Highly Efficient Absorption of CO_2 by Protic Ionic Liquids-Amine Blends at High Temperatures

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ABSTRACT: In view of the increasingly serious harm of CO_2 to the environment, it is highly desirable to develop effective CO_2 absorbents. In this work, we demonstrated an efficient absorption of CO_2 by blends of protic ionic liquids (PILs) plus amines. The density and viscosity of investigative four PILs-amine mixtures were measured. By systematically studying the effects of the solution ratio, temperature, CO_2 partial pressure, and water content on the absorption of CO_2, it is found that the 3-dimethylamino-1-propylamine acetate ([DMAPAH]-[OAc]) plus ethanediamine (EDA) mixture shows the highest CO_2 uptake of 0.295 g CO_2 per g absorbent at 50 °C and 1 bar and a further increase in the absorption of CO_2 to 0.299 g/g by adding water with a mass fraction of 20%. Furthermore, the absorption mechanism of CO_2 in the presence and absence of water has also been investigated by FTIR and NMR spectra.

protic ionic liquids-amine blends
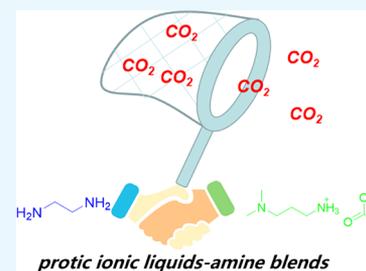
1. INTRODUCTION

It is well known that over emission of CO_2 is one of the primary causes of global warming and has led to serious environmental problems.[1] Flue gases from fossil fuel combustion are the most critical pathway for CO_2 emissions, and the development of CO_2 capture and storage technologies is one of the most promising ways to reduce the impact of greenhouse gases on environmental change.[2,3] However, the burning flue gas produces a CO_2 yield of less than 15%, while the high temperature of the flue gas and the low partial pressure of CO_2 result in a low thermodynamic driving force, which poses a great challenge for the development of efficient and low-cost CO_2 capture technologies.[4−6]

Ionic liquids (ILs) have many attractive natures, especially functionalized ILs with outstanding attributes like low heat capacity, high thermal stability, negative vapor pressure, outstanding CO_2 affinity, etc.[7−10] However, the use of ILs in industrial processes is limited by the high price and high viscosity of ILs.[11,12] Protic ionic liquids (PILs), a class of low-cost ILs, can avoid the limitations of functionalized ILs for CO_2 capture. Many amines thus are paired with carboxylic acids, phenol derivatives, or imidazole derivatives to form PILs.[13−15] For instance, a series of diamine carboxylate PILs with CO_2 absorption capacity were synthesized, with the CO_2 uptake reaching 0.33 mol CO_2/mol IL.[16] Li et al. reported the formation of three PILs from the ultra-strong base tetramethylguanidine (TMG) with imidazole (Im), pyrrole, and phenol, where [TMGH][Im] shows a maximum CO_2 absorption of 0.177 g CO_2/g IL at 30 °C and 1 bar.[15] Before this, we reported the use of 3-dimethylamino-1-propylamine (DMAPA)-based PILs to capture CO_2, acquiring a maximum absorption of 3.99 mol CO_2/kg IL.[17] However, it cannot be avoided that the viscosity of the ILs increases dramatically after

absorbing CO_2, and the absorption capacity of CO_2 also needs to be increased at high temperatures in the above processes.

Preliminary research studies show that adding amines can reduce the viscosity of ILs, resulting in faster absorption and mass transfer. Especially, the absorption of CO_2 can be enhanced by constructing mixed absorbents of ILs plus amine due to the good affinity between amine and CO_2.[18−20] After extensive studies,[21−23] DMAPA as an organic amine has a unique advantage in absorbing CO_2. In particular, DMAPA-based ionic liquids can effectively absorb CO_2 through intramolecular proton transfer.[24] But more than that, amine must have the advantages of low viscosity, high CO_2 capacity, fast adsorption rate, and so on when it is used to modify IL. Therefore, we note that EDA has preponderance and is widely praised for capturing CO_2. More importantly, EDA has the smallest molecular weight, which results in the high CO_2 capacity per unit mass.[25,26] Inspired by these,[18,19,27,28] we reported here four mixed PILs-amine absorbents for CO_2 capture at high temperatures, in which ethanediamine (EDA) and diethylenetriamine (DETA) were selected to confect the mixed absorbents along with PILs 3-dimethylamino-1-propylamium acetic acid [DMAPAH][OAc] or 3-dimethyla-mino-1-propylamium lactic acid [DMAPAH][LA]. The effects of the temperature, CO_2 partial pressure, and water content on the absorption of CO_2 in well-chosen PILs-amine blends were investigated. Furthermore, the absorption mechanism of CO_2
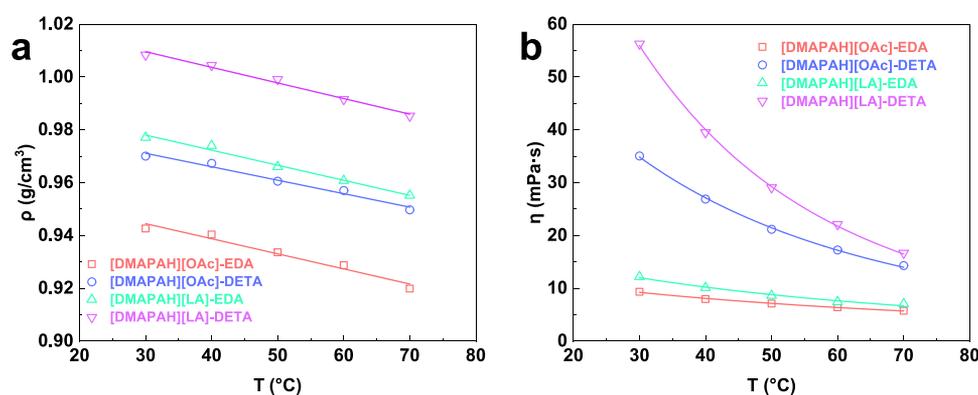
Figure 1. (a) Densities and (b) viscosities of four PILs-amine blends at various temperatures.

in the presence and absence of water has also been investigated by FTIR and NMR spectra.

2. RESULTS AND DISCUSSION

2.1. Characterization of Absorbents. The presented PILs were characterized by NMR and FTIR (Figures S1−S3). It was clearly shown that we successfully synthesized the PILs. Thermostability was also investigated (Figure S4). As shown in the figure, the thermostability of both ionic liquids is greater than 150 °C. The water content of the PILs was measured by a Karl Fischer method, and the PILs are almost anhydrous after deep dewatering (Table S1). In addition, the purities of [DMAPAH][OAc] and [DMAPAH][LA] are 99.0 and 94.5%, respectively, which were analyzed by ^{1}H NMR.

Physical properties of absorbents are essential characteristic parameters for industrial applications, so the densities and viscosities were measured at different temperatures and the results are shown in Figure 1 and listed in Tables S2 and S3.

Measurements of the four PILs-amine blends in a temperature range of 30−70 °C showed that the density decreased almost linearly with increasing temperature (Figure 1a). The viscosity of four PILs-amine blends decreased exponentially with the increase in temperature (Figure 1b). Densities and viscosities of four PILs-amine blends were fitted by eqs 1 and 2:[17]

$$\rho = a_0 + a_1 T \qquad (1)$$

$$\ln \eta = \ln \eta_0 - \frac{E_a}{RT} \qquad (2)$$

where a_0, a_1, and η_0 are undetermined parameters, E_a is the activation energy, and ρ and η are the densities and viscosities of the mixed absorbents, respectively. These parameters were obtained by fitting the experimental data into eqs 1 and 2, and the results are shown in Table 1. The E_a value decreased in the order [DMAPAH][LA]-DETA > [DMAPAH][LA]-EDA > [DMAPAH][OAc]-DETA > [DMAPAH][OAc]-EDA, which is consistent with the viscosity variation trend of absorbents.

The viscosities of four PILs-amine blends are in the range of 9.34−56.27 mPa·s at 30 °C, which are lower than most ILs CO_2 absorbents previously reported in the literature.[29,30] Notably, the viscosities of the PILs-amine blends are much lower than those of pure PILs. The low viscosity is more conducive to the mass transfer process for the absorption of carbon dioxide.

2.2. Effect of PILs and Amines on CO_2 Absorption. To explore the effect of PILs and amines on CO_2 absorption, CO_2

Table 1. Fitting Results of Densities and Viscosities for the Four PILs-Amine Blends

absorbents	parameters			
	a_0	a_1	E_a (kJ·mol^{-1})	$\ln \eta_0$
[DMAPAH][OAc]-EDA	1.12	−0.57	10.41	−1.91
[DMAPAH][OAc]-DETA	1.13	−0.51	19.74	−4.28
[DMAPAH][LA]-EDA	1.15	−0.57	12.67	−2.54
[DMAPAH][LA]-DETA	1.19	−0.59	26.42	−6.46
[DMAPAH][OAc]:EDA = 1:0.5	1.12	−0.51	28.50	−8.07
[DMAPAH][OAc]:EDA = 0.5:1	1.11	−0.61	16.80	−5.33

absorption was carried out at 30 °C and 1 bar for four different PILs-amine blends. As shown in Figure 2, the CO_2 absorption
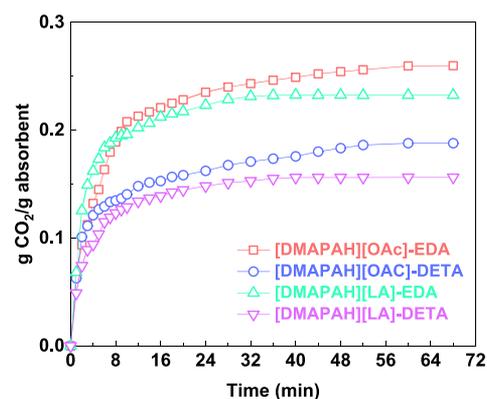
Figure 2. CO_2 absorption in four PILs-amine blends at 30 °C and 1 bar.

in [DMAPAH][OAc]-EDA, [DMAPAH][OAc]-DETA, [DMAPAH][LA]-EDA, and [DMAPAH][LA]-DETA reached the balance with the absorption amounts of 0.260, 0.188, 0.233, and 0.156 g CO_2/g absorbents, respectively. The absorption of CO_2 is higher than those of absorbents reported previously.[30,31] Since the acetate ion has a higher alkalinity than the lactate ion, therefore CO_2 uptake in [DMAPAH]-[OAc] is higher than that in [DMAPAH][LA].[32] Noteworthily, it was found that various degrees of foaming are clearly observed during the absorption processes, which leads to an increase in the apparent viscosity of the liquid, resulting in a decrease in the rate of CO_2 absorption, especially under low temperature conditions. According to the above results, [DMAPAH][OAc]-EDA, as a candidate, was selected to
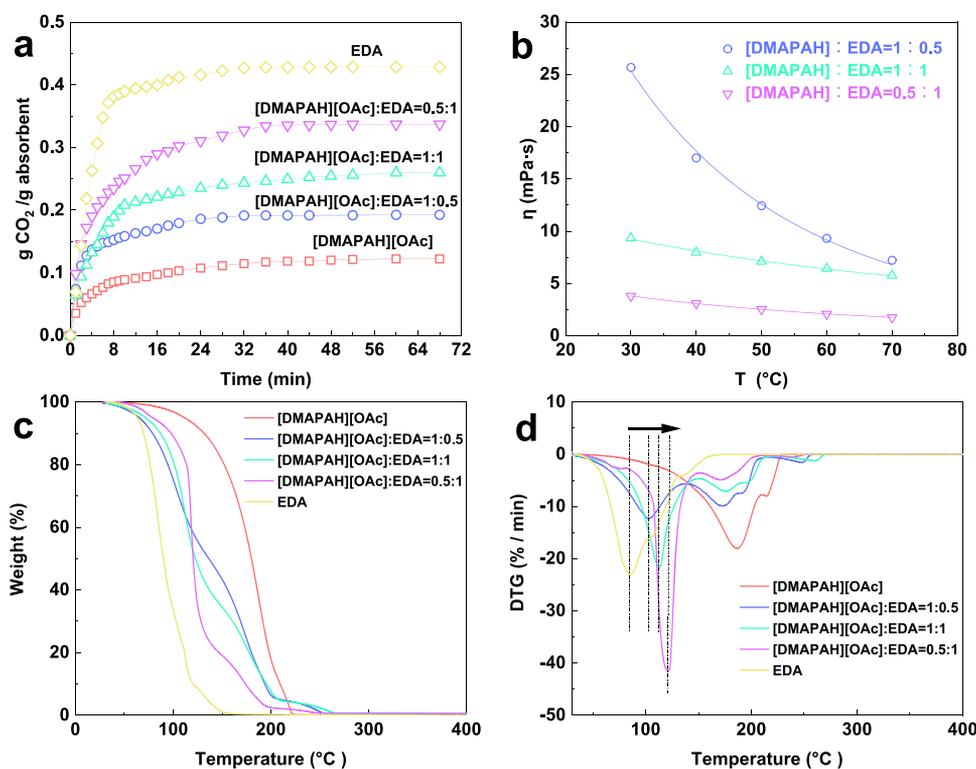
Figure 3. (a) CO_2 capture at 30 °C and 1 bar. (b) Viscosities at various temperatures. (c) TGA and (d) DTG of the [DMAPAH][OAc] and EDA blends with different mass ratios.

further investigate the effects of the temperature, CO_2 partial pressure, and water content on the CO_2 absorption.

The properties of [DMAPAH][OAc] and EDA blends with different mass ratios were studied. It is obvious that the introduction of EDA is beneficial to CO_2 capture (Figure 3a). The addition of EDA greatly enhances the CO_2 adsorption rate of the adsorbents. In addition, the viscosity of the absorbents decreased significantly with the increase in the EDA content (Figure 3b), which was favorable. This greatly reduces the mass transfer resistance of CO_2 in the absorbent. In general, EDA is an excellent CO_2 absorbent. However, it is limited by low thermal stability. Therefore, it is more attractive to enhance its thermal stability by making blends with ionic liquids. The TG curve clearly indicated an increase in the thermal stability of absorbents (Figure 3c). Interestingly, the absorbent obtains better thermal stability with adding a little IL ([DMAPAH][OAc]:EDA = 0.5:1), as shown in Figure 3d. In particular, the loss temperature of EDA therein is significantly improved (from about 85 to 115 °C). Overall, this demonstrates the potential of the protic ionic liquids-amine blends.

2.3. Effect of Temperature on CO_2 Absorption. The effect of temperature on CO_2 absorption by [DMAPAH]-[OAc]-EDA was investigated from 20 to 60 °C under atmospheric pressure. As shown in Figure 4, the CO_2 uptake of [DMAPAH][OAc]-EDA is 0.260 g CO_2/g absorbent at 30 °C and the absorption of CO_2 further increases to 0.295 g CO_2/g by enhancing the temperature to 50 °C. The absorption rate increased gradually with increasing temperature, and the absorption rate reached a maximum when the temperature is 60 °C. Particularly, blistering can be weakened observably by enhancing the temperature (Figure S5), which greatly reduced the mass transfer resistance during CO_2
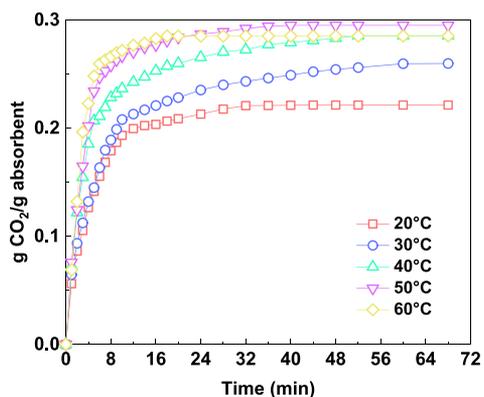
Figure 4. Absorption of CO_2 by [DMAPAH][OAc]-EDA at different temperatures and 1.0 bar.

absorption. The results above indicated that the influence of mass transfer is larger than the temperature during CO_2 absorption.

2.4. Effect of CO_2 Pressure on CO_2 Absorption. The partial pressure of CO_2 in the waste gas produced by the industrial application is low and CO_2 generally coexists with other gases, so it is necessary to study the effect of CO_2 partial pressure on the absorption of CO_2 by the PILs-amine. The CO_2 absorption performance of [DMAPAH][OAc]-EDA was thus investigated at 30 °C with different partial pressures of CO_2. As shown in Figure 5, the CO_2 uptake in [DMAPAH]-[OAc]-EDA decreased slightly with the decrease in the partial pressure of CO_2. It is worth noting that the CO_2 uptake at 0.1 bar CO_2 can reach 0.207 g CO_2/g absorbent, which shows a higher CO_2 absorption capacity than the functionalized ILs or some formulated absorbents reported in the literature.[15,33]
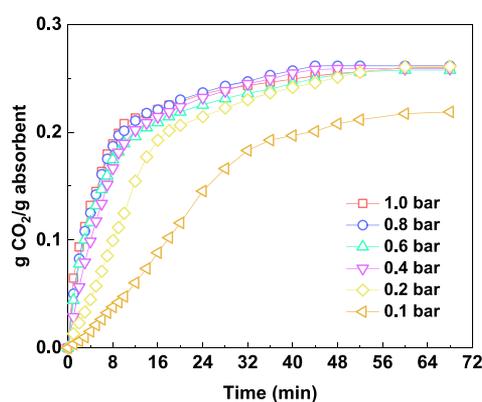
Figure 5. CO$_2$ absorption by [DMAPAH][OAc]-EDA at 30 °C and different partial pressures of CO$_2$.

Figure 6. Effect of the water content on the CO$_2$ absorption in [DMAPAH][OAc]-EDA-H$_2$O at 30 °C and 1 bar.

The absorption capacities of CO$_2$ in some functionalized ILs or some formulated absorbents are listed in Table 2. For these

Table 2. Comparison of the CO$_2$ Absorption Capacity of the Different Absorbents

absorbents	T (°C)	p (bar)	CO$_2$ uptake (g/g)	ref
[DMAPAH][OAc]-EDA	30	1	0.260	this work
[DMAPAH][OAc]-EDA	30	0.1	0.207	
[DMAPAH][OAc]-EDA	50	0.1	0.295	
[DMAPAH][For]	30	1	0.083	16
[DMAPAH][F]	30	1	0.159	31
[DMAPAH][4F-PhO]	30	1	0.176	17
[DMAPAH][Ac]	20	1	0.082	16
[DMAPAH][Py]	23	1	0.225	34
90% [DMAPAH][EOAc]	30	1	0.107	30
90% [DMEDAH][EOAc]	30	1	0.102	30
[P$_{4444}$][PhO]	40	1	0.096	35
[N$_{2222}$][PhO]	50	1	0.126	36
Li(TEPA)Tf$_2$N + Li(TEG)Tf$_2$N	80	0.1	0.060	37
[P$_{4442}$][Suc]	60	0.1	0.039	38
[N1111][Gly]	25	0.65	0.051	33
[N$_{1111}$][Gly]-H$_2$O (70 wt %)	25	0.64	0.178	33
[TMGH][Im]	30	0.1	0.050	15
[P$_{66614}$][2-Op]	20	0.1	0.100	39

absorbents reported in the literature, the CO$_2$ capacities are usually below 0.23 g/g.[30,34] Compared with these absorbents, the PILs-amine blends exhibited the better absorption performance of CO$_2$, especially under high temperature conditions.

2.5. Effect of the Water Content on CO$_2$ Absorption. The industrial flue gas is characterized not only by a high temperature and low CO$_2$ partial pressure but also by the fact that it contains water vapor, so it is also important to study the effect of the water content on the CO$_2$ absorption. As shown in Figure 6, when the water contents are in a range of 3−10 wt %, the absorption capacity and absorption rate of [DMAPAH]-[OAc]-EDA-H$_2$O changed slightly with the increase in the water content. When the content of water is 20 wt %, a maximal CO$_2$ absorption of 0.299 g/g is afforded. The appropriate water content can reduce the viscosity of the absorbent and can promote the mass transfer of CO$_2$. The absorbent also gained a higher CO$_2$ capture rate. In terms of absorption products, bicarbonate with a higher thermal
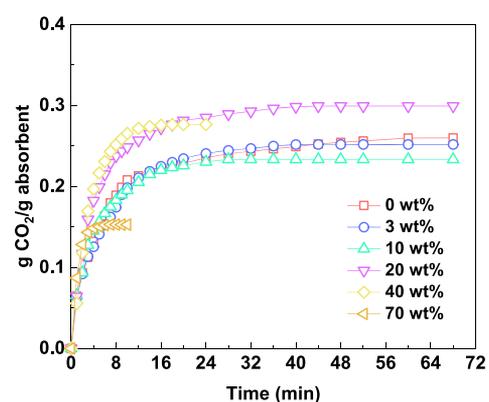
stability was produced when water was present, while the anhydrous [DMAPAH][OAc]-EDA generated carbamate, which was the reason for the increased viscosity of the absorbent.[15,40]

2.6. Mechanism of CO$_2$ Absorption in Mixed Systems. To investigate the mechanism of CO$_2$ absorption, FTIR was employed to investigate CO$_2$ absorption in [DMAPAH]-[OAc]-EDA and [DMAPAH][OAc]-EDA-H$_2$O (20 wt %). As shown in Figure 7a, the new peaks appeared after the absorption of CO$_2$ by [DMAPAH][OAc]-EDA. Concretely, new peaks at 1384 and 1044 cm^{-1} can be attributed to the C−O stretching vibration in carbamate.[41] The peaks at 1178 and 1429 cm^{-1} can be attributed to the deformation vibration of C−N and −NH$_3^+$,[42,43] respectively. The new peak at 1623 cm^{-1} is due to the stretching vibration of the C=O bond in the formation of carbamate after the absorption of CO$_2$, and the results suggested that carbamate is formed between the basic nitrogen atom of DMAPA and CO$_2$.[44,45] In addition, the appearance of a broader peak at 3135 cm^{-1} suggests the possible formation of zwitterions (NH$_2^+$COO$^-$) during the absorption of CO$_2$.[46] As shown in Figure 7b, the characteristic peaks of bicarbonate can be found at 1047 and 1157 cm^{-1} after capturing CO$_2$ with [DMAPAH][OAc]-EDA-H$_2$O (20 wt %).[15,47] Furthermore, the gradually broadening peaks in a range of 1419−1573 cm^{-1} are due to the continuous formation of −NH$_3^+$ during the reactions.[43]

To further obtain the absorption mechanism of CO$_2$, NMR spectroscopy was employed. As shown in Figure 8, after [DMAPAH][OAc]-EDA absorbed CO$_2$, a new carbon signal at 167.00 ppm was attributed to the carbonyl carbon in the generated carbamate.[48] In contrast, two peaks at 166.83 and 162.93 ppm were observed after CO$_2$ absorption in [DMAPAH][OAc]-EDA-H$_2$O (20 wt %), the former attributed to carbonyl carbon in carbamate and the latter due to bicarbonate formation.[49−51] These results are in good agreement with FTIR.

From FTIR and ^{13}C NMR analyses and combined with experimental results, we have presented a possible CO$_2$ absorption pathway for CO$_2$ absorption by [DMAPAH]-[OAc]-EDA and [DMAPAH][OAc]-EDA-H$_2$O. As shown in Figure 9, [DMAPAH][OAc] rearranged automatically into its balanced structure and the protons on the primary amine are transferred to the tertiary amine followed by exposure of the primary amine group and finally combining with EDA to rapidly absorb CO$_2$ and form zwitterions.[16,29,52] If there is a small amount of water in the reaction system, the zwitterions
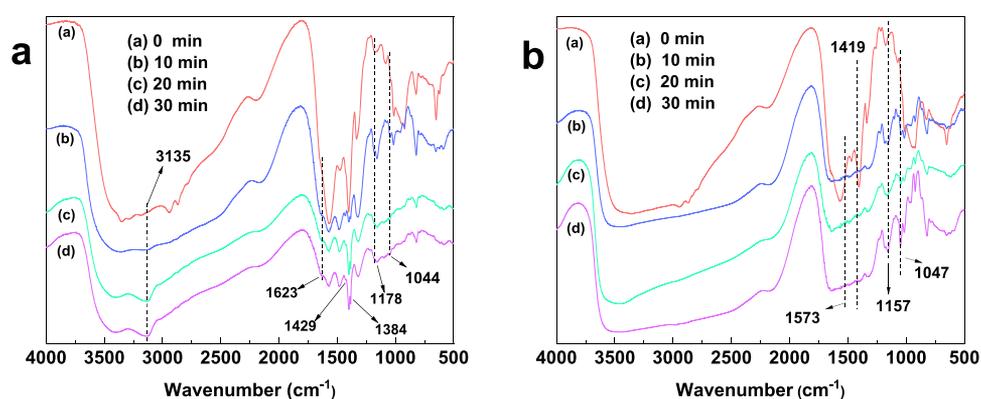
Figure 7. FTIR spectra of the (a) [DMAPAH][OAc]-EDA and (b) [DMAPAH][OAc]-EDA-H_2O systems before and after absorption of CO_2.
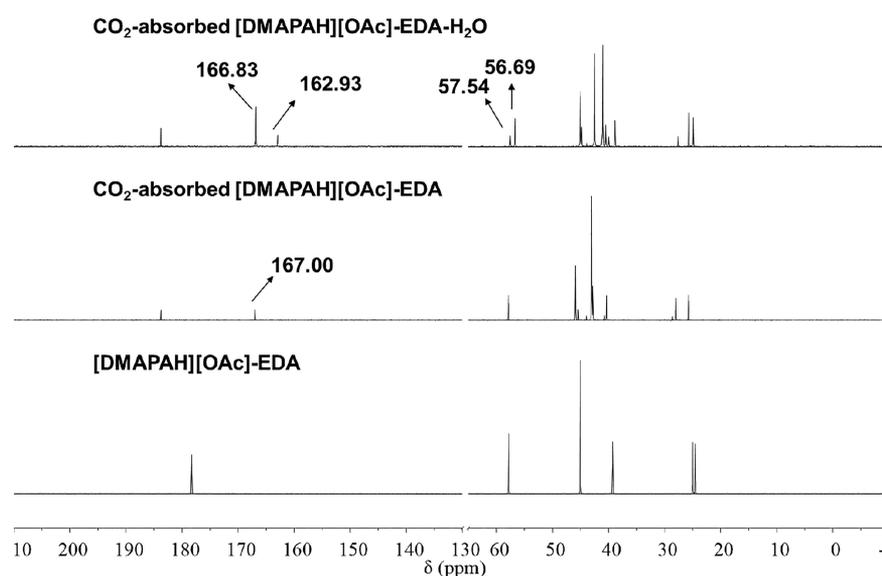
Figure 8. ^{13}C NMR spectra of the [DMAPAH][OAc]-EDA and [DMAPAH][OAc]-EDA-H_2O (20%) systems before and after CO_2 absorption.
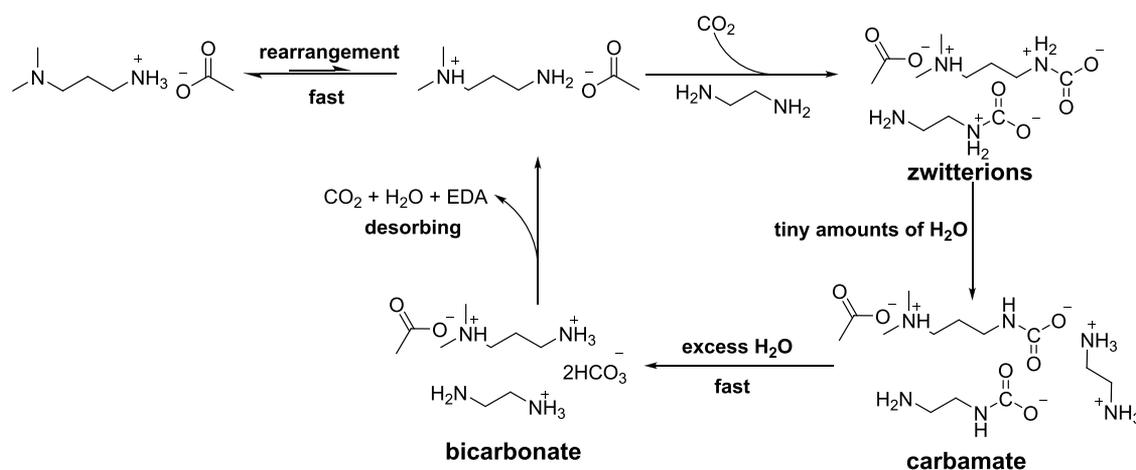
Figure 9. Schematic diagram of the proposed CO_2 absorption mechanism for the [DMAPAH][OAc]-EDA and [DMAPAH][OAc]-EDA-H_2O systems.

transfer into carbamate and the protonated EDA is generated. In contrast, the transfer rate of the zwitterions is slightly slower than that of the aqueous absorbent due to the absence of water assistance.[27,50] Carbamate can be further hydrolyzed to produce bicarbonate, which usually occurs in the presence of excess water. Furthermore, this step quickly and automatically takes place in the presence of water.[53] It is worth noting that the generation of primary amines by hydrolysis of carbamate makes more primary amines available for CO_2 absorption, further illustrating the speedy absorption rate and high CO_2 loading of the [DMAPAH][OAc]-EDA-H_2O mixture.

2.7. Recycling of Absorbents. To study the regeneration performance of absorbents, [DMAPAH][OAc]-EDA-H_2O (20 wt %) first absorbed CO_2 to reach saturation at 30 °C and 1 bar, and then the mixture of absorbents was desorbed by bubbling N_2 at 110 °C for 100 min. It can be seen from Figure 10 that the aqueous [DMAPAH][OAc]-EDA solution can be
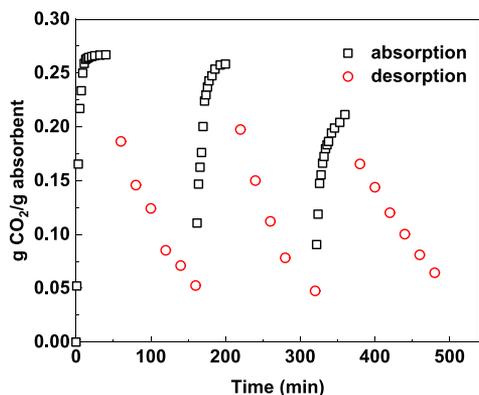
Figure 10. Recycling of the aqueous [DMAPAH][OAc]-EDA solution (mass fraction of water is 20%).

recycled. After the absorbent can be recycled three times, the absorption of CO_2 still exceeds 0.20 g/g. The reduced absorption performance may be due to insufficient desorption of the absorbent and oxidative degradation of EDA.

3. CONCLUSIONS

In conclusion, we demonstrated an effective CO_2 absorption using PILs-amine blends as the reversible absorbents. The experimental systems were used to study the effects of the absorbent composition, temperature, pressure, and water content on the CO_2 absorption performance. Good CO_2 absorption capacity in both the high-temperature and low-pressure range was acquired. Furthermore, TG, FTIR, and NMR have shown that there is a synergistic effect between [DMAPAH][OAc] and EDA for enhancing the absorption of CO_2. This work suggests that PILs-amine blends are promising candidates in the treatment of industrial high-temperature CO_2 gas.

4. EXPERIMENTAL SECTION

4.1. Materials. Chemicals of DMAPA (>99.0%), DETA (>99.0%), EDA (>99.0%), acetic acid (>99.0%), and lactic acid (>85%) were purchased from Energy Chemical Technology (Shanghai) Co., Ltd., China. CO_2 (>99.99%) and N_2 (>99.999%) were supplied by Guiyang Sanhe Special Gas Center, China. All chemicals were used directly without further purification. All mass measurements were performed on an electronic balance with an accuracy of ±0.1 mg (Sartorius BS224S). FTIR spectra were recorded on a Nicolet iS50 FTIR spectrometer. ^{13}C NMR and ^1H NMR spectra were recorded on a JNM-ECZ-400 spectrometer. The thermal stability was measured using an STA 449F5 simultaneous thermal analyzer

with a heat rate of 10 °C·min^{-1} in a N_2 atmosphere at a flow rate of 20 mL·min^{-1}.

4.2. Synthesis and Characterization of PILs. The PILs [DMAPAH][OAc] and [DMAPAH][LA] were prepared by dropping DMAPA into acetic acid or lactic acid at an ambient environment with strong stirring for 24 h, respectively, in a molar ratio of 1:1. PILs need to be vacuum dried at 60 °C for 48 h before use to remove water as much as possible. The structures of amines and PILs are shown in Scheme 1.

4.3. Preparation of PILs-Amine Blends. PILs-amine blends were prepared by mixing amine with the desired PILs in a 1:1 mass ratio. Typically, [DMAPAH][OAc]-EDA was obtained by intensive mixing of equal quantity of [DMAPAH]-[OAc] and EDA at room temperature for more than 24 h. In addition, the absorbents were prepared with various mass ratios of IL and amine as 1:0.5 and 0.5:1. According to the previously reported method,[22] the density and viscosity of the PILs-amine blends were determined by a pycnometer method and a Ubbelohde viscometer method, respectively. We used secondary water and ethanol to calibrate before measuring the absorbents. The above operation was repeated six times, and the difference was no more than 0.2 s each measurement. The average value is T, which is the outflow time of the absorbents. The aqueous solutions of [DMAPAH][OAc]-EDA were also prepared for the study of CO_2 absorption, and the mass fractions of water were 3, 10, 20, 40, and 70%, respectively.

4.4. Absorption and Desorption of CO_2. The absorption experiments were performed in a glass container with an inner diameter of 2 cm, and the installation diagram is shown in Figure 11. In a typical procedure, CO_2 gas was bubbled at a
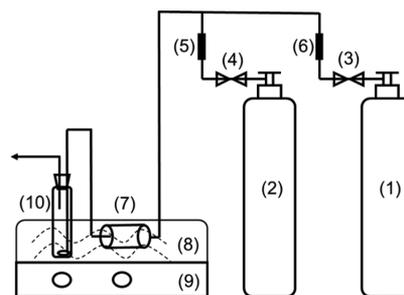
Figure 11. Experimental graph of CO_2 absorption. (1) N_2 gas cylinder; (2) CO_2 gas cylinder; (3) and (4) valve; (5) and (6) gas mass flow-meter; (7) gas premixing tank; (8) water bath; (9) magnetic stirrer; and (10) glass tube with round bottom.

flow rate of about 50 mL·min^{-1} through the absorbent in a glass vessel (10). The glass vessel was immersed in a water bath (8) at a temperature required. The CO_2 uptake was measured periodically with an electronic balance. Solvent loss caused by gas entrainment can be neglected due to the low gas flow rate. The influence of temperature on the CO_2 absorption was studied by varying the temperature from 20 to 60 °C at 1 bar. During the absorption of CO_2 under reduced pressure, the CO_2 partial pressure was controlled by adjusting the flow rates of pure CO_2 gas and N_2 gas. To study the effect of the water

Scheme 1. Structures of Ethanediamine (EDA), Diethylenetriamine (DETA), [DMAPAH][OAc], and [DMAPAH][LA]
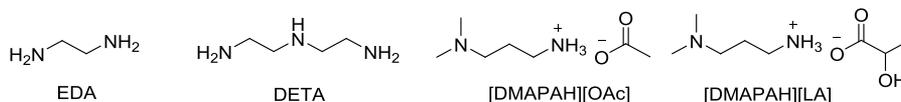
content on CO_2 absorption, CO_2 was bubbled through the mixed absorbent with different water contents. For the desorption of CO_2, absorbents after absorbing CO_2 were heated under a N_2 atmosphere to release CO_2. Reflux condensation avoided the loss of absorbents during regeneration, and the next absorption cycle used the regenerated absorbent directly.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05416.

Details about the structure characterization (NMR, TGA, FTIR, etc.) of absorbents (PDF)

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Notes

The authors declare no competing financial interest.

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