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Absorption and oxidation of H_2S in triethylamine hydrochloride · ferric chloride ionic liquids

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ABSTRACT

To explore environmentally benign solvents for absorbing and oxidizing H_2S, a series of triethylamine hydrochloride · ferric chloride ionic liquids ($Et_3NHCl \cdot FeCl_3$ ILs) were synthesized, the absorption and oxidation efficiency of H_2S in which were measured. The influence parameters, mole ratios of ILs and temperature, on the sulfur capacity of H_2S in the $Et_3NHCl \cdot FeCl_3$ ILs were investigated. The sulfur capacity of 1.5 $Et_3NHCl \cdot FeCl_3$ ILs at 303.15 K and 101.3 kPa is the highest (2.178 wt.%). The oxidation efficiency of H_2S in 1.5 $Et_3NHCl \cdot FeCl_3$ IL was up to 87.9%. The absorption and oxidation mechanism of H_2S in the ILs was studied. Fe (III) in the ILs was reduced to Fe (II) and H_2S was oxidized to sulfur at the same time. After bubbling air through the IL, $Et_3NHCl \cdot FeCl_3$ IL was regenerated, allowing the IL to be reused five times without clearly loss of capability.

1. Introduction

H_2S is produced along with coking coal, gasification, oil exploration, refining, natural gas development, sewage treatment, waste composting and many other chemical industrial processes [1]. It not only has the odor which threats to the atmospheric environment, but also it is an intense nerve gas. In addition, concrete and metal will be corroded by H_2S [2]. Currently, absorption/adsorption and oxidation of H_2S by ammonia [3], iron oxide [4], chelated iron [5], and zinc oxide [6] were applied broadly, but serious 'secondary pollution' would be caused by desulfurization equipments, complex operation processes and a large number of abandoned desulfurization solutions [7]. Many problems, such as low selectivity and efficiency, expensive desulfurizer and difficulty to recycle the sulfur affect the application of these methods.

With extremely low vapor pressures, high thermal and chemical stability, wide electrochemical window and tunable solvent power [8] for many organic and inorganic compounds, ionic liquids (ILs) can be used as environmentally benign solvents for a number of applications including gas solubility [9,10] and separations, cellulose processing, catalysis, extraction, and high-temperature pyrochemical processing [11,12]. ILs can potentially be used as liquid absorbents for inorganic and organic gases and as solvents for gas separations. Basic ILs with amino groups were synthesized and used to capture CO_2 [13–15] and SO_2 [16–21] and to promote hydrogenation of CO_2 [22]. Nowadays, one of the areas of active research is to explore the possibility of replacing task specific ionic liquids for conventional alkanolamine solutions in removal of H_2S in gas sweetening processes. At 9 MPa, the mole fraction of H_2S in [Bmim][PF_6] ionic liquid is about 0.7. At 2 MPa, the solubility (mole fraction of H_2S) in [Bmim][PF_6] ionic liquid decreases from about 0.84 at 298 K to about 0.2 at 403 K [23]. The solubility of H_2S in [Bmim][PF_6], [Bmim][BF_4] and [Bmim][Tf_2N] at 303.15–343.15 K was reported [24]. The solubility of H_2S in the studied ILs is in the order [Bmim][Tf_2N] > [Bmim][BF_4] > [Bmim][PF_6]. Pomeli [25] measured the solubility of H_2S in 1-butyl-3-methylimidazolium-based ILs and investigated the mechanism of H_2S in ILs at the molecular level using quantum chemistry. Shiflett [26] separated a certain component of the mixed gas selectively by bubbling different mole ratios of CO_2/H_2S into [Bmim][PF_6] ILs. The caprolactam tetrabutyl ammonium bromide (1:1, mole ratio) IL could physically absorb large amounts of H_2S gas, (5.40%, wt.%) at 303.15 K and 3.45% (3.45%, wt.%) at 363.15 K [27]. Fawzy [28] firstly reported the synthesis of triethylamine hydrochloride · ferric chloride ionic liquids ($Et_3NHCl \cdot FeCl_3$ ILs). The synthesis of diphenylmethane [29] from benzene and dichloromethane and dimethyl carbonate from methanol and urea by using $Et_3NHCl \cdot FeCl_3$ ILs as catalysts were reported, respectively. x $Et_3NHCl \cdot FeCl_3$ ($x = 1.4$–1.8) ILs exhibited remarkable abilities in effective desulfurization of thiophene in *n*-octane and fluid catalytic cracking (FCC) gasoline [29]. It is easy and environmentally friendly to synthesize the x $Et_3NHCl \cdot FeCl_3$ ILs, and the price of the ILs is very low also. Moreover, the IL is a good catalyst and oxidation agent.

In this manuscript, the effects of different mole ratios of Et_3NHCl and $FeCl_3$ on their sulfur capacity for absorption and oxidation of H_2S were systematically investigated. The oxidation efficiency of H_2S was measured. The recovery of sulfur and H_2S and recycle of the synthesized

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ILs were also conducted by increasing temperature and decreasing pressure and filtration. The theoretical basis of these absorption and oxidation processes was also explored.

2. Experimental

2.1. Materials

Triethylamine hydrochloride with purity > 99.0% was purchased from Jintan Huadong Chemical Research Institute, Nanjing, China. Ferric chloride hexahydrate with purity > 99.0% was purchased from Tianjin Yongda Chemical Reagent Co., Ltd., Tianjin, China. H_2S was obtained from Foshan Kodi Gas Chemical Industry Co., Ltd., Foshan, China, the purity of which was >99.5%.

2.2. Synthesis of $Et_3NHCl \cdot FeCl_3$ ILs

The different mole ratios of Et_3NHCl and $FeCl_3$ ILs were synthesized as previously reported [29], which was shown in Scheme 1. The x $Et_3NHCl \cdot FeCl_3$ ($x = 1.4$, 1.5, 1.6, 1.7 and 1.8) ILs were dried under a vacuum at 323.15 K until the mass remained constant.

2.3. Absorption and oxidation of H_2S

The ILs used here were dried under a vacuum for at least 24 h at 323.15 K prior to use, and the water content determined by Karl–Fischer titration was less than 100 ppm. The apparatus of absorption of H_2S in these ILs was prepared following procedures reported elsewhere [27]. H_2S gas was bubbled with a flow rate of 10 mL/min through predetermined amounts of the ILs (about 12 g) loaded in a glass vessel. After 2 h, the weight of the vessel and H_2S was stationary, and the equilibrium was reached. The off H_2S was treated by sodium hydroxide. These valves were closed, and the vessel was weighed by a balance with an uncertainty of ±0.0001 g to get the mass of H_2S absorbed and oxidized, through which the sulfur capacity (C) of H_2S in the ILs could be calculated. The sulfur capacity was calculated as follows (Eq. (1)):

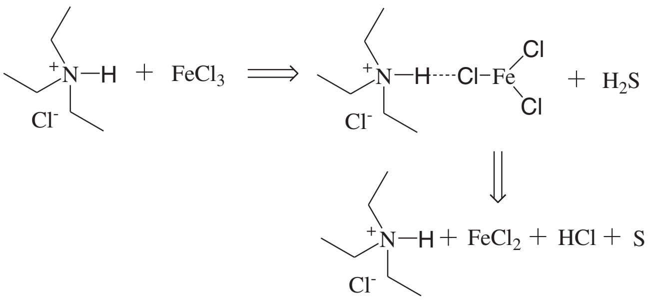
$$C = \frac{m_1}{m_2} \times 100\% \tag{1}$$

where m_1 and m_2 represent weight (g) of the H_2S absorbed (including the absorption and oxidation of H_2S) and ILs, respectively.

Sand core funnel (4.5–9 μm) was used to separate S and the ionic liquids. The oxidation efficiency of H_2S with the $Et_3NHCl \cdot FeCl_3$ ILs was calculated by Eq. (2).

$$\eta = \frac{n_1}{n_2} \times 100\% \tag{2}$$

where η represents the oxidation efficiency (%); n_1 is the amount of substance (mol) of H_2S oxidized by $Et_3NHCl \cdot FeCl_3$ ILs; and n_2 is the total amount of substance (mol) of H_2S absorbed and oxidized.



Scheme 1. Proposed reaction between $Et_3NHCl \cdot FeCl_3$ and H_2S.

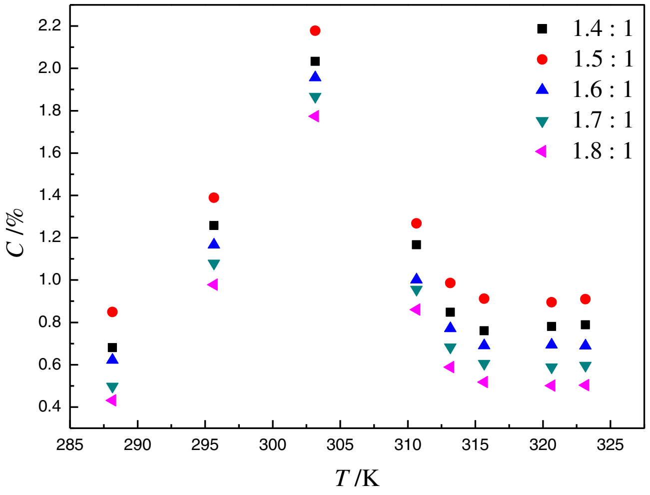


Fig. 1. Sulfur capacity of H_2S in different mole ratios of triethylamine hydrochloride and ferric chloride as a function of temperature.

2.4. Recycle of the $Et_3NHCl \cdot FeCl_3$ ILs

The absorption and desorption cycles were conducted to study the recovery of H_2S, sulfur and recycle of the ILs. Sand core funnel was used to separate S from the mixtures. After S was removed from ionic liquids, air was bubbled into the separated ionic liquids to oxide Fe (II) to Fe (III). The ionic liquid was regenerated. Experiments showed that the solubility of H_2S in the synthesized ILs is almost zero when the temperature rises to 373.15 K at 10.1 kPa vacuum. Consecutive absorption (303.15 K, 101.3 kPa) and desorption (373.15 K, 10.1 kPa vacuum) of H_2S and sulfur powder in recycled ILs were studied against times.

3. Results and discussion

3.1. Effect of the mole ratios of Et_3NHCl and $FeCl_3$ on the sulfur capacity of H_2S

The sulfur capacities of H_2S in different mole ratios of Et_3NHCl and $FeCl_3$ ILs from 1.4:1 to 1.8:1 versus temperature from 298.15 to 323.15 K were measured and shown in Fig. 1.

As it can be observed, the sulfur capacity of H_2S in 1.5 $Et_3NHCl \cdot FeCl_3$ IL is higher than that of other different mole ratios of Et_3NHCl and $FeCl_3$. The dynamic viscosity of $Et_3NHCl \cdot FeCl_3$ ILs increased sharply with the decrease of mole ratio of Et_3NHCl and $FeCl_3$ [29]. The high viscosity of the ILs limits the mass transfer of H_2S, which results in the sulfur capacity of H_2S decrease. However, the oxidation capacity increases with the decrease of mole ratio of Et_3NHCl and $FeCl_3$ due to the increasing content of $FeCl_3$. So the sulfur capacity of H_2S in 1.5 $Et_3NHCl \cdot FeCl_3$ IL is the highest because of these interrelated two factors. The maximum sulfur capacity value of H_2S in 1.5 $Et_3NHCl \cdot FeCl_3$ IL was 2.178% at 303.15 K and 101.3 kPa. According to Eqs. (1) and (2), the oxidation efficiency of

Table 1
Parameters for Eq. (3) and R-square values for the sulfur capacity of ILs with respect to temperature.

Entry	a ($\times 10^5$)	b ($\times 10^3$)	c ($\times 10^1$)	d ($\times 10^{-1}$)	e ($\times 10^{-4}$)	f ($\times 10^{-7}$)	R^2
1.4:1	4.665	−7.975	5.446	−1.857	3.162	−2.150	0.970
1.5:1	3.038	−5.259	3.633	−1.252	2.153	−1.478	0.968
1.6:1	3.849	−6.687	4.635	−1.602	2.763	−1.901	0.962
1.7:1	5.782	−9.907	6.779	−2.316	3.950	−2.690	0.969
1.8:1	11.81	−19.90	13.40	−4.509	7.580	−5.093	0.971