

Article

CO₂ Absorption Mechanism by Diamino Protic Ionic Liquids (DPILs) Containing Azolide Anions

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Abstract: Protic ionic liquids have been regarded as promising materials to capture CO₂, because they can be easily synthesized with an attractive capacity. In this work, we studied the CO₂ absorption mechanism by protic ionic liquids (ILs) composed of diamino protic cations and azolide anions. Results of ¹H nuclear magnetic resonance (NMR), ¹³C NMR, 2-D NMR and fourier-transform infrared (FTIR) spectroscopy tests indicated that CO₂ reacted with the cations rather than with the anions. The possible reaction pathway between CO₂ and azolide-based protic ILs is proposed, in which CO₂ reacts with the primary amine group generated from the deprotonation of the cation by the azolide anion.

Keywords: absorption; carbon dioxide; protic ionic liquids; azoles; water lean; insights



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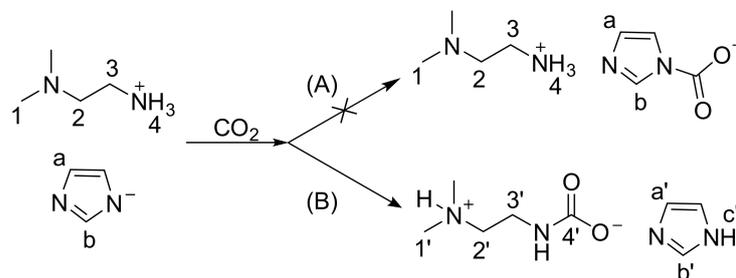
1. Introduction

In recent decades, the amount of carbon dioxide (CO₂) accumulated in the air has reached unbelievable levels, which is viewed as the main contributor to global warming, causing severe environmental problems, such as the rising atmospheric temperature, intense heat waves and drought. The vast majority of atmospheric CO₂ is mainly emitted from industrial activities by burning fossil fuels (coal and oil) to produce electricity [1]. An urgent demand to curb the atmospheric CO₂ concentration to avoid climate disaster has driven industry and the scientific community to explore efficient CO₂ capture technologies. A current, popular method used for CO₂ capture in industry is the amine-based scrubbing process, which mainly utilizes an aqueous solution of alkanolamine to chemically absorb CO₂ [2]. However, amine-based sorption systems have several drawbacks, such as high solvent volatility and equipment corrosion and a high energy penalty of absorbent regeneration [3]. Developing new and efficient sorption systems capable of addressing the above-mentioned drawbacks is one of the main challenges in the field of carbon capture and storage.

During the past decade, ionic liquids have been widely studied for CO₂ capture because of their attractive properties [4], such as negligible vapor pressure, high thermal stability, and tunable structures [5,6]. Among the ILs used for CO₂ absorption, aprotic ILs [7–9], such as azolide-based [10] and hydroxypyridine-based ILs [11], exhibit high CO₂ capacity. However, tedious procedures are needed to synthesize these aprotic ILs, resulting in high costs. Recently, protic ILs [12–14] have been investigated to capture CO₂ because they can be easily prepared and exhibit promising capacity.

In a recent article, Oncsik and co-authors reported on CO₂ capture by diamino protic ionic liquids (DPILs) formed by N,N-dimethylethylenediamine (DMEDA) with azoles, including imidazole (Im), 1,2,4-triazole (Tz) and pyrazole (Py). These DPILs showed a high gravimetric absorption capacity for CO₂ [15]. The authors also investigated CO₂ absorption mechanisms of these DPILs. On the basis of NMR and FTIR results, they believed that CO₂ reacted with anions, forming carbamate species, and CO₂ did not react with the diamino

cations. However, in contrast, we found that CO_2 reacted with the cations rather than with the azolide anions when CO_2 was captured by these DPILs (Scheme 1). The details are presented in the following sections.



Scheme 1. The reaction between [DMEDAH] [Im] and CO_2 .

2. Results and Discussion

Primarily, the CO_2 capacities of the protic ILs were investigated. [DMEDAH] [Py], [DMEDAH] [Im] and [DMEDAH] [Tz] could capture 0.231(0.82), 0.216 (0.77) and 0.190 (0.68) g CO_2 /g IL at 22 °C and 1.0 atm, respectively. The values in parentheses are the molar absorption capacities of ILs (mol CO_2 / mol IL). The capacities of these ILs were close to the values reported by Oncsik et al. (Table S1), suggesting that the protic ILs used in our study were successfully prepared. The absorption capacity of DMEDA was determined by using the DMEDA solution in sulfolane (30 wt.%). One mole of DMEDA could capture 0.90 mole of CO_2 at 1.0 atm and 22 °C. Moreover, the structure of the IL was further studied using NMR spectra. As shown in Figure 1A, the hydrogen peak of $-\text{NH}_3$ (H-4) can be clearly identified in the ^1H NMR spectra of [DMEDAH] [Im], and there was no N–H peak of imidazole in the spectra. The $-\text{NH}_2$ peak of DMEDA was also completely missing from the ^1H NMR spectra of [DMEDAH] [Im]. The ^1H NMR results again suggested that the IL [DMEDAH] [Im] was successfully obtained.

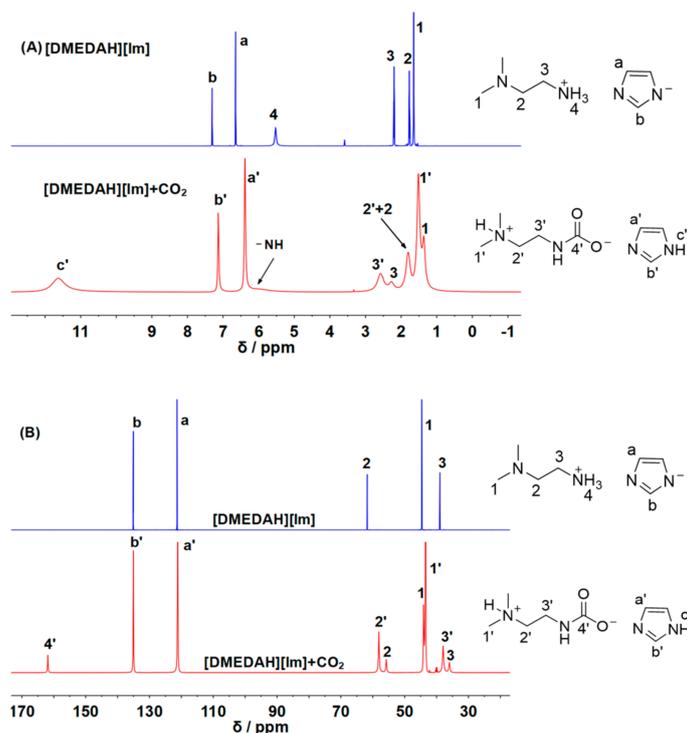


Figure 1. Spectra of ^1H (A) and ^{13}C (B) NMR of [DMEDAH] [Im] with and without CO_2 ; $\text{DMSO}-d_6$ was used as an external solvent.

In order to study the absorption mechanism, we investigated the ^1H NMR and ^{13}C NMR spectra of [DMEDAH] [Im] before and after CO_2 absorption. As shown in Figure 1A, there were several new peaks (H-1', H-3', and H-c') in the ^1H NMR spectrum after CO_2 absorption. H-c' (11.6 ppm) was the N-H hydrogen on the imidazole ring (Figure S1). Additionally, four new peaks (C-1', C-2', C-3', and C-4') can be observed in the ^{13}C NMR spectrum after CO_2 absorption. C-4' (161.9 ppm) was the peak of carbamate carbon [16,17]. The new peaks in the ^1H NMR (H-1', H-2', and H-3') (Figure S2A) and ^{13}C NMR (C-1', C-2', C-3', and C-4') (Figure S2B) spectra after CO_2 absorption were more obvious when deuterium oxide (D_2O) was used as the internal solvent to record the NMR spectra.

It would be difficult to explain these new peaks if CO_2 only reacted with the anion $[\text{Im}]^-$; thus, the ^1H - ^{13}C Heteronuclear Singular Quantum Correlation (HSQC) spectra (Figure 2) and ^1H - ^{13}C Heteronuclear Multiple Bond Correlation (HMBC) spectra (Figure 3) of [DMEDAH] [Im] after CO_2 absorption were studied in order to identify these new peaks. As can be seen in Figure 2A, H-1' was attached to C-1', H-2' was attached to C-2', and H-3' was attached to C-3'. As shown in Figure 3A, H-3' correlated with C-4' and C-2', and H-2' correlated with C-1' and C-3'. The correlation between H-3' and C-4' indicated that CO_2 was attached to the primary nitrogen in the cation. Furthermore, there were no correlations between C-4' and the hydrogen (H-a' or H-b') on the imidazole ring (Figure 3B), indicating that CO_2 did not react with the anion to form carbamate species. The similar new peaks can also be found in the NMR spectra of [DMEDAH] [Py] (Figure S3) and [DMEDAH] [Tz] (Figure S4) after CO_2 absorption. In the ^1H - ^{13}C HMBC spectra of [DMEDAH] [Py] (Figure S5) and [DMEDAH] [Tz] (Figure S6) after CO_2 absorption, correlation between H-3' and C-4' can also be observed, which again suggested that CO_2 was attached to the cation.

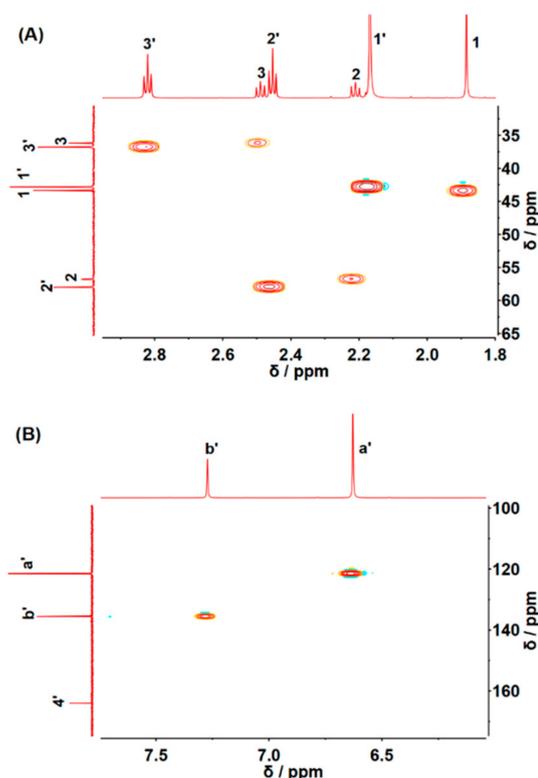


Figure 2. The ^1H - ^{13}C HSQC spectra of [DMEDAH] [Im] after CO_2 capture (A,B); D_2O was used as the internal solvent to record the spectra.

In order to further confirm the mechanism, the FTIR spectra of [DMEDAH] [Im] with and without CO_2 were investigated. As can be seen in Figure 4, a new peak at 1676 cm^{-1} , attributed to the C=O stretching of the carbamate, could be identified after CO_2 absorption. However, the C=O stretching peak of the carbamate formed by the reaction between $[\text{Im}]^-$

and CO_2 was near 1700 cm^{-1} [18,19]. Therefore, the peak at 1676 cm^{-1} implied that CO_2 was attached to the amino group in the cation and not attached to the anion $[\text{Im}]^-$. The N–H band related to $[\text{DMEDAH}]^+$ at 1584 cm^{-1} shifted to 1575 cm^{-1} after CO_2 absorption. The stretching vibration of N– COO^- could be observed at 1310 cm^{-1} after the reaction, which was different from the N– COO^- stretching band ($\sim 1293\text{ cm}^{-1}$) of the carbamate formed by the anion $[\text{Im}]^-$ and CO_2 [18]. These results again confirmed the interaction between CO_2 and the $[\text{DMEDAH}]^+$. Furthermore, we also studied the FTIR spectra of DMEDA solution (30 wt.%) in sulfolane (Sulf) before and after CO_2 uptake. As shown in Figure 5, an obvious peak at 1679 cm^{-1} can be observed after CO_2 uptake, which was the C=O stretching peak of the carbamate formed by CO_2 and the amino group of the DMEDA, indicating that the peak at 1676 cm^{-1} of the $[\text{DMEDAH}][\text{Im}] + \text{CO}_2$ system was from the DMEDA-based carbamate. These FTIR results again indicated that CO_2 reacted with the cation rather than the anion of $[\text{DMEDAH}][\text{Im}]$.

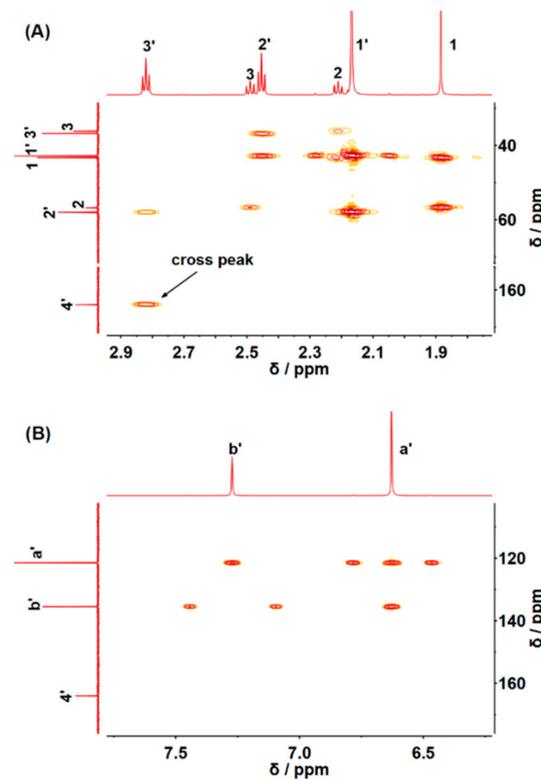


Figure 3. The ^1H - ^{13}C HMBC spectra of $[\text{DMEDAH}][\text{Im}]$ after CO_2 capture (A,B); D_2O was used as the internal solvent to record the spectra.

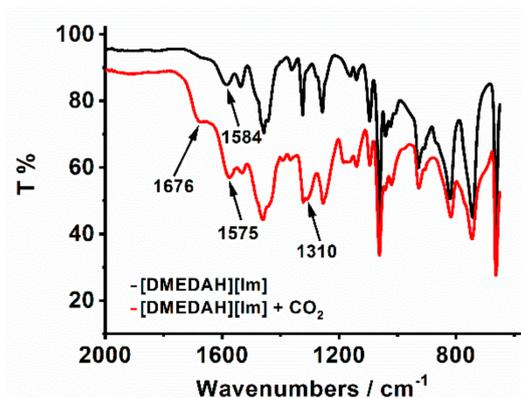


Figure 4. The FTIR spectra of $[\text{DMEDAH}][\text{Im}]$ before and after CO_2 absorption.

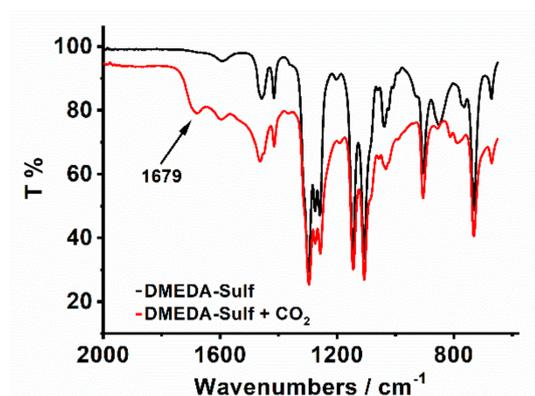
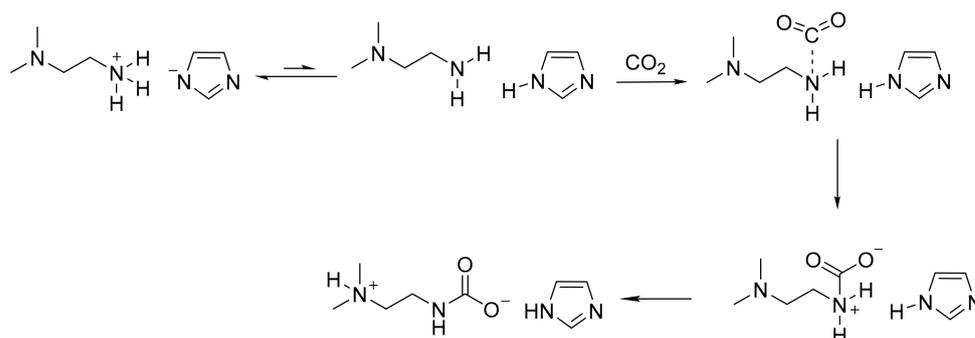


Figure 5. The FTIR spectra of DMEDA solution (30 wt.%) in sulfolane (Sulf) before and after CO₂ absorption.

The possible reaction pathway between CO₂ and [DMEDAH] [Im] is shown in Scheme 2. At first, there was an acid–base reaction between the cation and the anion in the ILs. The cation was deprotonated by the imidazolite anion, generating an amino group. When the absorbent interacted with CO₂, the final product was formed through nucleophilic addition of the amino group to CO₂ [20,21].



Scheme 2. The possible reaction pathway between CO₂ and [DMEDAH] [Im].

3. Materials and Methods

3.1. Material and Characterizations

Imidazole (Im, 98%), 1,2,4-Triazole (Tz, 98%), Pyrazole (Pz, 98%) and N,N-dimethylethylenediamine (DMEDA) (99%) were purchased from J&K Scientific Ltd. (Beijing, China). CO₂ ($\geq 99.99\%$) was obtained from Beijing ZG Special Gases Sci. and Tech. Co. Ltd. The ¹H NMR (600 MHz) and ¹³C NMR (151 MHz) spectra were recorded on a Bruker spectrometer with a 5 mm PABBO probe. A PerkinElmer Frontier spectrometer was used to record the FTIR spectra of the samples in the range of 650–4000 cm⁻¹ with a resolution of 4 cm⁻¹. Elemental analysis was conducted on Elemental Vario EL cube (Frankfurt, Germany).

3.2. Synthesis of Ionic Liquids

DMEDA and azole (1:1, molar ratio) were mixed in a glass vial. Each mixture was stirred at room temperature for 2 h to obtain a homogenous liquid.

Elemental analysis:

[DMEDAH] [Im]: found C 53.14%, H 10.02%, N 35.13%; estimated C 53.82%, H 10.32%, N 35.86%.

3.3. CO₂ Absorption

An ionic liquid (~1.0 g) was added to a glass tube with a diameter of 10 mm. The tube was equipped with a rubber lid and two needles. One needle was a CO₂ inlet, and

the other one was a CO₂ outlet. The glass tube was partially immersed in a water bath (22 ± 0.2 °C). CO₂ was bubbled into the IL through a needle at a flow rate of ~50 mL/min for 60 min. The weight of the tube was measured every 10 min with an analytical balance (±0.1 mg). The mass increase was attributed to the CO₂ captured by the IL.

4. Conclusions

In summary, the CO₂ absorption mechanism by the protic azolide ILs based on DMEDA has carefully been studied through various NMR and FTIR experiments. The results indicated that CO₂ reacted with the cations rather than with the azolide anions. We believe that the confirmation of the absorption mechanism is very important to the design of protic ILs in the future for CO₂ capture and utilization.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/pr9061023/s1>, Table S1: CO₂ capacities by DPILs, Figure S1: ¹H NMR spectra of imidazole in DMSO-*d*₆, Figure S2: ¹H (A) and ¹³C (B) NMR spectra of [DMEDAH] [Im] after CO₂ absorption; D₂O was used as the internal solvent to record the spectra, Figure S3: ¹H (A) and ¹³C (B) NMR spectra of [DMEDAH] [Py] before and after CO₂ absorption; DMSO-*D*₆ was used as the external solvent, Figure S4: ¹H (A) and ¹³C (B) NMR spectra of [DMEDAH] [Tz] before and after CO₂ absorption; DMSO-*D*₆ was used as the external solvent, Figure S5: The ¹H-¹³C HMBC spectra of [DMEDAH] [Py] after CO₂ capture; D₂O was used as the internal solvent to record the spectra, Figure S6: The ¹H-¹³C HMBC spectra of [DMEDAH] [Tz] after CO₂ capture; D₂O was used as the internal solvent to record the spectra.

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Sample Availability: Samples of the compounds are available from the authors.

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