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Cooperative CO_2 Absorption Isotherms from a Bifunctional Guanidine and Bifunctional Alcohol

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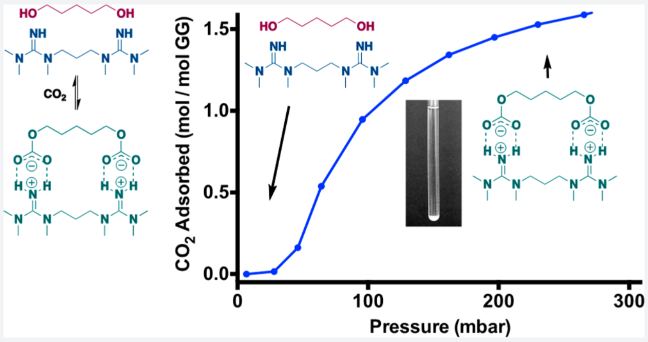
Ⓢ *Supporting Information*



ABSTRACT: Designing new liquids for CO_2 absorption is a challenge in CO_2 removal. Here, achieving low regeneration energies while keeping high selectivity and large capacity are current challenges. Recent cooperative metal–organic frameworks have shown the potential to address many of these challenges. However, many absorbent systems and designs rely on liquid capture agents. We present herein a liquid absorption system which exhibits cooperative CO_2 absorption isotherms. Upon introduction, CO_2 uptake is initially suppressed, followed by an abrupt increase in absorption. The liquid consists of a bifunctional guanidine and bifunctional alcohol, which, when dissolved in bis(2-methoxyethyl) ether, forms a secondary viscous phase within seconds in response to increases in CO_2. The precipitation of this second viscous phase drives CO_2 absorption from the gas phase. The isotherm of the bifunctional system differs starkly from the analogous monofunctional system, which exhibits limited CO_2 uptake across the same pressure range. In our system, CO_2 absorption is strongly solvent dependent. In DMSO, both systems exhibit hyperbolic isotherms and no precipitation occurs. Subsequent ^{1}H NMR experiments confirmed the formation of distinct alkylcarbonate species having either one or two molecules of CO_2 bound. The solvent and structure relationships derived from these results can be used to tailor new liquid absorption systems to the conditions of a given CO_2 separation process.

Large-scale CO_2 capture has been proposed as an important—and perhaps necessary—tool for limiting atmospheric CO_2 concentrations.[1] A number of commercial projects currently employ aqueous monoethanolamine or other liquid amine systems to separate CO_2 from other gases, including for natural gas processing or postcombustion capture.[2] Significant energy is required to desorb the CO_2, adding operational costs that have limited wider deployment of CO_2 capture technology.[3,4]

Chemists have developed a wide array of materials aimed at reducing the energy required for CO_2 capture.[5,6] Such materials include ionic liquids,[7,8] metal–organic frameworks,[9,10] and other sorbents.[11−15] These materials typically have hyperbolic isotherms where CO_2 uptake increases quickly at lower pressures, but levels off as available binding sites become saturated. This type of thermodynamic behavior presents a fundamental dichotomy: materials exhibiting high CO_2 affinity are often correspondingly difficult to desorb, while materials exhibiting low affinity may show poor CO_2 uptake or lack selectivity for CO_2 over other gases.

One strategy for overcoming this dichotomy is to design a material that transitions between high and low affinity binding. In the high affinity regime, the material would bind CO_2 strongly and selectively; in the low affinity regime, the CO_2 would readily desorb. This is commonly seen in nature, where hemoglobin uses this method to capture and release O_2. Cooperative diamine-functionalized metal organic frameworks use sterics and amine affinity to tune this transition from low to high affinity,[13] potentially improving the efficiency of CO_2 capture by allowing absorption/desorption cycles to occur over a narrower pressure or temperature range.[14] In another example, the Schneider and Brennecke groups reported an ionic liquid that melts upon CO_2 binding, exhibiting sigmoidal isotherms.[15] The associated heat of fusion (ΔH_{fus}) contributes to the heat required for CO_2 desorption. Still, examples of cooperative CO_2 absorption isotherms remain scarce. New strategies for obtaining cooperative isotherms would provide a valuable resource to design more efficient CO_2 capture materials.

Herein, we report a solution phase system comprising a bidentate guanidine (GG) and bidentate alcohol (AA) that exhibits cooperative isotherms at ambient temperature (Figure 1). Solution-based methods for CO_2 capture are of great interest, due, in part, to the possibility of incorporation within monoethanolamine CO_2 binding infrastructure.

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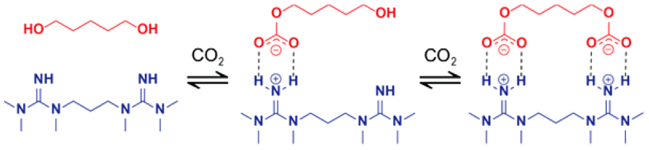
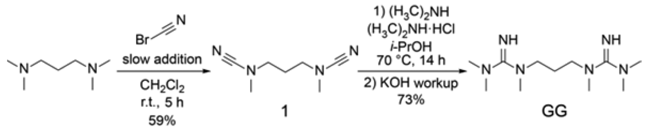


Figure 1. CO_2 binding by a bidentate alcohol and bidentate guanidine. A solution of 1,5-pentandiol (AA) and bis trimethylguanidine species (GG) may capture CO_2 in a cooperative fashion.

The 1,1′-(propane-1,3-diyl)bis(1,3,3-trimethylguanidine) (GG) 1,5-pentanediol (AA) system extends chemistry developed by Jessop, Heldebrant, and co-workers[16−18] in which an alcohol and strong organic base react with CO_2. The reaction forms the salt of a negatively charged alkyl carbonate species and a positively charged, protonated base. We hypothesized that, for a bifunctional system, binding of the first CO_2 molecule would generate an ionic interaction that facilitates binding of the second CO_2 molecule (Figure 1).

We measured CO_2 absorption isotherms for the system comprising the bifunctional guanidine shown in Figure 1 (GG) and a commercially available bifunctional alcohol (1,5-pentanediol, AA). The bifunctional guanidine GG was synthesized in two steps on multigram scale. First, 1,3-bis(dimethylamino)propane was reacted with cyanogen bromide to afford bis-cyanamide **1**.[19,20] Next, the bis-cyanamide was reacted with dimethylamine and dimethylamine·HCl to obtain the corresponding bis-guanidinium dichloride, which was treated with concentrated aqueous KOH to obtain 1,1′-(propane-1,3-diyl)bis(1,3,3-trimethylguanidine), GG (Scheme 1; see Supporting Information for details).

Scheme 1. Synthesis of Bifunctional Guanidine GG



To determine the potential for these bidentate species to exhibit cooperative isotherms, we conducted analysis on a gas sorption analyzer adjusted for a liquid system (3-Flex). (The physical dissolution of CO_2 in the solvent was measured independently and subtracted from the overall absorption to determine the chemically absorbed component. Additionally, an approximation of the initial flask volume was used due to the liquid phase of the analytes. See Supporting Information section II, p 16, for complete details.) In early experiments, we observed that solvent plays a large role in controlling CO_2 binding for the AA:GG system. Specifically, in bis(2-methoxyethyl) ether (diglyme) we observed an increased amount of CO_2 absorbed overall vs DMSO, as well as an inflection point—a transition from low affinity to high affinity—in the shape of the CO_2 absorption isotherm. We calculated a Hill coefficient of 2.4 for this isotherm, indicating cooperative binding of CO_2.[21] For measures of the CO_2 binding capacities of other system components, please see Table S2.

After observing the unique responses of the AA:GG system in diglyme, we sought to determine how the solvent was influencing binding. We examined an analogous monodentate CO_2 binding system to see how solvent related to CO_2-binding ability (Figure 2a). Analysis of the slope of the isotherm did not suggest a shift in CO_2 binding between low and high pressure regimes, and no precipitation was observed. It should be noted that, relative to the bidentate GG AA system, CO_2 absorption is suppressed across the entire isotherm.

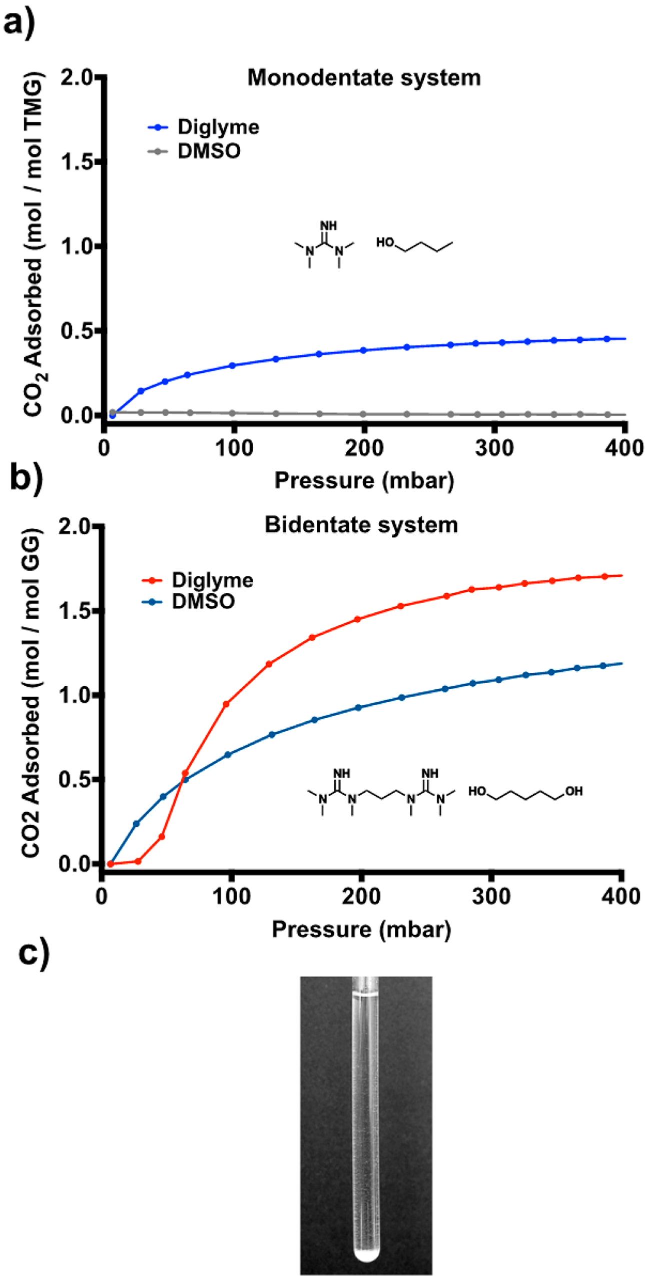


Figure 2. CO_2 absorption isotherms varying solvent and denticity. (a) 50 mM GG and 75 mM AA in diglyme and DMSO at 22 °C. (b) 50 mM *N,N,N′,N′*-tetramethylguanidine and 75 mM *n*-butanol in DMSO and bis(2-methoxyethyl) ether at 22 °C. (c) An NMR sample of a CO_2-saturated mixture of GG:AA, 1:1 ratio, evolves a viscous secondary phase (see Supporting Information section III for further details).

The altered shape of the AA:GG binding isotherm in diglyme relative to the monodentate suggested potential cooperativity in the bidentate system, as evidenced by the appearance of distinct low affinity and high affinity CO_2 binding regimes. (Figure 2a,b). This transition was always accompanied by the precipitation of a second phase from the CO_2 capture solution. This may explain, in part, why diglyme demonstrates a dramatic

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CO_2 absorption transition, whereas DMSO does not: the precipitation of the second phase (which contains CO_2) correlates with the binding mode change (Figure 2c). The selection of diglyme as a medium for CO_2 absorption agrees with solvent surveys reported for CO_2 capture with monoethanolamine.[22]

With a functional solvent determined, we next sought to ascertain the correct molar ratio of GG to AA to provide optimized CO_2 absorption (Figure 3a). In an interesting relationship, we found that 1:1 GG:AA displayed low affinity up to 68 mbar, where it sharply transitions to high affinity behavior. CO_2 absorption plateaus at approximately 1.1 mol/mol GG. In stark contrast, a relatively small change in ratio, 1:1.5 GG:AA, results in a very different isotherm. Here, low affinity behavior begins to transition earlier, at approximately 29 mbar, and CO_2 absorption levels at approximately 1.7 mol/mol GG. Increasing the ratio further does very little to change the CO_2 absorption profile: 1:2 GG:AA transitions to high affinity at 28 mbar, and CO_2 absorption levels at approximately 1.8 mol/mol GG. These data reinforce the hypothesis of the bimolecular requirement for CO_2 binding.

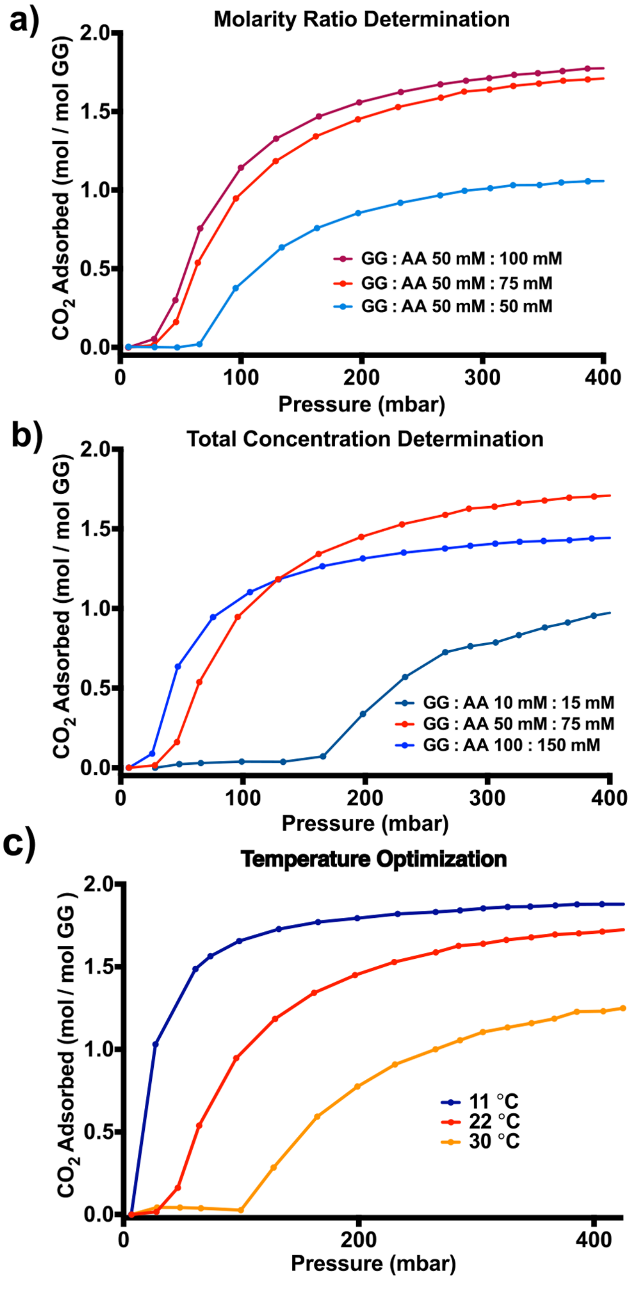

Figure 3. Evaluation of CO_2 absorption parameters. (a) Optimization of molar ratios of GG to AA in diglyme at 22 °C. (b) Optimization of concentrations of a 1:1.5 molar ratio of GG to AA in diglyme at 22 °C. (c) Temperature optimization of a 1:1.5 molar ratio of GG:AA in diglyme.

We next determined if concentration of GG:AA in diglyme would change the binding properties by potentially increasing the cooperativity and therefore the transition point (Figure 3b). A ratio of 10 mM GG to 15 mM AA resulted in a suppressed isotherm compared to higher concentrations, with an affinity switch occurring at 166 mbar. A ratio of 100 mM GG:150 mM AA resulted in a decreased pressure range of low affinity behavior, and a leveling off of CO_2 absorption at approximately 1.4 mol/mol GG, indicating some suppression of high affinity behavior relative to the 50 mM GG:75 mM AA regime. The Hill coefficient remained 2.4. This suppression may be due to the viscosity of the CO_2-rich phase prohibiting successful mixing with a magnetic stirring apparatus. In light of these results, 50 mM AA:75 mM AA was used for all further experiments.

As we had observed the formation of a distinct second phase, we hypothesized that the solubility of the second phase may be an important factor in determining the onset of the precipitation and the low to high affinity transition. To test this, we examined absorption as a function of solution temperatures (Figure 3c). We observed a striking temperature dependence on the cooperative CO_2 binding of our system. At 11 °C, a region of suppressed uptake—low CO_2 affinity—is not observed at the pressure regime assayed, though this does not preclude its existence. Conversely, at 30 °C the region of low affinity extends until 101 mbar, almost three times the pressure at which the shift to high affinity occurs at 22 °C. This results in a change in the capacity of ~0.06 mmol of CO_2 per mL of liquid at 165 mbar. While modest, this represents a large change in the overall capacity of 70% at a target CO_2 pressure over a very modest temperature range.

At all temperatures and concentrations assayed, the inflection in the CO_2 absorption isotherm, corresponding to the transition from low affinity to high affinity, coincided with visually observable precipitation of a second, viscous phase. This phase appeared to contain predominantly $A^-A^-G^+G^+$-2(CO_2) and led us to hypothesize that the captured CO_2 was precipitating. To clarify, we sought further characterization.

The precipitated phase was a highly viscous, turbid liquid (Figure 2c, Figure S9) that could be removed from the vial and analyzed, but would dissipate upon dissolution in other solvents, such as DMSO. ATR-IR analysis of the precipitate (Figure S7) showed that the phase was composed predominantly of alkylcarbonate and guanidinium functional groups, formed from the reaction of AA and GG with CO_2. These data indicate that there is limited solubility of the bis-alkylcarbonate and bis-guanidinium species, resulting in the formation of the new, CO_2-rich phase.

The ATR-IR data, as well as the suppression in CO_2 uptake, is consistent with previous observations by Heldebrant and coworkers that nonpolar solvents trigger CO_2 desorption by destabilizing the charged alkylcarbonate and guanidinium species.[17] Unlike the monofunctional system, bifunctional AA and GG appear to gain CO_2 affinity as correlating with the precipitation process. We hypothesize that the affinity is caused by two interrelated factors: (1) the linker couples binding of the first and second CO_2 molecules, so that the binding of the first molecules facilitates binding the second equivalent; (2) the resulting bis-cationic and bis-anionic species have relatively low solubility in diglyme. As increasing concentrations of CO_2 increase the concentration of the charged species, the charged species precipitate after reaching a solubility limit, designated by the temperature and solvent.

Based on these data, we can further understand the results seen in Figure 2. We hypothesize that DMSO, a strongly polar solvent, disrupts ion pairing between the cationic guanidinium and anionic alkylcarbonate functional groups of AAGG complex. Therefore, the charged functional groups remain dissociated and the binding of the first CO_2 molecule poorly facilitates binding of the second CO_2 molecule. DMSO disrupts other ionic interactions, especially by coordinating cations.[23,24] Alternatively, DMSO may act as a better solvent for the AAGG complex, altering the equilibria associated with the CO_2 absoprtion process.

To further confirm whether the cooperative binding observed was the result of a cooperative phenomenon between the AA and GG species, we used ^1H NMR to study CO_2 binding by AA and GG. For practical reasons, we used a cosolvent mixture of DMSO-d_6 and acetonitrile-d_3 to prepare NMR samples. A minimum of 20% (v/v) DMSO-d_6 was required to maintain a homogeneous solution, so samples were prepared ranging from 20 to 100% DMSO-d_6.

Exposure of solutions containing AA and GG to 1 atm of CO_2 led to the formation of two distinct alkylcarbonate species, mono-alkylcarbonate A^-A and bis-alkylcarbonate A^-A^- (Figure 4a). These species possess well-resolved resonances in the δ = 3.6−3.9 ppm region corresponding to protons adjacent to the newly formed alkylcarbonate functional groups (H_b and H_d). The species assignments were confirmed by ^1H TOCSY and ^{13}C NMR experiments (Supporting Information section III). To confirm our shift assignments, we synthesized phenyl carbonate analogues of A^-A and A^-A^-; the ^1H NMR spectra of these isolable analogues resemble closely that of the CO_2-bound species. We also observed unreacted diol, meaning that all three species (AA, A^-A, and A^-A^-) were present simultaneously. Additionally, signals corresponding to the bifunctional guanidine GG all shift downfield (Figure 4, dashed lines), indicating the formation of guanidinium species. (Unlike the alkyl carbonate species, distinct signals from these guanidinium species likely coalesce due to acid−base exchange between guanidine and guanidinium functional groups occurring much faster than the NMR time scale. Therefore, our assignment of mono-guanidinium and bis-guanidinium species by ^1H NMR remains putative.)

Supporting the hypothesis of cooperativity, we found that the relative concentrations of mono-alkylcarbonate A^-A and bis-alkylcarbonate A^-A^- vary as a function of solvent composition, as well as the concentration of unreacted diol, $[AA]_f$ (Figure 4c). The ratio of bis-alkylcarbonate to mono-alkylcarbonate ($[A^-A^-]/[A^-A]$) reflects their relative stability in solution, which we quantified via integration of H_d and H_b. The ratio increases as the proportion of DMSO-d_6 decreases (Figure 4d, blue circles). Moreover, the ratio diverges from what would be expected if CO_2 binding were statistically determined, that is, if the linkage had no influence on whether diol AA binds one or two CO_2 molecules. The stability of the bis-alkylcarbonate thus increases relative to the mono-alkylcarbonate at lower DMSO concentrations. This is consistent with our previous hypothesis that DMSO disrupts the ionic interaction between anionic alkylcarbonate and cationic guanidinium functional groups.

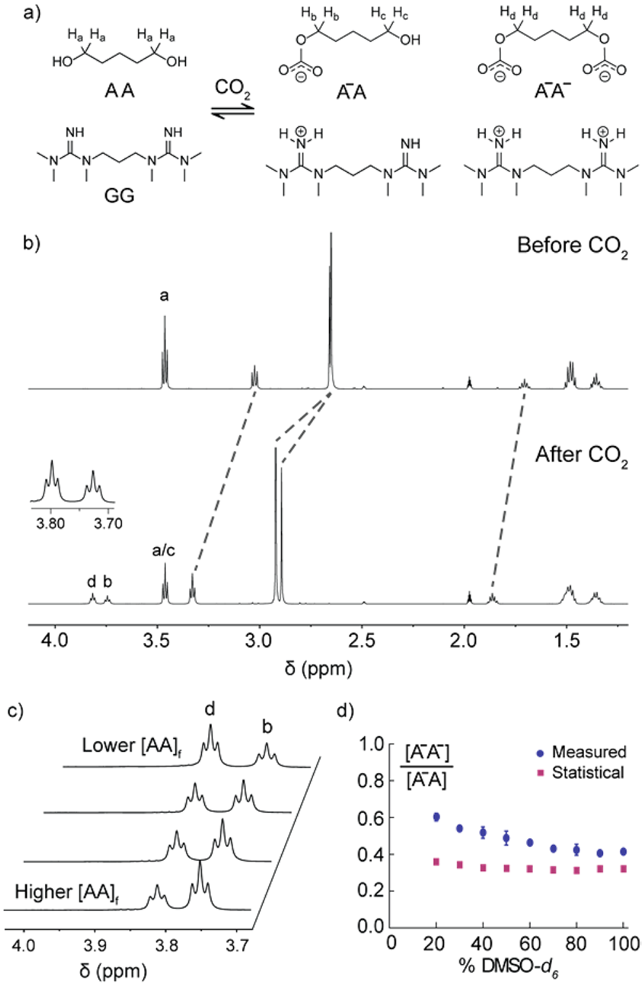

Figure 4. NMR analysis of CO_2 binding. (a) Species formed by AA and GG after exposure to 1 atm of CO_2. (b) ^1H NMR spectra before and after exposure to 1 atm of CO_2. Dashed lines correspond to GG or resulting guanidinium species. (c) Change in relative peak areas of H_b and H_d, which depend on solvent composition and final diol concentration, the latter shown. (d) Ratio of bis-alkylcarbonate A^-A^- to mono-alkylcarbonate A^-A versus solvent composition.

One common method to quantify the proximity advantage, or chelate effect, is to calculate the effective molarity (EM) of one binding partner with respect to the other.[25] We performed additional ^1H NMR experiments in which $[AA]_f$ was varied, and found that EM increases steadily as % DMSO-d_6 decreases, again suggesting that lower DMSO concentrations promote a stronger ionic interaction, agreeing with the bulk results observed in the isotherm as well as strongly supporting a cooperative mechanism (Figure S11).

In summary, we examined CO_2 binding by a system comprising a bifunctional guanidine and bifunctional alcohol. The system exhibits cooperative isotherms in diglyme, where CO_2 uptake is initially suppressed, but increases abruptly, with a corresponding precipitation of a viscous, CO_2-rich phase. The unique isotherm likely results from coordination between binding sites, and the limited solubility of bis-cationic and bis-anionic species formed. ^1H NMR studies confirmed that distinct mono-alkylcarbonate and bis-alkylcarbonate species are formed upon CO_2 binding. Lower DMSO-d_6 concentrations favor the bis-alkylcarbonate and suggest that a tighter initial ionic interaction promotes binding of the second CO_2 molecule. This, to our knowledge, represents the first description of a liquid with cooperative CO_2 binding. Two of the advantages of a cooperative technology are that (1) the affinity shift of an improved cooperative system would facilitate less energy-intensive absorption/desorption, a known challenge for existing CO_2 binding systems, and (2) the liquid nature of the system is compatible with existing infrastructure. This system further shows that the cooperative gas binding observed in biologically optimized systems may be mimicked chemically with properties distinct from other CO_2 binding liquids and found only in a handful of solid materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00418.

> Details regarding synthesis, isotherm measurements, thermodynamic model, and NMR experiments (PDF)

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Notes

The authors declare no competing financial interest.

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