Effect of Water Content on Properties of Homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O Mixtures and Their Application in Oxidative Absorption of H$_2$S

Jianhong Wang * and Renren Ding

Department of Environmental Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China; dingrenren@bipt.edu.cn
* Correspondence: wangjianhong@bipt.edu.cn; Tel.: +86-010-8129-2291

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Abstract: The potential of 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]Fe(III)Cl$_4$) for replacing an iron(III) chelate catalytic solution in the catalytic oxidation of H$_2$S is attributed to its no side reaction and no degradation of the chelating agent. The catalytic oxidation product of water in non-aqueous [bmim]Fe(III)Cl$_4$ possibly has an influence on the oxidative absorption of H$_2$S. Water and hydrophobic [bmim]Fe(III)Cl$_4$ mixtures at water volume percents from 40% to 70% formed separate phases after stirring, without affecting the oxidative absorption of hydrogen sulfide. Then, studies on the properties of homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures at water volume percents in the range of 5.88–30% and above 80% reveal that these mixtures are both Brønsted and Lewis acids at vol % (H$_2$O) $\leq$ 30%, and only Lewis acids at vol % (H$_2$O) $\geq$ 80%. Raman spectra showed that [bmim]Fe(III)Cl$_4$ was the dominating species at vol % (H$_2$O) $\leq$ 30%, in contrast, [bmim]Fe(III)Cl$_4$ decomposed into FeCl$_3$·2H$_2$O and [bmim]Cl at vol % (H$_2$O) $\geq$ 80%. Further research on oxidative absorption of H$_2$S by homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures demonstrated that [bmim]Fe(III)Cl$_4$ was reduced by H$_2$S to [bmim]Fe(II)Cl$_4$H and FeCl$_3$·2H$_2$O was reduced to FeCl$_2$, at the same time, H$_2$S was oxidized to S$_8$. In addition, the decrease in acidity caused by increasing the water content increased the weight percent of absorbed H$_2$S, and decreased volatile HCl emissions. However, it is difficult to prevent the suspended S$_8$ generated at vol % (H$_2$O) $\geq$ 80% from the formation of sulfur blockage. Therefore, oxidative absorption of H$_2$S by [bmim]Fe(III)Cl$_4$–H$_2$O mixtures is feasible at vol % (H$_2$O) < 80% without sulfur blockage.

Keywords: [bmim]Fe(III)Cl$_4$; hydrogen sulfide; water; homogeneous mixtures

1. Introduction

[bmim]Fe(III)Cl$_4$ (1-butyl-3-methylimidazolium tetrachloroferrate) is an ionic liquid with unusual properties, including low volatility, high thermal stability, high hydrophobicity [1], low viscosity [2], and low surface tension [3]. [bmim]Fe(III)Cl$_4$ has also been found to be a potentially suitable solvent for gas separation and a highly effective catalyst for many reactions [4–6].

There has been a considerable recent interest in the use of [bmim]Fe(III)Cl$_4$ as an alternative to an iron(III) chelating solution for catalytic oxidation of H$_2$S. Iron(III) chelating solutions have several disadvantages that are associated with liquid phase oxidation processes, including degradation of the chelating agent [7] and sulfur oxo-acid salt formation [8]. Liquid phase oxidation processes using [bmim]Fe(III)Cl$_4$, however, do not require a complexing agent. In addition, sulfur oxo-acid salts cannot form in acidic media [9]. Catalytic-oxidation of H$_2$S by [bmim]Fe(III)Cl$_4$ differs from other heterogeneous catalytic reactions in that it is comprised of two simultaneous reactions that occur in the same or a separate vessel [10].
A description of these reactions follows. \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) is reduced by \(\text{H}_2\text{S}\) and then oxidatively regenerated by air or oxygen. The two steps demonstrate that \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) is both a solvent and a catalyst. The overall reaction is shown in Equation (1).

\[
\text{H}_2\text{S} + 0.5\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}
\]

Apart from sulfur, which is easily recovered by filtration, only \(\text{H}_2\text{O}\) is generated. Since \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) is hydrophobic [1], mixtures of \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) and water should form two phases that should be easily separable. However, Lee et al. reported that 20% (v/v) of \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) and water were fully miscible after vigorous shaking [11]. Wang et al. also reported that a \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) can be dissolved in 80% (v/v) \(\text{H}_2\text{O}\), while it was difficult for even a spot of \(\text{H}_2\text{O}\) to be dissolved in pure \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) [12]. Additional studies indicated that the presence of water in ionic liquids that have no metal affected their physical and chemical properties. The surface tension of ammonium ionic liquids in aqueous solutions increased non-linearly with water content [13]. The viscosity of hydrophilic 1-butyl-3-methylimidazolium-based ionic liquids also strongly depends on water content [14]. In addition, high hydration numbers are observed for imidazolium-based ionic liquids in aqueous mixtures [15]. Furthermore, solute-induced dissolution of hydrophobic ionic liquids in water was observed by Rickert et al. [16]. Nevertheless, to our knowledge, there are no literature reports on the effect of water on the properties of metal-containing ionic liquids, such as \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\). Since aqueous mixtures of \([\text{bmim}]\text{Cl}\) influence the solution structures of two archetype proteins [17], and imidazolium perrhenate ionic liquids in aqueous hydrogen peroxide were proved to be efficient catalysts for the selective oxidation of sulfides to sulfoxones [18], it is possible that water in \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) has an influence on the oxidative absorption of \(\text{H}_2\text{S}\).

In this paper, we report our findings on the properties of homogeneous mixtures of \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) and \(\text{H}_2\text{O}\), and their effect on the oxidative absorption of \(\text{H}_2\text{S}\). Additional work on the regeneration of \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) from these aqueous homogeneous mixtures will be discussed in a future paper.

2. Results and Discussion

2.1. Effect of Water Concentration on the Formation of \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\)–\(\text{H}_2\text{O}\) Mixtures

The effect of water concentration on the formation of homogeneous \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\)–\(\text{H}_2\text{O}\) mixtures was studied by adding different amounts of water to \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\).

Figure 1 shows that dark brown homogeneous liquids are obtained at \(x(\text{H}_2\text{O})\) values from 5.88% to 30%. At \(x(\text{H}_2\text{O})\) values from 40% to 70%, however, the mixtures form two phases. The upper aqueous phase is brownish yellow and the lower oil phase is dark brown. The homogeneous liquids at \(x(\text{H}_2\text{O}) \geq 80\%\) are brownish yellow. Since there wasn’t the presence of structured water in the hydrophobic ionic liquid phase [19], it is very easy to separate water from \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\) in the two-phase mixtures without affecting the oxidative absorption of hydrogen sulphide. However, it is difficult to separate water from the homogeneous \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\)–\(\text{H}_2\text{O}\) mixtures without evaporation method [11,12]. On the one hand, the acidity of homogeneous \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\)–\(\text{H}_2\text{O}\) mixtures may change with the increment of water. On the other hand, as the \(x(\text{H}_2\text{O})\) in homogeneous mixtures was increased from lower concentrations (5.88–30%) to higher concentrations (≥80%), the colour of the mixture changed from dark brown to brownish yellow. This colour change may indicate that the structure of iron in mixtures at \(x(\text{H}_2\text{O}) \leq 30\%\) may be different from that at \(x(\text{H}_2\text{O}) \geq 80\%\), because the colour of each solution came from an optical frequency characteristic of a specific iron structure. Hence, the formation of homogeneous \([\text{bmim}]\text{Fe(III)}\text{Cl}_4\)–\(\text{H}_2\text{O}\) mixtures possibly affects the oxidative absorption of hydrogen sulfide.
These observations indicate that increasing the content of water causes a decrease in the amount of Lewis acids present. For example, when $x(H_2O)$ increases from 0% to 30%, the IR bands at 1487 and 1610 cm$^{-1}$ are attributed to Brønsted acids [22]. These assignments demonstrate that the homogeneous mixtures at $x(H_2O) \leq 30\%$ are simultaneously Brønsted and Lewis acids. In contrast, when $x(H_2O)$ reaches 80%, the intensity of the IR bands at 1540 and 1635 cm$^{-1}$ decrease, and are almost absent at $x(H_2O) = 90\%$. However, the IR bands at 1487 and 1610 cm$^{-1}$ are still present. These observations indicate that increasing the content of water causes a decrease in the amount of Brønsted acid present, resulting in the presence of almost exclusively Lewis acids at $x(H_2O) \geq 80\%$. Since the H at the 2 position on the imidazolium ring in [bmim]Fe(III)Cl$_4$ is easily removed in Brønsted acids [25], the absence of Brønsted acids was mainly caused by the decomposition of [bmim]Fe(III)Cl$_4$, as discussed below. On the other hand, Lewis acids resulted from FeCl$_3$ [23]. Therefore, it is possible that the FeCl$_3$ concentration decreased as the water content increased, causing a decrease in the quantity of Lewis acids present. For example, when $x(H_2O)$ increases from 80% to 90%, the pH of the homogeneous mixtures increases from 1.17 to 1.28. However, the acidity of the mixtures at $x(H_2O) \leq 30\%$ is too low (negative pH) to be precisely measured by a pH Meter.
2.3. Raman Spectral Analysis of Homogeneous [bmim]Fe(III)Cl4–H2O Mixtures

Raman spectra were used to investigate the structure of iron species in the homogeneous [bmim]Fe(III)Cl4–H2O mixtures. The Raman spectra for the homogeneous mixture at x(H2O) = 5.88% are shown in Figure 3. The peaks at 110, 136, 333, and 390 cm\(^{-1}\) correspond very well with literature values for Fe(III)Cl4\(^-\) in concentrated aqueous solution [26], indicating that Fe(III)Cl4\(^-\) is the predominant iron-containing species in the homogeneous mixtures at x(H2O) = 5.88% before oxidative absorption of H2S. Since homogeneous liquids at x(H2O) ≤ 30% are all dark brown, which corresponds to the colour of [bmim]Fe(III)Cl4 [1], [bmim]Fe(III)Cl4 was the dominating species at x(H2O) ≤ 30%.

Unfortunately, the peaks at 136, 333, and 390cm\(^{-1}\) disappeared for the homogeneous mixture containing 80% H2O. A new peak at 318 cm\(^{-1}\) appeared (see Figure 3), belonging to FeCl3·2H2O [26]. This peak provides strong evidence for the decomposition of [bmim]Fe(III)Cl4 into a new species, such as FeCl3·2H2O (see Equation(2)) at x(H2O) = 80%, which is consistent with Liu’s research [27].

\[
\text{FeCl}_3 \cdot 2\text{H}_2\text{O} \rightarrow \text{FeCl}_3 + 2\text{H}_2\text{O}
\] (1)

The colour of the homogeneous mixture at x(H2O) ≥ 80% demonstrates that FeCl3·2H2O is the iron compound present at x(H2O) ≥ 80%. Since both FeCl3·2H2O and hydrophilic [bmim]Cl [17] are soluble in water, the homogeneous mixtures at x(H2O) ≥ 80% are true solutions. These results come in complete opposition with previous works asserting that due to the hydrophobic property of [bmim]Fe(III)Cl4, the homogeneous mixture of [bmim]Fe(III)Cl4 and H2O may be an emulsion rather than a true solution [12].

2.4. Oxidative Absorption of H2S by Homogeneous [bmim]Fe(III)Cl4–H2O Mixtures

Oxidative absorption of H2S by homogeneous [bmim]Fe(III)Cl4–H2O mixtures was investigated at 60 °C. Figures 3 and 4 provide a good picture of the oxidative product. As can be seen in Figure 4, the characteristic feature of FeCl3·2H2O at 318 cm\(^{-1}\) in homogenous mixtures of 80% H2O disappears after oxidative absorption of H2S. Simultaneously, a new peak at 153 cm\(^{-1}\) belonging to FeCl2 [28], as well as new peaks at 219 and 473 cm\(^{-1}\), both due to S\(_8\) [29], appears. These results indicate that FeCl3·2H2O was completely reduced to FeCl2. Therefore, the reaction can be summarized by Equation (3).

\[
16\text{FeCl}_3 \cdot 2\text{H}_2\text{O} + 8\text{H}_2\text{S} \rightarrow 16\text{FeCl}_2 + \text{S}_8 + 16\text{HCl} + 32\text{H}_2\text{O}
\] (3)
Equation (3) shows that HCl is generated from the oxidative absorption of H$_2$S by homogeneous mixtures at $x$(H$_2$O) $\geq$ 80%. Consequently, it is apparent that the acidity of mixtures at $x$(H$_2$O) $\geq$ 80% is improved after oxidative absorption of H$_2$S and discharge of volatile HCl from the acidic mixtures. Furthermore, as shown in Figure 5c,d, homogeneous mixtures at $x$(H$_2$O) = 90% after oxidative-absorption of H$_2$S become colourless due to the complete reduction of FeCl$_3$·2H$_2$O and S$_8$, the oxidative product of H$_2$S, is suspended in the mixtures. Figure 6 shows that the surface tension of homogeneous mixtures at $x$(H$_2$O) $\leq$ 30% remains almost constant up to about 37 mN·m$^{-1}$, whereas, a remarkable increase in the surface tension is observed for homogeneous mixtures at $x$(H$_2$O) $\geq$ 80%, moreover, for homogeneous mixtures at $x$(H$_2$O) = 90%, the surface tension sharply increase to 56.57 mN·m$^{-1}$. At $x$(H$_2$O) $\geq$ 80%, the surface tension of homogeneous mixtures increases remarkably, resulting in the suspension of S$_8$ in the mixtures.

![Raman spectra for the homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixture at $x$(H$_2$O) = 80% before and after oxidative-absorption of H$_2$S.](image)

**Figure 4.** Raman spectra for the homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixture at $x$(H$_2$O) = 80% before and after oxidative-absorption of H$_2$S.

![Photo of homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures at different $x$(H$_2$O) values.](image)

**Figure 5.** Photo of homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures at different $x$(H$_2$O) values: (a) $x$(H$_2$O) = 30%; (b) $x$(H$_2$O) = 30% after bubbling H$_2$S; (c) $x$(H$_2$O) = 90%; and (d) $x$(H$_2$O) = 90% after bubbling H$_2$S.

However, it is difficult to prevent the suspended S$_8$ from the formation of sulfur blockage. Therefore, catalytic-oxidation of H$_2$S by homogeneous mixtures at $x$(H$_2$O) $\geq$ 80% suffers from at least two major drawbacks: (1) the slow rate of oxidation of free Fe(II) ions, such as FeCl$_2$ oxidation by O$_2$ [30], and (2) the sulfur blockage of suspended S$_8$. 

On the contrary, with the color deepening of homogeneous mixtures at $x(H_2O) = 30\%$ after oxidative absorption of $H_2S$, stable deposits of elemental sulfur, which is easy to be separated, is likely produced, as shown in Figure 5b. However, the characteristic peaks at 110, 136, 333, and 390 cm$^{-1}$ for FeCl$_4^-$ also exist in the homogeneous mixture at $x(H_2O) = 5.88\%$ after the absorption of $H_2S$ with the appearance of no new peaks in the IR spectra (see Figure 3). These results indicate that Fe(III)Cl$_4^-$ is also an essential component in the homogeneous mixture after oxidative absorption of $H_2S$. In fact, Fe(III)Cl$_4^-$ was probably changed to Fe(II)Cl$_4^{2-}$ [6], and $H_2S$ was oxidized to $S_8$ [24]. But the concentration of Fe(II)Cl$_4^{2-}$ and sulfur in mixtures at $x(H_2O) = 5.88\%$ after oxidative-absorption of $H_2S$ were too low to be detected by Raman spectroscopy (see Table 1). This was strengthened by the previous studies [21]. The Raman characteristic peaks of $S_8$ and Fe(II)Cl$_4^{2-}$ after oxidative-absorption of $H_2S$ by pure [bmim]FeCl$_4$ were not observed. However, at lower concentration of [bmim]FeCl$_4$ in the mixtures of [bmim]Fe(III)Cl$_4$, [bmim]Cl and water, the acidic strength decreased remarkably, resulting in higher concentration of Fe(II)Cl$_4^{2-}$ and sulfur, and hence the new features of $S_8$ and Fe(II)Cl$_4^{2-}$ after oxidative-absorption of $H_2S$ by the mixtures of [bmim]Fe(III)Cl$_4$, [bmim]Cl and water could be detected by a Raman Spectrometer.

In order to get the more catalytic oxidation product of $H_2S$ by homogeneous mixtures, the first absorption of $H_2S$ for 20 min and the second regeneration of $O_2$ for 40 min in the homogeneous mixtures at $x(H_2O) = 5.88\%$ were conducted for six consecutive cycles, then, the homogeneous mixtures at $x(H_2O) = 5.88\%$ were filtered and vacuum-dried. We get an amount of yellow powder. The XRD patterns of the yellow powder are shown in Figure 7. The yellow powder is observed with significant $S$ (23) peak reflection demonstrates that the powder is elemental sulfur.

![Figure 6. Surface tension of homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures at different $x(H_2O)$ at 25 °C.](image)

![Figure 7. XRD of the product from catalytic oxidation of $H_2S$ by homogeneous mixtures at $x(H_2O) = 5.88\%$.](image)
Our conclusion was strengthened by the fact that the product of oxidative absorption of H$_2$S using pure [bmim]Fe(III)Cl$_4$ was sulfur [24].

In addition, Fe(III)Cl$_4$ in DMSO was reduced to Fe(II)Cl$_4^{2-}$ in the oxidation of H$_2$S [31]. Finally, our previous research also showed H$_2$S was converted to S$_8$ by [bmim]FeCl$_4$ of [bmim]Fe(III)Cl$_4$–[bmim]Cl–H$_2$O mixtures, and [bmim]FeCl$_4$ in the process was converted to [bmim]Fe(II)Cl$_4$H [21]. Hence, the oxidation of H$_2$S by homogeneous mixtures at $x$(H$_2$O) $\leq$ 30% is written as Equation (4).

$$16\begin{array}{l}
\text{Fe(III)Cl}_4^2- \\
\\end{array} + 8\text{H}_2\text{S} \rightarrow 16\begin{array}{l}
\text{Fe(II)Cl}_3^+ \\
\\text{Cl}^- \\
\text{H}^+ \end{array} + \text{S}_8$$

(2)

Nguyen et al. suggested that [bmim]FeCl$_4$ could be reduced to give ([bmim]FeCl$_3$)*, which could be transformed into [Fe(II)Cl]$^+$([bmim]Cl)$_2$ $^-$. Similarly, our previous research also suggested [bmim]Fe(III)Cl$_4$ was firstly reduced by H$_2$S to give ([bmim]FeCl$_3$)*, which was then transformed into [bmim]Fe(II)Cl$_4$H as soon as it reacted with HCl (see Equations (5) and (6)).

$$16\text{[bmim]Fe(III)Cl}_4 + 8\text{H}_2\text{S} \rightarrow 16\text{[bmim]Fe(II)Cl}_3^* + \text{S}_8 + 16\text{HCl}$$

(5)

$$\text{([bmim]Fe(II)Cl}_3^* + \text{HCl} \rightarrow \text{[bmim]Fe(II)Cl}_4\text{H}$$

(6)

From Equation (4), an increase in the acidity of homogeneous mixtures after oxidation of H$_2$S is apparent due to the production of H$^+$. In addition, Fe(III)Cl$_4$ has a longer Fe(III)–Cl bond distance than FeCl$_3$ [6]. Therefore, it is likely that after oxidation of H$_2$S, H$^+$ and Cl$^-$ present in homogeneous mixtures becomes HCl. The existence of HCl is also strengthened by Equation (5), which shows that HCl comes from the intermediate species.

Trace amounts of volatile HCl from the mixtures during oxidative absorption of H$_2$S were indeed detected by ion chromatography. Effect of water concentration on oxidative absorption of H$_2$S by [bmim]Fe(III)Cl$_4$–H$_2$O mixtures without other additives at 60 °C was shown in Table 1. Table 1 shows an increase in weight percent of absorbed H$_2$S and a decrease in volatile HCl emissions with increasing water concentration were seen.

Table 1. Effect of water concentration on the weight percent of absorbed H$_2$S and volatile HCl emissions in homogenous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures at 60 °C.

| Water Concentration in Homogeneous Mixtures (v/v) % | 0     | 5.88  | 80     |
|-------------------------------------------------|-------|-------|--------|
| Weight percent of iron(III) in homogeneous mixtures (%) | 16.6  | 15.87 | 4.19   |
| Weight percent of absorbed H$_2$S in mixtures (%) | 0.78  | 0.82  | 1.15   |
| Concentration of volatile HCl in mixtures ($\times 10^{-6}$) | 841.11 | 326.86 | 52.16 |

Previous studies demonstrated that the oxidation of H$_2$S by Fe$^{3+}$ or an iron(III) chelate is a fast chemical reaction [20,32]. As soon as H$_2$S was absorbed, it was oxidized. In addition, many researchers have observed a high solubility of H$_2$S in a series of 1-butyl-3-methylimidazolium ([bmim]+)-based ionic liquids due to the formation of H$_2$S–Cl$^-$ or other complexes [33–35]. It can be seen from Table 1 that the concentration of iron(III) in mixtures is very high in comparison with chelated iron solutions [36]. A high concentration of absorbed H$_2$S in these mixtures is not seen, however. On the contrary, the concentration of iron decreases as the water content increases, resulting in an increase of the weight percent of absorbed H$_2$S. A key factor is that the [bmim]Fe(III)Cl$_4$–H$_2$O mixtures were not only an oxidizer but also a solution, thus, the low concentrations of absorbed H$_2$S in mixtures was most likely caused by the strong acidity of the mixtures. Figure 2 shows that the homogenous mixtures at $x$(H$_2$O) $\leq$ 30% are simultaneously Brønsted and Lewis acids. Moreover, their acidity was too strong to be measured by a pH Meter. Even when the water content of the mixtures increases to 80%, the pH only reaches 1.17. However, a highly acidic environment was disadvantageous to the
solubility of H₂S [20,32]. Consequently, the weight percent of absorbed H₂S in mixtures was very low in comparison with iron concentrations. Nevertheless, the decrease in acidity by increasing the water content improved the solubility of H₂S in the mixtures, and the weight percent of absorbed H₂S in mixtures was improved.

Similarly, decreasing acidity by increasing water content enhances the solubility of acidic HCl, and, thus, volatile HCl emissions decreased with increasing water content. However, during oxidative absorption of H₂S by homogenous [bmim]Fe(III)Cl₄–H₂O mixtures at 60 °C increasing water also led to more evaporation of water, which decreased the weight percent of absorbed H₂S in mixtures, according to the absorption measurements. Volatile HCl emissions and the evaporation of water indicated that the actual weight percent of absorbed H₂S in mixtures was higher than the measured value.

It’s worth mentioning that increasing x(H₂O) was favourable for increasing oxidative-absorption of H₂S and decreasing volatile HCl emissions, but suspended S₈ generated at x(H₂O) ≥ 80% was difficult to separate from the mixtures and the formation of the sulfur blockage.

3. Materials and Methods

3.1. Preparation of [bmim]Fe(III)Cl₄–H₂O Mixtures

[bmim]Fe(III)Cl₄ was synthesized via a literature method [1]. Mixtures of [bmim]Fe(III)Cl₄ and water were prepared by adding water to [bmim]Fe(III)Cl₄ with vigorous stirring for 24 h. Ten [bmim]Fe(III)Cl₄–H₂O mixtures were prepared in volume fractions of x(H₂O), where x(H₂O) = 5.88%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%.

3.2. Instruments

The acidity of each mixture was measured by a TENSOR 27 FT-IR Spectrometer (Bruker Optics, Ettlingen, Germany) using a method of determining the acidity of [bmim]Fe(III)Cl₄ ionic liquids [24]. Pyridine was used as a base infrared spectroscopy probe molecule to determine the acidity of ionic liquids. All of the infrared spectroscopy samples were prepared by mixing pyridine and ionic liquids at the ratio of one to five and then spreading as liquid films on KBr windows.

The iron structure of each mixtures was obtained using a laser confocal spectrometer (model labRAM Aramis, Horiba Jobin Yvon, France) with a He–Ne laser (632.8 nm). Raman samples were measured in glass capillaries with an inner diameter of 0.9–1.1 mm and 0.10–0.15 mm wall thickness.

The surface tension of each mixtures was measured by OCA 15 (Dataphysics, Filderstadt, Germany) at room temperature.

XRD of the powder was obtained using an X ray diffractometer (model Ultima IV, Rigaku, Tokyo, Japan).

3.3. Absorption Measurements

The apparatus of oxidation-absorption of H₂S in ionic liquids has been presented in detail [21]. H₂S from a commercial gas cylinder was first bubbled at a pressure of 0.05 Mpa and a flow rate of 15 mL/min through predetermined amounts of each liquid (about 3.5–4 g) loaded in a glass bubbling absorption tube (140 mm long, 20 mm maximum inner diameter), which was placed in a water bath at 60 °C, then bubbled into 200 mL of ultra-pure water in a tail gas absorber.

After 20 min, the glass bubbling absorption tube was weighed using an AL104 precision balance (Mettler Toledo, Shanghai, China) with an uncertainty of ±0.0001 g, to measure the mass of H₂S absorbed. From this mass, the H₂S absorbed per gram of ionic liquid was calculated. Then, a DX-600 ion chromatography apparatus (DIONEX Co., Sunnyvale, CA, USA) was used to analyse the Cl⁻ concentration in ultra-pure water, which had been absorbed along with H₂S. From this data, the concentration of volatile HCl per gram of ionic liquid was calculated.

If the ionic liquids absorbed H₂S was regenerated by O₂, O₂ was bubbled at a pressure of 0.05 Mpa and a flow rate of 30 mL/min through the ionic liquids absorbed H₂S for 40 min.
4. Conclusions

We have prepared homogeneous mixtures of [bmim]Fe(III)Cl$_4$–H$_2$O at $x$(H$_2$O) = 5.88–30% and above 80%, which showed the presence of both Brønsted and Lewis acids at $x$(H$_2$O) ≤ 30%, and only Lewis acids at $x$(H$_2$O) ≥ 80% by FT-IR. Raman spectra showed Fe(III)Cl$_4^-$ was the dominating iron species at $x$(H$_2$O) ≤ 30%, which was reduced by H$_2$S to Fe(II)Cl$_4^-$. FeCl$_3$·2H$_2$O was the primary iron compound at $x$(H$_2$O) ≥ 80%, which was reduced to FeCl$_2$. In addition, oxidative-absorption of H$_2$S by homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures demonstrated that increasing $x$(H$_2$O) increased the weight percent of absorbed H$_2$S and decreased the volatile HCl emissions. However, there are some disadvantages in oxidation of H$_2$S by homogeneous [bmim]Fe(III)Cl$_4$–H$_2$O mixtures at $x$(H$_2$O) ≥ 80%, including sulfur blockage of suspended S$_8$ and the slow regenerative rate of FeCl$_2$. Therefore, it is necessary that controlling the $x$(H$_2$O) below 80% ensures that oxidative-absorption of H$_2$S by [bmim]Fe(III)Cl$_4$ is performed well.

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References

1. Hayashi, S.; Hamaguchi, H. Discovery of a magnetic ionic liquid [bmim]FeCl$_4$. Chem. Lett. 2004, 33, 1590–1591. [CrossRef]
2. Yoshida, Y.; Saito, G. Influence of structural variations in 1-alkyl-3-methylimidazolium cation and tetrahalogenoferrate(III) anion on the physical properties of the paramagnetic ionic liquids. J. Mater. Chem. 2006, 16, 1254–1262. [CrossRef]
3. Zhang, Q.-G.; Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Huang, M. Studies on an ionic liquid based on FeCl$_3$ and its properties. Fluid Phase Equilib. 2004, 226, 207–211. [CrossRef]
4. Bica, K.; Gaertner, P. An iron-containing ionic liquid as recyclable catalyst for aryl grignard cross-coupling of alkyl halides. Org. Lett. 2006, 8, 733–735. [CrossRef] [PubMed]
5. Wang, H.; Yan, R.; Li, Z.; Zhang, X.; Zhang, S. Fe-containing magnetic ionic liquid as an effective catalyst for the glycosylation of poly(ethylene terephthalate). Catal. Commun. 2010, 11, 763–767. [CrossRef]
6. Nguyen, M.; Nguyen, L.; Jeon, E.; Kim, J.; Cheong, M.; Kim, H.; Lee, J. Fe-containing ionic liquids as catalysts for the dimerization of bicyclo[2.2.1]hepta-2,5-diene. J. Catal. 2008, 258, 5–13. [CrossRef]
7. Eng, S.J.; Motekaitis, R.J.; Martell, A.E. Degradation of coordinated β-diketonates as iron chelate catalysts during the oxidation of H$_2$S to S$_8$ by molecular oxygen. Inorg. Chem. Acta 2000, 299, 9–15. [CrossRef]
8. McManus, D.; Martell, A.E. The evolution, chemistry and applications of chelated iron hydrogen sulfide removal and oxidation processes. J. Mol. Catal. A Chem. 1997, 117, 289–297. [CrossRef]
9. Angelis, A.; Bellussi, G.; Pollesel, P.; Romano, U.; Perego, C. Process for the Removal of Hydrogen Sulfide, by Means of its Oxidation in the Presence of Hetero Polyacids. U.S. Patent 7,553,473 B2, 30 June 2009.
10. He, Y.; Yu, J.; Chen, L. Wet oxidation desulfurization of hydrogen sulfide with application of Fe-based ionic liquid. CIESC J. 2010, 61, 963–968. (In Chinese)
11. Lee, S.H.; Ha, S.H.; You, C.-Y.; Koo, Y.-M. Recovery of magnetic ionic liquid [bmim]FeCl$_4$ using electromagnet. Korean J. Chem. Eng. 2007, 24, 436–437. [CrossRef]
12. Wang, M.; Li, B.; Zhao, C.; Qian, X.; Xu, Y.; Chen, G. Recovery of [bmim]FeCl$_4$ from homogeneous mixture using a simple chemical method. Korean J. Chem. Eng. 2010, 27, 1275–1277. [CrossRef]
13. Domarńska, U.; Pobudkowska, A.; Rogalski, M. Surface tension of binary mixtures of imidazolium and ammonium based ionic liquids with alcohols, or water: Cation, anion effect. J. Colloid Interface Sci. 2008, 322, 342–350. [CrossRef] [PubMed]
14. Grishina, E.P.; Ramenskaya, L.M.; Gruzdev, M.S.; Kraeva, O.V. Water effect on physicochemical properties of 1-butyl-3-methylimidazolium based ionic liquids with inorganic anions. J. Mol. Liq. 2013, 177, 267–272. [CrossRef]
15. Singh, T.; Kumar, A. Cation-anion-water interactions in aqueous mixtures of imidazolium based ionic liquids. Vib. Spectrosc 2011, 55, 119–125. [CrossRef]
16. Rickert, P.; Stepinski, D.; Rausch, D.; Bergeron, R.; Jakab, S.; Dietz, M. Solute-induced dissolution of hydrophobic ionic liquids in water. Talanta 2007, 72, 315–320. [CrossRef] [PubMed]
17. Baker, G.A.; Heller, W.T. Small-angle neutron scattering studies of model protein denaturation in aqueous solutions of the ionic liquid 1-butyl-3-methylimidazolium chloride. Chem. Eng. J. 2009, 147, 6–12. [CrossRef]
18. Zhang, B.; Li, S.; Yue, S.; Cokoja, M.; Zhou, M.-D.; Zang, S.-L.; Kühn, F.E. Imidazolium perrhenate ionic liquids as efficient catalysts for the selective oxidation of sulfides to sulfoxones. J. Organomet. Chem. 2013, 744, 108–112. [CrossRef]
19. Kashin, A.S.; Galkin, K.I.; Khokhlova, E.A.; Ananikov, V.P. Direct observation of self-organized water-containing structures in the liquid phase and their influence on 5-(hydroxymethyl)furfural formation in ionic liquids. Angew. Chem. Int. Ed. Engl. 2016, 55, 2161–2166. [CrossRef] [PubMed]
20. Piché, S.; Larachi, F. Dynamics of pH on the oxidation of with iron(III) chelates in anoxic conditions. Chem. Eng. Sci. 2006, 61, 7673–7683. [CrossRef]
21. Wang, J.; Zhang, W. Oxidative absorption of hydrogen sulfide by iron-containing ionic liquids. Energy Fuels 2014, 28, 5930–5935. [CrossRef]
22. Yang, Y.L.; Kou, Y. Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe. Chem. Commun. 2004, 226–227. [CrossRef] [PubMed]
23. Yin, D.; Li, C.; Tao, L.; Yu, N.; Hu, S.; Yin, D. Synthesis of diphenylmethane derivatives in Lewis acidic ionic liquids. J. Mol. Catal. A Chem. 2006, 245, 260–265. [CrossRef]
24. Yao, R.; Li, P.; Sun, L.; He, Y.; Chen, L.; Yu, Y.; Mu, R.; Yu, J. Physicochemical properties of iron-based chloride imidazole ionic liquid and wet desulfurization mechanism of hydrogen sulfide. J. China Coal Soc. 2011, 36, 135–139. (In Chinese)
25. Sun, X.; Zhao, S.; Zhang, M. Characterization of [bmim]Cl/FeCl₃ ionic liquid with spectra. Pet. Sci. 2005, 2, 77–81.
26. Marston, A.; Bush, S. Raman spectral investigation of the complex species of ferric chloride in concentrated aqueous solution. Appl. Spectrosc. 1972, 26, 579–584. [CrossRef]
27. Liu, W.; Etschmann, B.; Brugger, J.; Spiccia, L.; Foran, G.; McInnes, B. UV–Vis spectrophotometric and XAFS studies of ferric chloride complexes in hyper-saline LiCl solutions at 25–90 °C. Chem. Geol. 2006, 231, 326–349. [CrossRef]
28. Jou, F.-Y.; Mather, A.E. Solubility of hydrogen sulfide in [bmim][PF₆]. Int. J. Thermophys. 2007, 28, 490–495. [CrossRef]
29. Jalili, A.H.; Rahmati-Rostami, M.; Ghotbi, C.; Hosseini-Jenab, M.; Ahmadi, A.N. Solubility of H₂S in ionic liquids [bmim][PF₆], [bmim][BF₄], and [bmim][TF₂N]. J. Chem. Eng. Data 2009, 54, 1844–1849. [CrossRef]
35. Pomelli, C.S.; Chiappe, C.; Vidis, A.; Laurenczy, G.; Dyson, P.J. Influence of the interaction between hydrogen sulfide and ionic liquids on solubility: Experimental and theoretical investigation. *J. Phys. Chem. B* 2007, 111, 13014–13019. [CrossRef] [PubMed]

36. Karimi, A.; Tavassoli, A.; Nassernejad, B. Kinetic studies and reactor modeling of single step H$_2$S removal using chelated iron solution. *Chem. Eng. Res. Des.* 2010, 88, 748–756. [CrossRef]