis of polyoxymethylene dimethyl ethers from methylal and trioxane catalyzed by Bronsted acid ionic liquids with different alkyl groups. *RSC Adv.* 2015, *5*, 57968–57974.