Functionalized Ionic Liquids for CO_2 Capture under Ambient Pressure

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Declarations of conflict of interest: none

Abstract

Ionic liquids (ILs) have been widely explored as alternative solvents for carbon dioxide (CO_2) capture and utilization. However, most of these processes are under pressures significantly higher than atmospheric level, which not only levies additional equipment and operation costs, but also makes the large-scale CO_2 capture and conversion less practical. In this study, we rationally designed glycol ether-functionalized imidazolium, phosphonium and ammonium ILs pairing with acetate (OAc^-) or Tf_2N^- anions, and found these task-specific ILs could solubilize up to 0.55 mol CO_2 per mole of IL (or 5.9 wt% CO_2) at room temperature and atmospheric pressure. Although acetate anions enabled a better capture of CO_2, Tf_2N^- anions are more compatible with alcohol dehydrogenase (ADH), which is a key enzyme involved in the cascade enzymatic conversion of CO_2 to methanol. Our promising results indicate the possibility of CO_2 capture under ambient pressure and its enzymatic conversion to valuable commodity.

1. Introduction

As carbon dioxide (CO_2) concentration is drastically rising in atmosphere due to fossil fuel burning, carbon capture, sequestration and utilization (CCSU) has become a viable option for CO_2 reduction and its conversion to valuable commodities such as formate/formic acid, formaldehyde, CO, bicarbonate, methanol, carboxylation products, and sugars, etc. (*1-3*). In particular, CO_2 reduction to methanol is an attractive route for preparing C1 building blocks, and can be achieved by chemical, electrochemical, photochemical, or enzymatic methods (*2, 4*). First three methods suffer from issues such as low selectivity and difficulty in preparing effective catalysts; for example, electrochemical methods need excessive overpotentials and yield mixtures of products (*2, 5*). On the other hand, enzymatic approaches have the advantages of high specificity, high selectivity and being environmentally benign. However, enzymatic CO_2 reduction in aqueous solutions is limited by poor CO_2 solubility in water (2.9 g/L at 25 °C) (*6*). Recently, various ionic liquid (IL) systems have evolved into emerging tools for capturing high concentrations of CO_2 (up to equal mole of the solvent). However, these ILs either are not compatible with enzymes (i.e. dehydrogenases), or chemically convert CO_2 to an unreactive substrate for enzymatic reductions.

Post-combustion capture of CO_2 can be achieved through a number of methods such as absorption, adsorption, cryogenic distillation, membrane separation, and microalgae growth (*7*). Conventional chemical absorption of CO_2 using amine solutions (e.g. monoethanolamine) are effective but have several drawbacks including equipment corrosion, amine volatility, high construction cost, amine degradation by SO_2, NO_2, and O_2 in the flue gas, and high energy input for absorbent regeneration (*7, 8*). The mixture of amines and ILs were found efficient for CO_2 capture, but monoethanolamine-carbamate salt began to precipitate from ILs (*9*). ILs have several favorable properties for CO_2 capture including low volatility, high thermal and chemical stability, various solvent polarity, and tunable structures for either physical or chemical gas absorption. CO_2 capture by ILs has been extensively reviewed by several groups (*10-13*). A process simulation study suggests that CO_2 absorption using 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) reduces the energy loss by 16%, the investment by 11% and equipment cost by 12% when compared with aqueous monoethanolamine process (*14*). This section intends to provide a brief overview of examples that are closely relevant to this project. In general, CO_2 has a much higher solubility in ILs than other gases (e.g. CO, O_2, N_2, CH_4, and C_2H_4), especially in ILs with fluorinated cations or anions; however, ILs have minimum solubility in CO_2 (*15-17*). The use of fluorinated ILs raises some environmental concerns due to their poor biodegradability. CO_2 dissolution in ILs can be through physisorption/physical interactions (e.g. electrostatic, van der Waals, and hydrogen bonding), or chemisorption/chemical reactions (*18*).

IL anions typically impose strong influence on CO_2 solubility (*19*). MD simulations indicate strong CO_2 interaction with anions (e.g. PF_6^-) but weak interaction with cations (e.g. $BMIM^+$) (*20, 21*). Another MD simulations (*22*) suggest that CO_2 molecules interact preferentially with the polar region of ILs, and coordinate with anions in a decreasing coordination order of $BF_4^- > Br^- > OAc^- >$ prolinate (BF_4^- has multiple coordination sites and small size). A decreasing CO_2 solubility corresponds to the order of anions: methide $> Tf_2N^- > OTf^- > PF_6^- \sim BF_4^- > dca^- > NO_3^-$ (25 °C with the same $BMIM^+$ cation; Tf_2N^- = bis(trifluoromethylsulfonyl)imide; dca^- = dicyanamide) (*23*), $PF_6^- > BF_4^- > NO_3^- > EtSO_4^-$ (*24, 25*), $NO_3^- > SCN^-$ (*26*), $OAc^- > Tf_2N^- > PF_6^- > BF_4^-$ (*27*), and $OAc^- >> MeSO_4^- > Cl^-$ (*28*). The Jalili group (*29, 30*) found CO_2 solubility following a similarly decreasing order of $Tf_2N^- > OTf^- > PF_6^- > BF_4^-$ in 1-(2-hydroxyethyl)-3-methylimidazolium based ILs at temperatures between 303.15 and 353.15 K and pressures up to 1.3 MPa. Ayad *et al.* (*31*) reported that ILs carrying the anion of tricyanomethanide $[C(CN)_3]^-$ led to a higher CO_2 solubility than other anions ($[C(CN)_3]^-$ > BF_4^- > Tf_2N^- > PF_6^- > SCN^-). Yokozeki *et al.* (*32*) observed similar CO_2 solubilities in ILs based on CF_3COO^-, PF_6^-, and BF_4^- anions. Zhang *et al.* (*33*) reported ~15% higher CO_2 solubility in 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate than in [HMIM][Tf_2N]. Fluorinated anions tend to dissolve more CO_2; hydrogen-bond basicity of anions is not correlated with the solubility (e.g. CO_2 solubility is similar in ILs containing BF_4^- and dca^- anions (*34*)); the order of anions could depend on the temperature (*23*). CO_2 can act as both a weak Lewis acid and a Lewis base; C-F bonds interact with Lewis acidic carbon atoms of CO_2 molecules (*35*). However, Carvalho *et al.* (*36*) argued that fluorinated molecules including ILs are not superior to eicosane in dissolving CO_2 except some fluorinated aromatic compounds. The issues with fluorinated compounds are their high cost and negative environment impact (*11, 37, 38*).

ILs carrying acetate anion (such as [BMIM][OAc]) could absorb less CO_2 than aqueous monoethanolamine but more than physical absorption (*39*); different chemisorption mechanisms have been put forward including deprotonation of imidazolium C-2 position leading to the coupling of carbene with CO_2 forming carboxylate (*40*), the formation of non-volatile (*41*) or electron donor-acceptor (oxygens of acetate as Lewis base interacting with CO_2) complexes (*42, 43*), multidentate binding between CO_2 and acetate (*44, 45*), carboxylate-induced ylide intermediate (of phosphonium) resulting in chemisorption of CO_2 (*46*) (which is similar to the role of phenolate (*47*)), acetate interacting with water and CO_2 to form bicarbonate (via ylide intermediate in some cases) (*39, 46*). Shiflett and co-workers (*32, 41, 48*) observed ~27 mol% (or 7.7 wt%) CO_2 dissolved in [EMIM][OAc] and [BMIM][OAc] at 25 °C and 0.1 MPa. Interestingly, they noticed very low vapor pressure above the mixture containing up to 20 mol% CO_2, implying the formation of non-volatile complex (but it is reversible). Similarly, Shaahmadi *et al.* (*49*) determined the CO_2 solubility in [BMIM][OAc] at atmospheric conditions (25 °C and 0.99 bar) as 27.3 mol% but observed a much lower solubility (1.5 mol%) in [BMIM][BF_4]. The Wallen group (*45*) pointed out the important role of cooperative C–H···O interaction as extra stabilizing factor in addition to Lewis acid–Lewis base interaction between CO_2 and carbonyl groups with H atoms attached to carbonyl carbon or α-carbon atom. Their ab initio calculations indicate that methyl acetate has a strong interaction with CO_2; they suggest that acetylation and incorporation of S=O bonds might be effective methods to design CO_2-philic solvents. On the other hand, [BMIM][CF_3COO] could dissolve much less CO_2 (e.g. 1.8 mol% at 25 °C and 0.1 MPa) due to the physisorption process (*32, 48, 50*). Ab initio calculations suggest that both oxygen atoms in acetate or trifluoroacetate interact with CO_2 while acetate is a stronger Lewis base than trifluoroacetate (*42*). However, Dupont and co-workers (*51*) argued that basic IL anions (e.g. acetate) do not act as nucleophiles to form covalent anion-CO_2 adducts, but promote the formation of carbonate/bicarbonate due to the presence of trace water in ILs. Butyrate anion-containing ILs were found having high CO_2 absorption capability than the acetate type (*52*).

The influence of cations on CO_2 solubility is usually less drastic than anions. In general, a higher CO_2 solubility can be found in an IL containing a longer alkyl chain (such as $BMIM^+$ vs $EMIM^+$, where $EMIM^+$ refers to 1-ethyl-3-methylimidazolium) (*25, 53-56*); a longer alkyl chain grafted to pyrrolidinium exhibited minimum impact on CO_2 dissolution under low pressures, but slightly increased CO_2 solubility at higher pressures (> 5 MPa) (*57*). Short ether-chain or hydroxyl-functionalized ILs have complicated effects on CO_2 dissolution (*58*). van Ginderen *et al.* (*59*) pointed out that ether oxygen atoms act as Lewis base to interact with the carbon atom (as Lewis acid) in CO_2 forming a 1:1 van der Waals complex. ILs carrying long branched-alkyl chains or ether groups (such as Ecoeng 500) have increased free volume and thus exhibited a high affinity toward CO_2 (which was comparable to [HMIM][Tf_2N] at all pressures) (*38*). Sharma *et al.* (*60*) reported a high CO_2 solubility in single ether-functionalized imidazolium ILs ([CH_3OCH_2-MIM]X), reaching ~0.9 mole CO_2 per mole of IL at 30 °C; CO_2 solubility increases with the type of anions as $BF_4^- < dca^- \sim PF_6^- \sim OTf^- < Tf_2N^-$. However, the Brennecke group (*61*) verified that such high CO_2 chemisorption results are in error, and ether-functionalized ILs only physically absorb CO_2. The Jalili group (*29, 30*) concluded that the solubility of CO_2 in a number of 1-(2-hydroxyethyl)-3-methylimidazolium based ILs was greater than corresponding $[EMIM]^+$-based ILs with the same anions. However, after comparing their solubility data with literature values, the Henni group (*27, 62*) implied that hydroxyl-functionalized ILs reduced CO_2 solubility while ether-functionalized ammonium ILs increased the solubility. On the other hand, some ether- and hydroxyl-functionalized ILs showed no impact on CO_2 solubility. Oligo(ethylene glycol)-grafted imidazolium ILs displayed similar dissolution power for CO_2 as alkyl-substituted ILs (*63*). The Gomes group (*64*) suggested that in ester or ester ether-functionalized imidazolium ILs could dissolve similar amounts of CO_2, methane and ethane as alkyl-substituted ILs. The same group (*65*) also found that CO_2 solubility was not influenced by hydroxyl or ester groups in ammonium ILs, and was even reduced (up to 48 % decrease in mole fraction) in functionalized pyridinium ILs; an unfavorable entropic contribution to the Gibbs energy of solvation was likely the reason. Makino *et al.* (*66*) reported that an ester-functionalized IL actually reduced CO_2 solubility compared with non-functionalized ILs while a short-ether-chain-grafted IL showed minimum impact on CO_2 solubility on the mole fraction scale, but a higher molarity-scale solubility due to a smaller molar volume of functionalized IL. The same group (*67*) revisited the effect of ether-functionalization of both cations and anions on CO_2 dissolution, and found the anion functionalization to introduce alkoxy sulfates was more effective to increase CO_2 solubility on both the mole fraction and molarity scales. In the presence of superbases, hydroxy-containing surfactants and polyethylene glycols could dissolve CO_2 via chemical absorption (*68*), and hydroxy-containing ILs could absorb equimolar CO_2 reversibly (*69*).

Most physisorption studies in ILs applied relatively high pressures (>10 bar), but this is not practical for commercial-scale processes due to the large consumption of energy and high capital cost. The partial pressure of CO_2 in flue gases is even below atmospheric pressure. At ambient pressure and temperature, the CO_2 solubility in conventional ILs is only up to ~3.3 mol% or 0.3 wt% (based on low-pressure Henry's constants of 30–50 bar for common PF_6^- and Tf_2N^- types of ILs (*70*)). The practical CO_2 absorption conditions should be close to flue gas temperature (~45 °C) and pressure (~0.15 bar) (*71*).

Based on the forementioned rationales, this study focused on the design and synthesis of ether-functionalized phosphonium and ammonium-based ILs paired with acetate or Tf_2N^- anions for CO_2 dissolution under ambient conditions. We further examined the compatibility of alcohol dehydrogenase (ADH) in 0.5 M aqueous solutions of these ILs, which provided some feasibility data about how these ILs could be further employed in the enzymatic conversion of captured CO_2.

2. Materials and methods

2.1. Materials

3-Aminopropyltrimethoxysilane (**1**), 3-aminopropyltriethoxysilane (**2**), and *N*-(6-aminohexyl) aminopropyltrimethoxysilane (**3**) were acquired from Gelest Inc. (Morrisville, PA). Chemglass Cajon® Airfree® Bubbler with O.D.×H = 9×220 mm (Supplier No. AF-0085-01; VWR Catalog Number 80064-292), ammonium acetate (ultrapure), and tributylphosphine (95%, Acros Organics) were purchased from VWR (Radnor, PA). Triethylene glycol monomethyl ether (≥97.0% GC), 1-(2-bromoethoxy)-2-(2-methoxyethoxy)ethane (≥94.0%), 1,2-epoxy-2-methylpropane (≥99%, known as isobutylene oxide,1,1-dimethyloxirane, and 2,2-dimethyloxirane), and imidazole (≥99.0%) were obtained from TCI America (Portland, OR). Polyethylene glycol monomethyl ether with M.W. ~350 (PEG-350) and benzenesulfonyl chloride (≥98%) was acquired from BeanTown Chemical (Hudson, NH). Lithium bis(trifluoromethylsulfonyl)imide provided by VWR (Radnor, PA) is the product of Biosynth International Inc. (Oakbrook Terrace, IL). Amberlyst® A-26 (OH) ion exchange resin was produced by Alfa Aesar (Tewksbury, MA). Alcohol dehydrogenase (ADH) from *Saccharomyces cerevisiae* (catalog #A7011) as lyophilized powder (contains buffer salts) with ⩾300 units/mg protein, and β-nicotinamide adenine dinucleotide (NADH), reduced disodium salt hydrate was purchased from Sigma-Aldrich (St. Louis, MO).

2.2. Synthesis and characterization of functionalized ILs

See *Supporting Information* for reaction schemes (Schemes S1-S8) and NMR characterizations.

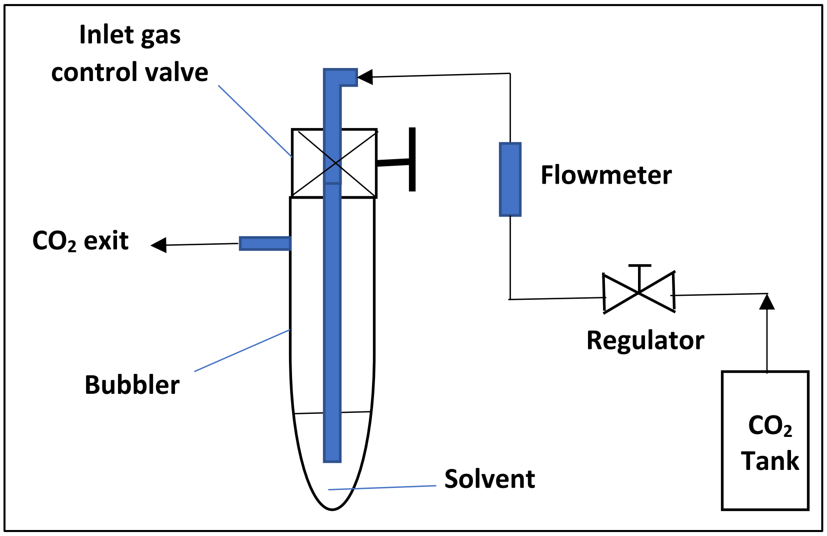


Figure 1 Flow diagram of CO_2 capture in ILs by using a bubbler.

2.3. CO_2 solubility determination

The CO_2 solubility in each solvent was determined by the bubbler setup shown in Figure 1. The empty bubbler was pre-weighed before adding 2.0–3.0 mL solvent, which was weighed again to determine the mass of each solvent. CO_2 (99.9%) was bubbled into the solvent through a regulator to control the flow rate at about 0.05 SCFM (standard cubic feet per minute). The bubbler was kept under ambient conditions (22 °C and atmospheric pressure). The bubbler containing the solvent and absorbed CO_2 was weighed on a balance every 15 min to observe the mass change over 1–3 h period. The absorption completed in 30-45 min in most cases. The mass of CO_2 captured was determined by subtracting the mass of bubbler and solvent before absorption from the total mass (bubbler + solvent + CO_2) after the absorption. The mass of CO_2 in each solvent was further converted into **CO_2 solubility (wt%)** and **mole of CO_2 per mol of solvent** by using the mass of each solvent.

2.4. Alcohol dehydrogenase (ADH) activity

A pre-determined amount of IL (final concentration as 0.5 M) was mixed with phosphate buffer (0.1 M, pH 6.5), 50 μL of 60 mM formaldehyde, and 50 μL of 20 mM NADH to make 980 μL solution. The absorbance of this mixture at 340 nm was determined as the blank. The reduction of formaldehyde to methanol was initiated by adding 20 μL of 500 mg/L ADH solution in phosphate buffer (0.1 M, pH 6.5) at room temperature (21 °C). The NADH absorbance in the reaction mixture at 340 nm was measured every 5 min to determine the initial reaction rate during the linear range. The molar absorptivity of NADH at 340 nm used in this study was 6,317 M^{-1} cm^{-1} at 25 °C and pH 7.8 (*72*). Relative ADH activity was calculated by dividing the ADH activity in 0.5 M solvent by the activity in phosphate buffer (0.1 M, pH 6.5).

3. Results and discussion

3.1. Design and synthesis of functionalized ILs

As discussed in Introduction, ether-functionalized ILs (i.e. containing alkoxy groups) tend to improve the CO_2 solubility, while hydroxy groups likely reduce or have no impact on the solubility. Poly(ethylene glycol)s (PEGs) typically contain multiple alkoxy groups; in addition, they are inexpensive solvents that have negligible vapor pressure, high chemical and thermal stability, and low toxicity. CO_2 solubility in PEGs increases with the molar mass of PEGs and pressure; however, longer PEG chains eventually lead to high solvent viscosity, therefore, up to PEG-400 is considered the optimum solvent (*73*). It was found that the mixing of PEG-600 or PEG-1000 with [BMIM][PF_6] could lead to higher viscosities than individual components (so called '"hyperviscosity") due to extensive hydrogen-bonding, but not in the case of PEG-200 and PEG-400 (*74*). Adding an alcohol such as 1-pentanol into PEG-200 could increase the CO_2 solubility (*75*). The addition of PEG-200 into an IL (i.e. [Choline][Pro]) could considerably improve CO_2 absorption and desorption rates (*76*). PEG-derived (*77*) or PEG-incorporated membranes (*78*) allowed a high CO_2 permeability and selectivity due to the CO_2-philic polyether. However, CO_2 solubility decreased in aqueous diethanolamine with the increase in PEG-400 concentration (*79*). Therefore, this study incorporated multiple alkoxy groups in IL cations paired with Tf_2N^- or OAc^- anions; both anions are known CO_2-philic in nature as discussed in Introduction.

Through the combination of previously established methods (see *Supporting Information*) (*80-85*), we synthesized glycol-functionalized ILs (see Table 1) based on imidazolium (**4**), phosphonium (**5**–**9**) and alkylammonium (**10** and **11**) paired with Tf_2N^- and/or OAc^- anions. As shown in Table 1, Tf_2N^--based ILs could be easily dried in vacuum oven to have 0.1 wt% or lower water, while the acetate type still contained 1.6–5.0 wt% water even after one week of extensive drying possibly due to strong hydrogen-bonding interaction between water and the acetate. Ether-functionalized ILs tend to have relatively lower viscosities (dynamic viscosities of 53–131 mPa s and kinematic viscosities of 41–109 mm^2/s at 30 °C) than alkyl analogues; due to higher flexibility of ether chains than rigid alkyl chains (*86*), the incorporation of ether chain in IL structures reduces intermolecular correlation (especially tail-tail segregation) and cation-anion specific interactions (*87, 88*).

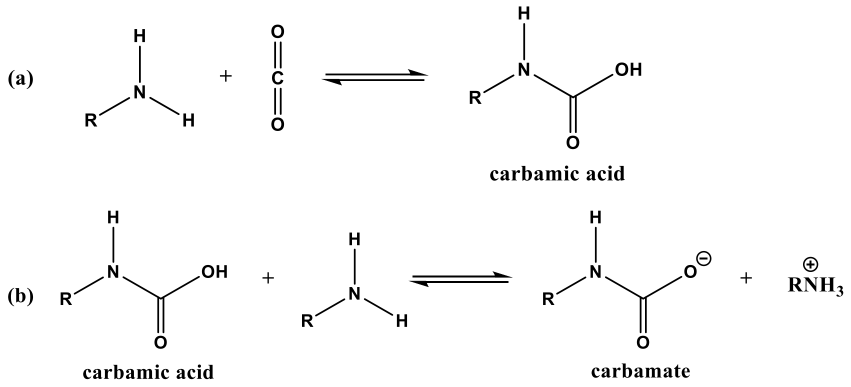
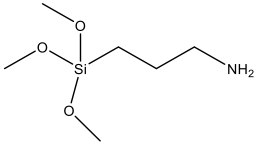
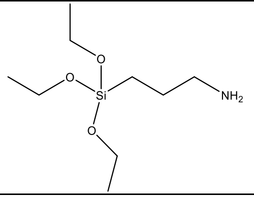
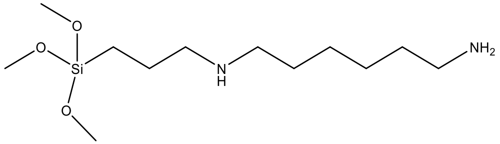
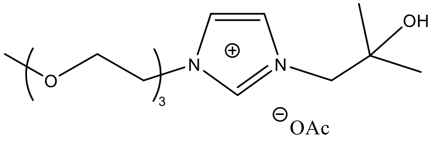
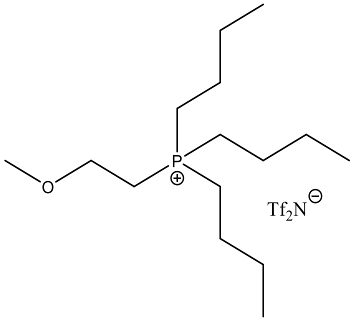
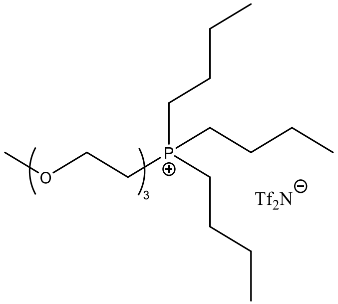
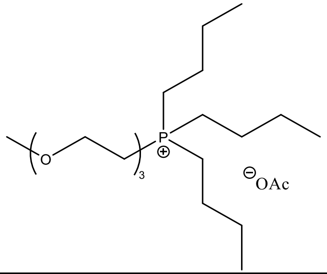
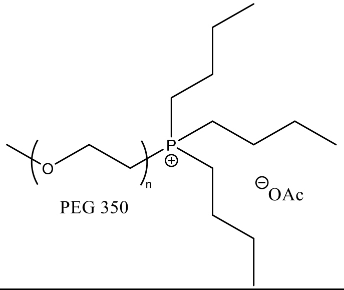
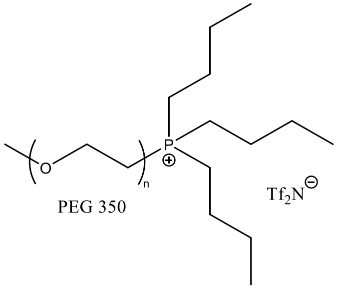
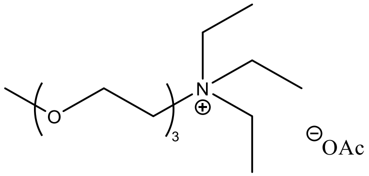
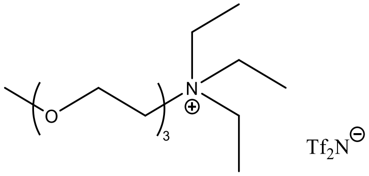


Figure 2 Reactions of amine with carbon dioxide.

Table 1 CO_2 solubility in functionalized solvents at room temperature and atmospheric pressure

	Structure	**Water content (wt%)** [a]	**Dynamic viscosity, kinematic viscosity, and density (30 °C)** [b]	**CO_2 solubility (wt%)**	**Mole of CO_2 per mol of solvent**
1		0.017	1.5535 mPa s 1.5496 mm^2/s 1.0025 g/cm^3	16.2	0.65
2		0.031	1.8538 mPa s 1.9697 mm^2/s 0.9411 g/cm^3	10.2	0.52
3		0.084	12.268 mPa s 12.637 mm^2/s 0.9708 g/cm^3	2.1	0.14
4		4.303	97.273 mPa s 88.385 mm^2/s 1.1006 g/cm^3 (11.17 wt% H_2O)	0.74	0.065
5		0.111	96.275 mPa s 78.277 mm^2/s 1.2299 g/cm^3	1.5	0.21

6		0.131	92.915 mPa s 76.811 mm^2/s 1.2097 g/cm^3	1.5	0.24
7		4.951	65.337 mPa s 66.359 mm^2/s 0.9846 g/cm^3	5.9	0.55
8		2.383	61.536 mPa s 60.838 mm^2/s 1.0115 g/cm^3	3.9	0.53
9		0.111	130.70 mPa s 109.27 mm^2/s 1.1961 g/cm^3	1.5	0.29

10		1.649	53.527 mPa s 50.194 mm^2/s 1.0664g/cm^3	5.3	0.37
11		0.09	54.900 mPa s 41.348 mm^2/s 1.3278 g/cm^3	1.3	0.15

Note: [a] The water content was determined by the coulometric Karl Fischer titration at 22 °C using Hydranal® Coulomat AG as the analyte. [b] The viscosity and density data at 30 °C were acquired by an Anton Paar SVM 3000 viscometer.

3.2. CO_2 solubility in ILs

Conventional chemical absorption of CO_2 using amine solutions (e.g. monoethanolamine) results in the formation of carbamate (*89*). Theoretically, 1 mole of primary amine could absorb 0.5 mol CO_2 to form carbamate (Figure 2) (*90*) while an excess CO_2 dissolved is due to physical absorption (*91*). On other other hand, Brennecke and co-workers (*92*) found that amino acid-anions could react with CO_2 at nearly 1:1 molar ratio to form carbamic acid (Figure 2a) while physical absorption of 1 bar CO_2 at 25 °C in amino acid-based ILs only accounted for 1–3% of total CO_2 uptake. In addition, Poly(dimethyl siloxane) (PDMS) (*93, 94*) and PDMS terminated with trimethylsilyl groups (*95*) are known as CO_2-philic solvents. Aminosilicones are commercially produced for textile and personal care application; aminosilicones and their mixtures with glycol could dissolve a significant amount of CO_2 (up to 21.8 wt% at 1 bar and 40 °C, or up to ~9 wt% at 0.1 bar and 45 °C) via chemisorption (*71, 96, 97*). Therefore, by using the bubbler setup illustrated in Figure 1 at room temperature and atmospheric pressure, we evaluated three commercial aminosilanes (see Table 1), namely 3-aminopropyltrimethoxysilane (**1**), 3-aminopropyltriethoxysilane (**2**), and *N*-(6-aminohexyl)aminopropyltrimethoxysilane (**3**), as substitutes of conventional aqueous amines because these aminosilanes are less volatile, low in viscosities (1.6–12.3 mPa s at 30 °C), and have both amino and silane CO_2-philic groups. The chemical absorption establishes the baseline for our physical absorption study using functionalized ILs. 3-Aminopropyltrimethoxysilane (**1**) showed a high capability of CO_2 absorption with 16.2 wt% CO_2 or 0.65 mol CO_2 per mole of solvent, which clearly demonstrated the chemical absorption. 3-Aminopropyltriethoxysilane (**2**) displayed a lower CO_2 solubility of 0.52 mol CO_2 per mole of solvent due to the bulkiness of trialkoxysilane group. Despite having two amine groups (primary and secondary), *N*-(6-aminohexyl)aminopropyltrimethoxysilane (**3**) only absorbed 0.14 mol CO_2 per mole of solvent because the mixture quickly turned into thick gel.

IL **4** consists of acetate anion and imidazolium cation functionalized with both *tert*-butanol and triethylene glycol ether, and exhibits weak ability of solubilizing CO_2 (0.065 mol CO_2 per mole of IL). The likely reason of poor CO_2 solubility is the presence of hydroxy group as discussed earlier. Ether-functionalized phosphonium-based ILs (**5**-**9**) enabled much higher CO_2 solubility (0.21–0.55 mol CO_2 per mole of IL) at ambient conditions; interestingly, a longer glycol chain (**6** *vs* **5**; **8** *vs* **7**) had a small impact on the CO_2 dissolution. However, the change of anion from Tf_2N^- to OAc^- drastically increased the CO_2 solubility (from 0.24 in IL **6** to 0.55 in IL **7**; from 0.29 in IL **9** to 0.53 in IL **8**). A similar trend was observed in glycol-functionalized ammonium-based ILs (10 and 11), where the CO_2 solubility increased from 0.15 in Tf_2N^--based IL **11** to 0.37 in acetate-based IL **10**. Therefore, even at room temperature and atmospheric pressure, glycol-functionalized ILs, especially those carrying acetate anions, could dissolve a considerable amount of carbon dioxide. A longer glycol chain on the cation imposes a minimum impact on the CO_2 solubility (ILs **5**, **6** and **9**; ILs **7** and **8**). However, different cation cores could have a drastic influence on the CO_2 dissolution; for example, phosphonium IL **7** could dissolve much more CO_2 than ammonium analogue **10** (0.55 vs 0.37 mol CO_2 per mol IL). Most CO_2 solubility data in ILs were reported at high pressures (>10 bar); there are limited literature results at atmospheric pressure that can be compared with. The CO_2 solubility in [EMIM][OAc] and [BMIM][OAc] at 25 °C and 0.1 MPa were reported to be about 27 mol% despite of much lower solubilities in [BMIM][BF_4] (1.5 mol%) (*32, 41, 48, 49*) and in [BMIM][CF_3COO] (1.8 mol%) (*32, 48, 50*). Our acetate-based IL **10** is comparable to [BMIM][OAc] and [EMIM][OAc] for CO_2 capture while ILs **7** and **8** could dissolve ~30 mol% more CO_2. In addition, our glycol-functionalized ILs are less viscous (**7**, **8** and **10**: 54–

65 mPa s at 30 °C) than [EMIM][OAc] (105.3 mPa s at 30 °C) (*98*) and [BMIM][OAc] (274 mPa s at 30 °C) (*99*). The CO_2 solubility in [BMIM][Tf_2N] at 25 °C and 1.01 bar was reported as 3.1 mol% (*19*), so it is comparable with functionalized Tf_2N^- based ILs **5**, **6**, **9** and **11**. Since oxygen (O_2) and nitrogen (N_2) are much less soluble in ILs compared with CO_2 (*19*), this IL method is highly applicable to direct air capture of CO_2.

The sorption of CO_2 was examined by FT-IR spectra to determine the nature of chemisorption and/or physisorption. As shown in Figure 3, CO_2 in 3-aminopropyltrimethoxysilane (**1**) displayed two characteristic IR bands at 1684 and 2338 cm^{-1}. The 1684 cm^{-1} band corresponds to the 2° carbamate carbonyl stretching following steps in Figure 2; previous studies have suggested that secondary carbamates absorb at 1705–1722 cm^{-1} (*100*), and ammonium carbamate absorbs at 1684 cm^{-1} (*101*). The 2338 cm^{-1} band represents CO_2 antisymmetric stretching mode, which indicates the physisorption of CO_2 (*102-104*). CO_2 in 3-aminopropyltriethoxysilane (**2**) showed similar IR bands (see Figure S1 in *Supporting Information*). In neat IL **7**, there is a strong IR band at 1575 cm^{-1} for acetate carbonyl, which became weakened when CO_2 was dissolved while the band at 1634 cm^{-1} was strengthened. The 1634 cm^{-1} band could be due to the interactions of acetate with CO_2 via different mechanisms such as the formation of non-volatile (*41*) or electron donor-acceptor (oxygens of acetate as Lewis base interacting with CO_2) complexes (*42, 43*), multidentate binding between CO_2 and acetate (*44, 45*), carboxylate-induced ylide intermediate (of phosphonium) resulting in chemisorption of CO_2 (*46*) (which is similar to the role of phenolate (*47*)). In IL **7**, CO_2 also exhibited the physisorption band at 2336 cm^{-1}. In two other acetate-based ILs (**10** and **8**, see Figures S1 and S2 respectively in *Supporting Information*), similar IR bands were observed except IL **10** showed a minimum band at 2338 cm^{-1}. In Tf_2N^--based IL **9**, only the physisorption of CO_2 band at 2338 cm^{-1} was shown, and the band at 1684 cm^{-1} was absent indicating no complexing interaction between CO_2 and Tf_2N^- anion (*54*). Carbonate and bicarbonate ions in aqueous solutions typically show strong infrared band in the region of 1300−1400 cm^{-1} (*104*). Figures 3, S1 and S2 suggest the absence of carbonate and bicarbonate anions in these solvents.

Other than CO_2, trace amounts of nitrogen oxides (NO_x) and sulfur dioxide (SO_2) can also be found in flue gases from burning fossil fuels. The solubility of SO_2 in Tf_2N^- based ILs tends to be much higher than that of CO_2, where the Henry law's constants of SO_2 physical absorption is more than one order of magnitude lower than that of CO_2 (*105*). In an acetate-carrying IL, [EMIM][OAc], SO_2 competes with CO_2 in dissolution, leading to a large decrease of CO_2 solubility (as much as 25%) in the presence of SO_2 (*106*). Anthony and co-workers (*19*) found the nitrous oxide (N_2O) solubility is similar to that of CO_2 in [BMIM][Tf_2N] due to quadrupole moments in both types of molecules. In summary, the presence of SO_2 and NO_x reduces the CO_2 solubility in ILs, especially with water in ILs (as ILs are generally hygroscopic) (*107*). Therefore, SO_2 and NO_x should be removed through the modifications of combustion process and the post-combustion treatment.

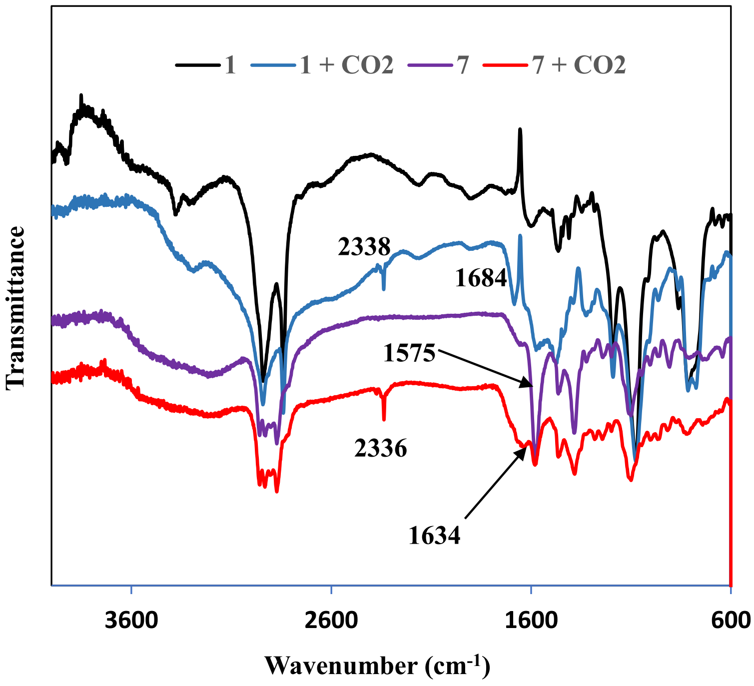


Figure 3 FT-IR spectra of CO2 dissolution in 3-aminopropyltrimethoxysilane (**1**) and IL **7** (The spectra were obtained through using a Thermo-Fisher Scientific Nicolet™ iS™ 5 FT-IR spectrometer equipped with an iD5 ATR (attenuated total reflection) accessory with 32 scans at a resolution of 2 cm^{-1} followed by 5-point smoothing.).

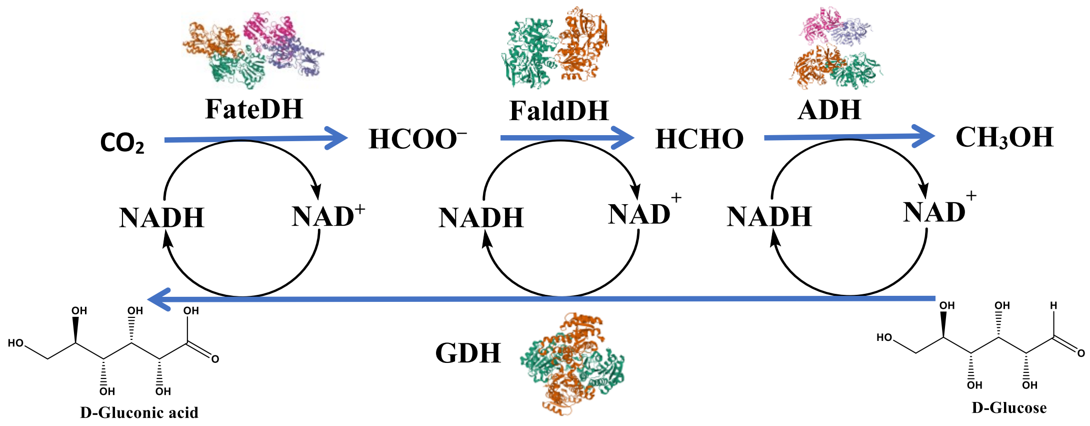
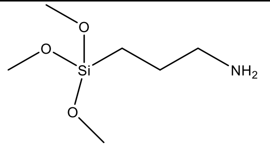
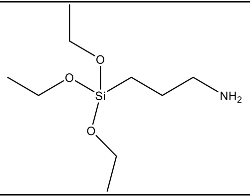
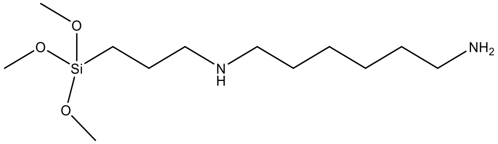
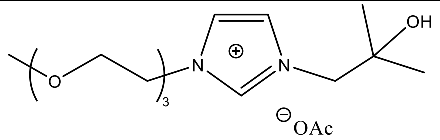


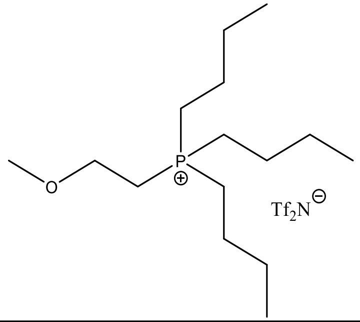
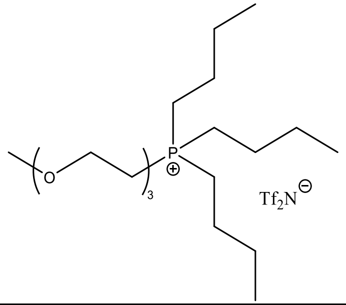
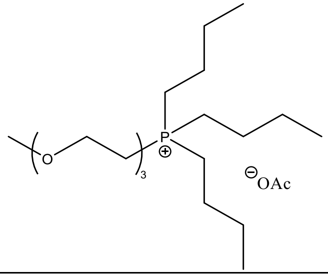
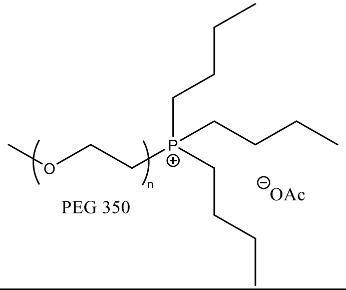
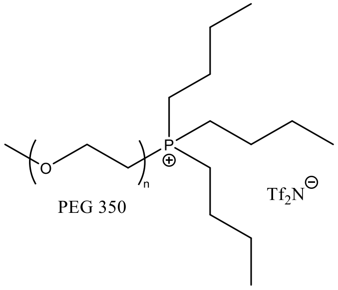
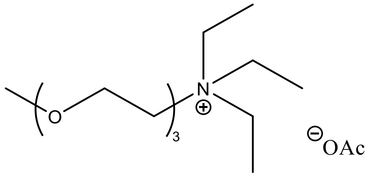
Figure 4 Enzymatic conversion of CO_2 to methanol using in situ regeneration of NADH. (Abbreviations of enzymes: FateDH—formate dehydrogenase; FaldDH—formaldehyde dehydrogenase; ADH—alcohol dehydrogenase; GDH— glucose dehydrogenase).

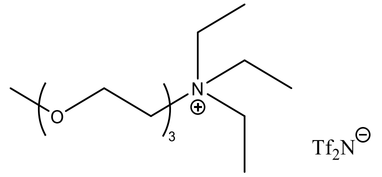
3.3. Alcohol dehydrogenase (ADH) activity in IL solutions

Carbon dioxide can be converted to methanol by a cascade enzymatic reaction involving three dehydrogenases (see Figure 4): formate dehydrogenase (FateDH) converting CO_2 to formate/formic acid, formaldehyde dehydrogenase (FaldDH) converting formate/formic acid to formaldehyde, and then alcohol dehydrogenase (ADH) converting formaldehyde to methanol (*108*). In each of these three reactions, reduced nicotinamide adenine dinuncleotide (NADH) acts as the terminal electron donor; with suitable electron donors, dehydrogenases are able to catalyze the reverse reactions (i.e. reduction). However, these reactions are usually carried out in aqueous buffers, where the solubility of CO_2 is very small. The low substrate (CO_2) availability becomes the bottleneck of the overall cascade reaction. In addition, the first reaction is usually considerably slower (e.g. 30 times (*109*)) than its reverse reaction (i.e. the oxidation of formate to CO_2), partly due to the low substrate solubility (*110*), but also due to low affinity of CO_2 with the enzyme (*109*).

Table 2 Relative alcohol dehydrogenase (ADH) activity in 0.5 M solution

	Structure	**Relative ADH activity in 0.5 M solution** [c]
1		0.54%
2		0.0%
3		0.0%
4		51%

5		85%
6		72%
7		1.1%
8		17%
9		59%
10		36%

11		75%

Note: The relative ADH activity was calculated from the division of ADH activity in the presence of 0.5 M silylether or IL by ADH activity in phosphate buffer (0.1 M, pH 6.5).

To demonstrate the concept of carrying out these reactions in functionalized IL solutions, we examined the last step of cascade reaction (ADH-catalyzed reduction of formaldehyde to methanol) in 0.5 M IL solutions (Table 2). Despite their chemical absorption power towards CO_2, aminosilanes (**1**–**3**) at 0.5 M concentration essentially completely inhibited the ADH activity possibly due to the strongly basic nature of amine groups. As shown in Table 2, Tf_2N^--based ILs (**5**, **6**, **9**, and **11**) are less inhibitory (59–85% relative activity) than acetate-containing ILs (**4**, **7**, **8**, and **10**) (1.1–51% relative activity). Interestingly, a longer glycol chain in Tf_2N^--based ILs (**5**, **6**, and **9**) led to a lower ADH activity (85% > 72% > 59%). Overall, ILs **5** and **6** showed the best performance in terms of high CO_2 solubility (0.21 and 0.24 mol CO_2 per mole of IL, respectively) and high ADH activity (85% and 72% relative activity, respectively). IL **10** performed the best among all acetate-based ILs for CO_2 capture (5.3 wt% CO_2, or 0.37 mol CO_2 per mole of IL) and ADH relative activity (36%). Therefore, strong CO_2-philic solvents often cause enzyme deactivating, and an optimized solvent for both CO_2 capture and enzyme compatibility can be obtained by designing the IL structure. It is well known that enzymes are more compatible with hydrophobic ILs (e.g. carrying Tf_2N^- and PF_6^- anions) than hydrophilic ILs containing basic anions such as acetate; a high concentration of acetate anion could form strong hydrogen bonds with enzymes to inactivate them (*111, 112*). Eckstein and co-workers (*113*) found that alcohol dehydrogenase from *Lactobacillus brevis* showed a higher reduction activity in a biphasic system with [BMIM][Tf_2N] than with methyl *tert*-butyl ether (MTBE). The Kroutil group (*114*) studied the reduction of ketones by alcohol dehydrogenase ADH-'A' from *Rhodococcus ruber* in aqueous ILs, and found 20% (v/v) [BMIM][Tf_2N] (~0.52 M) as a biphasic system reduced the enzyme activity to <60% of that in aqueous buffer while 20% (v/v) [BMIM][OAc] (~1.1 M) or [EMIM][OAc] (~1.3 M) as a homogeneous phase only slightly reduced the activity. Weibels *et al.* (115) compared the activity of yeast alcohol dehydrogenase in 0.5 M IL solutions during ethanol oxidation, and suggested that the enzymatic efficiency followed the Hofmeister series for anions: $Cl^- > Br^- > EtSO_4^- > OTf^- > BF_4^- > dca^- > SCN^-$, and for cations: $Me_4N^+ > Cholinium^+ > EMIM^+ > Et_4N^+ > Bu_4N^+ > guanidinium^+ > BMIM^+$. Bekhouche and co-workers (116) reported that formate dehydrogenase lost >50% of its activity in 10% (v/v) [BMIM][OAc] (~0.55 M). D'Oronzo *et al.* (*117*) observed that formate dehydrogenase's oxidation activities were preserved well in up to 40% (v/v) [BMIM][CH_3SO_3] but dropped quickly in >5% (v/v) [BMIM][OAc] (>0.28 M). It was rationalized that IL ions could have a direct binding with the protein resulting in conformational changes, and IL anions can bind with NAD^+ to disrupt the cofactor from binding with formate dehydrogenase. A more systematic evaluation of different dehydrogenases in different concentrations of various ILs is needed to fully understand how ILs influence the enzyme activity and stability.

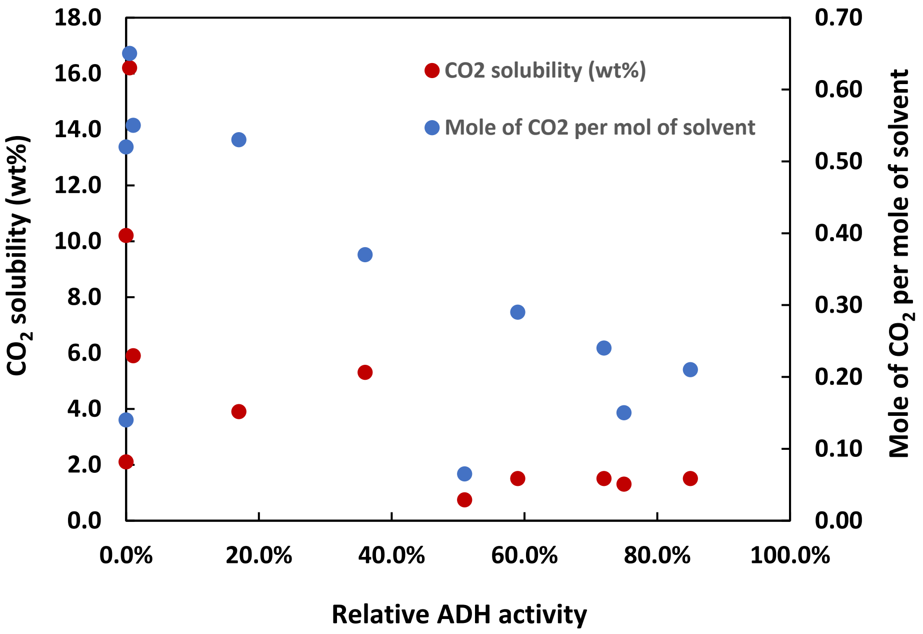


Figure 5 Correlation of solvent compatibility with ADH and CO_2 solubility.

To further illustrate the conflicting ability of solvents in dissolving CO_2 and maintaining high ADH activity, data in Tables 1 and 2 are plotted in Figure 5 to suggest that more CO_2-philic solvents are generally less ADH-compatible, especially when the CO_2 solubility is expressed in moles (except several solvents such as **3** and **4** in Table 1). *N*-(6-aminohexyl) aminopropyltrimethoxysilane (**3**) contains two amine groups and is probably too basic for ADH to maintain a high activity. Dual-functionalized IL (**4**) is more ADH-compatible (51% relative activity) than other acetate-based ILs (1.1–17%) because its hydroxy group interacts with acetate anion to minimize its enzyme-inactivating nature; for the same reason, the hydroxy group weakens the ability of acetate in dissolving CO_2. The Henni group (*27, 62*) pointed out that hydroxy-functionalized ILs reduced CO_2 solubility while ether-functionalized ammonium ILs increased the solubility.

4. Conclusions

Glycol ether-functionalized phosphonium and ammonium ILs carrying acetate and Tf_2N^- anions could dissolve up to 0.55 mol CO_2 per mole of IL (or 5.9 wt% CO_2) at room temperature and atmospheric pressure. Although acetate anions promoted a higher CO_2 solubility, Tf_2N^- anions allowed a higher compatibility with ADH. These preliminary results imply the feasibility of using functionalized ILs to capture CO_2 and convert it to methanol via an enzymatic route. Potential challenges of using ILs for CO_2 capture at an industrial scale include the high IL costs, relatively high IL viscosities, and IL biodegradability. Therefore, further studies should focus on the recycling and reusing of these ILs, and their potential environmental impact.

Disclosure statement

The authors declare no competing financial interest.

Funding

This material is partly based upon work supported by the National Science Foundation – Division of Chemistry under Grant No. [2244638]. Research reported in this publication was partly supported by the National Institute of General Medical Sciences of the National Institutes of Health under Award Number R15GM143682. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health.

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