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 CO_2 capture by deep eutectic solvents (DESs) formed between 1,3-bis(isopropyl)imidazolium 1,2,4-triazolide ([liPim][Triz]) and ethylene glycol (EG) is investigated in this study. [liPim][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 [liPim]⁺ cation, which may be due to the high steric hindrance of the C-2 site of the N-heterocyclic carbene liPim present in [liPim][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, CO₂ is mainly emitted from the combustion of fossil fuels. Reducing CO₂ emissions plays a key role in mitigating climate change and preventing detrimental effects of CO₂ on ecosystems. Carbon capture technology is one of the most promising methods to curb CO₂ 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. Nevertheless, this method suffers from inherent shortcomings, including degradation of amines and intensive energy cost for regenerating absorbents.

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. 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. The applications of DESs have been explored in various fields, and DESs are also emerging as promising candidates for CO₂ capture. DESs which capture CO₂ only through physical interactions are called physical-based DESs, state as DESs

mising chemisorption performances for CO₂, ^{25–28} such as azolide-based DESs^{29,30} and phenolate-based DESs. ^{31,32} The CO₂ 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 CO₂ resulting in the formation of carboxylate species. ^{33,34} Zhang *et al.* reported CO₂ 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 CO₂. ³⁵ Lee *et al.* investigated CO₂ 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 CO₂.³⁶

formed by ammonium/phosphonium halide salts as HBAs and

alcohols or carboxylic acids as HBDs. 15-18 The CO2 capacity of

physical-based DESs is low because of the weak interactions

between CO2 and solvents. With the aim of improving the CO2

capacity of DESs, chemical-based or functionalized DESs are

developed, which can chemically capture CO₂ through reactions

between CO₂ 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 CO₂ by forming carbamate species.^{20–24} Anion-functionalized DESs exhibit pro-

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

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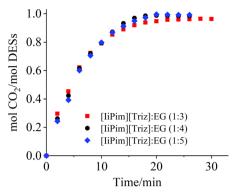


Fig. 1 CO₂ absorption by [liPim][Triz]-EG DESs at 25 °C and 1.0 atm.

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

Fig. 1 presents CO₂ 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 CO₂ 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 CO₂ 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 CO₂ to form a carboxylate species. Unexpectedly, mechanism results of [IiPim][Triz]-EG with and without CO₂ indicate that the carbene IiPim in DESs does not react with CO₂, 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 CO₂ absorption. In the ¹³C 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 CO₂ 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

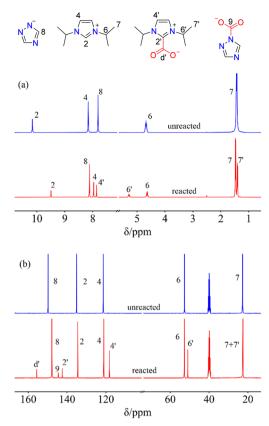


Fig. 2 The $^1\! H$ (a) and $^{13}\! C$ (b) NMR spectra of [liPim][Triz] in DMSO- d_6 with and without CO2.

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 CO2 and [IiPim][Triz]-based absorbents. Fig. 4 presents the FTIR spectra of the DMSO- d_6 solution of [IiPim] [Triz] before and after CO₂ 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 carbenebased carboxylate.40 These two peaks again reveal that CO2 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 ChemComm Communication

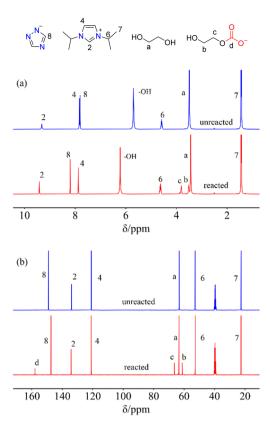


Fig. 3 The ¹H (a) and ¹³C (b) NMR spectra of [liPim][Triz]:EG (1:3) with and without CO2

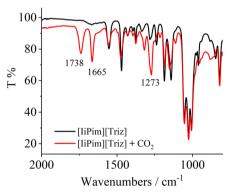
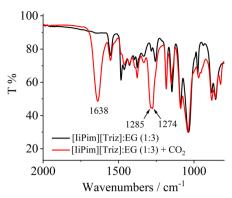


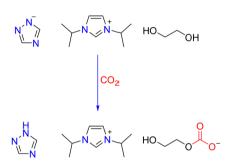
Fig. 4 The FTIR spectra of [liPim][Triz] in DMSO- d_6 (50 wt%) with and without CO2

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 CO2 and EG. The FTIR spectra of the [IiPim][Triz]:EG (1:4) + CO₂ (Fig. S4, ESI†) and [IiPim][Triz]:EG (1:5) + CO₂ (Fig. S5, ESI†) systems show similar peaks to that of [IiPim][Triz]:EG (1:3) + CO₂. However, the peaks around 1738 and 1665 cm⁻¹ are not detected in the spectra of [IiPim][Triz]-EG solvents after CO2 absorption, indicating once more that the reaction between CO₂ and the cation [IiPim]⁺ or the anion [Triz]⁻ can be neglected.

The possible CO₂ capture mechanism by [IiPim][Triz]-EG solvents used can be proposed based on the above spectral data,



The FTIR spectra of [liPim][Triz]:EG (1:3) with and without CO₂.



Scheme 1 The possible reaction mechanism between CO2 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 CO2 to form a carbonate. The reason why CO2 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 CO2 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 CO₂ can be released at a low temperature of 60 °C (Fig. S6, ESI†). During five absorption-desorption cycles (Fig. S7, ESI†), the decrease of CO₂ 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 CO₂ at 60 °C. The comparison between [IiPim][Triz]-EG and other DESs for CO₂ 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 CO2 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, CO₂ 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 CO₂ 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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