

CO₂ CaptureInternational Edition: DOI: 10.1002/anie.201602919
German Edition: DOI: 10.1002/ange.201602919Multi-Molar Absorption of CO₂ by the Activation of Carboxylate Groups in Amino Acid Ionic LiquidsFeng-Feng Chen⁺, Kuan Huang⁺, Yan Zhou, Zi-Qi Tian, Xiang Zhu, Duan-Jian Tao,* De-en Jiang, and Sheng Dai*

Abstract: A new strategy for multi-molar absorption of CO₂ is reported based on activating a carboxylate group in amino acid ionic liquids. It was illustrated that introducing an electron-withdrawing site to amino acid anions could reduce the negative inductive effect of the amino group while simultaneously activating the carboxylate group to interact with CO₂ very efficiently. An extremely high absorption capacity of CO₂ (up to 1.69 mol mol⁻¹) in aminopolycarboxylate-based amino acid ionic liquids was thus achieved. The evidence of spectroscopic investigations and quantum-chemical calculations confirmed the interactions between two kinds of sites in the anion and CO₂ that resulted in superior CO₂ capacities.

The emission of CO₂ from the combustion of fossil fuels has become an urgent issue because of the environmental threats posed by the “greenhouse effect”.^[1] Although current amine scrubbing technology in industry has the advantages of good reactivity, high capacity, and low cost, an inherent drawback is that it produces and releases volatile organic compounds.^[2] Thus, the discovery of new materials that can selectively and efficiently eliminate CO₂ is essential to realize practical carbon capture and sequestration. Ionic liquids (ILs) are the state-of-the-art solvent in this regard because of their unique properties, including extremely low volatility, high thermal stability, virtually unlimited tunability, and excellent affinity with acidic gases.^[3,4]

In light of the chemistry of alkanolamines’ reactivity with CO₂, grafting amine groups to the framework of ILs is a promising method of improving the absorption of CO₂ in

ILs.^[5–7] Davis et al.^[5] reported the first example of amine-functionalized cation-tethered ILs for CO₂ capture, in which 0.5 mol CO₂ per mol of IL could be absorbed through a carbamate mechanism. Brennecke et al.^[7a] further demonstrated that amino acid ILs, whose amine groups are tethered on anions in the vicinity of carboxylate groups, could capture almost 1 mol CO₂ per mol of IL by forming carbamic acid rather than carbamate. Subsequently, some other anion-functionalized ILs—including azolate ILs,^[7e] phenolate ILs,^[7f] methylbenzolate ILs,^[7j] and pyridinolate ILs^[7k]—have been examined as high-capacity absorbents for CO₂. Recently, capture of 2 mol CO₂ per mol of IL was achieved after 24–48 h by amino-functionalized amino acid ILs making use of two amino groups.^[8] However, note particularly that carboxylate groups in amino acid ILs are almost deactivated to interact with CO₂. Generally, a carboxylate anion can complex with CO₂ very efficiently. The dilemma is that the negative inductive effect of an amino group tethered on anions reduces the alkalinity of a carboxylate group. For example, the pK_b of an acetate anion is 9.24, whereas the pK_{b2} of glycinate is 11.66. Thereby, the challenge remains regarding whether a new method of activating carboxylate groups in amino acid ILs to capture CO₂ effectively can be developed.

Herein, we propose a new method to activate carboxylate groups in amino acid ILs to attract CO₂ very efficiently. The essence of our strategy is to reduce the negative inductive effect of amino groups by introducing electron-withdrawing sites to amino acid anions. Thus, robust absorption of CO₂ (up to 1.69 mol CO₂ per mol IL) could be achieved for the first time through multiple-site interactions between amino and carboxylate groups in amino acid anions and CO₂. The chemical structures of five aminopolycarboxylate-based ILs (APC-ILs) designed in this work are shown in Scheme 1. The anions of the APC-ILs could be viewed as N-substituted glycinate. These structures were confirmed by nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and mass spectrometry. The physico-chemical properties were characterized by thermogravimetry-differential scan-

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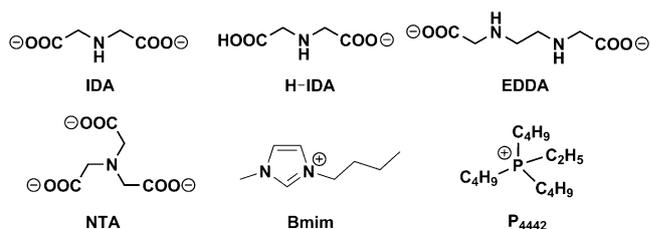
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Scheme 1. Chemical structures of the anion and the cation in aminopolycarboxylate-based ionic liquids.

ning calorimetry (TG-DSC), viscometer, and densimeter. The characterization results are presented in the Supporting Information (Table S1).

We first determined CO₂ absorption in these five APC-ILs in relation to time (Figure 1). Surprisingly, it was seen that two APC-ILs showed very high capacity for CO₂ capture under atmospheric pressure, which is significantly greater than 1:1 stoichiometry. For example, for [P₄₄₄₂]₂[IDA], capture of 1.69 mol CO₂ per mol IL, corresponding to a gravimetric

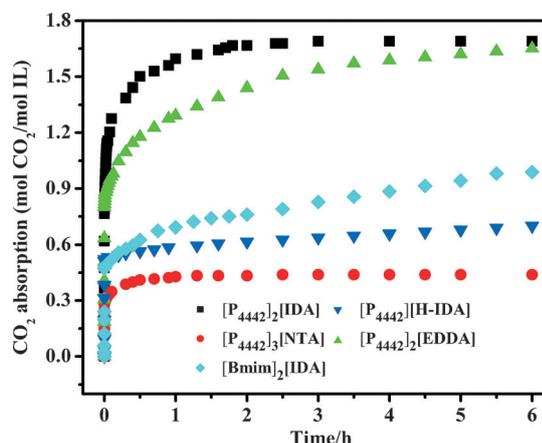


Figure 1. Absorption of CO₂ in the five synthesized APC-ILs over time at 40°C and 1 bar.

capacity of 13 %, was achieved at 40°C and 1 bar. Moreover, the effect of the pressure and the temperature on CO₂ capture by [P₄₄₄₂]₂[IDA] was investigated (Supporting Information, Figure S1). It was seen that CO₂ capacity decreased from 1.69 to 1.33 mol per mol IL when the partial pressure decreased from 1 bar to 0.4 bar. The mole ratio of CO₂ to IL decreased to 1.09 upon increasing the temperature to 80°C. Thus, the captured CO₂ was easy to release by heating or under reduced pressure. The repeated absorption of CO₂ in [P₄₄₄₂]₂[IDA] was carried out at 40°C and 1 bar (Supporting Information, Figure S3). As can be seen, the absorption capacity of CO₂ remained unchanged after five cycles, indicating that this CO₂ capture process by [P₄₄₄₂]₂[IDA] is highly reversible. Also, there was no obvious change in the characteristic bands of IR and NMR spectra between the fresh and reused [P₄₄₄₂]₂[IDA] ILs (Supporting Information, Figures S4–S6), demonstrating that [P₄₄₄₂]₂[IDA] for CO₂ capture is stable enough to be recycled.

Clearly, APC-IL [P₄₄₄₂]₂[IDA] has much higher absorption than traditional amino acid ILs (e.g., 0.52 for [P₄₄₄₂][Gly] and ca. 0.90 for [P₆₆₆₁₄][Pro]) and is also superior to most functionalized ILs and adsorbent materials in terms of CO₂ capacity either in molar ratio or mass ratio (Table 1). As is well known, an amino group tethered on an anion has been proved to be able to complex with equimolar CO₂. Therefore, the solubility of CO₂ in [IDA]-based ILs exceeds the limit of 1 mol mol⁻¹ apparently because carboxylate groups on the [IDA] anion function as additional active sites for attracting CO₂. Obviously, the difference between [IDA] and [Gly] is that only one more acetate group is substituted on the

Table 1: Absorption capacity of CO₂ in APC-ILs and other functionalized ILs under 1 bar.

| Ionic liquid | T [°C] | Solubility [mol/mol] | Solubility [g/g] | Ref. |
|--|--------|----------------------|------------------|------|
| [P ₄₄₄₂] ₂ [IDA] | 40 | 1.69 | 0.13 | – |
| [Bmim] ₂ [IDA] | 40 | 0.99 | 0.11 | – |
| [P ₄₄₄₂][H-IDA] | 40 | 0.70 | 0.08 | – |
| [P ₄₄₄₂] ₃ [NTA] | 40 | 0.44 | 0.02 | – |
| [P ₄₄₄₂] ₂ [EDDA] | 40 | 1.65 | 0.11 | – |
| [P ₄₄₄₂][Gly] | 40 | 0.52 | 0.07 | – |
| [P ₄₄₄₂][Ac] | 40 | 0.30 | 0.05 | – |
| [P ₄₄₄₂][Gly] + [P ₄₄₄₂][Ac] | 40 | 0.82 | – | – |
| [P ₄₄₄₂] ₂ [Oxalate] | 40 | 0.53 | 0.04 | – |
| [P ₆₆₆₁₄][2-Op] | 20 | 1.58 | 0.12 | [7k] |
| <i>i</i> PrNH-GlyNa ^[a] | 25 | 0.91 | – | [7h] |
| [P ₆₆₆₁₄][PhO] | 30 | 0.85 | 0.06 | [7f] |
| [P ₆₆₆₁₄][Im] | 23 | 1.00 | 0.08 | [7e] |
| [MTBDH][TFE] | 23 | 1.13 | 0.19 | [7b] |
| [P ₆₆₆₁₄][Pro] | 22 | ca. 0.9 | 0.07 | [7a] |
| [P ₆₆₆₁₄][2-CNpyr] | 40 | ca. 0.7 | 0.05 | [7g] |
| [aP ₄₄₄₃][Gly] ^[b] | 45 | ca. 1.1 | – | [6c] |
| [APbim][BF ₄] | 25 | ca. 0.5 | 0.08 | [5] |

[a] The absorption was carried out in PEG₁₅₀ solution. [b] The absorption was carried out on SiO₂ supporter.

nitrogen of [IDA] relative to [Gly]. However, the solubility of CO₂ in [P₄₄₄₂]₂[IDA] is still much higher than the sum for [P₄₄₄₂][Gly] (0.52) and [P₄₄₄₂][Ac] (0.30), as presented in Table 1. Therefore, the highly enhanced CO₂ capacity of [IDA]-based ILs cannot be explained simply as a combination of the capacities of amino acid anions and acetate anions.

To illustrate the underlying mechanism, we employed density functional theory calculations at the B3LYP/6-311++G(d,p) level with a Gaussian 09 program^[9] to investigate the interaction of [IDA], [Gly], and [Ac] anions with CO₂ (Figure 2). We found that after the amino group of [Gly] complexed with the first CO₂ ($\Delta H_1 = -68.7$ kJ mol⁻¹), a carbamic acid group was formed, sharing an intramolecular proton with the carboxylate group of [Gly]. That is to say, the shared proton weakened the basicity of the carboxylate group, and the electron-withdrawing amino group tethered in the vicinity of the carboxylate group further robbed its ability to attract CO₂. Thus, the strength of interaction between the carboxylate group of [Gly] and the second CO₂ ($\Delta H_2 = -19.6$ kJ mol⁻¹) was located in a range of weak physical absorption; for example, ΔH for CO₂ + [Bmim][PF₆] is -16.1 kJ mol⁻¹.^[4a] As a result, [Gly] cannot further attract a second CO₂ efficiently, and the limit of CO₂ solubility in amino acid ILs is always 1 mol mol⁻¹. However, comparing [IDA] with [Gly], the substituted acetate group of [IDA] can further interact with a second CO₂ very efficiently ($\Delta H_2 = -52.8$ kJ mol⁻¹) after the amino group complexes with the first CO₂ ($\Delta H_1 = -89.0$ kJ mol⁻¹). This value is much larger than the interaction of a free acetate anion with CO₂ ($\Delta H = -34.2$ kJ mol⁻¹, Supporting Information, Figure S7). More impressively, [IDA] can even attract a third and fourth CO₂ moderately around the carboxylate groups ($\Delta H_3 = -25.4$ kJ mol⁻¹ and $\Delta H_4 = -22.1$ kJ mol⁻¹). These interactions are also larger than the secondary interaction of [Gly] with

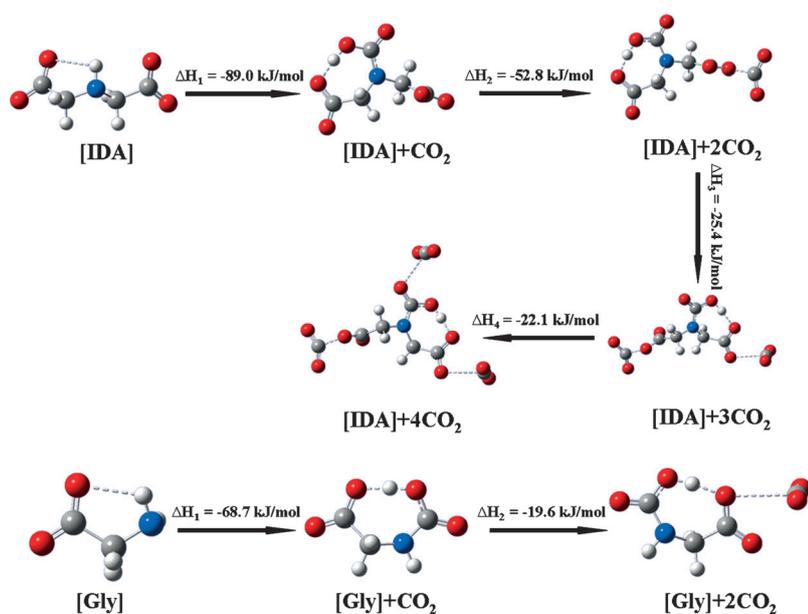


Figure 2. Multiple-site interaction of [IDA] and [Gly] anions with CO₂. O red, N blue, C gray, H white.

CO₂ (−19.6 kJ mol^{−1}). Accordingly, the multiple-site interactions between CO₂ and [IDA] were confirmed by the experimental enthalpy of CO₂ absorption at different absorption capacities, which is determined from the isotherms of CO₂ absorption (Supporting Information, Figure S2). Thus we believe there must be a positive cooperative effect between the substituted acetate group and the amino group of [IDA], resulting in the significant increase in CO₂ capacity.

Thereafter, we calculated the natural bond orbital (NBO) atomic charges of nitrogen, oxygen, and hydrogen in the anion, and the complex of the anion with CO₂. As shown in Figure 3, the proton shared by the carboxylate and carbamic acid in the complex possessed much more positive charge than that in the amine group, leading to the deactivated carboxylate group. We can estimate the CO₂ affinity of each carboxylate group from the absolute value of the sum of NBO charges of the two oxygen atoms, which is termed as |ΣeO|. [10] Larger |ΣeO| relates to a more negative charge distribution of the carboxylate group and stronger interaction with

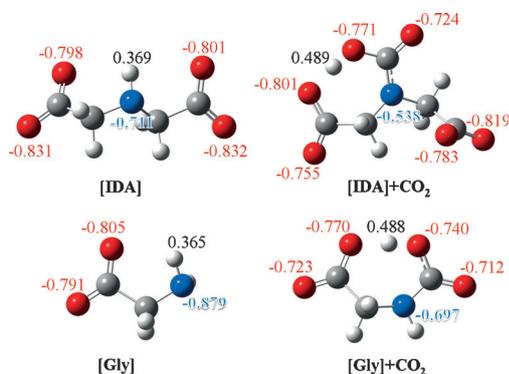


Figure 3. The NBO atomic charges of nitrogen, oxygen, and hydrogen in the anion, and the complex of the anion with CO₂ (blue N, red O, white H).

CO₂. In [Gly], |ΣeO| is 1.596|e|. After complexing with CO₂, it decreased by 0.103|e|, which was close to the increased positive charge of the proton (0.123|e|). The reduced negative charges of oxygen atoms weakened the affinity of the carboxylate with CO₂. Similarly, the shared proton in the [IDA]+CO₂ complex also resulted in the |ΣeO| of one carboxylate group decreasing from 1.629|e| to 1.556|e|. But the other carboxylate group was influenced insignificantly; therefore it could still complex with one more CO₂. Moreover, the NBO atomic negative charges of the nitrogen atoms in [IDA] and of the complex of [IDA]+CO₂ decreased significantly compared with those in [Gly] and the complex of [Gly]+CO₂, respectively. More negative charges coming from the nitrogen atoms concentrated on the oxygen atoms in [IDA] and the complex of [IDA]+CO₂. This shows that introducing an electron-withdrawing substituted acetate group can effectively reduce the negative inductive effect of an amino group in [IDA], thereby leading to an

enhanced interaction between the carboxylate group in [IDA] and CO₂. Hence, unlike the deactivated carboxylate group in [Gly], the carboxylate groups in [IDA] are activated to attract CO₂ very efficiently, which enables [IDA] to have multiple-site interactions with CO₂.

The multiple-site interaction between [IDA] and CO₂ was further verified by Fourier transform infrared (FTIR) and ¹³C NMR spectroscopy (Figure 4). In the IR spectrum, the N–H stretch of [IDA] (observed at 3347 cm^{−1}) disappeared after CO₂ absorption. Simultaneously, two new characteristic peaks were observed at 1630 cm^{−1} and 1423 cm^{−1}, which can be assigned to the asymmetrical stretching vibration of carbamic acid in the NH–CO₂ interaction and the carbonate ion in the O–CO₂ interaction, respectively. In contrast, only one new peak appeared at 1689 cm^{−1}, which corresponds to carbamic acid after CO₂ absorption by [P₆₆₆₁₄][Pro]. [7a] Furthermore, it is seen in Figure 4b that one new signal in the ¹³C NMR spectra at δ = 160.2 ppm appeared when [IDA] captured 0.8 mol CO₂ per mol IL, which is clearly indicative of carbamic acid formation between NH and CO₂. Subsequently, after 1.69 mol CO₂ uptake per mol IL, two new resonances were observed at δ = 156.8 and 163.5 ppm, respectively. The first new peak at δ = 163.5 ppm could likewise be assigned to carbamate carbonyl carbon atom. The second new resonance at δ = 156.8 ppm was attributed to the secondarily captured CO₂, which was thought to form a carbonate anion as a result of the strong interaction of CO₂ with the carboxylate group in [IDA]. Accordingly, the resonance of carboxylate carbons in [IDA] at δ = 171.8 ppm split into two peaks at δ = 169.2 and 174.4 ppm because of the different chemical environments after one of the carboxylate groups in [IDA] captured a second CO₂. Therefore, on the basis of previous reports [7] and the observed product, a plausible mechanism of CO₂ absorption by [IDA] can be proposed (Scheme 2), which exhibits a two-site interaction between [IDA] and CO₂.

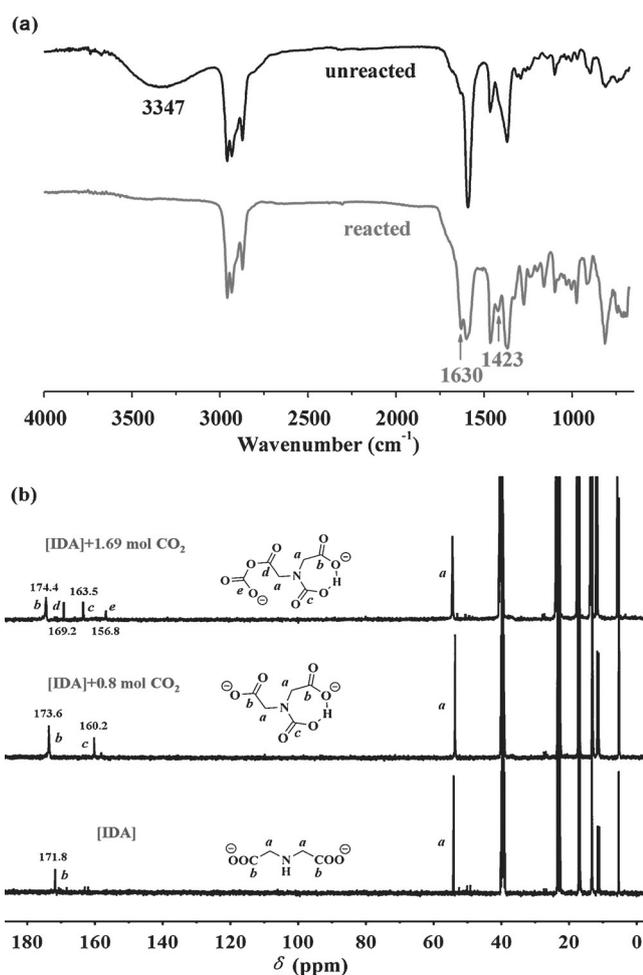
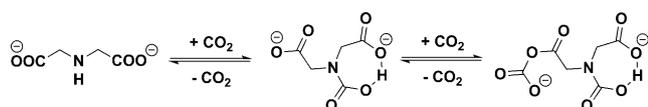


Figure 4. a) FTIR and b) ^{13}C NMR spectra of APC-IL $[\text{P}_{4442}]_2[\text{IDA}]$ before and after the capture of CO_2 .

On the basis of these results, another APC-IL $[\text{P}_{4442}]_2\text{-}[\text{EDDA}]$ also had a very high CO_2 capture capacity (1.65 mol CO_2 per mol IL). Its multiple-site interactions with CO_2 are shown in Figure S8 in the Supporting Information. However, for $[\text{P}_{4442}][\text{H-IDA}]$ —in which an acetic acid group, not an acetate group, was substituted on the nitrogen of the amino group—absorption capacity for CO_2 was only 0.70, similar to that of $[\text{P}_{66614}][\text{Pro}]$. The binding energies of $[\text{H-IDA}]$ with the first and second CO_2 were -39.4 and -13.7 kJ mol $^{-1}$, respectively (Supporting Information, Figure S9). The NBO charges calculations indicated that after the uptake of the first CO_2 , $|\Sigma e\text{O}|$ of the acetic acid group in the complex of $[\text{H-IDA}] + \text{CO}_2$ decreased significantly from $1.506|e|$ to $1.306|e|$ because of the formation of intramolecular hydrogen bonds (Supporting Information, Figure S10), so that the acetic acid



Scheme 2. The proposed mechanism of CO_2 absorption by $[\text{P}_{4442}]_2[\text{IDA}]$ through multiple-site interactions.

group in $[\text{H-IDA}]$ cannot capture a second CO_2 efficiently. $[\text{P}_{4442}]_3[\text{NTA}]$ also showed a relatively low CO_2 absorption capacity (0.44 mol CO_2 per mol IL) because of the lack of proton in the tertiary amine group. In addition, $[\text{Bmim}]_2\text{-}[\text{IDA}]$, which has the same anion of $[\text{IDA}]$ as that of $[\text{P}_{4442}]_2[\text{IDA}]$, exhibited the absorption capacity of only 0.99 mol CO_2 per mol IL. This is attributed to the difference caused by CO_2 absorption in viscosities. It was seen that the viscosity of $[\text{Bmim}]_2[\text{IDA}]$ increased significantly from 627.7 cp to 17346 cp after the capture of CO_2 , whereas the viscosity of $[\text{P}_{4442}]_2[\text{IDA}]$ increased only to 961.6 cp upon complexation (Supporting Information, Tables S2,S3). For $[\text{P}_{4442}]_2[\text{IDA}]$, it is difficult to form the intermolecular hydrogen-bonded network because of the absence of any acidic proton in the cation $[\text{P}_{4442}]$. In contrast, the C2-H of $[\text{Bmim}]$ could form strong intermolecular hydrogen bonding with carbamic acid after the capture of CO_2 and result in the dramatic increase in viscosity, thus leading to a lower CO_2 capacity.^[7e,11]

In summary, we have introduced a new strategy for multi-molar absorption of CO_2 by activating a carboxylate group in APC-ILs. Thus, extremely high CO_2 capacities (up to 1.69 mol CO_2 per mol IL) were achieved through multiple-site interactions between the amino group and carboxylate group in APC-ILs. Quantum-chemical calculations and spectroscopic investigations show that the reduction of the negative inductive effect of amino groups in APC-ILs can stimulate the carboxylate group to attract CO_2 very efficiently, resulting in a significant increase in CO_2 capacity. We believe that this highly efficient and reversible process by APC-ILs has great potential for the capture of CO_2 .

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