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Review

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Why are Ionic Liquids Attractive for CO_2 Absorption? An Overview

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As the climate debate is hotting up, so is the (re)search for finding powerful new materials for the efficient and cost-effective removal of CO_2 from flue-gas streams from power plants and other emission sources. Ionic liquids (ILs), exhibiting higher CO_2 solubility than conventional organic solvents, have received considerable interest as new CO_2 absorbents. The present paper evaluates the advantages and disadvantages of ILs, and provides an overview of the recent developments of ILs for CO_2 capture. In conventional ILs, CO_2 is absorbed by occupying the free space between the ions through physical absorption mechanisms. As another promising strategy, task-specific ILs have been studied that, by attaching functional groups to the ions, allow the formation of chemical bonds to improve the overall absorption capacity during the CO_2 capture process. Other strategies include using ILs as reaction media or as selective absorption materials.

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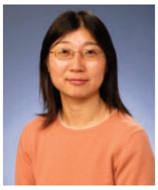
Introduction

As the world's fourth largest coal producer (405 million tonnes) and the largest coal exporter (233 million tonnes), Australia is abundant in coal.[1] A total of 84% of Australia's electricity (185 TW h) is generated from coal, which emitted 197 million tonnes CO_2 from 60 flue-gas streams, and contributed to 50% of the overall CO_2 emission of 398.6 million tonnes in 2006.[2] As the climate debate is hotting up, so is the (re)search for finding new methods and powerful materials for the efficient and cost-effective removal of CO_2 from flue-gas streams of power plants and other emission sources. Ideally, the absorbents would have high absorption capacity, fast absorption and desorption kinetics, balanced reaction enthalpy, high stability, and environmental friendliness. The present overview is intended to evaluate how ionic liquids (ILs) may be used as absorbents to capture CO_2 from flue-gas streams in the process of Post-Combustion Capture (PCC).

CO_2 capture technologies are categorized into chemical absorption, physical absorption, and membrane separation. Physicochemical data such as CO_2 absorption capacities and sorption enthalpies have been summarized by Chinn et al., who gave a straightforward comparison of ILs versus chemical absorbents and other physical absorbents.[3] Here, we compare ILs with some conventional chemical absorbents.

Currently, chemical absorption methods employing aqueous solutions of amines or ammonia are the technology of choice for CO_2 capture. These technologies display high CO_2 absorption capacities through forming chemical bonds. This method, however, presents several concerns.[3] (1) Intensive energy use is required to break the chemical bonds between the absorbents and the absorbed CO_2 in the regeneration step ($\Delta H = -80$ to $-64\,\mathrm{kJ\,mol^{-1}}$ (bicarbonate formation) or $-101\,\mathrm{kJ\,mol^{-1}}$ (carbonate formation)),[4] which represents a high operation expense due to the energy cost related to the desorption step. (2) Amines



Junhua Huang finished her Ph.D. study in 2002 on plastic crystals (interesting solid phases found in some ionic liquids) under the supervision of Professor Douglas MacFarlane at Monash University. She then studied biomimetic catalysis as a postdoctoral fellow in the group of Dr. Gerhard Swiegers at CSIRO Molecular and Health Technologies. In 2004, she joined CSIRO Energy Technology to research ionic liquids in energy storage devices. She is currently a project manager of developing ionic liquids for Post-Combustion Capture. Her research interests are new materials development in energy area and related physical chemistry, electrochemistry, and organic chemistry.

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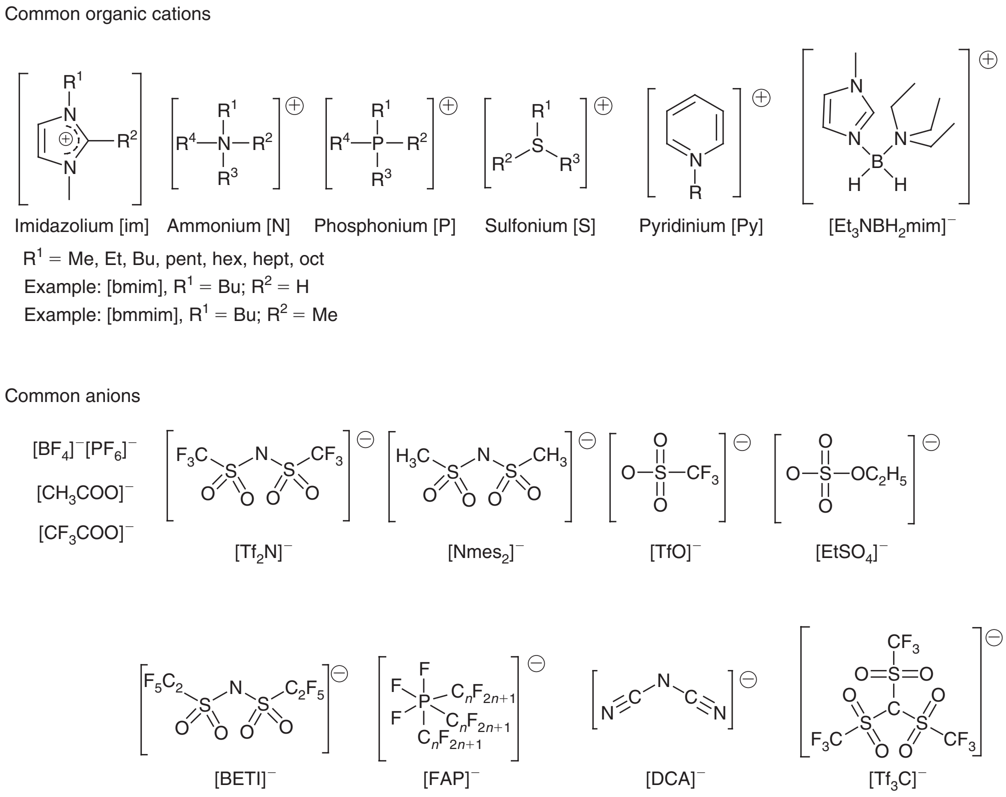

Scheme 1. Structures of cations and anions.

can rapidly corrode alloy steel pipes, pumps, etc. Therefore, the concentration of the amine absorbent in the solution is limited, and thus the CO_2 absorption capacity is reduced. (3) Amines and ammonia are prone to degrade either thermally or through chemical reactions, which causes the loss of active absorbents, produces extra waste streams, and therefore leads to additional operational cost. (4) Owing to their volatility, amines and ammonia are to some extent lost into the gas stream – replenishment thereby adds to the cost of the process and environmental impact.

Owing to the drawbacks of amine/ammonia solutions, ILs are considered to be promising alternatives. ILs are materials composed entirely of ions and demonstrating melting points below 100°C, in contrast to conventional molten salts which are solids up to hundreds of degrees.[5] ILs generally consist of nitrogen- or phosphorus-containing organic cations, with either cyclic or non-cyclic structures, where short-to-medium length alkyl chains are attached. A wide range of anions have been combined with cations to form compounds that are liquids around room temperature (Scheme 1).

Compared with amine/ammonia solutions, ILs have several advantages. (1) Less energy is required to remove the absorbed CO_2 from ILs in the regeneration step. This is attributed to a physical absorption mechanism. The enthalpy of CO_2 sorption is typically $\sim$10–20 kJ mol^{-1} for ILs.[6] This suggests that, compared with standard amine solutions, only a quarter of the energy is required to remove the same amount of CO_2 from ILs. (2) Many ILs are both thermally and chemically stable. Their decomposition temperature is normally above 300°C.[5] They are less likely to degrade via oxidation, to react with impurities, or to be corrosive. Therefore, the anticipated losses of IL absorbents are low and the waste streams are minimal. ILs can thus be recycled and reused repeatedly. (3) With a few exceptions, many ILs are found to be non-volatile solvents with negligible vapour pressure, indicating that these ILs are non-flammable and thus are able to be used safely. Their low volatility also prevents their losses into the gas streams. (4) ILs have been of great interest in recent years owing to the fact that, by tuning the structures of the ions (e.g. changing the length of the alkyl chain or choosing different anions), the physicochemical properties (e.g. melting point, viscosity, conductivity) can be changed according to the requirements of their intended use. Therefore, by carefully designing suitable chemical structures and/or by adding functional groups, desirable absorption capacity and other properties can be achieved.

Conventional Ionic Liquids

IL–CO_2 Systems

Here we define conventional ILs as the ILs that do not bear any functional groups and where the CO_2 absorption follows a physical absorption mechanism. Although ILs (molten salts) have been known to be used as CO_2 absorbents,[7] only in the past decade have IL–CO_2 systems been extensively studied. Brennecke et al. reported that supercritical CO_2 is highly soluble in ILs, whereas ILs do not dissolve in supercritical CO_2.[8] The maximum concentrations of CO_2 in several ILs were reported to be as high as 0.75 mol fraction. By contrast, the solubility of [bmim][PF_6] was measured to be less than 5×10^{-7} mole fraction in the CO_2-rich phase.[9] These properties allow CO_2 to be used to extract non-volatile organic products from ILs without being contaminated with ILs.[10,11]

CO_2 also shows a higher solubility in ionic liquids than other gases such as CO, O_2, N_2, H_2, CH_4, C_2H_4, and C_2H_6.[12–16] The Henry's constants of the different gases in [bmim][PF_6] and

Table 1. Henry's constants (bar, 10^5 Pa) for gases in [bmim][PF_6] and [bmim][BF_4] at 25°C[17–20]

Ionic liquid (IL)	CO_2	CO	O_2	N_2	H_2	CH_4	C_2H_4	C_2H_6
[bmim][PF_6]	53.4	>20000	8000	>20000	>1500	1690	173	355
[bmim][BF_4]	55.7	1728	1580	1703	2037	887	–	300

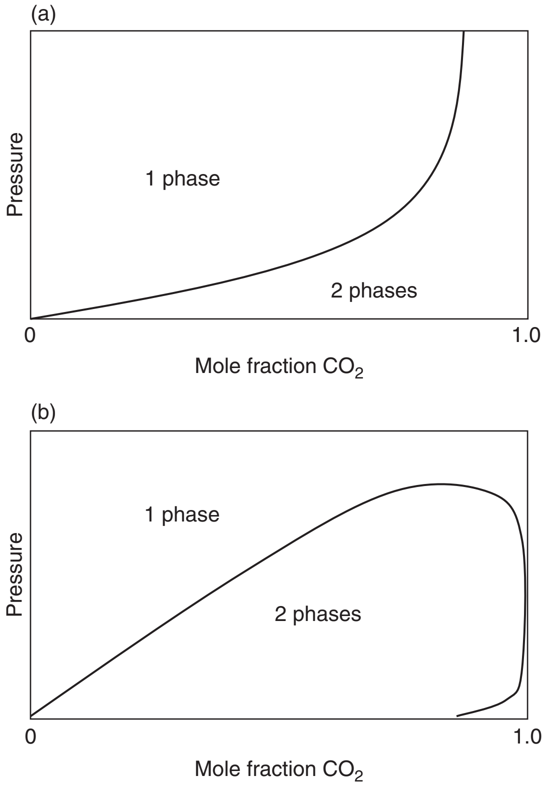

Fig. 1. Simplified profiles of phase diagrams of ionic liquid–CO_2 systems (a), and molecular organic solvent–CO_2 systems (b).

[bmim][BF_4] are compared in Table 1.[17–20] A lower Henry's constant indicates a higher solubility. The higher dissolution behaviour of CO_2 allows ILs to be used to separate CO_2 from gas mixtures.[21,22]

IL–CO_2 systems exhibit phase behaviours distinctly different from those of molecular organic solvent–CO_2 systems. First, CO_2 was reported to be more soluble in ILs than in organic solvents. The Henry's constants for CO_2 are 53.4 bar (10^5 Pa) and 55.7 bar in [bmim][PF_6] and [bmim][BF_4] at 25°C, respectively.[18,19] In comparison, the values are 84.3, 133.3, 104.1, 159.2, and 54.7 bar in heptane, cyclohexane, benzene, ethanol and acetone, respectively.[17]

Second, the phase diagrams of IL–CO_2 systems are strikingly different from those of molecular organic solvent–CO_2 systems. Brennecke et al. first reported the profile of the phase diagram for the [bmim][PF_6]–CO_2 system.[8] The profile was further verified by studying the dissolution behaviour of CO_2 in a series of ILs.[9,23] The phase diagram of CO_2–IL systems shows a two-phase region (the liquid phase of the IL–CO_2 mixture and the pure CO_2 phase) in the moderate-pressure range, and a single phase (the liquid phase of the IL–CO_2 mixture) in the high-pressure region (Fig. 1a). On the CO_2-rich side, the two-phase region remains even at high pressure. Increasing the pressure only slightly increases the solubility of CO_2. This phase behaviour was verified by the observation of the co-existence of two distinct phases in the [bmim][PF_6]–CO_2 system at a pressure as high as 3100 bar.[9] The phase-diagram profile of the IL–CO_2 mixtures, especially that under high pressure, was also confirmed by Equation of State calculations.[24,25] In comparison, the profile of the phase diagram of molecular organic solvents–CO_2 (Fig. 1b) generally shows an enclosed two-phase domain under moderate pressure. It is composed of a liquid phase of the mixture of the organic solvent and CO_2, and a vapour phase. The two-phase domain normally covers a wide range of compositions, and is enveloped with a critical point of a mixture. At higher pressure, it shows a single-phase region covering the entire composition range, indicating that the CO_2 molecules and the organic solvent are completely miscible in this region.[26–28]

Another distinct difference is that, unlike organic solvents where dilation is generally observed on gas dissolution, ILs do not show a significant volume expansion even when a high mole fraction of CO_2 is dissolved. For example, the volume of 1-methylimidazole expands by 103% on dissolution of a 0.70 mol fraction of CO_2, whereas the volume of [bmim][PF_6] increases by only 18% under the same conditions.[9] Brennecke et al. further compared the volume expansions of 10 ILs with molecular solvents. The volumes, on dissolution of a 0.4 mol fraction of CO_2, increase by 57 and 33% for acetonitrile and ethyl acetate, respectively, and 5–15% for the 10 ILs.[29]

Absorption Mechanism

Free Volume

The small volume expansion may originate from the distinct Coulombic interaction among the ions and special ionic organization in ILs. Bearing either positive or negative charges, the cations and anions all participate in Coulombic interaction and form a more rigid packing than molecular solvents. Not surprisingly, the thermal expansion coefficients of ILs are smaller, in the range of ~0.4–0.7 × 10^{-3} K^{-1}, whereas organic solvents generally exhibit larger thermal expansion coefficients between ~1.1 and 1.8 × 10^{-3} K^{-1}.[30] Molecular dynamics simulations suggest that, on addition of CO_2 into ILs, the arrangement of the ions does not appear to be perturbed.[6] These results again support the view that cations and anions are arranged to form a relatively rigid network, and that the ionic arrangement potentially contains a large amount of 'free volumes' available to accommodate CO_2 molecules. Berne et al. further studied the [bmim][PF_6]–CO_2 system by molecular dynamics simulations.[31] They reported that the size of the originally available cavities in [bmim][PF_6] is not big enough to accommodate a CO_2 molecule. By introducing CO_2, the $[PF_6]^-$ anions are rearranged by a small angular displacement, which does not significantly change the radial distribution functions, to form larger voids to hold CO_2 molecules. Thereby, CO_2 molecules occupy the positions above and below the imidazolium rings, or close to the long alkyl chains on the rings. As the larger 'free volumes' are generated by the rearrangement of the originally available cavities, the ILs do not exhibit significant volumetric expansion upon dissolution of CO_2, even at a high concentration. This also explains that, owing to the finite free volume originally available, only a certain amount of CO_2 can be accommodated even under an infinitely high pressure.[9] Berne et al., through calculations of the diffusion coefficients (D) of $[bmim]^+$, $[PF_6]^-$, and CO_2 molecules, suggested that, although the diffusion of CO_2 ($D = 4 \times 10^{-10}\,m^2\,s^{-1}$) is two orders of magnitude slower in the phase of IL–CO_2 mixture than in the supercritical CO_2 phase, CO_2 molecules are five times more mobile than the ions of $[bmim]^+$ and $[PF_6]^-$ ($D_{[bmim]^+} = 7.7 \times 10^{-11}\,m^2\,s^{-1}$ and $D_{[PF_6]^-} = 6.8 \times 10^{-11}\,m^2\,s^{-1}$).[31] Yokozeki et al. reported that the activation energy for CO_2 diffusion in $[bmim][PF_6]$ is $27.2 \pm 4.2\,kJ\,mol^{-1}$, smaller than the values of 38.4 ± 2.1 and $40.5 \pm 2.2\,kJ\,mol^{-1}$ for the diffusion of $[bmim]^+$ and $[PF_6]^-$, respectively.[24] These data provide the following physical picture: the cations and anions form a rigid network by Coulombic interactions and thus are less mobile; upon the addition of CO_2, the anions are slightly rearranged to form larger voids without causing significant structural change; the CO_2 molecules diffuse through the relatively rigid network and fill into these available free volumes without disturbing the arrangement of the ions.

Anions

The nature of the anions appears to be one of the other major factors dominating the dissolution of CO_2. Mechanic dynamic simulations on ILs containing $[PF_6]^-$ demonstrate a strong association between the carbon on the CO_2 molecule and the $[PF_6]^-$ anion, regardless of the structure of the cation.[6] In situ attenuated total reflection infrared spectroscopic study, again, reveals the interaction between the anion and CO_2. The interaction is suggested to be of a Lewis acid–base type where the anions act as Lewis bases and the CO_2 as the Lewis acid. According to Kazarian et al., the axes of O=C=O molecules dissolved in $[bmim][PF_6]$ (or $[bmim][BF_4]$) are perpendicularly orientated to the P–F (or B–F) bonds.[32] In addition, X-ray diffusion measurements on the $[bmim][PF_6]$–CO_2 system suggest that the interactions are dominated by those between $[PF_6]^-$ and CO_2. CO_2 is located in such a close proximity (3.57 Å) to $[PF_6]^-$ that the CO_2 molecule slightly penetrates into the space of $[PF_6]^-$ anion.[33]

The effect of the anions on the CO_2 solubility was further studied by Brennecke et al. for several ILs consisting of a common $[bmim]^+$ cation and different anions. They found that the solubilities of CO_2 in the ILs are in the order of the anions: $[NO_3]^- < [DCA]^- < [BF_4]^- \approx [PF_6]^- < [TfO]^- < [Tf_2N]^- < [Tf_3C]^-$, where $[TfO]^-$, $[Tf_2N]^-$, and $[Tf_3C]^-$ contain one, two, and three CF_3 groups, respectively. The authors suggested that the interaction between the CO_2 molecules and the anions, in particular those containing fluorinated alkyl groups, is the dominating factor in determining the solubility.[29]

The effect of the fluorination of the anion on dissolution of CO_2 was also demonstrated by comparing the solubilities of $[emim][Nmes_2]$ and $[emim][Tf_2N]$. The Henry's constant is 76 bar for $[emim][[Nmes_2]$, whereas the value for its fluorinated counterpart is 47 bar.[34] The effect of fluorination on CO_2 dissolution is further demonstrated by new fluorinated phosphate anions $[PF_3R_{F3}]^-$ (FAP) ($R_F = C_2F_5$ (eFAP), C_3F_7 (pFAP), or C_4H_9 (bFAP)).[35–37] These anions are the analogues of $[PF_6]^-$ where three fluorine atoms are replaced by three fluoroalkyl chains.[38] The Henry's constants of $[hmim][PF_6]$, $[hmim][eFAP]^{i}$, and [hmim][pFAP] are 37.0, 27.3, and 25.2 bar, respectively, at 25°C.[36,37] The COSMO-RS method (a conductor-like screening model for real solvents) was used to estimate the CO_2 solubilities in a large number of ILs. The results of this screening suggest that the ILs containing $[PF_3R_{F3}]^-$ (FAP) ($R_F = CF_3, C_2F_5, C_3F_7$) exhibit the lowest Henry's constants among all the listed anions.[39] Again, these data demonstrate that a longer fluoroalkyl chain in the anion corresponds to a higher CO_2 solubility. The compatibility of fluorinated entities with CO_2 has been known and is used to improve the 'CO_2-philicity' of organic compounds.[40] When interacting with hydrocarbon, CO_2 molecules act as a weak Lewis base where the oxygen atom on the CO_2 interacts with the C–H bond. When electronegative fluorine atoms are present, the C–F bond may interact with the Lewis acidic carbon atom on the CO_2 molecule.[40] Therefore, the enhanced CO_2 solubility may originate from a different nature of intermolecular interaction involving the fluorine atoms in the anions.

Not conflicting with the previous mechanism, it is interesting to see that the effects of the anions on CO_2 solubilities bear some resemblance to those on the thermal expansions of the ILs. Husson et al. compared the coefficients of thermal expansion of a series of imidazolium-based ILs having different anions. It is striking to see that, while the length of the alkyl chains on the imidazolium cations only slightly changes the coefficient of thermal expansion, the anions appear to be the dominant factor in determining the thermal expansion coefficients. Each anion exhibits a distinct range of thermal expansion coefficients regardless of the structures of the cations, e.g. $[EtSO_4]^-$, $[BF_4]^-/[PF_6]^-$, $[Tf_2N]^-$ each displaying a characteristic region of ~ 0.48–0.52×10^{-3}, ~ 0.57–0.65×10^{-3}, and ~ 0.65–$0.7 \times 10^{-3}\,K^{-1}$, respectively.[30] The trend of their thermal expansion coefficients corresponds well with the solubilities of CO_2 in the ILs in the order of $[EtSO_4]^- < [BF_4]^-/[PF_6]^- < [Tf_2N]^-$. As thermal expansion reflects the strength of intermolecular interaction, the CO_2 dissolution mechanism could essentially originate from the interactions between the ions.

Cations

Although anions dominate the dissolution of CO_2 in imidazolium-based ILs, the cations are believed to play a secondary role. Compared with the anions, the effect of the cations, most of the reported ones based on imidazolium, seems to be marginal. It is well agreed that a longer alkyl chain on an imidazolium ring is generally associated with a slightly higher solubility. This trend is more noticeable at higher pressure.[9] Comparing the ILs having different lengths of alkyl chains, the solubilities follow the order of $[bmim][Tf_2N] < [hmim][Tf_2N] < [omim][Tf_2N]$.[29] Consistently, the Henry's constants for the $[BF_4]^-$-based ILs are in the order of $[bmim][BF_4] > [hmim][BF_4] > [omim][BF_4]$. A longer alkyl chain on the imidazolium ring is also associated with a more negative sorption enthalpy and a more negative sorption entropy.[41] Again, the underlying reason for the observed trend is suggested to be related to a 'free volume' mechanism, as the IL with a longer alkyl chain exhibits a smaller density and a larger 'free volume'.[9]

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[i] It is worth noting that the absorption involving [hmim][eFAP] is classified as chemical absorption.[35]

It is known that the proton in the C2 position (C2–H) on the imidazolium ring is acidic.[42,43] Therefore, CO_2 may be dissolved via forming hydrogen bonds at the C2 positions. The effect of the proton in the C2 position has been studied by solubility measurements and mechanical dynamic simulations for several ILs with C2–H and their counterparts with a C2-methyl substituent.[6,29] Although the methyl group in the C2 position alters the arrangement of the anions, which are otherwise known to associate strongly at the C2 sites, it has a negligible effect on the CO_2 solubility at low pressure. Only above 70 bar do the ILs having C2–H exhibit slightly higher solubilities. The explanation is that the CO_2 molecules are located relatively far away (~5 Å or more) from the cations and are primarily associated with the anions; at higher pressure when a larger amount of CO_2 molecules is involved, some CO_2 molecules may occupy the secondary locations in proximity to the cations; CO_2 molecules are allowed to be located closer to the imidazolium rings having C2–H by 0.2–0.4 Å than to their methyl-substituted analogues. Thus ILs with C2–H display slightly higher CO_2 solubility at high pressure.[6]

The effect of fluorination of the alkyl chains on the cations has also been studied. The Henry's constants for [hmim][Tf_2N], [omim][Tf_2N], and their fluorinated analogues [$C_6H_4F_9$mim][Tf_2N] and [$C_8H_4F_{13}$mim][Tf_2N] are 31.6 bar[36] (or 35.0 bar[44]), 30.0 bar,[44] 28.4 bar, and 27.3 bar,[36] respectively. This implies that, while the fluorination of the alkyl chain on the cations slightly increases the solubility of CO_2, the effect is not as significant as the fluorination in anions. Controversially, Baltus et al. reported their Henry's constants of [$C_6H_4F_9$mim][Tf_2N] and [$C_8H_4F_{13}$mim][Tf_2N] to be 31.0 bar[45] and 4.5 bar,[44] respectively. This Henry's constant measured for [$C_8H_4F_{13}$mim][Tf_2N] is significantly lower compared with the result from Brennecke's report,[36] suggesting that fluorination of the cationic alkyl chain could also improve the solubility of CO_2 significantly.

Although most of the ILs studied are based on imidazolium cations, other cations, such as phosphonium,[46–48] boronium,[36] pyridinium,[37] and guanidinium,[49] have been studied to a less extent. The Henry's constants of several ILs having different structures of cations were estimated by COSMO-RS calculation. The results show a distinct order of CO_2 solubility as: imidazolium < pyridinium < guanidinium < thiouronium.[39] Conversely, experimental data suggest that the structure of the cation does not influence the CO_2 solubility as significantly as the nature of the anion. The Henry's constants of [bmpy][Tf_2N], [hmpy][Tf_2N], and [Et_3NBH_2mim][Tf_2N] are 33.0, 32.8, and 33.1 bar at 25°C, respectively,[36,37,45] and 33.0 bar for [$P_{(14)666}$][Tf_2N] at 30°C.[48] These values are not significantly different from the Henry's constants of [bmim][Tf_2N] (33.0 bar) and [hmim][Tf_2N] (31.6 bar) at 25°C.[36] The comparison implies again that the cations play a minor role in the dissolution of CO_2.

Absorption Kinetics

Gas diffusion in ILs is one of the dominant factors in determining the absorption/desorption rate. Whereas most of the research on IL–CO_2 systems has been focussed on their thermodynamic properties, we expect to see more studies on their kinetics. As mentioned before, Berne et al. used molecular dynamics simulations to estimate the diffusion coefficient of CO_2 in [bmim][PF_6] to be $4.0 \times 10^{-10}\,m^2\,s^{-1}$ whereas the diffusion coefficients for [bmim]$^+$ and [PF_6]$^-$ are 7.7×10^{-11} and $6.8 \times 10^{-11}\,m^2\,s^{-1}$, respectively.[31] Baltus et al. reported that the diffusion coefficients of CO_2 in [bmim][Tf_2N], [pmmim][Tf_2N], [bmpy][Tf_2N], and [bmim][BF_4] are in the range of $\sim 3\text{–}10 \times 10^{-10}\,m^2\,s^{-1}$. CO_2 diffuses the fastest in [bmim][Tf_2N] and the slowest in [bmim][BF_4].[45] The diffusion coefficients of CO_2 in [bmim][PF_6], [emim][TfO], [emim][Tf_2N], [emim][BETI],[50,51] and in [$P_{(14)666}$][Cl], [$P_{(14)666}$][DCA], [$P_{(14)666}$][Tf_2N],[48] as summarized in Table 2, are all at the level of $\sim 10^{-10}\,m^2\,s^{-1}$. Yokozeki et al., however, measured the diffusion coefficients of CO_2 in [bmim][PF_6] and [bmim][BF_4] to be 6.0×10^{-11} and $7.8 \times 10^{-11}\,m^2\,s^{-1}$, respectively,[24] which are nearly one order of magnitude lower than those reported by other groups (Table 2).

Table 2. Diffusion coefficients (D) of CO_2 in ionic liquids at 30°C

Ionic liquid (IL)	$D \times 10^{10}$ [$m^2\,s^{-1}$]		
[bmim][PF_6]	0.6^{A}[24]	2.7[51]	4.0[31]
[bmim][BF_4]	0.8^{A}[24]		
[emim][TfO]	5.2[51]		
[emim][Tf_2N]	6.6[51]	7.9[50]	
[emim][BETI]	4.6[51]		
[$P_{(14)666}$][Cl]	3.0[48]		
[$P_{(14)666}$][DCA]	3.0[48]		
[$P_{(14)666}$][Tf_2N]	6.2[48]		

^{A}At 25°C.

The diffusion coefficient of a gas is determined by temperature, the molecular size of the gas, and the viscosity of the IL. For a given gas, the temperature and the viscosity of the IL are the dominant factors. The diffusion coefficient is proportional to the inverse viscosity of the IL. For different ILs, the correlation of the viscosity with the diffusion coefficient was found to be different, e.g. for imidazolium ILs, the CO_2 diffusion coefficient D is correlated to the viscosity η by $D \propto \eta^{-0.6}$ whereas the correlation is $D \propto \eta^{-0.35}$ for phosphonium ILs.[48,51]

The relationship between CO_2 diffusion and the viscosity of IL casts a concern on the use of ILs in practical application. Owing to the exothermal nature of the absorption of CO_2, the absorption procedure is favoured at a lower temperature, at which the viscosities of ILs are relatively high. This not only puts a high demand on the circulating system, but also slows the absorption kinetics.

Concerns in Practical Applications

There are several other concerns for the practical application of ILs in PCC. Flue gases generally contain 20–25% H_2O, 10–15% CO_2, 5–8% O_2, and ~100 ppm SO_2.[4] Therefore, one of the major problems lies in the low CO_2 absorption capacity of ILs when the CO_2 partial pressure is below ambient pressure. Although ILs exhibit good absorption capacity at high pressure (above 10 bar), the solubility of CO_2 in conventional ILs is only up to 3.5 mol-% (~0.4 wt-%) at ambient temperature and pressure.[52] The CO_2 solubility may be increased 10-fold by increasing the CO_2 pressure to 10 bar. However, this is not a practical solution, because it will reduce the energy efficiency and magnify capital cost of a large-scale carbon capture process. The low absorption capacity for the conventional ILs is attributed to the physical nature of the absorption. Molecular dynamic simulation indicates that, under ambient conditions, there are only a limited number of CO_2 molecules able to be accommodated between the IL molecules, e.g. 10:192 (CO_2:[bmim][PF_6];

~5 mol-%).[53] In order to improve CO_2 solubility while maintaining the advantages of ILs, one way is to develop new ILs that exhibit the appropriate physical natures to accommodate a larger number of CO_2 molecules through a physical absorption mechanism. This requires a deeper understanding of the underlying absorption mechanism. Another way is to design and develop task-specific ILs bearing functional groups to introduce additional chemical absorption mechanisms. We will give an overview of the functionalized ILs in the next section.

Another concern is that other components in the flue gas may affect the CO_2 absorption capacity of ILs. Brennecke et al. reported that the water content could significantly decrease the solubility of CO_2 in ILs. For example, 0.54 mol fraction of CO_2 can be dissolved in dried [bmim][PF_6], whereas the solubility is only 0.13 mol fraction in water-saturated samples.[9] However, the effect of water on the dissolution of CO_2 is still controversial. The water content has also been reported to have negligible effect on or to enhance the CO_2 solubility.[29,47,54]

Some ILs could be better SO_2 absorbents than CO_2 absorbents.[55–60] The IL [hmim][Tf_2N] was reported to absorb 0.9 mol fraction of SO_2; under the same pressure of CO_2, the solubility of CO_2 is only 0.10 mol fraction.[55] For a practical application in power plants operating without a desulfurization unit, this would mean that SO_2 may compete with CO_2 in the absorption processes, and thus decrease the efficiency of ILs for CO_2 absorption.

In summary, conventional ILs exhibit distinct CO_2 dissolution behaviours (e.g. higher CO_2 solubility and smaller volume expansion) from those in organic solvents. This could originate from a free volume mechanism that the CO_2 molecules occupy the free cavities in the ILs that are originally available within the relatively rigid framework of the ions. Although the effect of the cationic structure seems to be less significant, the structure of the anion appears to be one of the dominant factors determining the CO_2 solubility. As physical absorbents, conventional ILs are appealing in CO_2 capture in PCC processes owing to their low sorption enthalpy, which indicates that less energy is required to remove CO_2 in the regeneration stage. However, a major concern with their practical application is that their CO_2 absorption capacity is still too low. This implies that a significantly larger amount of ILs is required as the CO_2 absorbents compared with the efficient amine or ammonia solutions. The advantage of the low sorption enthalpy for conventional ILs is thus offset. Therefore, it is imperative to improve the absorption capacity for the conventional ILs. Although there has been significant progress in understanding the CO_2 dissolution behaviours and in improving the CO_2 solubility, other important properties (e.g. viscosity, absorption and desorption rate, heat capacity) should be given more consideration in the future studies.

Functionalized Ionic Liquids

Owing to the limitations in absorption capacity seen for ILs where a physical absorption mechanism is prevailing, several research groups have initiated a new concept where the advantages of ILs are combined with the incorporation of functional groups to allow enhanced (chemical) binding of CO_2 to the absorbent. The functional groups intended for the anchoring have to be carefully selected with respect to the thermodynamics and kinetics of a reversible process (Fig. 2). Ideally, in the first step, the CO_2 should bind favourably to the functional group in a thermodynamic sense and the kinetics ($K_{(T)abs}$) should be sufficient for this process to operate at a fast enough absorption rate. Given this, the absorption step must not be too exothermic, so that the removal of CO_2 from the absorbent in the subsequent regeneration step can be conducted without high energy requirements. Conventional aqueous amine solutions have relatively large exothermic sorption enthalpies (−50 to $-80\,kJ\,mol^{-1}$).[3,4,61] Thus, functionalized ILs exhibiting less exothermic sorption enthalpy would be very attractive from a thermodynamic point of view.

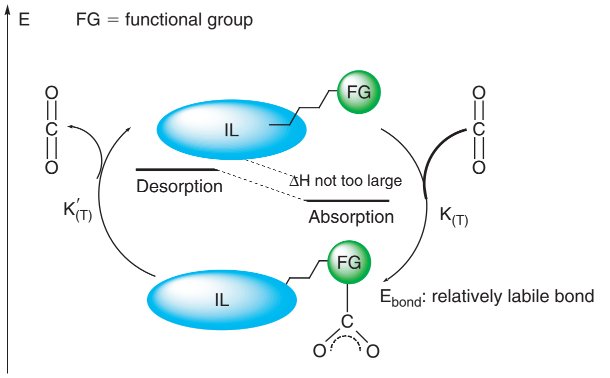


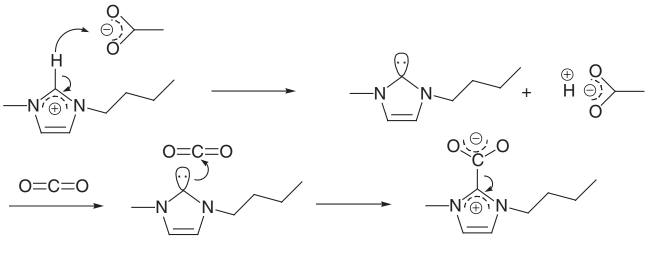
Fig. 2. Energy profile for the absorption/desorption of CO_2 in functionalized ionic liquids (ILs).

Carboxylate Functionality

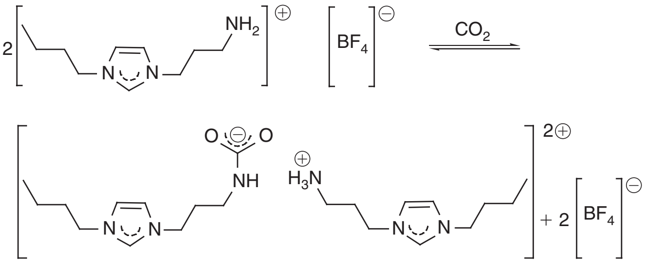
One of the first types of functionalized ILs tested as CO_2 absorbents are composed of acetate anions paired with imidazolium cations.[3,7] The very few examples studied contained substantial amounts of water, up to almost 2 mol per mol IL.[ii] Chinn et al. reported that [bmim][acetate] + 14 wt-% H_2O has a CO_2 absorption profile (CO_2 loading versus pressure) typical for a chemical absorption process with an initial steep rise and a subsequent plateau at higher pressures.[3] The absorption capacity for this material (4.6 wt-%) is intermediate between aqueous amines (9 wt-% for 30% mono ethanol amine (MEA) solution) and physical solvents like non-functionalized ILs (0.1–0.4 wt-%). In keeping with the favourable $\Delta H = -40\,kJ\,mol^{-1}$, the regeneration can be carried out under mild conditions with a suitable stripping gas. The authors put forward a mechanistic explanation where the acetate group interacts with the water and the CO_2 binds as a bicarbonate. Some support for this view comes from the ^{13}C NMR resonances at 173 and 171 ppm assigned by Zhang et al. to [HCO_3^-] and [CO_3^{2-}], although here the amine group is acting as the base rather than the CH_3COO^- group (see also section titled 'Combined functionalities', page 304).[46]

Maginn et al. also investigated [bmim][acetate], but explained the observed high absorption capacity by a different mechanism involving the deprotonation of the C2 position in the imidazolium ring followed by a coupling of the in situ carbene with CO_2 (Scheme 2).[62] The pK_a of imidazolium cations is in the range of 21–24 (in DMSO, H_2O)[63,64] and the (in situ) deprotonation and formation of carbenes from imidazolium cations can occur under relatively mild conditions.[42,43] However, sterically unprotected N-heterocyclic carbenes, which would be present according to the proposed mechanism in any slightly wet acetate or amino acid ILs, are unstable.[65,66]

[ii] Converted from the reported values in wt-%.



Scheme 2. Reaction of CO_2 at the C2 position in an in situ-generated carbene.[62]

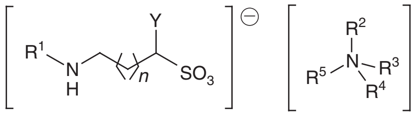


Scheme 3. Carbamate formation between CO_2 and [aminopropyl-mim][BF_4].[70]

Shiflett et al. did detailed experimental investigations on [bmim][acetate] + CO_2 with and without water presence.[67] Their spectroscopic analyses of the systems showed little support for the acetic acid and imidazolyl–acetate formation mechanism put forward by Maggin et al. However, the authors do not completely exclude some limited acetic acid formation on the basis of smells encountered during experiments. Their conclusion is a rare case of phase behaviour for this system, involving strong intermolecular interaction. In this regard, Beckmann and Wallen's contribution to the binding mechanisms for CO_2 with acetate-functional saccharides/polysaccharides is informative.[68,69] According to their observations, one of the explanations for enhanced solubility lies in the ambivalent nature of CO_2, which can act as a Lewis acid through its electron-deficient carbon and as a Lewis base through the electron-richer oxygen. This situation opens up the possibilities for multidentate binding between CO_2 and the acetate group where the acidic protons on the acetate moiety are involved.

Amine Functionality

The group of Davis was one of the first to design ILs around the idea of combining the advantages of normal ILs and those of amine solutions like MEA.[70] These ILs consist of an imidazolium-based cation that is tethered to an amine group through a (variable) alkyl chain (Scheme 3). The amine-functionalized ILs show a molar up-take of CO_2 of nearly 0.5 at 0.1 MPa over a period of 3 h. This is close to the theoretical maximum for amine-based absorbents operating under the carbamate formation scheme. In mass units, the absorption capacity of the material is significantly increased compared to [hmim][PF_6]. Importantly, the work also demonstrates the crucial desorption process, which can be carried out under practical conditions by heating under vacuum at 80–100°C. One of the disadvantages of this material is, however, the relatively high viscosity compared with other ILs and MEA solutions. This will have a negative impact on the overall energy balance of a PCC unit owing to higher demands on liquid circulating pumps.



R^1 = *n*-hexyl, 1,5-dimethylhexyl, 2-ethylhexyl,
2-heptyl, isopropyl, isobutyl, 2-hydroxyethyl

Y = methyl or H *n* = 1 or 2

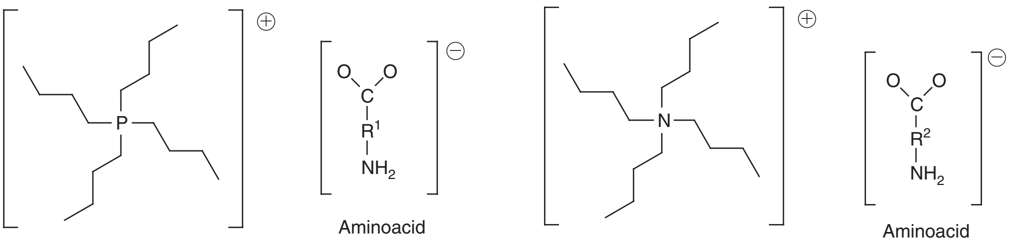
Scheme 4. Aminoalkyl sulfonium anion-based ionic liquids (ILs).[73]

Sanchez et al.[71] verified this concept by measuring the CO_2 absorption of several functionalized $[bmim]^+$ cations carrying (i) a primary amine group, (ii) a tertiary amine group, or (iii) a hydroxyl group. In addition, the amine-functionalized cations were paired with the $[BF_4]^-$ and the dicyanamide $[DCA]^-$ anions respectively. For the non-functionalized ILs, the CO_2 absorption does not vary significantly between the $[BF_4]^-$ and the $[DCA]^-$ anions. The materials show Henry's Law behaviour over the entire pressure range (0.1–1.0 MPa), indicative of physical absorption. By contrast, the functionalized derivatives display a sharp increase in CO_2 absorption up to 0.1 MPa, followed by a steady increase between 0.1 and 1 MPa, exhibiting a typical chemical absorption profile. At 0.1 MPa, CO_2 solubilities for [Ambim][BF_4] and [Ambim][DCA] are ~13 and 4 times higher than those observed for their respective non-functionalized counterparts, underpinning the significant role of the amine functionality as well as the effects of the anions. The material containing a tertiary amine function displays a far lower, but still sharp, increase. This observation demonstrates that the reactivity of higher substituted amines is reduced compared with simple primary amines.[72] Beyond 0.1 MPa, the absorption capacity of all of the amine-functionalized ILs still increases steadily after the involved amine functions reach saturated absorption. This is attributed to the physical absorption mechanism. In contrast, conventional amine solutions reach a maximum capacity at pressures $\geq$0.2 MPa. These ILs can be regenerated by heating under vacuum at 80°C.

Combined Functionalities

More recently, several groups took the concept of amino groups one step further by combining it with the introduction of acidic groups. Davis et al. put forward a new type of ionic soft materials containing an anion component that carries a secondary amine functional group and an $[SO_3]^-$ group on either end of an alkyl chain (Scheme 4).[73] CO_2 fixation via carbamate formation in these materials is evidenced by IR, ^{13}C NMR, and MS data. The incorporation of CO_2 into the anion is displayed in the mass spectrum. The corresponding mass peaks diminish over time when the binding is broken. Desorption of CO_2 was also observed for these compounds when they were exposed to vacuum at 80°C.

In a similar approach, Zhang et al. used the amino groups in naturally occurring amino acid anions (Scheme 5).[46,53] Because of their relatively high viscosities (227 to 744 mPa s), these materials were fixed to porous silica supports. This method achieves high surface area and allows for a faster absorption rate compared with the viscous neat materials. Absorption equilibria are typically reached after exposure to CO_2 for 100 min at ambient pressure and temperature. The maximum absorption capacity is demonstrated to be close to CO_2:IL = 0.5:1 (mol:mol). As expected for amine-functionalized materials, the absorption capacity suggests a carbamate formation mechanism



Aminoacid (R^1-NH_2): alanine, serine, glycine, leucine

Aminoacid (R^2-NH_2): alanine, glycine, valine

Scheme 5. Alkyl-phosphonium-[46] and -ammonium[74]-based amino acid ionic liquids (ILs).

for the amino acid ILs (Scheme S1). Evidence is provided by IR and ^{13}C NMR.[73] In order to reduce the high viscosities, the group tested these materials in the presence of 1 wt-% of water. In this case, the molar uptake of CO_2 is ~1.0 (calculated from the mass fraction), which suggests a bicarbonate formation mechanism. This view is supported by IR and NMR data.

In an attempt to obtain less viscous ILs for improved mass transfer, Wu et al. combined amino acid anions with symmetric tetraalkyl ammonium cations (Scheme 5).[74] Seven out of the nine examples are liquids at room temperature and display comparatively low viscosities (three examples $\leq$200 mPa s). These materials reached maximum CO_2 absorption (CO_2:IL = 0.5:1) within 1 h.

In an interesting twist to amino acid-based ILs, Weiss et al. discussed a fully reversible reaction where room-temperature ILs are formed when 1:1 molar mixtures of trialkyl amidines and alkylesters of amino acids are exposed to CO_2.[75] The binding of CO_2 in the starting non-ionic mixture follows a mechanism similar to that operating in mixed amine solutions containing a tertiary amine as a proton acceptor (Scheme S2). Here, the role of the latter is performed by the amidine. Absorption equilibria are typically established after a relatively short 0.5 h. The uptake of CO_2 exceeds the stoichiometric amount by ~10% as a consequence of additional physical absorption. Desorption of CO_2 occurs either on heating or by bubbling a replacement gas such as N_2. Although it appears to be a quite attractive alternative to aqueous amine solutions, the aldimine/amino acid ester mixture has, in contrast to ILs, the disadvantage of relatively high volatility, as indicated by mass loss in thermogravimetric analysis measurement.

It would be interesting from a molecular point of view to endeavour to compare the physicochemical properties, including CO_2 absorption measurements, between [R_4N][alkyl aminosulfonate][73] and the [R_4E][alkylaminocarboxylates] (E = N, P).[46,74] Both resemble each other in that: (i) they consist of common tetraalkyl ammonium (or phosphonium) cations; and (ii) the anionic components are, in a broader sense, both amino acids – the former featuring an $[SO_3]^-$ group and the latter a $[COO]^-$ group. The two groups differ in acidity, electron density delocalization, and thermal stability. Further, the difference in the reactivity of the secondary amine group and the primary amine group in these compounds has a strong effect on the individual absorption kinetics and thermodynamics.[72] Finally, the steric demands in the larger anions may shift the CO_2 absorption mechanism in the presence of water to bicarbonate formation.

In this context, it is also interesting to note the reports on the ILs of guanidinium lactate by the group of Suojiang Zhang. They found the solubility (in wt-%) of CO_2 in guanidinium lactate to be very low near ambient pressure ($<0.25\ \mathrm{mol\,kg^{-1}}$), suggesting a physical absorption mechanism.[49] At pressures up to 11 MPa, the solubility (in wt-% units) in guanidinium lactate is only slightly higher than that in [bmim][PF_6], but lower when compared in mole ratios (CO_2:[bmim][PF_6] = $0.75\ \mathrm{mol\,mol^{-1}}$; CO_2:tetramethyl guanidinium lactate = $0.57\ \mathrm{mol\,mol^{-1}}$). The reason may be that the tertiary nature of the amino functions is not very reactive with CO_2. The authors put forward molecular orbital calculations that show a much larger HOMO–LUMO energy gap (9.53 eV) between the guanidinium cation and CO_2 compared with the energy gap (6.07 eV) between 1-propylamine-3-butyl imidazolium and CO_2.[53]

An important feature that is common for all the above ILs carrying amino groups is that they have higher viscosities than their non-functionalized counterparts. The viscosity of [ethylamino-mim][PF_6] was found to be approximately two orders of magnitude higher than conventional imidazolium ILs.[76] Moreover, from the onset of CO_2 absorption, the viscosity is increased to a point where the absorption products become viscous gel-type materials or even solids. This presents a potential concern, because viscosity is a crucial parameter determining mass transport, and capital and energy costs for pump operation in any large-scale plant operation.[4]

The underlying reason for the increased viscosity parameter was addressed by Zhang et al. in a molecular dynamics simulation and *ab initio* calculation study of two representative ILs, [aminoethyl-mim][PF_6] and [aminopropyl-bim][PF_6].[77] Typically, in non-functionalized ILs, anions are preferably organized through interionic hydrogen bonds around the C2, C4, and C5 positions on the imidazolium rings. These interactions are responsible for the long-range ordering in the liquid, higher vapourization heat (non-volatile nature) and lower self-diffusion coefficients compared with conventional molecular solvents. By contrast, the introduction of a terminal –NH_2 group creates a new strong site for cation–anion interaction in addition to the C2, C4, and C5 sites. Further, anions interacting with the –NH_2 group may simultaneously interact with other cations through the C2, C4, C5, and –NH_2 sites. Thus the –NH_2 group causes the formation of compact liquid structures where ion fragments are relatively stably fixed and ion motions become more difficult. Hence, the creation of an additional site for cation–anion interaction by the presence of an –NH_2 group is believed to be responsible for the increased viscosities. Qualitatively consistent with the higher viscosities, the simulated self-diffusion coefficients of the ions (approx. $10^{-13}\ \mathrm{m^2\,s^{-1}}$) are two orders of magnitude lower than those of conventional imidazolium-based ILs.

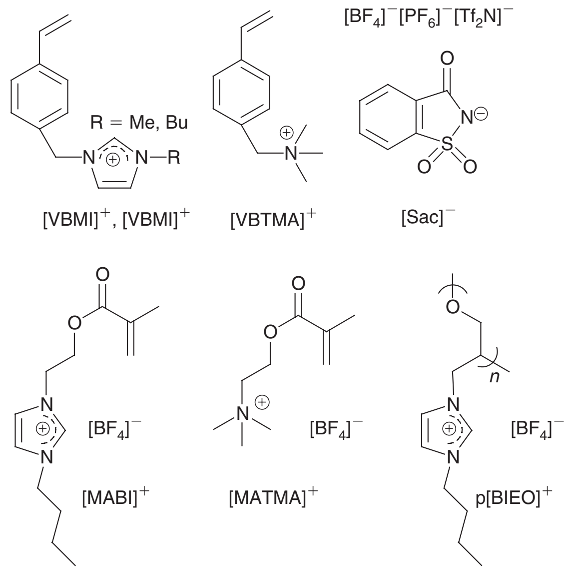
In an interesting approach to alleviate the problem of high viscosities, Zou et al. mixed [choline][proline] in polyethylene glycol 200 (PEG 200) to reduce the viscosity (Scheme S3).[61]

Adding PEG 200 as a solvent dramatically reduces the time for both absorption and desorption, e.g. from nearly 300 min (for neat IL) to only 50 min in an IL/PEG = 1:1 solution. This clearly demonstrates the impact of lower viscosities on the improvement of mass transfer. The thermodynamic data for the systems exhibit very negative values of sorption enthalpies and entropies (e.g. $\Delta H = -40$ to $-25.5\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S = -122$ to $-77\,\mathrm{J\,K^{-1}\,mol^{-1}}$), indicating exothermic formation of relatively strong bonds (similar to those in aqueous amine solutions) between the absorbents and CO_2.

Polymeric Materials

Using ILs as solvents, the group of Suobo Zhang turned to the biopolymers chitin and chitosan.[78] Chitin has two hydroxyl groups in the cellulose-like polymeric structure, whereas chitosan has an additional amine group (Scheme S4). The IL [bmim][Cl] was used as a solvent to break the strong inter- and intramolecular hydrogen bonds responsible for the otherwise limited solubility in organic solvents. For the chitosan solution, the measured absorption capacity exceeds the theoretical capacity, assuming all available amino groups participate in a stoichiometric reaction with CO_2. The difference arises from the contribution due to physical absorption of CO_2 in these liquids. Physical absorption is observed for the chitin IL solution. Although this approach does not deliver the high absorption capacities observed for neat (undiluted) functionalized ILs, it has the advantage of providing a fully recyclable, less corrosive and non-volatile CO_2 absorption medium.

Tang et al. also investigated polymeric materials for CO_2 absorption, but here a new concept was applied where imidazolium- or ammonium-based IL monomers were used as precursors to build polymeric organic salts (Scheme 6).[79,80] Six different cations $[VBTMA]^+$, $[MATMA]^+$, $[VBMI]^+$, $[VBBI]^+$, $[MABI]^+$, $[BIEO]^+$ combined with $[BF_4]^-$ were investigated. In the case of $[VBBI]^+$, the combinations with three other anions, $[PF_6]^-$, $[Tf_2N]^-$, and *o*-benzoic sulfimide $[Sac]^-$, were also studied. All of the polymeric ILs, except $[BIEO][BF_4]$, show higher absorption capacities for CO_2 (10.22 to 1.55 mol-%) than their respective monomers and the benchmark $[bmim][BF_4]$ (1.34 mol-%). Screening the influence of varying cations, anions and side-chain length shows that the structures of cations have the largest impact. Tang's work also demonstrates that the influence of the nature of the anion, in particular the claimed prerequisite of fluorine, is less significant than in the conventional ILs.[6] For example, the absorption capacities for the $[BF_4]^-$ and $[Tf_2N]^-$ compounds are very similar. The $[Sac]^-$ compounds, devoid of fluorine, are sorbents too. The absorption/desorption for these materials is reversible, showing no decline in kinetics or sorption capacity for the first four cycles. More importantly, the absorption (and also desorption) rates of the polymeric materials are much faster. Particle size has a significant impact on the absorption rate. For larger particles (>250 μm), the time to reach absorption equilibrium is >100 min, whereas for smaller particles (90–125 and <53 μm), the same capacity is achieved in less than 30 min. These polymeric ILs are also interesting for gas separation membranes, because they have a high gas absorption selectivity against O_2 or N_2.[80]



Scheme 6. Templates for polymeric ionic liquids.[79]

The present overview shows that, in the past 6 years or so, most of the research and development efforts to improve the CO_2 absorption capacities of ILs have concentrated on marrying some of the key advantages of physisorbent (conventional) ILs and chemisorbent aqueous amine solutions. The a priori most logical approach to this task, incorporation of amine functionalities into IL templates, by far dominates the progress of these efforts. According to the disseminated work, this approach has merit because high absorption capacities, sometimes even exceeding the mechanistic expectations, are achieved. The negligible vapour pressure is an important advantage over aqueous amine or ammonia solutions. As pointed out earlier, low volatility of the absorbent is crucial to the economic and environmental viability of a PCC process. Another advantage of functionalized materials is the reduced volume of the liquid stream, which reduces the demands on the pump circulation and therefore benefits in terms of capital, operational and energy costs.[iii]

At this stage, there are no data available reflecting the chemical (oxidative) stability and corrosiveness of the functionalized chemisorbent materials. This concern will remain to a certain extent, because the amine functionality may not be fully protected in the ILs.

The really problematic point that emerges is the significant increase in viscosity for the neat absorbents and, more seriously, during CO_2 absorption. Apart from higher fluid mechanical demands during pump circulation, the main disadvantage here concerns the reaction kinetics. These need to be fast in order to achieve high turnovers in the reversible absorption/desorption process.

For future studies, although absorption capacities are estimated reasonably well, it would be desirable, in particular from an engineering perspective, to quantify viscosities and densities of the materials. Moreover, as the desorption step of the process is very crucial with respect to the involved energy economics, the operating conditions such as pressure during CO_2 desorption should be given more emphasis.

Conclusions

In the present overview, we have summarized new and promising developments in IL materials for their application in CO_2

[iii] For example, the equivalent of a $2.5\,\mathrm{mol\,L^{-1}}$ MEA solution is replaced by less than half of the volume of $[aminobutylmim][BF_4]$, assuming a density of $1.3–1.4\,\mathrm{kg\,L^{-1}}$.

capture processes. We focus on the important aspect that different mechanisms of physical and chemical absorption account for different performances of these materials.

Conventional ILs operating under the physical absorption mechanism may suffer from relatively low CO_2 absorption capacities. However, this problem is currently being addressed by recognizing the underlying mechanistic reasons.

It is also clear that ILs containing functional groups operating under the chemical absorption mechanism can exhibit CO_2 absorption capacities matching those of common amine solutions. In some examples, they can even exceed the mechanistically expected capacities owing to the contributions from physical absorption.

It is clear from the recent reports in this area that most of the materials have the common advantage of robustness and low volatility over traditional absorbents so that the disadvantage of absorbent loss occurring for amine or ammonia solutions in a process of this scale could be overcome.

However, the common disadvantage for all of the ILs, particularly the functionalized ILs, is the higher viscosity compared with aqueous amine solutions, which slows absorption kinetics and causes higher operational cost.

On a more general note, the first promising steps have been made to greatly improve CO_2 absorption capacities by building chemical docking points (functional groups) into ILs. Therefore, this area is now opened up to the chemists' imagination for better design of the chemical structures of the docking points to tune the strength of the interaction between CO_2 and ILs (thermodynamic), and to adjust important properties like viscosity (kinetic).

Accessory Publication

The Accessory Publication contains additional illustrations relating to compounds discussed in the article and is available from the Journal's website.

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