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CO$_2$ 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 [iD] *

CO$_2$ 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$_2$ per mol DES at 1.0 atm and 25 °C. Surprisingly, mechanistic results disclose that CO$_2$ reacts with EG but does not bind with the C-2 site of the [IiPim]$^+$ 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 anthropogonic greenhouse gas emissions has been a global critical issue. As the major component of greenhouse, CO$_2$ is mainly emitted from the combustion of fossil fuels. Reducing CO$_2$ emissions plays a key role in mitigating climate change and preventing detrimental effects of CO$_2$ on ecosystems.[1] Carbon capture technology is one of the most promising methods to curb CO$_2$ 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.[2] Nevertheless, this method suffers from inherent shortcomings, including degradation of amines and intensive energy cost for regenerating absorbents.[3]

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.[4] 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.[5] The applications of DESs have been explored in various fields,[6,7] and DESs are also emerging as promising candidates for CO$_2$ capture.[8–10] DESs which capture CO$_2$ only through physical interactions are called physical-based DESs,[11–14] such as DESs

formed by ammonium/phosphonium halide salts as HBAs and alcohols or carboxylic acids as HBDs.[15–18] The CO$_2$ capacity of physical-based DESs is low because of the weak interactions between CO$_2$ and solvents. With the aim of improving the CO$_2$ capacity of DESs, chemical-based or functionalized DESs are developed, which can chemically capture CO$_2$ through reactions between CO$_2$ and components of the DESs.[19] 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$_2$ by forming carbamate species.[20–24] Anion-functionalized DESs exhibit promising chemisorption performances for CO$_2$,[25–28] such as azolide-based DESs[29,30] and phenolate-based DESs.[31,32] The CO$_2$ capture mechanisms of anion-functionalized DESs present various reaction pathways depending on the structures of the components of the DESs.[8]

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$_2$ resulting in the formation of carboxylate species.[33,34] Zhang *et al.* reported CO$_2$ 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$^+$ by the imidazolide anion [Im]$^-$ reacts with CO$_2$.[35] Lee *et al.* investigated CO$_2$ 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$_2$.[36]

Herein, we investigate CO$_2$ 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$_2$ is not attached to the C-2 site of the [IiPim]$^+$ 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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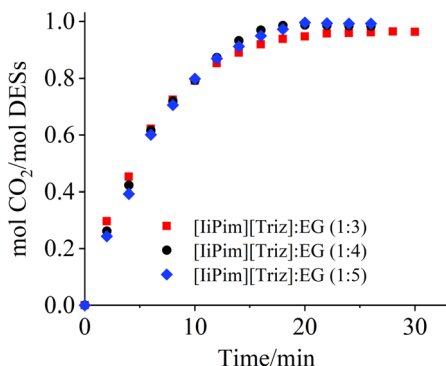
Fig. 1 CO_2 absorption by [IiPim][Triz]–EG DESs at 25 °C and 1.0 atm.

Fig. 2 The ^1H (a) and ^{13}C (b) NMR spectra of [IiPim][Triz] in DMSO-d_6 with and without CO_2.

structure effect of components on CO_2 absorption by imidazolium-based DESs.

Fig. 1 presents CO_2 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_2 per mol DES, respectively. As reported in the literature, the carbene derived from the [Emim]$^+$ cation in [Emim][2-CNpyr]-EG DESs can react with CO_2 to form a carboxylate Emim$^+$–COO$^-$.[36] Similarly, in [IiPim][Triz]-EG solvents, the acid–base reaction between the cation [IiPim]$^+$ and the anion [Triz]$^-$ 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_2 to form a carboxylate species. Unexpectedly, mechanism results of [IiPim][Triz]-EG with and without CO_2 indicate that the carbene IiPim in DESs does not react with CO_2, which is shown in the following sections.

The reaction between CO_2 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_2 are studied in DMSO-d_6 solvent. As shown in Fig. 2a, after capture, the hydrogen peaks related to the IiPim$^+$–COO$^-$ 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$^+$–COO$^-$ 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$^+$–COO$^-$ carboxylate. Moreover, the carbonyl carbon of [Triz]-based carbamate is found at 144.2 (C-9) ppm.[36,37] These new hydrogen and carbon peaks detected in the [IiPim][Triz] + CO_2 system suggest that CO_2 reacts with both the IiPim carbene and [Triz]$^-$ anion present in IL [IiPim][Triz].

The NMR results of the [IiPim][Triz]:EG (1:3) system are shown in Fig. 3. In the ^1H 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]$^-$ shifts downfield from 7.80 to 8.19 ppm upon CO_2 absorption. In the ^{13}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,[25,27] demonstrating that CO_2 reacts with EG in the [IiPim][Triz]:EG (1:3) solvent. The C-d signal is ascribed to the carbonyl carbon of O–COO$^-$.[29,36] Importantly, the hydrogen or carbon peaks related to the carboxylate IiPim$^+$–COO$^-$ are not detected in the NMR
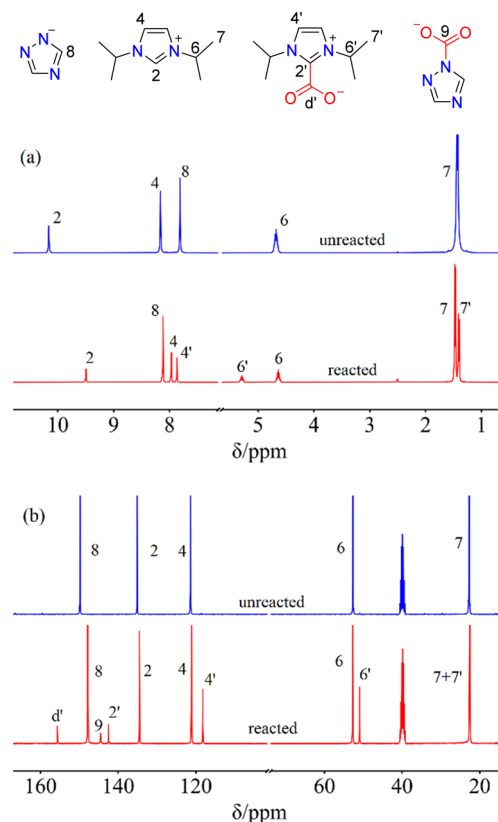
spectra of [IiPim][Triz]:EG (1:3) after CO_2 capture, and the carbonyl carbon of [Triz]-based carbamate is also not observed. Similarly, in the NMR spectra of the [IiPim][Triz]:EG (1:4) (Fig. S1, ESI†) and [IiPim][Triz]:EG (1:5) (Fig. S2, ESI†) systems after CO_2 uptake, the peaks of carboxylate and 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_2.

Fourier transform infrared (FTIR) spectroscopy is also used to study interactions between CO_2 and [IiPim][Triz]-based absorbents. Fig. 4 presents the FTIR spectra of the DMSO-d_6 solution of [IiPim][Triz] before and after CO_2 capture. New peaks at 1738, 1665, and 1273 cm^{-1} can be clearly seen. The peak at 1738 cm^{-1} is ascribed to the asymmetrical stretching band of the COO$^-$ group of [Triz]-based carbamate,[38,39] while the peak at 1665 cm^{-1} is the asymmetrical stretching band of the COO$^-$ group of carbene-based carboxylate.[40] These two peaks again reveal that CO_2 is attached to both the anion [Triz]$^-$ and the cation [IiPim]$^+$ present in IL [IiPim][Triz]. The peak that falls at around 1273 cm^{-1} can be attributed to the combination band of the ring stretching and N–H bending of 1,2,4-triazole,[41,42] which can be observed as well in the spectra of 1,2,4-triazole (Fig. S3, ESI†). The FTIR spectra of [IiPim][Triz]:EG (1:3) before and after capture are seen in Fig. 5. The new peak at 1638 cm^{-1} is attributed to the –COO$^-$ asymmetrical stretching of EG-based carbonate, and the peak appearing at 1285 cm^{-1} is the O–COO$^-$ stretching band.[25,27,29,36] The
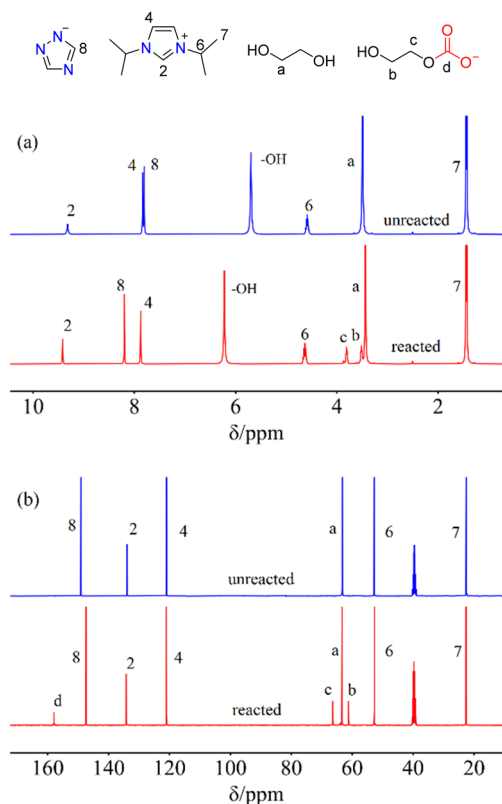
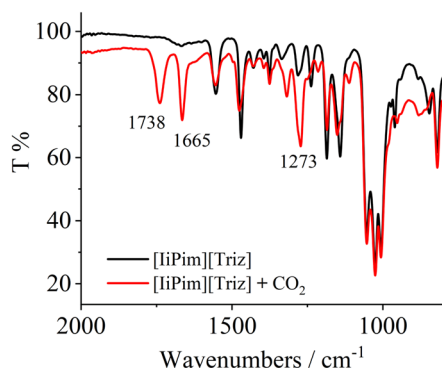**Fig. 3** The ^{1}H (a) and ^{13}C (b) NMR spectra of [IiPim][Triz]:EG (1 : 3) with and without CO_2.

Fig. 4 The FTIR spectra of [IiPim][Triz] in DMSO-d_6 (50 wt%) with and without CO_2.

Fig. 5 The FTIR spectra of [IiPim][Triz]:EG (1 : 3) with and without CO_2.

Scheme 1 The possible reaction mechanism between CO_2 and [IiPim]-[Triz]-EG DESs studied in this work.

combination band of 1,2,4-triazole ring stretching and N–H bending is observed at 1274 cm^{-1}. Therefore, the new peaks in Fig. 5 suggest that the reaction occurs between CO_2 and EG. The FTIR spectra of the [IiPim][Triz]:EG (1 : 4) + CO_2 (Fig. S4, ESI†) and [IiPim][Triz]:EG (1 : 5) + CO_2 (Fig. S5, ESI†) systems show similar peaks to that of [IiPim][Triz]:EG (1 : 3) + CO_2. However, the peaks around 1738 and 1665 cm^{-1} are not detected in the spectra of [IiPim][Triz]-EG solvents after CO_2 absorption, indicating once more that the reaction between CO_2 and the cation [IiPim]$^+$ or the anion [Triz]$^-$ can be neglected.

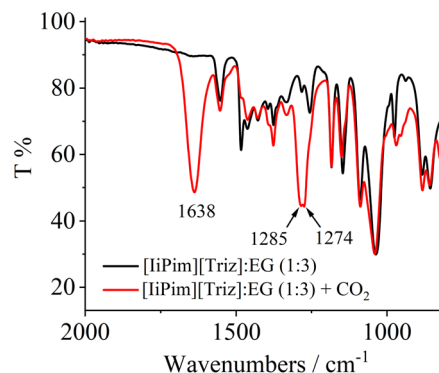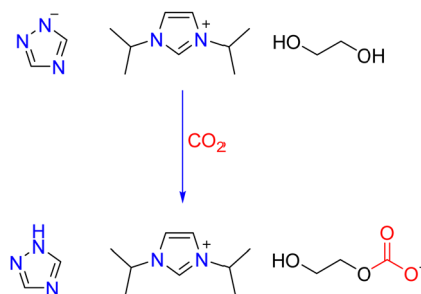The possible CO_2 capture mechanism by [IiPim][Triz]-EG solvents used can be proposed based on the above spectral data, as shown in Scheme 1. EG is deprotonated by the [Triz]$^-$ anion with the formation of the EG-based alkoxide anion, which can bind with CO_2 to form a carbonate. The reason why CO_2 is not attached to the C-2 site of the imidazolium ring in [IiPim][Triz]-EG DESs may be mainly because of the high steric hindrance of the C-2 site of the IiPim carbene with two isopropyl groups.[43] The steric hindrance of the –OH group of EG is lower in comparison with that of the C-2 site of the IiPim ring, so CO_2 is bonded to the O atom of EG rather than the C-2 site of the IiPim ring.

The regeneration of [IiPim][Triz]:EG (1 : 3) is also investigated. The absorbed CO_2 can be released at a low temperature of 60 °C (Fig. S6, ESI†). During five absorption-desorption cycles (Fig. S7, ESI†), the decrease of CO_2 capacity is low, suggesting the good reversibility of [IiPim][Triz]:EG (1 : 3) DESs. In addition, [IiPim][Triz]:EG (1 : 4) and (1 : 5) can also release captured CO_2 at 60 °C. The comparison between [IiPim][Triz]-EG and other DESs for CO_2 capture is shown in Table S1 (ESI†).

In summary, [IiPim][Triz]-EG DESs can efficiently capture CO_2 with a capacity of ∼1.0 mol CO_2 per mol DES. The mechanism results suggest that CO_2 is not bonded to the C-2 site of the [IiPim]$^+$ cation, which can be due to the higher steric hindrance of the C-2 site in comparison with the –OH group of EG. Moreover, CO_2 captured by [IiPim][Triz]-EG can be released at a low temperature of 60 °C. The findings in this work reveal that the steric hindrance can be a pivotal factor in tuning the CO_2 capture behaviors of imidazolium-based DESs.

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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