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

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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: 

\[ N_{\text{H}_2\text{S}} = 6.6 \times 10^{-2} \cdot \exp\left(-1064/T\right) \cdot C_{\text{H}_2\text{S}}^{1.120} \cdot C_{\text{[Bmim]3PMo12O40}}^{0.099} \]

For the aqueous solutions of peroxo phosphomolybdic acid and CuH2PMo11VO40, the absorption can be expressed as 

\[ N_{\text{H}_2\text{S}} = 2.68 \times 10^{-6} \cdot \exp\left(-790/T\right) \cdot C_{\text{H}_2\text{S}}^{0.252} \cdot C_{\text{PHMo}}^{0.131} \]

and 

\[ N_{\text{H}_2\text{S}} = 1.02 \times 10^{-6} \cdot \exp\left(607/T\right) \cdot C_{\text{H}_2\text{S}}^{0.510} \cdot C_{\text{CuH2PMo11VO40}}^{0.431} \]

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; Kozevnikov, 1998). As for the removal of H2S, HPC solution has been proved to be 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
remove H2S 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 H2S absorption in three systems were investigated by a double stirred, concentration gradient-less gas liquid reaction cell. The [Bmim]3PMo12O40/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 (H3PMo12O40) 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 (H2O2, 30%) was purchased from Laiyang Kant Chemical Co., Ltd., China; phosphoric acid (H3PO4, 85%) was purchased from Laiyang Kant Chemical Co., Ltd., China; molybdenum trioxide (MoO3) and copper oxide (CuO) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China; vanadium pentoxide (V2O5) was purchased from Tianjin Hongyan Chemical Reagents Factory, China.

The Preparation of Desulfurizers
The [Bmim]3PMo12O40/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 H2S 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 H2S was passed to the reaction cell at a flow rate of 100 mL min–1. The H2S concentration of the outlet gas was detected by a TH-990s hydrogen sulfide gas analyzer. The residual H2S gas was absorbed by aqueous NaOH solution.

Experimental Methods
The absorption processes of H2S in the three systems are 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 H2S absorption. The mass transfer coefficients of H2S in gas and liquid phase, macro reaction orders and activation energy were determined.

Determination of Gas and Liquid Phase Mass Transfer Coefficients of H2S
The absorption rate of H2S was determined as follows:

\[ N_{H2S} = \frac{V(C_1 - C_0)}{S} \]  

where \( N_{H2S} \) is the absorption rate of H2S, kmol m–2 s–1; \( C_1 \) and \( C_0 \) are the inlet and outlet concentrations of H2S in the reaction cell, respectively, kmol m–3; \( V \) is the gas flow rate, m3 s–1; \( S \) is the area of gas-liquid interface, m2.

The physical absorption rate of CO2 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:

\[ N_{CO2} = k_{LCO2}(C^* - C_L) \]

where \( N_{CO2} \) is the absorption rate of CO2, kmol m–2 s–1; \( k_{LCO2} \) is the liquid phase mass transfer coefficient of CO2, m s–1;
pCO2 is the gaseous phase partial pressure of CO2, Pa; H is the solubility coefficient of CO2, kmol m–3 Pa–1; C4 is the concentration of CO2 in the main body of liquid phase. The kLCO2 could be determined by Eq. (2), and then the liquid phase mass transfer coefficient of H2S was determined as follows (Weisweiler and Blumhofer, 1984):

\[ kLH2S = kLCO2(DH2S/DCO2)^{2/3} \]  

(4)

where \( kLH2S \) is the liquid phase mass transfer coefficient of H2S, m s–1; \( DH2S \) and \( DCO2 \) are the liquid diffusion coefficient of H2S and CO2, respectively, m2 s–1.

The absorption rate of H2S 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:

\[ N_{H2S} = kGH2S \cdot p_{H2S} \]  

(5)

where \( kGH2S \) is the gas phase mass transfer coefficient, kmol m–2 s –1 Pa –1; \( p_{H2S} \) is the gaseous phase partial pressure of H2S, Pa. So, \( kGH2S \) could be determined by measured \( N_{H2S} \) and \( p_{H2S} \).

**Determination of Macro Kinetic Equation of H2S Absorption**

The absorption rate of H2S 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:

\[ N_{H2S} = A \cdot \exp(-E/RT) \cdot C_{H2S}^a \cdot C_{absorbent}^b \]  

(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 H2S and absorbent, respectively.

**RESULTS AND DISCUSSION**

**The Gas and Liquid Phase Mass Transfer Coefficients of H2S**

The experimental results showed that the liquid phase mass transfer coefficient of CO2 at 25°C is:

\[ kLCO2 = 3.41 \times 10^{-5} \text{ m s}^{-1} \]

Hence, according to Eq. (4), the liquid phase mass transfer coefficient of H2S at 25°C is:

\[ kLH2S = 3.26 \times 10^{-5} \text{ m s}^{-1} \]

The measured gas phase mass transfer coefficient of H2S at 25°C is:

\[ kGH2S = 1.46 \times 10^{-10} \text{ kmol m}^2 \text{ s}^{-1} \text{ Pa}^{-1} \]

**The Macro Kinetic Characteristics of H2S Absorption in [Bmim]3PMo12O40/BmimCl Solution**

The effect of the concentration of [Bmim]3PMo12O40 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 [Bmim]3PMo12O40. In our previous work (Liu et al., 2017; Ma et al., 2017), the removal of H2S using [Bmim]3PMo12O40 and the BmimCl only played a role of solvent and reaction medium. The increase of the concentration of [Bmim]3PMo12O40 is benefit to the decrease of liquid phase mass transfer resistance, thus
promoting the absorption of H$_2$S. According to nonlinear fitting method, the relation between the concentration of [Bmim]$_3$PMo$_{12}$O$_{40}$ and absorption rate is:

$$N_{H2S} = 7.29 \times 10^{-9} C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}}^{0.099}, \quad R^2 = 0.986 \quad (7)$$

Therefore, the H$_2$S absorption rate in [Bmim]$_3$PMo$_{12}$O$_{40}$/BmimCl solution is proportional to the 0.099 power of the concentration of [Bmim]$_3$PMo$_{12}$O$_{40}$. This means that the kinetic reaction order of [Bmim]$_3$PMo$_{12}$O$_{40}$ in the process of H$_2$S absorption is 0.099.

The effect of the concentration of H$_2$S on the absorption rate is shown in Fig. 3. The H$_2$S absorption rate increased with the increase of the concentration of H$_2$S, and the correlation is close to linear relation. The increase of the concentration of H$_2$S could decrease the gas phase mass transfer resistance significantly. According to nonlinear fitting method, the relation between the concentration of H$_2$S and absorption rate is:

$$N_{H2S} = 7.07 \times 10^{-12} C_{H2S}^{1.120}, \quad R^2 = 0.992 \quad (8)$$

The H$_2$S absorption rate in [Bmim]$_3$PMo$_{12}$O$_{40}$/BmimCl solution is proportional to the 1.120 power of the concentration of H$_2$S. This means that the kinetic reaction order of H$_2$S is 1.120. Compared with the order of concentration of [Bmim]$_3$PMo$_{12}$O$_{40}$, it could be seen that the major limiting factor of H$_2$S absorption rate in [Bmim]$_3$PMo$_{12}$O$_{40}$/BmimCl solution is gas phase mass transfer resistance.

The effect of absorption temperature on the H$_2$S absorption rate is shown in Fig. 4. The increase of temperature was conductive to the absorption of H$_2$S in [Bmim]$_3$PMo$_{12}$O$_{40}$/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 H$_2$S 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 H$_2$S absorption in [Bmim]$_3$PMo$_{12}$O$_{40}$/BmimCl solution is:

$$N_{H2S} = 6.6 \times 10^{-2} \cdot \exp\left(-1064/T\right) \cdot C_{H2S}^{1.120}, \quad C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}}^{0.099} \quad (9)$$

The relatively low activation energy demonstrated that the absorption reaction of H$_2$S in [Bmim]$_3$PMo$_{12}$O$_{40}$/BmimCl solution was a diffusion controlled process.

### The Macro Kinetic Characteristics of H$_2$S 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 H$_2$S 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 H$_2$S removal. The relation between the concentration of PHPMo and absorption rate was determined using nonlinear fitting method as follows:

$$N_{H2S} = 5.033 \times 10^{-9} C_{\text{PHPMo}}^{0.131}, \quad R^2 = 0.962 \quad (10)$$

Therefore, the H$_2$S 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 H$_2$S absorption is 0.131.

As shown in Fig. 6, the increase of the inlet concentration of H$_2$S showed a positive influence on the H$_2$S absorption rate due to the decreased gas phase mass transfer resistance. In our previous work, the results showed that the increase of H$_2$S concentration had little effect on the H$_2$S removal efficiency within a certain range, and the H$_2$S removal efficiency would decrease with further increase of H$_2$S concentration. Therefore, an appropriate inlet concentration

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**Fig. 3.** The effect of the inlet concentration of H$_2$S on the absorption rate: $T = 80^\circ$C, $C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}} = 0.005$ 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: \( \text{CH}_2\text{S} = 576 \, \text{mg} \, \text{m}^{-3}, \text{C}_{[\text{Bmim}]\text{PMo}_{12}\text{O}_{40}} = 0.005 \, \text{mol} \, \text{L}^{-1}, r_G = 750 \, \text{r} \, \text{min}^{-1}, r_L = 220 \, \text{r} \, \text{min}^{-1} \).

Fig. 5. The effect of the concentration of PHPMo on the absorption rate: \( T = 25^\circ\text{C}, \text{CH}_2\text{S} = 750 \, \text{mg} \, \text{m}^{-3}, r_G = 750 \, \text{r} \, \text{min}^{-1}, r_L = 220 \, \text{r} \, \text{min}^{-1} \).

The H\(_2\)S absorption rate in aqueous PHPMo solution is proportional to the 0.252 power of the inlet concentration of H\(_2\)S.

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\(_2\)S 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\(_2\)S absorption in aqueous PHPMo solution is:

\[
N_{\text{H}_2\text{S}} = 2.68 \times 10^{-6} \cdot \exp(-790/T) \cdot \text{CH}_2\text{S}^{0.252} \cdot \text{CPHPMo}^{0.131}
\] (12)

The Macro Kinetic Characteristics of H\(_2\)S Absorption in Aqueous CuPMoV Solution

The effect of the concentration of CuPMoV on the absorption rate is shown in Fig. 8. The H\(_2\)S absorption rate
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:

\[ N_{\text{H}_2\text{S}} = 1.18 \times 10^{-8} \text{C}_{\text{CuH}_2\text{PMo}_{11}\text{V}_{40}}^{0.431}, R^2 = 0.985 \]  

(13)

Hence, the kinetic reaction order of CuPMoV in the process of H2S absorption is 0.431.

The effect of the inlet concentration of H2S on the absorption rate is shown in Fig. 9. A higher H2S concentration could promote the gas phase transfer process, and then increase the H2S absorption rate. According to nonlinear fitting method, the relation between the inlet concentration of H2S and absorption rate was determined as follows:

\[ N_{\text{H}_2\text{S}} = 4.63 \times 10^{-10} \text{C}_{\text{H}_2\text{S}}^{0.510}, R^2 = 0.989 \]  

(14)

Therefore, the H2S absorption rate in aqueous PHPMo solution is proportional to the 0.510 power of the inlet concentration of H2S.

As shown in Fig. 10, differing from the two systems above, the absorption temperature showed a negative effect on the H2S absorption rate. Although the increase of temperature could promote the molecular motion, the increased temperature would hinder the reaction between CuPMoV and H2S, which is exothermic reaction (Wang et al., 2006). Obviously, as for the reaction between CuPMoV and H2S, 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 KJ mol−1, and the macro
Fig. 8. The effect of the concentration of CuPMoV on the absorption rate: $T = 25^\circ C$, $C_{H_2S} = 600 \text{ mg m}^{-3}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

Fig. 9. The effect of the inlet concentration of H$_2$S on the absorption rate: $T = 25^\circ C$, $C_{CuPMoV} = 0.001 \text{ mol L}^{-1}$, $r_G = 750 \text{ r min}^{-1}$, $r_L = 220 \text{ r min}^{-1}$.

Kinetic equation of H$_2$S absorption in aqueous CuPMoV solution could be expressed as:

$$N_{H_2S} = 1.02 \times 10^{-6} \times [exp(607/T)] \times C_{H_2S}^{0.510} \times C_{CuH_2PMo11VO40}^{0.431}$$

(15)

CONCLUSIONS

Ionic liquids and heteropoly compounds have been found to be effective systems for H$_2$S removal due to their unique properties. In our previous work, three systems for H$_2$S 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$_2$S absorption using a double-stirred gas-liquid reaction cell. The gas and liquid phase mass transfer coefficients for H$_2$S in the reaction cell at $25^\circ C$ 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$_2$S 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 $N_{H_2S} = 6.6 \times 10^{-2} \times [exp(-1064/T)] \times C_{H_2S}^{1.120} \times C_{[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}}^{0.099}$. For the aqueous PHPMo solution, the orders of the reactions to PHPMo and H$_2$S 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 $N_{H_2S} = 2.68 \times 10^{-6} \times [exp(-790/T)] \times C_{H_2S}^{0.252} \times C_{\text{PHPMo}}^{0.131}$. For the aqueous CuPMoV solution, the orders of the reactions to PHPMo and H$_2$S were 0.131 and 0.252, and the activation
energy of the overall reaction was identified as –5.04 KJ mol$^{-1}$; these macro kinetics can be expressed with the equation $N_{H_{2}S} = 1.02 \times 10^{-6} \cdot \exp(607/T) \cdot CH_{2}S^{0.510} \cdot CCuH_{2}PMo^{11VO_{40}}^{0.431}$. The relatively low activation energy demonstrated that the absorption reactions of H$_2$S in all three systems were driven by diffusion.

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