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Highly Efficient and Reversible Absorption of SO_2 from Flue Gas Using Diamino Polycarboxylate Protic Ionic Liquid Aqueous Solutions

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Supporting Information

ABSTRACT: Ionic liquid (IL) aqueous solutions (aq) have emerged as promising candidates for SO_2 absorption. In this work, a new series of diamino polycarboxylate protic ionic liquids (DPPILs) aq with low viscosities and high stabilities were developed and used for SO_2 capture. All of the prepared absorbents could efficiently absorb low-concentration SO_2 in simulated flue gas. Among them, DPPILs aq based on citric acid (CA) presented the most excellent SO_2 desorption performance; nearly all absorbed SO_2 could be easily desorbed under mild conditions. Particularly, *N*,*N*-dimethylethylenediamine citrate [DMEDA][CA] showed the highest available absorption capacity toward 0.2 vol % SO_2 (up to 0.51 mol_{SO_2}/mol_{ILs} and 0.058 g_{SO_2}/g_{abs} in 50 wt % aq at 20 °C), which also presented satisfactory SO_2/CO_2 selectivity, reusability, and SO_2 removal efficiency. Fourier transform infrared and nuclear magnetic resonance spectroscopic analyses revealed that the protonation of $[DMEDA]^+$ and $[CA]^-$ promoted SO_2 absorption. Overall, the studied DPPILs aq with excellent physical properties, SO_2 absorption−desorption performance, and stability may have a great perspective in industrial SO_2 removal.

1. INTRODUCTION

Excessive sulfur dioxide (SO_2) in the atmosphere will create adverse effects on the environment and human health.[1] Currently, the flue gas desulfurization (FGD) process is deemed to be the most effective measure to control the atmospheric SO_2 concentration. Among commercially available processes, the limestone−gypsum method is the most widely used technique.[2] However, the shortcomings of this process are obvious, such as the non-renewability of absorbents and the production of waste effluents and solid byproduct ($CaSO_4$). Another widely used process is the ammonia scrubbing technique.[3] Nevertheless, the volatilization of the absorption agent is inevitable, which could cause secondary pollution to the environment, and the regeneration of absorbents is a high-energy-consumption process. Consequently, it is still highly desired to develop novel renewable, stable, and energy-saving absorbents for the FGD process.

Over the past few decades, ionic liquids (ILs) have been proposed as attractive candidates for acid gas capture as a result of their unique properties, such as high thermal stability, negligible vapor pressure, and tunable structure.[4−9] Han et al. first reported that tetramethylguanidinium lactate [TMG][L] could capture SO_2 with absorption capacity up to 0.978 mol_{SO_2}/mol_{ILs} at 40 °C and 8% SO_2 in 2004.[10] Subsequently, numerous ILs have been explored for SO_2 absorption, including guanidinium-derived,[11,12] imidazolium-derived,[13−15] hydroxyl-ammonium-derived,[16,17] and ether-functionalized ILs.[18,19] Although these ILs exhibited high SO_2 loading capacities (especially functional ILs), the ultrahigh viscosities and costs hampered their large-scale application.

To overcome the drawbacks of ILs mentioned above, a feasible and promising strategy is to develop IL aqueous solutions (aq) by mixing low-cost ILs with water. Huang et al. reported that the aq of hydroxylammonium dicarboxylate ILs could absorb SO_2 efficiently and the mixed absorbents showed low viscosities and satisfactory mass transfer performance.[20] Wu et al. developed a series of aqueous triethylenetetramine tetralactate [TETA][L] solutions for SO_2 absorption.[21] It was found that the absorption−desorption properties of SO_2 in ILs aq could be easily tuned by varying the compositions of ILs. In our previous work, a novel triamine-based IL aq was used for SO_2 capture, and the results showed that the excellent SO_2 absorption capacity, especially at very low partial pressures, was contributed to the chemical absorption originating from the pH-buffering effect.[22] Obviously, all of these benign absorbents were composed of protic ionic liquid (PILs), which could be easily synthesized by low-cost materials through direct acid−base neutralization in contrast to aprotic ionic liquids (APILs).[23,24] The capture of SO_2 using PILs aq is based on a buffer mechanism.[25,26] First, SO_2 dissolves in aq and undergoes hydration to form H_2SO_3. Subsequently, H_2SO_3 ionizes into H^+, HSO_3^-, and SO_3^{2-}. These processes could be promoted taking advantages of the protonation of free carboxylate anions ($-COO^-$) or amines in aq. Therefore, PILs aq used for efficient SO_2 absorption (especially for the flue gas with a low SO_2 concentration) should meet at least one of the following requirements: (1) the acids selected for synthesizing ILs should be weaker than H_2SO_3, implying that

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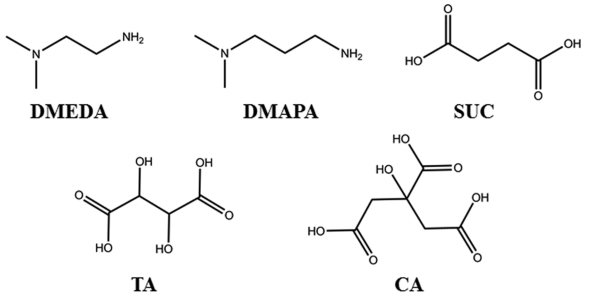
the pK_a values of the acids should be higher than 1.8, and (2) the basicities of amines should be strong enough.[27−29] Of note, if the acidities of the selected acids are too weak or the basicities of amines are too strong, it tends to cause irreversible absorption and enormous energy demand for absorbent regeneration. In addition, because SO_2 desorption is usually carried out at a high temperature, the thermostabilities and volatilities of PILs and the derived acids should also be well-considered.

Lately, diamino protic ionic liquids (DPILs) have attracted intensive attention owning to their exceptional characteristics, such as the higher stability and moderate alkalinity compared to traditional PILs.[30,31] Generally, DPILs were obtained by neutralizing organic bases containing both primary and tertiary amines with carboxylic acids.[32,33] DPILs with facilely tunable alkalinity through subtle combination bases and acids have been widely studied for CO_2 capture. These DPILs were found to readily achieve high CO_2 loading capacities and low absorption enthalpies, which indicated that DPILs are a promising candidate for acid gas capture with high capacity and energy savings.[34,35] Herein, we develop a series of diamino polycarboxylate protic ionic liquids (DPPILs) aq for SO_2 capture. To the best of our knowledge, DPPILs have not been synthesized and used for SO_2 absorption thus far. The corresponding DPPILs could be easily synthesized by neutralizing *N*,*N*-dimethylethylenediamine (DMEDA) and (3-dimethylamino)-1-propylamine (DMAPA) with succinic acid (SUC), tartaric acid (TA), and citric acid (CA) (see Scheme 1 for structures of amines and acids). DMEDA and DMAPA are the most common organic bases for DPIL synthesis, with the advantages of small molecular weight and moderate basicities. SUC, TA, and CA are all inexpensive and non-volatile poly(carboxylic acid)s. According to previous reports, polycarboxylate-based ILs tended to exhibit more excellent SO_2 absorption−desorption properties than monocarboxylate-based ILs.[20,36,37] In this work, the physical properties of the prepared absorbents were studied comprehensively. The influences of DPPIL structures, DPPIL concentrations, absorption temperature, and SO_2 concentration on the absorption performance were systematically investigated. The desulfurization performance of the studied absorbent on simulated flue gas was also evaluated. Moreover, the absorption mechanism was clarified by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H NMR).

Scheme 1. Structures of Amines and Acids Used To Synthesize DPPILs



2. EXPERIMENTAL SECTION

2.1. Materials. DMEDA (≥99%) and DMAPA (≥99%) were purchased from Aladdin Industrial Corporation. SUC (≥99.5%), TA (≥99.5%), and CA (≥99.5%) were provided by Tianjin Chemart Chemical Technology Co., Ltd. SO_2 (99.9%) and N_2 (99.99%) were supplied by Tianjin Dongxiang Specialty Gases Co., Ltd. All chemicals were used without further purification.

2.2. Preparation of SO_2 Absorbents. All DPPILs used in this work were synthesized by neutralizing equimolar diamines with poly(carboxylic acid)s referring to reports (the actual quantities of the starting materials are shown in Table S1 of the Supporting Information).[7,17] For instance, the preparation process of [DMEDA]-[CA] is as follows: 0.1 mol of DMEDA was dissolved in 50 mL of deionized water and loaded into a 250 mL flask, which was equipped with a reflux condenser and placed in an ice−water bath. Subsequently, 0.1 mol of CA dissolved in 50 mL of deionized water was added dropwise into the flask within 1 h under vigorous stirring. The reaction was stirred for 24 h at room temperature. Water was removed by rotary evaporation, and the water contents of the obtained DPPILs were determined below 1 wt % (Table S2 of the Supporting Information). Of note, the equivalence point pH values (Table S3 of the Supporting Information) of each neutralization reaction were determined by the titration method (0.1 mol/L aq), which were very close to those of 0.1 mol/L DPPILs aq (Table S3 of the Supporting Information), thus proving that the obtained stoichiometric ratios were the expected 1:1. Additionally, the corresponding DPPILs aq were obtained by mixing DPPILs with water at the certain mass ratios, as shown in Table 1.

2.3. Characterization. The ^{1}H NMR spectra of DPPILs were recorded on a 500 MHz spectrometer (Bruke Avance III, Germany), and the characterization results are shown in the Supporting Information, which presented that both primary and tertiary amines of DMEDA and DMAPA were protonated in neat DPPILs. It could be found that there were no obvious signals of neutral acids and bases in ^{1}H NMR spectra. Therefore, although there may be neutral bases and acids in DPPILs, their contents could be neglected and the protons from acids could be considered to be completely transferred

Table 1. Physical Properties (25 °C) of the Prepared SO_2 Absorbents

		density (g/mL)		viscosity (cP)	
absorbent	water content (wt %)	before absorption	after absorption	before absorption	after absorption
[DMEDA][SUC], 50 wt %	49.33	1.1623	1.1609	1.69	2.74
[DMEDA][TA], 50 wt %	50.41	1.1756	1.1734	1.97	3.03
[DMEDA][CA], 60 wt %	41.03	1.2163	1.2144	4.83	6.86
[DMEDA][CA], 50 wt %	50.63	1.1963	1.1955	2.33	4.41
[DMEDA][CA], 40 wt %	59.11	1.1722	1.1707	1.73	3.79
[DMEDA][CA], 30 wt %	69.29	1.1578	1.1566	1.44	2.47
[DMEDA][CA], 20 wt %	80.32	1.1530	1.1522	1.13	1.90
[DMAPA][SUC], 50 wt %	50.33	1.1732	1.1718	1.94	3.14
[DMAPA][TA], 50 wt %	49.86	1.1865	1.1844	2.17	3.31
[DMAPA][CA], 50 wt %	50.31	1.2102	1.2094	2.92	4.31

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to amines. Additionally, electrospray ionization mass spectrometry (ESI−MS, Agilent 1100 LC/DAD/MSD) was used to characterize the anions and cations in 50 wt % DPPILs aq. The results (Supporting Information) showed that the tertiary amines of DMEDA and DMAPA were not protonated completely in 50 wt % DPPILs aq, and the stable anions and cations were $[SUC]^-$, $[TA]^-$, $[CA]^-$, $[DMEDAH]^+$, and $[DMAPA]^+$. The densities of unreacted and 0.2 vol % SO_2 saturated (25 °C) absorbents were measured using a precalibrated (deionized water) 5 mL pycnometer. Each sample was determined 5 times to report the average, and the uncertainty was estimated to be less than ±1%. The viscosities of DPPILs aq before and after SO_2 absorption (0.2 vol % SO_2 and 25 °C) were measured by a viscometer (Brookfield DV-II+ Pro). Standard silicone oil was used to calibrate the viscometer. Each measure was repeated 5 times to obtain an average, and the uncertainty was estimated to be ±2.5%. The thermostability of DPPILs was evaluated by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) (NETZSCH). Furthermore, the absorption mechanism was clarified through FTIR (Bruker, TENSOR II, Germany) and ^{1}H NMR (500 MHz, Bruke Avance III, Germany) spectroscopies.

2.4. Absorption and Desorption of SO_2. The absorption and desorption experiments were carried out using the previously reported method.[28,29,38] The experimental system is shown in Figure 1. To

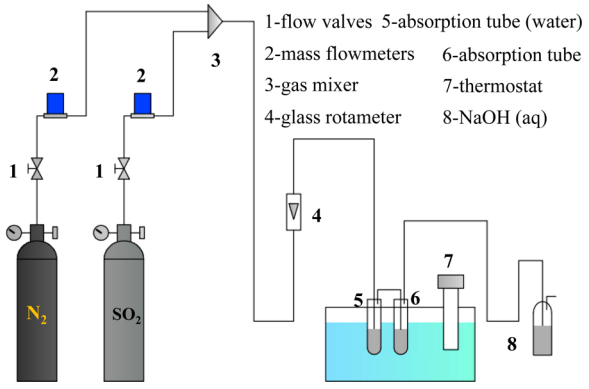

Figure 1. Schematic diagram of the absorption−desorption experimental system.

validate the feasibility of the absorption−desorption experimental system, the water loss ratios in the absorption tube (water), the outlet SO_2 concentrations of the absorption tube (water), and the water content variations of the absorbents during SO_2 absorption−desorption were determined and the results are summarized in Tables S4−S6 of the Supporting Information. In a typical absorption process, simulated flue gas (0.2 vol % SO_2 and 99.8 vol % N_2) at 100 mL/min was successively bubbled through two glass tubes loading about 2 g of deionized water (to offset the water evaporated) and DPPILs aq, respectively. The glass tubes were partly immersed in a thermostatic water bath with the desired temperature. The gas flow rates were controlled by mass flowmeters. The amount of absorbed SO_2 was measured using the iodine titration method (HJ/T 56-2000, a standard method of the State Environmental Protection Administration of China). For absorption under different SO_2 concentrations, the certain inlet SO_2 concentration was controlled by tuning the flow rate ratio of SO_2 and N_2. The desorption procedure was similar to that described above, only the simulated flue gas (100 mL/min) was replaced by pure N_2 (50 mL/min) and the desorption efficiency (*DE*) was calculated by the following equation:

$$DE = (R_a - R_d)/R_a \times 100\% \quad (1)$$

where R_a is the saturated molar SO_2 absorption capacity and R_d is the desorption residue. All measurements were repeated 3 times to obtain the averages, and it was estimated that the uncertainty of the results was less than ±5%. To evaluate the desulfurization performance of the studied SO_2 absorbent, the inlet and outlet SO_2 concentrations were determined by a gas analyzer (Testo 350) and the SO_2 removal efficiency (*RE*) was calculated by the following formula:

$$RE = (C_{in} - C_{out})/C_{in} \times 100\% \quad (2)$$

where C_{in} and C_{out} were the SO_2 concentrations in the inlet and outlet, respectively.

3. RESULTS AND DISCUSSION

3.1. Physical Properties of SO_2 Absorbents. The densities and viscosities of unreacted and 0.2 vol % SO_2 saturated DPPILs aq were determined at 25 °C. As shown in Table 1, the densities of the prepared absorbents increased with the increase of the molecular weight of DPPILs and the concentration of DPPILs in the mixed absorbents. The viscosity showed the same trend as the density. Additionally, it could be found that there were no significant differences in the densities and viscosities of these absorbents before and after SO_2 absorption. Of note, all absorbents prepared in this work presented extremely low viscosities (like water), whereas the viscosities of neat ILs were usually higher than 300 cP,[20] indicating that the viscosities of IL absorbents could be significantly reduced by mixing with water, and it could be inferred that the prepared absorbents with low viscosities could be potentially applied for the FGD process.

3.2. Absorption−Desorption of SO_2. *3.2.1. Absorption Mechanism.* In this work, FTIR and ^{1}H NMR were used to clarify the absorption mechanism of SO_2 in 50 wt % [DMEDA][CA] aq. The FTIR spectra before and after SO_2 absorption are shown in Figure 2. In comparison to the FTIR

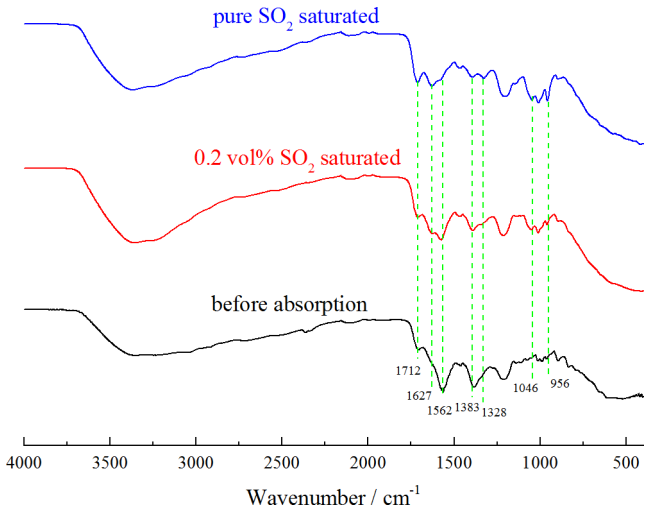

Figure 2. FTIR spectra of 50 wt % [DMEDAH][CA] aq before and after absorption of SO_2.

spectrum of the virgin absorbent, three characteristic peaks of absorbed SO_2 appeared after absorption. The new peak centered at 956 cm^{-1} could be attributed to the stretching vibration of S−O bonds in SO_3^{2-} or HSO_3^-, which indicated that the studied absorbent could capture SO_2 via chemical interaction.[22,39] The new peak at 1046 cm^{-1} could be assigned to the S═O stretching vibration of SO_2, H_2SO_3, HSO_3^-, or SO_3^{2-}.[40,41] The characteristic peak presented at 1328 cm^{-1} was ascribed to the asymmetry stretching vibration of dissolved SO_2.[42,43] Additionally, it was clear that captured SO_2 presented a significant effect on −COOH and $-COO^-$ in aq. More concretely, the symmetric (1562 cm^{-1}) and asymmetric (1383

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cm^{-1}) vibrations of $-COO^-$ were weakened gradually during SO_2 absorption, whereas the vibrations (1712 and 1627 cm^{-1}) associated with −COOH were enhanced notably, implying that −COOH was formed during the absorption process.[28,29,44] Meanwhile, in comparison to the ^1H NMR spectrum (Figure S1 of the Supporting Information) of the virgin absorbent, the spectrum of the 0.2 vol % SO_2 saturated absorbent presented a new peak at 9.97 ppm, which could be assigned to the H atom bonded to the N atom of $[DMEDA]^+$,[45,46] demonstrating that $[DMEDA]^+$ also played an important role in SO_2 capture. Therefore, on the basis of the above analysis and previous reports, a plausible SO_2 absorption mechanism was illustrated in Scheme 2.

Scheme 2. SO_2 Absorption Mechanism in 50 wt % [DMEDA][CA] aq

$$SO_{2(g)} \rightleftharpoons SO_{2(aq)}$$
$$SO_{2(aq)} + H_2O \rightleftharpoons H_2SO_3$$
$$H_2SO_3 \rightleftharpoons HSO_3^- + H^+$$
$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$$
$$[CA]^- + H^+ \rightleftharpoons CA$$
$$[DMEDA]^+ + H^+ \rightleftharpoons [DMEDA]^{2+}$$

3.2.2. Effect of Different DPPILs on SO_2 Absorption−Desorption. It was found that neat [DMEDA][TA] and [DMAPA][TA] were in a solid state within the range of 20−60 °C. Besides, for [DMEDA][SUC], [DMEDA][CA], [DMAPA][SUC], and [DMAPA][CA], although they could flow at 40 °C (gel at 20 °C), their viscosities increased rapidly and turned into gel in the process of absorption at 40 °C. Thus, only the absorption−desorption properties of DPPILs aq were discussed in the following sections. To investigate the influence of different DPPILs on SO_2 absorption−desorption properties, the absorption−desorption experiments were carried out at 20 °C, 1 atm, and simulated flue gas (0.2 vol % SO_2 and 99.8 vol % N_2) at 100 mL/min and 80 °C, 1 atm, and pure N_2 at 50 mL/min, respectively. For all 50 wt % DPPILs aq prepared in this work, the SO_2 absorption and desorption equilibriums could be achieved within 120 and 60 min as shown in Figures S2 and S3 of the Supporting Information, respectively, indicating that the prepared absorbents presented excellent mass transfer performance. The SO_2 absorption capacities (Table S7 of the Supporting Information) and desorption residues are shown in Figure 3. Obviously, all 50 wt % DPPILs aq could efficiently capture low-concentration SO_2. The SO_2 loading capacities were up to 0.67, 0.61, 0.53, 0.73, 0.67, and 0.54 mol_{SO_2}/mol_{ILs} for [DMEDA][SUC], [DMEDA][TA], [DMEDA][CA], [DMAPA][SUC], [DMAPA][TA], and [DMAPA][CA], respectively. It could be found that the SO_2 absorption capacities of DPPILs were closely related to the pK_a values (Table S8 of the Supporting Information) of diamines and poly(carboxylic acid)s selected for synthesizing ILs. The higher the pK_a values of the amines and acids, the higher the absorption capacities could be achieved. The SO_2 desorption residue showed the same trend as the absorption capacity. Of note, the SO_2 desorption efficiencies in 50 wt % [DMEDA]-[CA] and [DMAPA][CA] aq were up to 97 and 93% within 1 h, respectively, far higher than those of other DPPIL absorbents. The pH values of 50 wt % [DMEDA][CA] and [DMAPA][CA] aq were 4.68 and 5.17 at 25 °C, respectively,

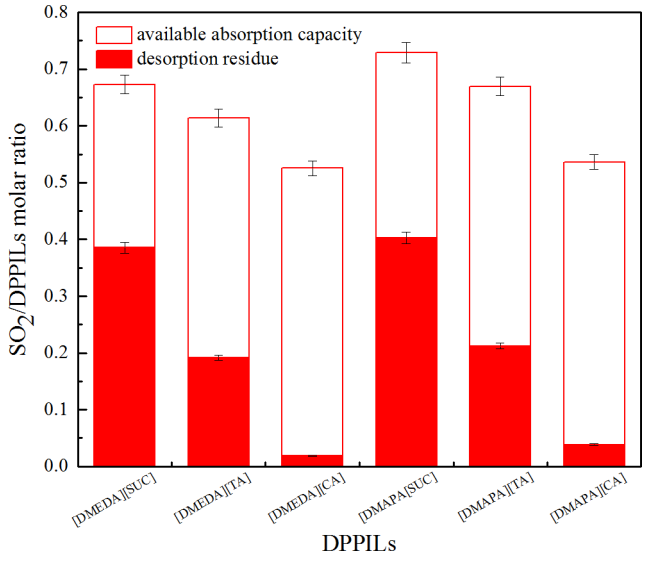

Figure 3. SO_2 absorption capacities and desorption residues of different DPPILs (aq, 50 wt %).

within the appropriate pH range (4.5−5.5) for the highly efficient and reversible SO_2 capture proposed by Huang et al.[20] The available absorption capacities of 50 wt % [DMEDA]-[SUC], [DMEDA][TA], [DMEDA][CA], [DMAPA][SUC], [DMAPA][TA], and [DMAPA][CA] aq were also calculated, with the values of 0.29, 0.42, 0.51, 0.33, 0.46, and 0.49 mol_{SO_2}/mol_{ILs}, corresponding to 0.045, 0.057, 0.058, 0.047, 0.058, and 0.053 g_{SO_2}/g_{abs}, respectively. Thus, considering the higher available capacity, [DMEDA][CA] was selected for subsequent studies.

3.2.3. Effect of the DPPIL Concentration on SO_2 Absorption−Desorption. The influence of the DPPIL concentration on SO_2 absorption−desorption was also investigated. As shown in Figure 4, the molar SO_2 absorption capacity of [DMEDA][CA] increased with the decrease of the DPPIL concentration and the increase of the water content of

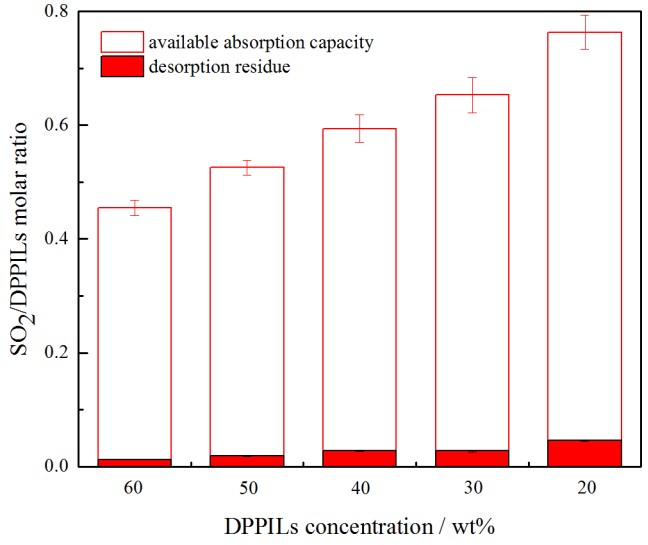

Figure 4. Molar SO_2 absorption capacities and desorption residues of [DMEDA][CA] aq with different concentrations at 20 °C and 0.2 vol % SO_2.

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the absorbent. For instance, the SO_2 loading capacity of [DMEDA][CA] increased from 0.46 to 0.76 mol_{SO_2}/mol_{ILs} as the DPPIL concentration decreased from 60 to 20 wt %. The solubility of 0.2 vol % SO_2 in deionized water was also measured at 20 °C, with the value of 0.0007 mol_{SO_2}/mol_{H_2O} (0.0025 g_{SO_2}/g_{H_2O}), which was negligible compared to those of the studied absorbents, indicating that DPPILs played the major role in SO_2 capture rather than water. Additionally, it could be found that the desorption residue also increased slightly with the decrease of the DPPIL concentration. Perhaps this was because, although the overall dissolution behavior of SO_2 in DPPILs aq cannot be described by Henry's law, the transfer of SO_2 molecules from flue gas to absorbent (converting to $SO_{2(aq)}$) could still be expressed by that. Thus, the $SO_{2(aq)}$ concentration in the absorbent could be considered as a constant value, whereas the concentrations of HSO_3^- and SO_3^{2-} decreased with the increase of the water content, resulting in the enhanced hydration of SO_2 and ionization of H_2SO_3 according to Le Chatelier's principle.[21] Furthermore, as shown in Figure 5, the gravimetric available

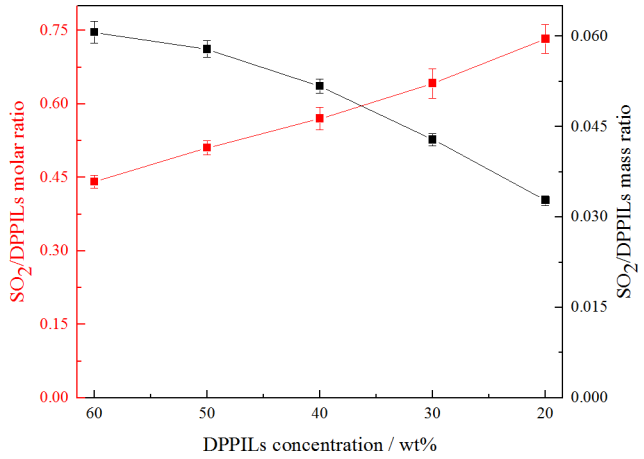

Figure 5. Available SO_2 capacities in [DMEDA][CA] aq with different DPPIL concentrations at 20 °C and 0.2 vol % SO_2.

capacities of [DMEDA][CA] aq decreased from 0.061 to 0.033 g_{SO_2}/g_{abs} as the DPPIL content decreased from 60 to 20 wt %, showing a contrary trend to the molar available SO_2 capacities. Of note, although a high concentration of DPPILs was beneficial to mass absorption capacity of SO_2, it could lead to an increase in cost and viscosity of the absorbent (more than 300 cP for 10 wt % [DMEDA][CA] aq); thus, 50 wt % [DMEDA][CA] aq was still used in subsequent investigations.

3.2.4. Effect of the Temperature on SO_2 Absorption. The temperature dependence of the SO_2 absorption by 50 wt % [DMEDA][CA] aq at 1 atm with 0.2 vol % SO_2 was investigated. It can be seen from Figure 6 that the SO_2 loading capacity significantly decreased with the increase of the temperature, which was consistent with previous reports.[47−49] For instance, the saturated SO_2 absorption capacity in 50 wt % [DMEDA][CA] aq was up to 0.53 mol_{SO_2}/mol_{ILs} at 20 °C, while it decreased to 0.18 mol_{SO_2}/mol_{ILs} at 60 °C. The results verified that absorbed SO_2 could be released and the absorbent can be easily regenerated by heat treatment.

3.2.5. Effect of the SO_2 Concentration on Absorption. The effect of the SO_2 concentration in simulated flue gas on the

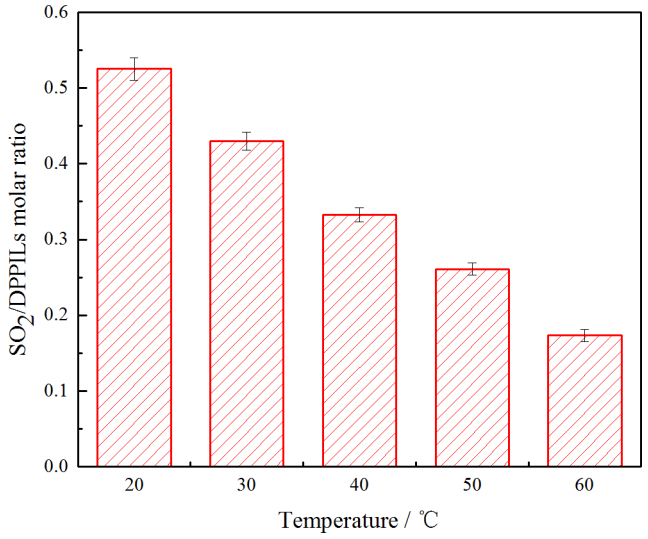

Figure 6. Effect of the temperature on SO_2 absorption in 50 wt % [DMEDA][CA] aq at 1 atm with 0.2 vol % SO_2.

absorption capacity was investigated at 40 °C. As depicted in Figure 7, the SO_2 absorption capacity elevated gradually with

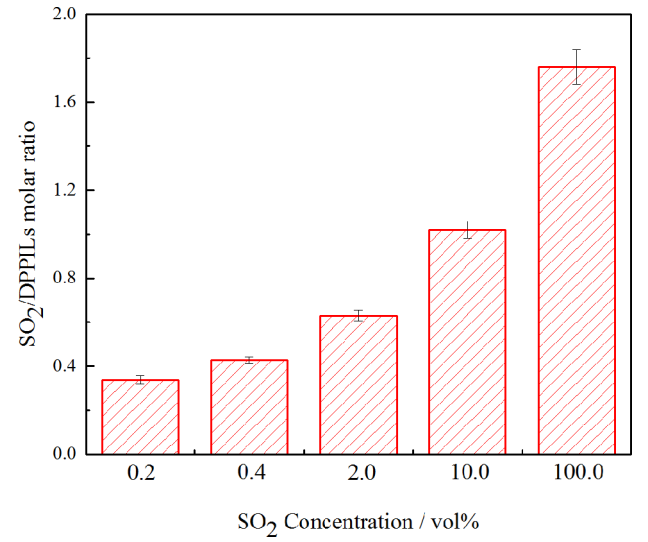

Figure 7. Effect of the SO_2 concentration on absorption in 50 wt % [DMEDA][CA] aq at 40 °C.

the increase of the SO_2 concentration in simulated flue gas. More specifically, the SO_2 absorption capacity of 50 wt % [DMEDA][CA] (aq) increased from 0.34 to 1.76 mol_{SO_2}/mol_{ILs} as the SO_2 concentration increased from 0.2 to 100 vol % at 40 °C. The results implied that the SO_2-saturated absorbent could be easily regenerated by reducing the SO_2 concentration. Additionally, it was clear that the SO_2 loading capacity increased more remarkably in the low SO_2 concentration range than in the high SO_2 concentration range, indicating that the studied absorbent may interact with SO_2 via chemical interaction according to previous reports.[20,22]

The absorption capacity of pure CO_2 in 50 wt % [DMEDA][CA] aq was also determined, with the value of 0.10 mol_{CO_2}/mol_{ILs} (0.008 g_{CO_2}/g_{abs}) at 40 °C and 1 atm. It was calculated that the gravimetric absorption capacity of pure SO_2 in 50 wt % [DMEDA][CA] aq was 25 times higher than

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Table 2. Comparison to Other IL Aqueous Solutions

absorbent	absorption (T_a, °C; SO_2, vol %)	SO_2 capacity mol/mol[a]	SO_2 capacity g/g[b]	desorption (T_d, °C; N_2, mL/min; t, min)	DE (%)	reference
[DMEDA][CA], 50 wt %	(40, 0.2)	0.34	0.039	(80, 50, 60)	97	this work
	(40, 0.4)	0.43	0.050			
[DMEAH][glutarate], 60 wt %	(40, 0.4)	0.36	0.058	(100, 70, 60)	84	20
$[TETA]L_4$, 70 wt %	(60, 3)	1.22	0.145	(100, 50, 300)	96	21
$[PEDETAH][SO_4]_{0.5}$, 30 wt %	(40, 0.4)	0.68	0.044	(110, −, 60)	95[c]	22
[BTMEDA]Cl, 23 wt %	(30, 100)	1.53	0.102	(60, 20, 60)	34	27

[a] mol_{SO_2}/mol_{ILs}. [b] g_{SO_2}/g_{abs}. [c] DE with pure SO_2-saturated absorption capacity as a reference.

that of CO_2, indicating that the studied absorbent exhibited considerable SO_2/CO_2 selectivity. Of note, the absorption capacity of 0.2 vol % SO_2 was still 4.8 times higher than that of pure CO_2, and the concentration of CO_2 in flue gas was usually within the range of 10−15% in practice, implying that the studied absorbent could be employed as the selective absorbent for SO_2 absorption.

For comparison, the SO_2 absorption−desorption properties of the studied absorbent and the previously reported ILs aq are shown in Table 2. The results presented that the studied absorbent exhibited competitive SO_2 solubility at low SO_2 partial pressure. Meanwhile, nearly all SO_2 captured by the studied absorbent could be easily desorbed under mild conditions, showing more excellent desorption efficiency than others, which implied that the studied absorbent could be used as the low-energy-consumption absorbent for the FGD process. Therefore, comprehensively considering the excellent absorption−desorption properties, simple synthesis process, and relatively low cost, it could be expected that the studied absorbent held the potential for industrial application.

3.2.6. Stability and Reusability of the SO_2 Absorbent. The stability and reusability of the absorbent are important for evaluating its industrial application prospects. In this work, the thermostability of neat [DMEDA][CA] was explored. As shown in Figure 8, the decomposition temperature (5% weight loss) of [DMEDA][CA] was up to 175 °C, far above the desorption temperature commonly used in practice (100−120 °C for amine methods), indicating that the studied absorbent was stable enough during the absorption−desorption process. To investigate the long-time stability of 50 wt % [DMEDA][CA] aq, the studied absorbent was first saturated with 0.2 vol % SO_2 and kept for 12 h at 40 °C and then absorbed SO_2 was desorbed by bubbling N_2 and kept for another 12 h at 80 °C. The procedure was repeated for 10 consecutive days, and the stability was evaluated by ^{1}H NMR (Figure 9). Clearly, in comparison to the spectrum of the virgin absorbent, there was no obvious difference in the spectra of the absorbent used for a long time, indicating that the studied absorbent could be stable for a long time. Additionally, the reusability of 50 wt % [DMEDA][CA] aq was also investigated, and the absorption−desorption experiments were conducted at 40 °C, 1 atm, and pure SO_2 at 50 mL/min and 80 °C, 1 atm, and pure N_2 at 50 mL/min. As depicted in Figure 10, the excellent absorption−desorption properties of 50 wt % [DMEDA][CA] aq did not change markedly during 5 consecutive absorption−desorption cycles. The SO_2 absorption capacities and desorption residues were (1.76, 0.021), (1.80, 0.019), (1.78, 0.024), (1.73, 0.0260), and (1.75, 0.025) mol_{SO_2}/mol_{ILs}, respectively. The results indicated that the studied absorbent exhibited satisfactory reusability. Of note, although the water content of the studied absorbent did not change obviously after 5 absorption−desorption cycles (less than 5 wt %; Table S6-2 of the Supporting Information), it is necessary to recover water by condensation reflux or replenish water to the absorbent regularly if the absorbent is used for a long time under industrial operating conditions.

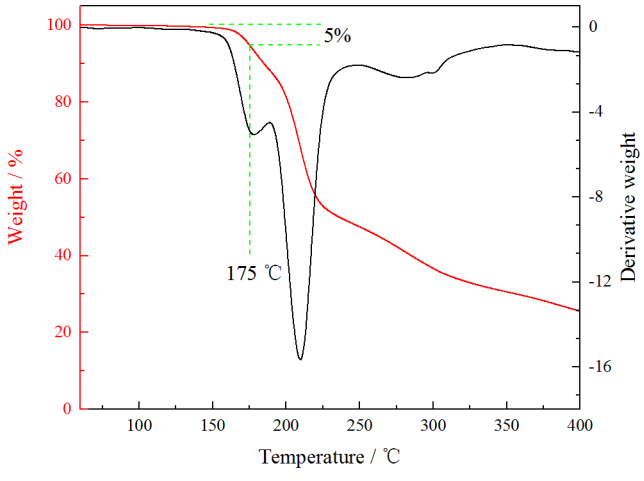

Figure 8. TGA and DTG curves of [DMEDA][CA].

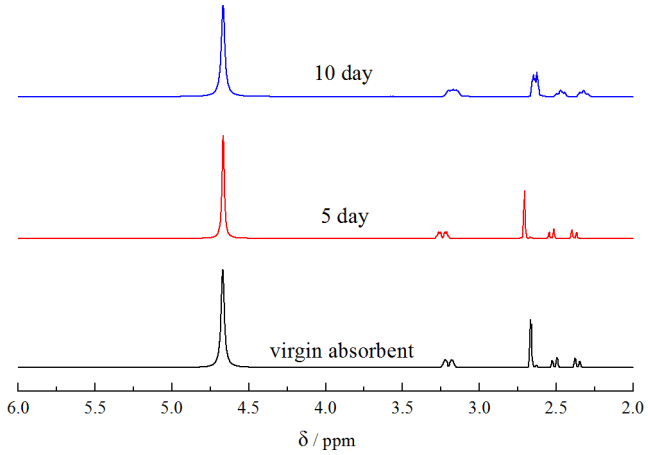

Figure 9. ^{1}H NMR spectra (DMSO-d_6) of 50 wt % [DMEDA][CA] aq for different days of reuse.

3.2.7. Desulfurization Performance. The time-dependent SO_2 removal efficiency (RE) curves in about 2 g of 50 wt % [DMEDA][CA] aq were determined. As shown in Figure 11, the curves (40 °C) were approximately horizontal at the initial period and RE values were higher than 99% (0−25 min), 98%

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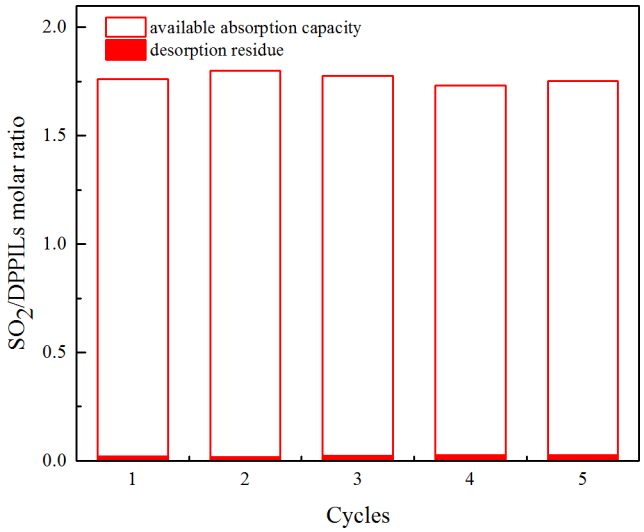

Figure 10. Reusability of 50 wt % [DMEDA][CA] aq.

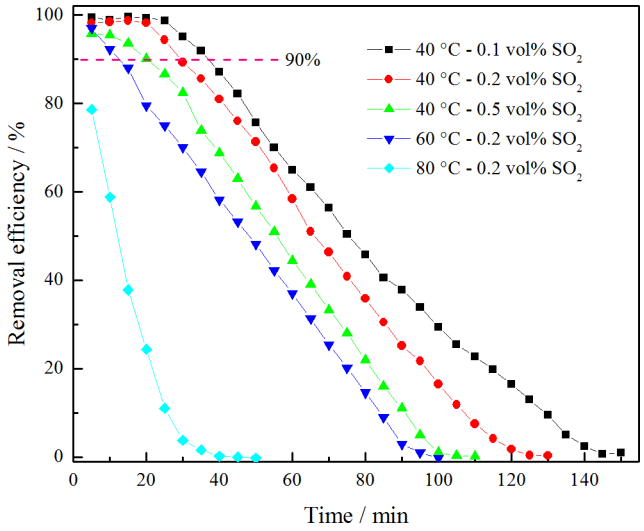

Figure 11. Desulfurization performance of 50 wt % [DMEDA][SUC] aq.

(0−20 min), and 95% (0−10 min) for the inlet SO_2 concentration of 0.1, 0.2, and 0.5 vol %, respectively, indicating that inlet SO_2 could be efficiently captured at 40 °C. Additionally, it could be found that the high temperature was not conducive to SO_2 removal. Concretely, for the simulated flue gas with 0.2 vol % SO_2, *RE* of 50 wt % [DMEDA][CA] aq decreased rapidly in the absorption process at 60 and 80 °C. Nevertheless, considering that industrial desulfurization was usually carried out at 40−60 °C (amine methods) and *RE* of the studied absorbent was higher than 90% at the initial absorption period for the simulated flue gas with 0.1−0.5 vol % SO_2 at 40−60 °C, the studied absorbent could be used as a promising substitute for the traditional amine absorbents. Meanwhile, it was noteworthy that the SO_2 concentration in flue gas was usually within 0.2 vol %, whereas the excellent desulfurization performance could be obtained even if the simulated flue gas was simply bubbled through the studied absorbent within this range. Therefore, in practical application, *RE* of the studied absorbent could be further improved by adjusting the number of column plates and the gas−liquid ratio to meet the stricter flue gas emission standards.

4. CONCLUSION

In summary, a novel series of DPPILs were synthesized and blended with water for efficient and reversible SO_2 absorption. All of the prepared absorbents presented low densities and viscosities, which were conducive to mass transfer. Effects of the DPPIL structure, DPPIL concentration, absorption temperature, and SO_2 concentration on the SO_2 absorption performance were comprehensively studied. It was found that all DPPILs aq could efficiently capture low-concentration SO_2. Among them, DPPILs aq based on CA showed the highest SO_2 desorption efficiencies, and the available SO_2 loading capacity could reach up to 0.51 mol_{SO_2}/mol_{ILs} (0.058 g_{SO_2}/g_{abs}) in 50 wt % [DMEDA][CA] aq at 20 °C and 0.2 vol % SO_2. The high DPPIL concentration, low absorption temperature, and high SO_2 concentration were beneficial for SO_2 capture. Moreover, 50 wt % [DMEDA][CA] aq also exhibited high SO_2/CO_2 selectivity and excellent reusability and stability. Importantly, the SO_2 removal efficiency of the studied absorbent could be higher than 98% at 40 °C for simulated flue gas with a SO_2 concentration within 0.2 vol %, even by a simple bubbling method. The spectroscopic investigation suggested that the protonation of $[DMEDA]^+$ and $[CA]^-$ promoted the SO_2 absorption. Comprehensively considering the simple synthesis process, low viscosity, excellent SO_2 absorption−desorption properties, and superior stability, we believed that the prepared absorbents have great potential to be applied in the practical FGD process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.9b01745.

Characterization results, actual quantities of starting materials (Table S1), water contents of neat DPPILs (Table S2), pH values (Table S3), water loss ratios (Table S4), actual SO_2 concentration (Table S5), water contents of the studied absorbents during absorption−desorption (Table S6), gravimetric SO_2 absorption capacities (Table S7), pK_a values (Table S8), ^1H NMR spectra of 50 wt % [DMEDA][CA] aq before and after SO_2 absorption (Figure S1), and time-dependent absorption−desorption curves of SO_2 in 50 wt % DPPILs aq (Figures S2 and S3) (PDF)

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Notes

The authors declare no competing financial interest.

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