



# Recent advances in anhydrous solvents for CO<sub>2</sub> capture: ionic liquids, switchable solvents, and nanoparticle organic hybrid materials

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CO<sub>2</sub> capture by amine scrubbing, which has a high CO<sub>2</sub> capture capacity and a rapid reaction rate, is the most employed and investigated approach to date. There are a number of recent large-scale demonstrations including the Boundary Dam Carbon Capture Project by SaskPower in Canada that have reported successful implementations of aqueous amine solvent in CO<sub>2</sub> capture from flue gases. The findings from these demonstrations will significantly advance the field of CO<sub>2</sub> capture in the coming years. While the latest efforts in aqueous amine solvents are exciting and promising, there are still several drawbacks to amine-based CO<sub>2</sub> capture solvents including high volatility and corrosiveness of the amine solutions as well as the high parasitic energy penalty during the solvent regeneration step. Thus, in a parallel effort, alternative CO<sub>2</sub> capture solvents, which are often anhydrous, have been developed as the third-generation CO<sub>2</sub> capture solvents. These novel classes of liquid materials include ionic liquids, CO<sub>2</sub>-triggered switchable solvents (i.e., CO<sub>2</sub>-binding organic liquids, reversible ionic liquids), and nanoparticle organic hybrid materials. This paper provides a review of these various anhydrous solvents and their potential for CO<sub>2</sub> capture. Particular attention is given to the mechanisms of CO<sub>2</sub> absorption in these solvents, their regeneration and their processability – especially taking into account their viscosity. While not intended to provide a complete coverage of the existing literature, this review aims at pointing the major findings reported for these new classes of CO<sub>2</sub> capture media.

**Keywords:** CO<sub>2</sub> capture, CO<sub>2</sub>-binding organic liquids, ionic liquids, nanoparticle organic hybrid materials, novel liquid solvent

**Abbreviations:** b<sub>2</sub>Nic, 1-butyl-nicotinic acid butyl ester; bmim, 1-butyl-3-methylimidazolium; bupy, 1-butylpyridinium; DCA, dicyanamide; doc, docusate; emim, 1-ethyl-3-methylimidazolium; hmim, 1-hexyl-3-methylimidazolium; Met, methionine; N<sub>2224</sub>, triethylbutylammonium; N<sub>4444</sub>, tributylmethylammonium; P<sub>66614</sub>, trihexyl(tetradecyl)phosphonium; pabim, 1-*n*-propylamine-3-butyl-imidazolium; Pro, proline; Tf<sub>2</sub>N, bis[(trifluoromethyl)sulfonyl]imide; TFO, trifluoromethanesulfonate.

## Introduction

Mitigation of anthropogenic CO<sub>2</sub> has become a global challenge to prevent the negative consequences associated with high atmospheric CO<sub>2</sub> concentration. One may capture CO<sub>2</sub> either from large point sources, such as power plants, or directly from the atmosphere (Keith, 2009; Orr, 2009). In this review paper, the focus will be on technologies used to capture CO<sub>2</sub> from flue gas streams, particularly via a post-combustion capture process. Various technologies that have been developed for post-combustion CO<sub>2</sub> capture include chemical absorption, physical and chemical adsorption, and membrane separation (MacDowell et al., 2010; Boot-Handford et al., 2014).

Amine scrubbing using aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), represents the most mature technology for post-combustion capture. It relies on chemical absorption and more specifically on the chemical reaction between CO<sub>2</sub> and the amine group of the solvent (Rochelle, 2009). Amine-based reagents exhibit favorable thermodynamic and kinetic properties for CO<sub>2</sub> absorption and are considered affordable since the solvents are already commercially available. Nevertheless, these materials are corrosive and tend to degrade during their regeneration, which is typically performed via heating (MacDowell et al., 2010; Boot-Handford et al., 2014). Moreover, during the thermal regeneration of the materials, not only is the solvent heated but also the water. The process is, therefore, impaired by a high parasitic energy penalty since water represents 70–85 wt% of the amine reagent. For all these reasons, alternative CO<sub>2</sub> capture solvents that are environmentally benign, thermally and chemically stable, and that exhibit high absorption capacity and fast kinetics, are coveted for effective CO<sub>2</sub> capture, from both process and cost points of view.

A number of alternative materials have, therefore, been proposed to substitute for the amine-based solvents including solid sorbents, advanced membranes, and novel liquid solvents (MacDowell et al., 2010; Boot-Handford et al., 2014). In particular, the recent investigation of novel anhydrous liquid materials, such as ionic liquids (ILs), CO<sub>2</sub>-triggered switchable absorbents [i.e., CO<sub>2</sub>-binding organic liquids (CO<sub>2</sub>BOLs)], and nanoparticle organic hybrid materials (NOHMs), provide an interesting selection of alternative solvents for CO<sub>2</sub> capture. Indeed, owing to their anhydrous nature, the energy required to recycle them is overall diminished compared to aqueous amine-based solvents. In addition, these absorbents could be directly used in the same type of reactor as that designed for amine-based solvents. This review paper provides an overview of the most recent advances in the field of anhydrous liquid materials for CO<sub>2</sub> capture. Each section of the paper is dedicated to a specific type of absorbent, i.e., ILs, CO<sub>2</sub>-triggered switchable absorbents and NOHMs. This paper does not provide an exhaustive review of all papers on the topic, but rather aims at presenting the major and most recent findings for each type of absorbent. In the case of ILs, the reader is invited to refer to these comprehensive reviews: Ramdin et al. (2012), Zhang et al. (2012), and Lei et al. (2014). The three classes of solvents, i.e., ILs, CO<sub>2</sub>-triggered switchable absorbents, and NOHMs – are discussed below starting from the most mature technologies to the most recently developed absorbents. Overall,

the materials presented here are still being investigated at the lab-scale and could represent the next generation of CO<sub>2</sub> capture materials.

## Liquids (ILs)

Ionic liquids are composed solely of cations and anions (no additional solvent) and typically melt below 100°C. As such, ILs differ from typical molten salts, which remain solid even at hundreds of degrees Celsius. The asymmetry of the cations accounts for the low melting points of ILs and the anions are responsible for ILs' physical properties (Dzyuba and Bartsch, 2002). Various combinations of cations and anions have been selected to synthesize a wide range of ILs – the number of potential ILs is on the order of 10<sup>18</sup>. Owing to the tunability of their physicochemical properties and structures, ILs can be employed in a wide variety of environmental and energy-related applications (Koel, 2009; MacFarlane et al., 2014). Typical examples of ILs employed for CO<sub>2</sub> capture consist of nitrogen- or phosphorous-containing organic cations. Examples of ILs are shown in **Scheme 1**. Besides negligible vapor pressure (~10 N m<sup>-2</sup>), ILs also exhibit high thermal stability over a wide temperature range, up to 300°C (Freemantle, 2010). Owing to these merits, ILs have been proposed for CO<sub>2</sub> capture. ILs for CO<sub>2</sub> capture can be classified into three major categories based on their CO<sub>2</sub> capture mechanisms: (i) conventional ILs, (ii) task-specific ILs (TSILs), and (iii) reversible ILs (RevILs). All these categories are described below. It must be noted that RevILs are discussed in the section dedicated to CO<sub>2</sub>-triggered switchable solvents.

## Conventional Ionic Liquids

Conventional ILs are characterized by the absence of any task-specific functional groups, i.e., groups that can chemically react with CO<sub>2</sub>, such as amines. Despite this feature, conventional ILs exhibit promising CO<sub>2</sub> capture capacity and selectivity. In fact, a key strength of these ILs is their facile regeneration via a mild treatment (e.g., low temperature heating 70–80°C, inert gas bubbling or pressure swing). Indeed, unlike amine-based solvents, which utilize strong chemical interactions between amine and CO<sub>2</sub> (–ΔH = 80–130 kJ mol<sup>-1</sup>), conventional ILs interact with CO<sub>2</sub> via relatively weak forces (–ΔH = ~15 kJ mol<sup>-1</sup>) (Ramdin et al., 2012). A detailed study of solubilities of various gases, including water vapor, Ar, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> in [bmim][PF<sub>6</sub>], was conducted by Anthony et al. (2002). Besides water vapor, CO<sub>2</sub> exhibited the highest solubility in [bmim][PF<sub>6</sub>], followed by CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. It was indicated that the large quadrupole moment of CO<sub>2</sub> makes it highly soluble in [bmim][PF<sub>6</sub>]. Anderson et al. (2007) also found that even common ILs, such as [hmmim][Tf<sub>2</sub>N], have excellent selectivity for CO<sub>2</sub> relative to N<sub>2</sub> and other components in flue gas streams based on physical absorption. Blanchard et al. (2001) determined the solubility of CO<sub>2</sub> in a series of imidazolium-based ILs in the pressure region of 1–100 bar, and the solubilities followed this order: [bmim][PF<sub>6</sub>] > [omim][PF<sub>6</sub>] > [omim][BF<sub>4</sub>] > [N-bupy][BF<sub>4</sub>] > [bmim][NO<sub>3</sub>] > [emim][EtSO<sub>4</sub>]. Interestingly, imidazolium-based ILs exhibited remarkable CO<sub>2</sub> capture capacity (Anthony et al., 2002; Kamps et al., 2003; Husson et al., 2010). Semi-empirical studies

were also conducted to determine the Henry constant of several ILs (Mortazavi-Manesh et al., 2011; Sistla and Khanna, 2011). Overall, it was found that the shape and size of ILs played a major role in the value of the Henry constant of ILs.

The solvating mechanisms of ILs for CO<sub>2</sub> are not fully understood, but several explanations have been put forth. Kazarian et al. (2000) found spectroscopic evidence of a Lewis acid–base intermolecular interaction between anions and CO<sub>2</sub> using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy, explaining the high CO<sub>2</sub> capture capacity in [bmim][PF<sub>6</sub>]. The anion acted as a basic site for CO<sub>2</sub>, allowing for weak Lewis acid–base interactions between anion and CO<sub>2</sub> to drive the capture of CO<sub>2</sub>. Cadena et al. investigated the effect of anions in alkylimidazolium-based ILs for CO<sub>2</sub> capture via experimental and molecular simulation studies. They revealed that the anions played a critical role in interacting with CO<sub>2</sub> (Cadena et al., 2004). Anthony et al. also investigated the effect of anions, focusing on [BF<sub>4</sub>]<sup>−</sup>, [PF<sub>6</sub>]<sup>−</sup>, and [Tf<sub>2</sub>N]<sup>−</sup>, with [bmim]<sup>+</sup> as a counterion. They observed that [bmim][Tf<sub>2</sub>N] exhibited relatively high capacity for CO<sub>2</sub>, while [bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>] had lower affinity for capturing CO<sub>2</sub> (Anthony et al., 2005). Among the anions, those with fluoride have drawn significant interest (Aki et al., 2004; Bara et al., 2009; Sistla and Khanna, 2011). For instance, a detailed study on the effect of anions on CO<sub>2</sub> capture was conducted focusing on the influence of fluorination on CO<sub>2</sub> solubility in ILs (Aki et al., 2004). The fluorinated anions, such as [BF<sub>4</sub>]<sup>−</sup>, [PF<sub>6</sub>]<sup>−</sup>, [Tf<sub>2</sub>N]<sup>−</sup>, [TfO]<sup>−</sup>, and [methide]<sup>−</sup>, were compared with non-fluorinated anions like [DCA]<sup>−</sup> and [NO<sub>3</sub>]<sup>−</sup> ([bmim]<sup>+</sup> used as a cation). The results indicated that ILs with fluorinated anions captured more CO<sub>2</sub>. In particular, ILs that had anions with fluoroalkyl groups, such as [TfO]<sup>−</sup>, [Tf<sub>2</sub>N]<sup>−</sup>, and [methide]<sup>−</sup>, showed the highest CO<sub>2</sub> solubilities. The reported order of solubility in different types of anions was: [NO<sub>3</sub>]<sup>−</sup> < [DCA]<sup>−</sup> < [BF<sub>4</sub>]<sup>−</sup> ≈ [PF<sub>6</sub>]<sup>−</sup> < [TfO]<sup>−</sup> < [methide]<sup>−</sup> < [Tf<sub>2</sub>N]<sup>−</sup>, where [TfO]<sup>−</sup>, [methide]<sup>−</sup>, and [Tf<sub>2</sub>N]<sup>−</sup> contain one, two, and three −CF<sub>3</sub> groups, respectively. On the other hand, Bara et al. (2009) observed a decrease CO<sub>2</sub>/N<sub>2</sub> selectivity in ILs fluorinated anions compared to their alkyl counterparts. Fluorination of the alkyl chains in cations, as well as anions, has also been investigated to increase CO<sub>2</sub> capture capacity (Baltus et al., 2003; Muldoon et al., 2007). A modeling study conducted by Sistla and Khanna (2011) also focused on the effect of fluorination on the Henry's constant of several ILs. In addition, the effects of anions with sulfate and phosphonium groups on CO<sub>2</sub> solubility were investigated. These ILs exhibited comparable CO<sub>2</sub> capture capacity to imidazolium-based ILs (Zhang et al., 2005; Ferguson and Scovazzo, 2007; Carvalho et al., 2010; Harper et al., 2011).

Although many studies pointed to the importance of the anion effect on CO<sub>2</sub> solubility, the cation effect has also been investigated (Blanchard et al., 2001; Aki et al., 2004). Blanchard et al. (2001) selected three ILs with different imidazolium-based cations [i.e., [hmim]<sup>+</sup>, [omim]<sup>+</sup>, and [bmim]<sup>+</sup>] and [Tf<sub>2</sub>N]<sup>−</sup> as an anion to investigate the cation effect on CO<sub>2</sub> solubility. It was found that longer alkyl chains noticeably increased CO<sub>2</sub> solubility. Hojniak et al. (2013) used dicationic supported ILs membranes based on imidazolium, pyrrolidinium, piperidinium, and morpholinium ions. They showed that increasing the cationic charge led to an

enhancement of selectivity toward CO<sub>2</sub> compared to N<sub>2</sub>. Another mechanism proposed to explain CO<sub>2</sub> solubility in ILs is the presence of a free volume that can accommodate CO<sub>2</sub> molecules. There is, however, no agreement on the location of this free volume as two theories have been proposed: (i) on the one hand, it is thought that the free volume is near the alkyl chain of the cation and (ii) on the other hand, some studies showed that the free volume could be located in the space between the cation and anion (Babarao et al., 2011; Zhang et al., 2011; Lei et al., 2014). Despite the uncertainty, the free volume is considered to play a significant role in CO<sub>2</sub> solubility. Further in-depth investigations on the nature of free volume are required, particularly focusing on the relationship between total pressure and molecular structure.

The cation and anion effects as well as the presence of a free volume are the most common drivers for CO<sub>2</sub> capture in conventional ILs. In addition to these, other parameters have been investigated to enhance CO<sub>2</sub> solubility. One of them is the introduction of ether groups, which has a dual purpose: (i) rendering ILs more flexible, thereby increasing free volume (Sarbu et al., 2000; Beckman, 2004) and (ii) enabling dipole–quadrupole interactions between the oxygen atoms of the ether groups and CO<sub>2</sub> (Ghosal et al., 1996; Van Ginderen et al., 2003). An example of IL with ether groups is [N<sub>4444</sub>][doc] for which a high CO<sub>2</sub> solubility was measured (Muldoon et al., 2007). The carbonyl groups and long branched alkyl groups in [N<sub>4444</sub>][doc] were also thought to contribute to its high CO<sub>2</sub> solubility, which was even higher than fluorinated ILs at high partial pressure of CO<sub>2</sub>. However, the extremely high viscosity of [N<sub>4444</sub>][doc] (12,100 cP at 25°C) is one of the challenges for its practical application. The positive impact of the presence of ether groups on CO<sub>2</sub> solubility was also observed by Makino et al. (2014) who used ammonium bis(trifluoromethanesulfonyl)amide IL systems to capture CO<sub>2</sub>. On the other hand, Bara et al. showed that imidazolium-based ILs with one to three oligo(ethylene glycol) substituents absorbed the same amount of CO<sub>2</sub> compared to their alkyl-substituted counterparts. However, their study pointed to a higher selectivity toward CO<sub>2</sub> compared to N<sub>2</sub> and CH<sub>4</sub> for ILs with ether groups (Bara et al., 2007).

The effect of other functional groups, such as carbonyl and ester, on CO<sub>2</sub> solubility in ILs has also been investigated. For instance, [b<sub>2</sub>Nic][Tf<sub>2</sub>N], a pyridinium-based IL with a butyl ester group, was studied by Muldoon et al. (2007) to analyze the effect of ester groups on CO<sub>2</sub> solubility. Results indicated that [b<sub>2</sub>Nic][Tf<sub>2</sub>N] had a noticeably higher CO<sub>2</sub> solubility than [hmim][Tf<sub>2</sub>N] under high partial pressure of CO<sub>2</sub>, which was the result of minor interactions between CO<sub>2</sub> and ester groups. This was contrary to the finding of Makino et al. (2014) whose study on ammonium bis(trifluoromethanesulfonyl)amide ILs showed that the presence of ester groups led to a decrease in CO<sub>2</sub> solubility.

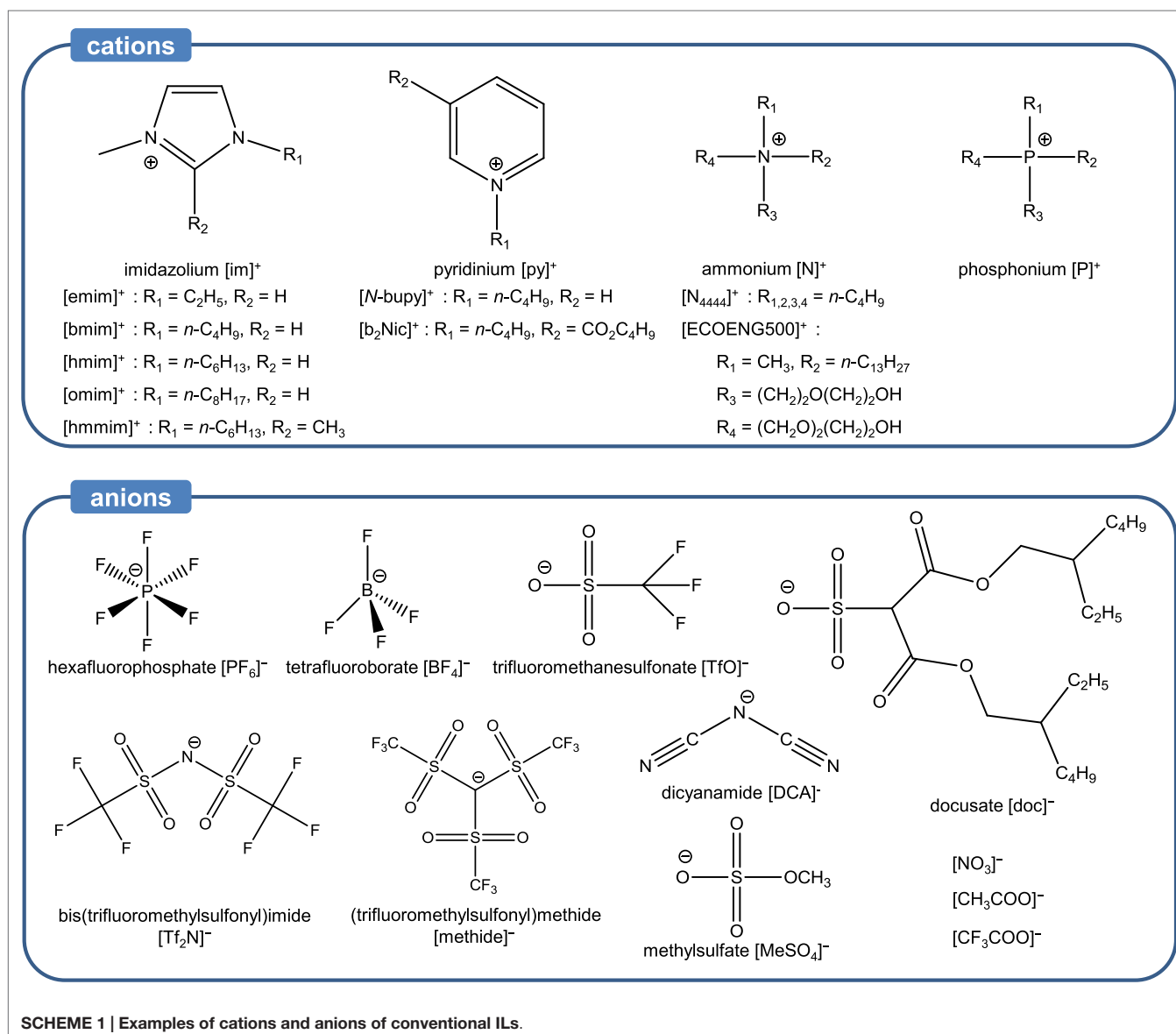
Overall, conventional ILs exhibit a very CO<sub>2</sub> capture capacity. Typically, at pressures between 9 and 30 bar at room temperature, capacities between 0.1 and 0.6 mol CO<sub>2</sub>/IL (or 3 and 16 wt%) have been reported for various conventional ILs (Zhang et al., 2012). This has to be compared to 0.3 mol CO<sub>2</sub>/MEA (or 7 wt%) at 1 bar and 25°C for 30 wt% MEA solvent. In addition, the absence of any functional groups can restrict the selectivity of the materials. These aspects have prompted the development of another class of

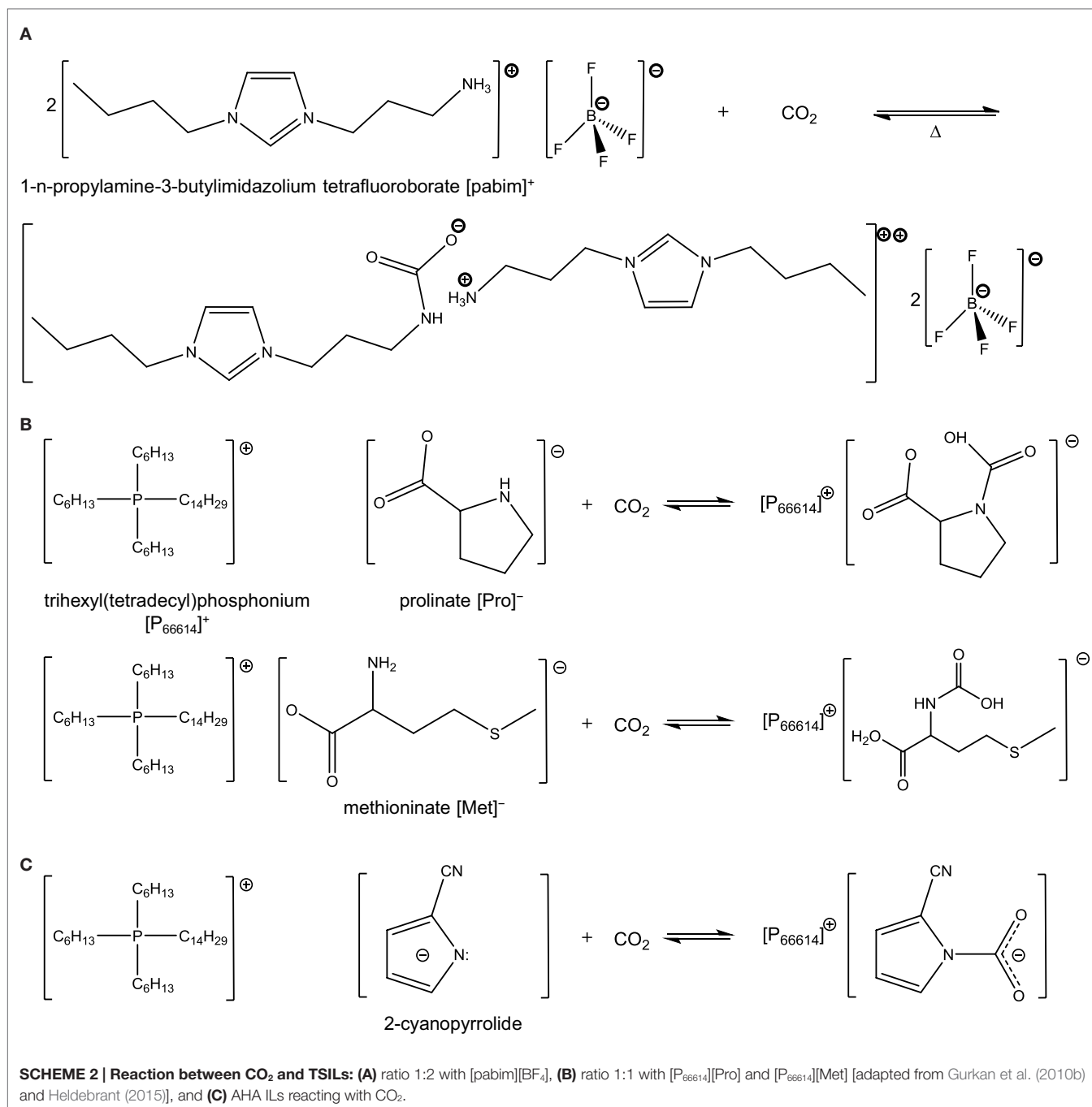
ILs referred to as task-specific ionic liquids (TSILs). These ILs are characterized by their amine or other functionalities that allow for relatively strong interactions with CO<sub>2</sub>. This type of ILs is discussed in the next section.

### Task-Specific Ionic Liquids

Task-specific ionic liquids are mostly similar to conventional ILs expect that they exhibit functional groups, which can capture CO<sub>2</sub> more rapidly. In most cases, the functional groups in question are amine groups but more recent studies have looked into other functionalities as well, which are discussed below. Regeneration of TSILs requires slightly more stringent conditions than conventional ILs, such as higher temperature or longer heat treatment in vacuum. In general, these treatments enable the complete recycling of the ILs with no or minimal loss of capture capacity and material. This is due to the chemical interactions involved in

the capture process. Interestingly though, a recent study showed that by properly selecting the structure of TSILs, and particularly the position of the amine group on the benzene-derived anion (i.e., para, meta, or ortho), one could tune the binding energy of CO<sub>2</sub> and hence the regeneration requirements (Luo et al., 2014b). Bates et al. (2002) synthesized the first type of TSILs, [pabim][BF<sub>4</sub>], shown in **Scheme 1A**. They successfully introduced the primary amines on cations, and it allowed for the formation of an ammonium carbamate salt, which reacted with CO<sub>2</sub> in the same way as in a conventional amine scrubbing process (**Scheme 2**). The molar equilibrium ratio of CO<sub>2</sub> to [pabim][BF<sub>4</sub>] was 1:2 and the weight gain due to CO<sub>2</sub> capture was 7.4%, compared to 0.1% in [hmim][PF<sub>6</sub>], a conventional IL. The findings pointed to the enhancement of CO<sub>2</sub> solubility at low pressure owing to the presence of the amine groups, while physical sorption occurred at high pressure.

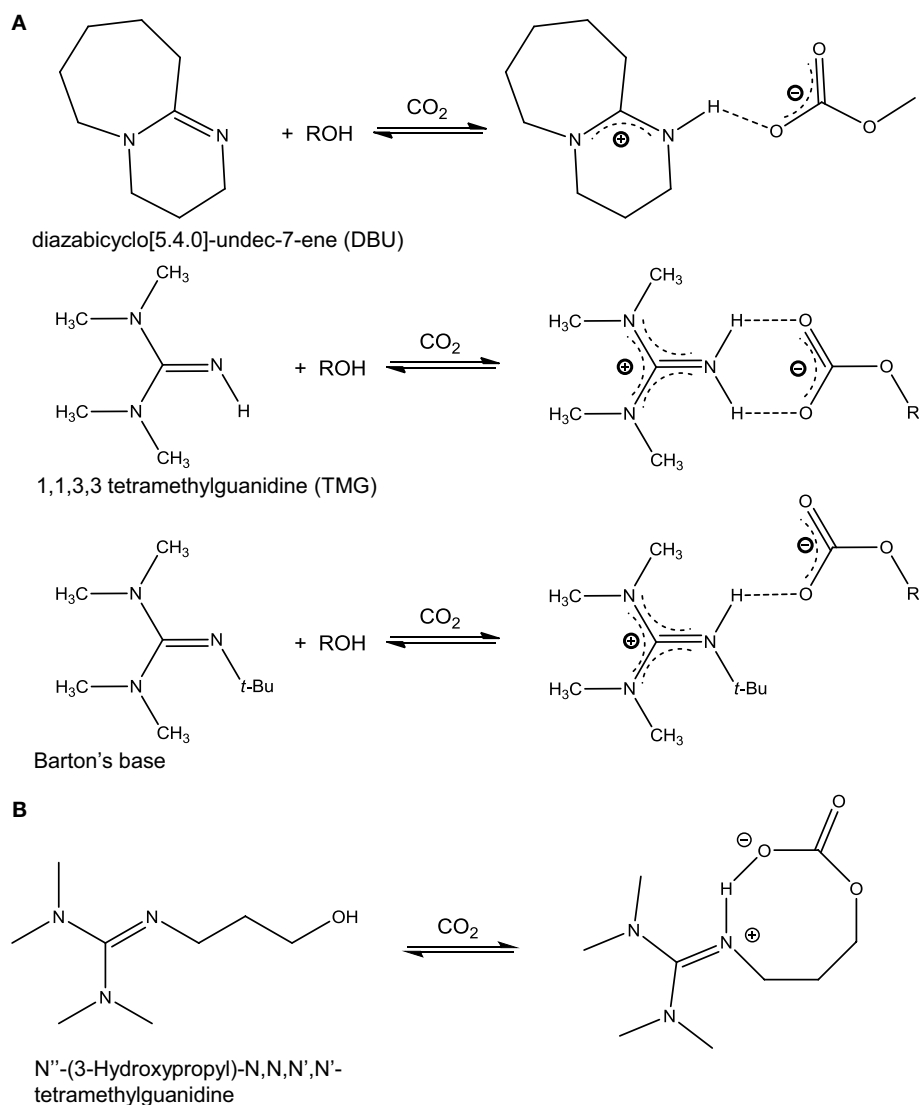




The first examples of TSILs all led to a CO<sub>2</sub> to ILs molar ratio of 1:2 as can be deduced from **Scheme 2A**. Later, Gurkan et al. reported the preparation of new amine-based TSILs resulting in an equimolar ratio between the two entities (Gurkan et al., 2010b). Such a behavior significantly enhanced the capacity of ILs. The way to reach such high solubility was to introduce the amine functionality on the anionic component and not on the cationic one as in “regular” TSILs. Specifically, the ILs used by Gurkan et al. consisted of [P<sub>66614</sub>]<sup>+</sup> and [Met]<sup>-</sup> or [Pro]<sup>-</sup> (**Scheme 2B**). Upon exposure to CO<sub>2</sub>, the amino group of the ILs reacted with

CO<sub>2</sub> and formed carbamic acid. More recently, a CO<sub>2</sub> to ILs molar ratio of 1.6:1 was reported by Luo et al. at 1 bar and 20°C (Luo et al., 2014a). The researchers used a pyridium-based anion functionalized with a hydroxide group. Both functionalities were hypothesized to react with CO<sub>2</sub> in a cooperative way. The cation used was [P<sub>66614</sub>]<sup>+</sup>.

Besides amines, nitrile functional groups have also been trialed as a way to improve the CO<sub>2</sub> selectivity and permeance in ILs. Mahurin et al. (2010) prepared a series of nitrile-containing ILs for supported IL membranes. These nitrile-containing



**SCHEME 3 | Reaction between CO<sub>2</sub> and CO<sub>2</sub>BOLs: (A)** CO<sub>2</sub>BOLs composed of two species, an alcohol and an amidine (top) or guanidine based (middle and bottom). Reaction with CO<sub>2</sub> leads to the formation of H-bonds [adapted from Heldebrant et al. (2008)]; **(B)** CO<sub>2</sub>BOLs composed of a single species. Reaction with CO<sub>2</sub> leads to the formation of a zwitterionic species [adapted from Park et al. (2011)].

ILs exhibited high CO<sub>2</sub> solubilities and selectivities over N<sub>2</sub>. Among them, 1-ethyl-3-methylimidazolium tetracyanoborate [emim][B(CN)<sub>4</sub>], exhibited the highest CO<sub>2</sub> solubility as well as permeance. The positive impact of nitrile groups was further confirmed by a modeling study by Gupta and Jiang (2014), which indicated that increasing the number of nitrile groups led to an increased CO<sub>2</sub> solubility. Among the various ILs tested, [bmim][B(CN)<sub>4</sub>] was identified as the most promising one. It was suggested that the presence of the nitrile group weakens the cation–anion interactions and this was correlated with an increase in CO<sub>2</sub> solubility. Carlisle et al. (2008) showed that nitrile-functionalized ILs exhibited enhanced CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> solubility selectivity compared to their alkyl-substituted counterparts.

Wang et al. (2011) studied the solubility of CO<sub>2</sub> in a triethylbutylammonium acetate TSIL ([N<sub>2224</sub>][CH<sub>3</sub>COO]) and its derived hydrated complexes. While in the dried TSIL the capture mechanism mainly involved Lewis acid-based interactions, in the case of the hydrated complexes, CO<sub>2</sub>, H<sub>2</sub>O, and the acetate component reacted to form the bicarbonate ion and acetic acid. The mole fractions reported at room temperature and a pressure of 1 bar ranged from 0.05 to 0.39.

Although amine-functionalized TSILs have allowed a noticeable improvement in terms of CO<sub>2</sub> capture capacities, they suffer from a relatively high viscosity. Furthermore, an increase in viscosity is typically observed in those materials upon reaction with CO<sub>2</sub> (Soutullo et al., 2007). A molecular simulation study reported that the high viscosity in neat TSILs (i.e., not yet exposed

to CO<sub>2</sub>) is caused by the strong H-bonding interactions between the anions and the amine groups of the cations (Yu et al., 2007). Another simulation study was conducted by Gutowski and Maginn (2008) to clarify the mechanism causing the dramatic increase in viscosity when TSILs are exposed to CO<sub>2</sub>. The authors suggested that it was due to the complexation of TSIL and CO<sub>2</sub> leading to an extensive H-bonding network, i.e., a salt bridge network connecting carbamate and ammonium species (Gutowski and Maginn, 2008).

Reducing the viscosity of TSILs has become one of the key challenges and many studies have been dedicated to this aspect. A reduction in the extent of this H-bonding network was observed on a representative IL of a new class of TSILs referred to as aprotic heterocyclic anion (AHA) ILs (Gurkan et al., 2010a; Wu et al., 2011; Seo et al., 2014). AHA ILs corresponds to ILs with pyrrolide-based anions (Gurkan et al., 2010a). These anions can react with CO<sub>2</sub> to form a carbamate (**Scheme 2C**). In this reaction, the CO<sub>2</sub> to IL ratio is 1. A key advantage of the reaction is that it does not lead to the formation of H-bonds, thereby addressing the viscosity issue. Experimental studies supported by computational measurements confirmed the absence of increase in viscosity in AHA ILs (Gurkan et al., 2010a; Wu et al., 2011). In addition, the CO<sub>2</sub> solubilities were in a similar range to that of many other “regular” TSILs (Wu et al., 2011). A recent study conducted on several AHA ILs with varying substituents on the pyrrolide anion evidenced that functionalization of these ILs could be used to tune the binding energy of CO<sub>2</sub> (Seo et al., 2014). When the cation in AHA ILs is imidazolium, it was found that the mechanism of CO<sub>2</sub> capture was not simply via the CO<sub>2</sub>-anion reaction. A parallel reaction also occurred in which a proton exchange took place between the anion and the cation leading to the formation of carbene species that could react with CO<sub>2</sub> (Seo et al., 2014).

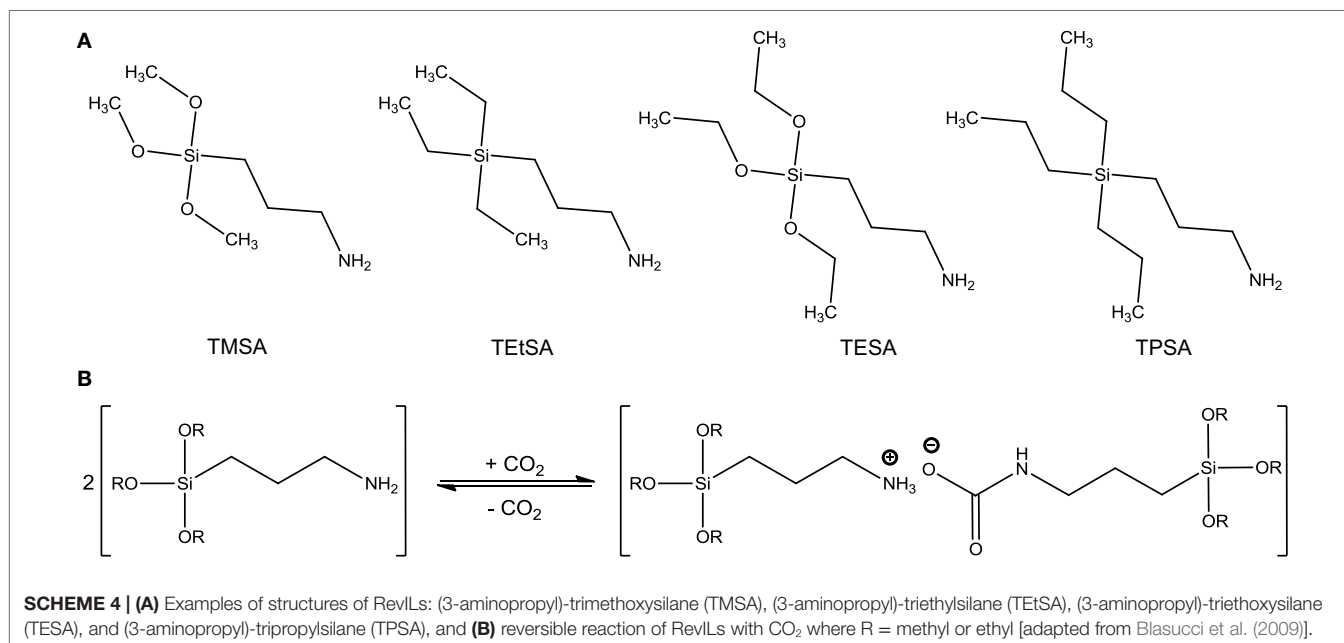
Besides the use of AHA ILs, another way to deal with the viscosity issue is to mix TSILs with a low-viscosity fluid. A range of

solvents have been tested including conventional ILs, alcohols (Liu et al., 2003), ketones (Zhang et al., 2007; Lei et al., 2012), organic acids (Bogel-Lukasika et al., 2010), water (Goodrich et al., 2011; Stevanovic et al., 2012) as well as alkanolamines (Camper et al., 2008; Sairi et al., 2011). For instance, Bara et al. (2010) dissolved a TSIL into a conventional RTIL, [hmim][Tf<sub>2</sub>N], to lower overall viscosity so that the sorbent could be employed in gas separation units. Following the same principle, other studies have looked at mixtures of alkanolamines and RTILs or TSILs to dramatically lower viscosity while increasing CO<sub>2</sub> capture capacity (Camper et al., 2008; Sairi et al., 2011). Goodrich et al. (2011) mixed [P<sub>66614</sub>][Pro] and water and observed a decrease in the overall viscosity of the mixture, while the decrease in CO<sub>2</sub> capture capacity was negligible. On the other hand, an enhancement of CO<sub>2</sub> capture in ILs in the presence of water was observed by Romanos et al. (2013). This trend was opposite to that observed by Stevanovic et al. (2012) with a different ILs. Overall, these studies show promising potential to integrate ILs and other solvents to address the viscosity issue but the simultaneous increase in CO<sub>2</sub> solubility is not systematic and depends on the solvent as well as the IL used.

## CO<sub>2</sub>-Triggered Switchable Solvents

### CO<sub>2</sub>-Binding Organic Liquids

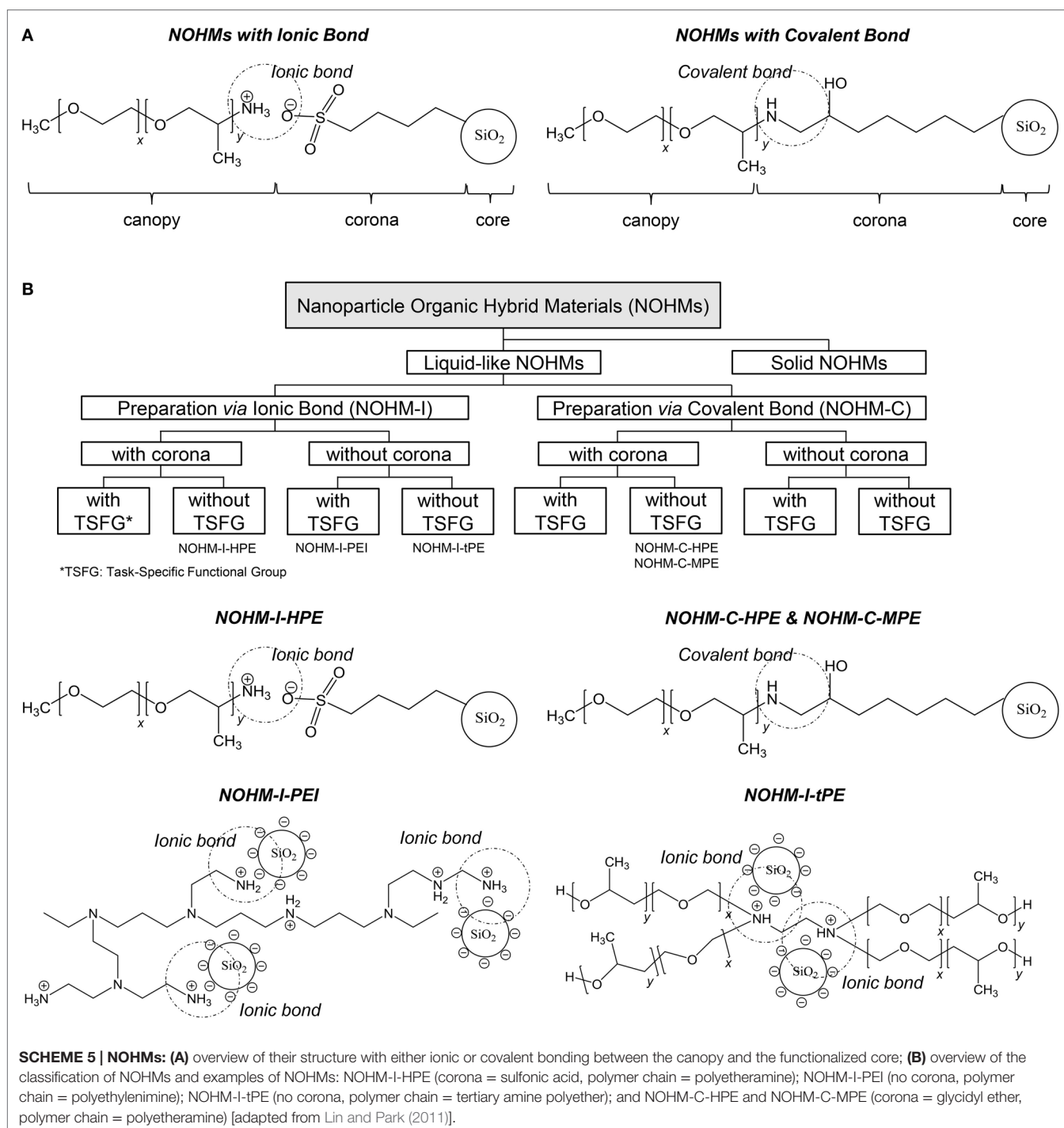
Another class of anhydrous solvents for CO<sub>2</sub> capture is that of CO<sub>2</sub>BOLs. CO<sub>2</sub>BOLs are organic liquids consisting of an alcohol and a strong amidine or guanidine base that can chemically capture CO<sub>2</sub> to form amidinium or guanidinium alkylcarbonate, respectively (Liu et al., 2006; Phan et al., 2008; Heldebrant et al., 2009). The reaction between CO<sub>2</sub> and CO<sub>2</sub>BOLs is shown in **Scheme 3**. Typically, the CO<sub>2</sub> capture capacity of CO<sub>2</sub>BOLs can be up to about 20 wt% (Heldebrant et al., 2008, 2009).



The first generation of CO<sub>2</sub>BOLs consisted of two distinct molecules, the strong base and the alcohol, and exhibited relatively high volatility. To address this aspect, it was decided to combine the two molecules into one single component forming either alkanolguanidine or alkanolamidine. The reaction of these species with CO<sub>2</sub> leads to the formation of zwitterionic species as shown in **Scheme 3B** (Heldebrant et al., 2010a, 2011; Kim and Park, 2010). While improvement was made on one front, it was found that single-component CO<sub>2</sub>BOLs

were highly viscous when loaded with CO<sub>2</sub> (>2,000 cP). As a result, a further advancement was the development of a low-viscosity single-component CO<sub>2</sub>BOLs (Koech et al., 2013). The best results were obtained with alkanolguanidines with an imidazolidine-based core.

One of the most interesting features of CO<sub>2</sub>BOLs is their low binding energy for CO<sub>2</sub>, which allows them to be regenerated without significant energy consumption. Initially focusing on the first generation of CO<sub>2</sub>BOLs, Heldebrant et al. (2008) reported the





free energies of CO<sub>2</sub>BOLs for CO<sub>2</sub> capture and they found that the binding energies for CO<sub>2</sub> in these materials were notably small, ranging from -9 to 2 kJ mol<sup>-1</sup> depending on the solvent. Because the CO<sub>2</sub>-binding energy of CO<sub>2</sub>BOLs was small, a relatively low temperature swing process could be applied to regenerate the solvents (90°C) over five cycles with no visible loss of activity and selectivity (Heldebrant et al., 2009). It must be noted though that some CO<sub>2</sub>BOLs required higher temperature for regeneration up to 160°C (Mathias et al., 2013). As the single-component CO<sub>2</sub>BOLs were developed, the product formed as a result of CO<sub>2</sub> capture was polar – zwitterionic species – and therefore the idea of using polarity-swing-assisted regeneration (PSAR) process was investigated to replace the common temperature swing approach (Mathias et al., 2013). The process consisted in adding an inert and non-polar anti-solvent to the CO<sub>2</sub>BOLs as the way to lower the polarity of the system, thereby releasing CO<sub>2</sub>. The non-polar solvent could then be separated from CO<sub>2</sub>BOLs by lowering the temperature to induce a phase separation. Overall, this process called for lower regeneration temperatures (about 85°C) and energies for CO<sub>2</sub> separation relative to conventional technology.

Heldebrant et al. (2011) studied the robustness and recyclability of alkanolganidines, alkanolamidines, and mixtures of these two types of CO<sub>2</sub>BOLs. Regeneration of the materials was tested for 10 cycles via heat treatment at 75°C under nitrogen atmosphere, in dry conditions, or in the presence of 10 mol% water. In both cases, the CO<sub>2</sub> uptake was not significantly decreased. This was confirmed by a subsequent study (Koech et al., 2013). It must be noted that BOLs have also been shown to capture SO<sub>2</sub> (Heldebrant et al., 2010b).

## Reversible Ionic Liquids

Other representative solvents of the switchable solvents family are RevILs (Blasucci et al., 2009, 2010; Blasuccia et al., 2010; Gonzalez-Miquel et al., 2012; Switzer et al., 2013, 2014). RevILs consist of silylated amines that react with CO<sub>2</sub> to form an IL. As CO<sub>2</sub> reacts with RevILs, an IL is formed, as shown in **Scheme 4**. This newly formed IL can, in turn, absorb CO<sub>2</sub> like a conventional IL. RevILs are distinguished from ILs in that the species are non-ionic prior to reaction with CO<sub>2</sub>, which makes them theoretically less viscous upon reaction with CO<sub>2</sub> compared to TSILs. RevILs also differ from CO<sub>2</sub>BOLs since CO<sub>2</sub> reacts with the N-containing group of RevILs, while it reacts with the alcohol group in the case of CO<sub>2</sub>BOLs. Nevertheless, it must be noted that some papers would classify single-component CO<sub>2</sub>BOLs as a sub-category of RevILs. In this review, the two are distinguished.

It was found that the CO<sub>2</sub> to amine ratio in RevILs could reach up to 0.7:1 (Switzer et al., 2013, 2014). The structural properties of silylated amines (i.e., length of the carbon chains, branched or unbranched, primary or secondary amines) strongly determine the viscosity (600–4,000 cP) and CO<sub>2</sub> solubility of RevILs (Blasuccia et al., 2010; Gonzalez-Miquel et al., 2012; Switzer et al., 2014). RevILs can be easily switched back to molecular liquids after exposure to CO<sub>2</sub> by purging with an inert gas to remove CO<sub>2</sub>, or heating up to 50–100°C, depending on the types of RevILs (Jessop et al., 2005; Blasucci et al., 2010; Blasuccia et al., 2010). Heat of reaction between 20 and 150 kJ/mol has been reported (Switzer et al., 2014).

## Nanoparticle Organic Hybrid Materials

The last set of anhydrous solvents for CO<sub>2</sub> capture discussed in this review is that of NOHMs. NOHMs are nanomaterials consisting of a nanocore functionalized with polymer chains (canopy). In some cases, a linker (corona) can be used to link the canopy to the core (Bourlinors et al., 2005; Bourlinos et al., 2005a,b, 2006; Rodriguez et al., 2008; Agarwal et al., 2009; Yu and Koch, 2010; Zheng et al., 2010). The canopy can be tethered onto the nanocore either covalently or ionically as shown in **Scheme 5A**. Various materials have been used as cores including oxide nanoparticles, metallic nanoparticles, carbon nanotubes, and polyoxometalates (Bourlinors et al., 2005; Bourlinos et al., 2005a,b, 2006; Rodriguez et al., 2008; Agarwal et al., 2009; Yu and Koch, 2010; Zheng et al., 2010). The corona is typically a silane or thiol compound, while polyethylene glycol, polyetheramine, and polyethyleneimine are examples of polymers used to form the canopy. Depending on their composition, NOHMs can exhibit liquid-, gel-, or solid-like properties. When applied for CO<sub>2</sub> capture, the focus has been on the former type of NOHMs, which corresponds to the category discussed in this review. Like ILs, NOHMs exhibit negligible vapor pressure owing to the bond existing between the canopy (or canopy plus corona) and the thermostable nanocore. The latter feature also confers NOHMs with a good thermal stability up to about 300°C, which is always higher than the parent polymer (Lin et al., 2014). Currently, NOHMs are classified based on their representative phase and synthesis methods as well as the existence of task-specific functional groups (see **Scheme 5B**) (Lin and Park, 2011).

It was found that CO<sub>2</sub> capture in NOHMs arises from two effects: an entropic effect and an enthalpic effect. The former contribution is due to the conformation of the polymer chains in NOHMs, which are better aligned and ordered than in pure polymers as they have to “fill out the gaps” between the nanocores (Park et al., 2011; Petit et al., 2012). Capture of CO<sub>2</sub> in NOHMs is, therefore, favored as it allows the solvents to return to a more relaxed state. This entropic effect can be tuned by changing the shape of the canopy – i.e., linear versus branched polymer – as well as the canopy grafting density – i.e., the number of polymer chain tethered onto the nanocore (Petit et al., 2012; Park et al., 2014). Nevertheless, the entropic contribution toward CO<sub>2</sub> capture remains minimal. On the other hand, the enthalpic effect is a major controlling factor and is related to the presence of functional groups along the polymer chains. As expected, it was found that ether groups – owing to Lewis acid-based interactions (Park et al., 2011) – enhanced CO<sub>2</sub> capture. This was also observed, albeit in a more pronounced way, in the case of the presence of amine groups (Lin and Park, 2011). It was found that NOHMs with polyethyleneimine could absorb up to 3 mmol/g of CO<sub>2</sub>, which is in the range of MEA-based aqueous solvents (Lin and Park, 2011). A good selectivity toward CO<sub>2</sub> compared to N<sub>2</sub> was also demonstrated (Lin and Park, 2011). The effect of another flue gas components, i.e., SO<sub>2</sub>, on the performance of NOHMs was also studied (Lin et al., 2013). No significant effect was observed in the presence of SO<sub>2</sub> in the range of concentration typically encountered in post-combustion plants (Lin et al., 2013).

**TABLE 1 | Overview of the properties, merits, and weaknesses of the reviewed anhydrous solvents with respect to CO<sub>2</sub> capture and compared to MEA aqueous solvent.**

|  | 30 wt% MEA aqueous solution   | Conventional ILs   | TSILs   | CO <sub>2</sub> BOLs   | NOHMs  |
|--|---|--|---|--|--|
| CO <sub>2</sub> -binding Energy (kJ/mol)   | ~80   | ~15  | 40–50   | –9 to 2  | Not reported but predicted to be between those reported for conventional ILs and TSILs   |
| Regeneration conditions tested or selected   | Thermal swing at 120–140°C  | Thermal swing at 70–80°C<br>Inert gas bubbling<br>Pressure swing     | Thermal swing at 80°C   | Thermal swing at 75–160°C<br>Polarity swing  | Thermal swing at 120°C for NOHMs with amine functional groups<br>Pressure swing for NOHMs without amine functional groups  |
| CO <sub>2</sub> capture capacity at 1 bar and 25–40°C (maximum reported)                 | 0.3 mol CO <sub>2</sub> /mol MEA<br>1.47 mmol/g (MEA + water)<br>7 wt%<br>108 g/L (MEA + water) | Henry's constant: 80 bar at 25°C for [emim][BF <sub>4</sub> ]        | 1.6 mol CO <sub>2</sub> /mol TSIL<br>2.6 mmol/g TSIL<br>11 wt%                            | 1.3 mol/mol of amidine DBU<br>4.3 mmol/g CO <sub>2</sub> BOL<br>19 wt%<br>147 g/L  | ~0.1 mmol/g organic component for NOHMs without amine functional groups<br>2.2 mmol/g organic component for NOHMs with amine functional groups (at 3.4 bar and 30°C)             |
| Commercial availability  | Commercially available<br>\$0.02/kg (from BASF)   | Some ILs commercially available<br><\$40/kg (Ramdin et al., 2012)    | Some TSILs commercially available<br>Usually synthesized via a two- or three-step process | Not commercially available<br>Formulation cost projected to be ~\$35/kg (Heldebrant, 2015)   | Not commercially available<br>Usually synthesized via a two-step process   |
| Estimated levelized cost of electricity (LCOE) increase compared to LCOE without capture | 75–100% (IEA, 2014; Heldebrant, 2015)   | Not reported   | Not reported  | 115% (current formulation – operated at 356 cP maximum viscosity)<br>68% (if 20 cP max viscosity formulation could be achieved) (Heldebrant, 2015) | Not reported   |
| Strengths  | Commercially available<br>High capture capacity<br>Fast kinetics<br>TRL 9                       | Low energy requirement for regeneration<br>Negligible vapor pressure | High capture capacity<br>Tunability<br>Negligible vapor pressure                          | High capture capacity<br>Low energy requirement for regeneration   | Low energy requirement for regeneration (for NOHMs w/o functional groups)<br>Tunability<br>Negligible vapor pressure<br>Electrolytic properties (for CO <sub>2</sub> conversion) |
| Weaknesses   | High energy penalty<br>Corrosive<br>Chemically/thermally unstable                               | Low capture capacity<br>TRL 2  | High viscosity<br>Not commercially available<br>TRL 1                                     | High viscosity<br>Not commercially available<br>TRL 1  | High viscosity<br>Not commercially available<br>TRL 1  |

In addition to the selectivity, the recyclability of NOHMs was tested via a vacuum pressure swing process (Lin and Park, 2011; Park et al., 2011). No degradation of the material was noticed and the efficiency for CO<sub>2</sub> capture was maintained for NOHMs deprived of task-specific functional groups. However, the presence of accessible amine groups led to a decrease in the capture capacity after the first cycle and it is anticipated that a mild thermal treatment, as in the case of TSILs, can lead to the release of chemisorbed CO<sub>2</sub>. The decrease in capture capacity upon the first cycle was related to the particular capture mechanism. The NOHMs exhibited amine groups, which reacted with CO<sub>2</sub> in the same way as observed with TSILs. The pressure swing cycle that was applied was, therefore, not sufficient to break the bond formed between the amine group and CO<sub>2</sub>. Given the similar chemistry of the tested NOHMs to that of TSILs, it is expected that a thermal swing can enable full recovery of the initial capture capacity. This discussion has been added to the revised manuscript. Overall, since NOHMs can capture CO<sub>2</sub> from two different effects of entropic and enthalpic contributions, one can desorb CO<sub>2</sub> from NOHMs via pressure, temperature, or pressure–temperature swing processes.

Like TSILs, a major obstacle to the applications of NOHMs in the large scale is their high viscosity (up to 15,000 cP). Reducing the size of the nanocore was, therefore, explored as a way to decrease the viscosity in NOHMs (Petit et al., 2013b). Indeed, it was recently proposed to use polysilsesquioxane (POSS) cages as the core particles instead of the typically used larger SiO<sub>2</sub> nanoparticles – POSS correspond to the smallest silica particles that exist. This approach led to a decrease in viscosity down to about 1,500 cP. Mixing NOHMs and water was also investigated as a way to decrease the viscosity of NOHMs. The viscosity was decreased down to about 8,000 and 500 cP for 15 and 70 wt% water contents, respectively. It was also found that water, while decreasing the CO<sub>2</sub> capture capacity, significantly helped reducing the viscosity of the NOHMs, thereby enhancing CO<sub>2</sub> diffusion (Petit et al., 2013a).

## Conclusion

Amine-based solvents have been selected to move to the next stage of development in terms of CO<sub>2</sub> capture with pilot-scale and demonstration-scale projects relying on these solvents. Aqueous amine-based solvents, such as MEA, have a great CO<sub>2</sub> capture capacity and fast kinetics, while still facing some challenges associated with their high volatility causing fugitive emissions and loss of materials, corrosive nature, and high water content leading to relatively high energy consumption. Thus, there has been a desire to develop alternative CO<sub>2</sub> capture solvents with a potentially lowered regeneration energy requirement.

In this review, we summarized new and promising developments in CO<sub>2</sub> capture media, focusing on novel liquid or liquid-like materials including ILs, CO<sub>2</sub>-triggered switchable solvents, and NOHMs. These materials exhibit low and/or negligible vapor pressure, which would minimize or eliminate the issues of fugitive emissions or loss of materials during CO<sub>2</sub> capture and solvent regeneration. In addition, being anhydrous, the problem of high parasitic energy consumption associated with water

vaporization would be circumvented. Finally, these new materials are highly tunable, and therefore, they can capture CO<sub>2</sub> via a range of chemical or physical mechanisms. This aspect allows for the CO<sub>2</sub>-binding energy to be tuned and for various desorption/regeneration processes to be used, such as thermal swing, pressure swing, polarity swing, or a combination of the three. A summary of the properties of the different anhydrous solvents discussed along with their merits/weaknesses is provided in **Table 1**. Overall, TSILs and CO<sub>2</sub>BOLs likely appear as the most promising candidates as alternative CO<sub>2</sub> capture solvents. TSILs have been around for quite some time and exhibit an excellent tunability along with a high capture capacity. It was estimated that ILs can reduce the energy loss by 16% (CO<sub>2</sub> capture with [bmim][Ac]), bringing the costs down for investment for the process by 11% (Zhang et al., 2012). A high capture capacity has also been reported with CO<sub>2</sub>BOLs, in some cases surpassing that of TSILs. CO<sub>2</sub>BOLs are characterized by a very low binding energy for CO<sub>2</sub>, and therefore benefit from a significantly lower energy requirement for solvent regeneration. In fact, it was calculated that, provided that the viscosity of CO<sub>2</sub>BOLs is below 20 cP, a 68% increase in the levelized cost of electricity could be reached with CO<sub>2</sub>BOLs as opposed to 75–100% typically reported for MEA aqueous solvent (Heldebrant, 2015). Comparatively to TSILs and CO<sub>2</sub>BOLs, relatively little effort has been dedicated to the study of NOHMs with task-specific functional groups for CO<sub>2</sub> capture. Given the tunability, chemistry, and zero vapor pressure, it is expected that they will behave similarly to TSILs. On the other hand, conventional ILs as well as NOHMs without task-specific groups are likely better suited for high-pressure separation processes rather than post-combustion CO<sub>2</sub> capture. It must be noted that while one can find commercially available ILs, the other solvents discussed in the review as well as the TSILs exhibiting the highest capture capacity are not yet produced at a large scale.

While TSILs, CO<sub>2</sub>BOLs, and NOHMs with task-specific groups exhibit real merits for CO<sub>2</sub> capture, it is also certain that they must be improved to meet the requirement of large-scale application for CO<sub>2</sub> capture. One of the key areas that should be further explored is the decrease of their viscosity. Many of these solvents are still highly viscous and while recent studies have shown ways to address this issue, their viscosities remain relatively high and do not allow them to be used in the same reactor set-up as amine solvents. In addition, further testing these materials using real flue gas streams is required to get an insight into their “real” performance. In addition, it becomes more and more important to couple experimental efforts to design materials with modeling work at the reactor and process scales to understand the set of key performance indicators a material must exhibit. Working across these scales will allow one to identify the most promising materials and provide guidance for materials scientists toward the design of improved solvents.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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