

# Advanced Theory and Simulation to Guide the Development of CO<sub>2</sub> Capture Solvents

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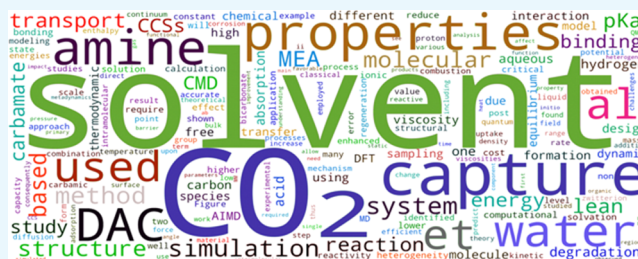
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**ABSTRACT:** Increasing atmospheric concentrations of greenhouse gases due to industrial activity have led to concerning levels of global warming. Reducing carbon dioxide (CO<sub>2</sub>) emissions, one of the main contributors to the greenhouse effect, is key to mitigating further warming and its negative effects on the planet. CO<sub>2</sub> capture solvent systems are currently the only available technology deployable at scales commensurate with industrial processes. Nonetheless, designing these solvents for a given application is a daunting task requiring the optimization of both thermodynamic and transport properties. Here, we discuss the use of atomic scale modeling for computing reaction energetics and transport properties of these chemically complex solvents. Theoretical studies have shown that in many cases, one is dealing with a rich ensemble of chemical species in a coupled equilibrium that is often difficult to characterize and quantify by experiment alone. As a result, solvent design is a balancing act between multiple parameters which have optimal zones of effectiveness depending on the operating conditions of the application. Simulation of reaction mechanisms has shown that CO<sub>2</sub> binding and proton transfer reactions create chemical equilibrium between multiple species and that the agglomeration of resulting ions and zwitterions can have profound effects on bulk solvent properties such as viscosity. This is balanced against the solvent systems needing to perform different functions (e.g., CO<sub>2</sub> uptake and release) depending on the thermodynamic conditions (e.g., temperature and pressure swings). The latter constraint imposes a “Goldilocks” range of effective parameters, such as binding enthalpy and pK<sub>a</sub>, which need to be tuned at the molecular level. The resulting picture is that solvent development requires an integrated approach where theory and simulation can provide the necessary ingredients to balance competing factors.



## INTRODUCTION

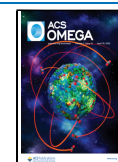
CO<sub>2</sub> capture from either major point sources, such as power plants, or directly from the environment is critical to alleviate adverse influences on the environment. Postcombustion carbon capture is an excellent choice since it requires no essential changes in the configuration of power plants.<sup>1–3</sup> In this category, chemical absorption using amine-based solvents has been extensively developed as a reliable capture/separation approach in postcombustion power plants. On the contrary, these same solvent types are deemed unattractive for direct capture from the environment due to undesirable properties such as insufficient uptake under low CO<sub>2</sub> partial pressures and high volatility. As such, solvents can be utilized as part of an environmental capture system<sup>4</sup> but not as a single component and will require different physical/chemical properties from a solvent designed for point source capture. This perspective will explore an atomic scale understanding of the chemistry of CO<sub>2</sub> capture solvents and how theoretical studies have been able to establish novel structure–activity relationships enabling us to tailor solvents for a wide range of different capture scenarios.

There has been extensive literature discussing technologies and materials using amine-based solvents for CO<sub>2</sub> capture.<sup>5,6</sup> Computational modeling of aqueous amines has also been reviewed.<sup>7</sup> However, the energy loss during water boiling and condensation to regenerate the aqueous amine-based solvent systems has placed limitations to a broader application. To minimize water content, different types of water-lean solvent systems have been developed as an alternative, including ionic liquids,<sup>8</sup> aminosilicones,<sup>9</sup> siloxylated amines,<sup>10</sup> etc., to reduce the energy requirements compared to aqueous solvents. Readers can refer to a few review articles of these ionic liquids<sup>11,12</sup> and water-lean solvents.<sup>1</sup>

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Molecular simulations have proven to be valuable tools that reveal atomic-level information across a variety of materials and applications. To advance the CO<sub>2</sub> capture solvents (CCSs), first-principles (or *ab initio*) calculations have been applied to study the CO<sub>2</sub> absorption mechanism,<sup>13,14</sup> make predictions of CO<sub>2</sub> absorption behaviors for new compounds,<sup>15</sup> interpret and rationalize experimental spectroscopic results,<sup>14</sup> etc. Classical molecular dynamics (CMD) simulations have been employed to study the transport properties in CO<sub>2</sub> solvents<sup>16</sup> or interpret structure–property relationships.<sup>13,17,18</sup> These approaches have succeeded in providing a better understanding of experimental results and further guiding the design of novel solvent systems.<sup>2,14</sup>

We will start by reviewing the computational methods used to study CCSs. We follow with a discussion on how challenges arise from the limitations of each method and how combinations of different methods are used to overcome them. We next elaborate on studies characterizing the reactivity, degradation, and CO<sub>2</sub> transport in CCSs as well as interfaces between CCSs and other organic and inorganic surfaces. Finally, we close with an analysis of structural heterogeneity and complexity at the nanoscale in CCSs.

## METHODOLOGY

To design a CO<sub>2</sub> capture solvent for a given application, a detailed knowledge of thermodynamics and kinetics of CCSs is required. In many cases obtaining all the properties for a large library of compounds is laborious and resource intensive. Alternatively, these properties can be obtained by using atomistic modeling. Most common methods used for atomistic simulations of CCSs are classical force fields (FFs) and density functional electronic structure theory (DFT)-based molecular dynamics (MD) methods. FF methods are most appropriate when chemical reactivity is not critical, so that the overall system can be modeled as a collection of molecules with fixed structure whereas, quantum mechanics-based approaches are needed when reactivity needs to be taken into account.

Force field based MD allows one to investigate properties, such as transport, viscosity, conductivity, etc., of system sizes of  $\sim 10^3$ – $10^4$  atoms and time scales of  $\sim 10$ – $10^3$  ns. A popular FF is the Optimized Potentials for Liquid Simulations (OPLS), developed by Jorgensen and co-workers.<sup>19</sup> This FF consists of bonded and nonbonded interaction terms:

$$U = U_{\text{bonded}} + U_{\text{nonbonded}} \quad (1)$$

The bonded interaction term includes two-body (bonds), three-body (angles), and four-body (dihedrals) terms:

$$U_{\text{bonds}} = \sum_{\text{bonds}} k_b (r_b - r_b^0)^2 \quad (2)$$

$$U_{\text{angles}} = \sum_{\text{angles}} k_a (\theta_a - \theta_a^0)^2 \quad (3)$$

$$U_{\text{dihedral}} = \sum_{\text{angles}} \sum_{n=1}^4 \frac{V_n}{2} [1 - (-1)^n \cos(n\varphi - \varphi_n)] \quad (4)$$

where  $r_b^0$  ( $\theta_a^0$ ) is the equilibrium value of a bond (angle), and  $k_b$  ( $k_a$ ) is the spring constant of a bond (angle). The nonbonded term further consists of Coulombic and van der Waals (vdW) interactions.

Many problems in CCSs however require reactive potentials to follow chemical reactivity including weak noncovalent

interactions, hydrogen bonds, induced polarizable bonds, and vdW dispersion effects. Proton transfers, redox processes, and degradation are typically observed reactions which impact the CO<sub>2</sub> adsorption thermodynamics and transport. Although reactive FFs (e.g., ReaxFF<sup>20</sup>) have been used to tackle such activated processes in CCSs,<sup>21</sup> the difficulty in robust parametrization has limited their widespread application.

On the other hand, electronic structure potentials, particularly, the ones from Kohn–Sham DFT, have been used more widely. In Kohn–Sham DFT, the electronic energy  $E[n]$  of a system is a functional of the electron density and can be expressed as

$$E[n] = T[n] + V_{\text{ext}}[n] + J[n] + E_{\text{xc}}[n] \quad (5)$$

where  $T[n]$ ,  $V_{\text{ext}}[n]$ ,  $J[n]$ , and  $E_{\text{xc}}[n]$  are the electron kinetic energy, the interaction energy between electrons and external potentials, e.g., electrostatic potentials by nuclei, the electrostatic interaction between electrons, and the exchange–correlation energy. The current state of the art allows for system models using DFT-based MD is on the order of  $10^2$ – $10^3$  atoms with simulation times on the order of  $10$ – $10^3$  ps.

In activated processes with a high barrier, larger than  $k_B T$ , where  $k_B$  is the Boltzmann constant and  $T$  is the temperature of the system, the *ab initio* molecular dynamics (AIMD) time scale ( $\leq 1$  ns) does not suffice to sample energetics accurately. Consequently, enhanced sampling methods are usually employed to overcome this problem. In this perspective, we will focus on enhanced sampling methods capable of overcoming barriers larger than  $k_B T$  along predetermining chemical descriptors that characterize sets of nuclear coordinates, namely, collective variables (CVs). Umbrella sampling<sup>22</sup> led the way for this category of methods. In this method, the CV space is split into segments (called “windows”) and one simulation is required for each window. Another prominent example, metadynamics<sup>23</sup> (and most importantly its well-tempered variant, WTmetaD<sup>24</sup> which has been shown to converge to the true free energy surface<sup>25</sup>), is capable of accelerating sampling by adding a history-dependent bias potential to the Hamiltonian of the system. In WTmetaD, the additive potential,  $V(S, t)$  is a sum of Gaussian functions with their height,  $w = w(t)$ , decreasing over time:<sup>26</sup>

$$V(S, t) = \int_0^t dt' w \exp\left(-\sum_{i=1}^d \frac{(S_i(R) - S_i(R(t')))^2}{2\sigma_i^2}\right) \quad (6)$$

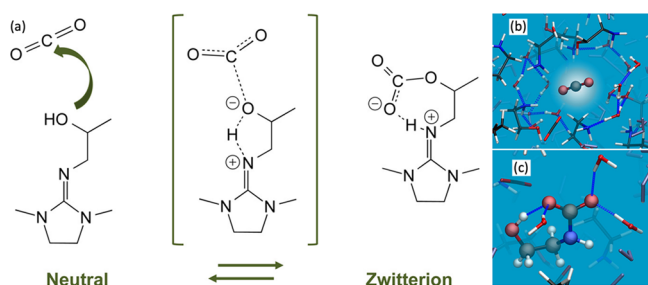
Metadynamics enables the sampling of configurations relevant with this CV, and only one simulation is required. Clearly, the choice of appropriate CVs becomes the most critical aspect of all enhanced sampling methods as it is should be limited in number and characterize all relevant states and slow degrees of freedom of the system.<sup>26</sup> In general, enhanced sampling methods have been successful in characterizing activated processes involving CCSs.<sup>27–33</sup>

### Computational Challenges and Methods to Address Them.

AIMD has been extensively used in the study of ionic liquids and their use in carbon capture to successfully identify both thermodynamically and kinetically favorable products<sup>29</sup> and to determine dynamic speciation in these systems<sup>28,34,35</sup>

As already mentioned above, accurate calculation of energy barriers corresponding to activated processes is possible when AIMD is used in conjunction with enhanced sampling methods.<sup>32,33</sup> In this context, we provide a structural

representation of the CCS before and after binding CO<sub>2</sub> in Figure 1.<sup>33</sup>



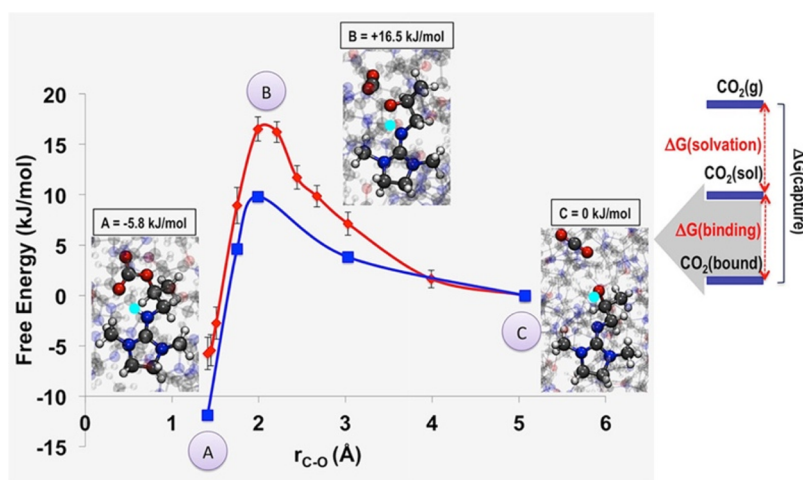
**Figure 1.** (a) Structure of neutral IPADM-2-BOL not binding CO<sub>2</sub> and zwitterionic binding CO<sub>2</sub>. Reprinted with permission from Cantu, D. C.; Lee, J.; Lee, M.-S.; Heldebrant, D. J.; Koech, P. K.; Freeman, C. J.; Rousseau, R.; Glezakou, V.-A. Dynamic Acid/Base Equilibrium in Single Component Switchable Ionic Liquids and Consequences on Viscosity, *J. Phys. Chem. Lett.* **2016**, *7* (9), 1646–1652 (ref 33). Copyright 2016 American Chemical Society. Snapshot of a MD simulation at room temperature (b) before and (c) after the formation of carbamate. Color code: black, C; blue, N; red, O; gray, H. Adapted with permission from Ma, C.; Pietrucci, F.; Andreoni, W. Capturing CO<sub>2</sub> in Monoethanolamine (MEA) Aqueous Solutions: Fingerprints of Carbamate Formation Assessed with First-Principles Simulations, *J. Phys. Chem. Lett.* **2014**, *5* (10), 1672–1677 (ref 35). Copyright 2014 American Chemical Society.

Using unbiased AIMD simulations, Han et al.<sup>36</sup> postulate that monoethanolamine (MEA) molecules should be represented explicitly to calculate heat of CO<sub>2</sub> absorption accurately. Ma et al.<sup>35</sup> argue that hydration effects have a significant role in determining the nature of the products of CO<sub>2</sub> capture in MEA aqueous solutions. They were also able to identify fingerprints of carbamate in vibrational spectra. An example of carbamate formation after CO<sub>2</sub> capture is provided in Figure 1. Sumon et al.<sup>27</sup> studied the mechanism of carbon capture by aqueous amines through investigating the dynamic conversion of intermediates in water. Sakti et al.<sup>31</sup> used a semiempirical

method (density-functional tight-binding, DFTB) coupled with metadynamics to calculate acid dissociation constants of aqueous amines commonly employed for carbon capture.

The study of bulk properties using AIMD is however difficult due to the length and time scale limitations compounded by the emergence of nanostructuring and slow dynamics of the system. In practice, one can employ CMD over a span of different CO<sub>2</sub> loadings and study the variation in transport and other bulk properties. In one of the early studies of nanostructuring as a result of solvent heterogeneity upon CO<sub>2</sub> capture, we identified domains of CO<sub>2</sub>-loaded solvent molecules and estimated the viscosity change using CMD.<sup>16,32,33</sup> Melnikov and Stein<sup>37</sup> also simulated CO<sub>2</sub>-loaded solvents (alkanolamines), noting that CO<sub>2</sub> absorption affects diffusion coefficients considerably.<sup>37</sup> Moosavi et al.<sup>38</sup> analyzed structural changes during CO<sub>2</sub> capture by MEA, while da Silva et al.<sup>39</sup> evaluated CO<sub>2</sub> affinities to both MEA and H<sub>2</sub>O. Kussainova and Shah<sup>40</sup> used CMD to study the absorption capacity of methyltriphenylphosphonium bromide (MTPPBr) and MEA-based deep eutectic solvents (DESs). Solvent structure analysis showed stronger interactions with CO<sub>2</sub> than the traditional MEA solvent. Rozanska et al. used a combination of DFT, continuum solvation, and CMD simulations to evaluate total solvation energies of CO<sub>2</sub> and select charged species (HO<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>) in a series of aqueous tertiary amines.<sup>41</sup> Turman-Cohen et al. used CMD to examine transport and structure properties<sup>42</sup> of species during CO<sub>2</sub> absorption in nonaqueous amines and noted that capturing the ionic speciation is critical for determining qualitative changes in fluidity.<sup>41,42</sup> Hwang et al.<sup>43</sup> used a combination of computational methods to study CO<sub>2</sub> uptake in aqueous MEA. AIMD was used to identify reactions and intermediate species, static DFT to evaluate interactions during the reaction between MEA and CO<sub>2</sub>, and CMD to assess how H<sub>2</sub>O molecules arrange themselves around MEA.

CMD simulations are often combined with a higher level of theory (e.g., static DFT calculations) to study CO<sub>2</sub> absorption in aqueous amines<sup>44,45</sup> or ionic liquids<sup>46</sup> for CO<sub>2</sub> capture.



**Figure 2.** Free energy (red) and energy (blue) profiles of CO<sub>2</sub> binding by IPADM-2-BOL at 40 °C obtained with Blue Moon ensemble simulations as a function of the CO<sub>2</sub> carbon to IPADM-2-BOL alcohol oxygen distance. In the images, dark gray is C, white is H, red is O, and blue is N. The H atom that moves between alcohol to guanidium base is highlighted in turquoise. The energy diagram on the right summarizes the whole capture and binding process. Reprinted with permission from Cantu, D. C.; Lee, J.; Lee, M.-S.; Heldebrant, D. J.; Koech, P. K.; Freeman, C. J.; Rousseau, R.; Glezakou, V.-A. Dynamic Acid/Base Equilibrium in Single Component Switchable Ionic Liquids and Consequences on Viscosity, *J. Phys. Chem. Lett.* **2016**, *7* (9), 1646–1652 (ref 33). Copyright 2016 American Chemical Society.

Recent work from our group used a combination of AIMD and CMD to (i) identify species present in solution, (ii) estimate their relative populations, (iii) derive classical force fields from the ab initio data, and (iv) assess how intermolecular interactions between them affect solvent viscosity<sup>2,3,47</sup> using either the nonequilibrium method<sup>48</sup> or Green–Kubo relations.<sup>49</sup> We concluded that understanding changes in the structure and transport properties as a function of CO<sub>2</sub> loading was a critical step toward mitigating viscosity bottlenecks for the development of postcombustion capture solvents.<sup>2</sup>

Proton transfer reactions have been identified as a critical chemical step in activating and binding CO<sub>2</sub> as well as the formation of ionic species that could impact solvent properties such as transport. Noroozi and Smith<sup>50</sup> also used this combination of methods to predict properties of reactive absorption in alkanolamines. They later used CMD and static DFT calculations to predict equilibrium constants and standard reaction enthalpies of a set of alkanolamines.<sup>51</sup> Cantu et al. employed this combination of methods with enhanced sampling to study how acid/zwitterion equilibrium impacts the viscosity of a class of water-lean solvents, namely, carbon dioxide binding organic liquids (CO<sub>2</sub>BOLs).<sup>32,33</sup> An example of the free energy profile of CO<sub>2</sub> binding by a CCS, obtained using AIMD with enhanced sampling methods, is depicted in Figure 2. Lastly, Afify and Sweatman<sup>52</sup> postulated that careful tuning of FF parameters is needed to study microwave heating during MEA regeneration. Scaling atomic charges to correctly predict dielectric properties of MEA resulted in very small diffusion coefficients and large bulk densities. Consequently, they could not predict microwave heating rates with accuracy and concluded that FFs parametrized for one property cannot guarantee accurate prediction of other properties.

An alternative, albeit more expensive, approach to CMD is reactive FFs such as ReaxFF.<sup>20,32,33,53</sup> These allow for reactivity, but they have not been used extensively for studies of CCSs. Also, ReaxFF presents challenges in describing polarization, charge transfer, dispersion interactions,<sup>54</sup> and conservation of energy.<sup>55</sup> Recently, progress has been made to overcome the latter.<sup>55,56</sup> Zhang et al.<sup>21</sup> used a DFT-trained ReaxFF<sup>20</sup> to calculate the change in the density of ionic liquids upon CO<sub>2</sub> uptake. The reactive FF led to a larger increase for the density with increasing CO<sub>2</sub> loading than nonreactive classical FFs. This is due to the presence of compact structures, resulting from reaction between CO<sub>2</sub> and glycine anions which could not be reproduced by a classical FF.<sup>21</sup>

Furthermore, combined quantum and molecular mechanics (QM/MM) methods have been employed to study CCSs and the reactivity between CO<sub>2</sub> and the solvent molecules as well. Kim et al.<sup>57</sup> investigated the mechanism of CO<sub>2</sub> absorption in blended amine solvents, pointing out that selection of the QM region is critical. They found that intermolecular interactions between neighbors can significantly lower the activation energy barrier for proton transfer. Wang et al.<sup>58</sup> used both AIMD and QM/MM simulations to study zwitterion formation during CO<sub>2</sub> capture by MEA in amine-blended solvents. They postulate that hydrogen bond capacity affects kinetics more than the dielectric constant of the solvent. Prasetyo and Hofer studied the solvation of CO<sub>2</sub> in NH<sub>3</sub><sup>59</sup> and H<sub>2</sub>O<sup>60</sup> using QM/MM with enhanced sampling. They identified a weak solvation shell due to ligand-exchange.<sup>59,60</sup> At last, Xie et al.<sup>61</sup> proposed a two-step mechanism involving the formation of a zwitterion

(a rate-determining step) as the most energetically favorable path to forming carbamate from CO<sub>2</sub> capture by MEA.

**Reactivity.** One of the main challenges of CO<sub>2</sub> capture is the thermodynamic state of the CO<sub>2</sub> molecule in solution, which depends on the CCS binding capacity and CO<sub>2</sub> partial pressure. The latter varies greatly with the field application: it is high in postcombustion gas streams (~0.5 bar) and in air (4 × 10<sup>-4</sup> bar).<sup>62</sup> Therefore, the design of effective carbon capture solvents first requires an analysis of the reactivity of the solvent and CO<sub>2</sub>. An optimal solvent should have a high reaction rate with CO<sub>2</sub>, low volatility, high capture capacity, and low solvent regeneration energy. The latter two properties are in competition, requiring a balance between adsorption (binding) and desorption. In addition to these requirements, the capture process must be able to operate at high temperatures and be environmentally benign. Unfortunately, there generally is a trade-off between the desirable properties of a carbon-capture solvent; for example, amine solvents can be energy efficient but are likely to form toxic degradation products such as nitrosamines.<sup>63</sup> In addition, the optimization of pilot postcombustion capture plants is costly and depends on the specific choice of solvent and its properties.<sup>64</sup> Furthermore, because the absorption process proceeds quickly in amine-based solutions, it is difficult to experimentally probe this process at the molecular level. This is where the synergy between experiments and computational work plays a key role for the design and optimization of solvents by including information at the molecular level.

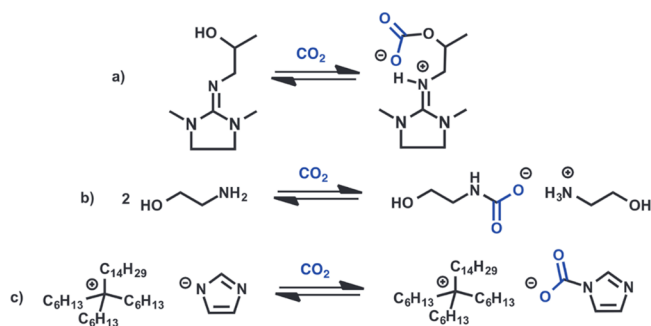
The CO<sub>2</sub> capture process consists of two primary steps: (i) solvation and (ii) subsequent binding to the solvent. Therefore, the capture free energy, Δ*G*(capture), is given by the sum of the individual free energies of each step:

$$\Delta G(\text{capture}) = \Delta G(\text{solvation}) + \Delta G(\text{binding}) \quad (7)$$

For many years, the state-of-the-art CCS was MEA because of its low cost, high CO<sub>2</sub> absorption capacity, and efficient CO<sub>2</sub> reaction rate.<sup>65–67</sup> With an increasing number of researchers studying and commercializing carbon capture solvents, vast improvements have been made in the efficiency and cost of second-generation amine solvents.<sup>68–70</sup> However, there is considerable room for improvement, as the energy required to regenerate aqueous amines remains high.<sup>71</sup> Depending on the composition and molecular structure of the solvent, binding of CO<sub>2</sub> will result in the formation of one of the following: alkylcarbonates from solvents with alcohols paired with non-nucleophilic superbases,<sup>72–74</sup> carbamates from 1° and 2° amines,<sup>9,75–78</sup> or azoline carboxylates.<sup>79–83</sup> All these chemical species form ions or zwitterions containing electrophilic sp<sup>2</sup>-hybridized anions. In each scenario, the solvent acts as a nucleophile, reacting with electrophilic CO<sub>2</sub> to form an adduct.

One of the most important properties to consider in the design of a CO<sub>2</sub> capture process is the heat, or enthalpy, of reaction between CO<sub>2</sub> and the solvent. This quantity is directly related to the amount of energy required for solvent regeneration, i.e., the breaking of the CO<sub>2</sub>–base adduct to release CO<sub>2</sub>. While previously many believed that a low or thermo-neutral heat of reaction with CO<sub>2</sub> was ideal, Mathias et al. demonstrated that there is a “Goldilocks” zone with an ideal enthalpy of solution for postcombustion capture and regeneration, that of –60 to –70 kJ/mol.<sup>84,85</sup> One of the limitations of mature CCSs, including MEA, is that they have enthalpies of solution much higher (more negative) than this range, which leads to higher solvent regeneration temperatures

and higher rates of degradation. In fact, solvent regeneration is a major bottleneck for reducing the energetic cost of aqueous solvent-based capture, requiring heating of the water content solution to temperatures in excess of 100 °C. Recent research has shown that removal of the water-co-solvent can reduce the regeneration temperature to below 100 °C, due to water having a heat capacity twice that of organic solvents.<sup>1</sup> Such “water-lean” solvents have exhibited other desirable properties for CO<sub>2</sub> capture (see Figure 3), such as a binding enthalpy tunable by tailored synthesis and anomalous CO<sub>2</sub> mass transfer, which will be discussed later in this section.



**Figure 3.** Representative binding modes of each solvent class with CO<sub>2</sub> (a) alkylcarbonate, (b) amine carbamate, and (c) azoline carboxylate. Reprinted from Heldebrant, D. J.; Koech, P. K.; Rousseau, R.; Glezakou, V.-A.; Cantu, D. C.; Malhotra, D.; Zheng, F.; Whyatt, G.; Freeman, C. J.; Bearden, M. D. Are Water-lean Solvent Systems Viable for Post-Combustion CO<sub>2</sub> Capture?, *Energy Procedia* 2017, 114, 756–763 (ref 86) under a Creative Commons Attribution-NonCommercial-No Derivatives 4.0 International License (CC BY-NC-ND 4.0) [<https://creativecommons.org/licenses/by-nc-nd/4.0>]. Copyright 2017 The Author(s). Published by Elsevier Ltd.

**Speciation and Equilibria.** Among the most tunable parameters for CCS design are the Lewis acid/base properties of the capture site (e.g., amine group) on the solvent molecule, as they are related to the CO<sub>2</sub> binding enthalpy as well as proton transfer thermodynamics. In particular, the protonation constant and protonation enthalpy of the capture solvent must be chosen such that they are within an optimal range for efficient adsorption and desorption of CO<sub>2</sub>, respectively. While  $pK_a$  can be readily measured experimentally, the ability to computationally predict  $pK_a$  for solvents, that have not yet been synthesized, aids in the design and screening of CCSs. There are two main approaches for calculating  $pK_a$  values: (i) the direct approach, in which reaction free energies are calculated directly in solution,<sup>87</sup> and (ii) the thermodynamic cycle approach, in which  $pK_a$  is estimated from gas-phase reaction free energies and solvation free energies of the reactants and products.<sup>87–89</sup> Computation of  $pK_a$  *ab initio* is particularly challenging; consequently, to date the most accurate computational models require some empirical parameters and work for only specific classes of solutes and narrow  $pK_a$  ranges.<sup>90</sup>

Early work by da Silva et al.<sup>91</sup> on the amine-H<sub>2</sub>O-CO<sub>2</sub> system established that continuum solvent models at the MP2 and B3LYP levels of theory can give accurate values for amines with the same numbers of intermolecular hydrogen bonds and amine hydrogens. Later work demonstrated that accurate temperature trends for amines could also be obtained by including a correction term to the free energy of protonation in solution; however, the correction requires the experimental

$pK_a$  value at 298 K.<sup>92</sup> Gangarapu et al.<sup>93</sup> tested various DFT exchange-correlation functionals and other *ab initio* methods (MP2 and G3) in conjunction with three different solvent models (the conductor-like polarizable continuum model (CPCM) and universal solvation models (SMD and SM8)) for the  $pK_a$ s of substituted MEAs, finding that the M11-L density functional is comparable to G3 and SCS-MP2. For screening purposes, Yamada et al.<sup>94</sup> have found that the conductor-like screening model for real solvents (COSMO-RS) at the BP/TZVP level of theory in conjunction with the RI approximation<sup>95–97</sup> is computationally efficient and sufficiently accurate for  $pK_a$  calculations of amines.

In general, the systematic errors of continuum-based  $pK_a$  calculations are either (i) constant-shift errors or (ii) errors proportional to  $pK_a$ . Constant-shift errors could be due to poor choice of  $G_{aq}(H^+)$  or poor electronic-structure treatment and the point charges of the solvation models. Nonempirical techniques for improving constant-shift errors are the extensive element-dependent parametrization of the continuum model (the SMx series)<sup>98</sup> and electrostriction by changing cavity radii with partial charges.<sup>98,99</sup> Errors proportional to  $pK_a$  were shown to be due to errors in  $\Delta_{solv}G(H^+)$  that arise from the inability of continuum models to capture hydrogen bonding between the solute and the solvent.<sup>100,101</sup> A few groups have had success in reducing this error by adding explicit water molecules in the cavity with the solute.<sup>102–104</sup> Jackson et al.<sup>105</sup> combined this approach with the direct method, mentioned above, to compute the  $pK_a$  of carbamic acid, finding that the  $pK_a$  of carbamic acid is similar to that of carbonic acid. The obtained value of  $pK_a = 5.2$  implies that the carbamic acid is not abundant at the pH for which aqueous-solvent-based CO<sub>2</sub> capture is most efficient (alkaline, pH > 9).

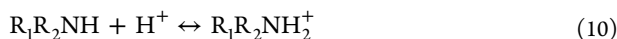
We note that while most theoretical  $pK_a$  values are computed from static quantum chemical calculations with implicit solvation, there has been a growing interest in using molecular dynamics with explicit solvent for such calculations. Several groups have found success by treating the solvent molecules with molecular mechanics and the solute with quantum mechanics (QM/MM).<sup>106–109</sup> For example, Uddin et al. used QM/MM molecular dynamics in conjunction with umbrella sampling and obtained astounding accuracy, with maximum and root-mean-square errors of 0.45 and 0.22  $pK_a$  units, respectively.<sup>109</sup> More recently, pure AIMD has been applied, where the entire system is treated quantum mechanically.<sup>33,110–114</sup> Because proton transfer occurs on the time scale of 100–200 ps, metadynamics is often employed to ensure adequate sampling.<sup>33,110–113</sup> While most of the aforementioned studies were not performed on CO<sub>2</sub> capture systems, Cantu et al.<sup>33</sup> used AIMD with metadynamics to compute the free energy barrier to switch between the ionic and neutral CO<sub>2</sub>-bound states in three water-lean solvents (see Figure 2). We expect that such dynamics-based methods for the computation of the  $pK_a$  of capture solvents will become increasingly more common with computational advances, as they have the potential for higher accuracy and minimal empiricism.

The basicity of the capture site is also related to the equilibrium constants for the formation of various species in solution and, consequently, the species distribution. All these factors determine the amount of CO<sub>2</sub> captured as well as the solvent regeneration energy. For primary and secondary amines, carbamic acids (R<sub>1</sub>R<sub>2</sub>NCOOH), carbamates (R<sub>1</sub>R<sub>2</sub>NCOO<sup>-</sup>), and bicarbonates (HCO<sub>3</sub><sup>-</sup>) can form upon

CO<sub>2</sub> absorption. Carbamic acid (R<sub>1</sub>R<sub>2</sub>NCOOH) is formed according to



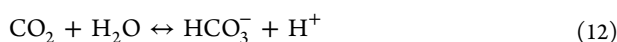
Depending on its acidity, the carbamic acid will be in a dynamic equilibrium by donating a proton to a second amine to form carbamate (R<sub>1</sub>R<sub>2</sub>NCOO<sup>-</sup>):



Thus, the overall pathway to carbamate formation upon CO<sub>2</sub> adsorption is given by

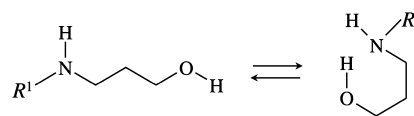


Alternatively, CO<sub>2</sub> can react with water to form bicarbonate (HCO<sub>3</sub><sup>-</sup>):



Here we have denoted the amine as R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>N, since this reaction may involve tertiary amines. In fact, for tertiary and some sterically hindered primary and secondary amines, CO<sub>2</sub> hydration to bicarbonate may be the dominant adsorption pathway. In terms of CO<sub>2</sub> binding capacity, bicarbonate formation is more efficient and forms the backbone of most direct air and seawater capture systems. Note that bicarbonate stoichiometrically consumes 1 mol of amine per mole of CO<sub>2</sub>, while carbamate formation consumes 2 mol of amine per mole of CO<sub>2</sub>. Moreover, bicarbonate formation is kinetically less favorable than carbamate formation, leading to primary and secondary amines having faster absorption rates than tertiary amines.<sup>115</sup>

The uptake binding, transport, and release of CO<sub>2</sub> also required quantitative knowledge of other reaction equilibria. As an example, Da Silva and Svendsen<sup>116</sup> studied the relative thermodynamic stability of the carbamates formed by various amines upon CO<sub>2</sub> capture, finding good agreement between experimental and DFT values at the B3LYP/6-311++G(d,p) level. In particular, continuum solvation models were more accurate for predicting the relative stabilities of molecules with similar structures, while free-energy calculations performed better when considering molecules with varying structures. While other groups have attempted to relate carbamate stability to a specific molecular characteristic, for example, steric hindrance,<sup>115,117</sup> they found that carbamate stability could not be correlated with a single molecular property and depends on intramolecular hydrogen bonding, solubility, steric effects, and possibly others. In fact, Puxty et al.<sup>118</sup> identified several amines with outstanding CO<sub>2</sub> absorption capacities, higher than what is expected based on pK<sub>a</sub> or steric hindrance alone. They attribute this phenomenon to the combination of steric hindrance and intramolecular hydrogen bonding. Specifically, all amines identified have a hydroxyl group within 2 or 3 carbons of the amino group that is free to move, see Figure 4. They provide two possible explanations for the enhanced capacities: (i) intramolecular hydrogen bonding destabilizes carbamate formation, and (ii) the formed carbamic acids are weak and do not deprotonate to consume a second amine. Interestingly, all the identified amines also exhibited initial absorption rates no more than 25% slower than MEA. Ma et al.<sup>34,119</sup> found that the formation of the zwitterion is the

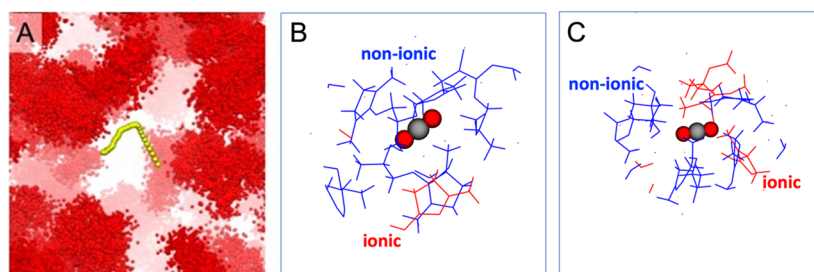


**Figure 4.** Linear and hydrogen-bonded structures for primary and secondary amines from Puxty et al. Reprinted with permission from Puxty, G.; Rowland, R.; Allport, A.; Yang, Q.; Bown, M.; Burns, R.; Maeder, M.; Attalla, M. Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines, *Environ. Sci. Technol.* **2009**, *43* (16), 6427–6433 (ref 118). Copyright 2009 American Chemical Society.

rate-limiting step for CO<sub>2</sub> capture in either MEA or 2-amino-2-methyl-1,3-propanediol (AMPD). Yamada et al.<sup>120</sup> also observed carbamate destabilization due to intramolecular hydrogen bonding in a computational study of alkanolamines. In particular, they examined the effects of alcohol and alkyl chain lengths on the carbamate/bicarbonate ratio, finding that only the alcohol chain length significantly affects intramolecular hydrogen bonding and stability. More specifically, increasing alcohol chain length strengthens intramolecular hydrogen bonding and reduces the carbamate/bicarbonate ratio, i.e., it destabilizes carbamate formation.

**Transport.** In addition to thermodynamic and kinetic properties, one must also consider transport properties of the CO<sub>2</sub>–solvent system, such as diffusivity, viscosity, and mass transfer. Generally, CO<sub>2</sub> uptake increases the viscosity of the solution, which directly impacts the overall capture cost and reduces CO<sub>2</sub> diffusivity. Nonetheless, the majority of the CO<sub>2</sub> capture research community has primarily focused on thermodynamic properties, as exemplified by the plethora of studies on pK<sub>a</sub>, equilibrium species distribution, reaction enthalpy, and solvent regeneration energy, at the expense of transport properties. As pointed out by Mota-Martinez et al.,<sup>63</sup> while improvement in thermodynamic properties of the solvent tend to lower operational costs for a plant, transport properties dictate the equally critical size of the process equipment and capital cost. Thus, while there has been an extensive effort to design better sorbent materials, only a few have been deployed on a large scale because gains in certain properties go hand-in-hand with losses in other properties. For example, water-lean solvents were designed to have lower specific heats and thus lower regeneration energies than aqueous solvents, but they tend to be more viscous.<sup>75–77,121</sup>

From a computational perspective, transport properties require the use of MD simulations, unlike the previously discussed equilibrium properties, which are typically modeled by QC methods. Moosavi et al.<sup>38</sup> studied CO<sub>2</sub> diffusion in MEA at various mole fractions with an AMBER force field,<sup>122</sup> using computed diffusion coefficients to estimate the dissolution point ( $\chi_{CO_2} = 0.036$ ). In an effort to offset the different disadvantages among different solvents, Yu et al.<sup>123</sup> studied the transport properties of mixtures of conventional capture solvents (MEA, methyldiethanolamine (MDEA), triethanolamine (TEA), diethanolamine (DEA), and 2-amino-2-methyl-1-propanol (AMP)) using the OPLS force field.<sup>124,125</sup> They evaluated ternary, quaternary, and quintuple amine systems with different weight fractions of each component. Using MD to quantify the interactive effects between diffusion and molecule motion, they conclude that ternary systems have higher synergy than quaternary and quintuple amine systems, with the MDEA-DEA-TEA system at a 3:1:1 ratio exhibiting the most improvement in transport



**Figure 5.** MD simulations of free CO<sub>2</sub> in IPADM-2-BOL at varied mole loadings: (A) superimposed frames from a 0.5 ns trajectory, with the yellow feature showing the trajectory of a CO<sub>2</sub> molecule in a solvent box, with only ionic species (in red) shown here; (B and C) snapshots of CO<sub>2</sub> and solvent/zwitterion molecules in its first solvation cell (CO<sub>2</sub>-free IPADM-2-BOL in blue, CO<sub>2</sub>-bound IPADM-2-BOL in red) at 15% and 30% mol loading, respectively. Reprinted with permission from Yu, X.-Y.; Yao, J.; Lao, D. B.; Heldebrant, D. J.; Zhu, Z.; Malhotra, D.; Nguyen, M.-T.; Glezakou, V.-A.; Rousseau, R. Mesoscopic Structure Facilitates Rapid CO<sub>2</sub> Transport and Reactivity in CO<sub>2</sub> Capture Solvents, *J. Phys. Chem. Lett.* **2018**, *9* (19), 5765–5771 (ref 16). Copyright 2018 American Chemical Society.

properties. Diffusivity and/or viscosity can be extracted from molecular trajectories. Following Wheeler and Newman, diffusivity can be calculated via the Green–Kubo method<sup>126</sup> from the velocity autocorrelation function, while Lin and Chen<sup>126</sup> and Koddermann et al.<sup>127</sup> computed viscosity from the pressure tensors, both of which are obtainable from MD simulations.

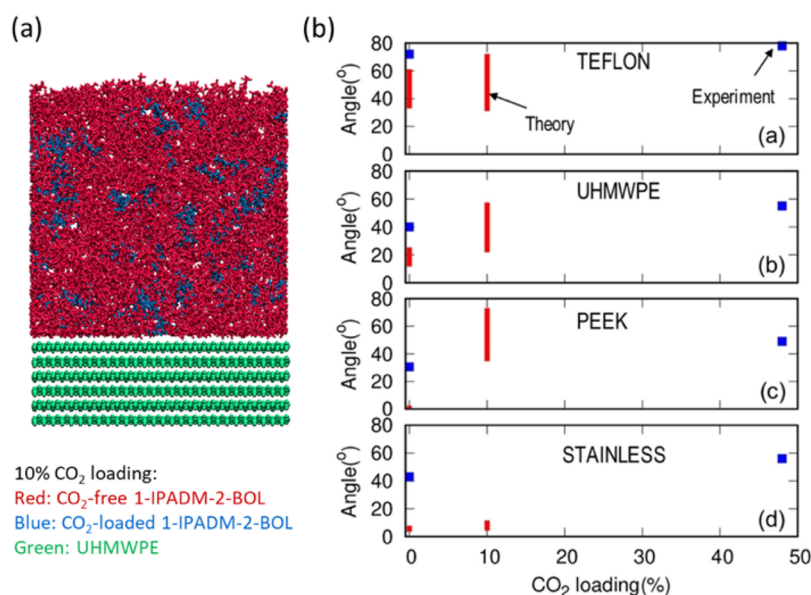
One of the main advantages, as well as one of the main challenges, of water-lean solvents is related to their transport properties, such as unexpectedly high CO<sub>2</sub> mass transfer<sup>86</sup> and high CO<sub>2</sub>-rich viscosities.<sup>127,128</sup> Glezakou and co-workers used MD simulations (with the OPLS force field<sup>19</sup>) to compute the viscosities of CO<sub>2</sub> binding organic liquids (CO<sub>2</sub>BOLs), a promising subclass of water-lean solvents that switches between ionic and nonionic forms upon binding and release of CO<sub>2</sub>.<sup>32,33</sup> They identified intramolecular hydrogen bonding as the primary molecular descriptor for viscosity<sup>33</sup> and used this knowledge to develop a reduced-order model for the quick screening of solvent libraries.<sup>32</sup> They additionally showed that these solvents exhibit a dynamic equilibrium between two CO<sub>2</sub>-bound states, a neutral acid and a zwitterionic base, demonstrating that *intermolecular* hydrogen bonding between zwitterions leads to high viscosities and *intramolecular* hydrogen bonding is an indicator of lower viscosity. Due to their relatively high viscosities, water-lean solvents were initially believed to have limited CO<sub>2</sub> mass transfer and thus to be unreasonable candidates for CO<sub>2</sub> capture. Mathias et al.<sup>129</sup> were the first to demonstrate the strangely high mass transfer of water-lean solvents in two CO<sub>2</sub>BOL solvent systems, revealing two kinetic anomalies. First, the liquid-film mass transfer coefficients  $k_g'$  of these systems were found to be comparable to those of water-based MEA, the current state-of-the-art solvent for postcombustion CO<sub>2</sub> capture, and another water-based solvent, piperazine (PZ). Second, they observed an inverse temperature dependence of the  $k_g'$  value, which implies that the physical solubility of CO<sub>2</sub> is higher in these water-lean solvents than in water, thus enabling comparable kinetic performance despite higher viscosities. This phenomenon was shown through a combination of liquid phase mass spectroscopy-based imaging and classical MD to be the result of nanostructuring of the liquid, which created nonionic domains/channels, see Figure 5, through which solvated nonbound CO<sub>2</sub> could diffuse freely, see section on structural heterogeneity below.<sup>16</sup>

Continued efforts to lower the viscosities of water-lean solvents have led to the design of pyridine- and diamine-based

solvents with CO<sub>2</sub>-rich viscosities lower than 150 cP at 40 °C.<sup>2,47</sup> For both solvent families, DFT was used to identify species where the acid/base equilibrium was shifted toward the nonionic carbamic acid and chemically modify the solvents to increase internal hydrogen bonding, whereas classical MD was used to verify that these modifications resulted in the projected viscosity reductions. Candidate molecules from both searches were indeed shown experimentally to lead to viable capture solvents for postcombustion applications.<sup>130</sup>

**Degradation.** Another set of challenges hindering the widespread application of solvent-based carbon capture are the harsh effects of industrial flue gas and process conditions on the solvent integrity. In addition to reacting with CO<sub>2</sub> and other flue gas components, the solvent interacts with a surrounding metal interface and dissolved metal atoms, resulting in corrosion and solvent degradation, both of which reduce the lifetime of the solvent and thus incurring significant capital costs. MEA has been shown to react irreversibly with CO<sub>2</sub> and other flue gas components,<sup>131,132</sup> which results in solvent loss.<sup>133</sup> A starting point for understanding the degradation mechanisms is the relative stabilities of the degradation products, which can be obtained from the Gibbs free energies of the various reactions. To this end, Vevelstad et al. utilized B3LYP and Hartree–Fock to examine oxidative degradation and thermal degradation with CO<sub>2</sub> in MEA, respectively, and the IEF-PCM model for solvation energies.<sup>134</sup> They identified oxalic acid, oxalamide, and 1-(2-hydroxyethyl)-imidazole (HEI) to be the most favorable oxidative degradation products and demonstrated that the thermal degradation pathway to 2-oxazolidone via carbamate is thermodynamically favorable. Yoon et al. furthered the study of thermal degradation pathways in the CO<sub>2</sub>–MEA system using AIMD with metadynamics, finding that the mechanisms are primarily dictated by the competition between inter- and intramolecular interactions.<sup>28</sup> They also highlight the importance of entropic contributions associated with solvent arrangement near intermediate species and dynamics to the degradation mechanism.

Additionally, carbon capture solvents and the carbonic acid formed by CO<sub>2</sub> and water are highly corrosive, necessitating the use of high quality corrosion-resistant hardware such as stainless steel, which also increases the costs of this solvent-based process.<sup>135</sup> To understand this issue, molecular modeling has aided in the prediction of amine degradation and possible mechanism of CO<sub>2</sub> capture.<sup>7,136</sup> Process modeling and simulations have been reviewed for the corrosive behavior



**Figure 6.** MD results for (a) a visual example of the interface between 1-IPADM-2-BOL solvent and polymer and (b) the simulated contact angles with experimental comparison. Reprinted with permission from Nguyen, M.-T.; Grubel, K.; Zhang, D.; Koech, P. K.; Malhotra, D.; Allec, S. I.; Rousseau, R.; Glezakou, V.-A.; Heldebrant, D. J. Amphiphilic Water-Lean Carbon Capture Solvent Wetting Behavior through Decomposition by Stainless-Steel Interfaces, *ChemSusChem* **2021**, *14* (23), 5283–5292 (ref 145). Copyright 2021 Wiley-VCH GmbH. (UHMWPE, ultrahigh molecular weight polyethylene; PEEK, polyetheretherketone).

of amine in CO<sub>2</sub> capture.<sup>137</sup> To help the design of corrosion inhibitor, various molecular modeling methods including DFT, MD and Monte Carlo (MC) simulations, artificial neural networks (ANN), and quantitative structure–activity relationship (QSAR) modeling have been employed to test the effectiveness of a wide range of organic corrosion inhibitors, as illustrated in detail in recent review articles.<sup>138,139</sup> In addition, theoretical and computational modeling methods have explored several less corrosive ionic liquids for both pre- and postcombustion CO<sub>2</sub> capture,<sup>140–142</sup> but a thorough understanding of solvent blends of different compounds still needs to be addressed. The use of carbon steel has also been studied to reduce the capital cost in carbon capture by replacing the costly stainless steel with less expensive materials.<sup>143,144</sup> The use of water-lean solvents can partially alleviate this corrosion issue; however, the CrO coating that is commonly used to reduce corrosion is a known oxidative catalyst for alcohols and amines, two chemical moieties that are ubiquitous in water-lean solvents.

Reducing the cost of the absorber and extending the lifetime of the solvent can be achieved by improvements in (i) the packing material and (ii) the solvent's ability to wet the packing. This amounts to selecting a solvent with low contact angles and surface tension and a packing material with reduced degradation effects. Due to lower water content, water-lean solvents exhibit lower surface tension and consequently lower contact angles than aqueous solvents.<sup>145</sup> Water-lean solvents also display comparable wetting behavior on hydrophilic (e.g., steel) and hydrophobic (e.g., plastic) surfaces, as illustrated in Figure 6. Removing or passivating the metal interface has been shown to reduce degradation activation energies, e.g., thermal, oxidation, or hydrolysis, and increase solvent lifetime up to 50%. AIMD simulations have demonstrated that replacing the metal with plastic reduces the strength of solvent–interface interactions, which consequently reduces intermolecular and

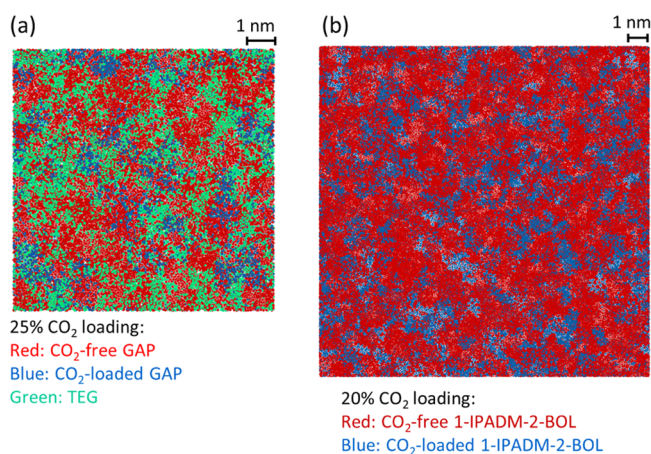
molecule–surface proton transfer processes that could promote degradation.<sup>145</sup>

**Structural Heterogeneity.** Structural heterogeneity is an intriguing property observed in many CCSs.<sup>79,146,147</sup> Due to the size limitation in AIMD simulations, the CMD approach plays an important role in simulating nanoscale properties to explore structural heterogeneity in CCSs. CMD has been successfully used in determining the structural heterogeneity in clean ionic liquid systems (no CO<sub>2</sub>) where polar and nonpolar regions form nanosized domains.<sup>146,148–150</sup> Heterogeneous structures in functionalized ionic liquids with CO<sub>2</sub> loadings have also been studied by CMD.<sup>79,151</sup> Similarly, micro-heterogeneous structures of neat and aqueous propylamine have also been investigated by CMD.<sup>147</sup> In all cases, the structural heterogeneity in such solvents has been shown to strongly affect their bulk properties and performance. For water-lean solvents, 1-((1,3-dimethylimidazolidin-2-ylidene)-amino)propan-2-ol (IPADM-2-BOL) shows a heterogeneous structure with regions of CO<sub>2</sub>-free solvent coexisting with clusters of zwitterionic carbonate ions. CMD simulations also indicate that CO<sub>2</sub> diffuses through the pockets and channels of the unreacted solvents. Such heterogeneous structures in fact enhance the diffusion and reactivity of CO<sub>2</sub>.<sup>16</sup> Following CMD simulations of CO<sub>2</sub>BOL systems, the structural analysis, such as the radial distribution functions, the internal/external hydrogen bonds, neighbor distribution, as well as the simulated viscosity, revealed the link between kinetic and thermodynamic properties of structural heterogeneity and identified two solvent states with different properties.<sup>17,18</sup>

In addition to single-component solvents, CMD simulations have been used to study mixtures of  $\gamma$ -aminopropyl (GAP) aminosilicone with a triethylene glycol (TEG) cosolvent system and revealed only negligible effects of diluents or cosolvents on the structurally heterogeneous system comprised by nanometer-sized CO<sub>2</sub>-rich regions and CO<sub>2</sub>-free regions.<sup>2</sup> An example of solvent heterogeneity is provided in Figure 7 for



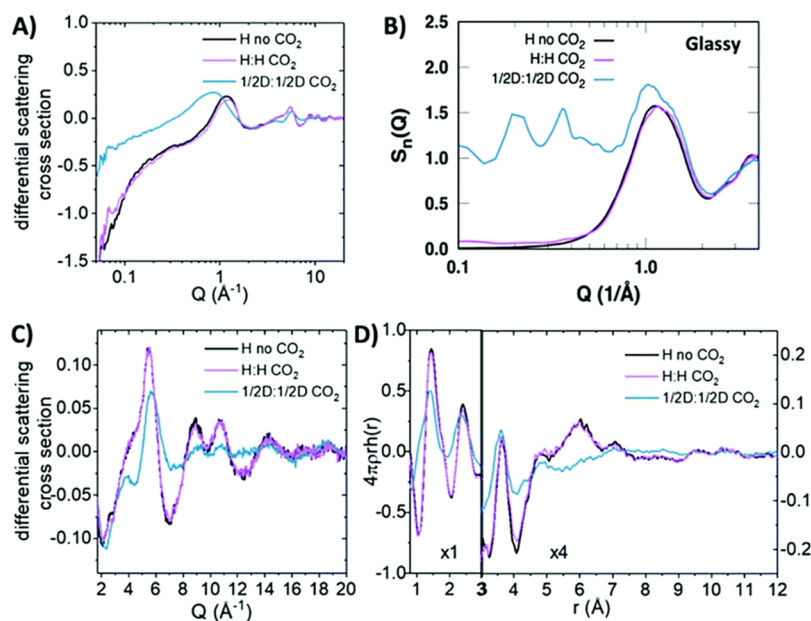
single-compound CO<sub>2</sub>BOLs solvent and diamine based GAP solvents.<sup>2</sup>



**Figure 7.** Structural heterogeneity in nanoscale of CO<sub>2</sub> capture solvents: (a) GAP-TEG solvent<sup>2</sup> and (b) the 1-IPADM-2-BOL solvent.<sup>18</sup> Figures produced based on numerical data taken from Cantu, D. C.; Malhotra, D.; Nguyen, M. T.; Koech, P. K.; Zhang, D.; Glezakou, V. A.; Rousseau, R.; Page, J.; Zheng, R.; Perry, R. J.; Heldebrant, D. J. Molecular-Level Overhaul of  $\gamma$ -Aminopropyl Aminosilicone/Triethylene Glycol Post-Combustion CO<sub>2</sub>-Capture Solvents, *ChemSusChem* **2020**, *13* (13), 3429–3438 (ref 2) and Bañuelos, J. L.; Lee, M.-S.; Ngyuen, M.-T.; Zhang, D.; Malhotra, D.; Cantu, D. C.; Glezakou, V.-A.; Rousseau, R.; Headen, T. F.; Dalgliesh, R. M.; Heldebrant, D. J.; Graham, T. R.; Han, K. S.; Saunders, S. R. Subtle changes in hydrogen bond orientation result in glassification of carbon capture solvents, *Phys. Chem. Chem. Phys.* **2020**, *22* (34), 19009–19021 (ref 18).

CMD results coupled with experimental measurements have suggested that the heterogeneous structures of CCSs can be found in many water-lean solvents, and they will benefit CO<sub>2</sub> transport by creating channels within the fluid for CO<sub>2</sub> to readily diffuse and react with the unreacted solvent molecules. Although it requires more studies to draw a definitive conclusion for such structure–property relationship and to be universally true for all water-lean CCSs, such similarity between many solvents is notable. Furthermore, to capture such structural heterogeneity in the simulations of other solvents in the future, it should also be noted that the size of the simulation box has to be adequately large.

Neutron scattering and diffraction techniques constitute an important tool for structural analysis, making available a wealth of information that can be used to understand complex structures in many types of matter. They have been used for CO<sub>2</sub> capture<sup>152</sup> to characterize water-lean solvents,<sup>18</sup> ionic liquids,<sup>153</sup> and other nonsolvent-based systems such as immobilized amines,<sup>154</sup> polymers,<sup>155</sup> metal-organic frameworks,<sup>156</sup> or nanoporous carbons.<sup>157</sup> Simulated neutron scattering data can be obtained by analyzing structures from molecular simulations<sup>158</sup> and used to interpret experimental results. For instance, simulated neutron diffraction has revealed different states in the 1-IPADM-2-BOL water-lean solvent in consistence with experimental observation, as illustrated in Figure 8.<sup>18</sup> The recent rapid development of quantum computers provides further opportunities to simulate and interpret neutron scattering data more efficiently.<sup>159</sup> Therefore, simulated neutron scattering from molecular simulations is able to reveal useful information for CCSs, but it still needs an efficient method to reduce the intense computing requirement.



**Figure 8.** Experimental and simulated neutron diffraction of H and 1/2D 1-IPADM-2-BOL mixtures with and without CO<sub>2</sub>. The data in this figure were all collected at 40 °C. Unless otherwise noted, the second component in the 1:1 molar mixture is fully loaded with CO<sub>2</sub>. (A) Differential scattering cross-section (DCS) plots over the entire measured Q-range (log scale). (B) Simulated neutron diffraction at different deuteration levels showing qualitative agreement with the experimental data. (C) DCS plots zoomed in over  $Q = 2\text{--}20 \text{ \AA}^{-1}$ . (D) Plot of  $4\pi r\rho h(r)$  vs  $r$  correlation, where  $h(r)$  is the Fourier transform of the DCS; the plot is magnified  $\times 4$  from 3 to 12 Å. Reproduced from Bañuelos, J. L.; Lee, M.-S.; Ngyuen, M.-T.; Zhang, D.; Malhotra, D.; Cantu, D. C.; Glezakou, V.-A.; Rousseau, R.; Headen, T. F.; Dalgliesh, R. M.; Heldebrant, D. J.; Graham, T. R.; Han, K. S.; Saunders, S. R. Subtle changes in hydrogen bond orientation result in glassification of carbon capture solvents, *Phys. Chem. Chem. Phys.* **2020**, *22* (34), 19009–19021 (ref 18) with permission from the PCCP Owner Societies. Copyright 2020 Royal Society of Chemistry.

## OUTLOOK

Theory and molecular simulation are at a point where they can accurately quantify and predict reactivity and local and extended structures that are pertinent to CCSs. Working with experiment, modeling has positively affected and guided solvent design for the next generation capture solvents to increase efficiency and lower costs via molecular design. Through our theoretical investigations of how capture solvents work, we have now acquired the critical knowledge that allows us to fine-tune the adsorption and transport solvent properties for particular applications. For instance, direct air capture will require much higher binding enthalpies than point-source capture due to the low partial pressures. Conversely, electrochemical-based capture methods can be combined with capture solvents but require a higher degree of ionicity, hence, favoring the formation of carbonates/carbamates over their neutral acid equivalence. All of these properties are controllable by manipulating the acid/base equilibria and species populations through molecular design.

While many studies have focused on thermodynamic properties, there is a pressing need to better understand and improve transport properties and solvent degradation pathways. Our team has shown that control of solvent acid/base properties and hydrogen bonding and its placement can lead to improved absorption capacity and lower viscosity. A shift from static QC calculations toward dynamics-based methods and enhanced sampling techniques was crucial for a more accurate treatment of solute–solvent interactions and coupled chemical equilibrium. Solvent heterogeneity, first observed in molecular simulation and validated by experiment, has a profound impact on transport properties, such as viscosity and diffusion, that are intimately connected to CO<sub>2</sub> uptake kinetics. Theoretical studies of CCSs are now a critical component of solvent design for both point-source and direct air capture. Ultimately, there is no single approach that can uniformly, i.e., in any environment in *ad hoc* conditions, allow the study of carbon capture reactions in the bulk of the solvent. Instead, a well-planned approach that combines different computational methodologies across time and size scales is needed to maintain a reasonable balance between chemical accuracy and computational efficiency. We firmly believe that such approaches will play even more imperative roles boosted by the rapid development of machine learning and quantum computing technologies.

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## Notes

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