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Authors: Phillip Koech, Deepika Malhotra, David J Heldebrant, David C Cantu, Feng Zheng, Vassiliki-Alexandra Glezakou, and Roger Rousseau

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# Reinventing design principles for developing low-viscosity carbon dioxide binding organic liquids (CO<sub>2</sub>BOLs) for flue gas clean up

Deepika Malhotra,<sup>a</sup> Phillip K. Koech,<sup>\*a</sup> David J. Heldebrant,<sup>a</sup> David C. Cantu,<sup>b</sup> Feng Zheng,<sup>a</sup> Vassiliki-Alexandra Glezakou,<sup>b</sup> Roger Rousseau<sup>b</sup>

Dedication ((optional))

Abstract: Anthropogenic carbon dioxide (CO<sub>2</sub>) emissions from point sources, such as coal fired-power plants, account for the majority of the greenhouse gases in the atmosphere. Capture and storage or utilization are required to mitigate adverse environmental effects. Aqueous amine-based CO<sub>2</sub> capture solvents are currently considered the industry standard, but deployment to market is limited by their high regeneration energy. In that context, water-lean solvent systems such as CO<sub>2</sub>binding organic liquids (CO<sub>2</sub>BOLs) are being developed to reduce this energy requirement for CO<sub>2</sub> capture. Many water-lean solvents such as CO<sub>2</sub>BOLs are currently limited by the high viscosities of concentrated electrolyte solvents, thus many of these solvents have yet to move towards commercialization. Historically, viscosity reduction has been achieved by systematic methods such as introduction of steric hindrance on the anion to minimize the intermolecular cation-anion interactions, fine-tuning the electronics, hydrogen bonding orientation and strength, and charge solvation. Conventional standard trial-and-error approaches, while effective, are time consuming and economically expensive. We rethink the metrics and design principles of low-viscosity CO2 capture solvents using a combined synthesis and computational modeling approach. We critically study the effects of viscosity reducing factors such as orientation of hydrogen bonding, introduction of higher degrees of freedom, and cation or anion charge solvation, and assess whether or how each factor affects viscosity of CO2BOL CO2 capture solvents. Ultimately, we found that hydrogen bond orientation and strength is the predominant factor influencing the viscosity in CO2BOL solvents. With this knowledge, a new CO2BOL variant, 1-MEIPADM-2-BOL, was synthesized and tested, resulting in a solvent that is approximately 60% less viscous at 25 mol% CO<sub>2</sub> loading than our base compound 1-IPADM-2-BOL. The insights gained from the current study redefine the fundamental concepts and understanding of what influences viscosity in concentrated organic CO<sub>2</sub> capture solvents.

#### Introduction

Carbon dioxide  $(CO_2)$  capture from anthropogenic sources such as power plants, petrochemical industries, and refineries and

 Energy Processes and Materials Division, Pacific Northwest National Laboratory, Richland, WA99352, USA, E-mail: phillip.koech@pnnl.gov

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subsequent storage or utilization is critical to mitigate any adverse environmental effects. Aqueous amine solvent technology is at the forefront of CO<sub>2</sub> capture from flue gas. However, the energy loss associated with boiling and condensing water to regenerate the solvent system currently limits its deployment to the market.<sup>1</sup> Various water-lean solvent systems designed to minimize water content, including taskspecific ionic liquids (TSILs),2,3 phase change materials, nanomaterial organic hybrids,<sup>5</sup> aminosilicones,<sup>6,7</sup> and siloxylated amines,<sup>8,9</sup> have been developed as alternatives to the energyintensive aqueous-amine solvents. Although the chemical reactivity of each of these water-lean solvent classes is different. they are projected to be drop-in replacements for aqueous solvents, yet operate in presence of little or no water.<sup>10</sup> Waterlean solvent systems have been projected to offer ~40% reductions in energy requirements compared to aqueous amines or other water-based solvents due to lower specific heat capacities and lower water content.<sup>11,12</sup> In the past decade, our group has focused on development of the water-lean solvent system known as CO<sub>2</sub> binding organic liquids (CO<sub>2</sub>BOLs).<sup>13,14</sup> CO<sub>2</sub>BOLs are predicated on Jessop's switchable solvents that utilize a nonionic base (amidines or guanidines) with nonionic aliphatic alcohols. CO2BOLs chemically fixate CO2 as zwitterionic amidium or guanidinium alkyl carbonate liquids.<sup>13,14</sup> These CO<sub>2</sub>BOL solvents have shown excellent CO<sub>2</sub> uptake capacity, CO<sub>2</sub> mass transfer comparable to that of aqueous solvents, and favorable thermodynamic properties, albeit at higher solution viscosities. Viscosities of CO2BOLs and other water-lean solvents have been shown to increase exponentially with CO<sub>2</sub> loading.<sup>4,7,8,12,14-16</sup> While thermodynamically favorable, the high viscosities of CO2-loaded CO2BOLs (~500 cP) currently prevents them from being economical.<sup>12</sup> Similarly, other waterlean solvents such as aprotic heterocyclic anions (AHAs) with viscosities of ~140 cP,17-19 azole-based TSILs with viscosities of 650 cP<sup>20,21</sup> and hydroxylated amidines (HAAMS) at viscosities >1000 cP<sup>22</sup> are likely to be uneconomical until solution viscosities can be substantially reduced.

We recently performed a comprehensive study on 1-((1,3dimethylimidazolidin-2-ylidene)amino)propan-2-ol (1-IPADM-2-BOL) to measure physical, thermodynamic, and kinetic property data. Additionally, Aspen Plus<sup>TM</sup> modeling and bench-scale testing were performed for both thermal and polarity swing assisted regeneration (PSAR) CO<sub>2</sub> release modes.<sup>10</sup> This study revealed that 1-IPADM-2-BOL has the potential to be an energetically viable CO<sub>2</sub> capture solvent, assuming viscosities could be reduced.

<sup>[</sup>b] Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA

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To address this challenge, our efforts are currently focused on not just designing less-viscous solvent systems for CO<sub>2</sub> capture, but to learn how to make less-viscous solvents at the molecular level while retaining adequate CO<sub>2</sub> capture capacity and low specific heat capacity and regeneration energy. Historically, a trial-and-error approach would be employed. As in our own previous work, such approaches using organic chemistry intuition have been shown to be effective,<sup>14</sup> though it was never clear why or how conventional viscosity-reducing structural motifs actually affected viscosity. The solvent development process can be accelerated using high throughput computational screening of solvent viscosities from a library of compounds to down select candidates for synthesis and testing. In this study, we apply an integrated computationally aided design, synthesis, and characterization efforts to assess the effects of molecular design principles that are commonly used to reduce viscosity in liquids. Each molecule consisting of the motif to be evaluated is modeled, synthesized, and measured, after which a critical assessment is made of not just whether, but how viscosity is affected in solution. Ultimately it is shown that each motif affects viscosity to some degree, but not through the molecular-level interactions they were designed for. Here, we rethink and simplify the design principles for viscosity reduction in organic CO<sub>2</sub> capture solvents.

We have previously shown that a critical indicator of the high viscosity of CO<sub>2</sub>BOLs is the hydrogen bonding network.<sup>23</sup> Hydrogen bonding and viscosity correlations in ionic liquids have also been discussed at length.<sup>24</sup> TSILs that possess N or O atoms capable of intramolecular hydrogen bonding have significantly lower CO<sub>2</sub>-rich viscosity compared to conventional ILs.<sup>25</sup> Upon CO<sub>2</sub> capture, CO<sub>2</sub>BOLs form a zwitterion capable of forming *intra*- or *inter*molecular hydrogen bonds, as shown in Figure 2. In recent computational studies, we have determined that a high population of molecules engaged in intramolecular H-bonds leads to higher viscosities.<sup>23,26</sup> Therefore understanding the effect of structural modifications on the inter-/intramolecular hydrogen bonding, and thereby on viscosity, is a critical aspect of our molecular design strategy.



Figure 2. Inter-vs. intramolecular hydrogen bonding forms in CO2BOLs.

#### **Results and Discussion**

Our current 1-IPADM-2-BOL molecule was used as a template to apply different functionalities in this study (Figure 1). A few molecular design criteria were kept to ensure adequate  $CO_2$  uptake and durability. First, the highly basic guanidine moiety was retained, as it has been shown to capture >90%  $CO_2$  from a (15%  $CO_2$ ) gas stream with acceptable solvent recirculation rates.<sup>11</sup> Second, the cyclic guanidine base core was retained to prevent hydrolysis of the reactive guanidinium moiety of the  $CO_2$ -bound  $CO_2BOL$ .<sup>15</sup> From this template, viscosity modifying motifs could be introduced to study the effects of maximizing or minimizing steric hindrance to prevent stacking, minimizing intermolecular cation/anion interactions, or fine-tuning electronic effects of the anion.



Figure 1. Generic structure representing structural motifs to reduce viscosity of  $\text{CO}_2\text{BOL}$  molecules.

In our recent computational studies,<sup>23,26</sup> we showed proof-ofprinciple that the molecular structure can be modified to increase intramolecular H-bonding in CO<sub>2</sub>-bound molecules that will in turn induce viscosity reductions.<sup>23</sup> Here, two guanidine-based CO2BOL variants (1-PADM-2-BOL and 1-IPADM-2-BOL) bearing linear and branched alkyl alcohol, respectively, in the side chain, were chosen as case study to validate the theorygenerated hypothesis. Internal H-bonding<sup>23</sup> was indeed found to be critical in reducing the viscosity: 1-IPADM-2-BOL is at least five times less viscous than 1-PADM-2-BOL at CO<sub>2</sub> loading of 25 mol% (Figure 3). This can be explained by the fact that 34% of CO<sub>2</sub>-bound 1-IPADM-2-BOL displayed an internal H-binding conformation, compared to less than 1% for 1-PADM-2-BOL.<sup>23</sup> Based on this finding, our molecular design strategy was to retain the high degree of internal hydrogen bonding while systematically evaluating each viscosity-reducing factor. Thus, the final design criteria were to retain the 2° alcohol moiety of the 1-IPADM-2-BOL template.

1-PADM-2-BOL Viscosity >>1,000 cP at 25 mol %CO<sub>2</sub>

1-IPADM-2-BOL Viscosity ~200cP at 25 mol %CO<sub>2</sub>

Figure 3. Viscosity of 1-PADM-2-BOL and 1-IPADM-2-BOL at CO\_2 loading of 25 mol%.

Once incorporated, the individual structural motifs in Figure 1 can be systematically studied to determine their impacts on viscosity. They are referred to as "viscosity-reducing factors" in the following discussion.

#### Viscosity-Reducing Factor 1: Steric Tuning of CO<sub>2</sub>BOLs

Intermolecular cation-anion interactions have been hypothesized to be a factor that contributes to high viscosities of concentrated organic electrolyte solutions such as CO<sub>2</sub>BOLs. It is believed that minimizing the ion pair interactions between different molecules could reduce the viscosity of the solvent. Our first strategy to investigate the viability of minimizing ion pair interactions was to break molecular symmetry by introducing different conformers to reduce stacking.

To investigate the potential effect of conformational flexibility of the guanidinium cation on viscosity, we designed 1-IPADM-3-BOL, which contains a six-membered tetrahydropyrimidine ring core while retaining the essential component of a high degree of internal hydrogen bonding (Scheme 1). The CO<sub>2</sub>-bound form of 1-IPADM-3-BOL has conformational flexibility as it can flip between two chair conformations,<sup>27</sup> leading to more degrees of freedom than the five-membered ring in 1-IPADM-2-BOL. The addition of boat and chair conformers was hypothesized to reduce the stacking ability of the molecule, thus minimizing ion pair association, which would translate to a lower viscosity solvent (Scheme 1).

We incorporated this motif, synthesizing 1-IPADM-3-BOL using our standard Vilsmeier salt protocol i.e., condensation of 1aminopropan-2-ol with Vilsmeier salt **2** (Scheme 1).<sup>14</sup> The structure of 1-IPADM-3-BOL was confirmed with <sup>1</sup>H and <sup>13</sup>C NMR characterization with the diagnostic peak of guanidine carbon (C=N) at 161.7 ppm. The CO<sub>2</sub>-bound substrate displayed a downfield chemical shift for  $-CH_2O$ - from 59.7 ppm to 63.3 ppm, which coincided with our earlier observations.<sup>14</sup> However, an up-field shift was reported for the signal corresponding to -C=N- from 161.7 ppm to 159.0 ppm, which could be attributed to the shielding effect induced by the conformational changes in the CO<sub>2</sub>-bound 1-IPADM-3-BOL.



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme 1. Synthetic methodology and conformational flexibility in $CO_2$ bound $1$-IPADM-3-BOL. \\ \end{array}$ 

The  $CO_2$  uptake of 1-IPADM-3-BOL was confirmed gravimetrically by bubbling  $CO_2$  through neat liquid at 25 °C. The

CO2 uptake capacity was found to be 8.7 wt% for 1-IPADM-3-BOL (Table 1), which was slightly lower than that of 1-IPADM-2-BOL at 9.0 wt%<sup>14</sup> which is attributed to the higher molecular mass of the former. The uptake capacity for CO<sub>2</sub>BOLs is less than 50 mol% mainly due increased viscosity which limits CO2 mass transfer. The CO2-rich 1-IPADM-3-BOL was found to be visually less viscous than 1-IPADM-2-BOL according to our preliminary falling-ball viscosity measurements (Supporting information-S1). However, formal viscosity measurements using our custom  $\Delta PVT$  (pressure volume temperature) cell (Figure 4) showed that the viscosity of 1-IPADM-3-BOL was higher at all loadings than that of 1-IPADM-2-BOL. The viscosity of 1-IPADM-3-BOL was calculated at 237 cP using a reduced-order model for CO2BOL viscosity26, comparable to the experimentally measured value of 318 cP. 1-IPADM-3-BOL is more viscous than 1-IPADM-2-BOL, with a calculated viscosity of 164 cP, and an experimentally measured on of 171 cP (Table 1). Computation and experiment indicate that this viscosity-reducing factor, increase in conformational flexibility, did not have the desired effect and may not be a viable strategy to reduce viscosity.



Figure 4. Viscosity vs. loading correlation for selected  $CO_2BOLs$ . 1-TMSIPADM-2-BOL was not tested because of its high viscosity.

It was initially unclear why 1-IPADM-3-BOL with higher degrees of flexibility would have a higher viscosity than 1-IPADM-2-BOL since both molecules are structurally similar. We turned to molecular dynamics (MD) simulations to determine the root cause of this anomaly. Our simulations clearly showed that the percentage of CO<sub>2</sub>-bound molecules with internal hydrogen bonding at 25% mol CO<sub>2</sub> loading (P<sub>int</sub>) for 1-IPADM-3-BOL was 21%, compared to the 34% for 1-IPADM-2-BOL. Thus, it was concluded that the increase in viscosity was due to the reduction in the P<sub>int</sub> and that the introduction of conformational flexibility

CO <sub>2</sub> BOLs	Wt% (CO <sub>2</sub> )	Mol% (CO <sub>2</sub> )	P <sub>int</sub>	η <sub>Experimental</sub> (25 mol%)	η <sub>Theory</sub> (25 mol%)
N OH N N- 1-IPADM-3-BOL	8.7	40	21%	318	237
N OH I	5.5	30	39%	ND*	143
HO N N N 1-MEIPADM-2-BOL	7.3	35.5	52%	75	99
N N H 1-IPADM-2-BOL	9.0	44 <sup>14</sup>	34%	171	164

plays a minimal role (if any) compared to the orientation and speciation of hydrogen bonding in this molecule.

 Table 1. Gravimetric weight capacities, P<sub>int</sub>, and viscosities for selected CO<sub>2</sub>BOLs (\*ND indicates not determined).

**Viscosity-Reducing Factor 2a:** Anion Charge Solvation Another viscosity reducing factor typically employed in solvent development is charge solvation. Weakening the cation-anion interactions by promoting either *intra-* or *inter*molecular interactions with other structural motifs may reduce the viscosity of concentrated organic solvents. We postulated that this could be achieved in two ways: anion (carboxylate) or cation (guanidinium) charge solvation. The first could be achieved via addition of a pendant highly oxophilic silane group to coordinate to oxygen in the alkylcarbonate anion. A second approach would be to introduce ether motifs that could promote solvation of cations through coordination by unpaired electrons in ether groups.<sup>28,29</sup> In order to validate this hypothesis, we introduced structural motifs that were believed to promote either cation or anion charge solvation.

With that goal, we designed silane-based  $CO_2BOL$  1-TMSIPADM-2-BOL, with an oxophilic silane moiety (Scheme 2, 8a). The rationale behind introducing the silane group into  $CO_2BOLs$  is based on the fact that silicon is highly oxophilic and may form a dative bond with the carbonate anion. The dative bond formation could thereby weaken the intermolecular cationanion interactions and lead to reduced solvent viscosity. Our synthesis of 1-TMSIPADM-2-BOL involved the addition of trimethylsilylmethylmagnesium chloride **3** to chloroacetaldehyde **4** to generate chlorotrimethylsilylpropan-2-ol **5** at room temperature (Scheme 2). The trimethylsilyl chlorohydrin **5** was reacted with sodium azide to furnish the corresponding azidoalcohol **6**, which underwent reduction catalyzed by palladium on carbon to generate silylamino alcohol **7**. The condensation of silylamino alcohol **7** with Vilsmeier salt **8** furnished **8a** (1-TMSIPADM-2-BOL).



Scheme 2. Synthetic methodology for the synthesis of 1-TMSIPADM-2-BOL.

The gravimetric CO<sub>2</sub> uptake ability of 1-TMSIPADM-2-BOL was evaluated by bubbling CO<sub>2</sub> into a neat sample at 25 °C, which gave a capacity of 5.5 wt%. This low CO2 uptake capacity can be attributed to destabilized or unbalanced charges of the zwitterion species, which favor the reverse reaction over the formation of the CO<sub>2</sub>-bound product. This result underscores the delicate balance that needs to be achieved in order to find an optimal material with both high CO<sub>2</sub> capture capacity and low CO2-rich solvent viscosity. The CO2 bound 1-TMSIPADM-2-BOL was found to be comparable in viscosity to 1-IPADM-2-BOL. The carbon dioxide capture ability of 1-TMSIPADM-2-BOL was further evaluated by both <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The CO<sub>2</sub>-free CO<sub>2</sub>BOLs' signals are consistent with those previously observed for alkanolouanidines with the quanidine carbon at 158.0 ppm. The characteristic peak for the CO<sub>2</sub>-bound 1-TMSIPADM-2-BOL had a downfield shift for the signal corresponding to -C=N- from 158.0 to 161.8 ppm, which is consistent with our previous report.14

Preliminary viscosity measurements using a falling-ball viscometer showed that 1-TMSIPADM-2-BOL was initially less viscous than 1-IPADM-2-BOL but the sample solidified at higher loadings (Figure S1 in supporting information). This observation was confirmed in that the initial low lean solvent viscosities that were predicted with the reduced model (143 cP Table 1). Figure 5 shows the radial distribution function of the interaction of the oxygen in the alkylcarbonate anion with either the guanidinium cation or the silicon in the TMS moiety. Here it can be seen that the carboxylate anion preferentially interacts with the guanidinium cation at ~2 Å and there is negligible interaction with the silicon at 5.5 Å. This observation is consistent with the calculated values of higher  $P_{int}$  for 1-TMSIPADM-2-BOL than 1-IPADM-2-BOL.

Ultimately, anion charge solvation may not be contributing towards viscosity reduction and internal hydrogen bonding is still the predominant factor in controlling the viscosity of CO<sub>2</sub>BOLs. It is unclear why 1-TMSIPADM-2-BOL solidified at higher CO<sub>2</sub>

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loadings, but regardless, this phase change suggests that this compound would not be viable in a solvent process and as such was not tested for formal viscosity measurements on the  $\Delta PVT$  cell.



Figure 5. Proposed alkylcarbonate-silane interaction in 1-TMSIPADM-2-BOL and plot of radial distribution vs. distance.

#### Viscosity-Reducing Factor 2b: Cation Charge Solvation

Conversely, we explored the viability of cation charge solvation. We envisioned that the introduction of ether functionalities could solvate positive charges by interaction with unpaired electrons on the -O- moiety. Ethereal groups such as those found in crown ethers have been shown to reduce solvent viscosity.<sup>29</sup> To test this concept, we designed 1-MEIPADM-2-BOL consisting of a methyl ether group proximal to the alcohol moiety (Scheme 4). Synthesis of 1-MEIPADM-2-BOL follows a similar reaction sequence as for 1-TMSIPADM-2-BOL, which begins with displacement of the chloride group of the commercially available 1-chloro-3-methoxypropanan-2-ol 9 using sodium azide to afford azido-alcohol 10 (Scheme 3). The azido-alcohol 10 is then reduced using a palladium-on-carbon catalyst and hydrogen gas to afford the amino alcohol 11, which was condensed with Vilsmeier salt 8 to yield 1-MEIPADM-2-BOL. The structure of 1-MEIPADM-2-BOL was successfully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, and the CO<sub>2</sub>-bound form of 1-MEIPADM-2-BOL exhibited downfield shift for -C=N- signal from 157.8 ppm to 160.1 ppm, which is in accordance with our previous observations.





Scheme 3. Synthetic scheme for 1-MEIPADM-2-BOL.

The CO<sub>2</sub> uptake for 1-MEIPADM-2-BOL was confirmed gravimetrically, yielding a capture capacity of 7.3 wt% (Table 1). Visual observations showed that the CO<sub>2</sub>-bound 1-MEIPADM-2-BOL was significantly less viscous than 1-IPADM-2-BOL. viscometer and ∆PVT Falling-ball cell measurements corroborated our visual observations of reduced viscosity of CO2-rich 1-MEIPADM-2-BOL solvent. 1-MEIPADM-2-BOL was found to be approximately 60% less viscous than our base compound 1-IPADM-2-BOL at higher loadings (Figure 4), indicating the ethereal moiety did provide a substantial decrease in viscosity. The reduced model also confirmed a lower CO<sub>2</sub>-lean solvent viscosity (99 cP calculated, 75 cP measured) compared to 1-IPADM-2-BOL (164 cP calculated, 171 cP measured).

Our initial conclusion was to attribute the decrease in viscosity to the proposed cation charge solvation, though this was not the case. The radial distribution coefficient for 1-MEIPADM-2-BOL obtained from molecular dynamics simulations (Figure 6) showed negligible intramolecular or intermolecular guanidinium interactions with the ether moiety, but preferential interaction between the alkylcarbonate anion with the guanidine moiety at ~1.8 Å. These results indicate that charge solvation did not exist and was not likely to play a significant role in viscosity.

The  $P_{int}$  value for 1-MEIPADM-2-BOL was calculated to be 52% from MD simulations, which is significantly higher than the 34% of 1-IPADM-2-BOL (Table 1). These simulations confirm that the viscosity reduction could not be attributed to any charge solvation and that viscosity in these solvents is mainly attributed to the hydrogen bonding in solution.

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Figure 6. Intramolecular interaction in 1-MEIPADM-2-BOL and plot of radial distribution vs. distance.

#### Conclusions

In this study, we systematically incorporated conventional structural motifs that are commonly used to reduce viscosity in electrolyte concentrated organic solvents. Synthesis, experimental testing and molecular simulation have shown that introduction of moieties that promote higher degrees of freedom or cation or anion charge solvation provides negligible contributions to viscosity for CO2BOL CO2 capture solvents. We found that hydrogen bond orientation and strength were the main parameters that influenced viscosity in CO<sub>2</sub>BOL solvents. In this study, a new CO<sub>2</sub>BOL variant 1-MEIPADM-2-BOL that is approximately 60% less viscous than our base compound 1-IPADM-2-BOL was discovered. The viscosity reduction was found to be simply due to an increase in intramolecular hydrogen bonding and not any of the viscosity reducing factors that we had set out to assess. Ultimately, this study highlights that the design criteria for lowering viscosity of water-lean CO2BOL solvents can be simplified and redefined to focus mainly on promoting a high degree of intramolecular hydrogen bonding. As a consequence, we are now working toward designing molecules that have an even higher degree of internal hydrogen bonding to continue to reduce the viscosity of CO<sub>2</sub>BOL solvents. We believe that this new understanding of molecularlevel interactions that govern viscosity will be applicable to other water-lean CO<sub>2</sub> capture solvents and will enable viscosity reductions in all solvent systems. These studies are the current focus of our group.

#### **Experimental Section**

**Experimental Details – General:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 500 MHz and 126 MHz (or 400 MHz and 101 MHz), respectively, using CDCl<sub>3</sub> as a solvent. The chemical shifts are reported in  $\delta$  (ppm) values (<sup>1</sup>H and <sup>13</sup>C NMR relative to CHCl<sub>3</sub>,  $\delta$  7.26 ppm for <sup>1</sup>H NMR and  $\delta$  77.0 ppm for <sup>13</sup>C NMR; multiplicities are indicated by s (singlet), d (doublet), t (triplet), sex (sextet), dd (doublet of doublets), m (multiplet) and br (broad). Coupling constants (*J*) are reported in Hertz (Hz). All reagents and solvents were employed without further purification. The products were purified using a flash chromatography system or a regular gravity glass column. Thin-layer chromatography (TLC) was developed on silica gel 60G F254 glass plates.

Experimental details for **ΔPVT** Cell<sup>26</sup>: For viscosity measurements: CO<sub>2</sub>BOL liquid viscosity as a function of CO<sub>2</sub> loading was measured using a custom flow cell developed infor simultaneous measurements of vapor/liquid house equilibrium and physical properties of nonaqueous solvents requiring less than 50 cc sample size. A sequence of quantitative injections of CO2 gas (Oxarc 99.99%) into the flow cell was performed at sub-ambient pressures. The amount of CO<sub>2</sub> absorption was determined from temperature and pressure measurements and the ideal gas equation of state. The liquid CO<sub>2</sub> loading was determined from the mass balance. A pump loop and an internal gas/liquid contactor were used to provide mixing and facilitate the approach to absorption equilibrium. An in-line viscosity sensor (Cambridge Viscosity, SPC-372 sensor head and VISCOpro 2000 viscometer) was used to obtain realtime viscosity data as the liquid sample was circulated inside the flow cell. The cell was made of stainless steel high vacuum components with an internal vapor volume of about 150 cc. The pump loop consisted of a gear pump (Micropump GA series) and a custom wetted wall stainless steel contactor (Ø1.27×12.4 cm) inside the cell. The cell pressure was measured using temperature-controlled capacitance diaphragm gauges with an accuracy of 0.2% (Nor-Cal CDG-100 series). The cell temperature was controlled within 0.1°C by a large circulating water bath. The operation range of the flow cell was 20°C-100°C and vacuum to 1 bar.

In a typical flow cell experiment, a known amount of CO2-free CO<sub>2</sub>BOL liquid sample was loaded into the cell under nitrogen protection and was allowed to reach an initial steady state at the testing temperature under the liquid's own vapor pressure. A small amount of CO<sub>2</sub> was injected quantitatively from a calibrated volume. The cell pressure was allowed to come to a new steady state under constant temperature. The change in liquid CO2 loading was calculated based on the cell pressure change and the known cell volume. The steady-state viscosity, equilibrium pressure, and liquid CO2 loading were recorded. Additional CO<sub>2</sub> injections were done to repeat the above process until a target CO<sub>2</sub> loading was reached. The liquid sample was regenerated in situ by raising the water bath temperature to 80°C and reducing the cell pressure using a vacuum pump (Edwards RV8). The operation of the cell was validated using a CO2BOL solvent with published viscosity and vapor/liquid equilibrium data.

**Computation:** Classical MD simulations of CO<sub>2</sub>BOL solvents at 25 mol% CO<sub>2</sub> loadings were done, as described in our previous work,  $^{23,26}$  to obtain the percentage of CO<sub>2</sub>-bound molecules with an internal hydrogen bond (P<sub>int</sub>) values, and radial distribution functions. Viscosities were calculated using the reduced model

presented in our recent work<sup>26</sup> using P<sub>int</sub> values obtained from classical MD.

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#### Layout 2:

## FULL PAPER



1-MEIPADM-2-BOL+CO<sub>2</sub> Percentage of internal hydrogen bonding P<sub>int</sub> 52% (~60 % less viscous) Deepika Malhotra,<sup>a</sup> Phillip K. Koech,<sup>\*a</sup> David J. Heldebrant,<sup>a</sup> David C. Cantu,<sup>b</sup> Feng Zheng,<sup>a</sup> Vassiliki-Alexandra Glezakou,<sup>b</sup> Roger Rousseau<sup>b</sup>

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Reinventing design principles for developing low-viscosity carbon dioxide binding organic liquids (CO<sub>2</sub>BOLs) for flue gas clean up