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Effect of Water Content on Properties of Homogeneous [bmim]Fe(III)Cl_4–H_2O Mixtures and Their Application in Oxidative Absorption of H_2S

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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_2S 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_2S. Water and hydrophobic [bmim]Fe(III)Cl_4 mixtures at water volume percents from 40% to 70% formed separate phases after srirring, without affecting the oxidative absorption of hydrogen sulfide. Then, studies on the properties of homogeneous [bmim]Fe(III)Cl_4–H_2O 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_2O) $\leq$ 30%, and only Lewis acids at vol % (H_2O) $\geq$ 80%. Raman spectra showed that [bmim]Fe(III)Cl_4 was the dominating species at vol % (H_2O) $\leq$ 30%, in contrast, [bmim]Fe(III)Cl_4 decomposed into $FeCl_3 \cdot 2H_2O$ and [bmim]Cl at vol % (H_2O) $\geq$ 80%. Further research on oxidative absorption of H_2S by homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures demonstrated that [bmim]Fe(III)Cl_4 was reduced by H_2S to [bmim]Fe(II)Cl_4H and $FeCl_3 \cdot 2H_2O$ was reduced to $FeCl_2$, at the same time, H_2S was oxidized to S_8. In addition, the decrease in acidity caused by increasing the water content increased the weight percent of absorbed H_2S, and decreased volatile HCl emissions. However, it is difficult to prevent the suspended S_8 generated at vol % (H_2O) $\geq$ 80% from the formation of sulfur blockage. Therefore, oxidative absorption of H_2S by [bmim]Fe(III)Cl_4–H_2O mixtures is feasible at vol % (H_2O) < 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_2S. 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_2S 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. [bmim]Fe(III)Cl_4 is reduced by H_2S and then oxidatively regenerated by air or oxygen. The two steps demonstrate that [bmim]Fe(III)Cl_4 is both a solvent and a catalyst. The overall reaction is shown in Equation (1).

$$H_2S + 0.5O_2 \rightarrow S + H_2O \quad (1)$$

Apart from sulfur, which is easily recovered by filtration, only H_2O is generated. Since [bmim]Fe(III)Cl_4 is hydrophobic [1], mixtures of [bmim]Fe(III)Cl_4 and water should form two phases that should be easily separable. However, Lee et al. reported that 20% (*v*/*v*) of [bmim]Fe(III)Cl_4 and water were fully miscible after vigorous shaking [11]. Wang et al. also reported that a [bmim]Fe(III)Cl_4 can be dissolved in 80% (*v*/*v*) H_2O, while it was difficult for even a spot of H_2O to be dissolved in pure [bmim]Fe(III)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 [bmim]Fe(III)Cl_4. Since aqueous mixtures of [bmim]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 sulfones [18], it is possible that water in [bmim]Fe(III)Cl_4 has an influence on the oxidative absorption of H_2S.

In this paper, we report our findings on the properties of homogeneous mixtures of [bmim]Fe(III)Cl_4 and H_2O, and their effect on the oxidative absorption of H_2S. Additional work on the regeneration of [bmim]Fe(III)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 [bmim]Fe(III)Cl_4–H_2O Mixtures

The effect of water concentration on the formation of homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures was studied by adding different amounts of water to [bmim]Fe(III)Cl_4.

Figure 1 shows that dark brown homogeneous liquids are obtained at $x(H_2O)$ values from 5.88% to 30%. At $x(H_2O)$ 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 $x(H_2O) \geq 80\%$ 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 [bmim]Fe(III)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 [bmim]Fe(III)Cl_4–H_2O mixtures without evaporation method [11,12]. On the one hand, the acidity of homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures may change with the increment of water. On the other hand, as the $x(H_2O)$ 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 $x(H_2O) \leq 30\%$ may be different from that at $x(H_2O) \geq 80\%$, because the colour of each solution came from an optical frequency characteristic of a specific iron structure. Hence, the formation of homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures possibly affects the oxidative absorption of hydrogen sulfide.

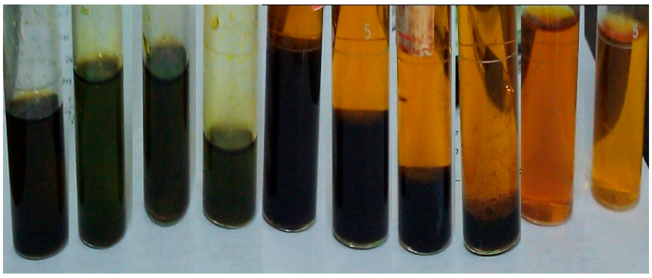


Figure 1. Effect of water volume percents on the formation of [bmim]Fe(III)Cl_4–H_2O mixtures. $x(H_2O)$ from left to right are: 5.88%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%.

2.2. *Acidity of Homogeneous [bmim]Fe(III)Cl_4–H_2O Mixtures*

Solution pH is widely recognized as a key variable for H_2S oxidation process using iron chelates [20]. Acidity is also a key variable for oxidation of H_2S by [bmim]Fe(III)Cl_4 [21]. Pyridine has been used as a probe molecule for the determination of the Lewis and Brønsted acidities of solid acids and ionic liquids by monitoring the bands in the range of 1400–1700 cm^{-1} arising from its ring vibration modes [22]. The principle of this experiment is as follows: if pyridine, a weak Lewis base, is mixed with acid, the interaction between these two compounds will exhibit a correlated band in IR spectra [23]. In this work, pyridine was added to homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures, then their acidity was measured by infrared spectroscopy.

As shown in Figure 2, when $x(H_2O)$ varies from 0 (pure [bmim]Fe(III)Cl_4) to 30%, the IR bands at around 1540 and 1635 cm^{-1} are attributed to Brønsted acids [22], while the IR bands at around 1487 and 1610 cm^{-1} are attributed to Lewis acids [21,24]. These assignments demonstrate that the homogenous 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.

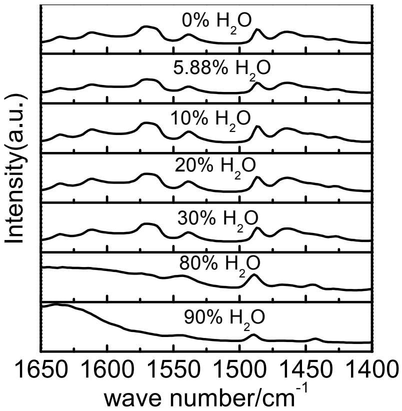


Figure 2. IR spectra of mixtures prepared from pyridine and [bmim]Fe(III)Cl_4–H_2O at different values for $x(H_2O)$.

2.3. Raman Spectral Analysis of Homogeneous [bmim]Fe(III)Cl_4–H_2O Mixtures

Raman spectra were used to investigate the structure of iron species in the homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures. The Raman spectra for the homogeneous mixture at $x(H_2O)$ = 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)Cl_4^- in concentrated aqueous solution [26], indicating that Fe(III)Cl_4^- is the predominant iron-containing species in the homogeneous mixtures at $x(H_2O)$ = 5.88% before oxidative absorption of H_2S. Since homogeneous liquids at $x(H_2O) \leq 30\%$ are all dark brown, which corresponds to the colour of [bmim]Fe(III)Cl_4 [1], [bmim]Fe(III)Cl_4 was the dominating species at $x(H_2O) \leq 30\%$.

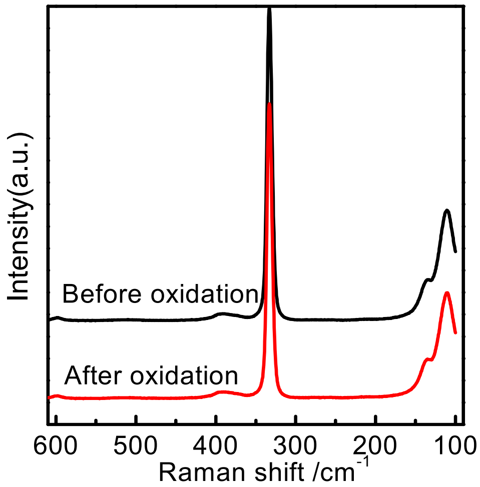
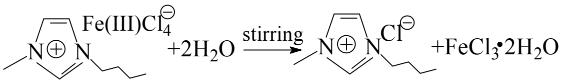


Figure 3. Raman spectra of homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures at $x(H_2O)$ = 5.88% before and after oxidative-absorption of H_2S.

Unfortunately, the peaks at 136, 333, and 390cm^{-1} disappeared for the homogeneous mixture containing 80% H_2O. A new peak at 318 cm^{-1} appeared (see Figure 3), belonging to $FeCl_3{\cdot}2H_2O$ [26]. This peak provides strong evidence for the decomposition of [bmim]Fe(III)Cl_4 into a new species, such as $FeCl_3{\cdot}2H_2O$ (see Equation(2)) at $x(H_2O)$ = 80%, which is consistent with Liu's research [27].



(1)

The colour of the homogeneous mixture at $x(H_2O) \geq 80\%$ demonstrates that $FeCl_3{\cdot}2H_2O$ is the iron compound present at $x(H_2O) \geq 80\%$. Since both $FeCl_3{\cdot}2H_2O$ and hydrophilic [bmim]Cl [17] are soluble in water, the homogeneous mixtures at $x(H_2O) \geq 80\%$ are true solutions. These results come in complete opposition with previous works asserting that due to the hydrophobic property of [bmim]Fe(III)Cl_4, the homogeneous mixture of [bmim]Fe(III)Cl_4 and H_2O may be an emulsion rather than a true solution [12].

2.4. Oxidative Absorption of H_2S by Homogeneous [bmim]Fe(III)Cl_4–H_2O Mixtures

Oxidative absorption of H_2S by homogeneous [bmim]Fe(III)Cl_4–H_2O 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 $FeCl_3{\cdot}2H_2O$ at 318 cm^{-1} in homogenous mixtures of 80% H_2O disappears after oxidative absorption of H_2S. Simultaneously, a new peak at 153 cm^{-1} belonging to $FeCl_2$ [28], as well as new peaks at 219 and 473 cm^{-1}, both due to S_8 [29], appears. These results indicate that $FeCl_3{\cdot}2H_2O$ was completely reduced to $FeCl_2$. Therefore, the reaction can be summarized by Equation (3).

$$16FeCl_3{\cdot}2H_2O + 8H_2S \rightarrow 16FeCl_2 + S_8 + 16HCl + 32H_2O \quad (3)$$

Equation (3) shows that HCl is generated from the oxidative absorption of H_2S by homogeneous mixtures at $x(H_2O) \geq 80\%$. Consequently, it is apparent that the acidity of mixtures at $x(H_2O) \geq 80\%$ is improved after oxidative absorption of H_2S and discharge of volatile HCl from the acidic mixtures. Furthermore, as shown in Figure 5c,d, homogeneous mixtures at $x(H_2O) = 90\%$ after oxidative-absorption of H_2S become colourless due to the complete reduction of $FeCl_3{\cdot}2H_2O$ and S_8, the oxidative product of H_2S, is suspended in the mixtures. Figure 6 shows that the surface tension of homogeneous mixtures at $x(H_2O) \leq 30\%$ remains almost constant up to about 37 $mN{\cdot}m^{-1}$, whereas, a remarkable increase in the surface tension is observed for homogeneous mixtures at $x(H_2O) = 80\%$, moreover, for homogeneous mixtures at $x(H_2O) = 90\%$, the surface tension sharply increase to 56.57 $mN{\cdot}m^{-1}$. At $x(H_2O) \geq 80\%$, the surface tension of homogeneous mixtures increases remarkably, resulting in the suspension of S_8 in the mixtures.

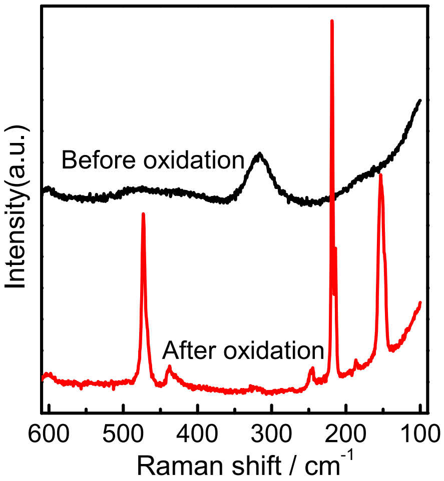


Figure 4. Raman spectra for the homogeneous [bmim]Fe(III)Cl_4–H_2O mixture at $x(H_2O) = 80\%$ before and after oxidative-absorption of H_2S.

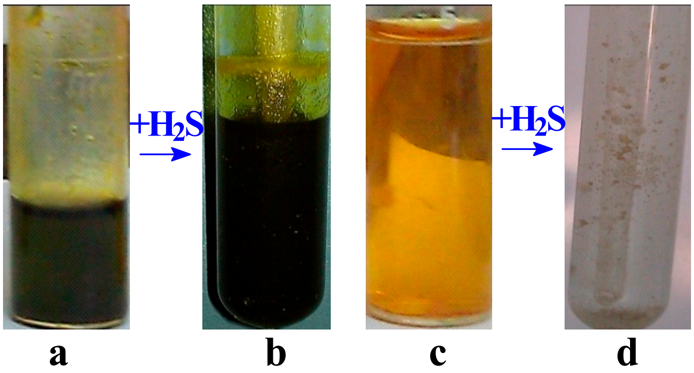


Figure 5. Photo of homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures at different $x(H_2O)$ values: (**a**) $x(H_2O) = 30\%$; (**b**) $x(H_2O) = 30\%$ after bubbling H_2S; (**c**) $x(H_2O) = 90\%$; and (**d**) $x(H_2O) = 90\%$ after bubbling H_2S.

However, it is difficult to prevent the suspended S_8 from the formation of sulfur blockage. Therefore, catalytic-oxidation of H_2S by homogeneous mixtures at $x(H_2O) \geq 80\%$ 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.

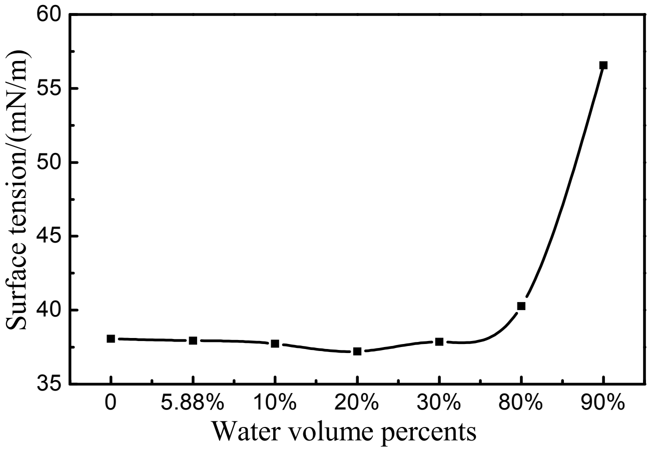


Figure 6. Surface tension of homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures at different $x(H_2O)$ at 25 °C.

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.

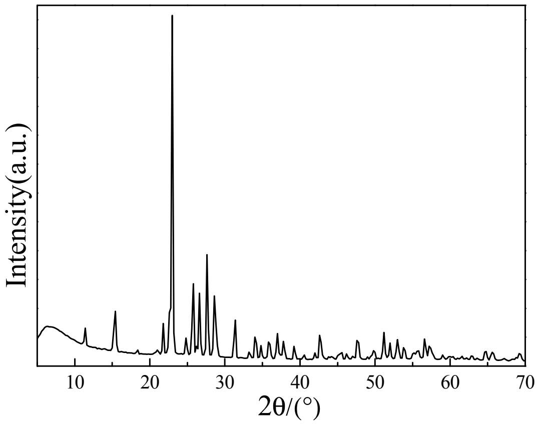
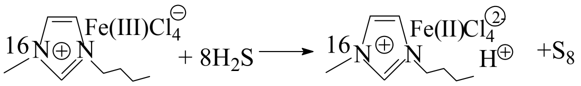


Figure 7. XRD of the product from catalytic oxidation of H_2S by homogeneous mixtures at $x(H_2O)$ = 5.88%.

Our conclusion was strengthened by the fact that the product of oxidative absorption of H_2S 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_2S [31]. Finally, our previous research also showed H_2S was converted to S_8 by [bmim]$FeCl_4$ of [bmim]Fe(III)Cl_4–[bmim]Cl–H_2O mixtures, and [bmim]$FeCl_4$ in the process was converted to [bmim]Fe(II)Cl_4H [21]. Hence, the oxidation of H_2S by homogeneous mixtures at $x(H_2O) \leq 30\%$ is written as Equation (4).



(2)

Nguyen et al. suggested that [bmim]$FeCl_4$ could be reduced to give ([bmim]$FeCl_3$)*, which could be transformed into $[Fe(II)Cl]^+[(bmim)Cl_2]^-$ [6]. Similarly, our previous research also suggested [bmim]Fe(III)Cl_4 was firstly reduced by H_2S to give ([bmim]$FeCl_3$)*, which was then transformed into [bmim]Fe(II)Cl_4H as soon as it reacted with HCl (see Equations (5) and (6)).

$$16[\text{bmim}]\text{Fe(III)Cl}_4 + 8\text{H}_2\text{S} \rightarrow 16([\text{bmim}]\text{Fe(II)Cl}_3)^* + \text{S}_8 + 16\text{HCl} \quad (5)$$

$$([\text{bmim}]\text{Fe(II)Cl}_3)^* + \text{HCl} \rightarrow [\text{bmim}]\text{Fe(II)Cl}_4\text{H} \quad (6)$$

From Equation (4), an increase in the acidity of homogeneous mixtures after oxidation of H_2S 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_2S, 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_2S were indeed detected by ion chromatography. Effect of water concentration on oxidative absorption of H_2S by [bmim]Fe(III)Cl_4–H_2O mixtures without other additives at 60 °C was shown in Table 1. Table 1 shows an increase in weight percent of absorbed H_2S 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_2S and volatile HCl emissions in homogenous [bmim]Fe(III)Cl_4–H_2O 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_2S 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_2S by Fe^{3+} or an iron(III) chelate is a fast chemical reaction [20,32]. As soon as H_2S was absorbed, it was oxidized. In addition, many researchers have observed a high solubility of H_2S in a series of 1-butyl-3-methylimidazolium ($[bmim]^+$)-based ionic liquids due to the formation of H_2S–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_2S 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_2S. A key factor is that the [bmim]Fe(III)Cl_4–H_2O mixtures were not only an oxidizer but also a solution, thus, the low concentrations of absorbed H_2S in mixtures was most likely caused by the strong acidity of the mixtures. Figure 2 shows that the homogenous mixtures at $x(H_2O) \leq 30\%$ 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 H_2S [20,32]. Consequently, the weight percent of absorbed H_2S in mixtures was very low in comparison with iron concentrations. Nevertheless, the decrease in acidity by increasing the water content improved the solubility of H_2S in the mixtures, and the weight percent of absorbed H_2S 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 H_2S by homogenous [bmim]Fe(III)Cl_4–H_2O mixtures at 60 °C increasing water also led to more evaporation of water, which decreased the weight percent of absorbed H_2S in mixtures, according to the absorption measurements. Volatile HCl emissions and the evaporation of water indicated that the actual weight percent of absorbed H_2S in mixtures was higher than the measured value.

It's worth mentioning that increasing $x(H_2O)$ was favourable for increasing oxidative-absorption of H_2S and decreasing volatile HCl emissions, but suspended S_8 generated at $x(H_2O) \geq 80\%$ 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)Cl_4–H_2O Mixtures

[bmim]Fe(III)Cl_4 was synthesized via a literature method [1]. Mixtures of [bmim]Fe(III)Cl_4 and water were prepared by adding water to [bmim]Fe(III)Cl_4 with vigorous stirring for 24 h. Ten [bmim]Fe(III)Cl_4–H_2O mixtures were prepared in volume fractions of $x(H_2O)$, where $x(H_2O)$ = 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)Cl_4 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 Yivon, France) with a He–Ne laser (632.8nm)). 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 H_2S in ionic liquids has been presented in detail [21]. H_2S 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 H_2S absorbed. From this mass, the H_2S 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 H_2S. From this data, the concentration of volatile HCl per gram of ionic liquid was calculated.

If the ionic liquids absorbed H_2S was regenerated by O_2, O_2 was bubbled at a pressure of 0.05 Mpa and a flow rate of 30 mL/min through the ionic liquids absorbed H_2S for 40 min.

4. Conclusions

We have prepared homogeneous mixtures of [bmim]Fe(III)Cl_4–H_2O at $x(H_2O)$ = 5.88–30% and above 80%, which showed the presence of both Brønsted and Lewis acids at $x(H_2O) \leq 30\%$, and only Lewis acids at $x(H_2O) \geq 80\%$ by FT-IR. Raman spectra showed Fe(III)Cl_4^- was the dominating iron species at $x(H_2O) \leq 30\%$, which was reduced by H_2S to Fe(II)Cl_4^-. $FeCl_3{\cdot}2H_2O$ was the primary iron compound at $x(H_2O) \geq 80\%$, which was reduced to $FeCl_2$. In addition, oxidative-absorption of H_2S by homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures demonstrated that increasing $x(H_2O)$ increased the weight percent of absorbed H_2S and decreased the volatile HCl emissions. However, there are some disadvantages in oxidation of H_2S by homogeneous [bmim]Fe(III)Cl_4–H_2O mixtures at $x(H_2O) \geq 80\%$, including sulfur blockage of suspended S_8 and the slow regenerative rate of $FeCl_2$. Therefore, it is necessary that controlling the $x(H_2O)$ below 80% ensures that oxidative-absorption of H_2S by [bmim]Fe(III)Cl_4 is performed well.

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