pH-Responsive and Buffering Macromolecule Aqueous Absorbent and Mathematic Model-Based Feasibility Evaluation for SO₂ Capture

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Abstract

An organic macromolecule, poly(1-vinylimidazole), with an appropriate polymerization degree was proposed and mixed with water to form a novel aqueous absorbent for SO₂ capture. This aqueous solution absorbent has the advantages of simple preparation, good physicochemical properties, environment-friendliness, high ability in deep removal of SO₂, and excellent reusability. Moreover, pH-responsive behavior, pH buffering absorption mechanism, and their synergistic effect on absorption performance were revealed. The solubilities of SO₂ in the absorbent were measured in detail, and the results demonstrated excellent absorption capacity and recyclability. Then, mathematic models that describe SO₂ absorption equilibrium were established, and the corresponding parameters were estimated. More importantly, on the basis of model and experimental data, the absorption and desorption could maintain high efficiency within a wide operating region. In summary, this work provided a low-cost, efficient, and unique absorbent for SO₂ capture and verified its technical feasibility in industrial application.

Keywords Poly(1-vinylimidazole) · pH buffer · pH responsibility · SO₂ capture · Flue gas desulfurization

Introduction

Combustion of fossil fuels leads to a large amount of sulfur dioxide (SO₂) emission, which causes serious environmental problems and is harmful to human health [1]. Therefore, a crucial task is to reduce SO₂ emission through flue gas desulfurization (FGD) on account of the principles of sustainable development and green chemistry [2].

Among all the FGD technologies, wet desulfurization [3, 4] and dry desulfurization [5, 6] are widely used in practice. The efficiency of dry desulfurization is lower than that of wet desulfurization, thereby preventing the large-scale

application of dry desulfurization. Limestone-gypsum as a kind of absorbent in one of the wet desulfurization methods has been widely used in practice [7–9]. However, limestone-gypsum has various inherent disadvantages, such as the production of a large amount of wastewater, high operating cost, useless byproducts that cause secondary pollutants, and intensive energy consumption. Another widely adopted wet desulfurization method is the use of organic amine, such as ethylenediamine [10], as absorbent in FGD. This method has a high desulfurization efficiency, and SO₂ can be desorbed from the system by heating so that the absorbents can be recycled. N-methylimidazole and N-methylpyrrolidone also showed great performance in SO₂ absorption [11]. However, the large loss of the absorption agent is inevitable because the organic solvents will volatilize into the gas stream, especially in the desorption process. The development of renewable and efficient absorbents with the absence of byproducts is highly valued for industrial application.

Recently, ionic liquids (ILs) have attracted widespread attention as promising absorbents for SO₂ removal and capture due to their unique properties [12–14], such as negligible vapor pressure, high thermal stability, and tunable structure. Wu et al. [15] first reported an IL—1,1,3,3-tetramethylguanidinium lactate ([TMG]L) for SO₂ absorption from a gas mixture of SO₂ and N₂, and the result showed

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that 1 mol [TMG]L could selectively capture 0.978 mol SO₂ at 40 °C. Later, many other ILs, including hydroxyl ammonium ILs [16, 17], ether-functionalized ILs [18–20], imidazolium-based ILs [21–23], guanidinium-based ILs [24–26], pyridinium-based ILs [27, 28], anion-functionalized ILs [29, 30], and, more recently, deep eutectic solvents [31–33], were investigated for SO₂ absorption.

Absorption capacity and absorption rate are two important aspects in assessing the absorption performance of absorbents. Despite the high absorption capacity of ILs, the high viscosities of most task-specific ILs induce the low heat and mass transfer performance of the SO₂ absorption process [34, 35]. In addition, water and O₂ are contained in flue gas; thus, part of SO₂ can be oxidized into SO₄^{2−} in the FGD process. Moreover, SO₄^{2−} will destroy the structure of the ILs and further affect the reusability of the absorbent [36, 37]. These limitations highlight the significance of developing new absorbents that have low viscosity and can adapt to the complex compositions of flue gas.

To take advantage of the non-volatility of ILs and the applicability of traditional organic amines, poly(1-vinylimidazole) (PVIM), an organic macromolecule with high thermal stability, was proposed and blended with water to form pH buffering aqueous solutions for SO₂ capture. The aqueous absorbents can reversibly and efficiently capture SO₂ because of the suitable basicity of each repeated imidazole group in PVIM [11]. The absorptive/desorptive capability and the reusability of the absorbents were investigated in detail. Then, equilibrium models were built according to the absorption mechanism. Parametric analysis was performed based on the models and the experimental data, and correlative thermodynamic parameters were obtained. The application feasibility of this absorbent was examined using the equilibrium models and the parameters.

Experimental Section

Materials

SO₂ gas (≥ 99.9%) and N₂ gas (≥ 99.99%) were supplied by Tianjin Shengtang Specialty Gases Co., Ltd. Ethanol (≥ 99.9%), acetone (≥ 99.9%), cyclohexane (≥ 99%), and azodiisobutyronitrile (AIBN, 99.9%) were purchased from Aladdin Industrial Corporation. 1-vinylimidazole (VIM) was obtained from Shanghai Meryer Chemical Technology Co., Ltd.

Synthesis of Poly(1-vinylimidazole)

PVIM was synthesized via conventional free radical polymerization [38]. In a 100 mL round-bottomed flask, VIM (10.00 g) was dissolved in a binary mixture of ethanol

(25.00 g) and cyclohexane (15.00 g) with a certain amount of AIBN as initiator. The molecular weight of PVIM was regulated by changing the dosage of AIBN, and the molar ratio of AIBN to VIM was selected as 3, 7, and 10%, respectively. The reaction was placed in a preheated oil bath at 75 °C with magnetic stirring under nitrogen atmosphere for 24 h. After the reaction, the mixture was precipitated into acetone, and the solid was separated by filtrate. Then, the solid was purified by dissolution in methanol and precipitation with acetone. The steps were repeated two times. Finally, the polymer was dried at 80 °C under vacuum for 24 h before use.

Characterization of PVIM

A series of PVIM with different molecular weights was prepared in this work. Absolute polymer molecular weights were determined using aqueous size exclusion chromatography using Malvern's OMNISEC and summarized in Table 1. The chemical structure of the as-prepared PVIM was confirmed by ¹H nuclear magnetic resonance (NMR) spectra and Fourier transform infrared (FTIR) spectra. ¹H NMR spectra were measured on a Bruker DPX 500 MHz spectrometer using DMSO as a solvent, and the spectra are illustrated in Fig. S1. FTIR spectra were recorded on a NEXUS870 FTIR spectrometer. The thermal stability of PVIM was investigated using TGA/DSC (STAR[®] System, Switzerland) from 0 to 500 °C at a scan rate of 10 °C/min under N₂ atmosphere, and the decomposition temperature was determined according to the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves.

Preparation of SO₂ Absorbents and Determination of Physical Properties

A range of absorbents was prepared by dissolving PVIM (30 wt%) with different molecular weights in water (70 wt%). The viscosities were measured using a Brookfield DV-II+ Pro viscometer, which was supplied by Brookfield Engineering Laboratories. The temperature was controlled by a water bath accurate to ± 0.1 K. The viscosities of these

Table 1 Viscosities of the absorbents with different molecular weights

Molar ratio of AIBN to VIM (%)	Molecular weight of PVIM	Viscosity (cP)
3	5000	307.6
7	4000	194.7
10	3100	131.6

The absorbents were aqueous solution of PVIM (30 wt%)

The viscosities were measured at 298.2 K

absorbents before absorption at 298.2 K are listed in Table 1. The uncertainty of viscosity measurements was estimated to be $\pm 1\%$.

Absorption of SO₂

The measuring methods employed to determine the absorption of SO₂ were similar to those used in other studies, and the diagram of the experimental apparatus is shown in Fig. 1 [39]. The whole test apparatus includes absorption and recording sections. The absorption section consists of two stainless steel chambers, the volumes of which are 161.752 cm³ (V_1) and 88.165 cm³ (V_2), respectively. The bigger chamber, which is called gas reserve, isolates SO₂ before it contacts with the absorbent in the smaller chamber. The smaller chamber, which is called equilibrium chamber, is equipped with a magnetic stirrer. The temperature of the chambers is controlled by a water bath with an uncertainty of ± 0.1 K. The recording section includes two pressure sensors of $\pm 0.2\%$ uncertainty (in relation to the full scale of 0–300 kPa), which are connected to a numeric instrument to record the pressure changes of the two chambers online.

In a typical absorption procedure, a known mass (w) of solvent was placed in the equilibrium chamber and nitrogen was then purged into the chamber to exclude the air. After a sufficient amount of time, the initial pressure in the equilibrium chamber was noted as P_0 . The air in the gas reserve was exhausted (< 10 Pa), and then the gas reserve received a certain amount of SO₂ from the gas cylinder. The pressure was measured as P_1 , which was much larger than P_0 . The needle valve between the two chambers was turned to introduce a certain amount of SO₂ into the equilibrium chamber. The absorption equilibrium was considered to have been achieved when the pressure of the equilibrium chamber stayed the same for at least 1 h. At this time, the pressure of the two cells was recorded as P'_1 for the gas reserve and P_2

for the equilibrium chamber. The SO₂ uptake ($n(P_s)$) could be calculated using the following formula:

$$n(P_s) = \rho_g(P_1, T)V_1 - \rho_g(P'_1, T)V_1 - \rho_g(P_s, T)(V_2 - V_a) \quad (1)$$

where $\rho_g(P, T)$, which is obtained from NIST standard reference data [40], represents the density of SO₂ in mol/cm³ at P and T ; V_a is the volume of the absorbent in cm³ at T ; and $\rho_g(P_s, T)$ is the density of SO₂ gas remaining in the equilibrium chamber when the absorption equilibrium was reached, and it could be calculated by the following equations:

$$\rho_g(P_s, T) = \rho_{12} - \rho_1 \quad (2)$$

$$y_2 = \rho_g(P_s, T) / \rho_{12} \quad (3)$$

where ρ_{12} and ρ_1 represent the density of the mixed gas and N₂ in the equilibrium chamber, respectively; y_2 is the mole fraction of SO₂ in the mixed gas, and ρ_{12} is a function of y_2 . The value of ρ_1 could be calculated using a generalized second virial coefficient [41]; the formula is as follows:

$$Z_1 = 1 + \frac{BP_c}{RT_c} \left(\frac{P_c}{T_c} \right) \quad (4)$$

$$\frac{BP_c}{RT_c} = B^{(0)} + \omega B^{(1)} \quad (5)$$

$$B^{(0)} = 0.083 - 0.422/T_r^{1.6} \quad (6)$$

$$B^{(1)} = 0.139 - 0.172/T_r^{4.2} \quad (7)$$

$$\rho_1 = P_0 / Z_1 RT \quad (8)$$

where Z_1 represents the compressibility factor of N₂; P_0 is the initial pressure of N₂ before SO₂ was introduced; and R

Fig. 1 Diagram of the experimental apparatus of SO₂ absorption: (1) N₂ gas cylinder; (2) SO₂ gas cylinder; (3) vacuum pump; (4) gas reserve chamber; (5) equilibrium chamber; (6) magnetic stirrers; (7)

constant temperature water bath; (8) residual gas absorption bottle (sodium hydroxide solution); (9), (10) pressure relief valve; (11)–(18) valve; (19), (20) pressure sensors

is the molar gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). The value of ρ_{12} could be calculated using the generalized second virial coefficient of gas mixture; the formula is as follows:

$$B_M = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (9)$$

$$y_1 = 1 - y_2 \quad (10)$$

$$B_{12} = \frac{RT_{c12}}{P_{c12}} (B^{(0)} + \omega_{12} B^{(1)}) \quad (11)$$

$$T_{c12} = (k_{12} - 1)^2 \times \sqrt{T_{c1} T_{c2}} \quad (12)$$

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2} \right)^3 \quad (13)$$

$$P_{c12} = \frac{Z_{c12} RT_{c12}}{V_{c12}} \quad (14)$$

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{V_{c12}} \quad (15)$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \quad (16)$$

$$Z_{12} = 1 + \frac{B_M P}{RT} \quad (17)$$

$$\rho_{12} = P_2 / Z_{12} RT \quad (18)$$

where Z_{12} represents the compressibility factor of the gas mixture of SO_2 and N_2 in the equilibrium chamber, and $k_{12}(0.08)$ is the binary interaction parameter. Relevant critical data are listed in Table S1. SO_2 was continually introduced into the equilibrium chamber to reach new equilibrium at different pressures. Unabsorbed SO_2 was then

introduced to the sodium hydroxide solution. The average uncertainty in absorption measurements was estimated to be within $\pm 2\%$.

pKa Value and Reaction Enthalpy Determination of PVIM

First, approximately 1 g PVIM was dissolved in water to form a dilute solution. Then, the solution was titrated by HCl aqueous solution (0.1 mol/L), and pH values were measured using a PHS-3C-01 pH meter. The uncertainty of the pH value measurements was ± 0.01 . The titration experiments were conducted under the temperature range from 25 to 70 °C.

In theory, every imidazole ring of the PVIM can bond with one H^+ , thus resulting in pH buffering effects. With the addition of HCl, H^+ can spontaneously bond to the position that has the strongest protonation ability, leading to a change in the pKa value of PVIM. To calculate the pKa value evolution and the molar reaction enthalpy ($\Delta_r H_m^0$), a mathematic model that describes the titration process was built using gPROMS software. The detailed mathematic model is listed in the Supporting Information.

Desorption of SO_2 and Recycling of the Absorbents

The diagram of the experimental apparatus for desorption and recycling of SO_2 is shown in Fig. 2. The whole apparatus consists of SO_2 and N_2 gas cylinders, a glass gas absorption tube (inner diameter of 40 mm) with a reflux condenser, a constant temperature oil bath with an uncertainty of $\pm 0.1 \text{ K}$, a pH sensor of ± 0.01 uncertainty (in relation to the full scale of 0–14), and a residual gas absorption bottle. The absorption tube is equipped with a magnetic stirrer, and the pH sensor is connected to a numeric instrument to record the pH evolution of the tube online.

The absorption process was operated at a temperature and a pressure of 298.2 K and 101.3 kPa, respectively. In a

Fig. 2 Diagram of the experimental apparatus for SO_2 desorption and recycling: (1) N_2 gas cylinder; (2) SO_2 gas cylinder; (3) numeric instrument; (4) pH sensor; (5) constant temperature water bath; (6) absorption tube (equipped with a reflux condenser); (7) residual gas absorption bottle (sodium hydroxide solution); (8), (9) pressure relief valve; (10)–(13) valve; (14), (15) rotor flow meter

typical procedure, a certain amount of absorbents (30–35 g) was charged into the gas absorption tube. After the air tightness of the experimental apparatus was checked, N_2 gas was released at a rate of 30 mL/min for 30 min to drive away the air in the experimental apparatus. Then, N_2 gas was cut off by closing the valve, and SO_2 gas was bubbled through the gas absorption tube at a rate of 40 mL/min. The weight changes of the tube combined with the absorbent during the absorption process were monitored using an electron analytical balance (Precision & Scientific FA2004, Shanghai, China) with an accuracy of ± 0.0001 g, and the molar ratio of absorbed SO_2 to VIM could be measured. The absorption equilibrium was considered to be reached when the pH value no longer changed, and then SO_2 gas was cut off.

The desorption of SO_2 from the absorbents was conducted by increasing the temperature of the oil bath to 373.2 K. The desorption equilibrium was considered to be reached when the pH value did not change. The experiments of the absorption (298.2 K and 101.3 kPa) and desorption (373.2 K and 101.3 kPa) cycles were repeated five times to test the reusability of the PVIM solution. Afterwards, the water in the absorbent was removed by rotary evaporation. Furthermore, to evaluate the absorption/desorption efficiency, another mathematic model that describes the absorption/desorption equilibrium is established and listed in the Supporting Information.

Results and Discussion

Physical Properties of the Absorbents

The molecular weights of PVIM synthesized in different conditions and the viscosities of the corresponding absorbents are listed in Table 1. The viscosity of the absorbents under the same concentration decreased with the decrease in the molecular weights of the PVIM. As is well accepted, low viscosity is favorable to the absorption efficiency of SO_2 . Thus, the absorbent with the lowest viscosity, which means the PVIM whose molecular weight is 3100, was used in the subsequent experiments.

The pH-responsive properties of many polymers were frequently reported to have physicochemical properties that can spontaneously change with the variation of pH value in a narrow range [42, 43]. Hence, the pH values and the corresponding viscosities of the absorbents during the absorption process at different temperatures ranging from 298.2 to 318.2 K were measured and listed in Table 2.

Notably, the viscosities not only decreased with the increase in temperature but also dramatically decreased when the absorbents changed from alkaline to acidic. For example, the viscosity at 298.2 K is 131.6 cP when pH is 9.1 and 2.42 cP when pH is 5.0, which is comparable

Table 2 Viscosities of the absorbents with various pH values

pH	Viscosity (cP)		
	298.2 K	303.2 K	318.2 K
9.1	131.6	126.5	119.3
7.2	16.43	15.62	14.73
5.0	2.42	2.03	1.85
2.2	1.44	1.24	1.16

Fig. 3 TGA and DTG curves of PVIM

to that of water (1.002 cP at 298.2 K) [44]. The reason for this phenomenon was investigated by dynamic light scattering. The size of micelles formed by PVIM could also respond to pH changes. As shown in Figure S2, the average size of the micelles in the solution varied from 248.1 to 4.2 nm when the pH values reduced from 9.1 to 2.2. This change is suspected to be caused by the protonation reaction of the PVIM. Before absorption, PVIM could associate with a little amount of H^+ ionized by H_2O , thus resulting in the original solution being alkaline. However, the strong hydrogen bonding interactions between the partial protonated polymers would cause a tight association. As a result, the PVIM aqueous solution before absorption exhibited a relatively high viscosity. When the concentration of the H^+ continued to increase during the absorption of SO_2 , more imidazole units of PVIM became protonated, which resulted in the weakening of association between polymers and enhanced the solvation interaction in water. Consequently, the absorbents possess notable pH-responsive properties. Moreover, lower viscosity can enhance the phase transfer between the gas–liquid two-phase and is favorable to the efficient absorption of SO_2 .

To verify the thermal stability of PVIM, the TGA and DTA curves of the PVIM are shown in Fig. 3. The PVIM first showed an obvious loss of weight at 375 °C, which means that the PVIM is stable enough under the operating conditions.

Absorption of SO₂

Absorption Mechanism

The proposed SO₂ absorption mechanism is illustrated in Scheme 1. Primarily, the gaseous SO₂ was dissolved in water, and the dissolved SO₂ could form H₂SO₃ through a hydration reaction. Then, H₂SO₃ was ionized to HSO₃[−], SO₃^{2−}, and H⁺, while the imidazole groups in each repeated unit could effectively bond the H⁺ through a protonated reaction, thus significantly promoting the solubility of SO₂ in the absorbent. To confirm the proposed absorption mechanism, the FTIR spectra of the absorbents before and after SO₂ absorption were studied, and the results are shown in Fig. 4. As can be seen from Fig. 4, three new peaks appeared at 961, 1151, and 1545 cm^{−1} after the absorption of SO₂. The absorption bond at 961 cm^{−1} corresponds to S–O stretching vibration in SO₃^{2−}, HSO₃[−], or similar species, thereby indicating the chemical interactions between SO₂ and the mixed absorbent [45]. The other peak at 1151 cm^{−1} can be assigned to the antisymmetric stretch of the dissolved SO₂, while the peak at 1545 cm^{−1} could be attributed to stretches of C–C and C–N in the ring after protonation [46]. Furthermore, a series of dispersed bonds in the region of 2800–2400 cm^{−1} after absorption could be assigned to NH⁺ [47]. In sum, the results of FTIR clearly prove the proposed absorption mechanism.

Absorption Capacity

To investigate the absorption capability of the absorbent, the equilibrium solubility of SO₂ in the absorbent was determined against SO₂ partial pressure at temperatures ranging from 298.2 to 328.2 K, and the results are shown in Fig. 5 (the solubility data are presented in Table S2). A detail that should be noted first is that each absorption equilibrium could be reached within 5 min, thereby indicating the low transfer resistance of the absorbent, which was attributed to the reduced viscosities in acidic conditions. The absorption isotherms shown in Fig. 5 demonstrated good absorption capability. The solubility of SO₂ in the absorbent increased drastically with the increasing SO₂ partial pressure under

Scheme 1 Absorption mechanism of SO₂ in the absorbents

Fig. 4 FTIR spectra of fresh absorbent and absorbent saturated with SO₂

low pressure (0–10.0 kPa), whereas it increased gradually and almost linearly under high pressure (10.0–100.0 kPa). For example, the SO₂ absorption capacity at 298.2 K is 0.431 mol SO₂ per kg absorbents at 0.3 kPa, 1.719 mol SO₂ per kg absorbents at 1.7 kPa, and 2.215 mol SO₂ per kg absorbents at 9.4 kPa. The large SO₂ solubility at low pressures can be primarily attributed to chemical absorption according to the proposed absorption mechanism. The strong bonding of H⁺ with PVIM could enhance the ionization of H₂SO₃ and significantly improve the content of HSO₃[−] and SO₃^{2−} in the system, while the linear increment of SO₂ solubility at high pressures was due to the complete protonation of PVIM.

In view of the relatively low SO₂ partial pressure in flue gas, a strong chemical interaction is essential, while the reaction equilibrium is always sensitive to temperature. As can be seen from Fig. 5, the increase in temperature has a negative influence on the solubility of SO₂ in the absorbent. For example, the solubility at 99.2 kPa is 3.409 and 2.468 mol SO₂ per kg absorbent at 298.2 and 328.2 K, respectively.

Fig. 5 Absorption isotherm of SO₂ by the absorbent at different temperatures

This phenomenon was consistent with the absorption mechanism we presented and the results obtained in most cases [48, 49]. Low temperature is not only beneficial to physical absorption but also shifts the protonation reaction equilibrium toward a positive direction. The results also indicated that the absorbed SO_2 could be released at high temperature.

In this absorbent, PVIM, as the major absorption component, could achieve the effective capture of SO_2 through the pH buffering effect, whereas water, a green solvent, was employed to realize the dissolution of PVIM and provide the reaction environment for the absorption. Given its easy preparation, low cost, and environment-friendliness, the absorbent can be regarded as a promising candidate for application. Moreover, considering that SO_2 capture is a continuous process of absorption–desorption, the suitable alkalinity of PVIM, which is the key point to enable the desorption at high temperature, was investigated in detail in the following sections.

Thermodynamic Analysis

To calculate the reaction equilibrium constant (K), acidity coefficient (pK_a), and the thermodynamic parameters of the protonation reaction of PVIM, acid titration experiments at different temperatures were conducted, and the experiment results are shown in Fig. 6. A corresponding reaction equilibrium mathematic model to describe the acid titration process was built using gPROMS software.

According to the absorption mechanism, PVIM could promote the capture of SO_2 through the reversible protonation reaction, while, as a macromolecule, the already protonated imidazole units would influence the bonding ability toward H^+ of other surrounding units via the inductive effect. Hence, we can reasonably consider that the pK_a value of the macromolecule would vary with the increment of the protonation degree.

Fig. 6 pH variation during $\text{HCl}_{(\text{aq})}$ titration process at 298, 313, and 328 K (solid line: experimental data; dash line: predicted results)

Given that the protonation reaction is an equilibrium process, the H^+ could spontaneously bond with the imidazole units that have the strongest bonding ability. Therefore, for a single PVIM molecule with a certain protonation degree, its corresponding pK_a value is constant (all the PVIM are assumed to have the same molecular weight). Thus, the average protonation degree of the PVIM is defined as:

$$\omega = c_{\text{VIMH}^+} / (c_{\text{VIM}} + c_{\text{VIMH}^+}) \quad (19)$$

At a certain ω , the calculated pK_a value can be approximately considered as the pK_a value of a single PVIM molecule with the same protonation degree.

Through parametric analysis of the experimental results, the pK_a values of the PVIM variation with the change in the protonation degree at different temperatures were calculated, and the results are illustrated in Fig. 7. The pK_a values of the PVIM decreased with the reduction of pH values of the aqueous solution and with the increase in the protonation degree of the PVIM. As can be seen in Fig. 7, the pK_a value decreased from 5.98 before the titration experiments to 4.46 when the protonation degree was 100% at 298 K. Thus, the pK_a value of the PVIM ranges from 4.46 to 5.98. The pK_a value is known to reflect the ability to dissociate H^+ . The decrease in the pK_a value along with the increase in the protonation degree indicates that the interaction between H^+ and PVIM becomes weaker. Subsequently, the molar reaction enthalpy, which is crucial for the design of industrial processes, was estimated using the van der Hoff equation. Furthermore, the molar Gibbs energy of reaction and molar reaction entropy can be calculated using Eqs. (20) and (21).

$$\Delta_r G_m^0 = -RT \ln K^0 \quad (20)$$

$$\Delta_r S_m^0 = (\Delta_r H_m^0 - \Delta_r G_m^0) / T \quad (21)$$

With the pK_a values integrated into these equations, the average values of $\Delta_r H_m^0$, $\Delta_r S_m^0$ and $\Delta_r G_m^0$ are presented in

Fig. 7 Relationship of pK_a value versus protonation degree at different temperatures

Table 3 Average molar reaction enthalpy, molar Gibbs energy of reaction, and molar reaction entropy at 298 K

	$\Delta_r H_m^0$ (kJ mol ⁻¹)	$\Delta_r G_m^0$ (kJ mol ⁻¹)	$\Delta_r S_m^0$ (J mol ⁻¹ K ⁻¹)
PVIMH ⁺	-40.30 ± 5	-34.13 ± 1.14	-20.69 ± 17.20

Fig. 8 Reusability of the absorbents in SO₂ absorption for five cycles

Table 3. Furthermore, in accordance with the calculated parameters and the mathematic model, the pH variation with the addition amount of HCl was obtained and illustrated in Fig. 6. The calculated results showed good agreement with the experimental data, which demonstrates the accuracy of calculated parameters.

Desorption of SO₂ and Reuse of the Absorbent

On the basis of previous analysis, the pH value of the system is a significant factor in evaluating the absorptive amount of SO₂. Hence, in this work, absorption/desorption capability and technological feasibility were studied by measuring the variation of the pH value and the weight change of the absorbent in the repeated absorptive/desorptive process. Experiments on the absorption and desorption cycles of SO₂ were conducted five times. The absorption or desorption equilibrium was considered to be achieved when the pH value of the absorbents no longer changed. After five cycles, almost no decline in the equilibrium absorption capacity of SO₂ occurred (see Fig. 8).

The solubility is 1.21 mol SO₂ per mole VIM for the first time and 1.17 mol SO₂ per mole VIM in the subsequent cycles. The desorption efficiency could reach 96.6% after the desorption. The slightly incomplete desorption may be due to the reflux water bringing back a small amount of SO₂. The pH changes in the absorption and desorption process are shown in the Supporting Information. The curves of the pH change with time are almost the same (see Figs. S3 and S4),

Fig. 9 Calculated and measured values of the molar ratio of SO₂ to VIM **Fig. 10** Variations of pH and solubility of SO₂ with time in the absorption process

which also proves that the absorption of SO₂ in the mixed absorbent is highly reversible and the absorbed SO₂ can be easily stripped out by heating.

According to the absorption mechanism, the absorptive amount of the SO₂ in the absorbents is closely related to the pH value and temperature, and can be calculated using the absorption equilibrium model and the obtained thermodynamic parameters. First, to validate the model, the absorptive amount of SO₂ that varied with the pH changes at 298 K was calculated and compared with the experimental data. As shown in Fig. 9, all the measured values are in good agreement with the calculated ones, which proves that the absorption equilibrium model is reliable. Taking the pH variation data into the model, the corresponding absorptive amount could be estimated.

The absorption of SO₂ in the absorbents at 298 K over time was estimated. As shown in Fig. 10, the absorption capacity had an approximately linear increase with time in the initial 30 min with the corresponding pH value interval of 9.02–1.51, which means that the absorbent could achieve

efficient capture of SO_2 in this pH region. However, the absorption efficiency decreased dramatically after 30 min, which suggested that the reactive absorption had been completed when the pH value was lower than 1.51. Similarly, the optimum pH value interval in the desorption process could be obtained.

The desorption of SO_2 from the absorbents over time was conducted at 383 K under the condition of heating reflux. High temperature has an inhibiting effect on the protonation reaction of PVIM, while the decrease in the partial pressure of SO_2 in the gas phase caused by steam stripping is the immediate cause of efficient desorption. With the proceeding of the desorption process, the desorption driving force decreased, and the pKa value of the PVIM increased gradually. Hence, the desorption rate gradually reduced as time proceeded. As shown in Fig. 11, in the initial 40 min of the desorption process and when the pH value of the system was lower than 4.80, the desorption efficiency could maintain a relatively high level and the residual amount was less than 10%. Therefore, the pH interval of 1.42–4.80 was considered a proper desorption operation range.

According to the absorption and desorption curves shown in Figs. 10 and 11, in a continuous operation process, both the absorption and desorption rates could maintain high when the pH value ranged from 1.51 to 4.80. In this region, the ratio of the available absorptive amount can reach up to 80%, the corresponding gas amount was 2.99 kg per mol absorbent, and, more importantly, the viscosity of the absorbent was comparable to that of water. All these results proved the applicability of the absorbent in the SO_2 capture process.

After five absorption–desorption cycles, the water in the absorbent was removed by rotary evaporation. The residual PVIM was dried under vacuum and analyzed by FTIR. As shown in Fig. 12, no noticeable change can be detected after the cycles, as indicated by a comparison with the fresh

Fig. 11 Variations of pH and solubility of SO_2 with time in the desorption process

Fig. 12 FTIR spectra of PVIM before use and after regenerating

PVIM, which further proves the excellent stability and reusability of the absorbent.

Conclusion

In this work, a novel macromolecule absorbent that was prepared by blending PVIM and water is first proposed for SO_2 absorption. This pH buffering absorbent combines the advantages of the non-volatility of ILs and the applicability of traditional organic amines. Furthermore, the unique pH-responsive characteristic of the absorbent provides it with a suitable physicochemical property in the absorption process. The results of the absorption and desorption experiments showed that the absorbent can capture SO_2 efficiently at low partial pressure and release SO_2 easily by heating reflux. As verified by FTIR, the reversible absorption of SO_2 was attributed to the reversible protonation reaction of PVIM due to its moderate alkalinity. Moreover, no obvious reduction in absorption capacity and chemical structure change were detected after several cycles, which demonstrated the reusability and recyclability of the absorbent. According to the thermodynamic analysis, the pKa value of the PVIM decreased with the increase in the protonation degree because of the inductive effect of the protonated units, but the pKa value still remained within an applicable range. With the use of the thermodynamic parameters, a technical feasibility study was conducted, and the absorbent was proven to be an excellent candidate for SO_2 capture in industrial application. In summary, this research provides an absorbent that has advantages of simple preparation, good physicochemical properties, environment-friendliness, high ability in deep removal of SO_2 , and excellent reusability. The unique properties of this absorbent are also revealed.

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