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# Assessment of Amine-Based CO2BOLs for Direct Air Capture

February 2024

Phillip K. Koech Dushyant Barpaga Deepika Malhotra Abhishek Kumar Andy Zwoster



Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory Richland, Washington 99354

## Abstract

Direct air capture (DAC) technologies extract  $CO_2$  from the atmosphere for  $CO_2$  storage, or utilization. Capturing  $CO_2$  from the air is the most expensive application of carbon capture because  $CO_2$  in the atmosphere is very dilute. There are limited number of  $CO_2$  capture technologies for DAC application. This project aims at developing an energy efficient sorbents for DAC, leveraging chemistries previously-developed at PNNL, including materials in the  $CO_2BOLs$  family. Three  $CO_2$  capture sorbents consisting of  $CO_2BOLs$  immobilized in mesoporous silica were designed, synthesized, and tested. These sorbents had 19-23 wt.% amine loadings which is lower than typical amine-based silica sorbents. The surface area and pore volumes of these solid were lower than those of the pristine silica support, which is expected due to  $CO_2BOLs$  immobilization in the pores of silica. The  $CO_2$  capture performance of these materials were evaluated using  $CO_2$  adsorption isotherms in the pressure range typically meaningful for DAC range (0-100 Pa). The values for  $CO_2$  capture were lower than the typical silica supported amines due to low amine loading and higher molecular weight with low amine density.

Liquid solvents were also evaluated for DAC applications. Properties for three different solvents, also in the CO<sub>2</sub>BOLs family, were measured. Property measurements included vapor pressure,  $CO_2$  uptake capacity, kinetics, and viscosity. The CO<sub>2</sub> uptake capacity for one of the most promising solvents, BEPBEGDA, was 13.2 wt%, corresponding to 97 mol%. The vapor pressure of the BEPBEGDA solvents was low at 80°C compared to other solvents, which is good from a DAC application standpoint. The effect of humidity on the CO<sub>2</sub> capture performance of these solvents was evaluated. This testing showed that presence of moisture doesn't have a negative effect on the CO<sub>2</sub> uptake performance and may make it slightly better. The CO<sub>2</sub> uptakes for all three solvents tested were slightly below that of the 0.1M NaOH solution tested under similar conditions. However, despite of the lower CO<sub>2</sub> uptake, it is expected that these liquid solvents will have lower regeneration temperature.

Future work will focus on optimization of the liquid solvents for DAC application to improve both  $CO_2$  capture efficiency and capacity without viscosity and vapor pressure increases. Testing of these solvents under DAC conditions in a representative a gas-liquid contactor will also be pursued. Further, solvent cost projections, techno-economic analyses and life cycle analyses are required to evaluate the economic viability of the potential solvent solutions.

### Summary

The first objective of this project was to design, synthesize and test a scalable amine-based solid sorbent capable of cost effectively removing  $CO_2$  from dilute gas streams such as ambient air. The main goal of this work was to lower the enthalpy of sorbent regeneration in direct air capture (DAC), which is the primary energy required in a DAC system. We designed, synthesized, and tested three CO<sub>2</sub> capture sorbent consisting of amine-based carbon dioxide binding organic liquids (CO<sub>2</sub>BOLs) immobilized in mesoporous silica. These three solid-supported CO<sub>2</sub>BOLs had amine loadings ranging from 19-23 wt.%, as determined by thermal gravimetric analysis (TGA). These loadings are lower than typical amine-based silica sorbents, due to the high molecular weight of the CO<sub>2</sub>BOLs. Further, the solid supported CO<sub>2</sub>BOLs had lower surface area and pore volumes compared to the pristine silica support. The CO<sub>2</sub> capture performance of these materials were evaluated using  $CO_2$  adsorption isotherms in a  $CO_2$  partial pressure range meaningful for DAC (0 to 1 mbar). When compared to  $CO_2$  adsorption isotherm measurements in the same partial pressure range, the CO<sub>2</sub>BOLs materials were comparable but slightly lower, largely due to low amine loadings, higher molecular weight, and low amine density. The results suggest that immobilized CO<sub>2</sub>BOLs in silica might require more optimization to removing CO<sub>2</sub> from ambient air that competitive with existing solutions.

2-EEMPA represents a leading CO<sub>2</sub>BOLs solvent for capturing CO2 from post combustion capture. However, the vapor pressure of 2-EEMPA is such that evaporative losses would become significant over time under dry DAC conditions. In order to lower the vapor pressure of 2-EEMPA, the amine density was increased from two to four, with corresponding increases in the molecular weight. Incorporation of CO<sub>2</sub>-philic and viscosity-lowering ether groups in the solvent ensures that the viscosity is maintained low enough to facilitate mass transfer. To this end the 2-EEMPA was modified to a symmetric dimer resulting in a tetramine, BEEMPA. The ether component of another the CO<sub>2</sub>BOLs solvent was converted to a novel diamine solvent BEPBEGDA rich in ether functionality for higher CO<sub>2</sub> uptake and lower vapor pressure. Finally, another solvent previously evaluated for post combustion CO<sub>2</sub> capture, EEDIDA, was dimerized to increase both amine density and molecular weight, resulting in BEEDIDA solvent.

To evalaute the CO<sub>2</sub> uptake capacity and viscosity of the three new DAC solvent candidates, gravimetric CO<sub>2</sub> uptake was performed using pure CO<sub>2</sub> gas. BEEMPA was viscous when loaded with pure CO<sub>2</sub> (7 wt% loading), to the extent that it was not flowable. The CO<sub>2</sub> uptake capacity of BEPBEGDA was the highest, at 13.2 wt%, corresponding to 97 mol%. This loading was partially attributable to its low viscosity. The vapor pressure of the BEPBEGDA and BEEDIDA solvents were measured using PNNL's custom built PVT apparatus. Both solvent vapor pressures were low, even at 80 °C, compared to other solvents. For comparison, the vapor pressure of 1 M NaOH solution at 37 °C is about 3 Torr, which is an order of magnitude higher than the vapor pressure of both the BEPBEGDA and BEEDIDA solvents at 80 °C, suggesting that these two solvents could have acceptable viscosity and volitile losses in direct air capture applications.

The vapor liquid equilibrium (VLE) of the three solvents were measured to determine the  $CO_2$  uptake, kinetics, and viscosity as a function of  $CO_2$  loading and temperature. The VLE isotherms of the BEEDIDA shows that the partial pressure of  $CO_2$  increases with temperature, indicating less  $CO_2$  uptake at higher temperatures. VLE also show that moisture from additional water can greatly enhance  $CO_2$  capture performance of the solvent, as observed when BEEDIDA was tested with 20 wt% water. However, the addition of water in BEEDIDA increased the viscosity of the solvent, suggesting that it may require further optimization. The  $CO_2$  uptake performance of BEPBEGDA followed the performance trend of EEMPA at 40 °C, but with a lower viscosity than

that of BEEDIDA. BEPBEGDA also had a slightly lower equilibrium  $CO_2$  uptake capacity when compared to BEEDIDA, but faster  $CO_2$  uptake kinetics.

The CO<sub>2</sub> capture performance of the three solvents were tested at 25 °C with ambient air using flow-through Parr reactor instrument, with a focus on BEPBEGDA and BEEDIDA. The CO<sub>2</sub> uptake with the BEPBEGDA solvent was about 20% higher than BEEDIDA, which can be partially attributed to the faster CO<sub>2</sub> uptake kinetics. The CO<sub>2</sub> capture performance of BEPBEGDA was slightly improved with increased humidity. The capture performance of both solvents was slightly lower that of the 0.1M NaOH solution tested under similar conditions. Despite of the slightly lower CO<sub>2</sub> uptake, it is expected that these liquid solvents will have lower regeneration temperature and minimum evaporative losses due their low vapor pressure.

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## Acronyms and Abbreviations

	<b>•</b> • • • • • • • • • • • • • • • • • •
CO <sub>2</sub> BOLs	Carbon dioxide binding organic liquids
DAC	Direct air capture
CO <sub>2</sub>	Carbon dioxide
2-EEMPA	N-(2-ethoxyethyl)-3-morpholinopropan-1-amine
BEEMPA	N,N'-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(3-morpholinopropan-1-amine
BEPBEGDA	N,N'-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(3-ethoxypropan-1-amine)
PNNL	Pacific Northwest National Laboratory
VLE	Vapor Liquid equilibrium
SAMMS	Self-Assembled Monolayers on Mesoporous Supports
MOFs	Metal Organic Frameworks
NMR	Nuclear Magnetic Resonance
BET	Brunauer, Emmett and Teller
TGA	Thermogravimetric analysis
MPMPA	3-methoxy-N-(pyridin-2-ylmethyl)propan-1-amine
PVT	Pressure Volume and Temperature
SBDAC	Solvent-based direct air capture
P&ID	Piping and instrumentation diagram

## Contents

## **Figures**

Figure 1. CO <sub>2</sub> Uptake and Regeneration Temperature for liquid CO <sub>2</sub> BOLs	1
Figure 2. Immobilized amine based CO <sub>2</sub> BOL	1
Figure 3. Two best performing $CO_2BOLs$ for post combustion $CO_2$ capture application	3
Figure 4. Triethoxypropylsilane modified CO <sub>2</sub> BOL amine and ether moieties	3
Figure 5. Synthesis of the triethoxypropylsilane modified CO <sub>2</sub> BOL components	4
Figure 6. Synthesis of silica supported CO <sub>2</sub> BOLs	4
Figure 7. Thermogravimetry analysis plots for amine-functionalized silica (MCM-41)	5
Figure 8. Nitrogen sorption at 77K of parent silica as well as the three amine- functionalized grafted silica samples. (left) N <sub>2</sub> uptake and (right) pore size distribution.	5
Figure 9. CO <sub>2</sub> sorption at various temperatures (288K - 318K) of a) MCM-41, b) L21- 150-R36 ( <b>11</b> ), c) L21-150-R37 ( <b>12</b> ), and d) L21-150-R38 ( <b>13</b> )	7
Figure 10. Vapor pressure at 20, 40, 60, and 80 °C for a) BEPBEGDA; b) BEEDIDA solvents.	9
Figure 11. VLE, Kinetics, and Viscosity isotherms as function of CO <sub>2</sub> loading for (a-c) BEEDIDIA; (d-f) BEPBEGDA	10
Figure 12. (a) Piping and instrumentation diagram (P&ID), (b) photograph of the solvent- based direct air capture apparatus	11
Figure 13. (a) Real time CO <sub>2</sub> capture performance (%) of the solvents (BEPBEGDA, BEEDIDA and 0.1 M NaOH) with time; (b) Cumulative CO <sub>2</sub> capture performance showing moles of CO <sub>2</sub> captured per moles of the solvent	12

## **Tables**

Table 1. Surface area and pore volume for amine-functionalized grafted samples as	
predicted from BET theory using nitrogen sorption at 77K.	6
Table 2. Gravimetric CO <sub>2</sub> Uptake for tetramine solvents for DAC	8

#### Introduction 1.0

DAC is a promising approach for atmospheric carbon dioxide removal, also referred to as negative emissions to mitigate environmental effects of climate change. However, due to the large amounts of CO<sub>2</sub> needed to be removed, DAC technologies will only become climate relevant at gigaton scales. There are limited  $CO_2$  capture technologies capable of removing  $CO_2$  from ambient air. One such technology involves amine functionalized sorbents that require regeneration at 100-120 °C. Carbon Engineering (CE) in Canada represents another approach, with a technology that uses alkali metal oxide sorbents regenerated by heating metal carbonates at around 900°C. Yet another DAC player is Global Thermostat (GT) in the U.S. The GT process uses a solid aminebased sorbent material, regenerated at around 100°C, while a Switzerland-based Climeworks uses a DAC design based on an adsorption/desorption process on alkaline-functionalized sorbents, in which adsorption is performed at ambient conditions and CO<sub>2</sub> desorption is performed through a temperature-vacuum-swing at 120°C resulting from the 85 kJ/mol heat of reaction for conventional amines compared to ~70 kJ/mol for our amine-based CO<sub>2</sub>BOLs. Our proposed amine based CO<sub>2</sub>BOLs immobilized in mesoporous silica technology has potential to lower regeneration temperature by up to 40 °C, corresponding to 30% energy reduction. Amine functionalized silica technologies can be scaled up easily following similar production protocols already established for PNNL's commercialized Self-Assembled Monolavers on Mesoporous Supports (SAMMs) technology. A novel carbon dioxide capture sorbent that comprises the best performing amine-based carbon dioxide binding organic liquids (CO<sub>2</sub>BOLs) immobilized on high surface area mesoporous silica (Figure 1) was developed. We have recently shown that aminebased CO<sub>2</sub>BOLs have high CO<sub>2</sub> capture capacity with low regeneration temperature ~75-80 °C. This low regeneration temperature is attributed to CO<sub>2</sub> capture via neutral carbamic acid. In this fashion, capture is accomplished without contribution from the heat of protonation from acid/base chemistry that is typical of carbamate binding as shown in Figure 2.<sup>1</sup>  $CO_2$  capture from ambient air requires a solid sorbent to minimize solvent evaporation. Amines immobilized in silica, metal organic frameworks (MOFs), and organic polymers have shown promise as CO<sub>2</sub> capture sorbents for DAC, however the regeneration temperature is high due to the carbamate binding mechanism.<sup>2</sup> Given this precedence, we expect that immobilizing amine-based CO2BOLs in silica will retain the unique carbamic acid mechanism and lower regeneration temperature as demonstrated by Yaghi and co-workers in amine-functionalized MOFs.<sup>3</sup>



**Mesoporous Silica** 





Figure 1. CO <sub>2</sub> Uptake and Regeneration
Temperature for liquid CO <sub>2</sub> BOLs

To achieve the project objective, we designed a CO<sub>2</sub> capture sorbent consisting of amine-based carbon CO<sub>2</sub>BOLs immobilized in mesoporous silica with potential to lower regeneration energy by 30% as shown in Figure 1. The team utilized liquid amine based CO<sub>2</sub>BOLs that have the best performance for CO<sub>2</sub> capture in flue gas streams (contains ~15% CO<sub>2</sub>), but not suitable for DAC due to evaporative losses at dry DAC conditions. These CO<sub>2</sub>BOL solvents have a lower enthalpy of regeneration 70-75 KJ/mol with lower solvent regeneration temperature 80 °C, compared to

100-120 °C for commonly used sorbents for DAC (Figure 2). Minor modification of these solvents with functional handles such silvl ethers enabled immobilization on high surface area mesoporous silica, xerogels or aerogels to minimize evaporative losses (Figure 1). The new sorbent materials were characterized using solid state nuclear magnetic resonance (NMR), and BET for surface area, and total pore volume measurements. Calorimetry was used to determine  $CO_2$  uptake capacity, heat of adsorption and kinetics of  $CO_2$  uptake.

## 2.0 Design, Synthesis and Testing of Solid Supported CO<sub>2</sub>BOLs

#### 2.1 Design

Design of solid supported sorbents utilized the active  $CO_2$  capture moieties for two best performing  $CO_2BOLs$ , that is 2-EEMPA and MPMPA (Figure 3.). The  $CO_2BOL$  solvents have two major components that is diamine and ether as shown in EEMPA Figure 3. To minimize the size of the amine added to the solid support the solvents components were evaluated separately as shown in Figure 4.



Figure 3. Two best performing CO<sub>2</sub>BOLs for post combustion CO<sub>2</sub> capture application.

Both amine and the ether components of each solvent were modified to include an alkyl triethoxysilane moiety as a functional handle for grafting onto silica (Figure 4). The triethoxysilane propyl group was used to modify these CO<sub>2</sub>BOL component because the starting chlorotriethoxypropylsilane is commercially available.



Figure 4. Triethoxypropylsilane modified CO<sub>2</sub>BOL amine and ether moieties.

#### 2.2 Synthesis and Characterization

The synthesis of alkyltriethoxysilane functionalized diamines (**3-5**) were achieved in one step reaction via alkylation of the commercially available morpholine amine **6** and aminopyridine **8** using 3-chloropropyltriethoxysilane **7** (Figure 5). The ether component of the CO<sub>2</sub>BOL was functionalized by alkylation of 3-ethoxyproylamine **9** using 2-bromoethoxyether **10**. The reactions were performed neat without additional solvent.



Figure 5. Synthesis of the triethoxypropylsilane modified CO<sub>2</sub>BOL components.

The mesoporous silica MCM-41 was grafted with synthesized organoalkoxysilanes (3-5) via dropwise addition to a suspension of MCM-41 in anhydrous toluene under reflux conditions in an inert atmosphere. The suspension was filtered and excess of organosilane was removed by washing the solids in a Soxhlet apparatus using 1:1 mixture of dichloromethane and diethyl ether for 24h to afford the  $CO_2BOLs$  functionalized mesoporous silica **11-13** Figure 6. The corresponding solid was analyzed using BET surface area,  $CO_2$  sorption and TGA analysis.



Figure 6. Synthesis of silica supported CO<sub>2</sub>BOLs.

#### 2.3. BET Surface area, CO<sub>2</sub> sorption and TGA data.

To estimate the amount of amine loaded onto silica, thermogravimetric analysis (TGA) of the amine-functionalized silica samples (**11-13**) was performed in air. As a baseline comparison, TGA of MCM-41 was also performed under similar conditions. A known mass of the samples was loaded onto alumina crucible and were heated in air at a rate of 10 °C/min and the corresponding change in weight was recorded. Compared to the pristine silica MCM-41, amine loading between 19-23 wt.% were estimated for the three samples as shown in Figure 7.



Figure 7. Thermogravimetry analysis plots for amine-functionalized silica (MCM-41)

The grafted samples were characterized via gas sorption to evaluate the porosity of the functionalized material as well as the  $CO_2$  capture performance. Initial sorption experiments with pure N<sub>2</sub> at 77K provided surface area and pore size information on the samples. As shown in Figure 8, the nitrogen uptake was lower for the grafted samples compared to the parent sample. Using BET theory, the available surface area and pore volume computed from the nitrogen sorption results (as shown in Table 1) corroborated the nitrogen sorption data. As expected, incorporation of the larger molecular weight functional moieties resulted in lower surface area and pore volume.



Figure 8. Nitrogen sorption at 77K of parent silica as well as the three amine-functionalized grafted silica samples. (left)  $N_2$  uptake and (right) pore size distribution.

Sample	Surface Area [m²/g]	Pore Volume [cm³/g]	
MCM-41	.790	.0.70	
L21-150-R36 ( <b>11</b> )	.340	.0.22	
L21-150-R37 ( <b>12</b> )	.13	.0.05	
L21-150-R38 ( <b>13</b> )	.134	.0.11	

Table 1. Surface area and pore volume for amine-functionalized grafted samples as predicted from BET theory using nitrogen sorption at 77K.

Pure  $CO_2$  sorption on the grafted samples was also collected via volumetric sorption apparatus. The data collection was limited to low partial pressures of CO<sub>2</sub> that correspond to the expected concentration of CO<sub>2</sub> in air (~0.04 kPa). On the parent silica MCM-41, the CO<sub>2</sub> uptake was more than an order of magnitude lower than amine-functionalized samples and reduced more dramatically as a function of increasing temperature (Figure 9a). On the sample with only a single secondary amine (11), the CO<sub>2</sub> uptake was ~10x higher at 0.04 kPa compared to MCM-41 (Figure 9b). However, for the other two samples where an additional tertiary amine was present, the  $CO_2$ uptake increased to ~100x higher at 0.04 kPa compared to MCM-41 (Figure 9 c-d). Clearly the incorporation of additional amines improves CO<sub>2</sub> uptake and highlights the importance of having a diamine in the 2-EEMPA solvent system. While these values may appear to be lower than typical reported values for amine-functionalized silica and other porous sorbents, most of the reported analysis using CO<sub>2</sub> isotherms are performed at higher pressure ranges, typically between 0-1, bar and not indicative of actual CO<sub>2</sub> performance in the DAC range. The CO<sub>2</sub> sorption isotherms were used to evaluate the heat of solution for four sample and were found to be 18.3, 38.0, 25.9, 25.9 kJ/mol for MCM-41, L21-150-R36 (11), L21-150-R37 (12), and L21-150-R38 (13), respectively. The higher heat of solution of the amine functionalized silica samples compared to MCM-41 is higher likely due to presence of amine.



Figure 9.  $CO_2$  sorption at various temperatures (288K - 318K) of a) MCM-41, b) L21-150-R36 (11), c) L21-150-R37 (12), and d) L21-150-R38 (13).

## 3.0 Synthesis and testing of improved CO<sub>2</sub>BOLs for DAC Application

#### 3.1 Design

The leading CO<sub>2</sub>BOLs solvents for post combustion CO<sub>2</sub> capture, 2-EEMPA (1) and MPMPA (2), shown in Figure 3, contain two amine functionalities, one secondary and one tertiary amine. Only the secondary amine binds CO<sub>2</sub>. Solvents for DAC application should have a high CO<sub>2</sub> uptake capacity, low vapor pressure to minimize evaporative losses and lower viscosity for effective mass transfer. To improve the performance for these water-lean amines in DAC application the amine density was increased from two to four with corresponding increases in the molecular weight, thus lowering the vapor pressure. Incorporation of CO<sub>2</sub>-philic and viscosity-lowering ether groups in the solvent ensures that the viscosity is maintained low enough to facilitate mass transfer. To this end three new solvents that is BEEMPA, BEPBEGDA and BEEDIDA were designed characterized and tested for DAC application.

#### 3.2 Solvent property testing

#### **Gravimetric CO**<sub>2</sub> uptake

To evaluate the  $CO_2$  uptake capacity and assess the  $CO_2$  rich viscosity of these new solvents, gravimetric  $CO_2$  uptake was performed using pure  $CO_2$  gas. The liquid solvents were sparged with  $CO_2$  using a syringe needle connected to a regulated  $CO_2$  cylinder, which pierced the rubber septa on the flasks. The flasks were sparged for 45 min to load  $CO_2$ , then the flask was weighed, and the gravimetric uptake was calculated. Timed sparge was standardized for consistent and comparable data, so all loadings presented herein are not considered equilibrium loadings (i.e., less viscous solvents could achieve higher loadings than more viscous ones). BEEMPA was viscous when fully loaded with  $CO_2$  to the extend that it was not flowable, thus this solvent was not tested in subsquent experiments. The  $CO_2$  uptake capacity for BEPBEGDA was the highest at 13.2 wt% corresponding to 97 mol%, this can be attributed to low viscosity and lower molecular weight (Table 2).

Molecule	CO₂ Uptake wt.%	CO₂ Uptake Mol%	
BEEMPA	7.1	67	
BEPBEGDA	13.2	97	
BEEDIDA	8.8	81	

Table 2. Gravimetric $CO_2$ Uptake for tetramine solvents for DA	Table 2. Gravimetric	CO <sub>2</sub> Uptake	for tetramine	solvents	for DAC
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#### Vapor Pressure, VLE, Kinetics and Viscosity

The vapor pressure of the BEPBEGDA and BEEDIDA solvents were evaluated using PNNL's custom built PVT apparatus with senstive pressure transducers that can record pressure changes as low as 0.03 Torr pressure. To accurately measure the vapour pressure of the solvents as a function of temperature, the solvents were first heated to 80 °C to release any dissolved CO<sub>2</sub>. After that the cell holding the solvents was evacuated and the pressure reading was recorded only when there was no increase in the pressure of the cell holding liquid. Figure 10 shows the vapor presure of the solvents BEPBEGDA and BEEDIDA as a function of four different temperatures and a corresponding exponential fit. It is obvious from Figure 10 that the vapor pressure of the solvents were very low, even at 80 °C, compared to other solvents. For comparison, the vapor pressure of 1 M NaOH solution at 37 °C is about 3 Torr that is at least one order of magnitude higher than the vapor pressure of both solvents even at 80 °C. The low vapor pressure is critical for direct air capture application as it means the amount of solvent in the vapor phase is low and that there will be negligible changes in the mass of the solvent when air flows over these solvents.



Figure 10. Vapor pressure at 20, 40, 60, and 80 °C for a) BEPBEGDA **17**; b) BEEDIDA **19** solvents.

The CO<sub>2</sub> absorption isotherms were obtained at a different temperature (20 °C, 40 °C, 60 °C, and 80 °C) using the PVT apparatus. To collect vapor liquid equilibrium (VLE), CO<sub>2</sub> uptake, kinetics, and viscosity isotherms as a function of CO<sub>2</sub> loading, a known mass of the solvent was first loaded into the PVT cell. After injection of the solvent, the solvent was heated up to 80 °C to remove any CO<sub>2</sub> or moisture previously taken by the solvent. Upon which, a small amount of pure CO<sub>2</sub> was step wise injected into the system and was allowed enough time for the CO<sub>2</sub> in the vapor phase to attain equilibrium. This was done automatically by monitoring the pressure profile of the cell after each injection and spacing the next CO<sub>2</sub> injection only after the system had attained equilibrium after previous injection. The temperature, pressure, and the viscosity of the cell were recorded and later analyzed to obtain corresponding isotherms for VLE, CO<sub>2</sub> uptake kinetics, and viscosity.

Figure 11 (a-c) shows the VLE,  $CO_2$  uptake kinetics, and viscosity of the BEEDIDA solvent at four different temperatures. For comparison, the performance of this solvent is compared to EEMPA, which is one of the state-of-the-art water lean amines developed at PNNL for carbon capture. For direct air capture applications 420 ppm of  $CO_2$  in air corresponds to a  $CO_2$  partial pressure of 42 Pa (0.42 mbar). Most of the sorbent measurements in the literature have been conducted over  $CO_2$  partial pressures between 0 and 13 mbar. The VLE isotherms of the BEEDIDA solvent shows that the partial pressure of  $CO_2$  increases with increased temperature, indicating less  $CO_2$  uptake at higher temperatures. The VLE of BEEDIDA solvent follows closely that of EEMPA at 40 °C with

slightly higher viscosity. It was observed that moisture in form of additional water could greatly enhance CO<sub>2</sub> capture performance of the solvent as was observed by the right shift of the VLE curve when BEEDIDA was tested with 20 wt% water added to it. The addition of water, however, also increased the viscosity of the solvent. Similarly, Figure 11 (d-f) shows the VLE, CO<sub>2</sub> uptake kinetics, and viscosity of the BEPBEGDA solvent at 4 different temperatures. The CO<sub>2</sub> uptake performance of the BEPBEGDA solvent also closely follows the performance of EEMPA at 40 °C but slightly lower viscosity than that of BEEDIDA. The BEPBEGDA solvent had slightly lower equilibrium CO<sub>2</sub> uptake when compared to BEEDIDA but faster CO<sub>2</sub> uptake kinetics. The isotherms from PVT instrument were used to calculate the heat of solution for the two solutions. Figure 11g shows the heat of solution for BEEDIDA and BEPBEGDA compared with EEMPA. The lower heat of solution of BEPBEGDA solution indicates possibility of ease of regeneration of the solvent in the capture process.



Figure 11. VLE, Kinetics, and Viscosity isotherms as function of CO<sub>2</sub> loading for (a-c) BEEDIDA; (d-f) BEPBEGDA; g) heat of solution for BEEDIDA and BEPBEGDA compared with EEMPA.

#### DAC solvent testing capability

A custom apparatus was built to test and compare the DAC capability of the solvents evaluated. Figure 12 shows a piping and instrumentation diagram (P&ID) and a photograph of the cart containing the solvent based direct air capture (SBDAC) apparatus. This set up consists of a three-way valve that switches between nitrogen and compressed air. A pressure regulator is used to control the pressure of the gas downside of the three-way valve. Next the gas flow through a humidity detector that monitors the humidity of the inlet gas. After this, a flow controller is used to control the flow of gases going into the parr reactor with a stirrer, where it is sparged into the solvent at a flow rate of 100 sccm. Before going into the parr reactor, the gases flow through an inlet  $CO_2$  analyzer that monitors the concentration of  $CO_2$  of the gas going in the parr reactor. The outlet from the parr reactor is then flowed through a condenser and to an outlet  $CO_2$  analyzer that measures the concentration of the  $CO_2$  in the gas coming out of the parr reactor. Measuring the inlet and outlet  $CO_2$  concentrations, as well as the flowrate of the gas going in, to enable calculation of the  $CO_2$  captured by the solvent.



Figure 12. (a) Piping and instrumentation diagram (P&ID), (b) photograph of the solvent-based direct air capture apparatus.

#### CO<sub>2</sub> capture performance in dry and humidified air

Before taking readings, a known weight of solvent was poured into the Parr reactor and heated at 80 °C overnight under N<sub>2</sub> to get rid of any dissolved CO<sub>2</sub>. Afterwards, the reactor was cooled to 25 °C and the three-way valve was then switched to compressed air. The inlet and the outlet CO<sub>2</sub> concentration were noted at fixed intervals for 3 h to compare the CO<sub>2</sub> capture performance of the solvents. Figure 13 (a-b) shows the CO<sub>2</sub> capture performance of the solvents at 25 °C and at 100 sccm of gas flow though the Parr reactor. Figure 13 a shows the % CO<sub>2</sub> capture for BEEDIDA and the BEPBEGDA solvents and compare their performance with 0.1 M NaOH. The CO<sub>2</sub> uptake performance of the BEPBEGDA solvent was about 20% higher than then BEEDIDA which might be due to the faster CO<sub>2</sub> uptake kinetics of BEPBEGDA as observed in the previous PVT runs. The effect of humidity was also studied on the CO<sub>2</sub> capture performance of the solvents, for this, the compressed air was bubbled through a beaker containing water that is pre-saturated with CO<sub>2</sub> to make it fully humid. It is seen that the presence of moisture doesn't have a negative effect on the CO<sub>2</sub> uptake performance of the BEPBEGDA solvent but makes it slightly better. The performance of both the long chain amines were slightly below the 0.1M NaOH solution tested under similar conditions. Despite having slightly lower  $CO_2$  uptake, we expect that these long chain amines to have lower regeneration energy without loss in solvent due to their low vapor pressure discussed in the previous section.



Figure 13. (a) Real time  $CO_2$  capture performance (%) of the solvents (BEPBEGDA, BEEDIDA and 0.1 M NaOH) with time; (b) Cumulative  $CO_2$  capture performance showing moles of  $CO_2$  captured per moles of the solvent.

## 4.0 Conclusion and Future Work

Three CO<sub>2</sub> capture sorbents, consisting of amine-based CO<sub>2</sub>BOLs immobilized in mesoporous silica, were designed, synthesized, and tested. These sorbents had amine loadings of 19-23 wt% which is lower than typical amine-based silica sorbents. The solid-supported CO<sub>2</sub>BOLs also had lower surface area and pore volumes compared to the pristine silica support. The CO<sub>2</sub> capture performance of these materials was lower than the typical silica supported amines due to low amine loading and higher molecular weight with low amine density. These results indicate that immobilized CO<sub>2</sub>BOLs in silica need more optimization, such as higher loadings, to be viable for DAC based CO<sub>2</sub> capture.

Three new novel liquid solvents (BEEMPA, BEPBEGDA and BEEDIDA) were also evaluated. Liquid solvents derived from the post-combustion CO<sub>2</sub>BOLs were used as starting points, and were modified and synthesized for DAC application. Solvent property measurements included vapor pressure, CO<sub>2</sub> uptake capacity, kinetics, and viscosity. The viscosity of BEEMPA was high when loaded with pure  $CO_2$  to 7 wt%, to the extend that it was not flowable. The  $CO_2$  uptake capacity for BEPBEGDA was the highest at 13.2 wt%. The vapor pressure of the BEPBEGDA and BEEDIDA solvents were low at 80 °C compared to other solvents making them suitable for DAC application. The CO<sub>2</sub> uptake performance of the BEPBEGDA solvent was about 20% higher than BEEDIDA which can be partially attributed to the faster CO<sub>2</sub> uptake kinetics of BEPBEGDA as observed in the VLE isotherm. The effect of humidity on the CO<sub>2</sub> capture performance of these solvents was evaluated which shows that presence of moisture doesn't have a negative effect on the CO<sub>2</sub> uptake performance of the BEPBEGDA solvent and may slightly improve it. The performance of both solvents was slightly below that of the 0.1M NaOH solution tested under similar conditions. Despite of the slight lower  $CO_2$  uptake, it is expected that these liquid solvents will have lower regeneration temperature and minimum evaporative losses due their low vapor pressure.

Future work will focus on optimization of the liquid solvents for DAC application to improve both CO<sub>2</sub> capture efficiency and capacity without viscosity and vapor pressure increase. Testing of these solvents under DAC conditions will also be pursued, using a representative gas-liquid contactor. Solvent cost projections, techno-economic analysis and life cycle analysis are also required to evaluate economic viability are also needed.

### 5.0 References

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## Pacific Northwest National Laboratory

902 Battelle Boulevard P.O. Box 999 Richland, WA 99354

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