Carbon Capture

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Tuning the Basicity of Ionic Liquids for Equimolar CO_2 Capture**

Congmin Wang,* Xiaoyan Luo, Huimin Luo, De-en Jiang, Haoran Li, and Sheng Dai*

The emission of carbon dioxide (CO_2) from fossil fuels has received worldwide attention because it has been implicated in climate change, which threatens economies and environments. Accordingly, new materials that can capture CO_2 from the burning of fossil fuels efficiently, economically, and with potential energy savings must be developed. The traditional technology for the capture of CO_2 in industry is chemical adsorption by an aqueous solution of amine, which has some advantages, such as low cost, good reactivity, and high capacity.[1] However, this process for the capture of CO_2 is highly energy intensive owing to the thermodynamic properties of water and high enthalpy of absorption.[2] It is estimated that the output of energy would drop by about 30 % when this capture technology was applied at coal-fired power plants, which significantly increases the cost of energy.[3] Currently, the goal is to design industrial attractive sorbent materials with high capacity and energy-saving for CO_2 capture.

Ionic liquids (ILs) offer a new opportunity for addressing this challenge to develop novel CO_2 capture systems because of their unique properties, including negligible vapor pressures, high thermal stabilities, and tunable properties.[4] A great deal of effort has focused on the experimental and theoretical studies on the physical absorption of CO_2 in ILs.[5] The enthalpy of CO_2 physical absorption by ILs is about 20 $kJ\,mol^{-1}$, indicating that only a quarter energy is required to release the physical absorbed CO_2 from ILs in the regeneration step relative to amine solution method.[6] However, the absorption capacity of CO_2 by these ILs is up to about 3 mol % under atmospheric pressure. Another strategy is based on the chemisorption for CO_2 capture by task-specific ILs. Davis and co-workers[7] reported the first example of CO_2 chemisorption that employs an amino-functionalized IL; in their work, 0.5 mol CO_2 was captured per mole of IL under ambient pressure. Subsequently, some other amino-functionalized ILs, including sulfone anions with ammonium cations and amino acid anions with imidazolium or phosphonium cations, were reported for the capture of CO_2.[8] Recently, a novel method for the capture of CO_2 in a 1:1 manner by superbase-derived protic ILs and substituted aprotic ILs using the reactivity of anion was reported.[9] Normally, the chemisorption has high absorption capacity for CO_2 along with high energy requirement for regeneration.[10] One commonly used parameter to access the regeneration energy requirement is the enthalpy of CO_2 absorption. We need reduce the enthalpy of absorption to design the energy-saving ILs for CO_2 capture. Then, how can we design suitable chemical structures of ILs to reduce the enthalpy of CO_2 chemisorption? Can we prepare highly stable ILs for energy-saving and equimolar CO_2 capture?

Herein, we present a strategy to tune the enthalpy of CO_2 absorption by tunable basic ionic liquids, which were prepared by neutralizing weak proton donors with different pK_a values with phosphonium hydroxide. We show that the stability of ILs, the enthalpy of absorption, and absorption capacity can be easily tuned by the basicity of ILs. Based on the relationship between the stability, the enthalpy of absorption, absorption capacity, and the basicity of ILs, highly stable ILs for CO_2 capture with desirable absorption enthalpy and high capacity were achieved, which opens the door to develop industrial attractive ILs for energy-saving and equimolar CO_2 capture.

Most studies on the chemisorption for CO_2 capture are based on the reactivity of two equivalents of amine per CO_2 using amino-functionalized ILs. Our approach is to make use of the reactivity of the anions in basic ILs to CO_2, thus equimolar CO_2 capture can be achieved. These basic ILs were prepared from the deprotonation of a variety of weak proton donors with phosphonium hydroxide, which was prepared by the anion-exchange method.[11] A complete CO_2 separation cycle should involve both the capture and the release of CO_2. Our method balances two processes by tuning the basicity of ILs. Considering both the effect of the basicity of the anion on the stability and the reactivity of the anion toward CO_2, eight kinds of weak proton donors with different pK_a values were selected, for which the pK_a values in DMSO range from 19.8 to 8.2 (Scheme 1).

The structures of these basic ILs were confirmed by NMR and IR spectroscopy (see Supporting Information). Thermal gravimetric analysis (TGA) revealed that the stability was significantly influenced by the basicity of these ILs. As seen in Table 1, the stability of ILs increased with the decrease of pK_a

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[*] Dr. C. Wang, X. Luo, Prof. H. Li
Department of Chemistry, Zhejiang University
Hangzhou 310027 (P. R. China)
Fax: (+86) 571-8795-1895
E-mail: chewcm@zju.edu.cn
Dr. C. Wang, Dr. D. Jiang, Dr. S. Dai
Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)
Fax: (+1) 865-576-5235
E-mail: dais@ornl.gov
Dr. S. Dai
Department of Chemistry, University of Tennessee
Knoxville, TN 37966 (USA)
Dr. H. Luo
Nuclear Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)

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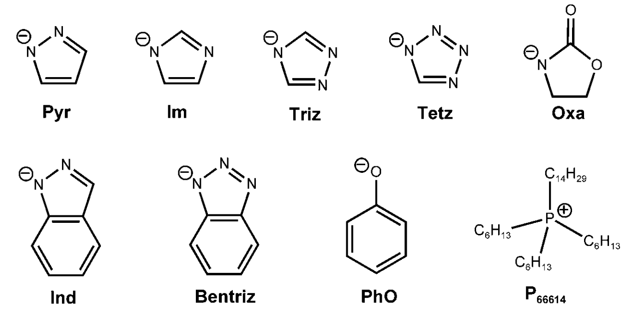


Scheme 1. Structure of anion and cation in tunable basic ILs for CO_2 capture.

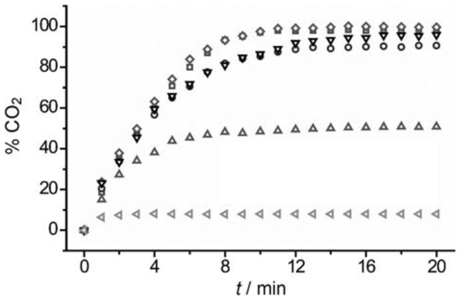


Figure 1. CO_2 absorption by some typical basic ILs: ◇ $[P_{66614}]$[Pyr], □ $[P_{66614}]$[Im], ▽ $[P_{66614}]$[Triz], ○ $[P_{66614}]$[Oxa], ◁ $[P_{66614}]$[Tetz], △ $[P_{66614}]$-[PhO].

Table 1: The effect of anion pK_a on the stability, absorption capacity, and absorption enthalpy.[a]

Ionic liquid	T_{dec} [°C]	Absorption capacity[b]	Absorption enthalpy[c]	pK_a in DMSO[d]
$[P_{66614}]$[Pyr]	182	1.02	91.0	19.8
$[P_{66614}]$[Im]	252	1.00	89.9	18.6 (14.5)
$[P_{66614}]$[Ind]	277	0.98	63.1	17.8
$[P_{66614}]$[Triz]	310	0.95	56.4	13.9
$[P_{66614}]$[Bentriz]	332	0.17	37.2	11.9
$[P_{66614}]$[Tetz]	340	0.08	19.1	8.2
$[P_{66614}]$[Oxa]	224	0.91	69.8	(12.5)
$[P_{66614}]$[PhO]	263	0.50	46.7	(10.0)

[a] The absorption was carried out at 23 °C for 20 min. [b] Mol CO_2 per mol IL. [c] Calculated values based on B3LYP/6-31++G(p,d) method. [d] Values given in brackets are in H_2O.

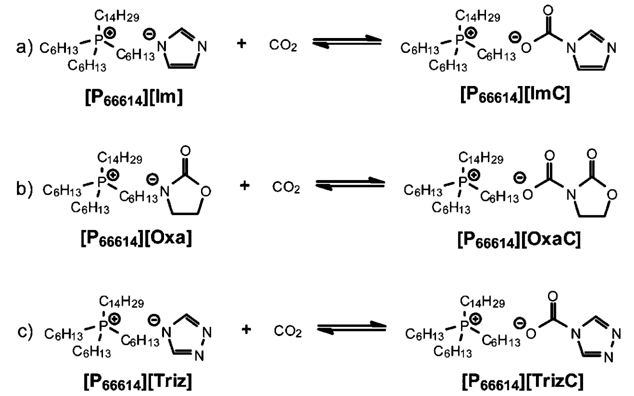
value of the corresponding weak proton donors. For example, the decomposition temperature of ILs increased from 182 °C to 340 °C when the pK_a values in DMSO of the corresponding weak proton donors decreased from 19.8 to 8.2. Thus, highly stable basic ILs (>300 °C), such as $[P_{66614}]$[Triz], can be obtained by tuning the basicity of ILs, which are significantly more stable than conventional strongly basic ILs (Supporting Information, Figure S1).[12]

The effect of the basicity of these ILs on CO_2 absorption was investigated (Table 1). It was clear that the absorption capacity of CO_2 was significantly affected by the basicity of these basic ILs. As seen in Table 1, the absorption capacity of CO_2 enhanced dramatically from 0.17 to 0.95 mol CO_2 per mole IL when the pK_a of the anion in DMSO increased from 11.9 to 13.9. The increase of the absorption capacity of CO_2 is not remarkable when the pK_a of the anion in DMSO further increased from 13.9 to 19.8. Similarly, the absorption capacity improved in case that the anion with the larger pK_a in H_2O was used due to its stronger reactivity to CO_2. It indicates that equimolar CO_2 absorption can be achieved by tuning the pK_a of the anion in these basic ILs.

An important feature of CO_2 absorption by these basic ILs is that the absorption kinetic is rapid. Figure 1 shows several typical CO_2 absorptions by different basic ILs as a function of time. The absorption of CO_2 was almost complete in 10 min (Figure 1) with all of these basic ILs, which is substantially faster than with conventional amino-functionalized ILs. Bara and co-workers[8f] reported that IL-amine solutions were capable of rapid capture of CO_2 because of the formation of an insoluble carbamate precipitate that helps to drive the capture reaction. This rapid absorption by these basic ILs should be due to the difference in viscosities caused by CO_2 absorption. During the absorption of CO_2 by amino-functionalized ILs, the viscosity of ILs increased dramatically, forming highly viscous gels or solids,[7,8b,c] thus leading to slow absorption kinetics. A molecular dynamics simulation indicates that the dramatic increase in viscosity is due to the formation of strong and dense hydrogen-bonded networks between the zwitterion and dication species formed during the reaction of CO_2 with the amino-tailored cation.[13] As opposed to the dramatic increase in viscosity during the absorption by amino-functionalized ILs, the viscosities of $[P_{66614}]$[Pyr], $[P_{66614}]$[Oxa], and $[P_{66614}]$[PhO] increased only to 555.1 cP, 1145.8 cP, and 645.4 cP upon uptake of CO_2. More interestingly, the viscosity of $[P_{66614}]$[Im] decreased from 810.4 cP to 648.7 cP upon uptake of CO_2. We believe that this decrease might be related to absence of strong hydrogen-bonded networks by these non-amino basic ILs.

During the capture of CO_2 in this study, these basic ILs reacted with CO_2 to form a liquid carbamate, or carbonate salt, which was verified by NMR and IR spectroscopy. For example, In comparison to fresh IL $[P_{66614}]$[Triz] and $[P_{66614}]$[Im], a new peak at 1736 cm^{-1} and 1711 cm^{-1}, attributable to a carbamate (C=O) stretch, formed by the absorption of CO_2, respectively (see the Supporting Information). Similarly, after the absorption of CO_2, a signal at 160.7 ppm and 163.0 ppm produced, which can be attributed to carbamate carbonyl carbon (see the Supporting Information). Based on previous reports[9,14] and the observed product, a absorption mechanism of CO_2 by these basic ILs can be proposed (Scheme 2). The mechanism involves the formation of carbamate or carbonate salt. Therefore, in contrast to CO_2 capture by amino-functionalized ILs, where two amine groups reacted with one CO_2 molecule, equimolar CO_2 absorption can be achieved for these basic ILs according to Scheme 2.

To investigate the effect of the basicity of ILs on the enthalpy of CO_2 absorption, we calculated the gas-phase reaction energetics according to Scheme 2 at the B3LYP/6-31++G(p,d) level of theory (see Table 1). The enthalpy of CO_2 absorption for $[P_{66614}]$[Triz] was $-56.4\,kJ\,mol^{-1}$, which is close to experimental values of $-50.0\,kJ\,mol^{-1}$ by in-situ IR spectroscopy (Supporting Information, Figure S2 and S3),



Scheme 2. The CO_2 absorption mechanism by typical basic ionic liquids.

where the pK_a of trizole was 13.9, while the enthalpy of CO_2 absorption for [P_{66614}][Im] increased to $-89.9\ kJ\,mol^{-1}$ when imidazole (pK_a 18.6) was used. In contrast, the enthalpy of CO_2 absorption for [P_{66614}][Tetz] decreased to only $-19.1\ kJ\,mol^{-1}$, where the pK_a of tetrazole decreased to 8.2, which is close to the enthalpy of CO_2 physical absorption.[6] To further investigate the relationship between the enthalpy of absorption and the basicity of the IL, we made a linear correlation between absorption enthalpy and the pK_a value of the anion in DMSO (Figure 2). The results show that a rough linear relationship between absorption enthalpy and the pK_a value can be obtained. It indicates that the enthalpy of CO_2 absorption by these basic ILs can be quantitatively tuned by varying the basicity of the IL, which should have some predictive value in future design for CO_2 capture. Furthermore, for these basic ILs, the changes of the enthalpy of CO_2 absorption agree with the variety of the absorption capacity (Figure 2).

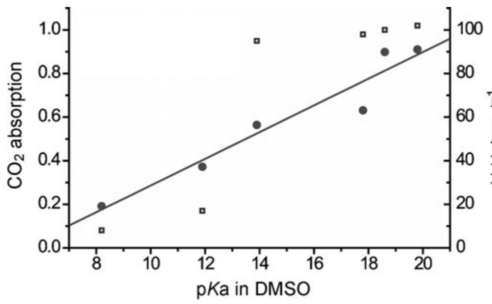


Figure 2. The relationship between CO_2 absorption capacity (□), absorption enthalpy (ΔH, ●), and the pK_a value of the anion in DMSO. The linear fit for the relationship between ΔH and pK_a of the anion in DMSO is shown; $R^2=0.930$.

As further evidence of the effect of the basicity of ILs on the enthalpy of absorption, we investigated the desorption of CO_2 by TGA. Generally, high absorption enthalpy would hinder the release of CO_2. As seen in Figure 3, for [P_{66614}][Im], the captured CO_2 started to lose the weight at 60 °C, and the release of CO_2 was almost complete at 150 °C. However, for [P_{66614}][Triz], the captured CO_2 was released between 40 °C to 120 °C, and no obvious weight loss was observed from 130 to 270 °C. The results indicate that the release of CO_2 is more facile when the basicity of ILs decreases, which agrees well with the trend of the enthalpy of absorption.

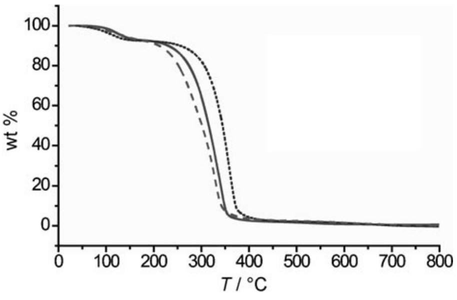


Figure 3. The effect of the anion of basic ionic liquids on the desorption of CO_2 by TGA: ----- [P_{66614}][Im], —— [P_{66614}][Ind], ••••• [P_{66614}][Triz].

Based on the relationship between the stability, absorption capacity, absorption enthalpy, and the basicity of ILs, we believe that [P_{66614}][Triz] is an ideal IL for CO_2 capture, as it shows high stability (> 300 °C), desirable enthalpy of absorption (ca. $56\ kJ\,mol^{-1}$), high absorption capacity (0.95 mole CO_2 per mole IL), and a rapid absorption rate. Thus, we selected [P_{66614}][Triz] as a sorbent material to investigate the stability of CO_2 absorption during the recycling of IL. The recycling of [P_{66614}][Triz] for CO_2 absorption is shown in Figure 4. It was seen that all the absorption capacities of IL remained steady, and absorption rates were rapid during 25 cycles. The results reveal that CO_2 absorption into and release from [P_{66614}][Triz] can be repeatedly cycled with high absorption capacity and rapid absorption rate, indicating that CO_2 capture process by [P_{66614}][Triz] is reversible.

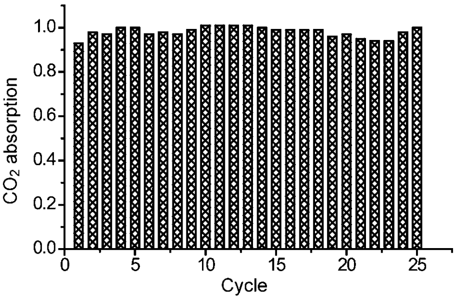


Figure 4. 25 cycles CO_2 absorption and desorption using [P_{66614}][Triz]. CO_2 absorption was carried out at 25 °C for 20 min, and desorption was performed at 80 °C under N_2 for 20 min.

In summary, we have developed a class of tunable basic ILs for energy-saving and equimolar CO_2 capture, which was prepared by neutralizing phosphonium hydroxide with eight kinds of weak proton donors with different pK_a values. The stability, absorption capability, and absorption enthalpy of ILs can be facilely tuned by varying the anions with different pK_a values. Thus, highly stable basic ILs [P_{66614}][Triz] for CO_2 capture with desirable enthalpy of absorption and high absorption capacity was achieved. Very interestingly, as opposed to the dramatic increase in viscosity, the change of the viscosity for these basic ILs is not remarkable during the absorption of CO_2, and rapid absorption rates were thereby obtained, which opens the door to achieving rapid absorption kinetics with ILs. The diversity of weak proton donors and the tunability of the anion provide an opportunity to develop other highly stable ILs for energy-saving and equimolar CO_2 capture. We believe that this equimolar, energy-saving, rapid, and reversible process by these tunable basic ILs provides an industrially attractive alternative for CO_2 capture.

Experimental Section

Trizole (Triz), tetrazole (Tetz), imidazole (Im), pyrazole (Pyr), oxazolidinone (Oxa), phenol (PhOH), indole (Ind), bentrizole (Bentriz), and trihexyl(tetradecyl)phosphonium bromide ($[P_{66614}]Br$) were purchased from Aldrich. An anion-exchange resin (Dowex Monosphere 550A (OH)) was obtained from Dow Chemical Company. All chemicals were obtained in the highest purity grade possible and used as received unless otherwise stated. All IL samples were dried under vacuum at 60 °C for more than 24 h to reduce possible traces of water.

^1H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 NMR spectrometer with tetramethylsilane as the standard. FT-IR spectra were measured using a Bio-Rad Excalibur FTS-3000 spectrometer. Mass spectra were obtained with a Bruker Esquire 3000 mass spectrometer equipped with ESI interface and ion-trap analyzer. HRMS were obtained on a Waters TOFMS GCT Premier instrument. The absorption of CO_2 was also monitored by in-situ FTIR spectroscopy (Bruker Optik GmbH, Matrix-MX) by analysis of the emerging of the C=O stretch at about 1736 cm^{-1} and the C=O stretch at about 1270 cm^{-1}. The enthalpy of CO_2 absorption by $[P_{66614}][Triz]$ was obtained by the variation in the natural logarithm equilibrium constant with temperature (Supporting Information, Figure S2). Viscosity was measured by a Brookfield DV-II + pro viscometer. Ionic conductivity was determined by an EC meter model 3084 from Amber Science Inc. Glass transition and decomposition temperatures were measured with a DSC Q 100 meter and TGA 2950 instrument, respectively.

A solution of $[P_{66614}]OH$ in ethanol was prepared from $[P_{66614}]Br$ using an anion-exchange resin. The tunable basic ILs were prepared by neutralizing $[P_{66614}]OH$ and weak proton donors such as trizole according to a literature method.[11] Equimolar trizole was added to the $[P_{66614}]OH$ solution in ethanol. The mixture was then stirred at room temperature for 12 h. Subsequently, ethanol and water were distilled off at 60 °C under reduced pressure. The product thus obtained was dried in high vacuum for 24 h at 60 °C. The structures of these basic ILs were confirmed by NMR and IR spectroscopy; no impurities were found by NMR. The water content of these basic ILs was determined with a Karl Fisher titration and found to be less than 0.1 wt %. The residual bromide content of these basic ILs was determined by a semi-quantitative Nessler cylinder method, which showed that the bromide content was lower than 0.15 wt %.

In a typical CO_2 absorption by basic ILs, CO_2 at atmospheric pressure was bubbled through circa 1.0 g ILs in a glass container at a flow rate of 60 $mL\,min^{-1}$. The glass container with an inner diameter of 10 mm 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. CO_2 captured was released by heating under bubbling molecular N_2.

All calculations were performed using the Gaussian 03 programs package.[15] For each set of calculations, we calculated geometry and energy optimizations for each free anion, the free CO_2 molecule, and each anion–CO_2 complex at the B3LYP/6-31G + + (d,p) level.[16]

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