Study on Macro Kinetics of the Desulfurization Processes of Heteropoly Compounds in Ionic Liquids and Aqueous Solutions

Xinpeng Liu^{1,2}, Rui Wang^{1*}

¹ Shenzhen Research Institute of Shandong University, Shenzhen, Guangdong 518057, China

² School of Environmental Science and Engineering, Shandong University, Qingdao, Shandong 266237, China

ABSTRACT

Ionic liquids and heteropoly compounds have been found to be effective systems for H₂S removal due to their unique properties. This study, which investigated the absorption kinetics of these new systems, continues our earlier research. Specifically, the macro kinetic characteristics of the H₂S absorption for three systems, viz., a [Bmim]₃PMo₁₂O₄₀/BmimCl solution, an aqueous solution of peroxo phosphomolybdic acid and an aqueous solution of CuH₂PMo₁₁VO₄₀, were determined using a gas-liquid reaction cell. The gas and liquid phase mass transfer coefficients were measured, and the activation energy was calculated. The H₂S absorption for the [Bmim]₃PMo₁₂O₄₀/BmimCl solution can be expressed as a macro kinetic equation: $N_{H_2S} = 6.6 \times 10^{-2} \cdot [\exp(-1064/T)] \cdot C_{H_2S}^{1.120} \cdot C_{[Bmim]_3PMo_{12}O_{40}}^{0.099}$. For the aqueous solutions of peroxo phosphomolybdic acid and CuH₂PMo₁₁VO₄₀, the absorption can be expressed as $N_{H_2S} = 2.68 \times 10^{-6} \cdot [\exp(-790/T)] \cdot C_{H_2S}^{0.252} \cdot C_{PHPMo}^{0.131}$ and $N_{H_2S} = 1.02 \times 10^{-6} \cdot [\exp(607/T)] \cdot C_{H_2S}^{0.510} \cdot C_{CuH_2PMo_{11}VO_{40}}^{0.431}$, respectively.

Keywords: H₂S; Absorption; Macro kinetics; Heteropoly compound; Ionic liquid.

INTRODUCTION

As a common toxic, corrosive gas existing in natural gas, refined gas, biogas and other industrial gases, hydrogen sulfide (H₂S) has threatened the environmental protection and human health seriously (Kashfi and Olson, 2013; Wiheeb *et al.*, 2013; Gupta *et al.*, 2016). In recent years, a large number of works has been focused on the removal of H₂S, and various desulfurization methods have been developed (Lu *et al.*, 2006; Ko and Hsueh, 2012; Wiheeb *et al.*, 2013). Among these methods, the wet methods which use solutions as desulfurizers play an important position in the field of H₂S removal due to their high sulfur load bearing and high desulfurization efficiency (Wang, 2003; Dubois and Thomas, 2010).

Heteropoly compounds (HPCs) have been applied in many fields such as fuel oils desulfurization (Ding and Wang, 2016; Huang *et al.*, 2019). The massive metal atoms existing in heteropoly anion lead to its unique reversible redox property (Pope and Müller, 1991; Kozhevnikov, 1998). As for the removal of H₂S, HPC solution has been proved as an excellent desulfurizer (Wang, 2003; Zou *et al.*, 2013; Kim *et al.*, 2014). Furthermore, studies reported that the oxygen atom in heteropoly anion could be replaced by O₂²⁻, and then

the peroxo heteropoly compound (PHPC) came into being (Ishii *et al.*, 1988; Yadav and Mistry, 2001). Compared with HPC, the PHPC possesses higher catalytic activity and oxidation property. The PHPC has been applied commonly as catalyst for oxidative desulfurization of fuel oil (Wang *et al.*, 2010a, b; Zhu *et al.*, 2011). However, there are few works on the application of PHPC on H₂S removal.

Ionic liquid (IL) has brought about the widespread attention of researcher in related fields because of its unique properties such as low vapor pressure, good thermal stability and dissolving ability for numerous compounds (Bai *et al.*, 2019). Compared with aqueous solution, the solution using IL as solvent could be operated at higher temperature which is higher than the boiling point of water without significant solvent loss. Hence, a series of researches on the desulfurization performance of IL have been reported (Pomelli *et al.*, 2007; Jalili *et al.*, 2009; Safavi *et al.*, 2013). Among these researches, the introduction of active substance has been recognized as an excellent choice to enhance the H₂S removal ability of IL-based desulfurizer (Guo *et al.*, 2011; Guo *et al.*, 2015; Huang *et al.*, 2016).

In our previous work, the H₂S removal performance of three HPC-based desulfurization systems, [Bmim]₃PMo₁₂O₄₀/BmimCl solution (Bmim: 1-*n*-butyl-3-methylimidazolium), aqueous solution of peroxo phosphomolybdic acid (PHPMo) and aqueous solution of CuH₂PMo₁₁VO₄₀ (CuPMoV), has been investigated (Ma *et al.*, 2016; Liu and Wang, 2017; Liu *et al.*, 2017; Ma *et al.*, 2017). The results showed that all the three systems can

* Corresponding author.

E-mail address: wangrui@sdu.edu.cn

remove H_2S with high efficiencies. In this work, to further understand the reaction characteristics of the desulfurization process of HPC-based system, the macro kinetic characteristics of H_2S absorption in three systems were investigated by a double stirred, concentration gradient-less gas liquid reaction cell. The $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}/\text{BmimCl}$ system has high thermostability under 250°C . The three systems were all stable under the temperature of this experiment. The relevant parameters of absorption process were determined, and the macro kinetic equations of practical importance were obtained.

EXPERIMENTAL

Materials

Phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) was purchased from Sinopharm Chemical Reagent Co., Ltd., China; 1-*n*-butyl-3-methylimidazolium chloride (BmimCl) was supplied by Shanghai Cheng Jie Chemical Co. Ltd., China; hydrogen peroxide (H_2O_2 , 30%) was purchased from Laiyang Kant Chemical Co., Ltd., China; phosphoric acid (H_3PO_4 , 85%) was purchased from Laiyang Kant Chemical Co., Ltd., China; molybdenum trioxide (MoO_3) and copper oxide (CuO) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China; vanadium pentoxide (V_2O_5) was purchased from Tianjin Hongyan Chemical Reagents Factory, China.

The Preparation of Desulfurizers

The $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}/\text{BmimCl}$ solution, aqueous PHPMo solution and aqueous CuPMoV solution were prepared according to our previous reports (Ma *et al.*, 2016; Liu and Wang, 2017; Liu *et al.*, 2017).

The Reaction Cell

As shown in Fig. 1, the double stirred, concentration gradient-less gas liquid reaction cell with an internal diameter of 3.82 cm and a height of 10 cm was used to investigate the macro kinetic characteristics of H_2S absorption in three systems. The temperature was controlled by thermostat water bath. The gas and liquid agitation was conducted by agitator and rotator, respectively. The stirring speed was adjusted to keep the interface smooth, so the area of gas-liquid interface could be identified as the area of absorption reaction. The specific stirring speed was identified by infrared digital tachometer. In our previous bubbling experiment, the slight foaming phenomenon will occur. However, in this work, the gas and liquid contact directly through the gas-liquid interface in the reaction cell, and no foaming phenomenon could be observed. In this experiment, the desulfurizer was used with relatively high concentration and large amount. As a result, the concentration of desulfurizer had little change in a certain period. A gas mixture (nitrogen as the carrier gas) containing a certain concentration of H_2S was passed to the reaction cell at a flow rate of 100 mL min^{-1} . The H_2S concentration of the outlet gas was detected by a TH-990s hydrogen sulfide gas analyzer. The residual H_2S gas was absorbed by aqueous NaOH solution.

Experimental Methods

The absorption processes of H_2S in the three systems are

Fig. 1. The double-stirred, concentration gradient-less gas liquid reaction cell: 1. agitator; 2. sealing plug; 3. temperature probe; 4. gas inlet; 5. gas outlet; 6. reaction cell; 7. rotator; 8. heating ring.

all mass transfer processes with chemical reaction, including the following three steps:

- 1) The hydrogen sulfide diffused from gas into gas-liquid interface.
- 2) The hydrogen sulfide dissolved and diffused into the liquid film at the interface, and reacted with the active component.
- 3) The reaction products diffused into liquid phase.

In this experiment, the double stirred gas-liquid reaction cell was used to investigate the macro kinetic characteristics of H_2S absorption. The mass transfer coefficients of H_2S in gas and liquid phase, macro reaction orders and activation energy were determined.

Determination of Gas and Liquid Phase Mass Transfer Coefficients of H_2S

The absorption rate of H_2S was determined as follows:

$$N_{\text{H}_2\text{S}} = V(C_1 - C_0)/S \quad (1)$$

where $N_{\text{H}_2\text{S}}$ is the absorption rate of H_2S , $\text{kmol m}^{-2} \text{ s}^{-1}$; C_1 and C_0 are the inlet and outlet concentrations of H_2S in the reaction cell, respectively, kmol m^{-3} ; V is the gas flow rate, $\text{m}^3 \text{ s}^{-1}$; S is the area of gas-liquid interface, m^2 .

The physical absorption rate of CO_2 in deionized water was determined using Eq. (1) under the same conditions. This process was limited by liquid phase mass transfer. The absorption rate can be expressed as:

$$N_{\text{CO}_2} = k_{\text{LCO}_2}(C^* - C_L) \quad (2)$$

$$C^* = H \cdot p_{\text{CO}_2} \quad (3)$$

where N_{CO_2} is the absorption rate of CO_2 , $\text{kmol m}^{-2} \text{ s}^{-1}$; k_{LCO_2} is the liquid phase mass transfer coefficient of CO_2 , m s^{-1} ;

p_{CO_2} is the gaseous phase partial pressure of CO_2 , Pa; H is the solubility coefficient of CO_2 , $\text{kmol m}^{-3} \text{ Pa}^{-1}$; C_L is the concentration of CO_2 in the main body of liquid phase. The k_{LCO_2} could be determined by Eq. (2), and then the liquid phase mass transfer coefficient of H_2S was determined as follows (Weisweiler and Blumhofer, 1984):

$$k_{\text{LH}_2\text{S}} = k_{\text{LCO}_2} (D_{\text{H}_2\text{S}}/D_{\text{CO}_2})^{2/3} \quad (4)$$

where $k_{\text{LH}_2\text{S}}$ is the liquid phase mass transfer coefficient of H_2S , m s^{-1} ; $D_{\text{H}_2\text{S}}$ and D_{CO_2} are the liquid diffusion coefficient of H_2S and CO_2 , respectively, $\text{m}^2 \text{ s}^{-1}$.

The absorption rate of H_2S in NaOH solution (1 mol L^{-1}) under the same condition was measured using the same method. This process was limited by gas phase mass transfer. The absorption rate can be expressed as:

$$N_{\text{H}_2\text{S}} = k_{\text{GH}_2\text{S}} p_{\text{H}_2\text{S}} \quad (5)$$

where $k_{\text{GH}_2\text{S}}$ is the gas phase mass transfer coefficient, $\text{kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$; $p_{\text{H}_2\text{S}}$ is the gaseous phase partial pressure of H_2S , Pa. So, $k_{\text{GH}_2\text{S}}$ could be determined by measured $N_{\text{H}_2\text{S}}$ and $p_{\text{H}_2\text{S}}$.

Determination of Macro Kinetic Equation of H_2S Absorption

The absorption rate of H_2S was correlated with the factors in the reaction by nonlinear fitting method, and then the kinetic reaction orders of the factors were determined. The activation energy of the overall reaction as well as the absorption rate equations were determined by the measured reaction rates at different temperatures as follows:

$$N_{\text{H}_2\text{S}} = A \cdot [\exp(-E/RT)] \cdot C_{\text{H}_2\text{S}}^a \cdot C_{\text{absorbent}}^b \quad (6)$$

where A is the pre-exponential factor; E is the activation energy, KJ mol^{-1} ; R is the molar gas constant, 8.314 J mol^{-1}

K^{-1} ; T is the thermodynamic temperature, K ; a and b are the reaction orders of the concentrations of H_2S and absorbent, respectively.

RESULTS AND DISCUSSION

The Gas and Liquid Phase Mass Transfer Coefficients of H_2S

The experimental results showed that the liquid phase mass transfer coefficient of CO_2 at 25°C is:

$$k_{\text{LCO}_2} = 3.41 \times 10^{-5} \text{ m s}^{-1}$$

Hence, according to Eq. (4), the liquid phase mass transfer coefficient of H_2S at 25°C is:

$$k_{\text{LH}_2\text{S}} = 3.26 \times 10^{-5} \text{ m s}^{-1}$$

The measured gas phase mass transfer coefficient of H_2S at 25°C is:

$$k_{\text{GH}_2\text{S}} = 1.46 \times 10^{-10} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$$

The Macro Kinetic Characteristics of H_2S Absorption in $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}/\text{BmimCl}$ Solution

The effect of the concentration of $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$ on the absorption rate was shown in Fig. 2, where T is the reaction temperature, r_G and r_L are the stirring rates in gas phase and liquid phase, respectively. It could be seen that the absorption rate increased with the increase of the concentration of $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$. In our previous work (Liu *et al.*, 2017; Ma *et al.*, 2017), the removal of H_2S using $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}/\text{BmimCl}$ solution has been proved to be achieved by the $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$, and the BmimCl only played a role of solvent and reaction medium. The increase of the concentration of $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$ is benefit to the decrease of liquid phase mass transfer resistance, thus

Fig. 2. The effect of $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$ concentration on the absorption rate: $T = 80^\circ\text{C}$, $C_{\text{H}_2\text{S}} = 576 \text{ mg m}^{-3}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

promoting the absorption of H₂S. According to nonlinear fitting method, the relation between the concentration of [Bmim]₃PMo₁₂O₄₀ and absorption rate is:

$$N_{\text{H}_2\text{S}} = 7.29 \times 10^{-9} C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}}^{0.099}, R^2 = 0.986 \quad (7)$$

Therefore, the H₂S absorption rate in [Bmim]₃PMo₁₂O₄₀/BmimCl solution is proportional to the 0.099 power of the concentration of [Bmim]₃PMo₁₂O₄₀. This means that the kinetic reaction order of [Bmim]₃PMo₁₂O₄₀ in the process of H₂S absorption is 0.099.

The effect of the inlet concentration of H₂S on the absorption rate is shown in Fig. 3. The H₂S absorption rate increased with the increase of the concentration of H₂S, and the correlation is close to linear relation. The increase of the concentration of H₂S could decrease the gas phase mass transfer resistance significantly. According to nonlinear fitting method, the relation between the inlet concentration of H₂S and absorption rate is:

$$N_{\text{H}_2\text{S}} = 7.07 \times 10^{-12} C_{\text{H}_2\text{S}}^{1.120}, R^2 = 0.992 \quad (8)$$

The H₂S absorption rate in [Bmim]₃PMo₁₂O₄₀/BmimCl solution is proportional to the 1.120 power of the inlet concentration of H₂S. This means that the kinetic reaction order of H₂S is 1.120. Compared with the order of concentration of [Bmim]₃PMo₁₂O₄₀, it could be seen that the major limiting factor of H₂S absorption rate in [Bmim]₃PMo₁₂O₄₀/BmimCl solution is gas phase mass transfer resistance.

The effect of absorption temperature on the H₂S absorption rate is shown in Fig. 4. The increase of temperature was conducive to the absorption of H₂S in [Bmim]₃PMo₁₂O₄₀/BmimCl solution. A higher temperature could decrease the viscosity of ionic liquid, and increase the molecular activity of reactants. As a result, the absorption of H₂S was promoted at higher temperature. Hence, according to the results above as well as Eqs. (6), (7) and (8), the

activation energy of the overall reaction was calculated as 8.84 KJ mol⁻¹, and the macro kinetic equation of H₂S absorption in [Bmim]₃PMo₁₂O₄₀/BmimCl solution is:

$$N_{\text{H}_2\text{S}} = 6.6 \times 10^{-2} \cdot [\exp(-1064/T)] \cdot C_{\text{H}_2\text{S}}^{1.120} \cdot C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}}^{0.099} \quad (9)$$

The relatively low activation energy demonstrated that the absorption reaction of H₂S in [Bmim]₃PMo₁₂O₄₀/BmimCl solution was a diffusion controlled process.

The Macro Kinetic Characteristics of H₂S Absorption in Aqueous PHPMo Solution

The effect of the concentration of PHPMo on the absorption rate is shown in Fig. 5. A higher concentration of PHPMo is in favor of the liquid phase mass transfer process of H₂S molecule, which is in agreement with the result of our previous work. Hence, a higher concentration of PHPMo should be chosen in the practical application of H₂S removal. The relation between the concentration of PHPMo and absorption rate was determined using nonlinear fitting method as follows:

$$N_{\text{H}_2\text{S}} = 5.033 \times 10^{-9} C_{\text{PHPMo}}^{0.131}, R^2 = 0.962 \quad (10)$$

Therefore, the H₂S absorption rate in aqueous PHPMo solution is proportional to the 0.131 power of the concentration of PHPMo. This means that the kinetic reaction order of PHPMo in the process of H₂S absorption is 0.131.

As shown in Fig. 6, the increase of the inlet concentration of H₂S showed a positive influence on the H₂S absorption rate due to the decreased gas phase mass transfer resistance. In our previous work, the results showed that the increase of H₂S concentration had little effect on the H₂S removal efficiency within a certain range, and the H₂S removal efficiency would decrease with further increase of H₂S concentration. Therefore, an appropriate inlet concentration

Fig. 3. The effect of the inlet concentration of H₂S on the absorption rate: T = 80°C, C_{[Bmim]₃PMo₁₂O₄₀} = 0.005 mol L⁻¹, r_G = 750 r min⁻¹, r_L = 220 r min⁻¹.

Fig. 4. The effect of temperature on the absorption rate: $C_{H_2S} = 576 \text{ mg m}^{-3}$, $C_{[Bmim]_3PMo_{12}O_{40}} = 0.005 \text{ mol L}^{-1}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

Fig. 5. The effect of the concentration of PHPMo on the absorption rate: $T = 25^\circ\text{C}$, $C_{H_2S} = 750 \text{ mg m}^{-3}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

of H_2S should be determined to achieve the highest utilization rate of desulfurizer without the decrease of H_2S removal efficiency. Based on nonlinear fitting method, the relation between the inlet concentration of H_2S and absorption rate was determined as follows:

$$N_{H_2S} = 1.33 \times 10^{-9} C_{H_2S}^{0.252}, R^2 = 0.989 \quad (11)$$

The H_2S absorption rate in aqueous PHPMo solution is proportional to the 0.252 power of the inlet concentration of H_2S .

The effect of temperature on the absorption rate is shown in Fig. 7. It could be seen that proper rise in temperature is beneficial to improve the H_2S absorption rate because of increased molecular activity at higher temperature. In

addition, considering the volatilization of solvent, a moderate temperature should be chosen for practical application. According to the results above as well as Eqs. (6), (10) and (11), the activation energy of the overall reaction was calculated as 6.57 KJ mol^{-1} , demonstrating that the absorption reaction was a diffusion controlled process. The macro kinetic equation of H_2S absorption in aqueous PHPMo solution is:

$$N_{H_2S} = 2.68 \times 10^{-6} \cdot [\exp(-790/T)] \cdot C_{H_2S}^{0.252} \cdot C_{PHPMo}^{0.131} \quad (12)$$

The Macro Kinetic Characteristics of H_2S Absorption in Aqueous CuPMoV Solution

The effect of the concentration of CuPMoV on the absorption rate is shown in Fig. 8. The H_2S absorption rate

Fig. 6. The effect of the inlet concentration of H_2S on the absorption rate: $T = 25^\circ\text{C}$, $C_{\text{PHPMo}} = 0.01 \text{ mol L}^{-1}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

Fig. 7. The effect of temperature on the absorption rate: $C_{\text{H}_2\text{S}} = 750 \text{ mg m}^{-3}$, $C_{\text{PHPMo}} = 0.01 \text{ mol L}^{-1}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

raise as the concentration of CuPMoV increased due to the decrease of liquid phase mass transfer resistance. Based on nonlinear fitting method, the relation between the concentration of CuPMoV and absorption rate was determined as follows:

$$N_{\text{H}_2\text{S}} = 1.18 \times 10^{-8} C_{\text{CuH}_2\text{PMo}_{11}\text{VO}_{40}}^{0.431}, R^2 = 0.985 \quad (13)$$

Hence, the kinetic reaction order of CuPMoV in the process of H_2S absorption is 0.431.

The effect of the inlet concentration of H_2S on the absorption rate is shown in Fig. 9. A higher H_2S concentration could promote the gas phase transfer process, and then increase the H_2S absorption rate. According to nonlinear fitting method, the relation between the inlet concentration of H_2S and absorption rate was determined as follows:

$$N_{\text{H}_2\text{S}} = 4.63 \times 10^{-10} C_{\text{H}_2\text{S}}^{0.510}, R^2 = 0.989 \quad (14)$$

Therefore, the H_2S absorption rate in aqueous PHPMo solution is proportional to the 0.510 power of the inlet concentration of H_2S .

As shown in Fig. 10, differing from the two systems above, the absorption temperature showed a negative effect on the H_2S absorption rate. Although the increase of temperature could promote the molecular motion, the increased temperature would hinder the reaction between CuPMoV and H_2S , which is exothermic reaction (Wang *et al.*, 2006). Obviously, as for the reaction between CuPMoV and H_2S , the negative effect of increased temperature is stronger than its positive effect. According to the results above as well as Eqs. (6), (13) and (14), the activation energy of the overall reaction was calculated as $-5.04 \text{ KJ mol}^{-1}$, and the macro

Fig. 8. The effect of the concentration of CuPMoV on the absorption rate: $T = 25^\circ\text{C}$, $C_{\text{H}_2\text{S}} = 600 \text{ mg m}^{-3}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

Fig. 9. The effect of the inlet concentration of H_2S on the absorption rate: $T = 25^\circ\text{C}$, $C_{\text{CuPMoV}} = 0.001 \text{ mol L}^{-1}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

kinetic equation of H_2S absorption in aqueous CuPMoV solution could be expressed as:

$$N_{\text{H}_2\text{S}} = 1.02 \times 10^{-6} \cdot [\exp(607/T)] \cdot C_{\text{H}_2\text{S}}^{0.510} \cdot C_{\text{CuH}_2\text{PMo}_{11}\text{VO}_{40}}^{0.431} \quad (15)$$

CONCLUSIONS

Ionic liquids and heteropoly compounds have been found to be effective systems for H_2S removal due to their unique properties. In our previous work, three systems for H_2S removal, a $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}/\text{BmimCl}$ solution, an aqueous PHPMo solution and an aqueous CuPMoV solution, exhibited excellent desulfurization performance. This study continues our earlier research by investigating the macro kinetic characteristics of the three systems' H_2S absorption

using a double-stirred gas-liquid reaction cell. The gas and liquid phase mass transfer coefficients for H_2S in the reaction cell at 25°C were $1.46 \times 10^{-10} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and $3.26 \times 10^{-5} \text{ m s}^{-1}$, respectively. For the $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}/\text{BmimCl}$ solution, the orders of the reactions to $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$ and H_2S were 0.099 and 1.120, respectively, and the activation energy of the overall reaction was identified as 8.84 KJ mol^{-1} ; these macro kinetics can be expressed with the equation $N_{\text{H}_2\text{S}} = 6.6 \times 10^{-2} \cdot [\exp(-1064/T)] \cdot C_{\text{H}_2\text{S}}^{1.120} \cdot C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}}^{0.099}$. For the aqueous PHPMo solution, the orders of the reactions to PHPMo and H_2S were 0.131 and 0.252, respectively, and the activation energy of the overall reaction was identified as 6.57 KJ mol^{-1} ; these macro kinetics can be expressed with the equation $N_{\text{H}_2\text{S}} = 2.68 \times 10^{-6} \cdot [\exp(-790/T)] \cdot C_{\text{H}_2\text{S}}^{0.252} \cdot C_{\text{PHPMo}}^{0.131}$. For the aqueous CuPMoV solution, the orders of the reactions to PHPMo and H_2S were 0.131 and 0.252, and the activation

Fig. 10. The effect of temperature on the absorption rate: $C_{H_2S} = 600 \text{ mg m}^{-3}$, $C_{CuPMoV} = 0.001 \text{ mol L}^{-1}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

energy of the overall reaction was identified as $-5.04 \text{ KJ mol}^{-1}$; these macro kinetics can be expressed with the equation $N_{H_2S} = 1.02 \times 10^{-6} [\exp(607/T)] \cdot C_{H_2S}^{0.510} \cdot C_{CuH_2PMoV}^{0.431}$. The relatively low activation energy demonstrated that the absorption reactions of H_2S in all three systems were driven by diffusion.

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