Equimolar CO_2 capture by imidazolium-based ionic liquids and superbase systems†

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Imidazolium-based ionic liquids continue to attract interest in many areas of chemistry because of their low melting points, relatively low viscosities, ease of synthesis, and good stabilities against oxidative and reductive conditions. However, they are not totally inert under many conditions due to the intrinsic acidity of hydrogen at the C-2 position in the imidazolium cation. In this work, this intrinsic acidity was exploited in combination with an organic superbase for the capture of CO_2 under atmospheric pressure. During the absorption of CO_2, the imidazolium-based ionic liquid containing an equimolar superbase reacted with CO_2 to form a liquid carboxylate salt so that the equimolar capture of CO_2 with respect to the base was achieved. The effects of ionic liquid structures, types of organic superbases, absorption times, and reaction temperatures on the capture of CO_2 were investigated. Our results show that this integrated ionic liquid–superbase system is capable of rapid and reversible capture of about 1 mol CO_2 per mole of ionic liquid. Furthermore, the captured CO_2 can be readily released by either heating or bubbling N_2, and recycled with little loss of its capture capability. This efficient and reversible catch-and-release process using the weak acidity of the C-2 proton in nonvolatile imidazolium-based ionic liquids provides a good alternative to the current CO_2 capture methods that use volatile alkanols, amines, or water.

Introduction

The emission of carbon dioxide (CO_2) has received worldwide attention because of its possible implications on climate change.[1] Accordingly, the development of novel sorbent materials and new technologies for CO_2 capture and storage is highly sought.[2] The traditional method for CO_2 capture is chemical absorption by aqueous amine solutions. The key advantages associated with this liquid-based method are high reactivity, low cost, and good absorption capacity.[3–6] However, the use of amines and water has some serious inherent drawbacks, including the loss of solvent, corrosion, and high energy demand for regeneration.[7,8] A potential alternative method is the capture of CO_2 by ionic liquids (ILs),[9–20] which have many unique properties, such as negligible vapor pressure, a broad range of liquid temperatures, high thermal stability, good CO_2 solubility, and tunable physicochemical characteristics.[21–37] Davis and coworkers proposed a new strategy for the chemical absorption of CO_2 under ambient pressure by amino-functionalized ILs.[38] The Han group studied the capture of CO_2 by task-specific ILs from renewable materials and the effect of the addition of polyethylene glycol.[39] Noble *et al.* reported the efficient and reversible capture of CO_2 by IL–alkanolamine solutions as tunable solvents.[40] More recently, the Brennecke group reported new IL capture systems based on amino acid anions.[41] However, the maximum capacity is generally limited to about 0.5 mol CO_2 per mole of IL, and the sorption kinetics is very slow because of the formation of solid or highly viscous gel products.[42,43] Consequently, alternative technologies and approaches capable of achieving rapid, reversible CO_2 capture with a higher sorption capacity are highly desired.

Recently, Jessop, Weiss, and their coworkers have developed an innovative CO_2-capture method using mixtures of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and an alcohol or alkylamine, an amidine, and amino acid esters or amino alcohol.[44–50] The important feature of this method is that a combination of proton acceptors such as DBU and proton donors such as alcohol or amine is necessary for CO_2 capture. It has some advantages, including good reactivity, high capacity, and less energy demand for the desorption of CO_2; however, one key drawback associated with this method for the capture of CO_2 is the volatile nature of its molecular constituents. Recently, Heldebrant *et al.*[51] developed a method for CO_2 capture by alkanolamidines, alkanolguanidines, and diamines, which was not volatile. We have recently reported a strategy to mitigate the volatility issue associated with alcohols in the DBU–alcohol carbon-capture system through the covalent attachment of alcohol groups to the structure of IL cations.[52] It is well known that the C-2 proton of imidazolium-based ILs has a weak acidity. Its pK_a in DMSO is about 24.0, and it can be exchanged with deuterium under mild conditions.[53–55] Could imidazolium-based ILs be used as proton donors for the capture of CO_2, eliminating the use of volatile alcohol or amine?

Herein, we report a new CO_2 sorption behavior by imidazolium-based ILs and superbase mixtures, using the weak

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acidity of the C-2 proton of imidazolium-based ILs. By replacing volatile alcohol or amine with conventional imidazolium-based ILs, the issues associated with volatilization of alcohol or amine can be mitigated. Superbases, neutral organic bases with proton affinities so high that their protonated conjugate acids (BH^+) cannot be deprotonated by hydroxide ion,[56,57] play a key role as proton acceptors, thereby providing a thermodynamic driving force for CO_2 capture. The effects of the IL structures, choice of superbases, sorption reactions, and reaction temperatures on the absorption/desorption of CO_2 were investigated. It was found that these novel integrated systems very effectively captured CO_2, which could be easily released *via* gentle heating or inert gas bubbling to regenerate the chemisorptive platform for future capture cycles.

Results and discussion

Absorption of CO_2

To investigate CO_2 absorption by imidazolium-based systems of ILs and superbases, six different ILs and four superbases were selected and explored (Fig. 1). The ILs were 3-butyl-1-methylimidazolium bis(trifluoromethanesulfonyl)amide, [bmim][Tf_2N]; 3-ethyl-1-methylimidazolium bis(trimfluoromethanesulfonyl)amide, [emim][Tf_2N]; 3-butyl-1-methylimidazolium tetrafluoroborate, [bmim][BF_4]; 3-butyl-1-methylimidazolium hexafluorophosphate, [bmim][PF_6]; 1-propyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide, [pdmim][Tf_2N]; and 1-butylpyridinium bis(trifluoromethanesulfonyl)amide, [bpy][Tf_2N]. The superbases were 1,8-diazabicyclo-[5.4.0]undec-7-ene, DBU; 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-a]pyrimidine, MTBD; tetramethyl guanidine, TMG; and 1-ethyl-2,2,4,4,4-pentakis-(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene), EtP_2(dma).

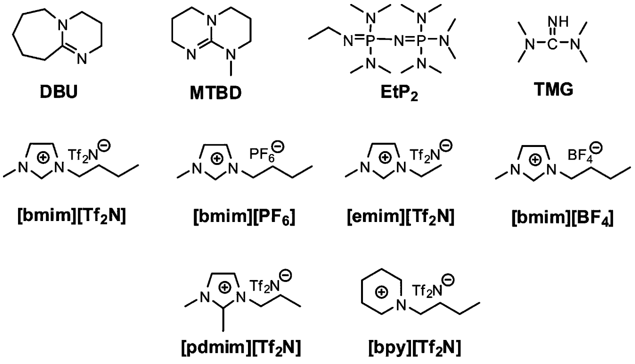


Fig. 1 Chemical structures of ionic liquids and superbases used in this work and their designations.

Table 1 The effect of different ionic liquids on CO_2 absorption[a]

RTIL	Superbase	Time/min	CO_2 absorption[b]	State
[bmim][Tf_2N]	DBU	30	0.99	Liquid
[bmim][BF_4]	DBU	90	0.80	Gel
[bmim][PF_6]	DBU	60	0.75	Gel
[emim][Tf_2N]	DBU	30	0.93	Liquid
[pdmim][Tf_2N]	DBU	30	0.64	Liquid
[bpy][Tf_2N]	DBU	30	0.29	Liquid

[a] 2 mmol ILs + 2 mmol superbase, 23 °C. [b] Moles CO_2 captured per mole superbase.

The DBU superbase was first combined with each of the ILs to study the effect of different ILs on the absorption of CO_2 under atmospheric pressure at 23 °C. It was clear that the influence of different ILs on CO_2 absorption was significant (Table 1). Among them, the absorption of CO_2 by both [bmim][Tf_2N]–DBU and [emim][Tf_2N]–DBU was excellent, where the absorption capacity of CO_2 approaches 1.0 mol per mole of IL in 30 min. However, the absorption molar ratio of CO_2 to IL reduced dramatically to 0.80 and 0.75, respectively, when [bmim][BF_4] and [bmim][PF_6] were used. This reduction of absorption capacity likely stems from reduced diffusion/absorption rates for CO_2 because of the increased viscosities of these systems. In contrast, when imidazolium-based ILs were replaced by pyridinium-based ILs ([bpy][Tf_2N]), only 0.25 mol CO_2 could be captured per mole of IL, which was probably caused by traces of water and the physical interaction between this system and CO_2. These results indicate that the C-2 proton of imidazolium-based ILs is critical to improving the capture of CO_2 by the IL–DBU system.

Table 2 shows the effect of employing different superbases on the absorption of CO_2, which was found to be quite strong. For the [bmim][Tf_2N]–EtP_2 system, a similar CO_2 absorption capacity of 1.0 mol per mole of superbase was achieved. The molar ratio of CO_2 to superbase increased to 1.08 when DBU was replaced by MTBD. However, the absorption capacity of CO_2 in the [bmim][Tf_2N]–TMG system reduced dramatically to 0.49 mol per mole of superbase, because of the formation of stronger hydrogen bonding between carboxylate salt and [$TMGH^+$].[58] We investigated the effect of some impurities such as trace of water and N_2 on the CO_2 absorption, which are listed in Table 2. As seen in Table 2, the effect of trace of water on the CO_2 absorption capacity was weak. During the absorption, a new singlet at 9.04 in the ^1H NMR spectra produced, which can be assigned to the proton of the bicarbonate, because DBU and water would react with CO_2 to form the bicarbonate.[58,59] Furthermore, it was clear in Table 2 that the effect of N_2 on the CO_2 absorption capacity was small. The CO_2 absorption capacity varied from 0.99 mol CO_2 per mol superbase to 0.96 mol CO_2 per mol superbase when pure CO_2 was replaced

Table 2 The effect of superbase, impurities, temperature, and recycling on the CO_2 absorption[a]

RTIL	Superbase	T/°C	CO_2 absorption[b]	State
[bmim][Tf_2N]	DBU	23	0.99	Liquid
[bmim][Tf_2N]	MTBD	23	1.08	Liquid
[bmim][Tf_2N]	EtP_2	23	1.00	Liquid
[bmim][Tf_2N]	TMG	23	0.52	Liquid
[bmim][Tf_2N]	DBU	55	0.78	Liquid
[bmim][Tf_2N]	DBU	80	0.66	Liquid
[bmim][Tf_2N]	DBU[c]	23	0.98	Liquid
[bmim][Tf_2N]	DBU[d]	23	0.96	Liquid
[bmim][Tf_2N]	DBU[e]	23	0.92	Liquid
[bmim][Tf_2N]	DBU[f]	23	0.87	Liquid
[bmim][Tf_2N]	DBU[g]	23	0.84	Liquid

[a] 2 mmol ILs + 2 mmol superbase, 30 min. [b] Moles CO_2 captured per mole superbase. [c] CO_2 including ~1% water. [d] The mixture of 50% CO_2 and 50% N_2. [e] The second recycling of IL-DBU. [f] The third recycling of IL-DBU. [g] The fourth recycling of IL-DBU.

by the mixture of 50% N_2 and 50% CO_2. The effect of reaction temperature on CO_2 absorption for the [bmim][Tf_2N]–DBU system was investigated and is also listed in Table 2. As seen in Table 2, CO_2 absorption decreased steadily as temperature increased from 23 to 80 °C. Therefore, the results show that the captured CO_2 can be easily stripped out by heating the system.

It is noted that absorption by imidazolium-based IL–superbase systems is weakly exothermic and that the effect of different ILs on the absorption rate is significant. The typical CO_2 absorption by [bmim][Tf_2N]–DBU and [bmim][PF_6]–DBU as a function of time is plotted in Fig. 2. The absorption was almost complete within the first 15 min of CO_2 bubbling with [bmim][Tf_2N]–DBU. This rapid CO_2 absorption may be related in part to the low viscosity of this system. Rapid absorption, in the range of tens of minutes, is a distinct advantage of the imidazolium-based IL–superbase method.

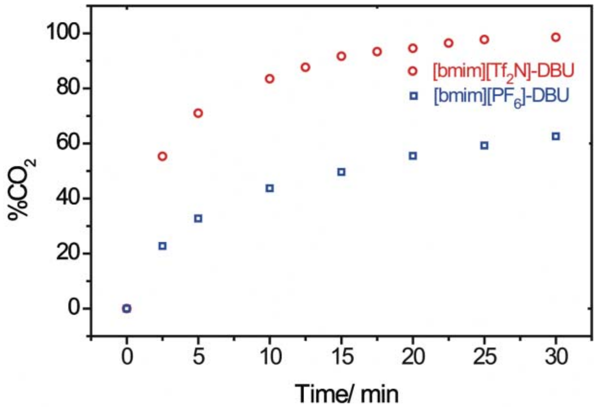


Fig. 2 The comparison of CO_2 absorption by [bmim][Tf_2N]–DBU (○) and [bmim][PF_6]–DBU (□) as a function of time at 23 °C.

It was known that CO_2 would react with DBU and activated C–H bonds to form the carboxylates.[46,60,61] During the absorption of CO_2 observed in this study, CO_2 reacted with imidazolium-based ILs and superbases to form the liquid amidinium carboxylate salt. The formation of amidinium carboxylate salt was verified by NMR and IR spectra of [bmim][Tf_2N]–superbase and the corresponding carboxylate salt [bmim][Tf_2N]–superbase+CO_2 (see ESI†). As seen in Fig. 3, after CO_2 bubbling, a new band for [bmim][Tf_2N]–MTBD+CO_2 was produced at 1669 cm^{-1}, which can be assigned to carboxylate stretches.[59,62] Furthermore, the ^{13}C spectrum of the product showed the carboxylate peak at 155.6 ppm, which is in agreement with the reported data by Louie *et al.*, also indicating the formation of the imidazolium carboxylate.[59,62] Based on previous reports related to the use of alcohol, active methylene compounds, or alcohol-functionalized ILs for the same reaction,[46,52,60,61] and the observed reaction product, we propose the reaction mechanism of CO_2 absorption by [bmim][Tf_2N]–MTBD, which is shown in Scheme 1. For the [bmim][Tf_2N]–MTBD system, the molar ratio of CO_2 to IL exceeds 1.0, which is the theoretical maximum for chemical absorption of CO_2, indicating that both chemical and physical absorption are present.

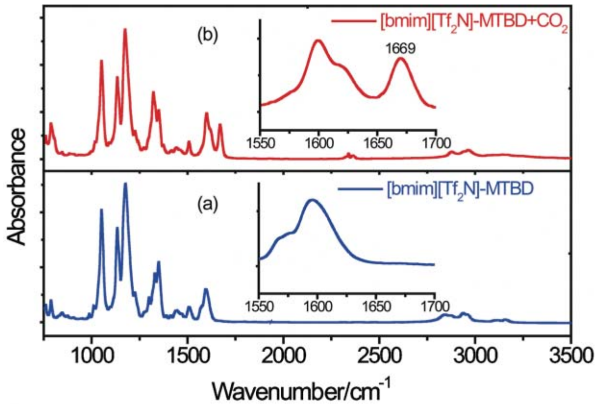
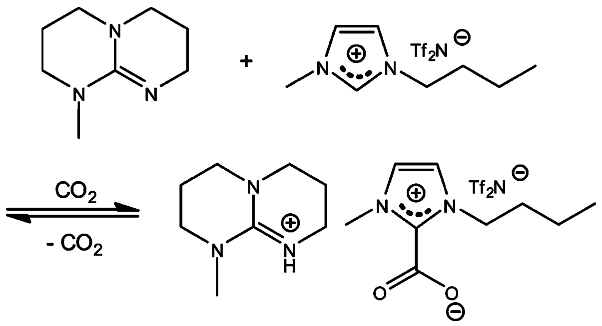


Fig. 3 The infrared spectra of [bmim][Tf_2N]–MTBD before and after the absorption: (a) [bmim][Tf_2N]–MTBD; (b) [bmim][Tf_2N]–MTBD+CO_2.



Scheme 1

Release of CO_2

The stabilities of the captured CO_2 in imidazolium-based IL–superbase systems were investigated by thermogravimetric analysis (TGA), which is an effective method for evaluating the release capability of CO_2.[63,64] Fig. 4 shows the scanning TGA results for various imidazolium-based IL–superbase+CO_2 systems with a 10 °C min^{-1} temperature ramping rate to 800 °C. As seen in Fig. 4, the decomposition of imidazolium-based IL–superbase+CO_2 systems was slow at low temperature, and the decomposition rate increased when the heating temperature reached about 60 °C. After reaching a temperature of 130 °C, the [bmim][Tf_2N]–DBU system lost approximately 10% of its total weight, indicating that the release of CO_2 was almost complete. Furthermore, no obvious weight loss was observed

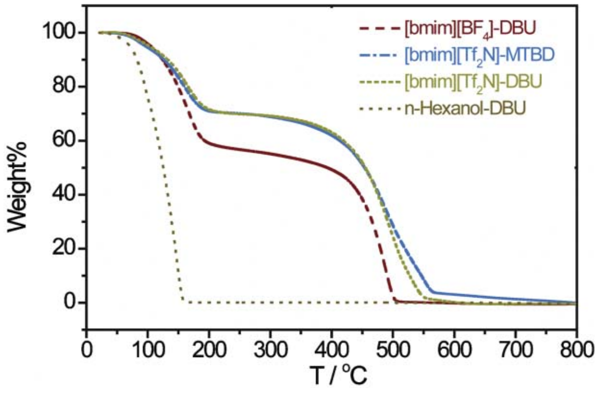


Fig. 4 Scanning TGA profiles for typical ionic liquids–superbase+CO_2 systems (N_2 atmosphere, 10 °C min^{-1} ramp rate).

from 220 to 360 °C due to the high stability of the ILs. Indeed, the decomposition of a number of imidazolium-based ILs such as [bmim][Tf$_2$N] has been reported to exceed 400 °C. Compared with the captured CO$_2$ in alcohol-functionalized IL–DBU systems, the [bmim][Tf$_2$N]–DBU system seems to exhibit a slightly higher thermal stability.[52] In sharp contrast to IL–DBU systems, the *n*-hexanol–DBU+CO$_2$ system began losing weight at 60 °C at a fast rate and had lost approximately 56% of its total weight when the temperature reached 130 °C. The volatilized *n*-hexanol and DBU would react with CO$_2$ to form the highly viscous *n*-hexanol–DBU+CO$_2$, which would result in an increase in the energy required for the release of CO$_2$ and in increased operating costs. Clearly, these results show that loss of the volatile *n*-hexanol or amine was avoided because of the use of imidazolium-based ILs during the release of CO$_2$.

The captured CO$_2$ was easy to strip out by heating or bubbling N$_2$ through the solution. For example, the release of CO$_2$ proceeded rapidly for the [bmim][Tf$_2$N]–DBU system at a temperature of 80 °C under bubbling N$_2$, and the CO$_2$ release was essentially complete within 20 min. Two cycles of absorption and release of CO$_2$ from [bmim][Tf$_2$N]–DBU were performed, and IR spectra were recorded (Fig. 5). The IR spectra show, from bottom to top, neat [bmim][Tf$_2$N]–DBU, CO$_2$ absorption by [bmim][Tf$_2$N]–DBU at 23 °C for 30 min, release of CO$_2$ at 80 °C under N$_2$ for 30 min, and CO$_2$ capture by [bmim][Tf$_2$N]–DBU at 23 °C for 30 min again. As seen in Fig. 5, the peak at 1668 cm^{-1} is visible when amidinium carbonate salt is formed, while this peak disappeared when stripped at 80 °C under bubbling N$_2$. In order to further investigate the effect of recycling imidazolium-based ILs and superbase on CO$_2$ capture, four cycles of absorption and desorption by DBU-[bmim][Tf$_2$N] were conducted, which also shown in Table 2. The results showed a slight loss of CO$_2$ absorption capability, indicating that the process of CO$_2$ capture by imidazolium-based IL-superbase systems is reversible.

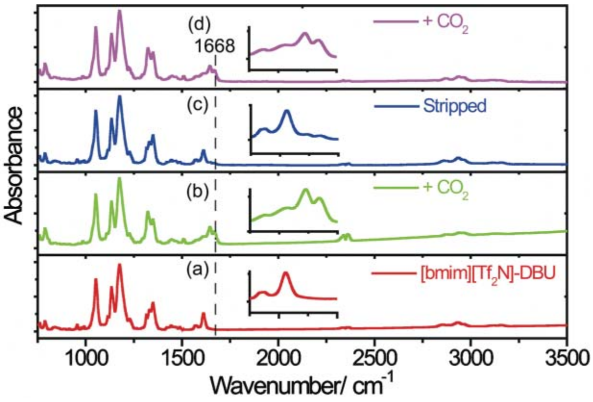


Fig. 5 The two cycles of absorption and release of CO$_2$ by [bmim][Tf$_2$N]–DBU system. From bottom to top: (a) [bmim][Tf$_2$N]–DBU; (b) CO$_2$ absorption at 23 °C; (c) stripped at 80 °C under N$_2$; (d) CO$_2$ absorption at 23 °C again.

Experimental

Materials and methods

DBU, MTBD, TMG, EtP$_2$(dma), and *n*-hexanol were purchased from Aldrich. All chemicals were obtained in the highest purity grade possible and were used as received unless otherwise stated. The [bmim][Tf$_2$N], [emim][Tf$_2$N], [bmim][BF$_4$], [bmim][PF$_6$], [bdmim][Tf$_2$N], and [bpy][Tf$_2$N] were prepared according to methods detailed in the literature.[65,66] IL samples were dried in vacuum at 353 K for more than 24 h to reduce possible traces of solvents and moisture. The water contents of the ILs were determined by Karl Fischer titration and were found to be less than 100 ppm. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 NMR spectrometer with tetramethylsilane as the standard. FT-IR data were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer at room temperature. The stability of IL–superbase+CO$_2$ was measured with a TGA 2950 at a 10 °C min^{-1} temperature ramping rate to 800 °C.

Absorption of CO$_2$

In a typical absorption of CO$_2$, CO$_2$ at atmospheric pressure was bubbled through IL–superbase solutions of about 1.0 g in a glass container with an inner diameter of 10 mm and at a flow rate of about 60 ml min^{-1}. The glass container was partly immersed in an oil bath at the desired temperature. The amount of CO$_2$ absorbed was determined at regular intervals by an electronic balance with an accuracy of ±0.1 mg. The IL–superbase systems were regenerated by heating or bubbling molecular N$_2$ through the solution.

Conclusions

In summary, the integrated systems consisting of imidazolium-based ILs and superbases are highly efficient for the capture of CO$_2$, eliminating the use of volatile alcohol, amine, or water. These systems reacted with CO$_2$ to form a liquid amidinium carboxylate salt using the acidity of the C-2 proton during the absorption of CO$_2$. The absorption of CO$_2$ by [bmim][T$_2$N]–MTBD and [bmim][Tf$_2$N]–DBU occurs rapidly, and the CO$_2$ capture capacity is about 1 mol per mole of IL, which is superior to capture by traditional ILs. Furthermore, the captured CO$_2$ is easy to release and recycle with a slight loss of its absorption capability. Considering the efficient and reversible process with the combination of imidazolium-based ILs and superbases, as well as the diversities of these ILs, this method has great potential for the capture of CO$_2$.

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