Performance of single-component CO_2-binding organic liquids (CO_2BOLs) for post combustion CO_2 capture

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ABSTRACT

We report the performance of multiple CO_2 binding organic liquids (CO_2BOLs) as solvent systems for post combustion gas capture. Alkanolguanidines and alkanolamidines are single component CO_2BOLs that reversibly bind CO_2 chemically as liquid zwitterionic amidinium/guanidinium alkylcarbonates. Select alkanolguanidines/alkanolamidines and guanidine/alcohol mixtures were tested for CO_2 capacity and solvent lifetime. Solvent performance of these three CO_2BOLs was assessed by batchwise CO_2 uptake and release over multiple cycles. We report each CO_2BOL's activity and solvent durability with and without water.

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1. Introduction

CO_2-binding organic liquids (CO_2BOLs) have been gaining attention as a plausible post-combustion CO_2 capture solvent system. Not to be confused with conventional ionic liquids (ILs) that physically dissolve CO_2 or ILs chemically modified with amines to chemically capture CO_2 [1–4], CO_2BOLs are organic liquids that convert into ionic liquids upon chemical capture of acid gases (e.g. CO_2, SO_2) [5–9]. CO_2BOLs consist of either a mixture of a strong organic amidine or guanidine base and an alcohol (dual component) or an alcohol functionalized strong organic amidine or guanidine base (single component) (Scheme 1). Amidine and guanidine bases are the primary bases utilized for CO_2 capture due to their strong basicity yet low reactivity towards carbon dioxide [10–12]. In contrast, primary and secondary amines function through direct amine/CO_2 insertion to form carbamates [8,13–16]. CO_2BOLs capture carbon dioxide by addition of CO_2 into an alcohol to form amidium or guanidinium alkylcarbonates. When the appropriate base and alcohol are used the resulting salt is an ionic liquid, a property well suited to industrial carbon dioxide capture applications [17–19]. Also of benefit is the readily reversible

CO_2 binding nature of CO_2BOLs; in most cases decarboxylation can be accomplished by the modest heating or simple inert gas bubbling.

Our first-generation materials were dual component blends of free alcohol and base (Scheme 1). We then functionalized the bases with alcohols, dubbed single component systems, in an effort to reduce the overall volatility of the material, increase the wt.% CO_2 uptake capacity and provide unimolecular phase behavior.

Here we investigate CO_2BOL robustness for various dual as well as single component CO_2BOLs. We report the relative volatility and wt.% carbon dioxide uptake of numerous single component alkanolamidines and a single alkanolguanidine vs. those of dual component systems (Fig. 1 and Tables 3–5). Because the binding efficiencies of CO_2BOL systems are influenced by simple acid–base chemistry, we also investigated and report for the first time the computationally estimated pK_a values of multiple alkylcarbonic acids in acetonitrile (Tables 1 and 2). To the best of our knowledge the alkanolamidines and alkanolguanidines chemically bound to carbon dioxide are the first examples of switchable zwitterionic liquids.

2. Materials and methods

2.1. NMR method

^{1}H NMR and ^{13}C NMR spectra were acquired on a Varian 300 MHz spectrometer. All samples were run in d-DMSO, $CDCl_3$ or

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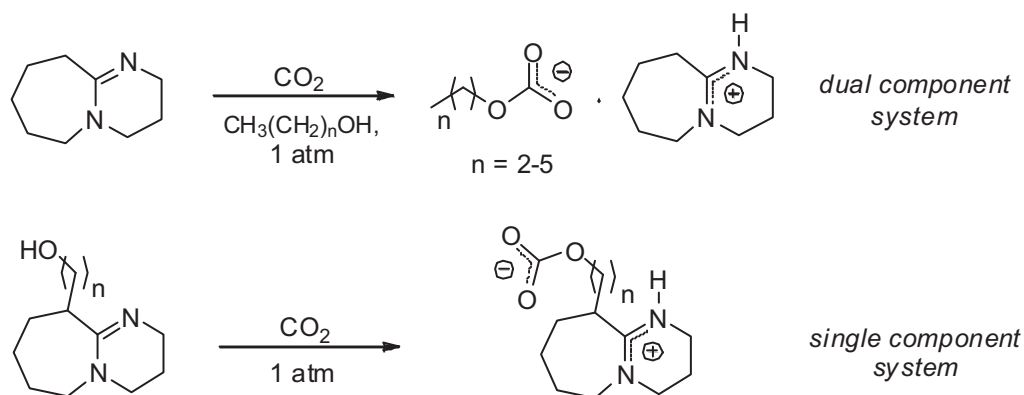
Scheme 1. Examples of dual and single component CO_2 BOLs with diazabicyclo[5.4.0]undec-7-ene (DBU) as the base core.
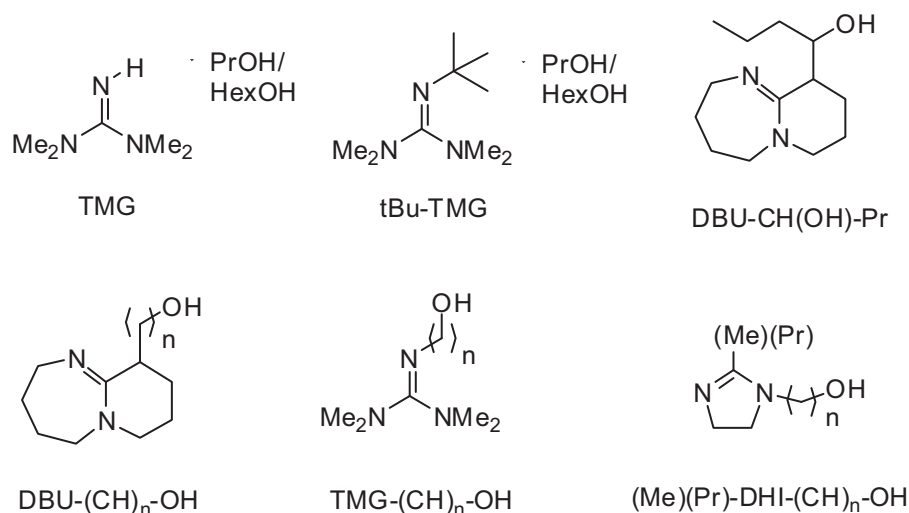

Fig. 1. Dual and single component CO_2 BOL systems developed and tested.

Table 1
Calculated and literature pK_a values of select compounds.

	pK_a_MeCN COSMO-RS	pK_a_MeCN Experimental	pK_a_MeCN Correlation 1	pK_a_MeCN Correlation 2
CH_3OCO_2H	20.5	5.7[a]	18.5	18.0
$CH_3CH_2OCO_2H$	22.3		19.9	19.7
$CH_3CH_2CH_2OCO_2H$	22.2		19.8	19.6
$(CH_3)_2CHOCO_2H$	22.6		20.1	19.9
$CH_3(CH_2)_3OCO_2H$	22.2		19.8	19.6
$CH_3(CH_2)_4OCO_2H$	22.2		19.8	19.6
$CH_3(CH_2)_5OCO_2H$	22.2		19.8	19.6
CH_3CO_2H	27.0	23.51[b]	23.6	24.2
$C_6H_5CO_2H$	24.2	21.51[b]	21.4	21.6
3,5-Dinitrobenzoic acid	18.8	17.00 [28]	17.2	16.4
3-Nitrobenzoic acid	21.3	19.20 [28]	19.1	18.8
Chloroacetic acid	20.8	18.80 [28]	18.7	18.2
Dichloroacetic acid	16.8	13.20 [28]	15.5	14.4
Trichloroacetic acid	12.7	10.75 [28]	12.3	10.4
DBU		24.3 [27]		
TMG		23.3 [28]		
Ph-TMG		20.8 [27]		
NEt_3		18.8 [27]		
Hünig's	18.6[c]			

[a] In methanol (see text for details).
[b] Ref. [34].
[c] Estimated using the PCM model [29,30].

Table 2
pK_a differences between alkylcarbonic acids and select organic bases.

Alkylcarbonic acid		ΔpK_a[a]				
		DBU	TMG	Ph-TMG	NEt$_3$	Hünig's
	pK_a	24.3[b]	23.3[b]	20.8[b]	18.8[b]	18.6[b]
CH$_3$OCO$_2$H	18.3[c]	6	5	2.5	0.5	0.3
CH$_3$CH$_2$OCO$_2$H	19.8[c]	4.5	3.5	1	−1	−1.2
CH$_3$CH$_2$CH$_2$OCO$_2$H	19.7[c]	4.6	3.6	1.1	−0.9	−1.1
(CH$_3$)$_2$CHOCO$_2$H	20.0[c]	4.3	3.3	0.8	−1.2	−1.4
CH$_3$(CH$_2$)$_3$OCO$_2$H	19.7[c]	4.6	3.6	1.1	−0.9	−1.1
CH$_3$(CH$_2$)$_4$OCO$_2$H	19.7[c]	4.6	3.6	1.1	−0.9	−1.1
CH$_3$(CH$_2$)$_5$OCO$_2$H	19.7[c]	4.6	3.6	1.1	−0.9	−1.1

[a] ΔpK_a = experimental pK_{aH} (base) – computationally estimated pK_a (acid).

[b] Experimental pK_{aH}.

[c] In the case of the alkylcarbonic acids, the average pK_a value of correlations 1 and 2 (Table 1) was used.

d-MeCN. All liquid reagents were handled and syringed under an N$_2$ environment at room temperature to an NMR tube.

2.2. Gravimetric method

150 mg samples of various CO$_2$BOLs were put in oven-dried pre-weighed micro GC vials containing a flea stir bar. Eleven vials were placed in a 160 mL stainless steel autoclave and sealed. The cell was pressurized with ~50 psi of CO$_2$ for 8–12 h under constant agitation. Once the cell was depressurized, each sample was massed for CO$_2$ uptake. All samples were stripped under a N$_2$ atmosphere by heating to 75 °C and then subsequently massed. This process was repeated 10 times.

2.3. pK_a calculations

Computations of pK_a values were carried out using the COSMO-RS [20] approach. Full DFT geometry optimization of the geometries of all neutrals and anions was done with the Turbomole software package [21] using B-P density functional [22,23] with TZVP quality basis set using the RI approximation [24]. The COSMO-RS calculations were done using the COSMO*therm* software [25].

3. Results and discussion

3.1. pK_a calculations of alkylcarbonic acids

To understand how the relative pK_a values of the acid and base of our CO$_2$BOLs affect carbon dioxide binding capacity, the pK_a values of alkylcarbonic acids must be understood. However, the instability of these acids makes the direct measurement of the pK_a values challenging. Eckert and Liotta recently showed an indirect method to measure the pK_a of methylcarbonic acid in methanol using a pH sensitive dye [26]. Despite efforts to apply this method to various alkylcarbonates it was found that only methylcarbonic acid (5.7 in methanol) could be measured. With no simple direct method to measure the pK_a values of larger alkylcarbonic acids, we turned to theory. The pK_a values of both linear and secondary alkylcarbonic acids were calculated in acetonitrile (MeCN) using the COSMO-RS approach (Table 1).

We first assessed the COSMO-RS approach with respect to a set of seven carboxylic acids with known MeCN pK_a vales within the anticipated range of the series of alkylcarbonic acids. We found a strong positive bias, i.e. all pK_a values computed directly are several units higher than the experimental ones (see Table 1). This is not exceptional or surprising but rather normal with computations in the condensed phase. In order to correct for this bias linear regression analysis was used based on the experimental and computed values of the seven known carboxylic acids (correlation 2) and a subset of five that excludes di-and trichloroacetic acid (correlation

1). The pK_a values of the alkylcarbonic acids obtained in such a way are listed in correlations 1 and 2. While it is not easy to determine which of the two sets is more appropriate for comparison, they are very similar and have uncertainties of at least 1 pK_a unit. Although the absolute uncertainties of correlations 1 and 2 are rather high, the uncertainties of their differences are significantly lower and allow detecting trends of pK_a values vs. molecular structure.

The linear and branched alkylcarbonic acids analyzed have similar pK_a values (19.6–20.1), save for methylcarbonic acid which is approximately two orders of magnitude more acidic (pK_a: 18.0–18.5). Alkylcarbonic acids are slightly more acidic than benzoic acid but less acidic than chloroacetic acid. The pK_a values of larger linear alcohols (C-2 plus) are close in proximity and correspondingly their carbonic acid derivatives also exhibit similar pK_a values (19.6–19.8). Isopropylcarbonic acid was found to be slightly less acidic than its linear counterpart. Table 2 shows the relative difference in pK_a between the conjugate acids of diazabicyclo[5.4.0]undec-7-ene (DBU), tetramethylguanidine (TMG), phenyltetramethylguanidine (Ph-TMG), triethylamine (TEA) and diisopropylethylamine (Hünig's base) and multiple alkylcarbonic acids. The strong bases DBU and TMG have ΔpK_a values ranging from 3.5 to 6 orders of magnitude less acidic than those of the alkylcarbonic acids. As such we suspect that alkylcarbonate salt formation/stabilization is observed when carbon dioxide is bubbled through solutions of DBU or TMG and alcohols due to the significant difference in pK_a values of the strong bases and corresponding alkylcarbonic acids. To further test this hypothesis we compared the ΔpK_a values of the aliphatic amine bases triethylamine and Hünigs bases, neither of which captures carbon dioxide in the presence of any alcohol. To our satisfaction the ΔpK_a values for these bases ranges from 0.5 to −1. This data suggests that the bases in CO$_2$BOL systems must have significantly greater pK_a values than the alkylcarbonic acids to successfully capture CO$_2$. We are currently studying the relationship between the magnitude of the ΔpK_a between a given base and alkylcarbonic acid and the carbon dioxide binding efficiency of that given mixture.
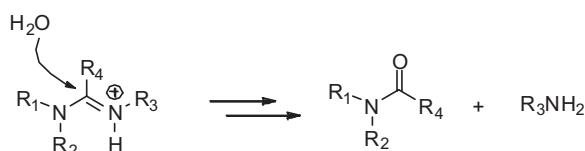
We predict that a base that is stronger than tertiary amines, yet less basic than amidines and guanidines, will yield a CO$_2$BOL that can be stripped of CO$_2$ more easily than previous systems. Individual bases or alcohol-functionalized base cores that have pK_a values of their conjugate acids near 20 or 21 pK_a units would be more favorable. To our knowledge there are no published accounts of liquid bases found in this pK_a range. Solid bases are unlikely to be executable as a liquid system, and therefore new advanced liquid bases will need to be developed.

3.2. Durability

High thermal and chemical stability are of the utmost importance for carbon dioxide capture reagents in post combustion gas

Table 3
Repeated gravimetric uptake of CO_2 for various CO_2BOLs under anhydrous conditions.

Entry		Cycle										
		1	2	3	4	5	6	7	8	9	10	Avg
	Dual component											
1	TMG/PrOH	22.7	20.6	26.6	24.0	25.8	29.1	25.3	26.9	18.9	34.8	25.5
2	TMG/HexOH	15.5	17.2	18.3	18.2	19.4	16.9	17.1	18.8	10.7	18.6	17.1
3	tBu-TMG/PrOH	17.0	9.6	10.0	0	0	0	0	0	0	0	12.2
4	tBu-TMG/HexOH	14.5	10.5	13.4	11.6	11.8	9.9	11.8	11.6	9.8	13.3	11.8
	Single component											
5	DBU–$(CH_2)_2$–OH	0.4	0.1	1.0	1.4	0.9	0.9	1.0	1.1	0.6	1.5	0.9
6	DBU–$(CH_2)_6$–OH	1.4	1.3	1.6	1.1	1.3	1.4	1.1	1.5	0.9	1.6	1.3
7	DBU–CH(OH)–Pr	1.3	2.1	1.2	1.6	1.6	1.0	1.5	1.4	1.3	1.9	1.5
8	TMG–$(CH_2)_6$–OH	4.5	6.5	7.4	6.7	7.2	4.2	4.4	4.3	3.0	7.3	5.6
9	Me–DHI–$(CH_2)_3$–OH	8.6	10.8	7.9	8.9	8.1	8.4	6.5	6.6	6.6	8.0	8.0
10	Me–DHI–$(CH_2)_6$–OH	7.3	10.6	9.7	7.1	10.0	10.5	10.1	9.8	7.5	9.4	9.2
11	Pr–DHI–$(CH_2)_6$–OH	5.0	4.6	5.7	7.1	7.0	4.3	6.3	6.9	5.6	8.0	6.1

Scheme 2. Degradation of amidines by water under acid conditions.

Scheme 3. Propyl alcohol substituted tetramethylguanidine reacts with carbon dioxide which further undergoes irreversible intramolecular cyclization.

capture. For CO_2BOLs the most sensitive portion is the imine functionality present in both amidine and guanidine bases (Scheme 2). Upon carbon dioxide binding of CO_2BOLs, the electrophilicity of the imine moiety increases as a consequence of protonation of the Lewis basic nitrogen to form the iminium ion. The iminium carbon is susceptible to nucleophilic addition reactions (Scheme 2). There are numerous examples of amidine and guanidine hydrolysis in the presence of water under highly acidic and basic conditions [31,32]. We have also observed an unwanted increase in the reactivity of imines under mildly acidic conditions. In a recent report, we observed that upon addition of CO_2 to propanol functionalized tetramethylguanidine the imine carbon undergoes irreversible nucleophilic attack by the weak alkylcarbonate (Scheme 3) [8]. Thus other nucleophilic chemical impurities present in post-combustion gas streams, such as water, may degrade CO_2BOL liquid systems over time.

To investigate the durability of CO_2BOLs the carbon dioxide uptake capacity of several single and dual component systems were measured gravimetrically under both wet and dry conditions (see Fig. 1 for structures). Samples were carboxylated/decarboxylated repeatedly over 10 cycles without water (Table 3) and with 10 mol% water (Table 4).

3.3. Anhydrous reaction conditions of dual and single component systems

Each dual component CO_2BOL is a non-viscous liquid mixture which becomes viscous after coming in contact with CO_2. In the absence of water, dual component systems show significantly greater carbon dioxide absorption than single component systems with a few exceptions (Table 3). Dual component blends exposed to carbon dioxide have relatively high gravimetric CO_2 uptake, averaging 25.5 wt.% for TMG/PrOH, 17.1 wt.% for TMG/HexOH, 12.2 wt.% for tBu-TMG/PrOH and 11.8 wt.% for tBu-TMG/HexOH. All these systems show little decrease in uptake capacity over 10 cycles, except for tBu-TMG/PrOH which shows complete loss of carbon dioxide uptake after just 3 cycles. To explain this irregularity control experiments were performed in which neat solutions of TMG/propanol, TMG/hexanol, tBu-TMG/propanol and tBu-TMG/hexanol were heated to 85 °C for 9 h in the absence of carbon dioxide. In all the solutions no chemical degradation

Table 4
Repeated gravimetric uptake of CO_2 for various CO_2BOLs with 10 mol% water added.

Entry		Cycle										
		1	2	3	4	5	6	7	8	9	10	Avg
	Dual component											
12	TMG/PrOH	21.4	25.6	29.5	33.0	31.9	22.3	22.0	25.8	21.8	23.6	25.7
13	TMG/HexOH	15.7	17.6	16.4	14.5	14.2	14.4	15.4	16.3	13.6	13.8	15.2
14	tBu-TMG/PrOH	16.8	0.8	0.1	0.8	0	0	0	0	0	0	5.9
15	tBu-TMG/HexOH	13.4	9.6	10.4	9.4	9.0	9.0	8.8	9.2	7.2	8.3	9.4
	Single component											
16	DBU–$(CH_2)_2$–OH	0.5	0.5	0.8	0.8	0.8	0.4	0.3	1.1	0.3	0.8	0.6
17	DBU–$(CH_2)_6$–OH	1.0	0.6	0.5	0.9	1.3	0.4	0.9	1.0	0.4	1.0	1.3
18	DBU–CH(OH)–Pr	3.1	0.9	1.2	1.6	0.8	1.7	1.1	1.7	1.0	1.5	1.5
19	TMG–$(CH_2)_6$–OH	9.7	5.2	6.9	4.8	8.3	4.0	6.9	7.9	7.6	3.1	6.4
20	Me–DHI–$(CH_2)_3$–OH	9.7	6.0	6.7	8.4	10.7	7.4	7.5	8.2	5.0	4.5	7.4
21	Me–DHI–$(CH_2)_6$–OH[a]	–	–	–	–	–	–	–	–	–	–	–
22	Pr–DHI–$(CH_2)_6$–OH	7.9	8.3	8.0	8.9	7.9	7.1	8.4	8.5	7.7	6.4	7.9

[a] This material was not analyzed.

was observed. In the hexanol containing solutions a mass loss of ~10 wt.% was observed, due to evaporation of hexanol. In the propanol cases some a significant amount of PrOH was lost, from 50 mol% to 20 mol% in the case of the TMG/PrOH mixture. However, in the tBu-TMG/PrOH blend all the alcohol had evaporated, explaining the rapid loss of CO_2 uptake capacity of this blend. This occurs most rapidly for the tBu-TMG/PrOH mixture due to a combination of the low volatility of propanol and the lack of hydrogen bonding between the base and alcohol that is present in the TMG/alcohol blends. The TMG-base cores show greater wt.% uptake over tBu-TMG cores due to devolatilizing hydrogen bonding and the inherently lower molecular mass of TMG.

The higher uptake capacity of the dual component materials vs. single component derivatives is likely due, in part, to the significantly higher viscosity of the latter. Indeed the single component CO_2BOLs become very viscous liquids or gels after exposure to CO_2. The linear alcohol single component derivatives possessing dihydroimidazole (DHI), TMG and DBU base cores absorb an average CO_2 wt.% of 6.1–9.2%, 5.6% and ~1%, respectively. The relatively low uptake of alcohol-substituted DBU samples is likely due to the particularly high viscosity of (and thus low gas diffusion into) these materials relative to the TMG- and DHI-based systems. The branched alcohol-functionalized DBU (DBU–CH(OH)–Pr) is the least active towards CO_2 capture. This is not wholly surprising as we have shown that secondary alcohols coupled with strong bases have far lower reactivity towards CO_2 than primary alcohols, an effect which we attribute to steric encumbrance [19]. In contrast to dual component systems, single component CO_2BOLs in the absence of CO_2 were as viscous as the carboxylated dual component CO_2BOLs.

To confirm our hypothesis that the viscous nature of the single component materials leads to poor diffusion of CO_2 therein, we performed the following experiment: the single component CO_2BOLs DBU–$(CH_2)_2$–OH and DBU–$(CH_2)_6$–OH were heated to 60 °C (thereby decreasing the viscosity), pressurized with CO_2 to 50 psi for 3 h and then allowed to cool to 25 °C under pressure. The carbon dioxide capacity for these compounds increased 5-fold from 0.9 wt.% for DBU–$(CH_2)_2$–OH to 6.0 wt.% and from 1.3 wt.% for DBU–$(CH_2)_6$–OH to 5.3 wt.%. Furthermore, the dual component analog of the above CO_2BOLs, DBU/HexOH, is a non-viscous liquid that shows excellent CO_2 capacity (17.2 wt.%) under similar conditions [19]. Thus we attribute to the low CO_2 uptake of single component systems vs. dual component systems to the viscosity of the former. These studies show that dual component systems have significantly higher CO_2 uptake than single component systems.

3.4. 10 mol% water reaction conditions of dual and single component systems

The durability of CO_2BOLs in the presence of water was studied using the same repeated absorption/desorption method while adding 10 mol% of water to each sample. To our satisfaction, comparable CO_2 binding capacities were obtained for the wet and dry samples, indicating a strong resistance of CO_2BOLs to hydrolysis (Table 5). In the presence of water, dual component systems again show significantly greater carbon dioxide absorption than single component systems with a few exceptions. Wet dual component blends exhibit gravimetric CO_2 uptakes averaging 25.7 wt.% for TMG/PrOH, 15.2 wt.% for TMG/HexOH, 5.9 wt.% for tBu-TMG/PrOH (four cycles) and 6.4 wt.% for tBu-TMG/HexOH. These systems also show excellent recyclability, suffering no significant decreases in uptake capacity between cycles with the exception of the dual component system tBu-TMG/PrOH, which, as with the anhydrous reaction conditions, looses activity due to evaporation of PrOH. The addition of water has no significant impact on the CO_2 uptake

Table 5
Percentage of CO_2BOL mass recovered after 10 cycles for anhydrous and 10 mol% H_2O samples.

Material	Mol% H_2O added	
	0%	10%
Dual component		
TMG/PrOH	29.5	20.3
TMG/HexOH	31.5	17.2
tBu-TMG/PrOH	0	36.6
tBu-TMG/HexOH	48.2	56
Single component		
DBU–$(CH_2)_2$–OH	95.6	92.6
DBU–$(CH_2)_6$–OH	95.1	98.7
DBU–CH(OH)–Bu	94.4	86.5
TMG–$(CH_2)_6$–OH	93	90.7
Me–DHI–$(CH_2)_3$–OH	95.6	96
Me–DHI–$(CH_2)_6$–OH	94.9	–[a]
Pr–DHI–$(CH_2)_6$–OH	80.9	74.4

[a] This material was not analyzed with 10 mol% H_2O.

capacity of the single component CO_2BOLs. Wet DHI, TMG and DBU base cores absorb CO_2 up to 11 wt.%, 8 wt.% and 2 wt.%, respectively.

Because solvents for post combustion CO_2 capture should ideally recycle indefinitely without evaporation or degradation, we also measured the percentage of the CO_2BOL solvents recovered after ten absorption/desorption cycles in the absence of a condenser to quantify the extent of potential evaporative losses (Table 5). For dual component systems significant losses (70–100%) were observed due to evaporation during stripping. The relative activity remained constant for TMG/propanol and hexanol and tBu-TMG/hexanol pairings because as solvent was lost, active material was still present to capture the same relative % CO_2 between cycles. Barton's base and propanol showed immediate deactivation in both 0% and 10% water which we attribute to evaporative loss of alcohol. The observed volatilization severely limits the applicability of dual component systems to post combustion gas capture unless large condensers are employed. In contrast, the single component CO_2BOLs exhibit <5% solvent loss after 10 absorption/desorption cycles in the absence of a condenser under both wet and dry conditions. The observed <5% can be mitigated by the addition of a condenser, and until continuous flow testing is performed this loss is not expected to significantly influence solvent makeup rates and process costs. To determine what, if any, degradation had occurred in these cycled samples $^1H/^{13}C$ NMR analysis was performed. No evidence for degradation of the samples for either wet or dry or single or dual component systems was observed, although there remains the possibility that volatile degradation products do form but evaporate. The continuous flow testing of single component CO_2BOLs for solvent lifetime and potential degradation products is ongoing.

Although a formal process economic assessment has yet to be performed, strictly on a material's property basis, CO_2BOLs have potential to be more efficient than aqueous based alkanolamine systems. A sample estimated process energy is calculated below (Table 6) in comparison to a baseline subcritical coal power plant study using 20% MEA scrubbing to remove 90% CO_2 [33]. In this calculation we compare MEA to tertbutyl 1,1,3,3 tetramethylguanidine (Barton's base) and 1-butanol, which has a heat of reaction with CO_2 of −85 kJ/mol (831 BTU/lb CO_2), it contains 15% by weight CO_2 and has a specific heat near 1.5 J/g/K. We choose an absorption temperature of 31 °C because cooler flue gas would condense out most of the water present in flue gas and higher CO_2 loading at lower temperatures. Stripping is performed in this calculation at 120 °C to match with MEA, however lower temperatures could be used. We calculate a 193 °C adiabatic heat increase of the organic solution (due to its lower specific heat and high loading) during CO_2 absorption. This heat increase will need to be exchanged and recovered. We also calculate a 383 BTU/lb CO_2 sensible heat increase

Table 6
Estimated energy requirements for MEA and Barton's/ BuOH.

	MEA	Barton's/BuOH
Amount of organic component in solvent (wt)	20%	100%
Heat of reaction in solvent (kJ/mol CO_2)	−85	−85
Specific heat of solvent (J/g solvent/K)	3.9	1.5
CO2 working capacity loading in solvent (wt)	6%	15%
Adiabatic increase in solvent temperature during absorption (°C)	29	193
Absorption temperature (°C)	55	31
Stripping temperature (°C)	120	120
Sensible heat from stripping temperature increase (BTU/lb CO_2)	1892	383
Theoretical regeneration energy if no absorption energy recovered (BTU/lb CO_2)	2722	1213
Recovered sensible heat (calculated from value below in the case of MEA [33])	71%	71%
Estimated regeneration heat energy with specified recovered sensible energy (BTU/lb CO_2)	1386	941

from CO_2 stripping, lower than MEA due to the low specific heat and high loading. We estimate that we can recover 71% of the sensible heat through heat exchangers similarly to the MEA case [33]. Computing the numbers, we estimate the total process to require 941 BTU/lb CO_2, in comparison to estimated process values for MEA at 1386 BTU/lb CO_2, or 32% lower. Again these numbers are not formal process values, however they show promise that on a material's property basis CO_2BOLs have potential to improve the efficiency of CO_2 capture in comparison to aqueous amine systems.

4. Conclusions

The pK_a values of both linear and secondary alkylcarbonic acids were computationally estimated in acetonitrile using the COSMO-RS approach and correlated by linear regression analysis based on the experimental and computed values of the seven known carboxylic acids. These pK_a values were then compared to those of numerous organic bases used in CO_2BOL systems. This data suggests that the bases in CO_2BOL systems must have significantly greater pK_a values than the alkylcarbonic acids to successfully capture CO_2. To investigate the durability of CO_2BOLs the carbon dioxide uptake capacity of several single and dual component systems were measured gravimetrically under both wet and dry conditions. These studies show that dual component systems have significantly higher CO_2 uptake than single component systems but are less durable due to ease of vaporization of the alcohol and base constituents. No hydrolysis or chemical degradation of either the dual or single component systems were observed. The robustness of the imine carbon suggests that alkanolamidines and alkanolguanidines are promising carbon dioxide capture reagents for flue gas streams.

Acknowledgements

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