



Article Measuring and Modeling the Solubility of Hydrogen Sulfide in rFeCl₃/[bmim]Cl

Huanong Cheng ^{1,*}, Na Li², Rui Zhang ², Ning Wang ², Yuanyuan Yang ², Yun Teng ², Wenting Jia ² and Shiqing Zheng ¹

- ¹ Institute of Computer and Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266000, China; zheng_sq1@163.com
- ² College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266000, China; li_na1@163.com (N.L.); zhang_r2@163.com (R.Z.); wang_n2@163.com (N.W.); yang_yy2@163.com (Y.Y.); teng_y1@163.com (Y.T.); Jia_wt1@163.com (W.J.)
- Correspondence: chn@qust.edu.cn

Abstract: The solubility of hydrogen sulfide in different mole ratios of ferric chloride and 1-butyl-3methylimidazolium chloride ionic liquid ($rFeCl_3/[bmim]Cl$, r = 0.6, 0.8, 1.0, 1.2, 1.4) at temperatures of 303.15 to 348.15 K and pressures of 100 to 1000 kPa was determined. The total solubility increased with the increase of pressure and the decrease of temperature. The solubility data were fitted using the reaction equilibrium thermodynamic model (RETM). The mean relative error between the predicted value and the measured value was less than 4%. Henry's coefficient and the equilibrium constant of chemical reaction at each temperature were calculated. Henry's coefficient first decreased and then increased with the increase of mole ratio, and increased with the increase of temperature. The equilibrium constant of the chemical reaction followed the same law as Henry's coefficient. The chemical solubility was related to both Henry's coefficient and the chemical equilibrium constant. H₂S had the highest chemical solubility in FeCl₃/[bmim]Cl at a mole ratio of 0.6 and a temperature of 333.15 K. The chemical solubility increased with the increase of pressure.

Keywords: ionic liquid; hydrogen sulfide; solubility; Henry's coefficient; reaction equilibrium constant

1. Introduction

Hydrogen sulfide (H₂S) is produced along with industrial production, natural gas development, biogas, and sludge treatment [1,2]. It is a toxic and harmful gas that not only causes damage to human health through odor and paralysis of nerves, but also damages the environment by forming acid rain. The liquid oxidation catalyst (LO-CAT) method [3] is a widely used wet oxidation desulfurization technology in which Fe(III) in the absorbent reacts with H_2S in the gas to become Fe(II), and H_2S becomes elemental sulfur. Then air is used to oxidize Fe(II) to generate Fe(III) to regenerate the absorbent. Compared with other desulfurization methods, the advantage of the LO-CAT method is that the raw material iron is cheap, easy to obtain, and harmless, and the desulfurization process is highly efficient [4]. However, the LO-CAT method still has some problems [5,6]: (1) Iron complex in the absorbent is easy to decompose, resulting in loss of oxidants. (2) The pH value of the absorbent solution has to be strictly controlled to prevent the iron ion from changing to iron hydroxide and iron sulfide precipitation during the reaction. (3) By-product salts, such as thiosulfate and sulfates, are formed due to overoxidation of H_2S in an alkaline or neutral solution. The by-product salts generated in the LO-CAT method process not only easily blocks the pipeline but also enters the wastewater, and it requires high energy consumption to treat the wastewater before it can be discharged into the environment.

In recent years, the green nature of ionic liquids has been widely recognized, and it is used as a solvent, catalyst, and extractant in various fields [7–10]. Due to the advantages of low vapor pressure and good solubility of ionic liquids, it is also used as a desulfurizer to



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). absorb H_2S . Some functional ionic liquids show excellent performance when absorbing H_2S [4,11–15]. The iron-based ionic liquid (Fe-IL) 1-butyl-3-methylimidazolium tetrachloro-ferrate ([bmim]FeCl₄) is one of them [16]. The good solubility of ionic liquids ensures high solubility of H_2S . Fe(III) acts as an oxidant and a catalyst. Therefore, the triple functional ionic liquid has great potential in absorbing H_2S .

Yukihiro Yoshida and Gunzi Saito's research [17] on [bmim]FeCl₄ shows that its thermal decomposition temperature can reach 553 K. The high decomposition temperature ensures that ferric iron can stably exist in the form of complexes when oxidizing hydrogen sulfide. Wang Jianhong [18] reported that [bmim]FeCl₄ is both Lewis acidic and Bronsted acidic. H_2S will not be overoxidized in an acidic environment [19]. Therefore, no thiosulfates and sulfates are produced during the oxidation of H₂S by [bmim]FeCl₄, which avoids the production of salty wastewater. This was confirmed by detecting H₂S-loaded [bmim]FeCl₄ by infrared spectroscopy, in which no S–O bond absorption peaks were found [16]. The surface tension of [bmim]FeCl₄ is small, and the deposited sulfur is easy to be separated from the desulfurizer [18]. Although ionic liquids are more expensive, Wang's study shows that the use of [bmim]FeCl₄ to catalyze the oxidation of hydrogen sulfide is more economical than traditional LO-CAT desulfurization [20]. This is because the vapor pressure of the ionic liquid is negligible, the loss of desulfurization liquid is very small, and there is no side reaction resulting in the post-treatment cost. The above studies show that $[Bmim]FeCl_4$ has the advantages of thermal stability, acidity, and low operating cost. It is a potential desulfurizer for solving the shortcomings of the chelated iron method.

 $[bmim]FeCl_4$ is synthesized by mixing anhydrous FeCl_3 and [bmim]Cl in an equimolar ratio. When the ratio is greater than 1, FeCl₄⁻ anions react with excess FeCl₃ to form $Fe_2Cl_7^-$. When the ratio is less than 1, unreacted Cl^- exists [21]. Therefore, there are different anion forms for different molar ratios. This paper uniformly uses $rFeCl_3/[bmim]Cl$ to represent them, where r represents the molar ratio of anhydrous $FeCl_3$ to [bmim]Cl. $rFeCl_3/[bmim]Cl$ has similar properties to $rAlCl_3/[bmim]Cl$. Their properties can be changed by changing the concentration of metal ions (mole ratio r) [22]. Li Jiguang [23] reported the density, viscosity, and conductivity of $FeCl_3/[bmim]Cl$ under different r's at a temperature ranging from 293 to 363 K. Studies have shown that the viscosity decreases sharply as the iron ion concentration increases at the same temperature. The density increases linearly, and the conductivity first increases and then slowly decreases. In addition to density and viscosity, solubility is an indispensable physical property when studying the H₂S absorption process. At present, the solubility data of hydrogen sulfide in rFeCl₃/[bmim]Cl are still lacking. The objectives of this work were to measure the solubility of hydrogen sulfide in rFeCl₃/[bmim]Cl (r = 0.6, 0.8, 1.0, 1.2, 1.4) at temperatures from 303.15 to 348.15 K and pressures from 100 to 1000 kPa. A model was proposed to fit the experiment data. Henry's coefficient and the equilibrium constant of the chemical reaction were calculated. The effects of temperature, pressure, and iron content on the absorption were investigated.

2. Materials and Methods

2.1. Chemicals

 H_2S gas of 99% mass purity was supplied by the Yuyan Gas Company. Anhydrous FeCl₃ of 99% mass purity was obtained from the Aladdin Reagent Company. All of the above were used as purchased without further purification. [bmim]Cl of 97% mass purity was purchased from the Macklin Reagent Company and was further purified by recrystallization in acetonitrile–ethyl acetate [17,24]. After that, it was filtered before being dried in a vacuum dryer for 24 h, then placed in a desiccator. No obvious impurities in the sample were confirmed by H¹ NMR (Figure S1 in the Supporting Materials section) [25].

rFeCl₃/[bmim]Cl was synthesized by a well-established procedure [26]. A certain mass of [bmim]Cl was added in a three-necked flask with stirring and N₂ atmosphere, and heated to 60 °C. Then different molar ratios of anhydrous FeCl₃ were added. After stirring for 6 h, a dark brown liquid rFeCl₃/[bmim]Cl with a molar ratio of 0.6 to 1.4 was

obtained. When r = 0.4, the resultant ionic liquid is too viscous and not suitable for practical application. Therefore, mole ratio starts at r = 0.6 in this work. The ionic liquid was dried in a vacuum drying oven at 333 K for 48 h, and the water content was determined below the detection limit (100 ppm) of a Karl Fischer titrator (Mettler Toledo, DL31). The results (Figure S2 in the Supporting Materials section) of the infrared spectrum (Bruker Tensor 27) for the synthesized *r*FeCl₃/[bmim]Cl were consistent with the literature [20,26], indicating that the structure of the synthesized iron-based ionic liquid cation was not changed. There was no –OH stretching vibration peak of 3300 cm^{-1} in the spectrum, indicating that the ionic liquid did not contain water. The ionic liquid was put into a desiccator with silica gel for later use.

2.2. Experimental Design

The experimental apparatus used to measure the solubility of H_2S in $rFeCl_3/[bmim]Cl$ was homemade and is shown in Figure 1. It consisted of a vacuum pump (1 in Figure 1, the same below), a high-pressure nitrogen cylinder (12), a high-pressure hydrogen sulfide cylinder (11), a buffer tank (13), a phase equilibrium kettle (16) made of Hastelloy (SL-Q100, Sen Long) with a magnetic-drive stirrer, and a tail gas absorption device (17). The volumes of the buffer tank and phase equilibrium kettle were 510.7 mL (V₁) and 122.8 mL (V₂), respectively. They were placed in two constant-temperature circulating water baths (14, 15) (HH-Sc, Changzhou Langyue Instrument Manufacturing Co., Ltd., Hangzhou, Zhejiang Province, China), respectively, and the temperature inside the kettle was measured by a TES 1320 TYPE-K thermocouple (9, 10) with an uncertainty of 0.03 K. The pressures in the buffer tank and the phase equilibrium kettle were measured by pressure sensors (2, 3) (YK-100B, -100–5000 kPa, PR Software V1.5, Xi'an Yunyi Instrument Co., Ltd., Xi 'an, Shaanxi Province, China) with an uncertainty of 3 kPa and transmitted to the computer.



Figure 1. Scheme of the experimental setup: 1, vacuum pump; 2, 3, pressure sensor; 4 to 8, valve; 9, 10, thermocouple; 11, H₂S gas cylinder; 12, N₂ gas cylinder; 13, buffer tank; 14, 15, water bath; 16, equilibrium kettle; 17, gas scrubber.

The operation of the apparatus was started by introducing a known mass of a Fe-IL weighed with an electronic balance (TG328-A, Shanghai Balance Instrument Factory) with an uncertainty of 0.3×10^{-7} kg to the phase equilibrium kettle, and the whole equipment (except the gas cylinder) was evacuated to pressures below 1.0 kPa by the vacuum pump, and the temperature was raised to 348 K. The Fe-IL inside the kettle was kept at this

temperature under vacuum for at least 4 h to remove trace amounts of water and volatile impurities. The temperature was then adjusted to the required value through the water bath, and a known amount of H₂S was introduced to the buffer tank from the H₂S gas cylinder. After 30 min of heat preservation, the pressure (P_1) in the buffer tank was recorded. Next, the gas from the buffer tank was released into the phase equilibrium kettle, and the remaining pressure in the buffer tank (P_2) was recorded after the valve was closed. Then the stir was turned on. The sign of reaching phase equilibrium was that the pressure in the equilibrium kettle remained unchanged for 1 h, and equilibrium pressure (P_3) was recorded. After the experiment, H₂S in the system was discharged into a saturated sodium hydroxide solution and purged with nitrogen for a long time.

The total solubility of H₂S in the Fe-IL solvent based on molality, $m_{H_2S,t}$, can be determined from the following equation:

$$m_{H_2S,t} = \frac{n_t}{w_{Fe-IL}} \tag{1}$$

where w_{Fe-IL} is the mass of rFeCl₃/[bmim]Cl added to the phase-balanced kettle; n_t denotes the integral molar quantity of H₂S, which is absorbed into the liquid at phase equilibrium; and n_t can be calculated by the difference between the molar quantity of gas filled into the phase equilibrium kettle and the molar quantity remaining at the equilibrium gas phase:

$$n_t = n_{add} - \frac{P_{H2S} \cdot (V_2 - \frac{w_{Fe-IL}}{\rho_{Fe-IL}(T)})}{Z_3 \cdot R \cdot T}$$
(2)

where P_{H2S} is the equilibrium partial pressure of H₂S in the equilibrium kettle, kPa; $\rho_{Fe-IL}(T)$ denotes the density of rFeCl₃/[bmim]Cl liquid in the phase equilibrium kettle at temperature *T*; $\rho_{Fe-IL}(T)$ is obtained according to the literature [23] (density data are shown in Table S1 in the Supporting Materials section); and *R* is gas constant with a value of 8.314 J·mol⁻¹·K⁻¹.

 P_{H2S} can be calculated by

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$$P_{H2S} = P_3 - P_0 - P_L, (3)$$

where P_0 is the pressure after the system is evacuated, and P_L is the partial pressure of the solvent in the equilibrium kettle.

For the Fe-IL in this work, the vapor pressure was very low, so $P_L = 0$. For the water solvent in the verification experiment, P_L cannot be ignored.

The molar quantity of H_2S filled into the phase equilibrium kettle, n_{add} , can be obtained by the real gas state equation:

$$n_{add} = \frac{\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right) \cdot V_1}{R \cdot T},\tag{4}$$

where Z_1 , Z_2 , and Z_3 are compression factors of H_2S at temperature *T* and pressures P_1 , P_2 , and P_3 , respectively. These compression factors are calculated using the Soave–Redlich–Kwong equation in Aspen Plus software (aspenONE[®] for Universities, Aspen Technology, Inc., Bedford, MA, USA).

3. Reaction Equilibrium Thermodynamic Model

Henry's coefficient is one of the important thermodynamic coefficients, which reflects the physical dissolution degree of the gas solute in the solvent. Henry's law [12,27] or the Krichevsky–Kasarnovsky equation [28] is usually used directly to estimate Henry's coefficient. The solubility used in these equations is physical. However, the solubility measured in this paper includes both physical dissolution and chemical dissolution, so the above equations cannot be used directly to estimate Henry's coefficient. Huang Kuan [29] put forward the reaction equilibrium thermodynamic model (RETM) for the estimation of

Henry's coefficient with both physical absorption and chemical absorption. This model introduces a reaction equilibrium constant to strip chemical dissolution. In this work, a new RETM model based on the absorption and reaction of H_2S in $rFeCl_3/[bmim]Cl$ (Fe (III)-IL) was derived as follows: H_2S is first absorbed into the ionic liquid. Since Fe (III)-IL is acidic, H_2S is not decomposed into HS^- or S^{2-} ionic state, but exists as an H_2S molecular state in liquid [30]. The H_2S molecule in the liquid undergoes redox reaction with Fe (III)-IL. It was reported [20] that when measuring the sulfur capacity, a large amount of iron is not reduced, so the redox reaction can be regarded as a reversible reaction. According to the literature [16,23], the reaction equation of H_2S being absorbed and oxidized by Fe (III)-IL is as follows:

$$H_2 S_{(g)} \rightleftharpoons H_2 S_{(l)},\tag{5}$$

$$H_2S_{(l)} + 2Fe(III) - IL_{(l)} \rightleftharpoons S_{(s)} + 2HFe(II) - IL_{(l)},$$
(6)

where g, l, and s are gas, liquid, and solid phases, respectively. Equation (5) means that H_2S in the gas phase is captured by the ionic liquid and then dissolved in the liquid phase, which obeys Henry's law:

$$P_{H2S} = H_m \cdot \gamma_{H_2S} \cdot \frac{m_{H_2S}}{m^0},\tag{7}$$

where P_{H2S} is the partial pressure of H₂S. The vapor pressure of the ionic liquid is negligible. Therefore, the gas phase in the phase equilibrium kettle is pure H₂S without solvent vapor. H_m denotes Henry's coefficient based on molality. m_{H_2S} denotes the molality of the physically dissolved H₂S in liquid phase. m^0 and P^0 are standard molality with a value of 1 mol/kg and standard pressure with a value of 100 kPa, respectively. γ_{H_2S} is the activity coefficient of H₂S physically dissolved in the liquid phase. Equation (6) reflects the process in which H₂S in the liquid phase is oxidized to sulfur by Fe(III), while Fe(III) is reduced to Fe(II). The chemical reaction equilibrium constant *K* of this reaction is expressed as follows:

$$K = \frac{\left(\frac{m_{Fe(II)}}{m^{0}}\right)^{2}}{\left(\frac{m_{Fe(III)}}{m^{0}}\right)^{2} \cdot \frac{m_{H_{2}S}}{m^{0}}},$$
(8)

where $m_{Fe(II)}$ and $m_{Fe(III)}$ denote the molality of Fe(II)-IL and Fe(III)-IL, respectively. The mass balance equations for H₂S and ionic liquids are given as follows:

$$m_{H_2S,t} = m_{H_2S} + m_{H_2S,r},\tag{9}$$

$$m_{Fe-IL} = m_{Fe(III)} + m_{Fe(II)}, \tag{10}$$

where $m_{H_2S,r}$ is the molality of H₂S involved in the reaction. According to the stoichiometric ratio, $m_{H_2S,r} = \frac{1}{2}m_{Fe(II)}$. m_{Fe-IL} is the initial molality of the ionic liquid, which is represented by Equation (11).

$$m_{Fe-IL} = \frac{1}{M_{Fe-IL}},\tag{11}$$

where M_{Fe-IL} is the molar mass of ionic liquid.

rFeCl₃/[bmim]Cl was actually a mixture except for r = 1. The average molar mass needed to be calculated. The calculation method is listed in Table 1.

Table 1. Calculation method for the molar mass (M) of different composition ratios of rFeCl₃/[bmim]Cl.

	Composition	Computational Formula
r < 1	[bmim]Cl, [bmim]FeCl ₄	$M_{Fe-IL} = r \cdot M_{[bmim]FeCl_4} + (1-r) \cdot M_{[bmim]Cl}$
r = 1	[bmim]FeCl ₄	$M_{Fe-IL} = M_{[bmim]FeCl_4}$
<i>r</i> > 1	[bmim]FeCl ₄ ,	$M_{Fe-IL} =$
	[bmim]Fe ₂ Cl ₇	$(2-r) \cdot M_{[bmim]FeCl_4} + (r-1) \cdot M_{[bmim]Fe_2Cl_7}$

Assuming that the liquid phase is an ideal solution, the value of γ_{H_2S} is set to 1. Combine Equations (7) to (11) together, and sort out the new RETM model:

$$m_{H_2S,t} = \frac{P_{H2S}}{H_m} + \frac{\sqrt{H_m \cdot P_{H2S} \cdot K} - P_{H2S} \cdot K}{2H_m - 2P_{H2S} \cdot K} m_{Fe-IL}$$
(12)

According to Equation (12), take *P* as the independent variable and $m_{H_2S,t}$ as the dependent variable, and the values of unknown quantity H_m and *K* can be obtained by using nonlinear regression to fit the solubility data in ORIGIN software. The accuracy of the model was characterized by mean relative error (*MRE*) and maximum relative error (*MD*).

$$MRE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{m_i^{\exp} - m_i^{fit}}{m_i^{\exp}} \right|,$$
 (13)

$$MD = Max \left(100 \left| \frac{m_i^{\exp} - m_i^{fit}}{m_i^{\exp}} \right| \right), \tag{14}$$

where *N* is the number of experiments per temperature, m_i^{exp} is the total solubility measured in the experiment, and m_i^{fit} is the total solubility calculated using the parameters obtained from the RETM model.

4. Results and Discussion

4.1. Experimental Method Validation

The solubility of H_2S in water was measured at temperatures 308.15, 323.15, and 343.15 K to verify the reliability of the experimental method. For the convenience of comparison with literature data, the solubility of H_2S in water is calculated by Equation (15) based on the molar fraction. The data obtained from the experiment are presented in the form of points in Figure 2. Henry's coefficients of H_2S in water [31] are reported to be 68,495.7 kPa at 308.15 K, 89,571.3 kPa at 323.15 K, and 120,576.8 kPa at 343.15 K. As shown in Figure 2, the lines with the slope of Henry's coefficients are drawn in a coordinate system with the equilibrium pressure of H_2S on the horizontal axis and the solubility on the vertical axis. The relative percentage deviations between the experimental values and the literature values at the three temperatures are all less than 3%, so the device has the ability to measure the solubility.

$$x_{H_2S} = \frac{n_t \cdot M_{H_2O}}{w_{H_2O}}$$
(15)



Figure 2. Comparison of experimental values and literature values of H₂S solubility in water.

The solubility of H_2S in $rFeCl_3/[bmim]Cl$ (r = 0.6, 0.8, 1.0, 1.2, 1.4) at temperatures of 303.15, 318.15, 333.15, and 348.15 K and pressures up to about 1.0 MPa is summarized in Figure 3. For detailed solubility data with uncertainty, see Table S2 in the Supporting Materials section. As can be seen, the total solubility of H_2S increases with increasing pressure and decreasing temperature at the same r, which is similar to the solubility of most gases. It not only shows that our experimental device is reliable, but also indicates that the phase equilibrium of iron-based ionic liquid and H_2S follows the same law as other traditional solvents.



Figure 3. Experimental results for the solubility of H_2S in $rFeCl_3/[bmim]Cl: (a)r=0.6$; (b)r=0.8; (c)r=1.0; (d)r=1.2; (e)r=1.4.

4.3. Modeling

The RETM model was used to fit the data of total solubility and pressure, and the fitting curve is shown in Figure 3. Henry's coefficients and the equilibrium constants calculated by the RETM model are listed in Table 2. The *MRE* of each group of forecasts does not exceed 4%, which indicates that the data predicted by the RETM model are in good agreement with the experimental data. The *MD* is 9.77%, which indicates that the requirement of engineering calculation is met.

	T/K				
	303.15	318.15	333.15	348.15	
<i>r</i> = 0.6					
H _m /kPa	325.7	604.9	966.6	1408.7	
K	0.04588	0.1585	0.3091	0.4082	
MRE/%	1.66	2.08	1.80	2.61	
<i>MD</i> /%	6.70	8.73	5.65	8.20	
r = 0.8					
H_m/kPa	313.6	505.7	832.7	1174.4	
K	0.0108	0.0242	0.0713	0.0940	
MRE/%	2.49	2.74	2.80	3.01	
MD/%	7.77	8.09	7.95	7.75	
r = 1.0					
H_m/kPa	330.8	471.6	575.9	803.4	
K	0.0049	0.0103	0.0175	0.0205	
MRE/%	3.17	1.95	2.56	1.78	
MD/%	9.77	7.56	8.48	7.83	
r = 1.2					
H_m/kPa	378.8	638.1	935.8	1484.8	
K	0.0063	0.0141	0.0359	0.0385	
MRE/%	2.84	1.86	3.11	3.07	
MD/%	9.35	9.05	6.67	6.05	
r = 1.4					
H_m/kPa	462.0	797.5	1697.3	3492.7	
Κ	0.0322	0.0855	0.3794	0.4917	
MRE/%	1.39	1.62	0.96	2.34	
<i>MD</i> /%	5.73	8.05	1.81	7.63	

Table 2. Henry's coefficients (H_m) and equilibrium constants (K) obtained by RETM model fitting and the mean relative error (MRE) and maximum relative error (MD) between the experiments and the fitting values at temperature T^{a} .

^a *T* is the equilibrium temperature in the equilibrium kettle, K. *r* is the molar ratio of anhydrous FeCl₃ to [bmim]Cl. H_m is Henry's coefficient of H₂S in Fe-IL based on molality, kPa. *K* is the chemical reaction equilibrium constant. *MRE* is mean relative error. *MD* is maximum relative error.

4.4. Influence of Molar Ratio

Henry's coefficients (H_m) at different temperatures and the molar ratio (r) obtained from Table 2 are plotted. The variation of H_m with r at different temperatures is shown in Figure 4. As we can see, with the molar ratio r = 1.0 of FeCl₃ and [bmim]Cl as the limit, H_m shows different trends for the composition of $r \le 1.0$ and $r \ge 1.0$. H_m decreases with the increase of r when $r \le 1.0$. Li Jiguang [23] measured the viscosity data of rFeCl₃/[bmim]Cl at 298.15 K. The viscosity decreased from close to 200 to 31.2 mPa·s when r increased from 0.6 to 1.0. Due to the sharp drop in viscosity, H_2S diffuses more freely in the liquid, and H_2S also moves more easily from the gas phase into the liquid phase [32]. Therefore, the physical solubility increases with the increase of iron content when $r \le 1.0$.

On the contrary, H_m increases with the increase of r when $r \ge 1.0$. The data measured by Li Jiguang [23] shows that the viscosity decreased from 31.2 to 27.4 mPa·s when rincreased from 1.0 to 1.5 at 298.15 K. The viscosity of $r\text{FeCl}_3/[\text{bmim}]\text{Cl}$ changes very little, which has little effect on the absorption of H₂S. While the density of the liquid continues to increase, from about 1.32 to about 1.42 g·cm⁻³, the free volume of the ionic liquid decreases to hold fewer H₂S molecules [33]. Therefore, the physical solubility decreases with the increase of iron content when $r \ge 1.0$.

The chemical reaction equilibrium constant (*K*) at different temperatures and the molar ratio (*r*) obtained from Table 2 are plotted. The variation of *K* with *r* at different temperatures is shown in Figure 5. Likewise, *K* shows a similar law to H_m . As shown in Figure 5, *K* decreases with the increase of *r* when $r \le 1.0$. In the ionic liquids consisting of $r \le 1.0$, the types of anions are Cl⁻ and FeCl₄⁻. Cl⁻ is a neutral ion, whereas FeCl₄⁻ is an acidic ion. Therefore, as *r* increases, the concentration of acid anion increases, which

is not conducive to the combination with acid molecule H₂S, resulting in a decrease in chemical reaction.



Figure 4. The effect of *r* on Henry's coefficient at different temperatures.



Figure 5. The effect of r on the chemical equilibrium constant at different temperatures.

In the case of $r \ge 1.0$, K increases with the increase of r. In ionic liquids composed of $r \ge 1.0$, the types of anions are FeCl_4^- and Fe_2Cl_7^- . Both of them are acidic anions [24]. Nguyen et al. [34] reported that Fe_2Cl_7^- exhibited higher catalytic activity than FeCl_4^- . Therefore, the chemical reaction is enhanced.

Chemical solubility is the amount of H_2S dissolved in the absorber for a chemical reaction. Consequently, the chemical solubility is determined by Henry's coefficient H_m and the equilibrium constant K. The oxidation of hydrogen sulfide to sulfur by rFeCl₃/[bmim]Cl is a reversible reaction. The amount of products is related to the concentration of reactants and the degree of reaction. The greater the concentration of the reactant and the degree of the reaction, the greater the amount of the product. H_m and K change with the iron content in the same law; that is, the concentration of reactants first increases and then decreases with the content of iron, while the reaction degree first decreases and then increases with the content of iron. This indicates that it is an offsetting process. The physical solubility can be calculated by Henry's coefficient from RETM, and the chemical solubility can be obtained by subtracting the physical solubility from the total solubility. In the experiment, it is difficult to measure solubility at the same equilibrium pressure at each temperature and iron content. For the convenience of comparison, the chemical solubility at 200 kPa is calculated by RETM. The changes in chemical solubility with r at different temperatures are graphically presented in Figure 6. The chemical solubility decreases first and then increases with the increase of r. The maximum chemical solubility appears when r = 0.6. For smaller

molar ratios *r*, it is not suitable for application due to very high viscosity [32] in the test temperature range.



Figure 6. Influence of iron content on chemical solubility at different temperatures at 200 kPa.

After the rFeCl₃/[bmim]Cl ionic liquid absorbs H₂S, the regeneration of the absorbent (ionic liquid) is the oxidation of Fe(II) to Fe(III) by oxygen, instead of desorption by rectification. The chemical solubility is the factor that measures the capacity of H₂S absorption. Therefore, r = 0.6 is the best molar ratio of anhydrous FeCl₃ to [bmim]Cl.

4.5. Influence of Pressure

Physical solubility and chemical solubility increase with the increase of pressure. For a given temperature and molar ratio, Henry's coefficient H_m and equilibrium constant K are fixed values. Physical solubility is directly proportional to pressure. The higher the pressure, the more dissolved H₂S, the more converted H₂S, and the greater the chemical solubility. For example, Figure 7 illustrates the physical solubility and chemical solubility of FeCl₃/[bmim]Cl at a mole ratio of 0.6 and at 333.15 K. Both physical and chemical solubilities increase as the pressure increases. Physical solubility changes more significantly. Under low pressure, the physical solubility is lower than the chemical solubility. Additionally, with the increase of pressure, the physical solubility gradually exceeds the chemical solubility.



Figure 7. Physical and chemical solubilities of H₂S in FeCl₃/[bmim]Cl at a mole ratio of 0.6 and at 333.15 K.

4.6. Influence of Temperature

Henry's coefficient H_m increases as the temperature rises under the same molar ratio and pressure. It means that the physical solubility decreases as the temperature increases. A rise in temperature intensifies molecular motion, making the molecules harder to fix in the liquid phase and thus not conducive to physical dissolution. The equilibrium constant of chemical reaction, K, increases with the increase of temperature. The increase of K indicates that the temperature rise causes the reaction to move in the positive direction. This means that the reaction of generating elemental sulfur is endothermic. However, the increase of K does not mean a greater chemical solubility, because only dissolved H_2S participates in the chemical equilibrium reaction. Although the K value is high, most of the dissolved H₂S is converted to elemental sulfur. However, the amount of H₂S converted is still small when the amount of H_2S dissolved is small. As a consequence, this leads to a low chemical solubility. For instance, the physical and chemical solubilities of H_2S in FeCl₃/[bmim]Cl at a mole ratio of 0.6 and at 200 kPa with temperature change are shown in Figure 8. With the increase of temperature, the physical solubility decreased from 0.61 to 0.14 mol·kg⁻¹ Fe-IL, and the chemical solubility first increased from 0.26 to 0.37 mol kg^{-1} Fe-IL and then decreased to $0.35 \text{ mol}\cdot\text{kg}^{-1}$ Fe-IL. The chemical solubility reaches its maximum at 333.15 K. This explains that the chemical solubility is not only related to the equilibrium constant but also influenced by Henry's coefficient.



Figure 8. Effects of temperature on physical and chemical solubilities in FeCl₃/[bmim]Cl at a mole ratio of 0.6 and at 200 kPa.

5. Conclusions

The experimental data for the solubility of H_2S in $rFeCl_3/[bmim]Cl$ (r = 0.6, 0.8, 1.0, 1.2, 1.4) were measured and presented in this work at temperatures from 303.15 to 348.15 K and pressures from 100 to 1000 kPa. The solubility of H_2S in $rFeCl_3/[bmim]Cl$ was well predicted by using the reaction equilibrium thermodynamic model. The chemical solubility of H_2S at $rFeCl_3/[Bmim]Cl$ is highest at 333.15 K. Additionally, the higher the pressure is, the greater the chemical solubility will be. These conclusions are helpful for H_2S absorption process simulation and process design in $rFeCl_3/[bmim]Cl$.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/pr9040652/s1: Figure S1: NMR of [bmim]Cl, Figure S2: Infrared spectrum of *r*FeCl₃[bmim]Cl, Table S1: Density data from the literature, Table S2: Total solubility (m_{H2S,t}) of H₂S in different composition ratios of rFeCl₃/[bmim]Cl.

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