

Ditetraalkylammonium Amino Acid Ionic Liquids as CO₂ Absorbents of High Capacity

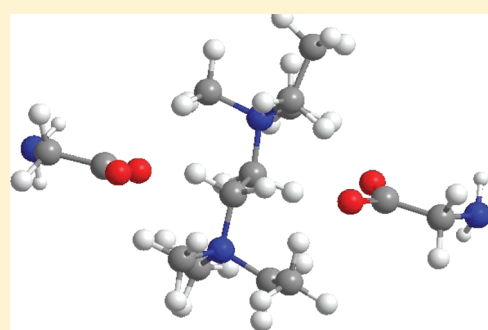
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 Supporting Information

ABSTRACT: By grafting butyl or ethyl onto tetramethylethylenediamine, quaternary ammonium salts with two positive charge centers were formed at the first step. Metathesis with Ag₂O followed. Through neutralization with glycine, L-alanine, or valine, a series of new ditetraalkylammonium amino acid ionic liquids (DILs) for CO₂ capture were generated. The structures of DILs, as shown in Figure 1, were verified by using ¹H NMR and EA. These DILs were found to be of quite high viscosity which militated against their industrial application in CO₂ removal. Drawing on the experience of mixed amines' aqueous solutions, these DILs were blended with water or N-methyldiethanolamine (MDEA) aqueous solutions to act as special absorbents of CO₂. Using a Double-Tank Absorption System, the absorption performance of these DIL solutions was investigated in detail. The experimental results indicated that among the three aqueous solutions of DILs (20%, 40%, and 80 wt %), the solution of 40% DIL had a higher absorption rate of CO₂ than the other two, demonstrating the different effects of concentration and viscosity on the absorption. The solution of 40% DIL or the 15% DIL + 15% MDEA had much higher capacity for CO₂ than the corresponding monocation tetraalkylammonium AAILs, due to the special structure of the dication which could influence the solubility of CO₂ in the aqueous solution.



1. INTRODUCTION

As a worldwide concern, the treatment of CO₂ has attracted more and more attention.¹ Many techniques for CO₂ removal have been developed. However, CO₂ is not just a greenhouse gas but also an important chemical resource widely used in many fields. Carbon dioxide can be transformed into an environmental-friendly extraction solvent in green chemical industries. Moreover, as a C1 resource, CO₂ can be transformed into some basic chemical materials, such as CO, syngas, and methanol.^{2–7} Therefore, the capture of CO₂ is good for both the environment and the recycling of carbon resource. At present, one of the most successfully and commercially utilized technologies for CO₂ recovery is the absorption of CO₂ by aqueous solutions of amines, including monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), etc.⁸ However, there are several shortcomings in the use of alkanolamine,^{9–11} such as equipment corrosion, easy heat decomposition, oxidation of amines, and secondary pollution due to its high volatility.

In view of the above-mentioned drawbacks of amines aqueous solutions, ionic liquids (ILs) are considered to be promising alternatives for the uptake of CO₂. Room temperature ionic liquids (RTILs) are novel type of green solvents with special properties^{12,13} such as low vapor pressure, wide liquid process temperature, high stability, and easy assembly. RTILs have aroused considerable

interest due to their potential application as new green solvents.¹² Compared with alkanolamines, RTILs have negligible volatility and remarkable thermal stability which can avoid loss of absorbents for CO₂ uptake. Many research groups, especially that of Brennecke,¹⁴ have carried out significant research on the solubility of CO₂ in ILs. They^{15,16} first reported that CO₂ was highly soluble in [bmim][PF₆](1-butyl-3-methylimidazolium hexafluorophosphate) with a mole fraction of 0.6 at 8 MPa. However, when the pressure of CO₂ was below ambient pressure, the solubility of CO₂ in conventional ILs was only up to 0.035 mol fraction. In general, the absorption of CO₂ by these traditional ILs was physical and had to be performed under extreme conditions such as very high pressure (90 bar or even higher) and very long time for the equilibrium to be reached (up to 24 h).

Inspiringly, the unique “assembly” character of ionic liquids makes rapid and efficient absorption of CO₂ in ILs possible. Introducing special groups which can greatly enhance CO₂ capture into the anion or the cation of ILs, functionalized ionic liquids by designing the structures of cation or anion according to

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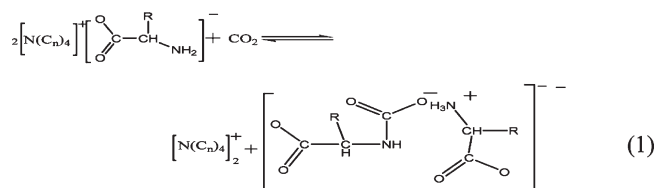
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the practical needs and special purposes are expected to have excellent performance in the uptake of CO₂. Bates et al.¹⁷ reported that the molar uptake of CO₂ per mole of [pNH₂bim][PF₆] (ionic liquid functionalized the cation with amine) during 3 h approached 0.5 under normal pressure and temperature. The absorption mechanism of CO₂ in the amine functionalized ionic liquid was also proposed as the primary amines. Since then, lots of functional ILs¹⁹ with the amino group in cation have been synthesized for CO₂ uptake. In 2005, amino-acid-based ILs [emim][amino acid] were prepared from 20 natural amino acids by Ohno's group.²⁰ Then, tetraalkylphosphonium amino acid ILs was also reported.^{19,20} Due to their high viscosities (245–745 mPa·s), tetraalkylphosphonium amino acid ILs had to be loaded on porous silica gel to absorb CO₂.²⁰ In 2010, Brennecke's group²¹ successfully used a computational molecular design approach to identify a new class of ILs based on the AHAs (aprotic heterocyclic anions), which were shown to react stoichiometrically and reversibly with CO₂ and to not suffer the large viscosity increases that have plagued previous attempts to create CO₂-complexing ILs.

Our research group have successfully synthesized nine tetraalkylammonium-based amino acid ionic liquids which could rapidly absorb CO₂ (the absorption equilibrium could all be reached within 60 min).²² In 2010, lysine, which had two amino groups in one molecule, was also used as anion to obtain tetramethylammonium lysine ([N₁₁₁₁][Lys]) and tetraethylammonium lysine ([N₂₂₂₂][Lys]).¹⁹ It was found that [N₁₁₁₁][Lys] and [N₂₂₂₂][Lys] had significant mole absorptivity of CO₂. The absorption mechanism of CO₂ in pure amino-acid-based ILs is similar to that of [pNH₂bim][PF₆], i.e., one CO₂ molecule is combined with two amino groups²³



The viscosity of amino acid ILs (AAILs) is still quite high.^{22–24} Generally, the diffusivity of CO₂ in the liquid is determined by the solvent's viscosity. The lower the viscosity of solvent is, the higher is diffusivity in the solvent and thus the faster absorption rate. The biggest flaw with the functionalized ILs is their high viscosity, which greatly hinders their application in CO₂ absorption. Drawing on the successful experience of the mixed amines in CO₂ uptake, combining functionalized ILs with water or MDEA solution is a good way to apply the functionalized ILs,¹⁸ since the amino acid ILs have high solubility in water. According to a US patent,²⁵ [bmim][BF₄] (1-butyl-3-methylimidazolium tetrafluoroborate) and [bmim][acetate] aqueous solutions and the hybrid of ionic liquid and MDEA (MEA) were used for the removal of CO₂. However, the absorption of CO₂ in these solvents was quite limited, since [bmim][BF₄] and [bmim][acetate] were not very good for the absorption of CO₂. In 2010, four functionalized amino acid ILs, tetramethylammonium glycinate ([N₁₁₁₁][Gly]), tetraethylammonium glycinate ([N₂₂₂₂][Gly]), tetramethylammonium lysinate ([N₁₁₁₁][Lys]), and tetraethylammonium lysinate ([N₂₂₂₂][Lys]), were mixed with aqueous solution of MDEA to form a new type of absorbents (AAILs + MDEA + water) for CO₂ capture. It was found that adding amino acid IL greatly enhanced CO₂ absorption in the MDEA aqueous solution.^{18,19}

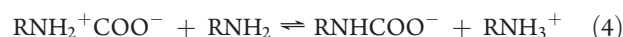
Practically, in the aqueous solution, the amino-acid-based ILs completely dissociate into hydrated cations and [H₂N-CHR-COO][−] anion. Since the amino acid anions react with CO₂ like the primary alkanolamine, [H₂N-CHR-COO][−] can be represented as RNH₂. In the aqueous solution of amino-acid-based ILs, the carbon dioxide absorption is usually described by the zwitterion mechanism.²⁵ First, zwitterion is obtained through the reaction of CO₂ with amino acid



Then, the zwitterion is deprotonated by the bases (denoted by B) in the solution



where B includes RNH₂, H₂O, OH[−], MDEA, etc. In the aqueous solutions of IL and MDEA, the amino acid first reacts quickly with CO₂ to form zwitterions which will transfer protons to MDEA. Therefore, the new CO₂ absorbent AAILs + MDEA + water combines the rapid absorption rate of AAILs and the high CO₂ capacity of MDEA. The equilibrium reactions in the liquid phase are suggested as follows¹⁹



Through eqs 4–10, the concentration of species can be calculated.

In recent years, dicationic ionic liquids have attracted increasing attention for their excellent properties. Some imidazolium-based dicationic ILs have been synthesized by Ohno and his co-workers,²⁷ who have also synthesized pyridinium- and ammonium-based dicationic ILs with a polyether linker.²⁸ Armstrong²⁹ synthesized 39 kinds of dication ionic liquids, combining cations which contain two imidazolium or pyrrolidinium cations joined via hydrocarbon linkage chains of different lengths (from 3 to 12 carbons long) and the anions including Br[−], NTf₂[−], BF₄[−], and PF₆[−]. The conductivity, glass transition temperature, melting point, surface tension, and shear viscosity in some dicationic ILs have been reported.³⁰ Some dicationic ILs have been applied as stationary phases for gas chromatography,^{31–33} as solvents for high-temperature organic reactions,³⁴ as high-temperature lubricants,^{35–38} and as electrolytes in secondary batteries³⁹ and dye sensitized solar cells.^{40,41} There are usually two ways to obtain functionalized ILs: cation or anion functionalized. As a medium for CO₂ capture, higher absorption capacity of the functionalized ILs is always preferred. In the present work, for the first time, dual-cations amino acid ILs were synthesized, in which the cation was equipped with two charges and the anions were functionalized with two appended amine groups. So far, most of the investigations on DILs^{29,37,42–44} have focused on their synthesis or their basic physicochemical properties, while little work has been done

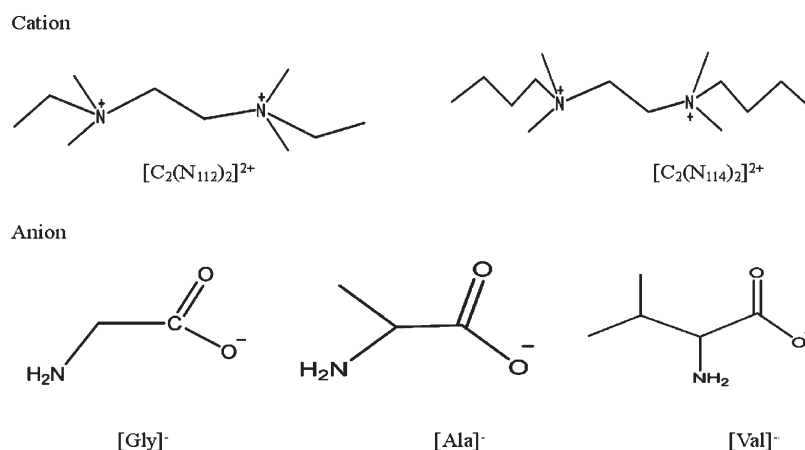


Figure 1. Cation and anion of the target ionic liquids.

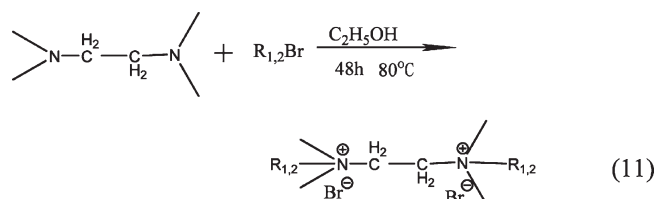
concerning the specific uses of DILs, especially the amino-acid-based DILs. In our work, DILs and their solutions were first applied in the absorption of CO_2 gas. Then, absorption of CO_2 in the DIL aqueous solutions and the DIL + MDEA aqueous solutions was investigated respectively to explore the effect of carbon structure and two positive charge centers on CO_2 uptake.

2. EXPERIMENTAL SECTION

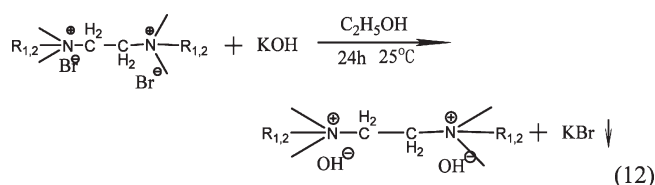
2.1. Materials. Tetramethylethylenediamine, 1-ethyl bromide, 1-butyl bromide, silver oxide, glycine, lysine, and valine of analytical grade were provided by Sinopharm Chemical Reagent. CO_2 (purity above 99.99%) was purchased from Jiangsu Topgrand Petrochemical industrial gas Co., Ltd.

2.2. Synthesis of Dicationic Ionic Liquids. The synthesis process of amino-acid-based DILs was as follows:

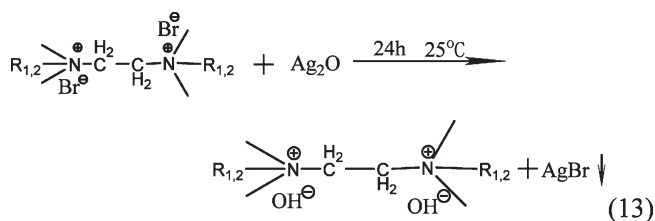
Step 1. Tetramethylethylenediamine and bromine alkane (methyl bromide or butyl bromide) reacted in ethanol at $80^\circ C$ for 48 h. The crude dication salt was then obtained through removing the solvent and unreacted reagents by rotary evaporator. After anhydrous drying over phosphorus pentoxide, pure dibromide salt was obtained eventually.



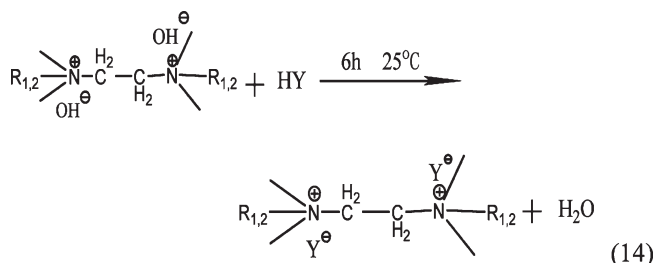
Step 2. Dication salt from Step 1 was mixed with potassium hydroxide in ethanol and stirred at room temperature for 24 h to obtain ditetraalkylammonium hydroxides. Since the solubility of potassium bromide in ethanol was quite low (0.034 g KBr/100 g ethanol at $25^\circ C$), the precipitated potassium bromide could be removed by filtration.



Step 3. The small amount of bromide ion in the solution generated from Step 2 was measured with the Mohr titration. One molar equivalent of the bromide salt dissolved in water would react with 1 mol equiv of solid silver oxide which was added intermittently. After being stirred in darkness at room temperature for 8 h, the upper supernatant was separated and treated by centrifugation at 4500 rpm for 15 min. Silver bromide which was nearly insoluble in ditetraalkylammonium hydroxides solution could be removed.



Step 4. As the concentration of OH^- in the solution generated from Step 3 was calibrated by 1 mol/L standard hydrochloric acid, OH^- reacted with amino acid at mole ratio of 1:1 for 6 h at ambient temperature. Then water was removed through rota-evaporation and vacuum drying over phosphorus pentoxide to obtain the crude products.



Step 5. The crude products were extracted by using the mixture of acetonitrile and chloroform (the volume fraction was 50%). By removing solvent through rota-evaporation and vacuum drying over phosphorus pentoxide, respectively, six pure ionic liquids would be obtained. The structures of the anion and the cation for the DILs are shown in Figure 1.

2.3. Characterization of Dicationic Ionic Liquids. The structures of synthesized DILs were identified by ^1H NMR spectroscopy (Varian XL-300) and EA (Elementar vario EL II). The thermal stability was measured with TGA

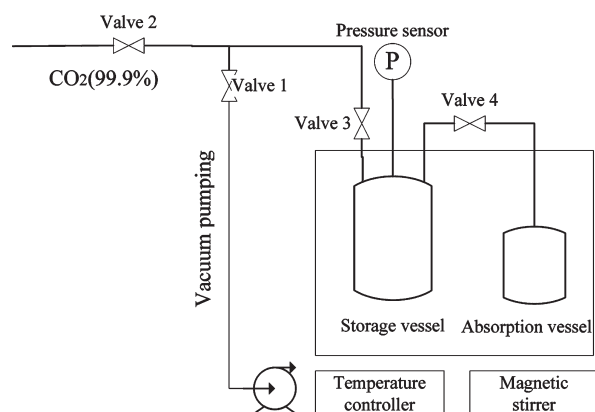


Figure 2. Schematic diagrams of gas absorption apparatus.

(Perkin-Elmer, 7 series thermal analysis system), and the samples were placed in aluminum pans and heated from room temperature to 500 at $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen. The amount of water was measured by using Karl Fisher coulometric titration (Brinkmann Metrohm 756 KF Coulometer). The Br concentration, which was found to be (240 to 285) ppm, was measured by the Mohr titration.

2.4. Experiments of CO_2 Absorption. Since all pure DILs are of high viscosity and low liquidity, they will be prepared as aqueous solutions for CO_2 uptake like the previous treatment for the amino-acid-based ILs.^{18,19} Considering the economic benefit and the reactivity, glycine is an excellent anion provider and CO_2 stabilizing agent. Therefore, $\text{C}_2(\text{N}_{114})_2\text{Gly}_2$ and $\text{C}_2(\text{N}_{112})_2\text{Gly}_2$ were chosen as functional absorbents for CO_2 capture. Two kinds of solutions were prepared as absorbents: (1) aqueous solutions of DILs with weight fraction of 20%, 40%, and 80% and (2) 15% DIL + 15% MDEA aqueous solutions. The densities of all the solutions were measured by density meter Anton Paar DMA 5000, with a precision of $0.000001\text{ g}\cdot\text{cm}^{-3}$. The viscosities of the solutions were measured by HAAKE Rheostress 600. The absorption reactor is made of stainless steel and can afford pressures up to 120 bar. The whole test device consists of an isothermal water bath, an absorption equilibrium system, and the data receiving sections. This device has two vessels, and the storage vessel (176.3 mL) isolates CO_2 before it contacts the samples in the absorption vessel (57.3 mL) which is equipped with a magnetic stirrer. The temperature of both vessels is controlled by the water bath. The pressure in the two vessels is monitored by using the pressure gauge (WIDEPLUS-8). Before the experiment, a known mass of the sample (about 4 g) was placed into the absorption vessel, and the whole device was degassed by a vacuum pump for at least 2 h. As shown in Figure 2, the two vessels were first separated by using a needle valve. When the storage vessel received the known amount of CO_2 , its initial pressure P_0 was measured by a pressure gauge. Then, the needle valve between the two vessels was turned on to let the CO_2 be introduced to the sample in the absorption vessel, and the CO_2 gas would be absorbed by the liquid in the bottom of the vessel. After the equilibration was reached, the CO_2 uptake could be calculated. A detailed description of the experiments has been presented in ref 19.

The amount of absorbed CO_2 can be calculated by the following equation

$$n_{\text{CO}_2} = \frac{P_0 V_S - P(V_S + V_A - V_L) + P_v V_L}{RT} \quad (15)$$

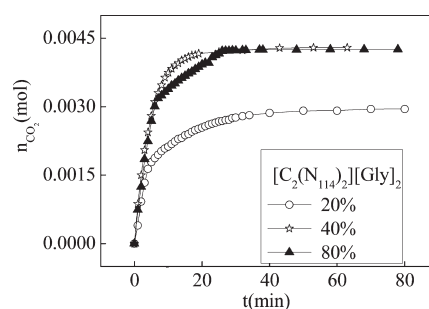


Figure 3. Absorption of CO_2 in aqueous solution of $\text{C}_2(\text{N}_{114})_2\text{Gly}_2$.

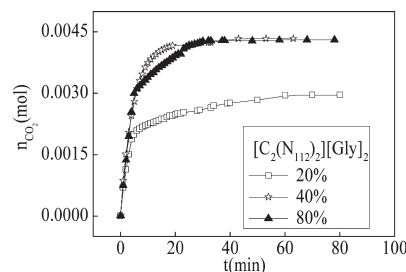


Figure 4. Absorption of CO_2 in aqueous solution of $\text{C}_2(\text{N}_{112})_2\text{Gly}_2$.

where V_S and V_A denote the volume of the storage vessel and the absorption vessel respectively. V_L represents the volume of liquid, and P_v represents the saturated vapor pressure of liquid. According to the Damping-Film Theory, for the isothermal absorption of gas, the relationship between the partial pressure of the gas versus the time can be described as follows

$$\ln(P - P_e)/(P_0 - P_e) = -ut \quad (16)$$

where P represents the partial pressure of CO_2 at time t . P_0 and P_e denote the partial pressure at the beginning and at the absorption equilibrium, respectively. u stands for the apparent absorption rate constant based on pressure. Taking part in the Peng–Robinson cubic equation of state, eq 16 will be written in the form of n —the amount of CO_2

$$\ln(n - n_e)/(n_0 - n_e) = -Kt \quad (17)$$

where, like u , K is also the apparent absorption rate constant. Noticeably, K strictly equals to u only for the ideal gas.

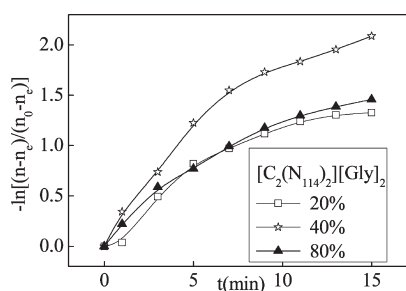
3. RESULTS AND DISCUSSION

3.1. The Characterization Results. The results of ^1H NMR, EA, TG, the water content, and the halide concentration of the sample are presented in the Supporting Information. The characteristic data are in good agreement with the expected structures and compositions.

3.2. Absorption of CO_2 in Solutions of Various Concentrations. Absorption of CO_2 by aqueous solutions of DILs with $P_0 = 97\text{ KPa}$ and $T = 298\text{ K}$ is illustrated in Figures 3 and 4. It was found that the two types of DILs, $\text{C}_2(\text{N}_{114})_2\text{Gly}_2$ and $\text{C}_2(\text{N}_{112})_2\text{Gly}_2$ had the same absorption trend in aqueous solutions. Among the three aqueous solutions of DIL (20%, 40%, and 80%), the 40% DIL aqueous solution had a higher absorption rate and larger absorption capacity for CO_2 than the 20% and 80% DIL aqueous solutions. A possible explanation is that compared with the 40% DIL aqueous solution, the 20% DIL

Table 1. Physical Property of the Absorbents

absorbents	<i>m</i> (g)	ρ (g·cm ⁻³)	μ (mP·s)	<i>n</i> _{CO₂} (mol)	α (mol _{CO₂} mol ⁻¹ _{Gly})
20% C ₂ (N ₁₁₂) ₂ Gly ₂	3.883	1.02243	4.58	0.0031909	0.6617
40% C ₂ (N ₁₁₂) ₂ Gly ₂	3.8995	1.04073	19.85	0.004296	0.4434
80% C ₂ (N ₁₁₂) ₂ Gly ₂	3.9923	1.07320	618	0.004254	0.2825
20% C ₂ (N ₁₁₄) ₂ Gly ₂	3.9968	1.02259	5.32	0.002950	0.6593
40% C ₂ (N ₁₁₄) ₂ Gly ₂	4.0012	1.04103	20.3	0.004107	0.4032
80% C ₂ (N ₁₁₄) ₂ Gly ₂	4.0037	1.074193	630	0.004082	0.2794

Figure 5. Apparent absorption rates in aqueous solution of C₂(N₁₁₄)₂Gly₂.

solution had less effective absorbent (RNH₂COO⁻), while the 80% DIL solution had higher viscosity which greatly hindered the absorption of CO₂. Generally, the viscosity of aqueous solutions increased with the uptake CO₂, further weakening the absorption performance. The absorption capacity of the DIL aqueous solutions was compared in Table 1, which showed that the 20% aqueous solution had the highest CO₂ load of 0.66 mol_{CO₂}/mol_{Gly} and the 40% DIL aqueous solution had the largest absorbing amount, while the viscosity of the 80% DIL aqueous solution was 30 times higher than that of the 40% DIL aqueous solution.

In general, the absorption rate of CO₂ in IL aqueous solutions is mainly influenced by the concentration and viscosity of the solution. High concentration of IL or low viscosity of solution both accelerates the absorption speed. For the IL aqueous solution, the viscosity is dominated by the IL's concentration, and a higher concentration of the IL leads to a higher viscosity of the solution. Therefore, the effect of the IL's concentration on the absorption rate is conflicting. As is displayed in Figure 5, for C₂(N₁₁₄)₂Gly₂, among the three different concentrations, the 40% DIL solution had the highest apparent absorption rate. The apparent absorption rate of the 80% DIL solution was close to that of the 20% solution during the early 6 min. As time went on, the apparent absorption rate of the 80% solution got gradually higher than that of the 20% DIL solution. A possible explanation is that the values of the concentration and viscosity of the 40% DIL aqueous solution were fitter for the absorption. As for the 20% and 80% DIL solutions, concentration played the leading role in the absorption, especially when the absorption time reached over 6 min. Noticeably, the case of C₂(N₁₁₂)₂Gly₂ (see Figure 6) was the same with C₂(N₁₁₄)₂Gly₂.

3.3. Effect of Different Lengths of Alkyl Chain. The absorption of CO₂ in 40% aqueous solutions of C₂(N₁₁₄)₂Gly₂ and C₂(N₁₁₂)₂Gly₂ were compared in Figure 7 and Figure 8, showing that the amount of absorbed CO₂ was a little larger and the uptake rate a little higher for C₂(N₁₁₂)₂Gly₂ aqueous solution than those of C₂(N₁₁₄)₂Gly₂. This could be explained that there were more molecules of C₂(N₁₁₂)₂Gly₂ under the same weight,

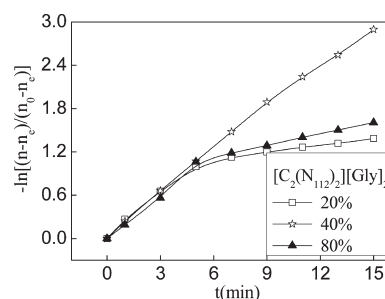
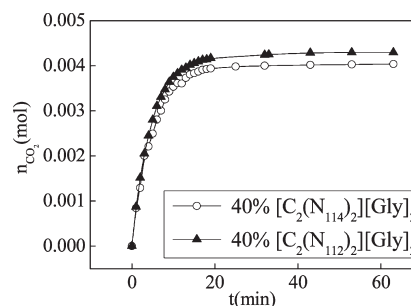
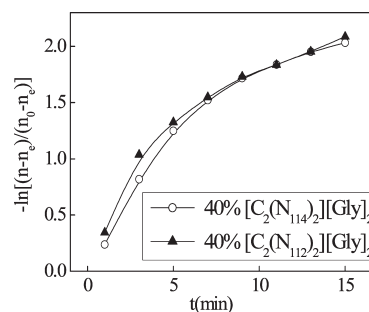
Figure 6. Apparent absorption rates in aqueous solution of C₂(N₁₁₂)₂Gly₂.Figure 7. Absorption of CO₂ in 40% DIL aqueous solution.

Figure 8. Apparent absorption rates of the absorbents.

rising from its lighter molecular weight. As shown in Figure 10, the molar absorption load of CO₂ in the C₂(N₁₁₄)₂Gly₂ aqueous solution was similar to that of the C₂(N₁₁₂)₂Gly₂ aqueous solution. Muldoon et al.²⁸ have reported the influence of alkyl chain length on absorption load. They compared the solubility of CO₂ in [C₈H₄F₁₃mim][Tf₂N] and [C₆H₄F₉mim][Tf₂N] and found that the solubility of CO₂ increased with the rise in the alkyl chain length, but the changes were not obvious.

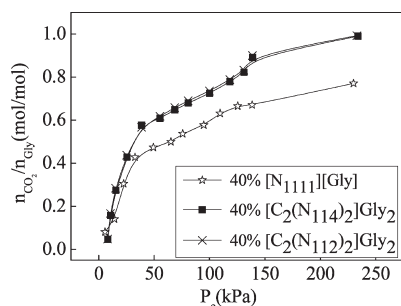


Figure 9. Absorption capacity of CO₂ in 40% ILs aqueous solution.

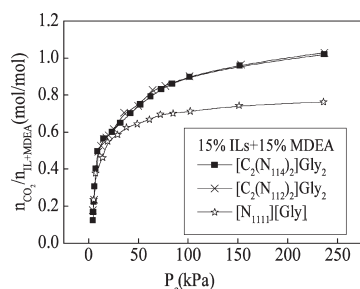


Figure 10. Solubility of CO₂ in 15% ILs + 15% MDEA aqueous solutions.

3.4. Effect of Different Cations on the Absorption Capacity of Aqueous Solutions. Due to the excellent absorption properties of the 40% DIL aqueous solution, its concentration was chosen to investigate the solubility of CO₂ under different pressure. The absorption load of dicationic and monocationic ILs in the 40% aqueous solution were compared in Figure 9. Since the DIL has two anions of glycine, the absorption loads of CO₂ were calculated by per mole anion. The solubility of CO₂ in aqueous solution could approach one mole CO₂ per mole DILs when the pressure is close to 250 kPa. It should be noted that the mole load of [N₁₁₁₁][Gly] aqueous solution was much lower than those of C₂(N₁₁₄)₂Gly₂ and C₂(N₁₁₂)₂Gly₂, indicating the significant influence of cation characteristic on CO₂ absorption in the aqueous solutions. That is, the dication of two positive charge centers could more effectively attract anions which contained the absorbed CO₂, such as RNH₂COO⁻. The absorption load of CO₂ was almost the same in C₂(N₁₁₄)₂Gly₂ and C₂(N₁₁₂)₂Gly₂ aqueous solutions.

3.5. Effect of Different Cations on the Absorption Capacity of Mixed Absorbent. At present, an effective chemical method for CO₂ uptake usually employs aqueous solutions of alkanolamine, including monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), etc. Among them, MDEA of high load performance is mainly used, but the slow absorption rate hindered its application in the industrial process. It has been proved that adding functionalized amino acid ionic liquids into MDEA aqueous solution could significantly improve the absorption performance of MDEA.²⁰ The absorption characteristics of 15% [N₁₁₁₁][Gly] + 15% MDEA aqueous solution have been investigated in detail.^{18,19} In the present work, the absorption characteristics of the DILs + MDEA aqueous solutions were also examined and compared with those of MIL ([N₁₁₁₁][Gly]). As shown in Figure 10, the CO₂ load of all the IL + MDEA solutions increased with the rise in the equilibrium

pressure in the same way. When the pressure was less than 25 kPa, the CO₂ load increased most rapidly with the rising pressure; when the pressure was between 25–100 kPa, the increase of CO₂ load with the pressure was moderate; when the pressure was over 100 kPa, there was only slight increase in CO₂ load with the still rising pressure. Obviously, the absorption performance of CO₂ in these solutions was similar to each other when the pressure was less than 20 kPa. When the pressure reaches over 20 kPa, the CO₂ load of DILs mixtures were higher than that of MIL mixtures and the difference became more noticeable with the further increasing pressure, indicating the potential use of DIL in CO₂ uptake under high pressure. This proved that the charge of ionic liquids had significant influence on the absorption of CO₂. In certain concentration range, CO₂ solubility increases with the rise in the number of electric charges. Practically, according to Schumpe's model,⁴⁵ the physical solubility of gas in solution can be affected by the concentration and the specific parameters of ions.

■ ASSOCIATED CONTENT

S Supporting Information. The results of ¹H NMR, EA, TG, the water content, and the halide concentration of the sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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