Reversible and robust CO_2 capture by equimolar task-specific ionic liquid–superbase mixtures

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Received 4th January 2010, Accepted 12th February 2010
First published as an Advance Article on the web 16th March 2010
DOI: 10.1039/b927514b

Integrated sorption systems consisting of 1 : 1 mixtures of an alcohol-functionalized ionic liquid and a superbase were found to be effective for CO_2 capture under atmospheric pressure, eliminating the use of volatile *n*-alkanols or water. Conversely, by using the current approach, there is no longer a requirement for maintaining scrupulously dry conditions. The effect of ionic liquid structure, choice of superbase, their relative ratios, the sorption temperature, and the reaction time on the absorption and release of CO_2 were investigated. Our results demonstrate that (i) this integrated ionic liquid–superbase system is capable of rapid and reversible capture of nearly one mole of CO_2 per mole of superbase, (ii) the captured CO_2 can be readily released by either mild heating or bubbling with an insert gas (N_2, Ar), and (iii) this novel CO_2 chemisorption platform can be recycled with minimal loss of activity. This efficient and fully reversible catch-and-release process using non-volatile, task-specific ionic liquids provides an excellent alternative to current CO_2 capture technologies, which are based largely around volatile alkanols or alkylamines. Furthermore, our integrated ionic liquid–superbase system can be used as a novel medium for supported liquid membranes, for which they demonstrate both good selectivity and permeability in model CO_2/N_2 gas separations.

Introduction

Emissions of carbon dioxide (CO_2), arguably the most significant anthropogenic greenhouse gas, have received worldwide attention because of the possible implications for climate change. Consequently, the development of efficient, reversible and economic capture technologies for CO_2 is becoming increasingly important.[1,2] One of the most popular technologies for the capture of CO_2 is chemical absorption by a weakly basic aqueous solution of monoethanolamine. Despite the numerous advantages, such as high reactivity, low cost and good absorption capacity, the use of monoethanolamine has some serious inherent drawbacks, including solvent loss, corrosion and high energy demand for regeneration.[3-7] An alternative method to monoethanolamine is the use of chilled ammonia.[8] However, the very low temperatures necessary to minimize evaporative losses of NH_3 result in an increased energy usage and unfavorable operating costs.[9] Recently, an innovative CO_2 capture system based on the formation of amidinium or guanidinium alkylcarbonate salts with good reactivity and high absorption capacity has shown interesting promise.[10–14] This CO_2 capture system consists of an alcohol and an amidine (or guanidine) superbase. Compared with aqueous solution systems, the low specific heat and reduced hydrogen bonding in alkylcarbonate salts result in a less energy intensive CO_2 release.[15] Unfortunately, volatilization of alcohol, as well as the recombination of CO_2 with volatilized species (*i.e.*, alcohols and/or base), can lead to the loss of organic solvents and increased operating costs associated with preventing CO_2 recombination losses during desorption. Hence, there remains a strong need to develop alternative technologies and approaches for the efficient and reversible capture of CO_2 without incurring the loss of volatiles (*e.g.*, alcohols or water).

Within the last few years, room temperature ionic liquids (RTILs) have attracted significant attention for their potential as alternative media for the capture of CO_2,[16–23] due to their unique properties, such as negligible vapor pressure, high thermal stability, non-flammability and excellent CO_2 solubility.[24–34] A large number of experimental and theoretical studies on the solubility of CO_2 in RTILs have been carried out, with a focus on imidazolium-based RTILs, and the results have shown that imidazolium RTILs have remarkable absorption capacities, particularly at relatively high pressures.[35–41] In reality, however, the physical solubility of CO_2 in RTILs still has some way to go before industrial adaptation because of the need for high pressures to enhance gas sorption. The Davis group has proposed a novel strategy for the chemisorption of CO_2 that employs an amino-functionalized, task-specific ionic liquid (TSIL), and their results show that 0.5 moles of CO_2 can be captured per mole of TSIL over 3 h under ambient pressure.[42] Han and co-workers studied the absorption and desorption of CO_2 by RTILs from renewable materials with polyethylene glycol. They demonstrated that the molar ratio of CO_2 to neat RTIL could slightly exceed 0.5, and that addition

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of polyethylene glycol significantly enhanced the rates of CO_2 absorption and desorption.[43] Furthermore, Noble *et al.*[44] have reported the capture of CO_2 by RTIL–alkanolamine solutions as tunable solvents and found that an RTIL solution containing 50 mol% monoethanolamine was capable of efficient and reversible capture of 0.5 moles of CO_2 per mole of monoethanolamine to give an insoluble carbamate precipitate, which helped to drive the capture reaction. Although these approaches have made important strides, the maximum absorption capacity is generally limited to about 0.5 moles of CO_2 per mole of RTIL, and an additional inert solvent is needed to enhance the CO_2 diffusion and capture rates due to the formation of highly viscous gels or solids during CO_2 capture by RTIL-based systems.[15,45,46] Consequently, alternative TSIL systems able to achieve rapid, reversible CO_2 capture at higher sorption capacities are highly sought, particularly those that eliminate the need for additional inert co-solvents.

Herein, we report CO_2 sorption behavior and CO_2/N_2 separation performance using integrated systems consisting of 1 : 1 mixtures of alcohol-containing TSILs and an appropriate superbase. By incorporating alcohol groups into non-volatile RTIL cations, the issues associated with the volatilization of the alcohol can be mitigated. Superbases, neutral organic bases with proton affinities so high that their protonated conjugate acids (BH^+) cannot be deprotonated by the hydroxide ion,[47,48] play a key role as proton acceptors, thereby providing a thermodynamic driving force for CO_2 capture. The effects of the RTIL and superbase choice, their molar ratios, the sorption temperature and the reaction time on the absorption/desorption of CO_2 were investigated. It was found that these novel integrated systems were very effective for the capture of CO_2, which could easily be released *via* gentle heating or inert gas bubbling to regenerate the chemisorptive platform for future capture cycles. The selective membrane separation of CO_2 and N_2 using this TSIL–superbase system was also demonstrated in this work.

Results and discussion

Absorption of CO_2

To investigate the gas separation performance and CO_2 absorption of the RTIL–superbase system, two RTILs (1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[Im_{21}OH][Tf_2N]$) and 2-hydroxyethyl(dimethyl)-isopropylammonium bis(trifluoromethylsulfonyl)imide ($[N_{ip,211}OH][Tf_2N]$)) and four superbases (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), 2-*tert*-butylamino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) and 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-$2\lambda^5,4\lambda^5$-catenadi(phosphazene) (EtP_2(dma))) were selected and explored (see Fig. 1 for the structures and their designations). The DBU superbase was first combined with each of the RTILs to investigate the effect of different RTILs on the absorption of CO_2 under atmospheric pressure at 20 °C (see Table 1). It was seen that the absorption of CO_2 by both $[Im_{21}OH][Tf_2N]$–DBU and $[N_{ip,211}OH][Tf_2N]$–DBU was excellent. A CO_2 to DBU molar ratio of 1.04 was achieved when the TSIL $[Im_{21}OH][Tf_2N]$ was used, which is at least 20 times greater than that in neat $[Im_{21}OH][Tf_2N]$.[37] CO_2 underwent a reaction with $[Im_{21}OH][Tf_2N]$ and DBU to form the liquid amidinium alkylcarbonate salt during the absorption reaction of CO_2, which was identified by NMR. Based on previous reports related to use of neutral alcohols for the same reaction[11,12] and the observed reaction products, we propose the reaction mechanism shown in Scheme 1, where CO_2 is absorbed by the RTIL–superbase system. For this RTIL–superbase combination, the molar ratio of CO_2 to DBU exceeds 1.0, which is the theoretical maximum for the chemical absorption of CO_2, indicating that both chemical and physical absorption mechanisms are active.

Table 1 The CO_2 absorption of different RTIL–superbase systems[a]

RTIL	Superbase	Time/min	CO_2 absorption[b]	State
$[Im_{21}OH][Tf_2N]$	DBU	30	1.04	Liquid
$[N_{ip,211}OH][Tf_2N]$	DBU	30	1.02	Liquid
$[Im_{21}OH][Tf_2N]$	MTBD	30	1.02	Liquid
$[N_{ip,211}OH][Tf_2N]$	MTBD	30	0.98	Liquid
$[Im_{21}OH][Tf_2N]$	BEMP	60	0.81	Gel
$[Im_{21}OH][Tf_2N]$	EtP_2(dma)	60	0.49	Gel

[a] 4 mmol RTIL + 4 mmol superbase, 20 °C. [b] Moles of CO_2 captured per mole of superbase.

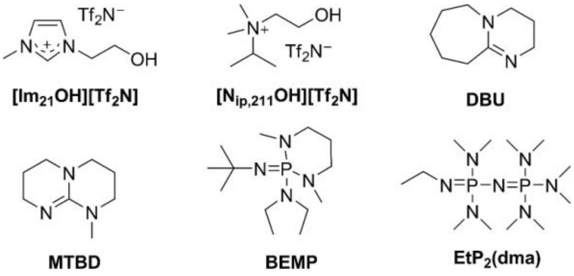
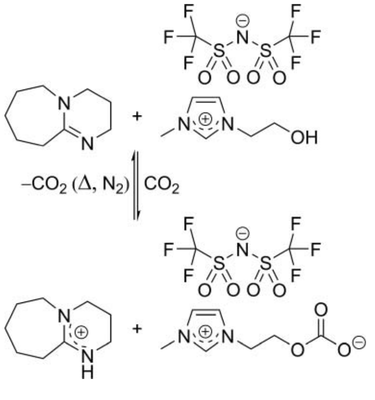


Fig. 1 The chemical structures of the RTILs and superbases used in this work, and their designations.



Scheme 1

The entries in Table 1 also illustrate the effect of employing different superbases on the efficiency of CO_2 absorption in the presence of an equivalent of alcohol-bearing TSIL. Essentially, unit CO_2 absorption capacity was achieved when either a bicyclic amidine (DBU) or a guanidine (MTBD) superbase was used, whereas CO_2 absorption in the presence of a phosphazene-type superbase was reduced by roughly 20% and 50% in the cases of BEMP and EtP_2(dma), respectively. This distinctly diminished performance may be related in part to the excessive viscosity of the latter RTIL–superbase systems and their corresponding alkylcarbonate salts. Specifically, while the $[Im_{21}OH][Tf_2N]$–DBU and $[Im_{21}OH][Tf_2N]$–MTBD systems remain fluid at all stages of CO_2 capture, the corresponding systems containing BEMP or EtP_2(dma) produce gelatinous phosphazenium alkylcarbonate systems, which clearly hampers subsequent CO_2 absorption.

An important feature of CO_2 absorption by RTIL–superbase systems is that the absorption is mildly exothermic, lending toward a favorably rapid absorption rate. Fig. 2 shows a typical CO_2 absorption by the $[Im_{21}OH][Tf_2N]$–DBU system as a function of time. From Fig. 2, it is clear that for this system, absorption is nearly complete within the first 10 min of CO_2 exposure. Explicitly, the CO_2 absorption increases initially to nearly 80% uptake within 5 min, with almost no additional uptake evident beyond 10 min. This rapid CO_2 sorption, in the range of a handful of minutes as opposed to tens of minutes to hours, is a distinct advantage of the alcoholic RTIL–superbase platform.

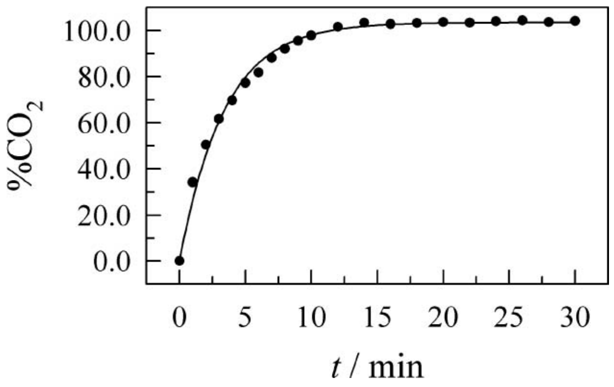


Fig. 2 A plot of percentage CO_2 uptake by $[Im_{21}OH][Tf_2N]$–DBU as a function of time at 20 °C. The points are the actual data and the curve shown is the fit: $\%CO_2 = 103(1 - e^{-0.294t})$ ($N = 21$, $r^2 = 0.992$).

Table 2 shows the effect of the RTIL–superbase molar ratio on the absorption of CO_2, which was found to be quite strong for some systems. For the $[Im_{21}OH][Tf_2N]$–DBU system, the CO_2 absorption increased only modestly from 1.04 to 1.11 moles of CO_2 per mole of DBU as the RTIL–superbase molar ratio increased from 1.0 to 1.2, with little increase thereafter. However, the absorption of CO_2 relative to superbase increased dramatically from 0.49 to 0.75 when the molar ratio of $[Im_{21}OH][Tf_2N]$ to EtP_2(dma) went from 1.0 to 1.5. This increase most likely stems from the increased diffusion/absorption rates for CO_2 due to the reduced viscosity when excess RTIL is present. In this case, these conditions help the system remain liquid as the CO_2 is captured. The data in Table 2 also show the pronounced effect of temperature on the absorption of CO_2 for the $[Im_{21}OH][Tf_2N]$–DBU system. The CO_2 absorption was found to decrease steadily with increasing temperature from 20 to 75 °C. Therefore, the results show that the captured CO_2 can be stripped out simply by heating.

Table 2 Effects of molar ratio and temperature on the capture of CO_2 by $[Im_{21}OH][Tf_2N]$–superbase systems[a]

Superbase	Molar ratio[b]	$T/°C$	CO_2 absorption[c]	State
DBU	1.2	20	1.11	Liquid
DBU	1.5	20	1.13	Liquid
EtP_2(dma)	1.0	20	0.49	Gel
EtP_2(dma)	1.5	20	0.75	Liquid
DBU	1.0	35	0.96	Liquid
DBU	1.0	50	0.85	Liquid
DBU	1.0	75	0.68	Liquid

[a] Superbase (4 mmol), 30 min. [b] Molar ratio of $[Im_{21}OH][Tf_2N]$ to superbase. [c] Moles of CO_2 per mole of superbase.

Release of CO_2

The stabilities of the CO_2-captured RTIL–superbase systems were further studied by thermogravimetric analysis (TGA), which is an effective method for evaluating CO_2 release capability.[49,50] Fig. 3 shows the scanning TGA results for various RTIL–superbase–CO_2 systems with a 10 °C min^{-1} temperature ramping rate to 800 °C. The decomposition of the RTIL–superbase–CO_2 systems was slow at low temperature, with no increase in the decomposition rate being observed until the heating temperature reached approximately 50 °C. After reaching a temperature of 120 °C, the $[Im_{21}OH][Tf_2N]$–DBU system lost approximately 12 wt%, indicating that the release of CO_2 was almost complete. Furthermore, no obvious weight loss was observed from 200 to 350 °C due to the high stability of the RTILs. Indeed, the decomposition temperature (T_{dcp}) of a number of alcohol-containing RTILs has been reported to be around 400 °C.[51] In stark contrast, the n-hexanol–DBU–CO_2 system started to decompose at 50 °C with a fast reaction rate and lost approximately 44 wt% when the temperature reached 120 °C. The volatilized n-hexanol and DBU would react with CO_2 to form highly viscous n-hexanol–DBU–CO_2, which would result in an increase in the energy required for the release of the CO_2 and so increase operating costs. Clearly, these results show that loss of the volatile alcohol component is avoided because of the use of TSILs during the release of CO_2.

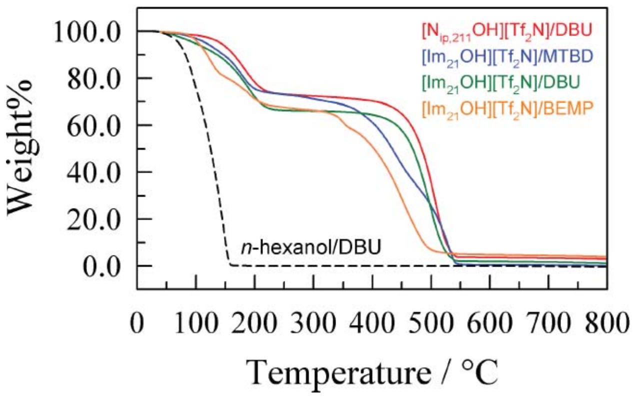


Fig. 3 Scanning TGA profiles for selected RTIL–superbase–CO_2 systems (N_2 atmosphere, 10 °C min^{-1} ramp rate).

The captured CO_2 was easy to strip out by heating or by bubbling N_2 through the solution. Fig. 4 shows the effect of time on the release of CO_2 under heating for the $[Im_{21}OH][Tf_2N]$–DBU system. The results show that the release of CO_2 proceeded rapidly at a temperature of 120 °C. For example, the CO_2 release was essentially complete within 15 min at 120 °C. Fig. 4 also reveals that CO_2 absorption into and release from the $[Im_{21}OH][Tf_2N]$–DBU solution can be repeatedly recycled with only a slight loss of absorption capability, indicating that the process of CO_2 absorption by RTIL–superbase systems is reversible.

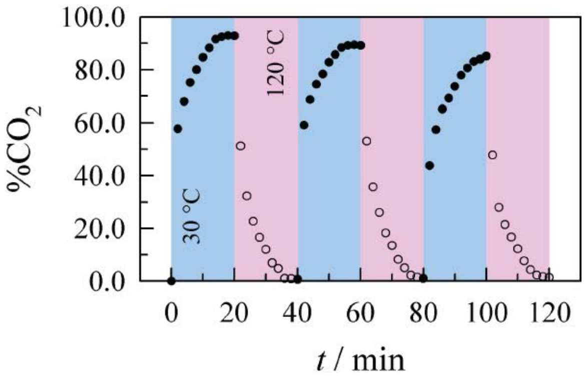


Fig. 4 Three consecutive cycles of CO_2 absorption (cyan, 30 °C) and release (pink, 120 °C) by the $[Im_{21}OH][Tf_2N]$–DBU system. In this representation, 100% CO_2 uptake denotes 1.0 mole of CO_2 per mole of $[Im_{21}OH][Tf_2N]$.

Selective separation of CO_2 and N_2

The selective separation of CO_2 and N_2 in these RTIL–superbase systems was investigated using a non-steady-state permeation method. Each RTIL–superbase solution was loaded onto a porous polymer support to form a supported ionic liquid membrane (SILM) for the measurement of permeance and selectivity. The feed pressure was typically 35 kPa, the permeate pressure was initially about 40 mTorr. By measuring the pressure of the permeate side as a function of time, we could calculate the permeance, Q_i, of the SILM for each gas by using the following equation:

$$Q_i = \frac{V}{\mathrm{R}TA(P' - P'')} \times \frac{dP''}{dt} \qquad (1)$$

where V is the permeate volume, R is the Boltzmann gas constant, T is the absolute temperature, A is the membrane area, P' is the upstream pressure, P'' is the downstream pressure and dP''/dt is the rate of gas pressure increase on the permeate side. The selectivity was obtained by calculating the ratio of the CO_2 permeance over N_2 permeance.

$$\alpha_i = \frac{Q_i}{Q_j} \qquad (2)$$

Here, Q_i and Q_j are the permeances of CO_2 and N_2, respectively.

In conventional industrial processes of CO_2 capture from flue gas streams, significant energy consumption is associated with the cooling of the flue gas to ambient temperature prior to the release of CO_2.[50] Therefore, an ideal CO_2 capture system should be capable of operating at elevated temperature. As indicated in Table 3, both the $[Im_{21}OH][Tf_2N]$–DBU system and the $[Im_{21}OH][Tf_2N]$–MTBD system exhibited good performance for the separation of CO_2 and N_2 at elevated temperatures. For example, the CO_2 permeance was measured to be 1.43×10^{-9} mol m^{-2} s^{-1} Pa^{-1} at 90 °C, with a CO_2/N_2 selectivity of 7.1. This permeance value is comparable to that of $[Im_{21}][Tf_2N]$, a widely used RTIL for SILM-based CO_2 separation. An even better performance, with a CO_2 permeance of 1.89×10^{-9} mol m^{-2} s^{-1} Pa^{-1} and a CO_2/N_2 selectivity of 8.0, was achieved when a $[Im_{21}OH][Tf_2N]$–MTBD SILM was used. In contrast, the CO_2 permeance for the $[Im_{21}OH][Tf_2N]$–DBU SILM was only 1.20×10^{-11} mol m^{-2} s^{-1} Pa^{-1} at room temperature because the RTIL–superbase strongly absorbs CO_2 but does not easily release it, as previously discussed.

Table 3 The selective separation of CO_2 and N_2 by $[Im_{21}OH][Tf_2N]$–superbase membranes[a]

Superbase	T/°C	CO_2 permeance/ mol m^{-2} s^{-1} Pa^{-1}	CO_2/N_2 selectivity
DBU	20	1.20×10^{-11}	—
DBU	90	1.43×10^{-9}	7.1
MTBD	85	1.89×10^{-9}	8.0

[a] The feed pressure was 35 kPa.

Experimental

Materials

MTBD, DBU, BEMP, EtP_2(dma) and n-hexanol were purchased from Aldrich. All chemicals were obtained in the highest purity grade possible and used as received, unless otherwise stated. The RTILs $[Im_{21}OH][Tf_2N]$ and $[N_{ip,211}OH][Tf_2N]$ were synthesized according to methods detailed in the literature.[51–54]

Absorption of CO_2

In a typical absorption of CO_2, CO_2 at atmospheric pressure was bubbled through about 2.0 g of RTIL–superbase solution in a glass container with an inner diameter of 10 mm at a flow rate of about 30 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 RTIL–superbase system was regenerated by heating or bubbling N_2 through the solution.

Gas permeation experiments

Gas permeation experiments were performed using a customised test apparatus.[55] The RTIL–superbase membrane was prepared by immersing a 47 mm Supor-100 polyethersulfone membrane (Pall Corp.) in 1 mL of RTIL–superbase solution. The membrane was then placed in a vacuum desiccator for 12 h for de-gassing. After removal from the desiccator, the membrane was carefully wiped with filter paper to eliminate excess RTIL–superbase solution. The permeation properties of the RTIL–superbase membrane was then analyzed in a stainless steel permeation cell that consisted of feed and permeate chambers separated by the membrane. Single gas permeance measurements were separately acquired for CO_2 and N_2 at 90 °C. Both the feed and permeate sides were initially evacuated to approximately 40 mTorr, followed by the introduction of the gas to the feed side at a pressure of 35 kPa. The pressure of the permeate side was recorded as a function of time for 30 min.

Conclusions

In summary, TSIL–superbase systems are highly efficient for the capture of CO_2, eliminating the use of volatile alcohols or water. The capture of CO_2 by $[Im_{21}OH][Tf_2N]$–DBU occurs rapidly, and the CO_2 capture capacity is more than 1 mole per mole of superbase, which is superior to those captured by traditional RTILs. The captured CO_2 is easily released and the system recyclable with only a slight loss of activity. This efficient and reversible process by the combination of TSILs and superbases provides a potential method for the capture of CO_2 in industry.

Acknowledgements

This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. The authors thank Dr Je Seung Lee for his kind assistance with CO_2 sorption measurements. C. M. W. also gratefully acknowledges the support of the National Natural Science Foundation of China (nos. 20704035 and 20773109).

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