Active chemisorption sites in functionalized ionic liquids for carbon capture

Journal:	*Chemical Society Reviews*
Manuscript ID	CS-SYN-06-2015-000462.R4
Article Type:	Review Article
Date Submitted by the Author:	06-May-2016
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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Active chemisorption sites in functionalized ionic liquids for carbon capture

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Development of novel technologies for efficient and reversible capture of CO_2 is highly desired. In the last decade, CO_2 capture using ionic liquids has attracted intensive attention from both academia and industry, and has been recognized as a very promising technology. Recently, a new approach has been developed for highly efficient capture of CO_2 by site-containing ionic liquids through chemical interaction. This perspective review focuses on the recent advances in chemical absorption of CO_2 using site-containing ionic liquids, such as amino-based ionic liquids, azolate ionic liquids, phenolate ionic liquids, dual-functionalized ionic liquids, pyridine-containing ionic liquids and so on. Other site-containing liquid absorbents such as amine-based solutions, switchable solvents, and functionalized ionic liquid-amine blends are also investigated. Strategies have been discussed for how to activate the existent reactive sites and develop novel reactive sites by physical and chemical methods to enhance CO_2 absorption capacity and reduce absorption enthalpy. The carbon capture mechanisms of these site-containing liquid absorbents are also presented. Particular attention is paid to the latest progress of CO_2 capture in multiple-site interactions by amino-free anion-functionalized ionic liquids. In the last section, future directions and prospects for carbon capture by site-containing ionic liquids are outlined.

1. Introduction

Up to now, energy conversion is based largely on the burning of fossil fuels–coal, oil, and natural gas. During these processes, carbon is released into the atmosphere in the form of gaseous CO_2, and 30 gigatons (Gt) of CO_2 is emitted per year as a result of the use of these fossil fuels at present. [1-2] It is known that CO_2 emissions from fossil firepower plants contribute about 30% to this,[3] and CO_2 concentration in most of the flue gases is approximately 15%.[4-5] As CO_2 is one of the most abundant greenhouse gas (GHG), the increased concentration of CO_2 may not only results in serious environmental problems, such as higher earth surface temperature and more frequent and severe climatic disturbance, but also leads to a pronounced change in our ecosystem because some plant species are more sensitive to the CO_2 concentration than others.[6] The Intergovernmental Panel on Climate Change (IPCC) perceives that climate change is a long-term challenge, but one that requires urgent action given the pace and the scale by which greenhouse gases are accumulating in the atmosphere and the risks of a more than 2 °C temperature rise. [7] Today we need to focus on the fundamentals and on the actions to control and minimize the emissions of CO_2, otherwise the risks we run will get higher with every year. In addition, CO_2 is also an attractive renewable carbon resource, which is nontoxic, cheap, and nonflammable. [8-9] Thus, development of novel materials and green processes for the efficient, reversible and economical capture of CO_2 is highly desired for environmental protection and valuable chemicals production.

Carbon dioxide capture and storage (CCS) is a technology aimed at reducing GHG emissions generated by the burning of fossil fuels during industrial and energy-related processes. [10-11] CCS involves the capture, transport and long-term storage of CO_2. During these decades, several technologies have been developed for CCS, such as liquid absorption, solid adsorption, and membrane absorption. The sorption processes are typically classified in chemical and physical sorption, also referred to as chemisorption and physisorption, respectively, according to the bonding between CO_2 and sorbent (Fig. 1). However, most physical sorbents for CO_2 such as organic liquids, [12-15] activated carbons, [16-17] zeolite 13X, [18-22] unmodified periodic mesoporous silicas, [22-23] porous organic polymers (POPs), [24] and traditional metal organic frameworks (MOFs) [25] require high pressure and/or temperature gradient between the sorption and desorption stages to enable both efficient sorption performance and near complete

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desorption of CO_2, because of the weak interaction between sorbate and sorbent. Moreover, they exhibit relatively low selectivity toward CO_2 and generally low tolerance to water vapor in the gas feed, and their CO_2 separation performance decreases drastically with increasing temperature. An ideal sorbent for capturing CO_2 from post-combustion flue gas would exhibit a high selectivity for CO_2, high CO_2 sorption capacity, minimal regeneration energy, and long-term stability under the operating conditions.[26] Thus, the chemical sorption of CO_2 from such a low pressure stream of gases by active site-containing sorbents is an effective method for the capture of CO_2.

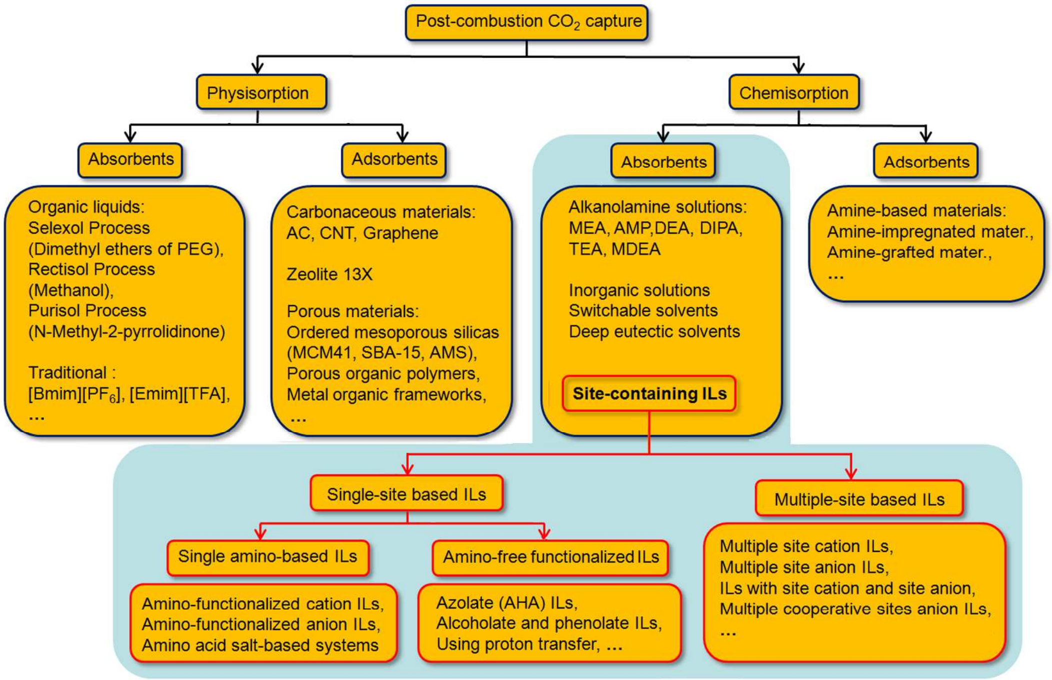


Fig. 1 Schematic representation of post-combustion CO_2 capture through physisorption and chemisorption.

Ionic liquids (ILs) are completely composed of ions and generally are liquid below 100 °C.[27] Those ILs that are liquid at room temperature are called room temperature ionic liquids (RTILs).[28] In recent years, RTILs have been widely used in the areas of chemistry and chemical engineering as better catalyst[29-30] and solvent for organic synthesis,[31-35] nanomaterials preparation,[36-38] extraction separation,[39-41] and energy conversion.[42-45] They exhibit the following outstanding properties: extremely low vapor pressure, wide liquid temperature range, non-flammability, high thermal stability, and excellent solvation capacity.[46-56] Since the pioneer work of Brennecke *et al*.[57] on the solubility measurements of CO_2 in 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim][PF_6]$) at 298.2 K and pressure up to 40 MPa, a great deal of efforts have been made to investigate the solvation of CO_2 in conventional ILs based on a physical mechanism (i.e, no chemical reaction takes place) with main focus on the understanding and improvement of CO_2 solubility.[58-64] The main conclusions obtained are as follows: (1) anions play a key role in determining CO_2 solubility in ILs; (2) fluorination on the cations and anions increases CO_2 solubility, and cation-fluorination has a lesser extent than anion-fluorination; (3) cations with long alkyl chain or ether linkage improve CO_2 solubility. [65-68] Nonetheless, even with these improvements, CO_2 capacity in ILs resulted from physical dissolution at low partial pressure from post-combustion flue gas is too low to develop a practical separation process. The reason for such a low capacity is due to the fact that no chemical interaction sites are included in these ILs.

Large scale application of conventional ILs for CO_2 capture from flue gas is mainly hindered by the low CO_2 absorption capacity under post-combustion conditions, where the partial pressure of CO_2 is rather low (~ 0.15 bar) and the solubility of CO_2 is lower than 0.05 mole of CO_2 per mole of IL even for the best conventional ILs.[66] To overcome this limitation, other strategies have been developed based on the chemical reaction of CO_2 with active site-containing ILs. For example, Davis *et al.* [69] reported the first example of CO_2 chemisorption by a "task-specific" IL (TSIL), now preferably known as a kind of functionalized ILs. This functionalized IL, tethered with an amino group on an imidazolium cation, was found to be able to capture 0.5 mole of CO_2 per mole of IL under ambient pressure. Since this breakthrough on CO_2 absorption, there have been many derivative publications, including the strategies uisng other functionalized ILs such as amino-based ILs, amino acid-based ILs, azolate-based ILs, phenolate-based ILs, and pyridine-containing ILs. The rapid increase of number of publications devoted to the relevant CO_2 chemisorption with active site-containing ILs in recent years evidences the potential and practical importance of site-containing ILs. More importantly, the potential of these site-containing ILs is further emphasized by the fact that their physical and chemical properties may be finely tuned by designing both the cation and the anion structures.[70]

By analysis of the relevant publications for CO_2 chemisorption, it is clear that the research interests have been mainly concentrated on the following aspects: (1) the design and synthesis of new ILs, especially the task-specific ILs with enhanced absorption performance by functionalization with an amine or other groups; (2) the measurements and estimation of physical/chemical properties of the multi-component systems containing IL, CO_2 and other compounds, and the development of suitable thermodynamic models; (3) the investigation on the transport properties, absorption kinetics, and the mechanism for CO_2 capture with functionalized ILs.

A number of significant progresses have been achieved in the capture of CO_2 by functionalized ILs, and several critical reviews in this area have been published.[27,66,71-83] For example, absorptive and membrane technologies for CO_2 capture using ILs and IL-based composites have been reviewed by Noble *et al.*[71] The use of ILs as alternative fluids for CO_2 capture and natural gas sweetening has been reviewed by Atilhan *et al.*, [75] and CO_2 chemisorption by functionalized ILs has been reviewed by Wang *et al.*[77] However, CO_2 capture by ILs is a fast-developing field with many new publications, and the most state-of-the-art research is already not covered by recent reviews. In addition, it is highly important to understand the strategies for improving CO_2 capture by designing the structures of site-containing ILs.

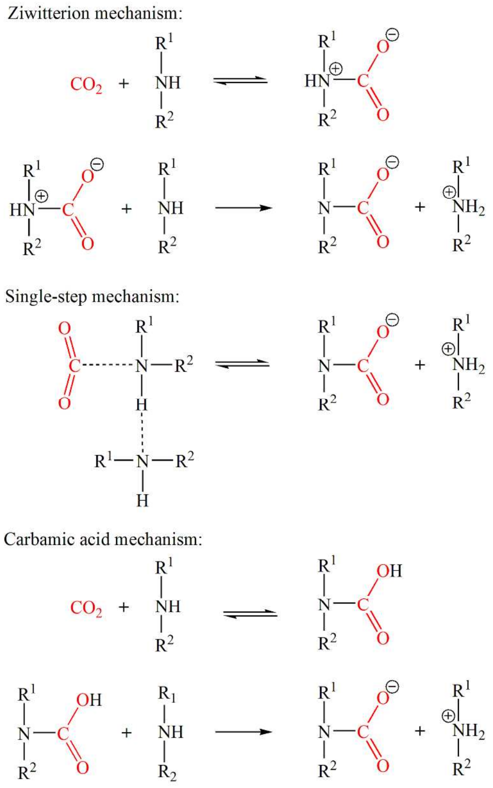
In this review paper, we are unable to discuss all the related aspects mentioned above, but mainly focus our attention on the recent advances in CO_2 chemisorption by active site-containing ILs. Since various active site-containing ILs have been used to capture CO_2, we classify these ILs into single site-containing ILs and multiple site-containing ILs through different absorption mechanisms. In order to compare the CO_2 capacities of different site-containing ILs, we have calculate the absorption capacity of all the investigated ILs and ILs-based mixtures based on a mol CO_2/kg IL basis. These data are listed in Tables 1, 2 and 3 together with the original data based on a mol CO_2/mol IL basis. Owing to the different experimental conditions and chemical materials used by different authors, the results might have some derivations without detailed evaluations. Also, some data have been taken approximately from the figures or curves published in the literatures, which are marked with "~". However, this will comprehensively reflect, to a great extent, the overall CO_2 capture performance of ILs and IL-based mixtures. Then the strategies for developing novel active sites, enhancing CO_2 absorption capacity, and reducing absorption energy have been discussed based on this classification to indicate that the desirable carbon capture with high capacity and low energy requirements can be achieved by carefully designing the structures of active site-containing ILs. Finally, the future directions and prospects for CO_2 chemisorption by active site-containing ILs are presented

2. Single amino-based ILs

Up to now, lots of functionalized ILs or task-specific ILs based on different kinds of reactive sites have been developed for efficient and reversible capture of CO_2 through single active site chemical interaction between a functional group and CO_2. The single active site-containing ILs can be simply classified into single amino-containing ILs and amino-free functionalized ILs with single active site.

2.1 Amino-containing cation-functionalized ILs

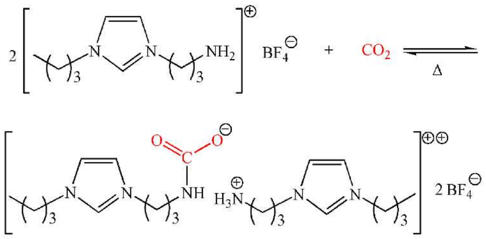
In industry, aqueous monoethanolamine (MEA) has been most widely used as liquid absorbent for CO_2 for more than 50 years, where the absorption is based on chemical interactions.[84-87] The mechanism for the reactions between CO_2 and amines have been extensively studied as shown in Scheme 1.[88-90] It is known that the reaction of CO_2 and MEA is stoichiometrically limited to 0.5 mole of CO_2 per mole of amine. However, the measured molar ratio of CO_2 to MEA in 30 wt% aqueous MEA solution is 0.90 at 40 °C and 20 bar (Table 1, entry 1-2), which indicates that the absorption of CO_2 exceeds the above mentioned limitation.[86] The reason is that MEA reacts with CO_2 to form carbamates through a 1:2 mechanism, while up to 1:1 mechanism can be achieved in the presence of water considering hydrolysis of the zwitterion (see Section 3.3.3). Although the absorption of CO_2 in aqueous amine solutions can achieve higher capacities, some serious inherent drawbacks are also involved, including solvent loss, corrosion, ethanolamine degradation, and high energy demands for the regeneration of amine, which is not consistent with the sustainable principles.[86-91]



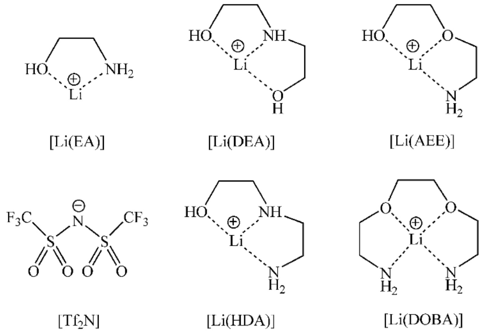
Scheme 1 The reaction of primary and secondary amines with CO_2. Adapted with permission from ref. 88. Copyright 2010 American Chemical Society.

In the year of 2002, Davis *et al.* [69] reported the first example of CO_2 chemisorption by a task-specific IL 1-propylamide-3-butyl imidazolium tetrafluoroborate ([apbim][BF_4]) tethered with an amino group on an imidazolium cation, taking the lead from the conventional aqueous amine technology. In their work, 0.5 mole of CO_2 per mole of IL was captured under ambient pressure (Table 1, entry 3). The amino group on the cation of [apbim][BF_4] was reacted with CO_2 in a carbamate mechanism similar to the aqueous amine system, resulting in a stoichiometry of one CO_2 molecule to two amines, as shown in Scheme 2. [69] The kinetics of CO_2 absorption in the amino-functionalized IL 1-

(3-aminopropyl)-3-methylimidazolium tetrafluoroborate ([apmim][BF_4]) was studied by Sánchez *et al.*[92] and it was found that although viscosity was increased dramatically upon complexation with CO_2, [93-94] the absorption of CO_2 was enhanced remarkably compared to the physical absorption in 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]). A number of amino-functionalized imidazolium ILs with different anions were also synthesized and investigated as potential absorbents for CO_2 capture. [95-96] For example, Baek *et al.* [95] synthesized a series of 1-(2-aminoethyl)-3-methylimidazolium ([aemim]$^+$) ILs and showed that absorption capacity of 0.45 mole of CO_2 per mole of IL was reached at 30 °C and 1 bar (Table 1, entries 4–8), indicating the predominance of a 1 : 2 mechanism, whereby one CO_2 reacted with two IL molecules to form a carbamate group. Han *et al.* [97] investigated the switchable basicity of [aemim][BF_4] by CO_2, while Mu *et al.* [98] performed the theoretical investigation on this reaction mechanism. Subsequently, sulfonate anions coupled with amino-functionalized ammonium cations were also explored to be effective for CO_2 capture. [99] Li *et al.* [100] studied the CO_2 capture by NaY zeolite supported [apmim][Br] through 1 : 2 mechanism. Sánchez *et al.* [101] showed that very low CO_2 absorption capacity was achieved at 30 °C and 1 bar by tertiary amino-based ILs, while CO_2 capture by primary amino-based ILs could achieve at 1:2 stoichiometry.

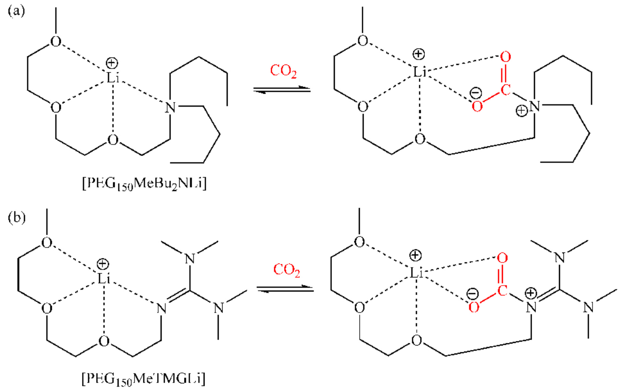


Scheme 2 Proposed reaction between amino-functionalized IL [apbim][BF_4] and CO_2. Reprinted with permission from ref. 69. Copyright 2002 American Chemical Society.



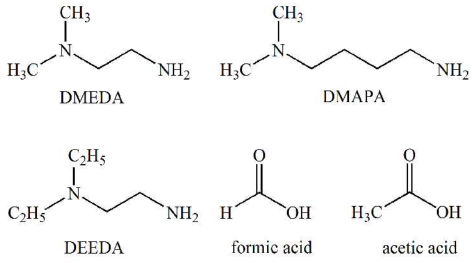
Scheme 3 Structures and abbreviations of different cations and anion of alkanolamine based ILs in ref. 102.

In the year of 2012, Wang *et al.* [102] presented a new kind of tunable alkanolamine-based ILs by making use of the multidentate coordination interactions of alkanolamine (e.g. ethanolamine (EA), diethanolamine (DEA), 2-(2-aminoethoxy)ethanol (AEE), 2-hydroxyethylenediamine (HDA), and 2,2′-(ethylenedioxy)bis(ethylamine) (DOBA)) with alkali metallic ions in a quasi-aza-crown ether fashion (Scheme 3). It was found that high capacity and rapid kinetics could be achieved by tuning the chelation of the alkali metal salt. For example, the molar ratios of CO_2 to [Li(EA)][Tf_2N], [Li(DEA)][Tf_2N], and [Li(AEE)][Tf_2N] were 0.54, 0.52, and 0.55 at 40 °C and 1 bar, respectively, indicating that 0.5 mole of CO_2 was captured by one mole of IL through carbamate mechanism (Table 1, entries 9–11). He *et al.* [103] reported the other kinds of triethylene glycol (PEG_{150}) chelated ILs, which could efficiently capture CO_2 through formation of zwitterionic adducts stabilized by Li^+ in a 1:1 manner (Scheme 4). It was shown that one mole of [$PEG_{150}MeBu_2NLi$][Tf_2N] and [PEG_{150}MeTMGLi][Tf_2N] was able to rapidly capture 0.66 and 0.89 mole CO_2, respectively, while [$PEG_{150}MeNH_2Li$][Tf_2N] gave rise to CO_2 uptake approaching 1:2 stoichiometry as expected from the proposed mechanism (Table 1, entries 12–14).[103] Thus, tertiary amino-functionalized ILs with multidentate cation coordination have a much better performance.



Scheme 4 The reaction of CO_2 with [$PEG_{150}MeBu_2NLi$]$^+$ (a) or [PEG_{150}MeTMGLi]$^+$ (b). Reprinted with permission from ref. 103. Copyright 2014 Yang and He; licensee Beilstein-Institut.

Recently, MacFarlane *et al.*[104] synthesized a series of amino-functionalized imidazolium protic ionic liquids (PILs) by the neutralization of dimethylethylenediamine (DMEDA), diethylethylenediamine (DEEDA), or 3-(dimethylamino)-1-propylamine (DMAPA) with formic acid or acetic acid (Scheme 5). The CO_2 absorption capacities as high as 13% w/v were observed with a mole ratio of IL to CO_2 close to the theoretical value (1 : 0.5 mol) for carbamate formation (Table 1, entries 15–19).

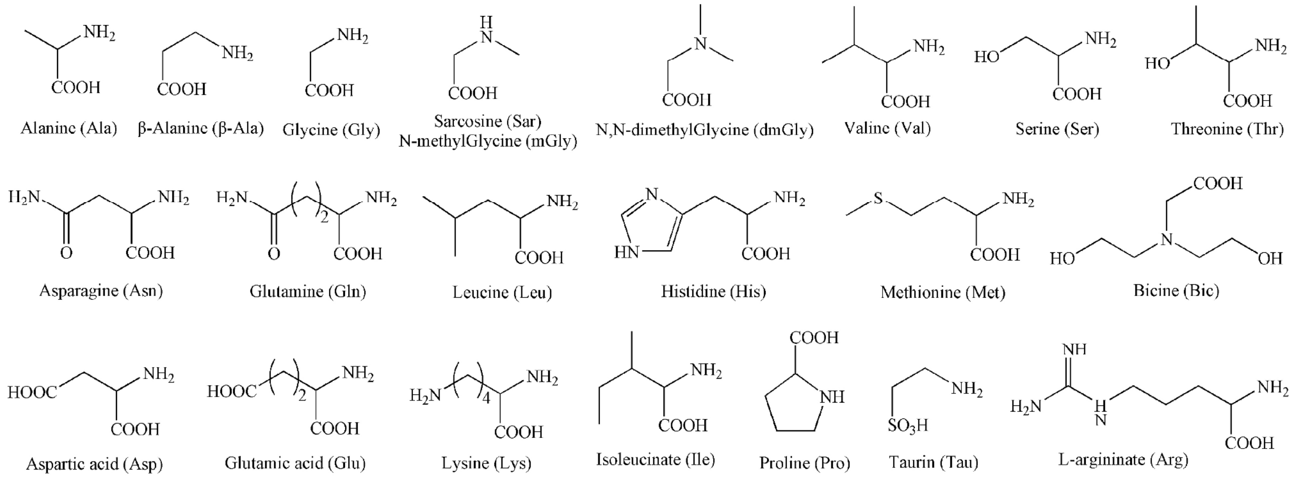


Scheme 5 Structures and abbreviations of different amines and acids used in ref. 104 to synthesis PILs for CO_2 capture.

2.2 Amino-containing anion-functionalized ILs

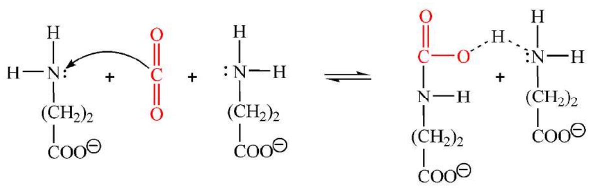
2.2.1 Amino acid-based ILs (AAILs)

Amino acids (AA), which consist of a carboxyl group (–COOH) and a primary amine (–NH_2) functional group (Scheme 6), have low cost, low environmental impact, high biodegradability, negligible volatility and high biological activity.[105] They are easy to obtain in large quantities at a relatively high purity. Ohno *et al.*[51] reported a series of ILs composed of imidazolium cations and AA anions for the first time through [OH]-exchange followed by acid-base neutralization, which seems to be suitable for preparing various pure ILs compared with conventional methods.



Scheme 6 Structures and abbreviations of amino acids and derivatives.

Through 1:2 mechanism. Considering the fact that the disadvantages of CO_2 capture by amino-functionalized ILs is its slow absorption kinetics and low CO_2 absorption capacities due to the relatively high viscosity of the ILs, Zhang *et al.*[106] reported the first example of CO_2 chemical absorption by porous SiO_2 supported tetrabutylphosphonium AAILs ($[P_{4444}][AA]$) with an amino group tethered to the anion. These ILs were synthesized by the reaction of tetrabutylphosphonium hydroxide $[P_{4444}][OH]$ with AAs, including $[P_{4444}][Gly]$, $[P_{4444}][Ala]$, $[P_{4444}][\beta\text{-}Ala]$, $[P_{4444}][Ser]$, and $[P_{4444}][Lys]$. The supported absorption of CO_2 by these ILs were investigated, and it was found that about 0.6 mole of CO_2 per mole of IL could be captured (Table 1, entries 20–22), resulting from the reaction mechanism of two amino groups with one CO_2 (Scheme 7). Wu *et al.*[107-108] reported a series of tetraalkylammonium AAILs, which were the first samples of amino-functionalized ILs with low viscosity. The capture capacities by $[N_{2222}][Ala]$ (81 mPa s), $[N_{2222}][\beta\text{-}Ala]$ (132 mPa s), and $[N_{2224}][Ala]$ (29 mPa s) were all found to approach 0.5 mole CO_2 per mole IL at ambient pressure and 40 °C (Table 1, entries 23–25)



Scheme 7 Proposed absorption mechanism of CO_2 by $[P_{4444}][\beta\text{-}Ala]$. Reprinted with permission from ref. 106. Copyright 2006 Wiley-VCH.

Li *et al.*[109] investigated CO_2 absorption by imidazolium AAILs immobilized on the nanoporous polymethylmethacrylate (PMMA) microspheres. The results showed that 1-ethyl-3-methylimidazolium based ILs such as [Emim][Gly] and [Emim][Ala] could capture about 0.5 mole of CO_2 per mole of the IL (Table 1, entries 26–27), due to the reaction mechanism of two amino groups with one CO_2.[109] Khanna *et al.*[110] studied some other imidazolium AAILs, including [Bmim][Met], [Bmim][Leu], [Bmim][Gly], [Bmim][Val], [Bmim][Ala] and [Bmim][Pro], which showed the capture performance through 1:2 mechanism (Table 1, entries 28–33). Compared with the amino group tethered to the cation, Ren *et al.*[111] found from molecular dynamics simulation that AAILs with an anion-tethered strategy was greatly benefit to the CO_2 capture from the viewpoint of interfacial adsorption and transfer.

In the subsequent studies, some other amino-functionalized ILs, such as cholinium prolinate ([Cho][Pro]) (Table 1, entry 34),[112] were explored for CO_2 capture in PEG_{200} (Mw = 200 g mol^{-1}) solution. However, all these systems are believed to proceed via a 1 : 2 (CO_2 : amine) stoichiometry, and these processes are atom inefficient. How can we enhance CO_2 absorption capacity by making use of the tunability of functionalized ILs?

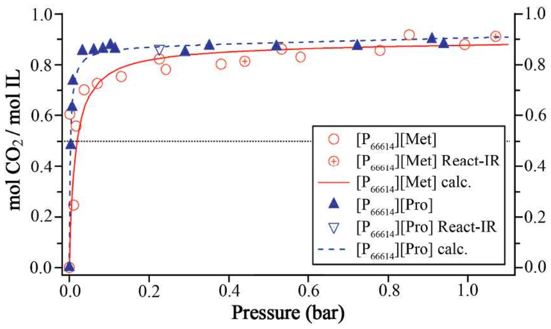
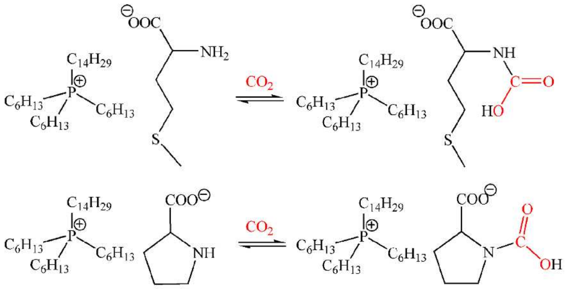


Fig. 2 CO_2 absorption by $[P_{66614}][Pro]$ and $[P_{66614}][Met]$ at 22 °C. Adapted with permission from ref. 113. Copyright 2010 American Chemical Society.

Through 1:1 mechanism. To enhance the absorption of CO_2 by ILs, other amino-functionalized ILs were designed and synthesized to prevent nucleophilic attack of the amino group on the carboxylic acid group of carbamic acid. For instance, two trihexy(tetradecyl)phosphonium ILs, $[P_{66614}][Met]$ and $[P_{66614}][Pro]$, were synthesized by Brennecke *et al.*[113-114] and used to absorb CO_2 (Fig. 2). It was shown that nearly 1:1

stoichiometry could be achieved during the reactions between these ILs and CO_2 (Scheme 8) (Table 1, entries 35–36), which is higher than other amino-functionalized ILs and even aqueous amine absorbents previously used. The *ab* initio calculations and FT-IR spectra verified the 1:1 reaction stoichiometry.



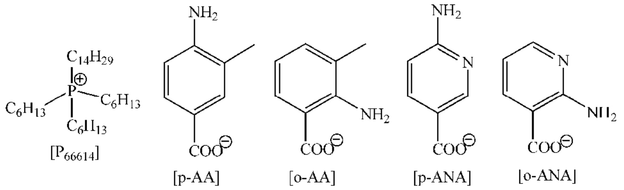
Scheme 8 Reaction schematics of CO_2 with [P_{66614}][Met] (top) and [P_{66614}][Pro] (bottom). Adapted with permission from ref. 113. Copyright 2010 American Chemical Society.

In a subsequent work, Brennecke *et al.* [115-116] prepared other kinds of [P_{66614}]-based ILs with amino acid anions, such as [P_{66614}][Gly], [P_{66614}][Sar] and [P_{66614}][Ile]. CO_2 absorption isotherms of these ILs were measured by using a volumetric method and nearly equimolar absorption capacities were shown (Table 1, entries 37–39). Riisager *et al.* [117] also reported that [N_{66614}]-based IL [N_{66614}][Met] could absorb 1.0 mole CO_2 per mole IL at room temperature and 1 bar CO_2, which corresponds to a 1:1 mechanism (Table 1, entry 40). However, the CO_2 absorption of [P_{66614}][Ala] and [P_{66614}][Tau] was greater than 0.5 mole of CO_2 per mole of IL, [116] which would be the capacity if 1:2 reaction mechanism was dominant (Table 1, entries 41–42).

Matsuyama *et al.* [118] reported three kinds of [P_{4444}]-based AAILs with a series of glycinate anions, such as [P_{4444}][Gly], [P_{4444}][mGly], and [P_{4444}][dmGly]. Their results showed that CO_2 was only physically dissolved in [P_{4444}][dmGly], while chemical structures of [P_{4444}][Gly] and [P_{4444}][mGly] were changed after CO_2 absorption and CO_2 complexes were formed. Similarly, Wassell *et al.* [119] showed that very low CO_2 absorption capacities were achieved at 25 °C and 5 bar by [P_{4444}][dmGly] and [P_{4444}][Bic], which contain tertiary amino groups in the anions, while CO_2 capture by other AAILs followed 1:1 stoichiometry (Table 1, entries 43–49). Romanos *et al.* [120] reported CO_2 absorption at 40 °C and 1 bar by some supported ionic liquid phase systems (SILPs) consisting of micron size IL droplets within an envelope of silica nanoparticles (Table 1, entry 50–54). These ILs includes [N_{1112}][Pro], [N_{1113}][Pro], [$Me_2N(CH_2CH_2OH)_2$][Pro], and [$Me_2N(CH_2CH_2OH)_2$][Tau]. Maier *et al.* [90] investigated CO_2 absorption by [$Me_2N(CH_2CH_2OH)_2$][Tau] at 37 °C using surface- and bulk-sensitive experimental techniques. In their work, CO_2 was found to be bound in the bulk as carbamate (with nominally 0.5 mole of CO_2 per mole of IL) up to ~2.5 bar CO_2, and as carbamic acid (with nominally 1 mole of CO_2 per mole of IL) at higher pressure (Table 1, entry 55–56).

2.2.2 Other amino-based anion ILs

Several other kinds of anion-functionalized methylbenzolate-based ILs and nicotinate-based ILs with amino group at the para or ortho position were designed by Wang *et al.* [121] and applied for 1:1 CO_2 capture (Scheme 9). It was found that the ILs with the amino group at the para or ortho position exhibited both higher capacity and lower enthalpy (Fig. 3). For example, the absorption capacities by [P_{66614}][*p*-AA] and [P_{66614}][*p*-ANA] were, respectively, 0.94 and 0.78 mole of CO_2 per mole of IL, while [P_{66614}][*o*-AA] and [P_{66614}][*o*-ANA] could absorb CO_2 only at the level of 0.60 and 0.56 mole CO_2 per mole IL (Table 1, entries 57–60). These results suggest that the absorption was significantly affected by the nature of anion, due to different entropic driving forces for the reaction with CO_2.



Scheme 9 Structures of the ILs for CO_2 capture. Reprinted with permission from ref. 121. Copyright 2014 American Chemical Society.

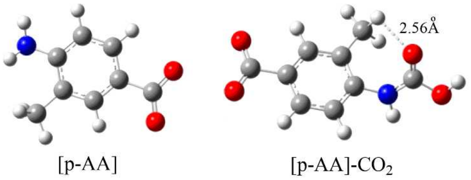


Fig. 3 The optimized structure of [p-AA] and [p-AA]–CO_2. Reprinted with permission from ref. 121. Copyright 2014 American Chemical Society.

2.3 Amino acid salt-based systems

In order to prevent nucleophilic attack of the amino group on the carboxylic acid group of carbamic acid, sodium N-alkylglycinates and alaninates with PEG_{150} as a suitable solvent were investigated for CO_2 absorption by He *et al.* [122] (Scheme 10). The results showed that a high CO_2 capacity up to 1:1 stoichiometry could be obtained by the steric hindrance controlled absorbent sodium N-isopropylglycinate (*i*PrNH-GlyNa), while CO_2 was captured by non-modified sodium glycinate to produce a 1:2 (CO_2 : amine) stoichiometry (Table 1, entries 61–68). However, *n*Pr_2N-GlyNa, without an N-H group, demonstrated a low CO_2 capacity (Table 1, entry 67). IR and NMR spectroscopy showed that CO_2 was captured by *i*PrNH-GlyNa in the form of carboxylate anions and –COOH. Density functional theory (DFT) calculations indicated that enthalpy change for the formation of the carbamic acid was −10.4 kcal mol^{-1}. In a later work, the same group used crown ether (e.g. 15-crown-5 and 18-crown-6) instead of PEG to coordinate the metal ion for the formation of alkali metal onium salt/crown ether systems, which could absorb CO_2 in similar 1:1 reaction stoichiometry in PEG_{300} (Mw = 300 g mol^{-1}) solution (Table 1, entries 69–77).[123]

Cite this: DOI: 10.1039/c0xx00000x

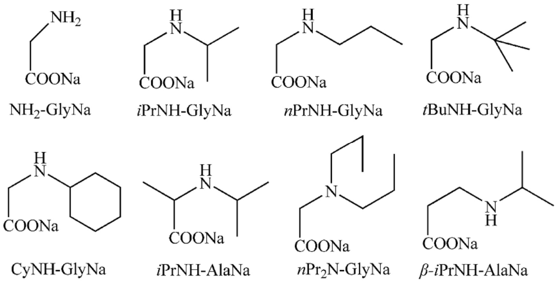
www.rsc.org/xxxxxx

Table 1 CO_2 chemisorption by amino-functionalized ILs or ionic salts with single active site.

Entry	Absorbent [a]	Conditions			Mw (g mol^{-1}) [b]	Absorption capacity		Active site [d]	Ref.
		T (°C)	P (bar)	*t* (min)		mol CO_2/mol IL	mol CO_2/kg IL [c]		
1	MEA	– [e]	– [e]	– [e]	61.1	0.5	8.18	–H**N**(H)	86
2	MEA-H_2O (30 w_{MEA}%)	40	20	– [e]	61.1	0.90	14.73 (4.42)	–H**N**(H)	86
3	[apbim][BF_4]	22	1	180	269.1	~0.5	~1.86	–H**N**(H)	69
4	[aemim][BF_4]	30	1	– [e]	213.0	0.41	1.92	–H**N**(H)	95
5	[aemim][PF_6]	30	1	– [e]	271.1	0.46	1.70	–H**N**(H)	95
6	[aemim][Tf_2N]	30	1	– [e]	406.3	0.49	1.21	–H**N**(H)	95
7	[aemim][TfO]	30	1	– [e]	275.3	0.47	1.71	–H**N**(H)	95
8	[aemim][DCA]	30	1	– [e]	192.2	0.42	2.19	–H**N**(H)	95
9	[Li(EA)][Tf_2N]	40	1	60	348.2	0.54	1.55	–H**N**(H)	102
10	[Li(DEA)][Tf_2N]	40	1	60	392.2	0.52	1.33	–**N**(H)–	102
11	[Li(AEE)][Tf_2N]	40	1	60	392.2	0.55	1.40	–H**N**(H)	102
12	[$PEG_{150}MeNH_2Li$][Tf_2N]	25	1	20	450.3	0.45	1.00	–H**N**(H)	103
13	[$PEG_{150}MeBu_2NLi$][Tf_2N]	25	1	20	562.5	0.66	1.17	–**N**R_3	103
14	[PEG_{150}MeTMGLi][Tf_2N]	25	1	20	548.5	0.89	1.62	–**N**R_3	103
15	[DEEDAH][HCOO]	20	1	– [e]	162.2	0.47	2.90	–H**N**(H)	104
16	[DMEDAH][HCOO]	20	1	150	134.2	0.38	2.83	–H**N**(H)	104
17	[DMAPAH][HCOO]	20	1	– [e]	162.2	0.28	1.73	–H**N**(H)	104
18	[DEEDAH][Ac]	20	1	– [e]	176.3	0.30	1.70	–H**N**(H)	104
19	[DMAPAH][Ac]	20	1	– [e]	176.3	0.33	1.87	–H**N**(H)	104
20	[P_{4444}][Gly] [f]	– [e]	1	100	333.5	~0.6	~1.80 (0.74)	–H**N**(H)	106
21	[P_{4444}][Ala] [f]	– [e]	1	100	347.5	~0.67	~1.93 (0.81)	–H**N**(H)	106
22	[P_{4444}][β-Ala] [f]	– [e]	1	100	347.5	~0.6	~1.73 (0.72)	–H**N**(H)	106
23	[N_{2222}][Ala]	40	1	60	218.3	~0.45	~2.06	–H**N**(H)	107
24	[N_{2222}][β-Ala]	40	1	60	218.3	~0.50	~2.29	–H**N**(H)	108
25	[N_{2224}][Ala]	40	1	30	246.4	~0.48	~1.95	–H**N**(H)	108
26	[Emim][Gly] [g]	40	1	40	185.2	0.49	2.65 (1.33)	–H**N**(H)	109
27	[Emim][Ala] [g]	40	1	40	199.3	0.45	2.26 (1.13)	–H**N**(H)	109
28	[Bmim][Met]	25	2	– [e]	287.4	0.42	1.46	–H**N**(H)	110
29	[Bmim][Leu]	25	2	– [e]	269.4	0.38	1.41	–H**N**(H)	110
30	[Bmim][Gly]	25	2	– [e]	213.3	0.38	1.78	–H**N**(H)	110
31	[Bmim][Val]	25	2	– [e]	255.4	0.39	1.53	–H**N**(H)	110
32	[Bmim][Ala]	25	2	– [e]	227.3	0.39	1.72	–H**N**(H)	110
33	[Bmim][Pro]	25	2	– [e]	253.3	0.32	1.26	–**N**(H)–	110
34	[Cho][Pro] [h]	35	1	60	218.3	~0.6	~2.75 (1.38)	–**N**(H)–	112
35	[P_{66614}][Met]	22	1	– [e]	632.1	~0.9	~1.42	–H**N**(H)	113
36	[P_{66614}][Pro]	22	1	– [e]	598.0	~0.9	~1.51	–**N**(H)–	113
37	[P_{66614}][Gly]	22	1	– [e]	557.9	1.26	2.26	–H**N**(H)	115
38	[P_{66614}][Sar]	22	1	– [e]	571.9	0.91	1.59	–H**N**(H)	115
39	[P_{66614}][Ile]	22	1	– [e]	614.0	0.97	1.58	–H**N**(H)	115
40	[N_{66614}][Met]	22	1	240	615.1	1.0	1.63	–H**N**(H)	117
41	[P_{66614}][Ala]	22	1	– [e]	571.9	0.66	1.15	–H**N**(H)	115
42	[P_{66614}][Tau]	22	1	– [e]	608.0	~0.8	~1.32	–H**N**(H)	116
43	[P_{4444}][Gly]	25	5	– [e]	333.5	1.02	3.06	–H**N**(H)	119
44	[P_{4444}][Ala]	25	5	– [e]	347.5	1.10	3.17	–H**N**(H)	119
45	[P_{4444}][Val]	25	5	– [e]	375.6	1.07	2.85	–H**N**(H)	119
46	[P_{4444}][Ile]	25	5	– [e]	389.6	1.07	2.75	–H**N**(H)	119
47	[P_{4444}][Pro]	25	5	– [e]	373.6	1.01	2.70	–**N**(H)–	119
48	[P_{4444}][Bic]	25	5	– [e]	421.6	0.44	1.04	–	119
49	[P_{4444}][dmGly]	25	5	– [e]	361.5	0.24	0.66	–	119
50	[N_{1112}][Pro] [i]	40	1	– [e]	202.3	0.74	3.66 (1.47)	–**N**(H)–	120
51	[$Me_2N(CH_2CH_2OH)_2$][Pro] [i]	40	1	– [e]	248.3	0.48	1.93 (0.77)	–**N**(H)–	120
52	[$Me_2N(CH_2CH_2OH)_2$][Pro] [j]	40	1	– [e]	248.3	0.54	2.17 (0.87)	–**N**(H)–	120
53	[$Me_2N(CH_2CH_2OH)_2$][Tau] [i]	40	1	– [e]	258.3	0.50	1.94 (0.77)	–H**N**(H)	120
54	[$Me_2N(CH_2CH_2OH)_2$][Tau] [j]	40	1	– [e]	258.3	0.53	2.05 (0.82)	–H**N**(H)	120
55	[$Me_2N(CH_2CH_2OH)_2$][Tau]	37	~2.5	– [e]	258.3	~0.4	~1.55	–H**N**(H)	90
56	[$Me_2N(CH_2CH_2OH)_2$][Tau]	37	~4	– [e]	258.3	0.92	3.56	–H**N**(H)	90
57	[P_{66614}][*p*-AA]	30	1	60	634.0	0.94	1.48	–H**N**(H)	121
58	[P_{66614}][*o*-AA]	30	1	– [e]	634.0	0.60	0.95	–H**N**(H)	121
59	[P_{66614}][*p*-ANA]	30	1	– [e]	621.0	0.78	1.23	–H**N**(H)	121
60	[P_{66614}][*o*-ANA]	30	1	– [e]	621.0	0.56	0.88	–H**N**(H)	121
61	NH_2-GlyNa [k]	25	1	20	97.1	0.43	4.43 (0.62)	–H**N**(H)	122

62	*i*PrNH-GlyNa [k]	25	1	25	139.1	0.91	6.54 (1.23)	–**N**(H)–	122
63	*n*PrNH-GlyNa [k]	25	1	30	139.1	0.59	4.24 (0.80)	–**N**(H)–	122
64	*t*BuNH-GlyNa [k]	25	1	25	153.2	0.85	5.55 (1.13)	–**N**(H)–	122
65	CyNH-GlyNa [k]	25	1	25	179.2	0.68	3.79 (0.87)	–**N**(H)–	122
66	*i*PrNH-AlaNa [k]	25	1	30	153.2	0.73	4.77 (0.97)	–**N**(H)–	122
67	*n*Pr$_2$N-GlyNa [k]	25	1	30	181.2	0.48	2.65 (0.61)	–**N**R$_3$	122
68	*β*-*i*PrNH-AlaNa [k]	25	1	15	153.2	0.65	4.24 (0.86)	–**N**(H)–	122
69	ProNa/15-crown-5 [l]	25	1	25	357.4 [m]	0.89	2.49 (1.35)	–**N**(H)–	123
70	ProK/18-crown-6 [l]	25	1	10	417.5 [m]	0.99	2.37 (1.38)	–**N**(H)–	123
71	ValK/18-crown-6 [l]	25	1	10	419.6 [m]	0.79	1.88 (1.10)	–H**N**(H)	123
72	MetK/18-crown-6 [l]	25	1	20	451.6 [m]	0.75	1.66 (1.00)	–H**N**(H)	123
73	GlyK/18-crown-6 [l]	25	1	20	377.5 [m]	0.75	1.99 (1.11)	–H**N**(H)	123
74	ThrK/18-crown-6 [l]	25	1	15	421.5 [m]	0.73	1.73 (1.01)	–H**N**(H)	123
75	AlaK/18-crown-6 [l]	25	1	15	391.5 [m]	0.71	1.81 (1.03)	–H**N**(H)	123
76	LeuK/18-crown-6 [l]	25	1	10	433.6 [m]	0.68	1.57 (0.93)	–H**N**(H)	123
77	SerK/18-crown-6 [l]	25	1	15	407.5 [m]	0.63	1.55 (0.89)	–H**N**(H)	123

[a] Full names of absorbents can be found in Table S1. [b] Molecular weight of pure MEA, IL or salt. [c] Values shown in brackets are based on the total weight of solution or IL + support. [d] Active site atoms are shown in bold font, and transfer proton atoms are shown in brackets. [e] Data are not mentioned in the literature. [f] Immobilization of IL on porous silica gel (SiO$_2$) support (molar ratio of IL : SiO$_2$ is 1:8). [g] Immobilization of IL on nanoporous PMMA support (mass ratio of IL : PMMA is 1:1). [h] Mixed with PEG$_{200}$ (mass ratio of IL : PEG$_{200}$ is 1:1). [i] Supported by HDK-T30 (hydrophilic), and mass ratio of IL : support is 40:60. [j] Supported by HDK-H20 (hydrophobic-50% SiOH), and mass ratio of IL : support is 40:60. [k] Mixed with PEG$_{150}$ (molar ratio of salt : PEG$_{150}$ is 1:4), and absorption by PEG$_{150}$ is subtracted. [l] Mixed with PEG$_{300}$ (molar ratio of salt : crown ether : PEG$_{300}$ is 1:1:2). [m] Molar mass of the 1:1 molar mixture.



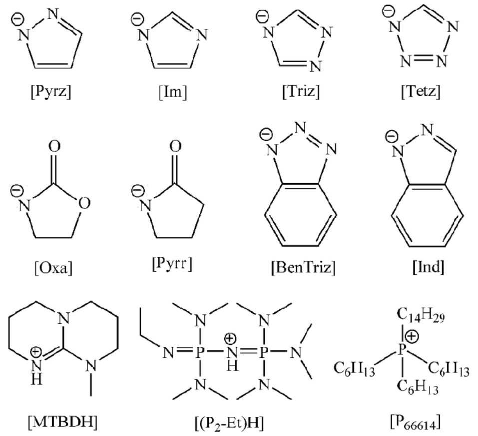
Scheme 10 Structure of various amino acid salts. Adapted with permission from ref. 122. Copyright 2012 Wiley-VCH.

3. Amino-free ILs with single active site

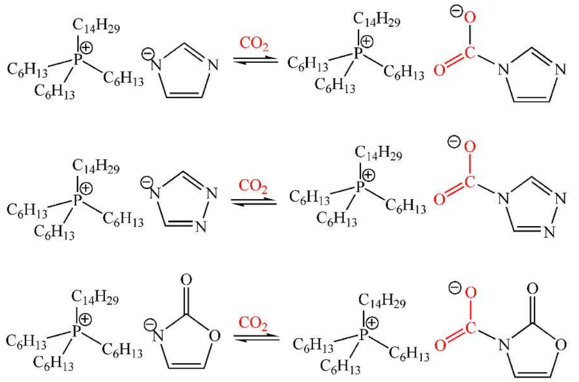
Generally, CO$_2$ capture by amino-functionalized ILs makes use of the reaction of the amino group on the cation or the anion with CO$_2$. In the studies of amino acid–based ILs that exhibited equimolar CO$_2$ uptake, remarkable increase in viscosity was observed after CO$_2$ absorption, which makes it quite challenging to use those particular ILs for CO$_2$ capture in any practical applications. [106,124-125] From molecular simulations in analogous systems, Gutowski *et al.* [93] concluded that the dramatic viscosity increase was attributable to the formation of a strong, pervasive hydrogen-bonded network. How can we develop novel amino-free functionalized ILs to improve CO$_2$ chemisorption?

3.1 Azolate ILs (or aprotic heterocyclic anion ILs)

A strategy was presented by Dai and Wang *et al.* [125-126] for equimolar CO$_2$ capture by a series of azole-based amino-free anion-functionalized ILs. These ILs were prepared from the neutralization of a superbase such as 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine (MTBD), 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene) (P$_2$-Et) or trihexyl(tetradecyl)phosphonium hydroxide ([P$_{66614}$][OH]) solution with such weak proton donors as imidazole (Im), pyrazole (Pyrz), 1,3,4-trizole (Triz), tetrazole (Tetz), indole (Ind), 2-oxazolidone (Oxa), pyrrolidone (Pyrr) and bentrizole (BenTriz) (Scheme 11). They exhibited equimolar CO$_2$ capture under atmospheric pressure (Table 2, entries 1–11). The absorption was significantly affected by the nature of the anion, due to the different driving forces for the reaction with CO$_2$ (Scheme 12). For example, the CO$_2$ absorption by [P$_{66614}$][Pyrz], [P$_{66614}$][Im], [P$_{66614}$][Ind], [P$_{66614}$][Triz], [P$_{66614}$][BenTriz], and [P$_{66614}$][Tetz] were 1.02, 1.00, 0.98, 0.95, 0.17 and 0.08 mole CO$_2$ per mole IL, respectively. It is clearly indicated that the absorption molar ratios of CO$_2$ to IL was decreased from 1.02 to 0.08, when the p*K*a value of the anions in DMSO decreased from 19.8 to 8.2.[125] Thus, high CO$_2$ absorption capacity could be achieved by tuning basicity of the ILs. However, CO$_2$ absorption by imidazolate ILs with different cations such as [MTBDH],[126] [(P$_2$-Et)H],[126] [P$_{66614}$],[125] and [TMGH] (Table 2, entry 12),[127] were 1.03, 0.96, 1.00 and 1.00 mole CO$_2$ per mole IL, respectively, indicating that the effect of cations on the absorption of CO$_2$ was weak. More interestingly, the viscosity of [P$_{66614}$][Im] was found to decrease from 810.4 cP to 648.7 cP upon uptake of CO$_2$. A molecular dynamics (MD) simulation was carried out by Jiang *et al.* [128] on the neat and fully CO$_2$ saturated [P$_{66614}$][Im] to reveal the microscopic origin for the decrease in viscosity after CO$_2$ absorption.

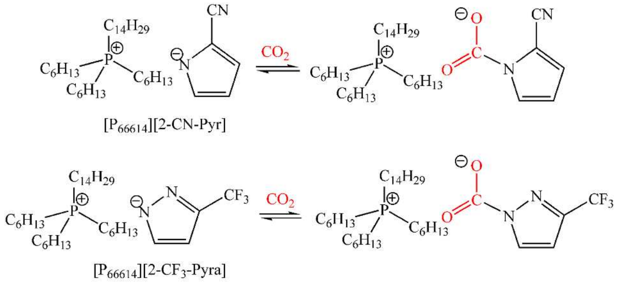


Scheme 11 Structures of anions and cations in various azolate amino-free anion-functionalized ILs in ref. 125 and ref. 126.



Scheme 12 CO_2 absorption mechanism by typical azolate ILs. Reprinted with permission from ref. 125. Copyright 2011 Wiley-VCH.

Other groups also performed deeper studies on the performance of CO_2 absorption by this kind of ILs, which were also named aprotic heterocyclic anion (AHA) based ILs or azolide ILs. [89,127,129-134] For example, Maginn *et al.* [129] investigated CO_2 capture by a class of anion-functionalized ILs with substituted AHAs. In their work, the absorption capacities of both trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide ($[P_{66614}][2\text{-CN-Pyr}]$) and trihexyl(tetradecyl)phosphonium 3-(trifluoromethyl) pyrazolide ($[P_{66614}][2\text{-}CF_3\text{-Pyra}]$) could reach about 0.9 mole of CO_2 per mole of IL (Table 2, entries 13–14). DFT calculations [129] and MD simulations [135] indicated that the high absorption capacity of CO_2 was ascribed to the chemical interaction between CO_2 and the nitrogen atom with negative charge on the anion (Scheme 13).



Scheme 13 CO_2 capture by $[P_{66614}][2\text{-CN-Pyr}]$ and $[P_{66614}][2\text{-}CF_3\text{-Pyra}]$.

In addition, Brennecke *et al.* [136] studied the reaction kinetics of CO_2 absorption into $[P_{66614}][Pro]$, $[P_{66614}][2\text{-CN-Pyr}]$, and $[P_{66614}][2\text{-}CF_3\text{-Pyra}]$. Recently, they also investigated CO_2 absorption performance by a series of $[P_{66614}]$-based ILs with other substitute AHAs, and calculated the reaction enthalpy for each IL afterward. [131,134] It was found that the parent benzimidazolate anion ($[BnIm]^-$) provided the strongest reaction with CO_2 and higher capacity compared to its substituted-counterparts, such as $[6\text{-BrBnIm}]^-$ and $[2\text{-}SCH_3BnIm]^-$ (Table 2, entries 15–17). Hatton *et al.* [137] investigated a series of [2-CN-Pyr]-based tetraalkylammonium and tetraalkylphosphonium ILs (Fig. 4). Among the investigated ILs, $[P_{2228}][2\text{-CN-Pyr}]$ was found to have the lowest viscosity (95 cP at 40 °C) and highest gravimetric CO_2 absorption capacity (114 mg CO_2 per g IL at 40 °C). Thereafter, a very recent report from Brennecke *et al.* [138] showed that [2-CN-Pyr]-based tetraalkylphosphonium ILs with shorter alkyl chains on the cations exhibited slightly stronger CO_2 binding ability than the ILs with longer alkyl chains (Table 2, entries 18–23), and they attributed this to the difference in reaction entropy, as well as the variation in the relative degree of ionicity.

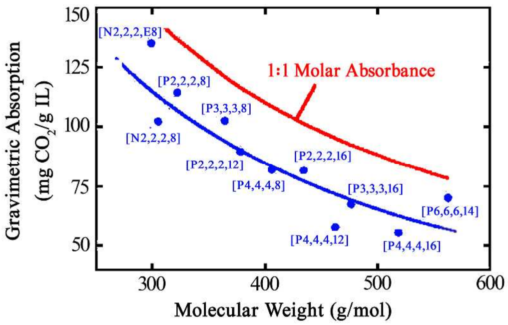
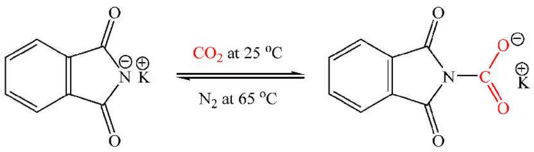


Fig. 4 The measured CO_2 absorption capacity as a function of molecular weight (Mw) at 40 °C. The blue curve indicates that the trend shown by the experimental data is similar to that calculated for complete chemisorption of one molar equivalent of CO_2, given by the red curve. Reprinted with permission from ref. 137. Copyright 2015 American Institute of Chemical Engineers.

Despite the great progress mentioned above, which shows the basicity of the anion is a determining factor for CO_2 capture and the capacity can be controlled by tuning the basicity of ILs, strategies for achieving equimolar and energy-saving CO_2 capture are still highly desirable. In this context, Li *et al.* [132] designed several quasi IL solutions with alkali metal salts of 1,2,4-triazole (TrizM). The results based on 5% TrizM in PEG indicated 1:1 stoichiometric chemical absorption of CO_2 by TrizM and low absorption enthalpies (Table 2, entries 24–26). He *et al.* [139] mixed some phthalimide salts (weak basicity, p*K*a=8.3 in H_2O) with PEG_{150}, and found that potassium phthalimide (K[Phth]) exhibited an extremely high CO_2 capacity, approaching almost equimolar absorption with easy desorption (Scheme 14, Table 2, entries 27–31).



Scheme 14 The formation of carbamate salt by K[Phth] in PEG_{150}. Reprinted with permission from ref. 139. Copyright 2014 Wiley-VCH.

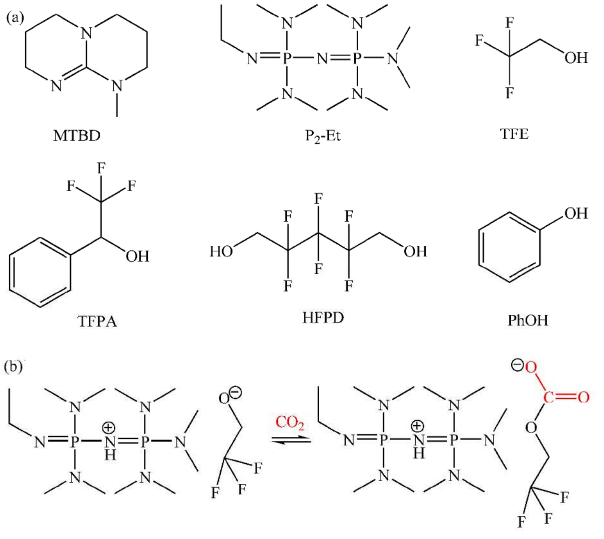
To understand the high reactivity in azolate ILs and design azolate CO_2 capture materials, Wu *et al.* [130] used DFT and a Langmuir-type adsorption model to study azolate anion–CO_2 interactions. These authors found that CO_2 needed to bend by more than 40^o to overlap its π^* orbital more efficiently with the nitrogen lone pair on the azolate anion to form a $\sigma_{C\text{-}N}$ bond. Strong interaction of CO_2 with the IL anions corresponds to chemisorption whereas weak interaction indicates physisorption. Recently, a predictive estimate with a clear distinction between physi- and chemisorption has been simply obtained according to geometries optimized in the presence of a solvation model [140] instead of optimizing it only in gas phase. [125,131,141] Promising anions with reversible CO_2 absorption property can be defined by a reaction Gibbs free energy of absorption in the range from −30 to 16 kJ mol^{-1}.[140]

3.2 Alcoholate and phenolate ILs

3.2.1 Alcoholate ILs

It is known that the absorption of CO_2 in aqueous NaOH solution is a chemisorption process, thus CO_2 reacts with hydroxide ions (OH^-) and is then converted into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). [142-143] Recently, Omar *et al.* [144] measured the solubility of CO_2 in 55 wt% aqueous solution of tetrabutylammonium hydroxide ($[N_{4444}][OH]$) by using high pressure solubility cell. Wu *et al.* [145] found that CO_2 capacities by two kinds of resins such as D201 (OH^-) and D202 (OH^-) were very high due to their most basic anion, OH^-. However it should be noted that the sorption of CO_2 by OH^- is nearly irreversible.

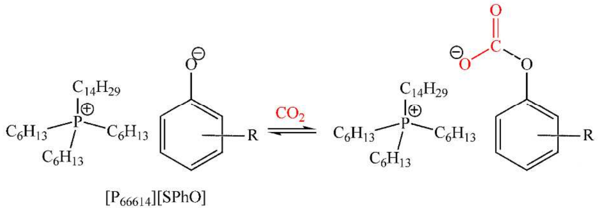
Dai *et al.* [126] presented a new strategy for equimolar CO_2 capture by a series of anion-functionalized PILs, which were directly prepared from the neutralization of a superbase with weak proton donors such as trifluoroethanol (TFE), 1-phenyl-2,2,2-trifluoroethanol (TFPA), and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (HFPD) (Scheme 15). It was found that the superbase played a key role as a strong proton acceptor to directly deprotonate the weak proton donor, thereby providing a thermodynamic driving force for the reaction of the active protic ILs with CO_2. This system showed an equimolar CO_2 capture under atmospheric pressure, and most systems remained as liquids after reaction with CO_2. For example, the absorption capacities of [MTBDH][TFE], $[(P_2\text{-Et})H]$[TFE], and [MTBDH][TFPA] were 1.13, 1.04, and 0.93 mole of CO_2 per mole of IL, respectively (Table 2, entries 32–34). The release of CO_2 was easy at 80 °C under bubbling N_2, and these protic ILs could be recycled without a significant loss in capacity. In addition, those authors pointed out that these superbase derived protic ILs had lower viscosities than the amino-functionalized ILs, either tethered with an amino group on the cation [69] or on the anion. [106] Thereafter, Liu *et al.* [146] used [DBUH][TFE], which could adsorb CO_2 with maximum CO_2/IL molar ratio of 1.01 at atmospheric pressure and room temperature (Table 2, entries 35), to catalyze CO_2 conversion into high-value chemicals.



Scheme 15 (a) Structure of the superbases, fluorinated alcohols, and phenol used as building blocks of superbase derived PILs; (b) Reaction of $[(P_2\text{-Et})H]$[TFE] with CO_2. Adapted with permission from ref. 126. Copyright 2010 Wiley-VCH.

3.2.2 Phenolate ILs

Wang *et al.* [141] investigated CO_2 chemisorption by a series of phenolate ILs prepared from $[P_{66614}][OH]$ and different substituted phenols (Scheme 16). As the basicity of these ILs is significantly affected by the electron-withdrawing ability, position, and quantity of the substituted group in their anions, the capacity of CO_2 absorption should be affected in the same way: the stronger the electron-withdrawing ability of the substituent on the anion, the lower the absorption enthalpy and absorption capacity of CO_2. For example, the absorption capacities of $[P_{66614}]$[4-Me-PhO], $[P_{66614}]$[4-H-PhO], $[P_{66614}]$[4-Cl-PhO], $[P_{66614}][4\text{-}CF_3\text{-PhO}]$, $[P_{66614}][4\text{-}NO_2\text{-PhO}]$, and $[P_{66614}]$[2,4,6-Cl-PhO] were found to be 0.91, 0.85, 0.82, 0.61, 0.30 and 0.07 mole of CO_2 per mole of IL, respectively (Table 2, entries 36–48). Furthermore, the absorption enthalpy and absorption capacity of CO_2 decreased with increasing quantity of the electron-withdrawing substituent. Later, Dai and He *et al.* [123] used PhOLi, PhONa or PhOK and crown ether to form alkali metal onium salt/crown ether systems and similar 1:1 reaction stoichiometry was reported (Table 2, entries 49–51). Hu *et al.* [147] reported some low-viscous fluorine-substituted phenolate ILs with high performance for CO_2 capture (Table 2, entries 52–55). CO_2 absorption by other phenolate ILs was also reported, and the results were listed in Table 2, entries 56–59.



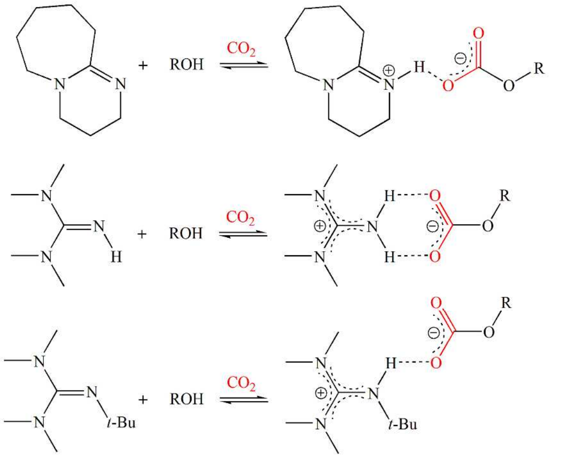
Scheme 16 CO_2 absorption by phenolate ILs. Adapted with permission from ref. 141. Copyright 2012 Wiley-VCH.

3.3 Proton transfer

Acidic protons in –N(H), –O(H), and C2(H) of imidazolium have a potential transfer property, which could activate the N, O, and C atoms to react with CO_2 for carbon capture. For example, by the transfer of hydrogen atom on amino group (e.g. –NH, –NH_2), the CO_2 absorption capacity of amino-functionalized ILs can achieve up to 1:1 stoichiometry (see Section 2). Furthermore, other acidic protons transfer are necessary in the following cases for carbon capture.

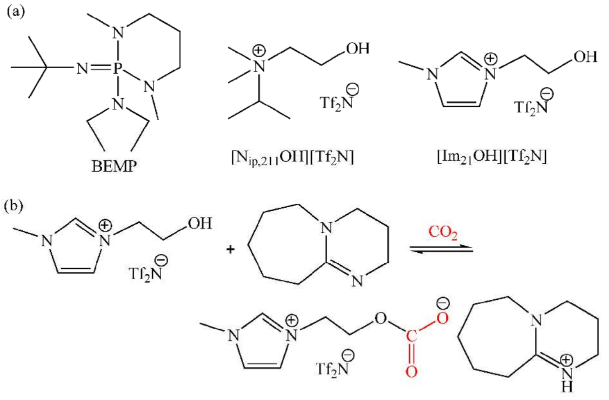
3.3.1 Proton of hydroxyl group

Switchable solvents or CO_2-binding organic liquids (CO_2BOLs) are based on a liquid mixture of an alcohol and a strong organic amidine or guanidine base (e.g. 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU)) to chemically bind CO_2 to form an amidinium or guanidinium alkylcarbonate salt through proton transfer from alcohol to superbase, thus a capacity of nearly 1:1 stoichiometry can be achieved (Scheme 17). [148-154] In recent years, some other kinds of active site-containing organic liquids, such as alkanol functionalized guanidines and amidines, [155-157] mixture of amidine or guanidine superbase with poly(ethyleneglycol) (PEG), [158] mixture of DBU with amino-containing alcohol, [159] ternary deep eutectic solvents, [160] and alkoxide-functionalized imidazolium betaines [161] or N-heterocyclic olefin [162] in THF were also explored for chemical capture of CO_2. One key problem associated with this strategy is the volatility of their molecular constituents, resulting in the loss of the absorbents.



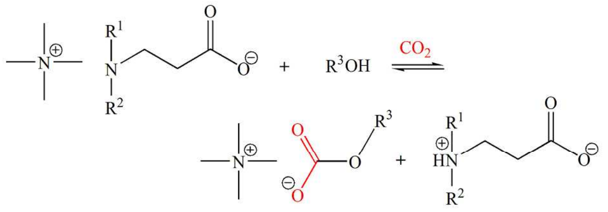
Scheme 17 Proposed hydrogen bonding of cation with anion for salts made from DBU, TMG and Barton's base with ROH and CO_2. Adapted with permission from ref. 148. Copyright 2008 Royal Society of Chemistry.

Besides the carbon capture by amino-functionalized ILs through proton transfer from –NH– group, Dai *et al.* [163] reported another type of proton transfer from alcohol –OH group. They investigated the integrated systems consisting of 1:1 mixtures of a hydroxyl functionalized IL and a superbase, and found that these systems were capable of rapid and reversible capture of CO_2 in 1:1 stoichiometry (Scheme 18, Table 2, entries 60–63). For example, the absorption capacities of $[Im_{21}OH][Tf_2N]$-DBU, $[Im_{21}OH][Tf_2N]$-MTBD, $[Im_{21}OH][Tf_2N]$-BEMP, and $[N_{ip,211}OH][Tf_2N]$-DBU were 1.04, 1.02, 0.81 and 1.02 mole of CO_2 per mole of IL, respectively. In addition, in their work, volatility of the alcohol was mitigated by tethering a hydroxyl group to the cation of a non-volatile IL.



Scheme 18 (a) Structures of the hydroxyl functionalized ILs and BEMP; (b) Formation of carbonate between CO_2 and $[Im_{21}OHmim][Tf_2N]$ in the presence of DBU.

Recently, a kind of tetramethylammonium-based ILs with *β*-amino acid anions was reported by Kim *et al.* [164] When each of these ILs was mixed with an alcohol (30 w_{IL}%) and used to absorb CO_2, the absorption capacities of 0.97, 1.01 and 1.02 mole of CO_2 per mole of IL were observed, respectively, for $[N_{1111}]$[*n*-BuNHEtCOO], $[N_{1111}]$[*n*-Bu_2NEtCOO] and $[N_{1111}]$[*n*-Bu_2NEtNHEtCOO] (Table 2, entries 64–69). The formation of methylcarbonate species in a 1:1 mechanism was confirmed in methanol (Scheme 19).



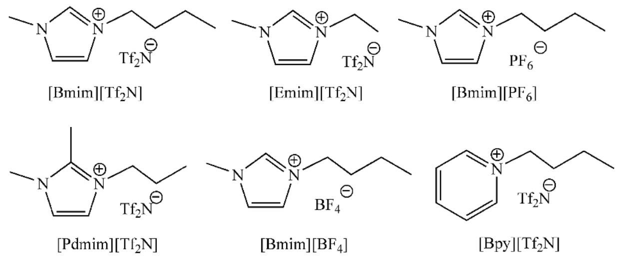
$[N_{1111}]$[*n*-BuNHEtCOO] : R^1=n-butyl, R^2=H; Methanol : R^3=CH_3
$[N_{1111}]$[*n*-Bu_2NEtCOO] : R^1=R^2=*n*-butyl; Ethylene glycol : R^3=CH_2CH_2OH
$[N_{1111}]$[*n*-Bu_2NEtNHEtCOO] : R^1=2-(diethylamino)ethyl, R^2=H.

Scheme 19 Possible alkylcarbonate pathway for the interactions of ILs with CO_2 in alcohol. Adapted with permission from ref. 164. Copyright 2013 Wiley-VCH.

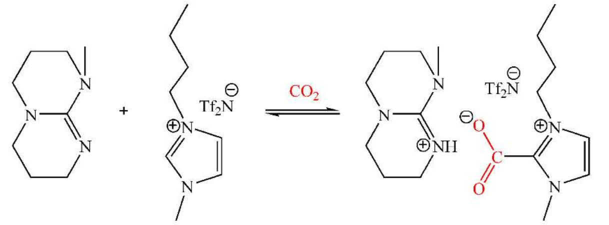
3.3.2 C-2 proton of imidazolium-based ILs

N-heterocyclic carbenes (NHCs), which are widely used compounds in chemistry since 1991, [165-166] have been reported to reversibly form carboxylate adducts with CO_2 at 1 atm in nearly 1:1 stoichiometry through NHC−CO_2 reaction mechanism. [167-168] However, the priori NHC is not stable although the ILs are relatively stable. [169] The well-known weak acidity of the proton at C-2 position of the alkylimidazolium rings is prone to a fairly strong hydrogen-bond interaction with an anion.[170-173] Introduction of an increasingly basic anion will cause progressively stronger interactions with the C-2 proton on the imidazolium, and an anion with high enough basicity has the potential to abstract the proton to produce an NHC along with a neutralized form of the anion. [174] Thus, it is one of the major pathways for reactivity of imidazolium species, in particular of imidazolium ILs.[175]

Imidazolium IL-superbase mixtures. By utilizing the intrinsic acidity of hydrogen at the C-2 position in the imidazolium cation, Dai *et al.* [176] presented another approach for CO_2 capture by liquid mixtures of 1,3-dialkylimidazolium ILs and a superbase (Scheme 20). During the absorption of CO_2, the imidazolium-based IL containing an equimolar superbase reacted with CO_2 to form a liquid dicationic-dianionic complex containing zwitterionic imidazolium carboxylate salt through proton transfer from the C-2 of imidazolium to the superbase, thus equimolar capture of CO_2 with respect to the base was observed (Scheme 21). Among these absorptions, the CO_2 capacities in $[Bmim][Tf_2N]$-DBU, $[Bmim][Tf_2N]$-MTBD, and $[Bmim][Tf_2N]$-(P_2-Et) were 0.99, 1.08, and 1.00 mole of CO_2 per mole of IL, respectively (Table 2, entries 70–73), while the absorption molar ratios of CO_2 to IL were reduced to 0.80 and 0.75, respectively, in $[Bmim][BF_4]$-DBU and $[Bmim][PF_6]$-DBU (Table 2, entries 74–75) because of the increased viscosities of these systems. However, the ILs with a ‘‘blocking’’ group (e.g., –CH_3) at the C-2 position would not experience the reaction in Scheme 21. These results indicate that the C-2 proton of imidazolium-based ILs is critical to improving the capture of CO_2 by the imidazolium IL–superbase system.

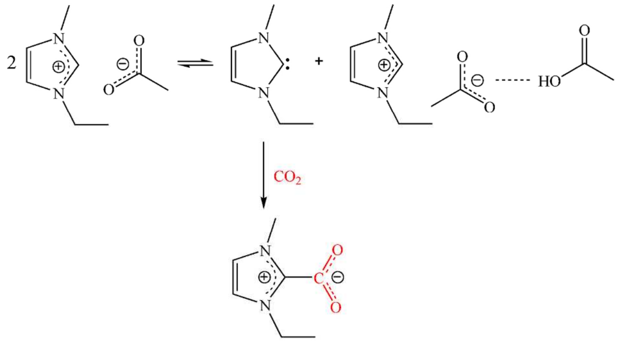


Scheme 20 Structures of ILs. Adapted with permission from ref. 176. Copyright 2010 Royal Society of Chemistry.



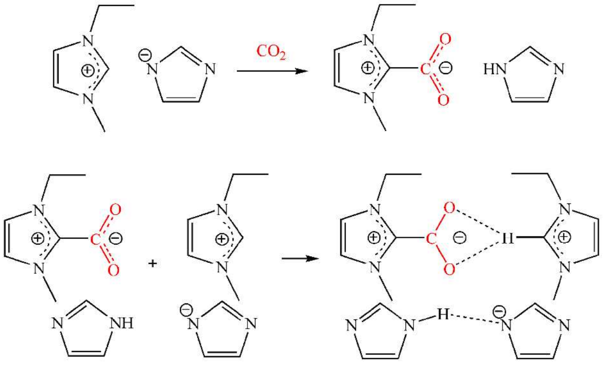
Scheme 21 The mechanism of CO_2 absorption by [Bmim][Tf$_2$N]–MTBD. Adapted with permission from ref. 176. Copyright 2010 Royal Society of Chemistry.

Imidazolium-based carboxylate ILs. Another example of CO_2 absorption using weak acidity of the proton at the C-2 position of imidazolium ring is the absorption by alkylimidazolium ILs with carboxylate anion, such as [Emim][Ac] [177-180] and [Bmim][Ac]. [177,181-187] It was shown that the molar ratios of CO_2 to these alkylimidazolium carboxylate ILs were 0.36 for [Emim][Ac] [177-179] and 0.38 [177,184] for [Bmim][Ac] [177,184] at atmospheric pressure (Table 2, entries 76–77), while the CO_2 capacities by [Emim][TFA] [179] and [Bmim][TFA] [188-189] were very low. Maginn *et al.* [181] studied the absorption of CO_2 in [Bmim][Ac] for the first time and proposed a NHC−CO_2 mechanism for the chemical reaction of the gas with the IL based on NMR results. Recently, Rogers *et al.* [190] showed that the C-2 proton could be abstracted to some extent in neat 1,3-dialkylimidazolium ILs if they were paired with a basic enough anion such as acetate even in the absence of any external base. Their experimental evidence sheds light on the interactions of [Emim][Ac] with CO_2 to form [Emim][H(Ac)$_2$][Emim$^+$-COO$^-$] complex (Scheme 22). [169] In fact, Shiflett *et al.* [184,191] smelled acetic acid after bubbling CO_2 through [Emim][Ac], [Eeim][Ac], and [Bmim][Ac]. In addition, Besnard *et al.* [192] provided the evidence for the formation of the complex in the liquid phase by using Raman and IR spectroscopy complemented by DFT calculations and NMR (^1H, ^{13}C, ^{15}N) spectroscopy. The molar fraction of CO_2 absorbed by [Emim][Ac] and [Bmim][Ac] were not far from the theoretical maximum of 0.33 molar fraction that corresponds to the reaction described in Scheme 22. [169] Gomes *et al.* [193] reported that there were both chemical reaction (major) and physical solubility (minor) during the carbon capture in dry [Bmim][Ac]. Furthermore, the absorption and desorption experiments showed that the complex formation was reversible. [184,191] Further studies indicated that there were three different formats of NHC−CO_2 formed in the reaction of [Emim][Ac] with CO_2 under both high pressure (10 MPa) and high temperature (125 °C). [194] CO_2 capture by other carboxylate-based 1,3-dialkylimidazolium ILs was also investigated (Table 2, entries 78–81), [177,191,195] and it is useful to consider the basicity of the carboxylate anion following the above mentioned mechanism.[195] However, Shi *et al.* [196] and Mu *et al.* [197] selected [P$_{4444}$][Ac] and [BPy][Ac] (1-butyl-pyridinium acetate) as the absorbents for carbon capture in order to eliminate the NHC−CO_2 reaction path available in imidazolium acetate ILs. Their results indicated that the high experimental CO_2 solubility was due to the strong CO_2−[Ac]$^-$ chemical interaction.



Scheme 22 Proposed reaction mechanism of CO_2 with [Emim][Ac]. Adapted with permission from ref. 169. Copyright 2011 Wiley-VCH.

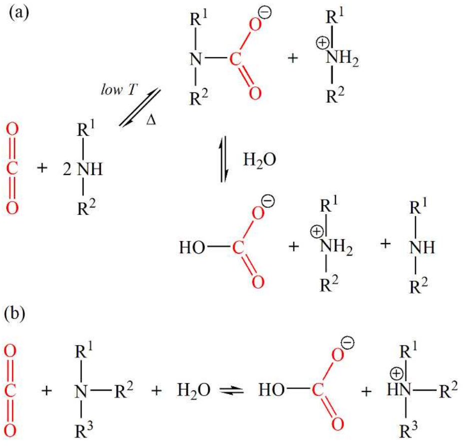
Imidazolium-based AHAILs. Given the fact that the basicity of AHAs is higher than that of acetate, AHA-based imidazolium ILs were developed by Luo *et al.* [198] and Brennecke *et al.*[174] It was shown that these ILs were effective for CO_2 capture and exhibited an unusual behavior compared to that expected from the previously reported [P$_{66614}$][AHA] ILs. [125,129] For example, the capacities of CO_2 absorption by [Bmim][Im], [Emim][Im], and [HO-emim][Im] (1-hydroxylethyl-3-methylimidazolium imidazolate) were 0.54, 0.54, and 0.55 mole of CO_2 per mole of IL at 40 °C and 1 bar, respectively (Table 2, entries 82–84).[198] The mechanism of the studied ILs was proposed as the formation of the carboxylation reactions on C-2 position of the imidazolium rings. A strong interaction between the newly formed carboxylate portion of the zwitterion and the C-2 proton of another cation was also formed, leading to a 0.5 molar ratio of CO_2 to the ILs (Scheme 23). Brennecke *et al.* [174] proposed that [Emim][AHA] ILs acted as both the base and carbene sources and this led to two separated equilibrium reaction pathways (anion−CO_2 and NHC−CO_2), with a major one being the NHC−CO_2 reaction. This NHC−CO_2 reaction mechanism was similar to that suggested by Luo *et al.*, [198] and the presence of the imidazolium-carboxylate species and carbamate anion species was verified using ^1H and ^{13}C NMR spectroscopy. [174]



Scheme 23 Scheme of the reaction mechanism for [Emim][Im] with CO_2. Adapted with permission from ref. 198. Copyright 2013 American Chemical Society.

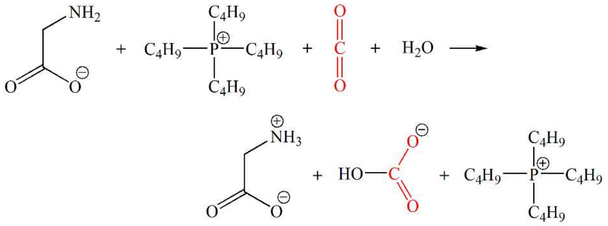
3.3.3 Protons of water in functionalized IL-H_2O blends

It is well-known that anhydrous primary and secondary amines can chemically absorb CO_2 to form carbamate through a 1 : 2 mechanism, while tertiary amines cannot react with CO_2 under dry conditions (Scheme 1). [199] In the presence of water, the reaction mechanisms of amines with CO_2 become different, and there are multiple equilibrium reactions in the liquid phase (Scheme 24). [76,86,200] That is a fraction of the carbamate species formed is hydrolyzed to form bicarbonate (HCO_3^-), and tertiary amines directly catalyze hydration of CO_2 to form bicarbonate, although tertiary amines do not combine with CO_2 directly. [200] Thus, the CO_2 loading capacity for primary and secondary amines lies in the range 0.5–1 mole of CO_2 per mole of amine, but that for tertiary amines lies on 1 mole of CO_2 per mole of amine, although the absorption rate is slow. Previous publications for functionalized IL-H_2O blends not only showed the reduced viscosity compared with pure ILs (see Section 5.1.2), but also showed the different CO_2 absorption mechanisms from the absorption by anhydrous functionalized ILs.

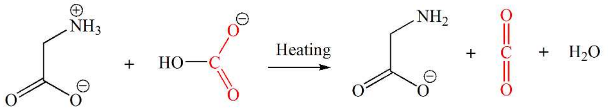


Scheme 24 General reaction schemes for the chemical absorption of CO_2 by a) primary or secondary and b) tertiary amine-containing solvents. Adapted with permission from ref. 200. Copyright 2010 Wiley-VCH.

Amino-based IL-H_2O blends. A number of studies have revealed the absorption of CO_2 in aqueous solutions of amino acid alkaline salts absorbents. [201-208] Zhang *et al.* [106] reported the first example of CO_2 chemical absorption by porous SiO_2 supported [P_{4444}][AA] with a small amount of water (1 w_{H2O}%) because of the high viscosity of pure AAILs. It was found that [P_{4444}][Gly] could absorb equimolar amounts of CO_2 (Table 2, entries 85) in the presence of water based on a 1:1 mechanism (Scheme 25). Furthermore, Zhang *et al.* investigated CO_2 capture by a series of aqueous IL solutions with different concentration of AAIL (Table 2, entries 86–90). [209-210] Although some other studies showed CO_2 absorption in aqueous AAILs through the carbamte mechanism, [210-211] Davis *et al.* [212] demonstrated that a carbamate was formed as a transitory species during the initial absorption, but the carbonate/bicarbonate emerged and predominated when CO_2 absorption surpassed a threshold stoichiometry. Thus, CO_2 absorption mechanism in AAILs with and without water were different. CO_2 capture by other aqueous solutions of AAILs, such as [P_{66614}][Pro], [116] [N_{2222}][Gly], [212] [N_{1111}][Gly], [209,212-213] and [Emim][Gly], [214] was also widely investigated. It is the case that could also been found for alkanolamines and other amino-functionalized carbon capture agents in wet environments (Scheme 24). [200] Jing *et al.* studied the regeneration performance and CO_2 absorption/desorption mechanism of aqueous [Hmim][Gly] [215] and [N_{1111}][Gly] [216] solutions (Scheme 26). It can be seen that when thermal regeneration reaction occurred, $2HCO_3^-$ was decomposed into 1 H_2O, 1 CO_2, and 1 CO_3^{2-}. Gly was subsequently deprotonated by CO_3^{2-} to form [Gly] and HCO_3^- in the solution. As mentioned above, amino-functionalized ILs, either tethered with a tertiary amino group on the cation [101] or on the anion, [118-119] showed less reactive activity on carbon capture. Kim *et al.* [164] reported a kind of tetramethylammonium-based IL [N_{1111}][n-$Bu_2NEtCOO$] bearing the tertiary amino-containing anion. When this IL was mixed with water (30 w_{IL}%) for CO_2 absorption, the molar ratio of CO_2 to [N_{1111}][n-$Bu_2NEtCOO$] was 0.95 (Table 2, entries 91), indicating the formation of bicarbonate species in a 1:1 mechanism in water. They also showed that the primary and secondary amino-based ILs could reach equimolar CO_2 absorption capacities (Table 2, entries 92–93).



Scheme 25 Reaction mechanism for [P_{4444}][Gly] with CO_2 in the presence of water. Adapted with permission from ref. 106. Copyright 2006 Wiley-VCH.



Scheme 26 The overall reaction for CO_2 desorption in aqueous solutions of [Gly]-based IL. Adapted with permission from ref. 216. Copyright 2015 Elsevier Ltd.

Cite this: DOI: 10.1039/c0xx00000x

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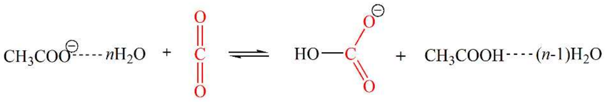
Table 2 CO_2 chemisorption by amino-free functionalized ILs or ionic salts with single active site.

Entry	Absorbent [a]	Conditions			Mw (g mol^{-1}) [b]	Absorption capacity		Active site [d]	Ref.
		T (°C)	P (bar)	*t* (min)		mol CO_2/mol IL	mol CO_2/kg IL [c]		
1	[MTBDH][Im]	23	1	30	221.3	1.03	4.65	$-\mathbf{N}^{-}-$	126
2	[(P$_2$-Et)H][Im]	23	1	10	407.5	0.96	2.36	$-\mathbf{N}^{-}-$	126
3	[MTBDH][Pyrr]	23	1	30	238.3	0.92	3.86	$-\mathbf{N}^{-}-$	126
4	[(P$_2$-Et)H][Pyrr]	23	1	30	424.5	0.86	2.03	$-\mathbf{N}^{-}-$	126
5	[P$_{66614}$][Pyrz]	23	1	20	550.9	1.02	1.85	$-\mathbf{N}^{-}-$	125
6	[P$_{66614}$][Im]	23	1	20	550.9	1.00	1.82	$-\mathbf{N}^{-}-$	125
7	[P$_{66614}$][Ind]	23	1	20	601.0	0.98	1.63	$-\mathbf{N}^{-}-$	125
8	[P$_{66614}$][Triz]	23	1	20	551.9	0.95	1.72	$-\mathbf{N}^{-}-$	125
9	[P$_{66614}$][Bentriz]	23	1	20	602.0	0.17	0.28	$-\mathbf{N}^{-}-$	125
10	[P$_{66614}$][Tetz]	23	1	20	552.9	0.08	0.14	$-\mathbf{N}^{-}-$	125
11	[P$_{66614}$][Oxa]	23	1	20	569.9	0.91	1.60	$-\mathbf{N}^{-}-$	125
12	[TMGH][Im]	30	1	40	183.3	1.00	5.46	$-\mathbf{N}^{-}-$	127
13	[P$_{66614}$][2-CN-Pyr]	22	1	– [e]	575.0	0.9	1.57	$-\mathbf{N}^{-}-$	129
14	[P$_{66614}$][3-CF$_3$-Pyra]	22	1	– [e]	618.9	0.9	1.45	$-\mathbf{N}^{-}-$	129
15	[P$_{66614}$][BnIm]	22	1	– [e]	601.0	0.91	1.51	$-\mathbf{N}^{-}-$	131
16	[P$_{66614}$][6-BrBnIm]	22	1	– [e]	679.9	0.90	1.32	$-\mathbf{N}^{-}-$	131
17	[P$_{66614}$][2-SCH$_3$BnIm]	22	1	– [e]	647.1	0.73	1.13	$-\mathbf{N}^{-}-$	131
18	[P$_{2224}$][2-CN-Pyr]	22	0.15	– [e]	266.4	0.80	3.00	$-\mathbf{N}^{-}-$	138
19	[P$_{2228}$][2-CN-Pyr]	22	0.15	– [e]	322.5	0.80	2.45	$-\mathbf{N}^{-}-$	138
20	[P$_{22212}$][2-CN-Pyr]	22	0.15	– [e]	378.6	0.73	1.92	$-\mathbf{N}^{-}-$	138
21	[P$_{44412}$][2-CN-Pyr]	22	0.15	– [e]	462.8	0.72	1.59	$-\mathbf{N}^{-}-$	138
22	[P$_{44418}$][2-CN-Pyr]	22	0.15	– [e]	546.9	0.64	1.17	$-\mathbf{N}^{-}-$	138
23	[P$_{66614}$][2-CN-Pyr]	22	0.15	– [e]	575.0	0.62	1.08	$-\mathbf{N}^{-}-$	138
24	TrizLi [f]	10	1	120	75.0	0.90	12.00 (0.60)	$-\mathbf{N}^{-}-$	132
25	TrizNa [f]	10	1	120	91.1	0.96	10.54 (0.53)	$-\mathbf{N}^{-}-$	132
26	TrizK [f]	10	1	120	107.2	0.96	8.96 (0.45)	$-\mathbf{N}^{-}-$	132
27	[DBUH][Phth] [g]	25	1	40	299.4	0.98	3.27 (1.31)	$-\mathbf{N}^{-}-$	139
28	[TMGH][Phth] [g]	25	1	40	262.3	0.98	3.74 (1.38)	$-\mathbf{N}^{-}-$	139
29	Na[Phth] [g]	25	1	30	169.1	0.96	5.68 (1.55)	$-\mathbf{N}^{-}-$	139
30	K[Phth] [g]	25	1	30	185.2	0.96	5.18 (1.51)	$-\mathbf{N}^{-}-$	139
31	K[Sacc] [g]	25	1	30	221.3	0.38	1.72 (0.57)	$-\mathbf{N}^{-}-$	139
32	[MTBDH][TFE]	23	1	10	253.3	1.13	4.46	$R-\mathbf{O}^{-}$	126
33	[(P$_2$-Et)H][TFE]	23	1	10	439.4	1.04	2.37	$R-\mathbf{O}^{-}$	126
34	[MTBDH][TFPA]	23	1	60	329.4	0.93	2.82	$R-\mathbf{O}^{-}$	126
35	[DBUH][TFE]	r.t.	1	– [e]	252.3	1.01	4.00	$R-\mathbf{O}^{-}$	146
36	[P$_{66614}$][4-Me-PhO]	30	1	30	591.0	0.91	1.54	$Ph-\mathbf{O}^{-}$	141
37	[P$_{66614}$][4-MeO-PhO]	30	1	30	607.0	0.92	1.52	$Ph-\mathbf{O}^{-}$	141
38	[P$_{66614}$][4-H-PhO]	30	1	30	577.0	0.85	1.47	$Ph-\mathbf{O}^{-}$	141
39	[P$_{66614}$][4-Cl-PhO]	30	1	30	611.4	0.82	1.34	$Ph-\mathbf{O}^{-}$	141
40	[P$_{66614}$][4-CF$_3$-PhO]	30	1	30	645.0	0.61	0.95	$Ph-\mathbf{O}^{-}$	141
41	[P$_{66614}$][4-NO$_2$-PhO]	30	1	30	622.0	0.30	0.48	$Ph-\mathbf{O}^{-}$	141
42	[P$_{66614}$][3-Cl-PhO]	30	1	30	611.4	0.72	1.18	$Ph-\mathbf{O}^{-}$	141
43	[P$_{66614}$][2-Cl-PhO]	30	1	30	611.4	0.67	1.10	$Ph-\mathbf{O}^{-}$	141
44	[P$_{66614}$][2,4-Cl-PhO]	30	1	30	645.9	0.48	0.74	$Ph-\mathbf{O}^{-}$	141
45	[P$_{66614}$][2,4,6-Cl-PhO]	30	1	30	680.3	0.07	0.10	$Ph-\mathbf{O}^{-}$	141
46	[P$_{66614}$][3-NMe$_2$-PhO]	30	1	30	620.0	0.94	1.52	$Ph-\mathbf{O}^{-}$	141
47	[P$_{66614}$][1-Naph]	30	1	30	627.0	0.89	1.42	$Ph-\mathbf{O}^{-}$	141
48	[P$_{66614}$][2-Naph]	30	1	30	627.0	0.86	1.37	$Ph-\mathbf{O}^{-}$	141
49	PhOLi/12-crown-4 [h]	25	1	5	276.3 [l]	0.75	2.71 (0.85)	$Ph-\mathbf{O}^{-}$	123
50	PhONa/15-crown-5 [h]	25	1	15	336.4 [l]	0.84	2.50 (0.90)	$Ph-\mathbf{O}^{-}$	123
51	PhOK/18-crown-6 [h]	25	1	10	396.5 [l]	0.90	2.27 (0.90)	$Ph-\mathbf{O}^{-}$	123
52	[P$_{4444}$][PhO]	40	1	5	352.5	0.77	2.18	$Ph-\mathbf{O}^{-}$	147
53	[P$_{4444}$][2-F-PhO]	40	1	5	370.5	0.67	1.81	$Ph-\mathbf{O}^{-}$	147
54	[P$_{4444}$][3-F-PhO]	40	1	5	370.5	0.74	2.00	$Ph-\mathbf{O}^{-}$	147
55	[P$_{4444}$][4-F-PhO]	40	1	5	370.5	0.84	2.27	$Ph-\mathbf{O}^{-}$	147
56	[MTBDH][PhO]	23	1	300	247.3	0.49	1.98	$Ph-\mathbf{O}^{-}$	126
57	[(P$_2$-Et)H][PhO]	23	1	300	433.5	0.45	1.04	$Ph-\mathbf{O}^{-}$	126
58	[N$_{2222}$][PhO]	50	1	– [e]	223.4	0.64	2.86	$Ph-\mathbf{O}^{-}$	222
59	[P$_{66614}$][PhO]	23	1	20	577.0	0.50	0.87	$Ph-\mathbf{O}^{-}$	125
60	[Im$_{21}$OH][Tf$_2$N]-DBU [i]	20	1	30	559.6 [l]	1.04	1.86	$R-\mathbf{O}(H)$	163
61	[Im$_{21}$OH][Tf$_2$N]-MTBD [i]	20	1	30	560.5 [l]	1.02	1.82	$R-\mathbf{O}(H)$	163

62	[Im$_{21}$OH][Tf$_2$N]-BEMP [i]	20	1	60	681.7 [l]	0.81	1.19	R–**O**(H)	163
63	[N$_{ip,211}$OH][Tf$_2$N]-DBU [i]	20	1	30	564.6 [l]	1.02	1.81	R–**O**(H)	163
64	[N$_{1111}$][*n*-BuNHEtCOO]-CH$_3$OH [j]	40	1	– [e]	250.4 [l]	0.97	3.87 (1.33)	R–**O**(H)	164
65	[N$_{1111}$][*n*-Bu$_2$NEtCOO]-CH$_3$OH [j]	40	1	– [e]	306.5 [l]	1.01	3.30 (1.10)	R–**O**(H)	164
66	[N$_{1111}$][*n*-Bu$_2$NEtNHEtCOO]-CH$_3$OH [j]	40	1	– [e]	349.6 [l]	1.02	2.92 (0.96)	R–**O**(H)	164
67	[N$_{1111}$][*n*-BuNHEtCOO]-EG [j]	40	1	– [e]	280.4 [l]	0.96	3.42 (1.32)	R–**O**(H)	164
68	[N$_{1111}$][*n*-Bu$_2$NEtCOO]-EG [j]	40	1	– [e]	336.5 [l]	0.98	2.91 (1.07)	R–**O**(H)	164
69	[N$_{1111}$][*n*-Bu$_2$NEtNHEtCOO]-EG [i]	40	1	– [e]	379.6 [l]	1.03	2.71 (0.97)	R–**O**(H)	164
70	[Bmim][Tf$_2$N]-DBU [i]	23	1	30	571.6 [l]	0.99	1.73	**C**-2(H)	176
71	[Emim][Tf$_2$N]-DBU [i]	23	1	30	543.6 [l]	0.93	1.71	**C**-2(H)	176
72	[Bmim][Tf$_2$N]-MTBD [i]	23	1	30	572.6 [l]	1.08	1.89	**C**-2(H)	176
73	[Bmim][Tf$_2$N]-(P$_2$-Et) [i]	23	1	30	758.8 [l]	1.00	1.32	**C**-2(H)	176
74	[Bmim][BF$_4$]-DBU [i]	23	1	90	378.3 [l]	0.80	2.11	**C**-2(H)	176
75	[Bmim][PF$_6$]-DBU [i]	23	1	60	436.4 [l]	0.75	1.72	**C**-2(H)	176
76	[Emim][Ac]	25	1	– [e]	170.2	0.36	2.12	**C**-2(H)	177
77	[Bmim][Ac]	25	1	– [e]	198.3	0.38	1.92	**C**-2(H)	177
78	[Bmim][CH$_3$CH$_2$COO]	25	1	– [e]	212.3	0.28	1.32	**C**-2(H)	177
79	[Bmim][(CH$_3$)$_2$CHCOO]	25	1	– [e]	226.3	0.28	1.24	**C**-2(H)	177
80	[Bmim][(CH$_3$)$_3$CCOO]	25	1	– [e]	240.3	0.31	1.29	**C**-2(H)	177
81	[Eeim][Ac]	25	1	– [e]	184.2	0.32	1.74	**C**-2(H)	191
82	[Bmim][Im]	40	1	5	206.3	~0.54	~2.62	**C**-2(H)	198
83	[Emim][Im]	40	1	3	178.2	~0.54	~3.03	**C**-2(H)	198
84	[HO-emim][Im]	40	1	60	194.2	~0.55	~2.83	**C**-2(H)	198
85	[P$_{4444}$][Gly]-H$_2$O (1 w_{H2O}%)	– [e]	1	200	333.5	~1.0	~3.00 (2.97)	H**O**(H)	106
86	[N$_{1111}$][Gly]	25	0.65	– [e]	148.2	0.17	1.15	–	209
87	[N$_{1111}$][Gly]-H$_2$O (20 w_{H2O}%)	25	0.63	45	148.2	0.25	1.69 (1.35)	H**O**(H)	209
88	[N$_{1111}$][Gly]-H$_2$O (35 w_{H2O}%)	25	0.63	45	148.2	0.31	2.09 (1.36)	H**O**(H)	209
89	[N$_{1111}$][Gly]-H$_2$O (50 w_{H2O}%)	25	0.63	45	148.2	0.40	2.70 (1.35)	H**O**(H)	209
90	[N$_{1111}$][Gly]-H$_2$O (70 w_{H2O}%)	25	0.64	45	148.2	0.60	4.05 (1.22)	H**O**(H)	209
91	[N$_{1111}$][*n*-Bu$_2$NEtCOO]-H$_2$O [k]	40	1	– [e]	236.4	0.95	4.02 (1.21)	H**O**(H)	164
92	[N$_{1111}$][*n*-BuNHEtCOO]-H$_2$O [k]	40	1	– [e]	292.5	0.94	3.21 (0.96)	H**O**(H)	164
93	[N$_{1111}$][*n*-Bu$_2$NEtNHEtCOO]-H$_2$O [k]	40	1	– [e]	335.5	1.01	3.01 (0.90)	H**O**(H)	164
94	[C$_1$C$_4$Pyrro][Ac]	80	0.98	– [e]	201.3	0.01	0.05	–	219
95	[C$_1$C$_4$Pyrro][Ac]-H$_2$O (35 mol$_{\mathrm{H2O}}$%)	30	0.09	– [e]	201.3	0.12	0.60 (0.57)	H**O**(H)	219
96	[C$_1$C$_4$Pyrro][Ac]-H$_2$O (60 mol$_{\mathrm{H2O}}$%)	30	0.15	– [e]	201.3	0.06	0.30 (0.26)	H**O**(H)	219
97	[C$_1$C$_4$Pyrro][Ac]-H$_2$O (85 mol$_{\mathrm{H2O}}$%)	30	0.64	– [e]	201.3	0.01	0.05 (0.03)	–	219
98	[Eeim][Ac]-H$_2$O (20.8 mol$_{\mathrm{H2O}}$%)	27	2	– [e]	184.2	0.27	1.47 (1.43)	H**O**(H)	191
99	[Eeim][Ac]-H$_2$O (20.8 mol$_{\mathrm{H2O}}$%)	27	0.75	– [e]	184.2	0.21	1.14 (1.11)	H**O**(H)	191
100	[Eeim][Ac]-H$_2$O (20.8 mol$_{\mathrm{H2O}}$%)	27	0.07	– [e]	184.2	0.10	0.54 (0.53)	H**O**(H)	191
101	[Eeim][Ac]-H$_2$O (35.0 mol$_{\mathrm{H2O}}$%)	27	0.10	– [e]	184.2	0.08	0.43 (0.41)	H**O**(H)	191
102	[Eeim][Ac]-H$_2$O (53.3 mol$_{\mathrm{H2O}}$%)	27	0.16	– [e]	184.2	0.06	0.33 (0.30)	H**O**(H)	191

[a] Full names of absorbents can be found in Table S2. [b] Molecular weight of pure IL or salt. [c] Values shown in brackets are based on the total weight of solution. [d] Active site atoms are shown in bold font, and transfer proton atoms are shown in brackets. [e] Data are not mentioned in the literature. [f] Mixed with PEG$_{200}$ (mass ratio of IL : PEG$_{200}$ is 5:95), and absorption by PEG$_{200}$ is subtracted. [g] Mixed with PEG$_{150}$ (molar ratio of IL : PEG$_{150}$ is 1:3), and absorption by PEG$_{150}$ is subtracted. [h] Mixed with PEG$_{300}$ (molar ratio of salt : crown ether : PEG$_{300}$ is 1:1:2). [i] Molar ratio of IL : superbase is 1:1. [j] EG is ethylene glycol, and mass ratio of IL : alcohol is 30:70. [k] Mass ratio of IL : H$_2$O is 30:70. [l] Molar mass of the 1:1 molar mixture.

Acetate-based IL-H$_2$O blends. Effect of water on the CO$_2$ absorption by 1,3-dialkylimidazolium acetate ILs,[169,193,217-218] or other carboxylate Ils [119,219,221] has been investigated in many publications. It is known that the carboxylate anions are stable in aqueous conditions below 100 °C, [119] and there is a different solubility mechanism for CO$_2$ in this kind of ILs in the presence of water. For example, aqueous acetate-based ILs could chemically bind CO$_2$ to form HCO$_3^-$ and protonated acetate species (Scheme 27). [218] By combining experimental data with molecular simulation, Gomes *et al.* [193] reported that the presence of water not only rendered the chemical reaction between CO$_2$ and IL less favorable but also lowered the (physical) solubility of the CO$_2$ as it competes by the same solvation sites of the IL.

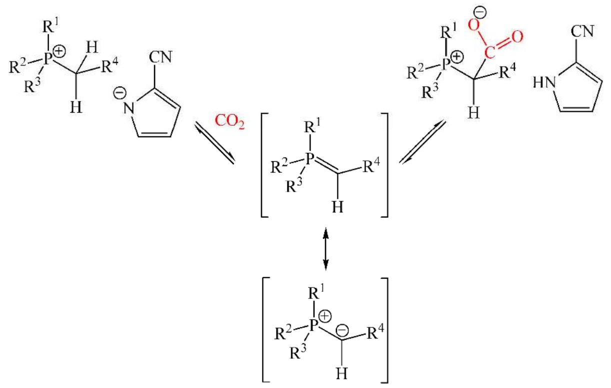


Scheme 27 The reaction mechanism of [Ac]-*n*H$_2$O (*n*>1) with CO$_2$. Adapted with permission from ref. 218. Copyright 2011 American Chemical Society.

Shiflett *et al.* [191] found that the reaction was irreversible because the formed bicarbonate was stable unless heated and/or reacted with acetic acid to form acetate. Furthermore, Wu *et al.* [218] claimed that the reaction product acetic acid accompanied with a small amount of water was more stable than pure acetic acid. However, Wassell *et al.* [119] suggested that there would be a reaction between acetic acid and acetate to form the stable protonated dimeric anion. They showed that mixture of [N$_{2224}$][Ac] [218] or [P$_{4444}$][HCOO] [119] with equimolar H$_2$O was an excellent reversible liquid absorbent for CO$_2$. In addition, no chemical reaction was involved between CO$_2$ and dry 1-butyl-1-methylpyrrolidinium acetate ([C$_1$C$_4$Pyrro][Ac]), except for its water mixture (Table 2, entries 94–97). [219] It was also found that although the reaction was possible only in the presence of water, excess water displaced equilibrium toward the reactants and decreased the absorption. [219] This has been supported by many investigations that the absorption capacity of CO$_2$ in aqueous [Emim][Ac],[178,193] [Bmim][Ac],[193] [N$_{2224}$][Ac],[218] [Eeim][Ac], [191] [C$_1$C$_4$Pyrro][Ac] [219] and other [Ac]-based ILs solutions decreased with the increase of water content (Table 2, entries 81, 98–102).

3.3.4 Protons on the α-carbon of the phosphorus center

Previous studies on CO_2 absorption by azole-based anion-functionalized ILs showed that the cation was innocent to the CO_2 chemistry and the basic N on the anion reacted with CO_2 to form a carbamate ($-NCO_2^-$) (Scheme 12).[129] This reaction channel certainly dominates at room temperature. However, based on their recent investigation on the CO_2 absorption at elevated temperature, Brennecke *et al.*[223-224] provided the evidence for an additional CO_2 reaction pathway with the cation, that is dramatically different, for the ILs with phosphonium and ammonium cations. It was found that at elevated temperature, phosphonium azolide ILs reacted with CO_2 through both the anticipated anion mechanism (Scheme 13) and the reaction with the cation in a mechanism involving an ylide intermediate (Scheme 28). The reaction was caused by an interaction between the anion and the cation allowing for proton transfer. Thus, phosphonium cations paired with AHA anions reacted with CO_2 through different mechanisms at higher temperatures (e.g. 60 °C). However, stripping of CO_2 from the cation would be more energy intensive than that from the anion due to the stability of each species. This may not be a significant drawback for phosphonium AHAs since the additional cation reaction is relatively minor.



Scheme 28 Proposed reaction mechanism of phosphonium with CO_2. Adapted with permission from ref. 223. Copyright 2014 Wiley-VCH.

4. Multiple site-functionalized ILs

Generally, tethering the CO_2-philic reactive sites on the cation or anion of ILs is important to improve the carbon capture. It is easy to conclude that more sites on one IL would achieve large CO_2 capacity.

4.1 Multiple site-functionalized cation

Wang *et al.*[102] presented a new kind of tunable alkanolamine-based ILs (Scheme 3) by using multidentate coordination interactions between alkanolamine and alkali metallic ions in a quasi-aza-crown ether fashion. The results indicated that high capacity and rapid kinetics could be achieved by tuning the chelation of the alkali metal salt. The absorption molar ratios of CO_2 to [Li(HDA)][Tf_2N] and [Li(DOBA)][Tf_2N] were 0.88 and 0.90 at 40 °C and 1 bar, respectively, suggesting that almost equimolar CO_2 absorptions were obtained (Table 3, entries 1–2, Fig. 5). Zhang *et al.*[225] reported that 1.05 mole CO_2 could be captured by one mole dual amino ionic liquid (DAIL) through carbamate mechanism (Table 3, entry 3). In this IL, two primary amino groups were tethered on the imidazolium-based cation.

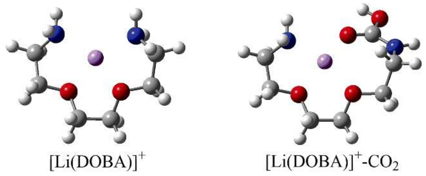
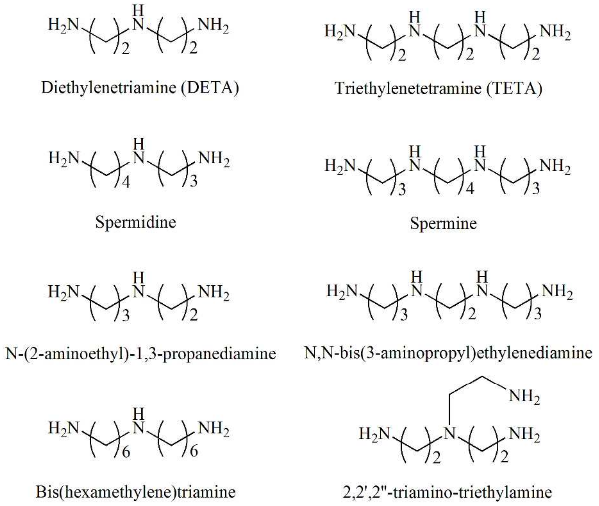
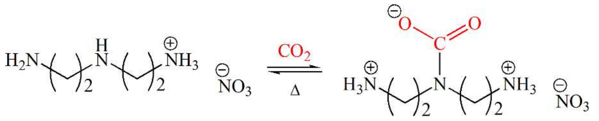


Fig. 5 The optimized structures of $[Li(DOBA)]^+$ before and after the absorption of CO_2. Reprinted with permission from ref. 102. Copyright 2012 Royal Society of Chemistry.

In 2002, Steed *et al.*[226] reported, for the first time, a crystal structure analysis of 16 complexes of polyammonium cations with nitrate, phosphate or sulfate anion (Scheme 29). Recently, Clyburne *et al.*[227] re-synthesized a kind of multiamino-based IL [DETA][NO_3] by mixing diethylenetriamine (DETA) with nitric acid and investigated its performance to capture CO_2 from ambient air (Scheme 30). At the nearly same time, Meng *et al.*[228] reported several ammonium ILs with multiamino-based cations. Their results showed that aqueous [TETA][NO_3] with three unprotonated amino groups on its cation, could be used to absorb 1.49 mole CO_2 per mole IL at 15 °C and 1 bar through carbamate mechanism detected using *in situ* FT-IR (Table 3, entry 4).



Scheme 29 Chemical structures of polyamines. Adapted with permission from ref. 226. Copyright 2002 Royal Society of Chemistry.

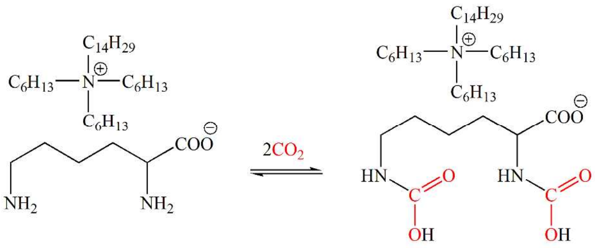


Scheme 30 Thermally reversible reactions of [DETAH][NO_3] with CO_2 to yield the corresponding carbamate salts. Adapted with permission from ref. 227. Copyright 2015 American Chemical Society.

4.2 Multiple site-functionalized anion

4.2.1 Multiamino-based anion

AAILs with the anion tethered with two primary amino groups were first reported by Brennecke *et al.*[116] In their work, [P_{66614}][Lys] with two amino groups on its anion could absorb 1.37 mole CO_2 per mole IL at room temperature (22 °C) (Table 3, entry 5). The authors pointed out that [P_{66614}][Lys] absorbed significantly less than 1 mole of CO_2 per mole of amine, much lower than the other ILs in this work, indicating a stronger effect of the 1:2 mechanism. Riisager *et al.*[117] synthesized some [N_{66614}]-based AAILs and investigated their super-equimolar CO_2 absorption capacity of 2 mole CO_2 per mole of IL (CO_2 : amine = 1:1) at 1 bar through carbamic acid mechanism detected using *in situ* FT-IR and DFT calculation (Scheme 31). It was found that the ILs such as [N_{66614}][Lys], [N_{66614}][His], [N_{66614}][Asn], and [N_{66614}][Gln], which have two amino groups on each anion, exhibited a remarkable CO_2 absorption capacity (2.0±0.1 mole of CO_2 per mole of IL) after 24–48 h gas saturation at 22 °C and 1 bar, while [N_{66614}][Met] could only absorb 1.0 mole CO_2 per mole IL under the same ambient conditions (Table 3, entries 6–10 vs Table 1, entry 40). Besides tetraalkylammonium and tetraalkylphosphonium AAILs, Li *et al.* [109] and Khanna *et al.* [110] investigated some imidazolium AAILs based on [Arg], [109-110] [Lys], [110] and [His] anions. [110] It was shown that CO_2 capture by these ILs could reach only slightly higher capacities than the single amino-containing anion-functionalized ILs under the same conditions (Table 3, entry 11 vs Table 1, entries 26–27, and Table 3, entries 12–14 vs Table 1, entries 28–33). According to 1:2 mechanism, the experimental CO_2 sorption capacities of these ILs presents an obvious discrepancy with their theoretical values, probably because of the strong cation-anion interaction and low reactive activity of amino group on these anions,[110] compared with the ILs based on [P_{66614}] or [N_{66614}] cation.

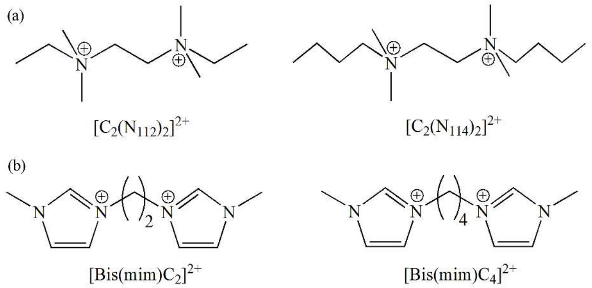


Scheme 31 The formation of the [N_{66614}][Lys]–CO_2 adduct. Adapted with permission from ref. 117. Copyright 2014 Wiley-VCH.

4.2.2 Dicationic ILs with two active site-containing anions

In this kind of ILs, the cation was equipped with two charges and the anions were functionalized with two appended active site-containing groups. Dicationic ILs have attracted increasing attention due to their excellent properties such as higher thermal stability, shear viscosity, surface tensions, and liquid density compared to monocationic ILs.[229-233]

ILs with one dication and two AA anions. Zhang *et al.*[210] reported a new CO_2 absorption example for the first time by using dicationic amino acid-based ILs (AA-DILs), in which the ditetraalkylammonium cation was equipped with two charges and the anions were finterfacialunctionalized with two appended amino groups (Scheme 32a). Since the high viscosity and low liquidity of all the pure AA-DILs hindered CO_2 from approaching into the IL, they were prepared as aqueous solutions for CO_2 uptake.[118,198,210,234-235] It was found that the aqueous solutions containing 40% [$C_2(N_{112})_2$][Gly]$_2$ or [$C_2(N_{114})_2$][Gly]$_2$ had higher absorption rates, and the absorption capacities were 0.443 and 0.403 mole of CO_2 per mole of [Gly], respectively (Table 3, entries 15–16).[210] Similar CO_2 absorption capacities could be achieved by other aqueous solutions containing 60% imidazolium-based AA-DILs, such as [Bis(mim)C_2][Pro]$_2$, [Bis(mim)C_4][Pro]$_2$, [Bis(mim)C_2][Gly]$_2$, and [Bis(mim)C_4][Gly]$_2$, (Scheme 32b, Table 3, entries 17–20) through 1:2 mechanism.[211]



Scheme 32 Structures of cations studied in ref. 210 (a) and ref. 211 (b).

ILs with one dication and two AHA anions. Luo *et al.* [195,226] developed a series of imidazolate-based DILs, such as [Bis(mim)C_2][Im]$_2$, and [Bis(mim)C_4][Im]$_2$.[198,236] These ILs exhibited significant equimolar capture capacities of CO_2 at 40 °C and 1 bar through two carboxylation reactions on C-2 position of the imidazolium rings, which were nearly twice that of the monocationic analogues (Scheme 23; Table 3, entries 21–22 vs Table 2, entries 82–83).[198]

4.2.3 IL with one diolate-based anion and two cations

Dai *et al.* [126] developed some superbase drived anion-functionalized protic ILs (Scheme 15) from the neutralization of a superbase with weak proton donors, such as TFE and HFPD, as an alternative absorbent for CO_2 capture. It was noted that compared with [MTBDH]$^+$[TFE]$^-$, by which the CO_2 absorption capacity is 1.13 mole CO_2 per mole IL, a superbase-drived diolate IL [MTBDH]$^+_2$[HFPD]$^{2-}$ showed a CO_2 capacity of more than 2.04 due to the presence of two CO_2-reactive groups (Table 3, entry 23 vs Table 2, entry 32).

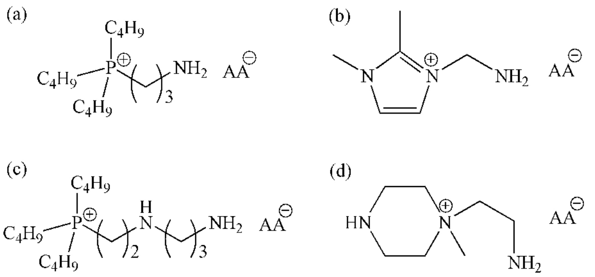
4.3 ILs with active site-containing cation and active site-containing anion

4.3.1 Amino-based cation and AA anion

Due to the designability of ILs, the structure of the anion and/or cation in an IL can be designed to include more amino groups to increase CO_2 absorption efficiency. From this point of view, dual amino-functionalized ILs that consist of an amino-based cation and an amino acid anion were developed for equimolar CO_2 capture by Zhang *et al.* [124] to improve CO_2 capture (Scheme 33a). Supported by porous SiO_2, the chemisorption of CO_2 by dual amino-functionalized phosphonium ILs, (3-aminopropyl) tributylphosphonium AAILs ([aP_{4443}][AA]), was almost complete within 80 min. The CO_2 absorption capacities of [aP_{4443}][Gly] and [aP_{4443}][Ala] were found to approach 1 mole of CO_2 per mole of IL, due to the reaction of both the cation and the anion with CO_2 (Table 3, entries 24–25).

For this kind of dual-amino functionalized ILs, the theoretical absorption capacity is about 1.5 mole of CO_2 per mole of IL because of the 1:1 mechanism of the amino-tethered anion and the 1:2 mechanism of the amino-tethered cation.[113] Mu *et al.* reported another kind of dual amino-functionalized AAIL with 1-aminoethyl-2,3-dimethylimidazolium cation and taurinate anion [aemmim][Tau] (Scheme 33b).[234] The results showed that CO_2 absorption capacity reached about 0.9 mole CO_2 per mole of IL at ambient pressure (Table 3, entry 26). They explained the reason why the absorption capacity could not reach 1.5 mole of CO_2 per mole of IL by the fact that the complex formed between the amino-tethered anion and CO_2 was not stable and reacted with another amino gorup on the anion, leading to both 1:2 mechanism of the amino-tethered anion and the amino-tethered cation, thus about 1 mole of CO_2 per mole of IL was obtained through the absorption experiments.

Wu *et al.* [237] investigated CO_2 capture by several porous silica supported N-(3-aminopropyl)aminoethyl tributylphosphonium AAILs ([apaeP$_{444}$][AA], where [AA] = [Lys], [Gly], [Ser], [Ala], [Asp], and [His]) (Scheme 33c), through 1:2 mechanism (Table 3, entries 27–32). It was shown that the experimental CO_2 sorption capacities were lower than the theoretical values (1.5−2.0 mol CO_2), which may be resulted from the following factors: (1) The −NH− group tethered to the phosphonium cation may have less reactivity to react with CO_2 than the $-NH_2$ group; (2) Some amino groups form hydrogen bonds among themselves and therefore may become inactive for CO_2 capture.[237] Similarly, Xia *et al.* [238] synthesized and characterized four kinds of porous silica supported 1-(2-aminoethyl)-1-methylpiperazin-1-ium AAILs ([AEMP][AA]), where [AA] = [Gly], [Ala], [Pro], and [Leu]) (Scheme 33d). The absorption capacity was found to reach about 1.5 mole of CO_2 per mole of IL at room temperature and normal pressure through 1:2 mechanism (Table 3, entries 33–36).



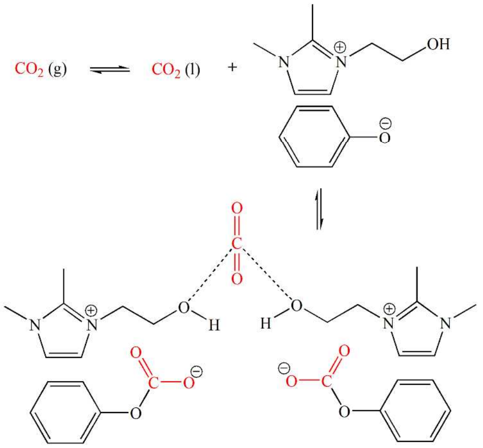
Scheme 33 Structures of the dual amino-functionalized ILs [aP$_{4443}$][AA] (a), [aemmim][AA] (b), [apaeP$_{444}$][AA] (c), and [AEMP][AA] (d).

4.3.2 Amino-based cation and AHA anion

Another example for CO_2 absorption by dual functionalized IL through dual site interaction mechanism is 1-aminopropyl-3-methylimidazolium imidazolate ([apmim][Im]) with amino-functionalized cation and imidazolate anion.[198] It was found that this IL exhibited an equimolar capacity (Table 3, entry 37) during the absorption of CO_2 through formation of carboxylate (Scheme 23) and carbamate (Scheme 2).

4.3.3 OH-based cation and phenolate anion

The solubilities of CO_2 in OH-based cation-functionalized ILs were determined previously and very little physical capacity was achieved under ambient conditions. [58,239-242] In addition, Luo *et al.* [198] showed that the capacities of CO_2 absorption by [Emim][Im] and [HO-emim][Im] were very similar at 40 °C and 1 bar (Table 2, entries 83–84). However, Vafaeezadeh *et al.* [243] found that up to 1.5 mole of CO_2 per mole of IL could be achieved under ambient conditions by 1-(2-hydroxyethyl)-2,3-dimethylimidazolium phenolate ([OH-emmim][PhO]) (Scheme 34; Table 3, entry 38). This might be ascribed to the fact that the "2-methylated" imidazolium is more stable than "2-H" imidazolium under the applied basic condition, and the later is susceptible to form carbene in the basic media.



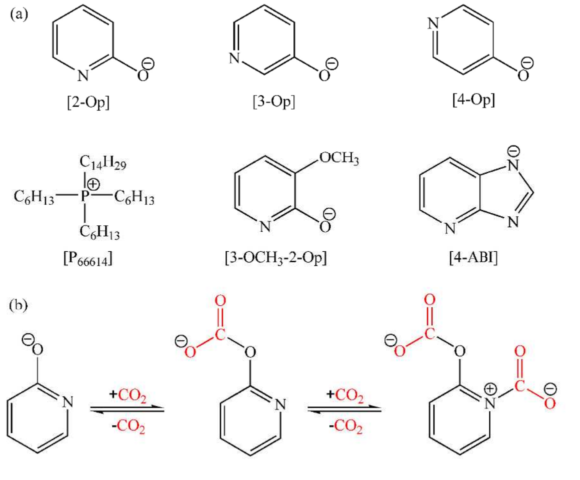
Scheme 34 The proposed mechanism for CO_2 absorption by [OH-emmim][PhO]. Adapted with permission from ref. 243. Copyright 2015 The Royal Society of Chemistry

4.4 Multiple cooperative sites on the anion

A strategy for significant improvement of CO_2 capture by new anion-functionalized ILs using multiple site cooperative interactions was reported by Wang *et al.*[244-245] An extremely high CO_2 capacity and excellent reversibility were achieved by introducing another interacting site on the phenolate and imidazolate anions.

4.4.1 Hydroxypyridine-based ILs

The structures of these pyridine-containing ILs were shown in Scheme 35a. The molar absorption ratios of CO_2 to [P$_{66614}$][2-Op], [P$_{66614}$][4-Op], [P$_{66614}$][3-Op], [P$_{66614}$][3-OCH$_3$-2-Op], and [P$_{66614}$][4-ABI] were found to be 1.58, 1.49, 1.38, 1.65 and 1.60 at 20 °C and 1 bar, respectively (Table 3, entries 39–43). IR spectra of [P$_{66614}$][2-Op]–CO_2 showed that two new peaks at 1670 cm^{-1} and 1650 cm^{-1} could be assigned to the asymmetrical stretching vibration of carboxylate anion from N−CO_2 and O−CO_2 interactions, respectively. In addition, two new signals produced in the ^{13}C NMR spectra of [P$_{66614}$][2-Op]–CO_2 at 166.6 and 159.3 ppm could be attributed to the carbonyl carbon of carbamate and carbonate, respectively (Fig. 6). Thus, the authors suggested that the superior CO_2 capacity was resulted from the multiple-site cooperative interactions between two kinds of interacting sites in the anion and CO_2 (Scheme 35b).



Scheme 35 (a) Structures of the pyridine-containing anion-functionalized ILs in ref. 244. (b) The plausible mechanism of CO_2 absorption by $[P_{66614}]$[2-Op] through multiple-site cooperative interactions. Adapted with permission from ref. 244. Copyright 2014 Wiley-VCH.

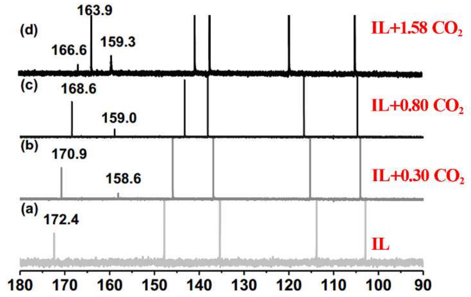
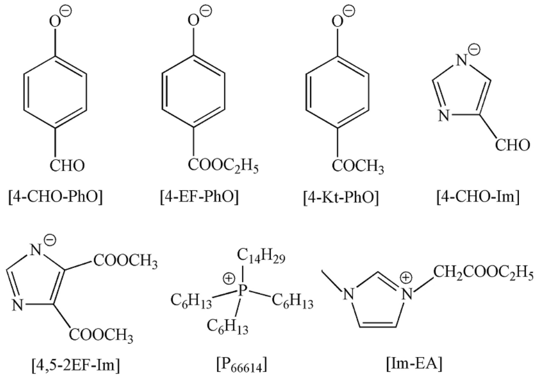


Fig. 6 ^{13}C NMR spectra of $[P_{66614}]$[2-Op] during the absorption of CO_2. Adapted with permission from ref. 244. Copyright 2014 Wiley-VCH.

4.4.2 Carbonyl-containing anion-functionalized ILs

Scheme 36 shows the structures of carbonyl-containing anion-functionalized ILs. [245] It was found from Wang's work that, the molar absorption ratios of CO_2 to $[P_{66614}]$[4-Kt-PhO], $[P_{66614}]$[4-EF-PhO], $[P_{66614}]$[4-CHO-PhO], and $[P_{66614}]$[4-CHO-Im] were 1.04, 1.03, 1.01, and 1.24 at 20 °C and 1 bar, respectively (Table 3, entries 44–47), while the molar ratios of CO_2 to $[P_{66614}]$[PhO], $[P_{66614}]$[Im], and [Im-EA][Tf_2N] were 0.81, 0.98, and 0.06 under the same conditions. Quantum mechanical calculations (Fig. 7) and spectroscopic investigations showed that such a high CO_2 capacity was originated from the enhanced C–H•••O hydrogen bonding interaction, indicating that the carbonyl group that was attached to the anion was very important.



Scheme 36 The structures of the cation and the anions in the carbonyl-containing ILs. Adapted with permission from ref. 245. Copyright 2014 The Royal Society of Chemistry.

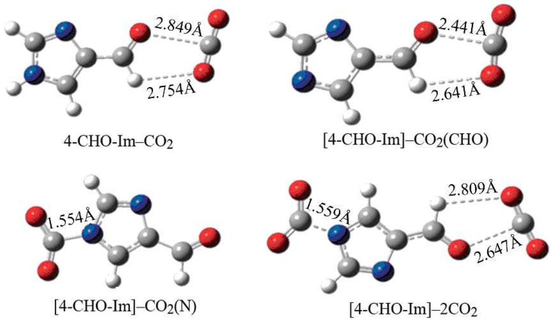


Fig. 7 The optimized structures of neutral 4-CHO-Im–CO_2 complex and anion [4-CHO-Im]–CO_2 complexes at the B3LYP/6-31++G(d,p) level. Adapted with permission from ref. 245. Copyright 2014 The Royal Society of Chemistry.

4.5 Functionalized IL-amine blends

The high volatility of MEA and high viscosity of IL limited their use in carbon capture for industrial applications. Since the first work reported by Nobel *et al.* [246] in 2008, the combination of non-functionalized RTILs with water-free amines to form special hybrid solvents for thermally reversible capture of CO_2 is becoming a popular research topic due to the unique properties of the blends.[247-254] RTIL-amine hybrids offer significant advantages over conventional aqueous amine solutions, especially in regard to the energy required to process CO_2. Unlike RTILs, functionalized ILs which contain active sites in their cations or anions could achieve higher CO_2 capture capcity. Thus, functionalized IL-amine hybrids may open a door to achieve highly efficient and reversible CO_2 cpature for industrial processes.

4.5.1 AAIL-amine blends

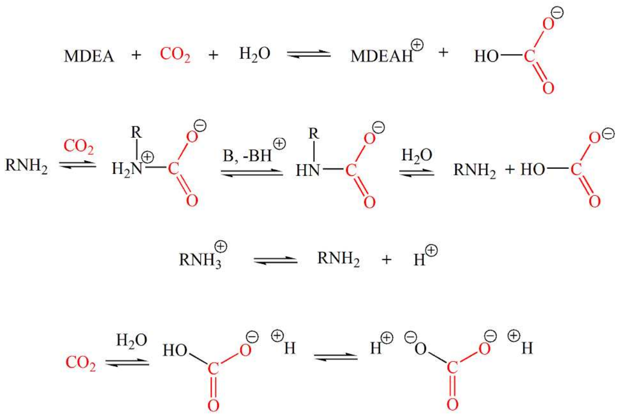
Until now, the most studied functionalized IL-amine blends is AAILs mixed with aqueous amine solutions. For the first time, Zhang *et al.* [209] investigated CO_2 capture in aqueous solutions containing N-methyldiethanolamine (MDEA) and AAILs such as $[N_{1111}]$[Gly], $[N_{2222}]$[Gly], $[N_{1111}]$[Lys] and $[N_{2222}]$[Lys]. It was found that the absorption capacities of [Lys]-based IL/MDEA/H_2O solutions were larger than that of [Gly]-based IL/MDEA/H_2O solutions due to the two amino groups in one [Lys] anion (Table 3, entries 48–51). These authors also studied the effect of AAIL concentration,[255] temperature and pressure,[256] and thermal regeneration of the blends[257] on CO_2 absorption performance. Their results indicated that low concentration (5–10 wt%) of the IL in 30 wt% MDEA aqueous solution dramatically increase the absorption rate, while high IL concentration slows it down due to the high viscosity of the IL.[255] Thus the use of aqueous MDEA solutions activated by AAIL can lead to high absorption speed, high stability of the functionalized ILs, and large absorption capacity of the blends. In addition, Fu *et al.* [258] found that the saturated CO_2 loading decreased with increasing mass fraction of [Bmim][Gly] in aqueous MDEA solutions, indicating that relatively low concentration of [Bmim][Gly] was propitious for high CO_2 loading (Table 3, entries 52–55). Zhou *et al.* [259] used aqueous solution of 2-amino-2-methyl-1-propanol (AMP) promoted by $[N_{1111}]$[Gly] to capture CO_2, and they found that addition of $[N_{1111}]$[Gly] into aqueous AMP solution accelerated the absorption rate. Li *et al.* [260-261] confirmed that the enhanced absorption capacity and higher regeneration efficiency could be achieved by a aqueous solution consisting MEA and [C_2OHmim][Gly].

Table 3 CO_2 chemisorption by multiple active sites functionalized ILs and functionalized IL-based blends.

Entry	Absorbent [a]	Conditions			Mw (g mol^{-1}) [b]	Absorption capacity		Active site [d]	Ref.
		T (°C)	P (bar)	*t* (min)		mol CO_2/mol IL	mol CO_2/kg IL [c]		
1	[Li(HDA)][Tf$_2$N]	40	1	60	391.2	0.88	2.25	–**N**(H)–, –H**N**(H)	102
2	[Li(DOBA)][Tf$_2$N]	40	1	60	435.3	0.90	2.07	–H**N**(H) [2]	102
3	DAIL [f]	30	1	– [e]	249.2	1.05	4.21 (0.42)	–H**N**(H) [2]	225
4	[TETA][NO$_3$] [g]	15	1	– [e]	209.3	1.49	7.12 (2.85)	–**N**(H)– [2], –H**N**(H)	228
5	[P$_{66614}$][Lys]	22	1	– [e]	629.0	1.37	2.18	–H**N**(H) [2]	116
6	[N$_{66614}$][Lys]	22	1	1440	612.1	2.1	3.43	–H**N**(H) [2]	117
7	[N$_{66614}$][Asn]	22	1	2880	598.0	2.0	3.34	–H**N**(H) [2]	117
8	[N$_{66614}$][Gln]	22	1	2880	612.1	1.9	3.10	–H**N**(H) [2]	117
9	[N$_{66614}$][His]	22	1	2880	612.0	1.9	3.10	–**N**(H)–, –H**N**(H)	117
10	[P$_{66614}$][Lys]	22	1	2880	629.0	1.6	2.54	–H**N**(H) [2]	117
11	[Emim][Arg] [h]	40	1	40	284.4	0.52	1.83	–H**N**(H) [2]	109
12	[Bmim][Arg]	25	2	– [e]	312.4	0.62	1.98	–H**N**(H) [2]	110
13	[Bmim][Lys]	25	2	– [e]	284.4	0.48	1.69	–**N**(H)–, –H**N**(H)	110
14	[Bmim][His]	25	2	– [e]	293.4	0.45	1.53	–H**N**(H) [2]	110
15	[C$_2$(N$_{112}$)$_2$][Gly]$_2$ [i]	25	1	120	322.4	0.89	2.76 (1.66)	–H**N**(H) [2]	210
16	[C$_2$(N$_{114}$)$_2$][Gly]$_2$ [i]	25	1	120	378.6	0.81	2.14 (1.28)	–H**N**(H) [2]	210
17	[Bis(mim)C$_2$][Pro]$_2$ [i]	40	1	120	420.5	~0.9	~2.14 (1.28)	–**N**(H)– [2]	211
18	[Bis(mim)C$_4$][Pro]$_2$ [i]	40	1	120	448.6	~0.8	~1.78 (1.07)	–**N**(H)– [2]	211
19	[Bis(mim)C$_2$][Gly]$_2$ [i]	40	1	120	340.4	~0.8	~2.35 (1.41)	–H**N**(H) [2]	211
20	[Bis(mim)C$_4$][Gly]$_2$ [i]	40	1	120	368.4	~0.9	~2.44 (1.47)	–H**N**(H) [2]	211
21	[Bis(mim)C$_2$][Im]$_2$	40	1	60	326.4	0.75	2.30	**C**-2(H) [2]	198
22	[Bis(mim)C$_4$][Im]$_2$	40	1	30	354.5	0.95	2.68	**C**-2(H) [2]	198
23	[MTBDH]$_2$[HFPD]	23	1	60	518.5	2.04	3.93	R–**O**$^-$ [2]	126
24	[aP$_{4443}$][Gly] [j]	– [e]	1	80	334.5	~0.94	~2.81 (1.15)	–H**N**(H) [2]	124
25	[aP$_{4443}$][Ala] [j]	– [e]	1	80	348.5	~0.92	~2.64 (1.11)	–H**N**(H) [2]	124
26	[aemmim][Tau]	30	1	– [e]	264.4	~0.9	~3.40	–H**N**(H) [2]	234
27	[apaeP$_{444}$][Lys] [k]	25	1	60	448.7	1.73	3.86 (1.93)	–**N**(H)–, –H**N**(H) [2]	237
28	[apaeP$_{444}$][Gly] [k]	25	1	60	377.6	1.29	3.42 (1.71)	–**N**(H)–, –H**N**(H) [2]	237
29	[apaeP$_{444}$][Ser] [k]	25	1	60	407.6	1.19	2.92 (1.46)	–**N**(H)–, –H**N**(H) [2]	237
30	[apaeP$_{444}$][Ala] [k]	25	1	60	391.6	1.14	2.91 (1.46)	–**N**(H)–, –H**N**(H) [2]	237
31	[apaeP$_{444}$][Asp] [k]	25	1	60	435.6	1.07	2.46 (1.23)	–**N**(H)–, –H**N**(H) [2]	237
32	[apaeP$_{444}$][His] [k]	25	1	60	457.6	1.01	2.21 (1.11)	–**N**(H)–, –H**N**(H) [2]	237
33	[AEMP][Gly] [l]	– [e]	1	40	218.3	1.50	6.87 (1.37)	–**N**(H)–, –H**N**(H) [2]	238
34	[AEMP][Ala] [l]	– [e]	1	– [e]	232.3	1.57	6.76 (1.35)	–**N**(H)–, –H**N**(H) [2]	238
35	[AEMP][Pro] [l]	– [e]	1	– [e]	258.4	1.54	5.96 (1.19)	–**N**(H)–, –H**N**(H) [2]	238
36	[AEMP][Leu] [l]	– [e]	1	– [e]	274.4	1.47	5.36 (1.07)	–**N**(H)–, –H**N**(H) [2]	238
37	[apmim][Im]	40	1	20	207.3	0.75	3.62	–H**N**(H), **C**-2(H)	198
38	[OH-emmim][PhO]	25	1	120	234.3	1.58	6.74	R–**O**(H), Ph–**O**$^-$	243
39	[P$_{66614}$][2-Op]	20	1	– [e]	578.0	1.58	2.73	Ph–**O**$^-$, –**N**=	244
40	[P$_{66614}$][4-Op]	20	1	– [e]	578.0	1.49	2.58	Ph–**O**$^-$, –**N**=	244
41	[P$_{66614}$][3-Op]	20	1	– [e]	578.0	1.38	2.39	Ph–**O**$^-$, –**N**=	244
42	[P$_{66614}$][3-OCH$_3$-2-Op]	20	1	– [e]	608.0	1.65	2.71	Ph–**O**$^-$, –**N**=	244
43	[P$_{66614}$][4-ABI]	20	1	– [e]	602.0	1.60	2.66	–**N**$^-$–, –**N**=	244
44	[P$_{66614}$][4-Kt-PhO]	30	1	– [e]	619.0	1.04	1.68	Ph–**O**$^-$, –C=**O**	245
45	[P$_{66614}$][4-EF-PhO]	30	1	– [e]	649.0	1.03	1.59	Ph–**O**$^-$, –C=**O**	245
46	[P$_{66614}$][4-CHO-PhO]	30	1	– [e]	605.0	1.01	1.67	Ph–**O**$^-$, –C=**O**	245
47	[P$_{66614}$][4-CHO-Im]	30	1	40	578.9	1.24	2.14	Ph–**O**$^-$, –C=**O**	245
48	[N$_{1111}$][Gly]-MDEA [m]	25	1	– [e]	148.2	~0.7 [p]	(~1.28)	–H**N**(H), H**O**(H)	209
49	[N$_{2222}$][Gly]-MDEA [m]	25	1	– [e]	204.3	~1.0 [p]	(~1.28)	–H**N**(H), H**O**(H)	209
50	[N$_{1111}$][Lys]-MDEA [m]	25	1	– [e]	219.3	~1.15 [p]	(~1.35)	–H**N**(H) [2] , H**O**(H)	209
51	[N$_{2222}$][Lys]-MDEA [m]	25	1	– [e]	275.4	~1.3 [p]	(~1.34)	–H**N**(H) [2] , H**O**(H)	209
52	MDEA [n]	30	1	– [e]	119.2 [o]	0.82 [p]	(2.07)	H**O**(H)	258
53	[Bmim][Gly]-MDEA (5 w_{IL}%) [n]	30	1	– [e]	213.3	0.80 [p]	(2.20)	–H**N**(H), H**O**(H)	258
54	[Bmim][Gly]-MDEA (10 w_{IL}%) [n]	30	1	– [e]	213.3	0.78 [p]	(2.33)	–H**N**(H), H**O**(H)	258
55	[Bmim][Gly]-MDEA (15 w_{IL}%) [n]	30	1	– [e]	213.3	0.73 [p]	(2.34)	–H**N**(H), H**O**(H)	258

[a] Full names of absorbents can be found in Table S3. [b] Molecular weight of pure IL. [c] Values shown in brackets are based on the total weight of solution or IL + support. [d] Active site atoms are shown in bold font, transfer proton atoms are shown in brackets, and number of active sites are shown in square brackets. [e] Data are not mentioned in the literature. [f] Mixed with H_2O (mass ratio of IL : H_2O is 10:90). [g] Mixed with H_2O (mass ratio of IL : H_2O is 40:60). [h] Immobilization of the IL on nanoporous PMMA support (mass ratio of IL : PMMA is 1:1). [i] Mixed with H_2O (mass ratio of IL : H_2O is 60:40). [j] Immobilization of the IL on porous SiO_2 support (molar ratio of IL : SiO_2 is 1:8), and absorption by SiO_2 is subtracted. [k] Immobilization of the IL on porous SiO_2 support (mass ratio of IL : SiO_2 is 1:1). [l] Immobilization of the IL on porous SiO_2 support (mass ratio of IL : SiO_2 is 1:4). [m] Mixed with H_2O (mass ratio of IL : MDEA : H_2O is 15:15:70). [n] Mixed with H_2O, and mass fraction of MDEA in solution is 30 %. [o] Molecular weight of MDEA. [p] Mole of CO_2 per mole of (IL + amine).

The mechanism of CO_2 absorption by AAIL-amine blends has been studied in many investigations. Typically, Zhang *et al.* [209] suggested an absorption mechanism by AAIL-MDEA blends through zwitterion mechanism which was first proposed by Caplow [262] and later reintroduced by Danckwerts (Scheme 1).[263] Then, the formed zwitterion was deprotonated by a base (including RNH_2, H_2O, OH^-, and MDEA) present in solution. Thus, a carbamate was formed, and the absorption rate was increased greatly compared with the aqueous MDEA solution.[209] In addition, multiple equilibrium reactions were suggested in the liquid phase of IL−amine−CO_2 (Scheme 37):



Scheme 37 Multiple equilibrium reactions suggested in the liquid phase of AAIL-amine-CO_2, where B is a base.

4.5.2 Acetate IL-amine blends

Besides the AAIL-amine blends, several other workers investigated carbon capture by the blends of acetate ILs and aqueous amines. For example, Baj *et al.* [264] showed that three-component system of [Bmim][Ac]/MEA/H_2O had the potential to capture CO_2, and the CO_2 absorption capacity was mainly a function of MEA concentration. Murugesan *et al.* [265] studied the uptake of CO_2 in the aqueous mixtures of $[H_2N(CH_2CH_2OH)_2][Ac]$ and MEA at three different temperatures (25 °C, 30 °C and 40 °C) and high pressure. Zheng *et al.* [266] determinated the solubilities of CO_2 in [Emim][Ac]/piperazine (PZ)/H_2O systems. It was shown that the addition of PZ highly improved the absorption ability of hybrid absorbent, while [Emim][Ac] had little effect on the CO_2 absorption ability at highly concentrated PZ aqueous solution. Recently, Kortunov *et al.* [267] revealed the mechanism for the reaction of CO_2 with 1,3-dialkylimidazolium acetate ILs in amine solutions at ambient pressure and temperature. *In situ* ^{13}C and ^1H NMR spectroscopy was used by the authors to provide real-time insights on CO_2−IL and CO_2−amine reaction pathways.

5. Activation of reactive sites

Since a primary motivation of this work is to review active site-containing ILs for designing novel kinds of IL-based systems and improving the efficiency of CO_2 capture from flue gases through chemical interaction, it is necessary to further improve the absorption of CO_2 in ILs with CO_2-philic reactive sites. Below we will concentrate our attention on how to activate the reactive sites by physical and chemical methods.

5.1 Activation of reactive sites by physical methods

One of the most important physical properties of ILs is viscosity.[268-269] Active site-containing ILs, especially those with amino groups tethered on the cation or anion, show relatively high viscosities, which even increased significantly after CO_2 absorption to form highly viscous gels or solids.[69,99,112,124] This will affect the distribution of CO_2 in the ILs and increase the energy input for heat and mass transfers. Thus the high viscosity is one of the major technical barriers for the application of CO_2 absorption by ILs.[93,99,106,115] In order to deal with the high viscosity of neat functionalized ILs, activate the reactive sites and enhance the absorption efficiency of CO_2, IL-supported materials, IL-based solutions and IL-IL mixtures have been developed and used for the absorption of CO_2.

5.1.1 Immobilization of ILs on supports

CO_2 capture by supported amines through dipping (also named impregnation-vaporization method) have been widely investigated to enhance selectivity and chemical adsorption capacity of CO_2.[270] However, alkanolamines are prone to degradation during the regeneration because they are volatile and their amino group are thermal instable. Zhang *et al.*[106,124] reported CO_2 absorption by phosphonium AAILs immobilized on porous SiO_2 for the first time. For the sake of simplicity, the porous silica gel was first pretreated, and then mixed with phosphonium AAILs dissolved in ethanol in an ideal molar ratio, followed by evaporation of the ethanol and drying of the sample. It was noted that in the neat $[aP_{4443}][AA]$, less than 0.2 mole of CO_2 per mole of IL was absorbed after 2 h (Fig. 8a), while the ratio of chemical absorption of CO_2 by supported $[aP_{4443}][AA]$ was close to 1 mole of CO_2 per mole of IL, and the absorption was almost complete in 80 min with SiO_2 absorption subtracted (Fig. 8b; Table 3, entries 24–25).[124] These results indicate that the supported amino-functionalized ILs could release interactive sites and result in kinetically beneficial for the absorption of CO_2. The same method was also used in other researchers' work.[237,271] Xia *et al.* [238] investigated the type of porous silica support on the performance of CO_2 capture by AAILs. It was found that the absorption capacity of AAIL supported on 300–400 mesh SiO_2 was twice that of 50–100 mesh SiO_2 with a certain mass ratio of IL to SiO_2 because of the large surface area and pore volume for the former. Glover *et al.* [272] provided a preliminary analysis for the use of tetraalkylammonium taurinate ILs supported on an ordered mesoporous silica as a composite CO_2 sorbent. Other supports were also used to increase the CO_2 capture performance. For example, Zhu *et al.* [273] presented CO_2 adsorption at relatively high temperature by alumina or silica supported basic $[P_{4444}]$-based ILs with anions such as imidazolate and 3-aminopyrazolate. After these ILs were immobilized on alumina or silica, equimolar CO_2 capture was realized at 120 °C for the first time. Li *et al.*[109] developed imidazolium AAILs supported on a kind of nanoporous microspheres (polyminterfacialethylmethacrylate, PMMA) as robust sorbents for CO_2 capture, which exhibited fast kinetics as well as good sorption capacity (Table 1, entries 26–27). Li *et al.* [100] investigated CO_2 capture by NaY zeolite supported [apmim][Br] through 1:2 mechanism. Different from the strategies mentioned above, Vafaeezadeh *et al.* [274] investigated CO_2 capture by $[aemim][BF_4]$ supported on amino functionalized-silica gel, and the increased sorption rate and capacity could be obtained.

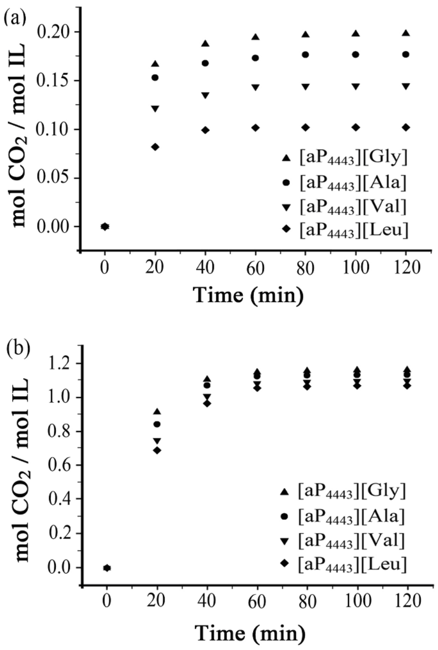


Fig. 8 (a) Direct and (b) supported absorption of CO_2 by [aP$_{4443}$][AA] ILs. Modified with permission from ref. 124. Copyright 2009 Wiley-VCH.

5.1.2 Using IL-based solutions

Using IL-based PEG solutions. Han *et al.*[112] presented another strategy for CO_2 absorption where the mixture of an amino-functionalized IL [Cho][Pro] and PEG$_{200}$ was employed, and the result was shown in Table 1, entry 34. It can be seen that in the neat IL [Cho][Pro], the absorption was almost complete after 240 min. However, 50 min was enough to finish the absorption of CO_2 when PEG$_{200}$ was used as a solvent due to the significant decrease in the viscosity of this system. This demonstrates that the addition of solvent is kinetically beneficial for the absorption and desorption of CO_2 (Fig. 9). It is the fact that PEGs has many distinctive properties, such as inexpensive, thermally stable, negligible vapor pressure, toxicological innocuous, and environmental benign. In addition, although CO_2 physical absorption capacity by PEGs is poor, it would promote the chemical absorption of CO_2 by ILs. Thus, similar strategy was used for CO_2 capture by other groups to eliminate diffusion limitation.[122-123,132,136,275-277] For example, Li *et al.*[132] designed several quasi IL solutions with alkali metal salts of TrizM in PEGs or DMSO. Although higher absorption capacity and rapid rate were achieved by TrizM-DMSO solutions, they did not have good long-term durability due to the volatility of DMSO.

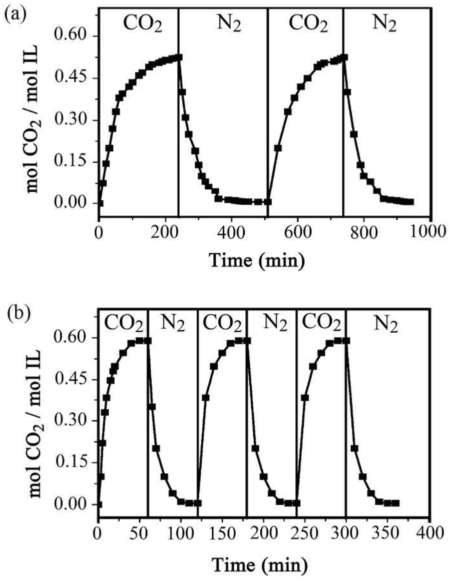


Fig. 9 Cycles of CO_2 absorption by [Cho][Pro] at 323.15 K (a) and by 1:1 mixtures of [Cho][Pro] and PEG$_{200}$ at 308.15 K (b). Modified with permission from ref. 112. Copyright 2008 The Royal Society of Chemistry.

Using IL-based water solutions. The presence of water in ILs may significantly affect physical properties of ILs like viscosity,[78,278] and therefore may have a considerable impact on the CO_2 capture.[106,116,279] CO_2 absorption in several IL/H_2O mixtures has been reported,[119,228,280-285] and MD simulations have been applied to explore the underlying mechanism in the hydrated systems.[277,284,286-287] Earlier studies [116,212] have shown that the viscosity of both pure IL and CO_2-complexed IL decrease with increasing water content, as it can be expected. Recently, Brennecke *et al.* [131] determined solubility of water in a kind of AHAIL [P$_{66614}$][2-CNPyr], and a series of IL/H_2O mixtures below the saturation limit was prepared and used for CO_2 absorption. It was shown that although CO_2 absorption was marginally affected by the addition of water in [P$_{66614}$][2-CNPyr] at low H_2O contents under ambient pressure, an increase of the H_2O content resulted in a slightly increased solubility of CO_2 and the slope of the isotherm was altered significantly (Fig. 10). The authors believed that the enhanced CO_2 solubility could be ascribed to the changes in the activity of the IL-CO_2 complex upon addition of water. Molecular simulations indicated that small amounts of water strongly solvated the CO_2 reaction with [2-CNPyr]$^-$ anion by formation of hydrogen bonds with the COO$^-$ group, and water was much stronger associated with the reacted anion compared to the unreacted one.[135] Phenolate ILs were also demonstrated a modest increase in CO_2 capacity with the addition of water.[141] Thus, the presence of water in the amino-free IL would increase the amount of the CO_2–IL complex in order to maintain phase and reaction equilibria.[131] The effect of water on the performance of CO_2 absorption by AAILs and [Ac]-based Ils [193] was different from that by AHAILs (see Section 3.3.3). However, addition of a large amount of water to form aqueous IL solutions was also used in many investigations to reduce the viscosity of ILs,[80,210-211,225] since the maximal absorption capacity of water was merely 0.02 mole of CO_2 per mole of water.[211,288-289]

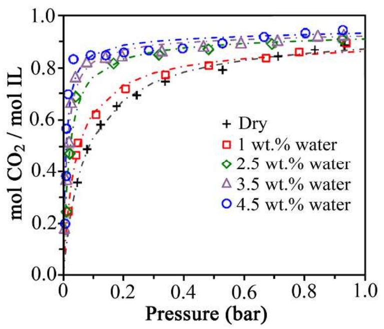


Fig.10 CO_2 capacity in amino-free IL $[P_{66614}]$[2-CNPyr] with different water contents at 22 °C. Adapted with permission from ref. 131. Copyright 2014 American Chemical Society.

5.1.3 Using IL-IL mxitures

Because of the non-volatile nature of ILs, low-viscosity conventional ILs have been used as good solvents for the capture of CO_2 by higher viscosity functionalized ILs. When two ILs are mixed together, double salt ionic liquids (DSILs) [290] are formed. Up to now, few studies have been carried out on the absorption of CO_2 in the mixed ILs, and most of them are only physical absorbents. [291-294] Inspired by the fact that absorption molar ratio of CO_2 to IL could be reached to 0.36 in [Emim][Ac] through the formation of zwitterionic 1,3-dialkylimidazolium-2-carboxylate, while that in [Emim][TFA] was only about 0.04 through physical interaction,[179] Shiflett *et al.* [179] for the first time mixed [Emim][Ac] and [Emim][TFA] with 1:1 molar ratio, and determined CO_2 solubility in the mixture. They found that the solubility was 0.39 mole of CO_2 per mole of IL, which is close to the sum of CO_2 capacity by each pure IL. The results indicated that the $[TFA]^-$ anion is not capable of deprotonating the imidazolium cation, but is capable of stabilizing the proton by the formation of $[H(Ac)(TFA)]^-$. Thereafter, mixtures of ILs, [Emim][Ac] and [Emim][$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate), were prepared by Soto *et al.* [295] at an approximate molar fractions of 0.25, 0.50, and 0.75, and used for CO_2 absorption. It was shown that the absorption of CO_2 in the mixture of [Emim][Ac] + [Emim][$EtSO_4$] reached the level in the mixture consisting of an IL with chemisorption and an IL with physisorption investigated by Shiflett *et al.*[179] Furthermore, the addition of [Emim][$EtSO_4$] to [Emim][Ac] prevented the solidification of the product resulting from the chemical reaction between CO_2 and [Emim][Ac].[295] Zhang *et al.* [296] used a mixture of a functional IL [aemim][BF_4] and low-viscosity conventional ILs such as [Emim][BF_4] and [Bmim][BF_4], to investigate CO_2 absorption and regeneration performance of binary ILs. These researches do show the potential to use one common IL with good physical properties as the solvent for another functionalized IL with desired chemical properties in CO_2 capture processing.[297]

5.1.4 Absorption under low temperature and high CO_2 pressure

Low temperature and high CO_2 pressure are most helpful for CO_2 absorption in ILs, especially in the traditional ILs. For the functionalized ILs, the main factor affecting the absorption of CO_2 is the functional group. Based on le Chatelier's principle, as the reaction between functional group and CO_2 is exothermic, the concentrated CO_2 could be desorbed from the CO_2 captured ILs by increasing temperature or decreasing CO_2 partial pressure.[112,125] Thus, the formation of carbamate or carbamic acid is more stable under low temperature and high pressure.

Brennecke *et al.* [129] determined the CO_2 absorption isotherms by $[P_{66614}]$[2-CNpyr] in the temperature range from 22 to 100 °C and CO_2 partial pressure range from 0 to 1 bar (Fig. 11). The steep initial slopes observed at low pressure reflected chemical reaction between CO_2 and the IL, and the gradual slopes found at higher pressure indicated the contribution of weaker physical absorption. The absorption capacity was approached 1 mole of CO_2 per mole of $[P_{66614}]$[2-CNpyr] at the highest pressure and lowest temperature, indicating that the capture performance is consistent with a 1:1 reaction stoichiometry. Similar results was achieved for such site-based ILs as $[P_{66614}]$[2-Op], in which 1.58 mole CO_2 per mole IL could be uptaken at 20 °C and 1 bar.[244]

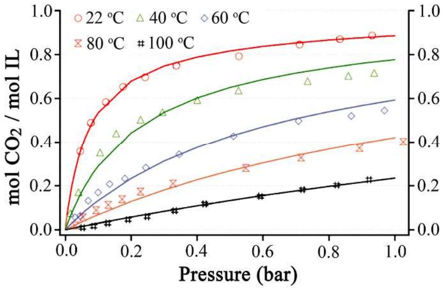


Fig. 11 CO_2 uptake capacity by $[P_{66614}]$[2-CNpyr]. Lines indicate fits to a Langmuir-type isotherm model. Modified with permission from ref. 129. Copyright 2010 American Chemical Society.

However, Maier *et al.* [90] recently investigated CO_2 absorption by amino-functionalized IL $[Me_2N(CH_2CH_2OH)_2]$[Tau] at 37 °C using surface- and bulk-sensitive experimental techniques. From a combination of isothermal uptake under equilibrium conditions up to 6 bar CO_2 and infrared spectroscopy measurements, CO_2 absorption in the bulk of this IL was found to be stepwise: in the first step, the amount of captured CO_2 was increased to ~0.4 mol per mol IL at 2.5 bar, indicative of carbamate formation, with a nominal storage capacity of 0.5 mol CO_2; in the second step, a value of ~0.92 mol CO_2 per mol IL was obtained at the pressure above 4 bar, indicative of the reaction into carbamic acid, with a nominal storage capacity of 1.0 mol CO_2 (Fig. 12). These results indicate that the mechanism of CO_2 absorption by this kind of amino-functionalized IL could be changed from 1:2 to 1:1 reaction stoichiometry under high temperature and led to higher absorption capacity (Scheme 38).

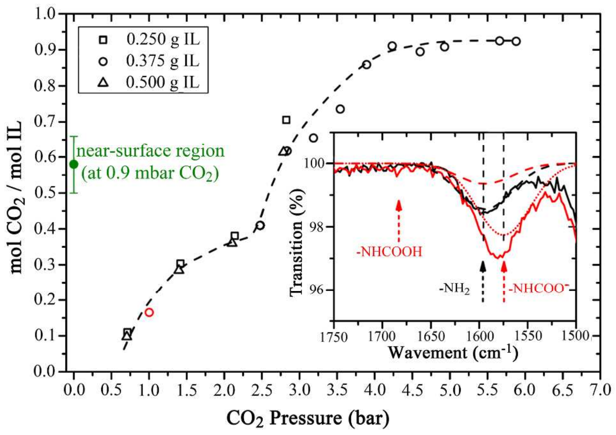
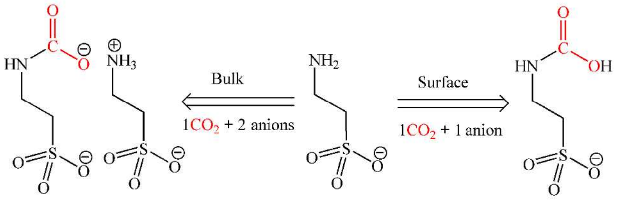


Fig. 12 Bulk isothermal absorption curve of CO_2 by $[Me_2N(CH_2CH_2OH)_2][Tau]$ at 37 °C. Inset: IR spectra for the degassed IL (black) and the IL after equilibrium absorption at 1 bar CO_2 (red). Adapted with permission from ref. 90. Copyright 2014 American Chemical Society.



Scheme 38 CO_2 reaction with [Tau] anion (middle) to form carbamic acid (right) or carbamate (left). Modified with permission from ref. 90. Copyright 2014 American Chemical Society.

5.2 Activation of reactive sites by chemical methods

It is known that CO_2 absorption mechanism is highly dependent on the activity of the CO_2-philic sites of ILs, and activation of reactive sites often leads to impressive carbon capture performance in chemical processes. Therefore, it is important to activate the CO_2-philic sites. By analysis of numerous publications, several effective ways have been summarized to activate CO_2-philic sites of ILs through careful design of the cations and the anions structures.

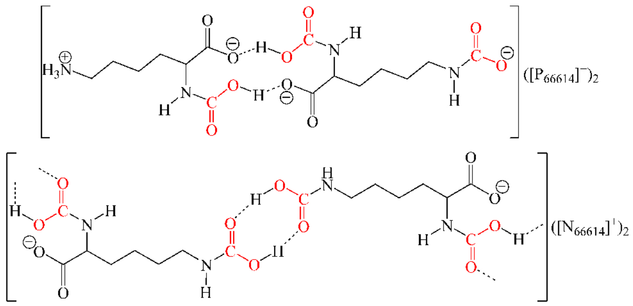
5.2.1 Using the anion-tethered strategy

In view of the fact that CO_2 capture by AAILs can reach equimolar capacity (amine:CO_2 = 1:1) while that by amino-functionalized cation ILs can only reach half of molar capacity (amine:CO_2 = 2:1), Schneider *et al.* [298] used first principles computation to contrast the effect of cation and anion tethering on the chemistry of amino-functionalized ILs. It was shown that the tethering location may have a direct electronic effect on the energetics of the amino-CO_2 bond. The cation-tethered amino groups were calculated to react slightly less exothermically with CO_2 than did MEA, while the anion-tethered react slightly more exothermically.[298] Moreover, it was also found that when an amino group was tethered to the anion of an IL, its basicity was stronger than when it was tethered to the cation.[299] Ren *et al.*[111] found through MD simulation that AAILs with an anion-tethered strategy was greatly benefit to the CO_2 capture from the viewpoint of interfacial sorption and transfer. Thus, anion tethering has promise for increasing acid gas carrying capacity over cation tethering.[245,300]

5.2.2 Using bulky cations

Phosphonium ILs are attractive for use in gas capture processes because of their relatively high thermal stability and low viscosity compared to ammonium ILs.[125,129,301-302] For amino-functionalized ILs, both 1:1 and 1:2 reaction stoichiometry mechanisms have been proposed. Zhang *et al.* [106] reported that the capacities of CO_2 absorption by phosphonium AAILs such as $[P_{4444}]$[Gly], $[P_{4444}]$[Ala], and $[P_{4444}]$[β-Ala] were all around 0.6 mole of CO_2 per mole of IL (Table 1, entries 20–22), resulting from the reaction of two amino groups with one CO_2. Wu *et al.* [107-108] and Li *et al.* [109] also investigated the CO_2 absorption by AAILs with ammonium cation $[N_{2222}]$ or imidazolium cation [Emim], respectively, and the capacity of about 0.5 mole of CO_2 per mole of IL was observed, which was ascribed to the reaction of two amino groups with one CO_2. However, Brennecke *et al.* [115] showed nearly equimolar absorption capacities of CO_2 by $[P_{66614}]$-based AAILs, such as $[P_{66614}]$[Gly], $[P_{66614}]$[Sar] and $[P_{66614}]$[Ile] (Table 1, entries 37–39). Dai and He *et al.* [123] prepared a series of integrated systems of alkali metal onium salts/crown ether/PEG_{300}, thus bulky cations were formed through coordination and 1:1 stoichiometry capacity was achieved. Why is CO_2 so soluble in bulky cation-based ILs? We can rationalize these experimental observations by the fact that for the ILs with large-sized cation (e.g. $[P_{66614}]$[AA]), it is difficult for two amino groups to approach each other so that only carbamic acid is formed according to 1:1 stoichiometry. When the size of the ILs is small (e.g. $[P_{4444}]$[AA]), the formed carbamic acid can undergo further reaction with another amino group to form a neutral carbamate in 1:2 stoichiometry.[109,123]

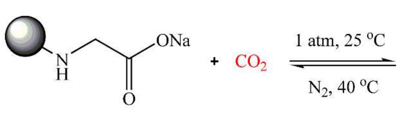
Another example is CO_2 absorption by AAILs containing [Lys] anion and $[P_{66614}]$ or $[N_{66614}]$ cation. In such ILs, there are two amino groups on the anion. Riisager *et al.* [117] reported that $[N_{66614}]$[Lys] showed a remarkable CO_2 absorption capacity (2.1 mole of CO_2 per mole of IL) after 24 h gas saturation at 22 °C and 1 bar, while $[P_{66614}]$[Lys] could only absorb 1.6 mole CO_2 per mole of IL after 48 h gas saturation under same conditions (Table 3, entry 6 vs entry 10), which is in good agreement with the earlier results.[116] Through in *situ* ATR-FTIR study, they proposed that $[N_{66614}]$[Lys]–CO_2 and $[P_{66614}]$[Lys]–CO_2 adducts were consisting of two different anion structures because of the competitive formation of strongly hydrogen-bonded complexes with the formed carboxylic acids in the phosphonium IL (Scheme 39). Therefore, careful consideration of both physical properties and chemical reactivity of the ILs with amino acid anions is necessary when designing ILs for CO_2 separation.



Scheme 39 The proposed structures of the $[P_{66614}]$[Lys]–CO_2 and $[N_{66614}]$[Lys]–CO_2 adducts. Adapted with permission from ref. 117. Copyright 2014 Wiley-VCH.

5.2.3 Using steric hindrance

Steric hindrance plays an important role in the capture of CO_2. He *et al.* [122-123] reported a series of integrated systems through mixing some N-substituted amino acid sodium salts with PEG_{150}, in which PEG_{150} could be used not only as a solvent, but also as a ligand to coordinate the sodium cation to form bulky cation. *i*PrNH-GlyNa-PEG_{150} containing bulky N-substituent was found to be the best absorbent for the rapid and reversible capture of CO_2 at a 1:1 stoichiometry, and the process was assumed to proceed via the formation of carbamic acid rather than the ammonium carbamate (Scheme 40). This is the first example of steric hindrance controlled CO_2 absorption.



Scheme 40 CO_2 capture via the formation of carbamic acid rather than ammonium carbamate by sodium N-alkylglycinate in PEG_{150}. Adapted with permission from ref. 122. Copyright 2012 Wiley-VCH.

5.2.4 Tuning the basicity of functionalized ILs

In the investigation of CO_2 absorption by ILs, it is emphasized that anion structure of ILs plays a major role, fluorination of the cation and the anion is beneficial to the physical solubility of CO_2,[58,303-305] and the functionalized groups are beneficial to the chemical absorption of CO_2.[106,113-177] Wang and Dai *et al.* [125] presented a useful strategy to tune CO_2 chemisorption by making use of the basicity of tunable amino-free anion-functionalized ILs such as azolate ILs which were prepared by neutralizing $[P_{66614}][OH]$ with weak proton donors with p*Ka* values in DMSO ranging from 19.8 to 8.2. It was found that there was a quantitative relationship between the absorption enthalpy of CO_2 and the p*Ka* value, indicating that the absorption enthalpy of CO_2 can be quantitatively tuned by varying the basicity of the ILs (Fig. 13).

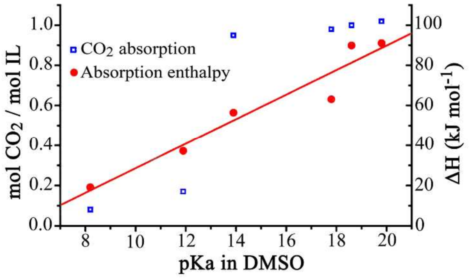


Fig. 13 The relationship between CO_2 absorption capacity (□), absorption enthalpy (ΔH, ●), and the pKa value of the azolate anion in DMSO. Adapted with permission from ref. 125. Copyright 2011 Wiley-VCH.

Considering the fact that the ILs with various functionalized groups or substituents can offer remarkable variations in binding energies, Wang *et al.* [141] and Brennecke *et al.* [131] reported another strategy to tune the reactivity of the interaction sites in phenolate Ils [141] and AHA ILs,[131] respectively, by the introduction of substituents in which steric hindrance and electronic interaction could be modified to tune the basicity of the ILs. As shown in Fig. 14, the CO_2-absorption capacity decreased with the decrease of the pKa value of the anion in the phenolate ILs. Wu *et al.* [222] found that in order to synthesize a functional IL to chemically capture SO_2 or CO_2, an organic acid with a larger pKa value than sulfurous acid and carbonic acid would be chosen and neutralized with a strong base. Through quantum chemical calculations, Xing *et al.* [299] demonstrated two effective ways to enhance the basicity of ILs: by weakening the cation-anion interaction strength, and by employing the anion-tethered strategy. These findings indicate that CO_2 absorption could be facilely tuned by varying the basicity of the ILs — another useful feature for the rational design of ILs for acid gas absorption.[306] Thus, CO_2 capture with a low absorption enthalpy and a high absorption capacity can be achieved by tuning the basicity of the ILs.

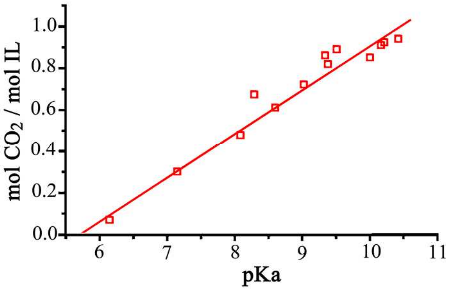


Fig. 14 The relationship between CO_2-absorption capacity and pKa value of the anion in the phenolate ILs. Adapted with permission from ref. 141. Copyright 2012 Wiley-VCH.

5.2.5 Using cooperation strategy

Previous modeling and experimental results indicate that the capacity of an anion-functionalized IL to chemically absorb CO_2 is a function of both the reaction pathway and the basicity of the anion.[125,141,307] Generally, CO_2 chemisorption by functionalized ILs is based on the interaction between CO_2 and the electronegative nitrogen (e.g. imidazolate) or oxygen atom (e.g. phenolate) of an IL, resulting in equimolar stoichiometry at low pressure.[71-73] Recently, Wang *et al.* [230-231] developed a new method for the capture of CO_2 through cooperative interactions using several pyridine-containing or carbonyl-containing anion-functionalized ILs, in which two kinds of interacting sites were included. It was shown that the molar ratios of CO_2 to $[P_{66614}][PhO]$ and pyridine were 0.85 and 0.013, respectively, while the adsorption capacity of CO_2 by $[P_{66614}][2\text{-}Op]$ is 1.58 mol CO_2 per mol IL, which is significantly higher than the sum of that by $[P_{66614}][PhO]$ and that by pyridine.[244] Quantum chemical calculations, spectroscopic investigations, and calorimetric data suggested that multiple site cooperative interaction between two kinds of interacting sites in the anion resulted in the superior CO_2 capacities, which originated from the π-electron delocalization that increased Mulliken atomic charge of the nitrogen atom (Fig. 15).

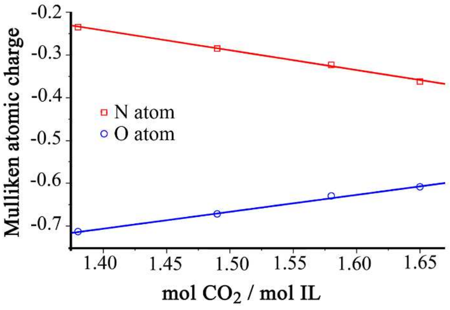


Fig. 15 The linear relationship between CO_2 absorption capacity and Mulliken atomic charges of the nitrogen and oxygen atoms in the anion of pyridine-containing ILs. Adapted with permission from ref. 244. Copyright 2014 Wiley-VCH.

6. Conclusions and remarks

The efficient, reversible, and economical capture of CO_2 from flue gas is highly desired for environmental protection and valuable chemicals production. ILs with outstanding properties have been widely used in the capture of CO_2. It is shown that the presence of strong CO_2-philic reactive sites is essential for ILs to be used in the capture of CO_2 from post-combustion flue gas via chemical interactions. In this critical review, we focus our attention on the recent advances in chemical absorption of CO_2 using site-containing ILs, including amino-based ILs, AAILs, AHAILs, phenolate ILs, dual-functionalized ILs, pyridine-containing ILs and among others. It can be seen from Tables 1, 2 and 3 that the mole CO_2 per kg uptake values of IL-based systems is always inferior to that of MEA due to the high molar masses of ILs. Although it is a difficult task to judge if one of these systems presented has a realistic potential for CCS application, some of the mentioned systems with low CO_2/mass uptake values or other major disadvantages mayt not be promising. Those ILs with amino groups or with big cations are examples due to their high viscosity or high molar mass. However, some ILs with high CO_2/kg uptake values and low viscosity like [MTBDH][Im] (4.65 mol CO_2/kg IL) and [TMGH][Im] (5.46 mol CO_2/kg IL) would be promising for CCS application, which contain small cations but strong CO_2-philic anions. Futhermore, strategies have been discussed for how to activate the existent reactive sites and how to develop novel strong CO_2-philic reactive sites by physical and chemical methods to enhance CO_2 absorption capacity and reduce absorption enthalpy. The absorption mechanisms of these site-containing ILs have been also discussed.

However, this field is still in its infancy and a number of issues need to be investigated in the future. At least, the following aspects should be included.

(1) The active site-containing ILs are very efficient for CO_2 capture, especially for the uptake at low CO_2 partial pressure in the flue gas. Thus design and preparation of novel kinds of CO_2-philic site-containing ILs with high stability, high activity, low viscosity, high reversibility and low price are highly encouraged.

(2) Although there are some quantitative relationships between CO_2 absorption capacity, absorption enthalpy, and basicity of ILs, it is a wise choice to investigate the interactions of CO_2 with active sites of functionalized ILs and their structural effects by various techniques such as ^{1}H-, ^{13}C NMR, quantum chemical calculation, MD simulation and among others in order to have a deeper understanding for their absorption mechanism.

(3) Due to the presence of other components such as N_2, O_2, NO_x, SO_x, steam and dust in the flue gas, how to increase the selectivity of CO_2 and improve the absorption capacity is critical to the development of novel active site-containing ILs.

(4) As CO_2 is a useful carbon resource and the industrial exhaust gases provide a CO_2-rich source, the conversion of CO_2 into value-added chemicals through activation by site-containing ILs under ambient conditions is a great challenge for CCS, and should be considered forever.[308]

(5) Creating novel CO_2-philic site-containing ILs with desired properties is of great importance to offer an alternative for the development of new site-containing solid adsorbents, liquid absorbents, membrane materials, and their integrated systems (mixed with PEGs or water, etc) towards efficient and low energy processes for carbon capture and sequestration.

Generally, compared with the traditional absorbents such as aqueous alkanolamine solutions, the synthesis of most functionalized ILs is still complex and their price is relatively high, which is the main shortcomings for CO_2 capture in CCS. However, the high absorption capacity and excellent reversibility will enable these ILs-based systems to be more competitive, due to the large energy consumption in the recovery and reuse of alkanolamine solutions.[85] In addition, several other relevant aspects of ILs such as corrosiveness and toxicity should not be ignored even they are not related with the capacity in carbon capture. Fortunately, the designability of structure and property of ILs can make these ionic absorbents to overcome some of the above mentioned disadvantages. Therefore, the development of highly efficient, reversible, and not expensive site-containing ILs is required for realizing the large scale application of ILs in the absorption of CO_2 from flue gases. Although some issues still exist in these capture processes, we believe that the strategies for CO_2 capture through active site-containing ILs described in this review can form a useful base for the future development of capture technology for CO_2 including other acid gas such as SO_2, H_2S, and NO_x.

Acknowledgements

We acknowledge the support from the National Natural Science Foundation of China (No. 21403059 and No. 21133009), the International Science & Technology Cooperation Program of China (No. 2014DFA61670), and the Natural Science Foundation of Henan Province (No. 142300413213).

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