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# CO<sub>2</sub> capture by imidazolium-based deep eutectic solvents: the effect of steric hindrance of N-heterocyclic carbenes†

Mingzhe Chen, Yi Zhou, Qing Lu and Dezhong Yang \*

**CO<sub>2</sub> capture by deep eutectic solvents (DESs) formed between 1,3-bis(isopropyl)imidazolium 1,2,4-triazolide ([IiPim][Triz]) and ethylene glycol (EG) is investigated in this study. [IiPim][Triz]-EG DESs exhibit a capacity of ~1.0 mol CO<sub>2</sub> per mol DES at 1.0 atm and 25 °C. Surprisingly, mechanistic results disclose that CO<sub>2</sub> reacts with EG but does not bind with the C-2 site of the [IiPim]<sup>+</sup> cation, which may be due to the high steric hindrance of the C-2 site of the N-heterocyclic carbene IiPim present in [IiPim][Triz]-EG DESs.**

The climate change mainly caused by the unexpected amount of anthropogenic greenhouse gas emissions has been a global critical issue. As the major component of greenhouse, CO<sub>2</sub> is mainly emitted from the combustion of fossil fuels. Reducing CO<sub>2</sub> emissions plays a key role in mitigating climate change and preventing detrimental effects of CO<sub>2</sub> on ecosystems.<sup>1</sup> Carbon capture technology is one of the most promising methods to curb CO<sub>2</sub> emissions, and various carbon capture technologies have been developed. The current benchmark industrial technology for carbon capture is the amine-based process using aqueous alkanolamines as absorbents.<sup>2</sup> Nevertheless, this method suffers from inherent shortcomings, including degradation of amines and intensive energy cost for regenerating absorbents.<sup>3</sup>

In the past decade, deep eutectic solvents (DESs) have drawn a great deal of interest because of their unique characteristics, such as low volatility, easy synthesis procedures, and tunable structures.<sup>4</sup> Most DESs are formed by combining hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) due to the intermolecular hydrogen bonds between HBAs and HBDs.<sup>5</sup> The applications of DESs have been explored in various fields,<sup>6,7</sup> and DESs are also emerging as promising candidates for CO<sub>2</sub> capture.<sup>8–10</sup> DESs which capture CO<sub>2</sub> only through physical interactions are called physical-based DESs,<sup>11–14</sup> such as DESs

formed by ammonium/phosphonium halide salts as HBAs and alcohols or carboxylic acids as HBDs.<sup>15–18</sup> The CO<sub>2</sub> capacity of physical-based DESs is low because of the weak interactions between CO<sub>2</sub> and solvents. With the aim of improving the CO<sub>2</sub> capacity of DESs, chemical-based or functionalized DESs are developed, which can chemically capture CO<sub>2</sub> through reactions between CO<sub>2</sub> and components of the DESs.<sup>19</sup> Most of the chemical-based DESs are synthesized by introducing amino groups or basic anions into components of DESs. The DESs containing amino groups can chemically capture CO<sub>2</sub> by forming carbamate species.<sup>20–24</sup> Anion-functionalized DESs exhibit promising chemisorption performances for CO<sub>2</sub>,<sup>25–28</sup> such as azolide-based DESs<sup>29,30</sup> and phenolate-based DESs.<sup>31,32</sup> The CO<sub>2</sub> capture mechanisms of anion-functionalized DESs present various reaction pathways depending on the structures of the components of the DESs.<sup>8</sup>

Chemical-based DESs containing imidazolium ionic liquids are also used for carbon capture. The C-2 site of the imidazolium cation can be deprotonated by basic anions to form N-heterocyclic carbene (NHC), which can react with CO<sub>2</sub> resulting in the formation of carboxylate species.<sup>33,34</sup> Zhang *et al.* reported CO<sub>2</sub> capture by DES DBN-BmimCl-Im (DBN: 1,5-diazabicyclo[4.3.0]non-5-ene; BmimCl: 1-butyl-3-methylimidazolium chloride; Im: imidazole), and the results suggest that the Bmim carbene formed through the deprotonation of Bmim<sup>+</sup> by the imidazolate anion [Im]<sup>−</sup> reacts with CO<sub>2</sub>.<sup>35</sup> Lee *et al.* investigated CO<sub>2</sub> capture by DESs composed of an imidazolium ionic liquid [Emim][2-CNpyr] ([Emim][2-CNpyr]: 1-ethyl-3-methylimidazolium 2-cyanopyrrolide) and ethylene glycol (EG), and the Emim carbene present in [Emim][2-CNpyr]-EG DESs is also found to bind with CO<sub>2</sub>.<sup>36</sup>

Herein, we investigate CO<sub>2</sub> capture by DESs consisting of EG and 1,3-bis(isopropyl)imidazolium 1,2,4-triazolide ([IiPim][Triz]) to gauge the role of the steric hindrance of the C-2 site of imidazolium cations. Interestingly, the mechanistic studies disclose that CO<sub>2</sub> is not attached to the C-2 site of the [IiPim]<sup>+</sup> cation present in DESs, which may be due to the high steric hindrance of the IiPim carbene (IiPim: 1,3-bis(isopropyl)imidazol-2-ylidene). These findings of our work may provide deep insights into the

School of Science, China University of Geosciences, Beijing 100083, China.  
E-mail: yangdz@cugb.edu.cn

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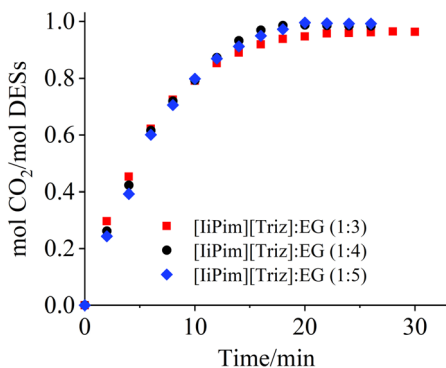


Fig. 1 CO<sub>2</sub> absorption by [IiPim][Triz]-EG DESs at 25 °C and 1.0 atm.

structure effect of components on CO<sub>2</sub> absorption by imidazolium-based DESs.

Fig. 1 presents CO<sub>2</sub> capture by DESs [IiPim][Triz]-EG. [IiPim][Triz]:EG (1:3), (1:4), and (1:5) could capture 0.96, 0.98, and 0.99 mol CO<sub>2</sub> per mol DES, respectively. As reported in the literature, the carbene derived from the [Emim]<sup>+</sup> cation in [Emim][2-CNpyr]-EG DESs can react with CO<sub>2</sub> to form a carboxylate Emim<sup>+</sup>-COO<sup>-</sup>.<sup>36</sup> Similarly, in [IiPim][Triz]-EG solvents, the acid-base reaction between the cation [IiPim]<sup>+</sup> and the anion [Triz]<sup>-</sup> can also form a carbene IiPim. Therefore, it is reasonable if one assumes that the carbene IiPim present in [IiPim][Triz]-EG can also react with CO<sub>2</sub> to form a carboxylate species. Unexpectedly, mechanism results of [IiPim][Triz]-EG with and without CO<sub>2</sub> indicate that the carbene IiPim in DESs does not react with CO<sub>2</sub>, which is shown in the following sections.

The reaction between CO<sub>2</sub> and [IiPim][Triz] was first studied using nuclear magnetic resonance (NMR) spectra. [IiPim][Triz] is solid at room temperature, so the interactions between [IiPim][Triz] and CO<sub>2</sub> are studied in DMSO-*d*<sub>6</sub> solvent. As shown in Fig. 2a, after capture, the hydrogen peaks related to the IiPim<sup>+</sup>-COO<sup>-</sup> carboxylate can be observed, which are at 7.86 (H-4'), 5.29 (H-6'), and 1.41 (H-7') ppm. The carbon peaks (Fig. 2b) related to the IiPim<sup>+</sup>-COO<sup>-</sup> carboxylate are found at 142.2 (C-2'), 117.9 (C-4'), 50.6 (C-6') and 155.3 (C-d') ppm. The C-d' peak is the carbonyl carbon of the IiPim<sup>+</sup>-COO<sup>-</sup> carboxylate. Moreover, the carbonyl carbon of [Triz]-based carbamate is found at 144.2 (C-9) ppm.<sup>36,37</sup> These new hydrogen and carbon peaks detected in the [IiPim][Triz] + CO<sub>2</sub> system suggest that CO<sub>2</sub> reacts with both the IiPim carbene and [Triz]<sup>-</sup> anion present in IL [IiPim][Triz].

The NMR results of the [IiPim][Triz]:EG (1:3) system are shown in Fig. 3. In the <sup>1</sup>H NMR spectra (Fig. 3a), new peaks at 3.51 (H-b) and 3.80 (H-c) ppm can be found, and the proton (H-8) of the [Triz]<sup>-</sup> shifts downfield from 7.80 to 8.19 ppm upon CO<sub>2</sub> absorption. In the <sup>13</sup>C NMR spectra (Fig. 3b), there are new peaks at 61.0 (C-b), 66.2 (C-c), and 157.7 (C-d) ppm. These new hydrogen and carbon signals are attributed to the hydrogens and carbons of the EG-based carbonate species,<sup>25,27</sup> demonstrating that CO<sub>2</sub> reacts with EG in the [IiPim][Triz]:EG (1:3) solvent. The C-d signal is ascribed to the carbonyl carbon of O-COO<sup>-</sup>.<sup>29,36</sup> Importantly, the hydrogen or carbon peaks related to the carboxylate IiPim<sup>+</sup>-COO<sup>-</sup> are not detected in the NMR

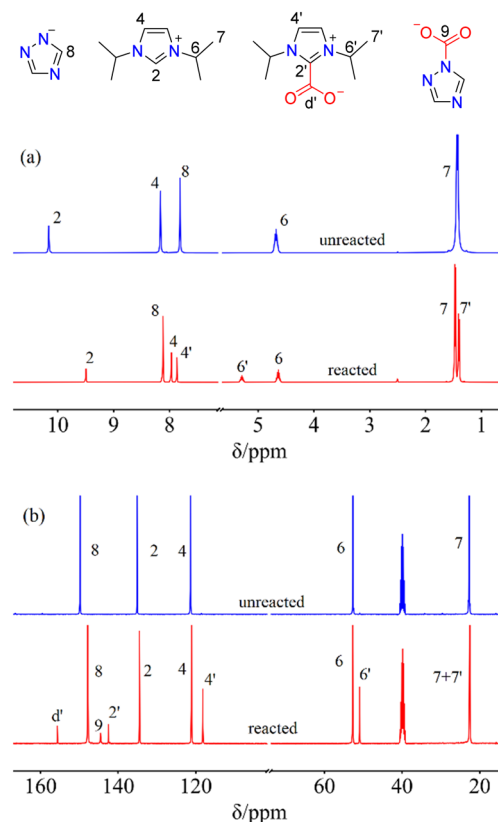


Fig. 2 The <sup>1</sup>H (a) and <sup>13</sup>C (b) NMR spectra of [IiPim][Triz] in DMSO-*d*<sub>6</sub> with and without CO<sub>2</sub>.

spectra of [IiPim][Triz]:EG (1:3) after CO<sub>2</sub> capture, and the carbonyl carbon of [Triz]-based carbamate is also not observed. Similarly, in the NMR spectra of the [IiPim][Triz]:EG (1:4) (Fig. S1, ESI<sup>†</sup>) and [IiPim][Triz]:EG (1:5) (Fig. S2, ESI<sup>†</sup>) systems after CO<sub>2</sub> uptake, the peaks of carboxylate and carbamate species are also not observed. Therefore, the above NMR results confirm that the IiPim carbene in [IiPim][Triz]-EG DESs does not react with CO<sub>2</sub>.

Fourier transform infrared (FTIR) spectroscopy is also used to study interactions between CO<sub>2</sub> and [IiPim][Triz]-based absorbents. Fig. 4 presents the FTIR spectra of the DMSO-*d*<sub>6</sub> solution of [IiPim][Triz] before and after CO<sub>2</sub> capture. New peaks at 1738, 1665, and 1273 cm<sup>-1</sup> can be clearly seen. The peak at 1738 cm<sup>-1</sup> is ascribed to the asymmetrical stretching band of the COO<sup>-</sup> group of [Triz]-based carbamate,<sup>38,39</sup> while the peak at 1665 cm<sup>-1</sup> is the asymmetrical stretching band of the COO<sup>-</sup> group of carbene-based carboxylate.<sup>40</sup> These two peaks again reveal that CO<sub>2</sub> is attached to both the anion [Triz]<sup>-</sup> and the cation [IiPim]<sup>+</sup> present in IL [IiPim][Triz]. The peak that falls at around 1273 cm<sup>-1</sup> can be attributed to the combination band of the ring stretching and N-H bending of 1,2,4-triazole,<sup>41,42</sup> which can be observed as well in the spectra of 1,2,4-triazole (Fig. S3, ESI<sup>†</sup>). The FTIR spectra of [IiPim][Triz]:EG (1:3) before and after capture are seen in Fig. 5. The new peak at 1638 cm<sup>-1</sup> is attributed to the -COO<sup>-</sup> asymmetrical stretching of EG-based carbonate, and the peak appearing at 1285 cm<sup>-1</sup> is the O-COO<sup>-</sup> stretching band.<sup>25,27,29,36</sup> The

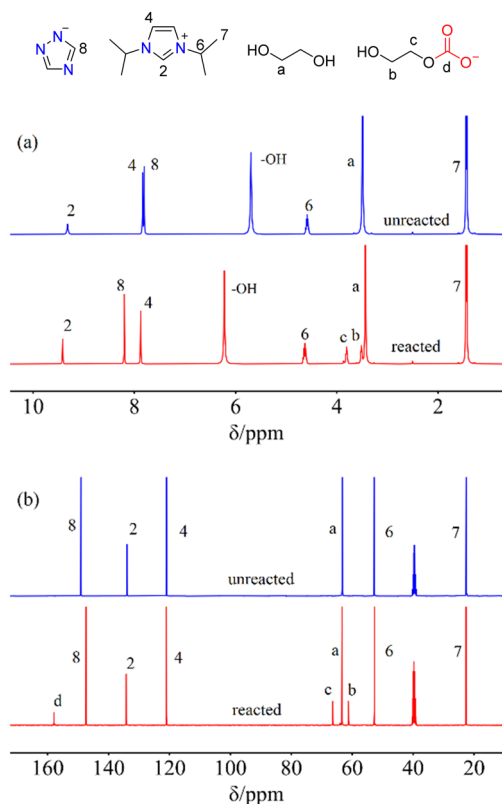


Fig. 3 The  $^1\text{H}$  (a) and  $^{13}\text{C}$  (b) NMR spectra of [liPim][Triz]:EG (1:3) with and without  $\text{CO}_2$ .

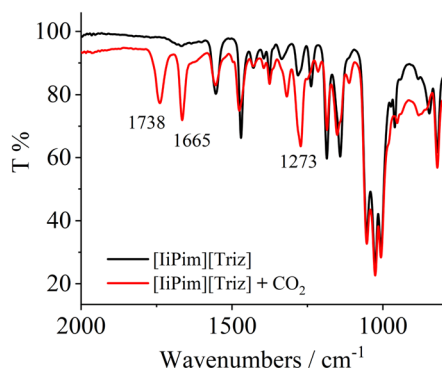


Fig. 4 The FTIR spectra of [liPim][Triz] in  $\text{DMSO}-d_6$  (50 wt%) with and without  $\text{CO}_2$ .

combination band of 1,2,4-triazole ring stretching and N–H bending is observed at  $1274\text{ cm}^{-1}$ . Therefore, the new peaks in Fig. 5 suggest that the reaction occurs between  $\text{CO}_2$  and EG. The FTIR spectra of the [liPim][Triz]:EG (1:4) +  $\text{CO}_2$  (Fig. S4, ESI†) and [liPim][Triz]:EG (1:5) +  $\text{CO}_2$  (Fig. S5, ESI†) systems show similar peaks to that of [liPim][Triz]:EG (1:3) +  $\text{CO}_2$ . However, the peaks around  $1738$  and  $1665\text{ cm}^{-1}$  are not detected in the spectra of [liPim][Triz]:EG solvents after  $\text{CO}_2$  absorption, indicating once more that the reaction between  $\text{CO}_2$  and the cation [liPim] $^+$  or the anion [Triz] $^-$  can be neglected.

The possible  $\text{CO}_2$  capture mechanism by [liPim][Triz]:EG solvents used can be proposed based on the above spectral data,

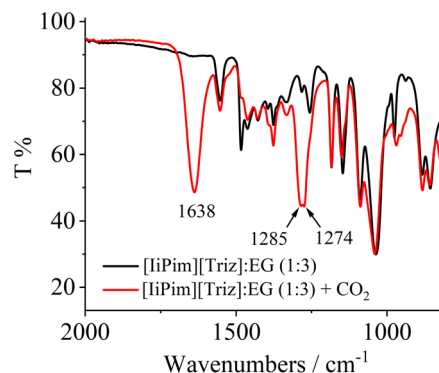
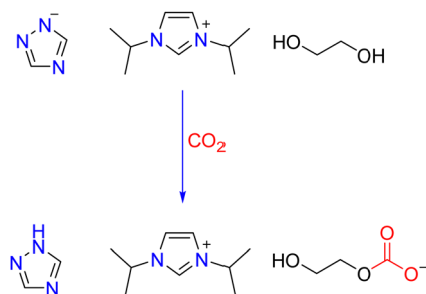


Fig. 5 The FTIR spectra of [liPim][Triz]:EG (1:3) with and without  $\text{CO}_2$ .



Scheme 1 The possible reaction mechanism between  $\text{CO}_2$  and [liPim]-[Triz]-EG DESs studied in this work.

as shown in Scheme 1. EG is deprotonated by the [Triz] $^-$  anion with the formation of the EG-based alkoxide anion, which can bind with  $\text{CO}_2$  to form a carbonate. The reason why  $\text{CO}_2$  is not attached to the C-2 site of the imidazolium ring in [liPim][Triz]:EG DESs may be mainly because of the high steric hindrance of the C-2 site of the liPim carbene with two isopropyl groups.<sup>43</sup> The steric hindrance of the –OH group of EG is lower in comparison with that of the C-2 site of the liPim ring, so  $\text{CO}_2$  is bonded to the O atom of EG rather than the C-2 site of the liPim ring.

The regeneration of [liPim][Triz]:EG (1:3) is also investigated. The absorbed  $\text{CO}_2$  can be released at a low temperature of  $60\text{ }^\circ\text{C}$  (Fig. S6, ESI†). During five absorption-desorption cycles (Fig. S7, ESI†), the decrease of  $\text{CO}_2$  capacity is low, suggesting the good reversibility of [liPim][Triz]:EG (1:3) DESs. In addition, [liPim][Triz]:EG (1:4) and (1:5) can also release captured  $\text{CO}_2$  at  $60\text{ }^\circ\text{C}$ . The comparison between [liPim][Triz]:EG and other DESs for  $\text{CO}_2$  capture is shown in Table S1 (ESI†).

In summary, [liPim][Triz]:EG DESs can efficiently capture  $\text{CO}_2$  with a capacity of  $\sim 1.0\text{ mol CO}_2$  per mol DES. The mechanism results suggest that  $\text{CO}_2$  is not bonded to the C-2 site of the [liPim] $^+$  cation, which can be due to the higher steric hindrance of the C-2 site in comparison with the –OH group of EG. Moreover,  $\text{CO}_2$  captured by [liPim][Triz]:EG can be released at a low temperature of  $60\text{ }^\circ\text{C}$ . The findings in this work reveal that the steric hindrance can be a pivotal factor in tuning the  $\text{CO}_2$  capture behaviors of imidazolium-based DESs.

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## Data availability

The data associated with this work can be found in the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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