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CO₂-binding organic liquids (CO₂BOLs) for post-combustion CO₂ capture.

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Abstract

CO₂-binding organic liquids (CO₂BOLs) chemically bind and release CO₂ more efficiently than aqueous alkanolamine systems. CO₂BOLs are comprised of alcohols and organic amidine or guanidine bases, which chemically bind CO₂ as liquid amidinium or guanidinium alkylcarbonate salts. CO₂BOLs have high CO₂ binding capacities (19% by weight, 147 g CO₂/L) compared to that of 30% monoethanolamine solution in water (7% by weight, 108 g CO₂/L) because they are liquid with or without bound CO₂ and do not require any added solvent such as water.

The dissolution of CO₂ into and out of the liquid phase limits the rate of CO₂ capture and release. Absorption of CO₂ is selective over nitrogen in both concentrated and dilute gas streams making these systems applicable to post- and pre-combustion CO₂ capture. The free energy of CO₂ binding in these systems is small and is independent of the choice of alcohol. The free energies of these systems are dependent on the choice of base; -9 kJ/mol for diazabicyclo[5.4.0]undec-7-ene (DBU) and Barton's base and +2 kJ/mol for 1,1,3,3-tetramethylguanidine. The specific heats of the organic CO₂BOLs are over 50% lower than that of water, resulting in a 50% reduction in the energy needed to strip out CO₂ as compared to aqueous alkanolamine solutions. CO₂BOLs have been recycled for five cycles without losing activity or selectivity towards CO₂.

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1. Introduction

The primary chemical CO₂-scrubbing agents in post-combustion systems are aqueous alkanolamines. While alkanolamines effectively bind CO₂ in systems where the CO₂ concentrations rarely exceed 5-15 volume %, these systems have inherent drawbacks such as corrosion, suboptimal gravimetric and the volumetric CO₂ capacity, solvent loss, and the high specific heat of water.¹ In the case of monoethanolamine (MEA) systems, the concentration of MEA is limited by system

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corrosion and rarely exceeds 30 wt %.² The 30 wt% loading of the CO₂ absorbing MEA limits the maximum CO₂ volumetric (≤ 108 g/L) and gravimetric capacity (≤ 7 wt%) of the aqueous MEA based CO₂ scrubbers.² The 30% MEA loading limit necessitates a large excess of water as a solvent to dissolve the MEA, the CO₂ carrier. The pumping and heating of this excess water greatly increases the energy requirements for CO₂ scrubbing. The energy requirements for CO₂ stripping from aqueous MEA systems are also increased by the high specific heat of water ($4 \text{ J g}^{-1} \text{ K}^{-1}$).³ Thermal stripping of CO₂ from aqueous systems at temperatures greater than 100 °C leads to large evaporative losses of solvent, which has to be recovered. Switching to organic, high-boiling, liquid compounds that chemically bind CO₂ would reduce solvent loss during CO₂ stripping, reduce the high specific heats associated with water, and reduce system corrosion as well as improve volumetric and gravimetric capacity for CO₂ capture compared to aqueous MEA systems.

We recently reported an innovative CO₂-selective solvent system, known as CO₂ binding organic liquids (CO₂BOLs).⁴ CO₂BOLs are liquid mixtures of an alcohol and a strong amidine or guanidine base that chemically bind CO₂ to form the respective liquid amidinium or guanidinium alkylcarbonate salt (Figure 1).⁵⁻⁸ CO₂BOLs are liquids when CO₂ is bound or not; no superfluous inert solvent is needed to dissolve the CO₂ carrier. The first CO₂BOL in our study (DBU:1-hexanol) is capable of chemically binding 1 mol of CO₂ per mol DBU (15 wt. %) with an additional physical adsorption of 0.3 mol of CO₂ per mol of DBU (4 wt. %) bringing the theoretical maximum CO₂ capacity to 19 wt. % and 147 gCO₂/L liquid. The chemical and physical binding of CO₂ gives CO₂BOLs potentially twice the CO₂ gravimetric capacity and a 36 % increase in volumetric capacity than current 30% MEA solutions in water (7 wt. %, 108 g/L liquid).

CO₂BOLs chemically bind CO₂ as a liquid alkylcarbonate in contrast to the aqueous alkanolamines that bind CO₂ as a bicarbonate or carbamate salt.² Aqueous carbamate and bicarbonate salts have high hydrogen bonding which increases the binding enthalpy of CO₂. The reduced hydrogen bonding in organic alkylcarbonate salts decreases the enthalpy, meaning that less energy is needed for thermal stripping of CO₂. Certain CO₂BOLs have been shown to release chemically bound CO₂ slowly even at room temperature.^{5,6}

The alcohol and base components can be changed to produce a CO₂BOL with the desired physical and chemical properties, such as specific weight capacity, volumetric capacity, CO₂ stripping temperature, or any other desired physical properties. All linear alcohols and certain secondary alcohols are suitable for CO₂BOL systems. Organic bases such as amidines, guanidines, phosphazines, and possibly some amines are suitable base choices. The structures of the four bases discussed in this study are shown in Figure 2.

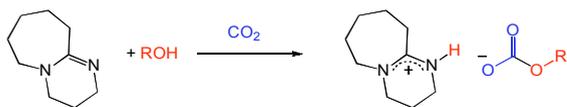


Figure 1. Reversible binding of CO₂ with an amidine (DBU) and alcohol.⁴ Reproduced by permission of The Royal Society of Chemistry

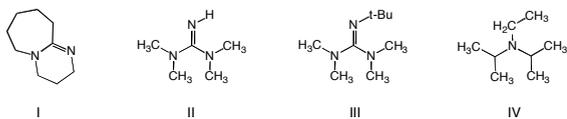
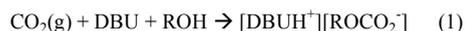


Figure 2. Bases investigated in this study. I. Diazabicyclo[5.4.0]-undec-7-ene (DBU), II. 1,1,3,3-Tetramethylguanidine (TMG), III Barton's base, IV Hunig's base.⁴ Reproduced by permission of The Royal Society of Chemistry

2. Results and discussion

CO₂BOLs are liquids before CO₂ is present and trap CO₂ as liquid amidinium or guanidinium alkylcarbonate salts and do not require superfluous solvents to dissolve the solid CO₂ absorbents like aqueous MEA based systems. The first CO₂BOL; DBU:1-Hexanol is capable of chemically capturing one mole of CO₂ per mol DBU (15 wt. %) at room temperature, but it can also physically adsorb 0.3 equivalents (4 wt. %) bringing the theoretical capacity to 19 wt % and 147 gCO₂/L liquid. This combined chemical and physical adsorption captures more CO₂ by weight and volume than a 30% aqueous MEA system (7 wt. %, 108 g/L liquid). The weight and volumetric capacity of CO₂BOLs can be increased by switching to smaller alcohols such as methanol and lighter bases such as TMG.

The uptake of CO₂ by these CO₂BOL mixtures is mildly exothermic and appears to be dependent on the rate of CO₂ diffusion into the CO₂BOL liquid. Initial kinetic investigations of CO₂ uptake were performed using changes in the conductivity of an acetonitrile solution of an amidine or guanidine bases and an alcohol CO₂BOL over time. CO₂BOLs are non-conductive until CO₂ is present; the resulting amidinium or guanidinium alkylcarbonate salt produces conductivity change (Equation (1)) Figure 1).⁵⁻⁷



The rate of CO₂ uptake at 28 °C was complete within 20 seconds regardless of the choice of base (DBU or TMG) or the choice of alcohol (ethanol, 1-propanol, 1-butanol, 1-pentanol, or 1-hexanol). However, the rate of uptake was strongly dependent on the stirring rate, indicating that the reaction was limited by the rate of mass-transfer of CO₂ from the gas phase into the solution rather than by the reaction of the dissolved CO₂ with the base and alcohol. We attempted to increase the rate of mass-transfer of CO₂ into solution by exclusively using liquids pre-saturated with CO₂ and by increasing the stir-rate to 500 rpm, but the rate remained dependent on the stir-rate. The process is as rapid as mass transport (mixing) will allow, which is clearly promising for CO₂ capture applications.

CO₂BOLs are selective for CO₂ binding in the presence of concentrated and dilute nitrogen. Our previous investigations showed that DBU:1-hexanol was able to capture CO₂ selectively from a mixture of CO₂ and N₂ at 1 atm.⁹ The ability to capture CO₂ at reduced partial pressures of CO₂ shows that CO₂BOLs have potential for post-combustion CO₂ capture. Capture of CO₂ in concentrated gas streams was demonstrated by placing a 1:1 molar ratio of DBU and 1-hexanol under 50 psi N₂ in a stainless steel pressure vessel. The solution was stirred at a constant rate and was monitored for changes in temperature and pressure as well as conductivity to indicate chemical capture of CO₂. There was no decrease in pressure or change in conductivity until 1 molar equivalent (50 psi) of CO₂ was introduced to the system bringing the total pressure to 100 psi. A pressure drop of 50 psi (Figure 3) was observed with a concurrent spike in the conductivity of the solution indicating that CO₂ was being consumed and the [DBUH⁺][ROCO₂⁻] salt was formed. The demonstrated selective capture of CO₂ in 50% CO₂/N₂ pressurized streams suggests CO₂BOLs can be designed for pre-combustion CO₂ capture.

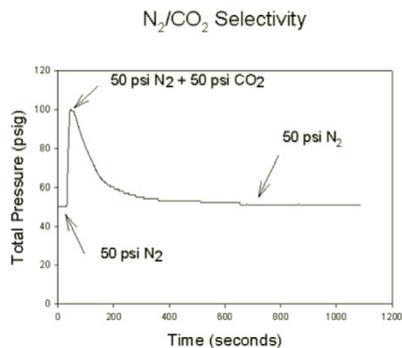
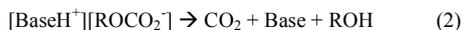


Figure 3. Selectivity of DBU:1-hexanol for CO₂ in an N₂/CO₂ mixture.⁴ Reproduced by permission of The Royal Society of Chemistry

CO₂ Release

CO₂ stripping from CO₂BOLs (equation 2) was studied on an automated burette system. Pre-CO₂-saturated CO₂BOLs were plunged into a pre-heated oil bath under agitation and examined for CO₂ evolution. Decarboxylations at 90 °C were nearly complete within 1 minute at 250 rpm. from DBU and TMG CO₂BOLs with 1-hexyl, 1-pentyl, and 1-butyl alcohols. CO₂ evolution from all CO₂BOLs was determined to be first order with respect to the CO₂BOL salt concentration in solution. The chain length of the linear alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol) did not affect the rate of CO₂ evolution from DBU CO₂BOLs. The CO₂ evolution did appear to be dependent on the stirring rate of the solution, suggesting mass-transfer limitations of CO₂ escaping from solution, instead of limitation due to the decarboxylation of the alkylcarbonate anion. The Arrhenius plot of the first order rate constant yielded an E_{act} for CO₂ release of between 23-33 kJ/mol.



The total volume of CO₂ released in the burette was correlated to the stripping temperature. At room temperature, CO₂BOLs do not decarboxylate under a static atmosphere.⁹ Gentle heating or sparging with an inert gas is required to remove CO₂ from CO₂BOLs because of the thermodynamic equilibrium between dissolved and gaseous CO₂.⁵ On average, the DBU and TMG CO₂BOLs with 1-hexyl, 1-pentyl, and 1-butyl alcohols evolved 0.25 equivalents of CO₂ at 50 °C, 0.50 equivalents at 70 °C, 0.65 equivalents at 90 °C, and up to 1 equivalent near 130 °C.

Nearly 60% of the energy for CO₂ scrubbing from power plants involves the thermal stripping of CO₂ from the scrubber.² The high energy requirements for alkanolamine solutions are due to the high specific heat of the solvent water (4.18 J g⁻¹ deg⁻¹).¹⁰ The specific heat of the organic DBU/1-hexanol CO₂BOL is 1.5 J g⁻¹ deg⁻¹. This is similar to other ionic liquids such as 3-ethyl-1-methyl-imidazolium tetrafluoroborate (1.28 J g⁻¹ deg⁻¹) and 3-butyl-1-methyl-imidazolium tetrafluoroborate (1.66 J g⁻¹ deg⁻¹).¹¹ The low specific heats associated with CO₂BOLs mean that CO₂ stripping at comparable temperatures to MEA, require up to 60% less energy, reducing the energy needed for CO₂ scrubbing.

Lifetime

The DBU/1-hexanol CO₂BOL was exposed to five capture and release cycles of CO₂ using an automated gas burette system to verify the robustness and reproducibility of the CO₂BOL system. The DBU/1-hexanol was loaded in a flask and CO₂ was sparged through the liquid for 5 minutes, making the [BaseH⁺][ROCO₂⁻] salt. After CO₂ uptake had ceased, the flask was connected to the burette system and then decarboxylated by dipping the flask into a pre-heated oil bath at 90 °C. (Figure 4). After CO₂ evolution had ceased, the flask was cooled to 25 °C and the flask was disconnected from the burette and then promptly carboxylated again by sparging CO₂ through the liquid for 5 minutes. This process was performed a total of 5 times, with no observable loss of CO₂ binding capacity. Formal measurements are underway to determine the lifetime of CO₂BOLs on mock flue gas streams.

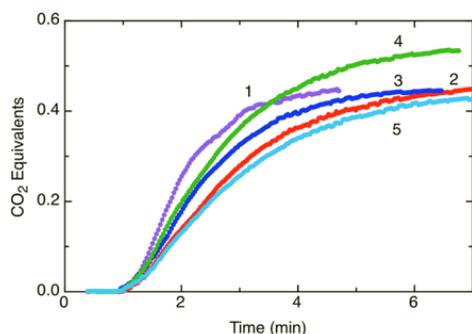


Figure 4. Lifetime/repeated CO₂ release from DBU and 1-Hexanol at 90 °C. Heating begins at 1 minute.⁴ Reproduced by permission of The Royal Society of Chemistry

Evaporative losses of solvent with aqueous MEA systems² will not be observed with CO₂BOLs as long as high boiling alcohols and bases are employed. Even if the CO₂ is stripped from CO₂BOLs at the same temperature as MEA systems (117 °C) this is far below the boiling point of both 1-hexanol (159 °C) and DBU (256 °C). The volatility of the CO₂BOL components can also be reduced by switching to even higher boiling alcohols such as 1-octanol and 1-decanol.

In our initial report, we showed that while the introduction of water with the CO₂ stream could produce large amounts of the bicarbonate salt, the bicarbonate salt could be stripped at the same temperature as an MEA system. Any water in the CO₂ stream competes with the alcohol. A large excess of alcohol can drive the formation of the CO₂BOL and not the bicarbonate.

The thermally stable CO₂BOL bicarbonate salt, [DBUH⁺][HCO₃⁻] rather than the CO₂BOL alkylcarbonate [DBUH⁺][ROCO₂⁻] will be produced if large amounts of water are present. In our previous studies, the CO₂ source had minimal water content. Industrial gas streams can contain up to 15% water.¹² CO₂ can be stripped from the [DBUH⁺][HCO₃⁻] bicarbonate salt at 121 °C, which is comparable to temperatures used for stripping CO₂ from MEA systems. The [DBUH⁺][HCO₃⁻] bicarbonate salt was measured to have a specific heat of 1.5 J g⁻¹ deg⁻¹, which is 60% less than that of water, meaning that even stripping of CO₂ from the [DBUH⁺][HCO₃⁻] bicarbonate salt is more energy efficient than stripping of aqueous MEA systems.

Thermodynamics

Approximate thermodynamic data for fifteen CO₂BOLs were determined by ¹H NMR spectroscopic measurements of the CO₂ binding equilibrium (equation 1, Table 2). The concentrations of CO₂BOLs with and without CO₂ bound were measured

in *d*-MeCN because the viscosity of the neat CO₂BOLs results in very broad ¹H NMR peaks. Placing CO₂BOLs into an organic solvent results in a slightly lower CO₂ capacity¹³ than neat systems⁷. The α-hydrogens of the free *RCH₂OH* and bound *RCH₂OCO₂* were evaluated over a temperature range of 24-60 °C, and the reaction enthalpy was extrapolated from the slope of the Van't Hoff plot of the measured equilibrium. Barton's base was measured over 25-50 °C because of curvature of the Van't Hoff plot, attributed to the temperature range being too large.

The data show very clear trends (Table 2.). The ΔH and ΔG values are almost independent of the choice of alcohol. Linear alcohols have almost identical pK_a values in *d*-MeCN, so the similarities were expected. Iso-propanol has slightly larger ΔG values because of its steric bulkiness which destabilizing the alkylcarbonate anion. Tert-butanol and other tertiary alcohols are unable to form detectable amounts of [BaseH⁺][ROCO₂⁻], almost certainly due to steric crowding which destabilizes the alkylcarbonate anion.

Table 2. Thermodynamics of the capture of CO₂ by select CO₂BOLs in MeCN, estimated by NMR spectroscopic determination of equilibrium constants.^{a,4} Reproduced by permission of The Royal Society of Chemistry

Base/Alcohol pair	ΔH, kJ/mol ^a	ΔS, J/molK ^b	ΔG, kJ/mol ^c	% CO ₂ absorption in MeCN at 25 °C
DBU/HexOH	-140	-440	-9.4	87
DBU/PentOH	-120	-390	-7.5	82
DBU/BuOH	-140	-450	-9.7	88
DBU/ PrOH	-130	-420	-7.8	83
DBU/ <i>i</i> -PrOH	-140	-450	-5.7	76
DBU/linear alcohol ^d	-136	-425	-8.6	-
TMG/HexOH	-160	-530	1.6	42
TMG/PentOH	-210	-710	0.7	47
TMG/BuOH	-180	-590	2.4	38
TMG/PrOH	-170	-590	2.3	39
TMG/ <i>i</i> -PrOH	-160	-550	5.5	25
TMG/linear alcohol ^d	-180	-610	1.7	-
Barton's/HexOH	-83	-250	-11	90
Barton's/PentOH	-52	-150	-8.7	85
Barton's/BuOH	-60	-180	-8.0	83
Barton's/PrOH	-53	-160	-9.0	86
Barton's/ <i>i</i> -PrOH	-76	-240	-7.7	82
Barton's/linear alcohol ^d	-72	-210	-9.2	-

^aData rounded to two significant figures. ^bCalculated at 25 °C from NMR integrations using $\Delta G = -R^*T \ln K_{eq}$, $K_{eq} = \frac{[\text{BaseH}^+][\text{ROCO}_2^-]}{P_{\text{CO}_2}[\text{Base}][\text{ROH}]}$. ^cCalculated at 25 °C using $\Delta G = \Delta H - T\Delta S$. ^dAverage of the unrounded values for PrOH, BuOH, PentOH, HexOH

The CO₂ binding energies are strongly correlated to the choice of base. Averages for the three bases paired with linear alcohols are listed in Table 2. The dependence of the enthalpy of the reaction with respect to base is correlated to the order of decreasing exothermicity: TMG > DBU > Barton's base. TMG was the weakest Bronsted base of the three chosen in this study with a pK_{aH} (of the conjugate acid, meaning the pK_a of the conjugate acid of TMG in MeCN) of 23.3^{14,15} CO₂ binding with TMG and linear alcohols had the most favorable reaction enthalpy because of greater hydrogen bonding in [TMGH⁺][ROCO₂⁻] than in the corresponding DBU and Barton's CO₂BOLs (see discussion below and Figure 5). This greater hydrogen bonding in the TMG CO₂BOLs would also be expected to lower the entropy of the reaction. The ΔS term is the major factor for the positive ΔG and the resulting weakest capture of CO₂ of the three bases. DBU was the intermediate Bronsted base (pK_{aH} in MeCN is 24.3).^{18,19} Barton's base was the strongest of the three Bronsted bases (estimated pK_{aH} in MeCN is 25.3).¹⁶ DBU and Barton's base were very close in their capability to bind CO₂. DBU had a much more favorable reaction enthalpy (-140 kJ/mol for DBU vs. -83

kJ/mol for Barton's) due to greater hydrogen bonding capability, compared to Barton's base, which has a more favorable entropy ($-390 \text{ J/mol}\cdot\text{K}$ for DBU vs. $-185 \text{ J/mol}\cdot\text{K}$ for Barton's base), effects which are attributed to steric repulsion between the cation and anion. For comparison, the enthalpy of Barton's base is comparable to that of a 30 wt. % MEA solution in water at 40°C (-80 kJ/mol CO_2).¹⁷ The entropy and enthalpy terms contribute to the overall reaction energetics but they are not linearly correlated to the pK_{aH} of the bases used to bind CO_2 with linear alcohols.

Hydrogen bonding contributes significantly to the stabilization of the CO_2 BOL alkyl carbonate salt structures. Too much hydrogen bonding (as shown in the case of TMG) can decrease the ΔG of CO_2 binding by a larger than desired decrease in the entropy of the system. The selection of a suitable base for a CO_2 BOL must consider the availability and strength of hydrogen bonds when CO_2 is bound. As shown in Figure 5, the alkylcarbonate salts of DBU and Barton's base appear to have less hydrogen bonding compared to TMG because $[\text{TMGH}^+]$ has two hydrogen-bond donor sites while DBU and Barton's base have only one. The 6-member ring of the TMG alkylcarbonate salt is entropically favorable and similar to other 6 member rings of carboxylates and amidines.¹⁸ The highly delocalized cations of amidines and guanidine bases in general are weak hydrogen bond donors and acceptors¹⁹ compared to localized amines such as triethylamine. Hydrogen bonds in the anion could also explain the preference for amidines and guanidines to bind CO_2 with water rather than alcohols. Crystal structures of the bicarbonate $[\text{DBUH}^+][\text{HOCO}_2^-]$ ²⁰ have more extensive hydrogen bonding than the methylcarbonate $[\text{DBUH}^+][\text{CH}_3\text{OCO}_2^-]$ and its CO_2 binding is enthalpically more favorable.⁷

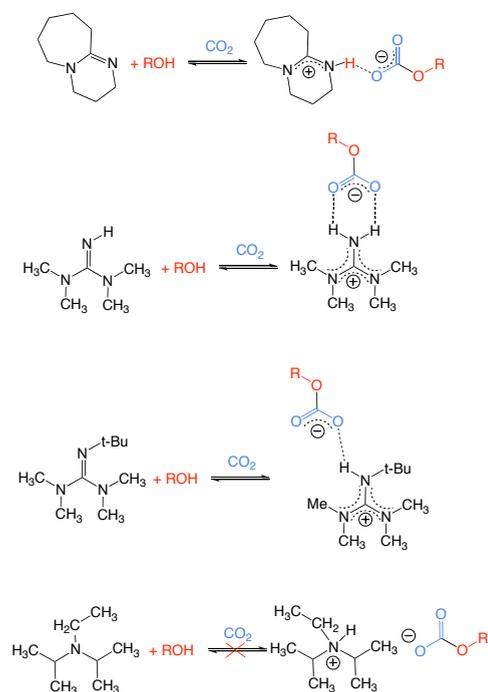


Figure 5. Proposed hydrogen bonding of cation with anion for salts made from DBU, TMG and Barton's base with ROH and CO_2 .⁴ Reproduced by permission of The Royal Society of Chemistry

The hydrogen bonding of the salts can also explain the reaction entropies. The ΔS term for Barton's base is less negative because the bulky tert-butyl group forces the alkylcarbonate anion farther away from the Barton H^+ cation, reducing available hydrogen bonding. The decreased steric crowding around the protonated nitrogen in DBU compared to Barton's base results in a more ordered system and in turn a more negative ΔS term. The ΔS term is most negative for TMG, due to the highly ordered 6-member hydrogen-bonding ring that is entropically unfavorable. This data clearly shows that the pK_{aH} of bases in CO_2 BOLs is not a valid predictor of the strength of CO_2 binding; the hydrogen bonding and the reaction entropy must be included in the selection process.

The thermodynamics confirm that choice of a linear alcohol with a chain length greater than two carbons has a minimal effect of the binding energies of CO_2 . We have shown that while alcohol choice does not alter the thermodynamic properties of CO_2 BOLs, the choice of alcohol can affect physical properties such as melting point and viscosity.^{5,6} CO_2 BOLs can be molecularly tuned to meet desired physical properties because of the ability to change the alcohol without major effects on CO_2 binding.

Triethylamine and Hünig's base were not able to form CO_2 BOLs under ambient conditions, and we anticipate that this is true for all tertiary amines. Hünig's base and other tertiary amines should be basic enough (pK_{aH} 's in MeCN $\sim 18.1 - 18.8$)^{21,22} to be protonated by the alkylcarbonic acid in CO_2 BOLs, but it remains unclear because there are no known pK_a 's of alkylcarbonic acids. Tertiary amines can form CO_2 BOLs at high pressures. Triethylamine in methanol produces the $[NEt_3H^+][CH_3OCO_2^-]$ salt at high pressures, but the salt is rapidly decarboxylated when the pressure is reduced to atmospheric conditions.²³ It is possible that the high pressure formation of a tertiary amine CO_2 BOL could be used for precombustion CO_2 capture.

The delocalized amidinium and guanidinium alkylcarbonate salts result in weakened interactions between the cation and anion of the ionic liquid. We hypothesize that the delocalization of both the cation and anion are key to the chemical and physical properties of these liquids. Formal investigations into the effect of the delocalization of the cation and anion on properties such as viscosity, melting point, as well as thermodynamic properties binding and release of CO_2 are underway.

3. Conclusions

CO_2 BOLs are a new class of liquid, organic, CO_2 capture agents that can continually bind and release CO_2 with a high gravimetric and volumetric CO_2 capacity up to 19 % by weight and 147 g/L liquid. CO_2 BOLs are neat mixtures of alcohols and strong organic bases that require no solvent. The rate of CO_2 binding and stripping from CO_2 BOLs appears to be mass-transfer limited by the rate of CO_2 movement into and out of the liquid phase. CO_2 uptake was selective in both dilute and concentrated streams, suggesting CO_2 BOLs are applicable to post- or pre-combustion scrubbing systems. CO_2 BOLs chemically bind CO_2 as alkylcarbonate salts with binding energies of less than 10 kJ/mol, which are weaker than the binding energies of the bicarbonate and carbamate salts in aqueous systems. The organic CO_2 BOLs have low specific heat compared to aqueous systems, resulting in less energy required for stripping of CO_2 when compared to aqueous alkanolamine systems. If water is present in the gas stream, CO_2 BOL bicarbonate salts will be formed, however they can be broken down at the same temperatures as MEA systems, but over 50% more efficiently due to the lower specific heat of CO_2 BOLs and CO_2 BOL bicarbonates than water and MEA.

The energetics of CO_2 binding are unrelated to choice of alcohol, but they are dependent on the choice of base, however they are not linearly correlated to the pK_{aH} of the base. CO_2 BOLs can be fine tuned to produce the desired chemical and physical properties by appropriate selection of the alcohol and base components. All of these properties suggest CO_2 BOLs are energy efficient CO_2 capture systems.

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