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Water-Lean Solvents for Post-Combustion CO_2 Capture: Fundamentals, Uncertainties, Opportunities, and Outlook

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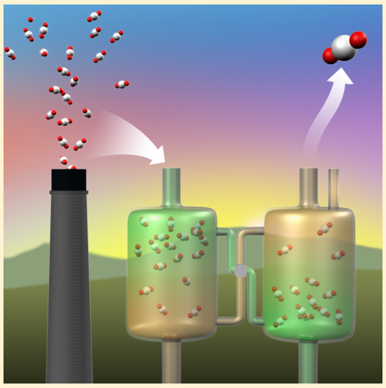
ABSTRACT: This review is designed to foster the discussion regarding the viability of postcombustion CO_2 capture by water-lean solvents, by separating fact from fiction for both skeptics and advocates. We highlight the unique physical and thermodynamic properties of notable water-lean solvents, with a discussion of how such properties could translate to efficiency gains compared to aqueous amines. The scope of this review ranges from the purely fundamental molecular-level processes that govern solvent behavior to bench-scale testing, through process engineering and projections of process performance and cost. Key discussions of higher than expected CO_2 mass transfer, water tolerance, and compatibility with current infrastructure are presented along with current limitations and suggested areas where further solvent development is needed. We conclude with an outlook of the status of the field and assess the viability of water-lean solvents for postcombustion CO_2 capture.



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1. INTRODUCTION

Capturing CO_2 from the exhaust of coal-fired power plants is a daunting task, requiring selective removal from a dilute gas stream of 10^6 lb/h of a molecule that is considered thermodynamically and kinetically stable. There are commercial

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solvent technologies containing proprietary blends of aqueous amines such as Econamine FG+, KS-1, Oase Blue, and Cansolv that may achieve this task.[1] The Achilles' heel of amine blends is the energy loss involved with regenerating the solvent (i.e., boiling and condensing 10^6 lb/h of water). This energy loss translates to a sizable parasitic load on a coal-fired plant, requiring the plant to burn more coal to get back to its nameplate capacity.[2] Unsurprisingly, a considerable amount of research has focused on the design of more efficient technologies to lessen this parasitic load. Liquid systems are the lowest hanging fruit from a time and cost perspective, as they have the potential to use aqueous amine infrastructure, with potential for more rapid ascent up the development ladder than porous solids or membranes.

The past decade has seen a renaissance in solvent development with concentrated organic "water-lean" solvents. Water-lean solvents are designed to maintain the chemical selectivity of water-based solvents along with promises of step changes in efficiencies achieved by lower specific heats of organics than that of water. Many solvents promise transformative gains in efficiency, but the majority of these systems are still in the early stages of development and lack the rudimentary data to enable rigorous modeling for large-scale performance projections. A few solvents have been studied at a meaningful scale, though it should be noted that they often lack published results, and the formulations of these solvents are often a trade secret.

Unsurprisingly, the viability of organic solvents for CO_2 has been the subject of much debate and met with skepticism. The debate stems primarily from the limited availability of data but also from misconceptions and unknowns of a first-of-a-kind technology. Water-lean solvents are thought by some to be too costly, exhibit negligible rates of CO_2 mass transfer, have poor water tolerance, and require costly and exotic infrastructure. Fortunately, there has been considerable work in solvent development that indicates that many of these are misconceptions. Some of the notable solvents have been shown to use conventional infrastructure, demonstrate acceptable water tolerance, and exhibit faster CO_2 mass transfer than their aqueous counterparts.[3] Conversely, advocates have their own misconceptions, with some believing that thermo-neutral capture is not only desirable but also feasible, while others claim efficiency gains over monoethanolamine (MEA) from simple small-scale benchtop experiments.

In either case, there is insufficient understanding at the molecular level of how the unique thermodynamic and physical properties of water-lean solvents manifest or how to control them. Similarly, little is known of how CO_2 diffuses in and out of solution or the kinetics and mechanism of binding. Ultimately, there is a sizable knowledge gap of how these solvents function and whether the projected efficiency gains are achievable.

In this review, we take a different approach from other reviews on the subject[4−7] and attempt to foster discussion on water-lean solvent systems by separating fact from fiction for the skeptic and advocate alike. We highlight the unique physical and thermodynamic properties of leading candidate water-lean solvents, with an emphasis on how those properties would translate to projected efficiency gains. We also assess the molecular-level processes that govern solvent behavior and how this knowledge can be used to refine performance. Known limitations of each solvent are identified along with opportunities for further advancement. We conclude with an outlook of the field and prospects for postcombustion CO_2 capture.

2. FUNDAMENTALS OF WATER-LEAN SOLVENTS

In this section, we introduce water-lean solvents and recap what is known about their behavior and the stage of their development. We begin by identifying the solvent formulations and binding chemistry with CO_2. We then highlight the unique physical and thermodynamic properties that can be exploited for efficiency gains.

2.1. Thermodynamic Considerations

One of the biggest misconceptions in the design of water-lean CO_2 capture solvents is that a low or thermo-neutral heat of reaction with CO_2 is ideal. This misconception has been refuted by the thermodynamic modeling work of Mathias,[8,9] who set out to identify the optimal thermodynamic range for known and hypothetical CO_2 capture solvents. In this study, Mathias aimed to identify suitable CO_2 capture solvents using only the CO_2 absorption strength (identified using the CO_2 partial pressure) and the enthalpy of solution. Known and hypothetical solvents were set into this model with absorption set at 40 °C and with CO_2 loadings (mol CO_2/mol solvent) of 0.15. Mathias discovered a simple exponential relationship between the enthalpy of solution and the solvent strength (Figure 1), which enabled validation of this relationship for known solvents but to also create hypothetical families of solvents with varied properties such as absorption capacity and enthalpy of solution. Mathias' study used Aspen Plus and varied only the thermodynamic properties in the flow sheet to determine the changes in solvent performance as a function of the solvent circulation rate.

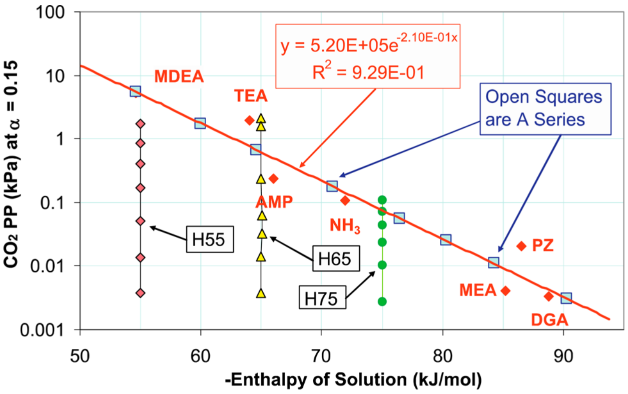

Figure 1. Relationship between the CO_2 partial pressure and the heat of solution for seven common solvents. The calculations were done at 40 °C, a CO_2 loading of 0.15, and a solvent strength of 7 M. Reproduced with permission from ref 8. Copyright 2013 Elsevier.

Mathias et al. identified what is best described as a "Goldilocks'" zone, where optimal solvents were neither too low nor too high in enthalpy of solution or CO_2 capacity. For solvent-based technologies, the solvent circulation rate and reboiler duty are the most critical parameters that define an efficient process. Solvents that have low enthalpies and high CO_2 partial pressures would require higher solvent recirculation rates, which greatly increase reboiler duty and pumping costs, in addition to the costs associated with more solvent. These costs can be prohibitive when considering that water-based solvents require circulation rates on the order of 10^6 kg/h. Conversely, a solvent with a high enthalpy of solution and low CO_2 partial pressure would entail a high reboiler duty to release CO_2 from the solvent and could suffer from higher rates of oxidative and

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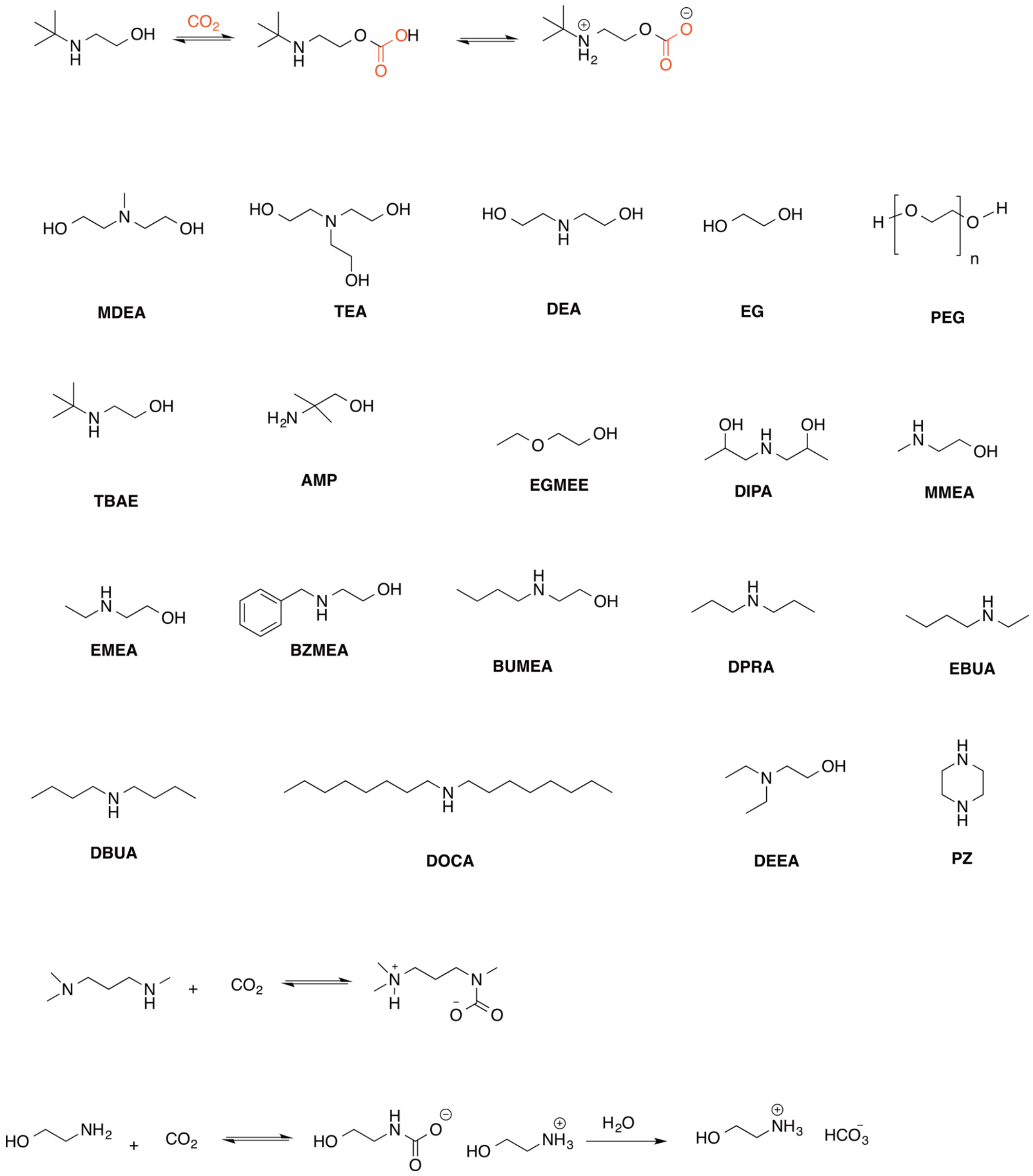

Figure 2. Reaction of aqueous MEA with CO_2, and structures of commonly used alkanolamines and amines.

thermal degradation. Rochelle has argued, however, that a high heat of reaction may be beneficial from an energy perspective. He suggests that a high enthalpy of solution would provide a high degree of thermal compression of CO_2, which could save energy compared to mechanical compression of CO_2 to a supercritical state.[10−12] Rochelle's conclusions may be viable for water-based solvents where regeneration temperatures are well above 100 °C but may be less advantageous for water-lean solvents that can regenerate below 100 °C. Here, processes could be made more efficient by using lower quality heat to regenerate the solvents (lower pressure steam), but they could also provide increased solvent durability due to lower thermal-degradation or evaporative losses.[13] It should be noted that water-lean solvents entail a lower specific heat than those of aqueous solvents, resulting in larger temperature bulges in the absorber column, though this could easily be handled by introduction of intercooling.

Mathias defines the optimal thermodynamic range of solvents as between −60 and −70 kJ/mol binding enthalpy. Unsurprisingly, the best-performing hypothetical solvents lie along the line of first-generation amine solvents such as methyldiethanolamine (MDEA), triethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP), MEA, and piperazine (PZ).[8] We emphasize that this Goldilocks' range may not apply universally to all solvent platforms, though we highlight it here because the majority of solvents covered in this review fall in this range. We also highlight this range to dispel the misconceptions that a low heat of reaction with CO_2 is desirable for a working process or that a high heat of reaction would be beneficial to water-lean solvents.

2.2. Volatility Considerations

Volatility is one of the biggest parameters that skeptics have voiced concern over. All liquids, including water-based solvents, may suffer substantial evaporative losses into the gas being treated. Evaporative losses of a custom and costly water-lean solvent would burden a process with substantial solvent makeup rates and costs, on the order of millions of tons and millions of dollars per year per individual power plant. Further, these emissions may introduce significant environmental impacts if the gas being treated is released to the atmosphere.

In the case of power plant flue gas scrubbing, solvent losses occur primarily in the absorber. A 550 MW coal-fired power plant produces about 7 million lb/h of gas, and most or all of that gas must pass through the solvent in the absorber column to capture more than 10^6 lb/h of CO_2.[2] Here, the vapor pressure of the solvent is critical. Any solvent, whether it be water or organic, will evaporate until vapor−liquid equilibrium is established. As the flow and pressure of the exhaust is constant, the solvent will continuously evaporate. Solvents with low vapor pressures would have slower (but not negligible) evaporative rates, while solvents with high vapor pressures would suffer from substantial rates of evaporative losses. Monoethanolamine (MEA), which is relatively nonvolatile (0.009 bar at 338.9 K),[14] would lose roughly 225 t per year to evaporation, which adds a significant cost burden to a working process even though MEA can be considered one of the cheapest amine solvents.[15]

In the stripper, the rich solvent is heated to release CO_2 until a desired lean loading is achieved. As in the absorber, solvent will evaporate and approach vapor−liquid equilibrium at the higher temperature of the stripper. However, the CO_2 and any water or solvent vapor are sent to a compressor, where the CO_2 is compressed to high pressure (nominally 2200 psi) for geological sequestration.[2] In this process, most liquids such as water or solvent are condensed as part of the compression process and are separated from the CO_2.[2] These liquids are recovered and typically pumped back to the process. As such, evaporative losses from the stripper are much lower than in the absorber.

We highlight volatility for two purposes. First, we point out that fugitive emissions occur primarily from the absorber side of a working process, and solvent vapor pressure is a critical parameter. Second, we note that the majority of water-lean solvents presented in this review have taken volatility into consideration. It is understood that any water-lean solvent would require either solvent reclaimer or other type of emissions treatment to minimize emissions to mitigate any adverse environmental impact, though such technologies are not a focus of this review.

2.3. Solvent Chemistries

We present here various formulations of water-lean solvents grouped by their chemical functionality (i.e., binding mechanism with CO_2), not in chronological order. There is much synergy between formulations in their binding mechanisms, with many variants of similar concepts. The solvents differ in their distinctive physical or thermodynamic properties that translate into unique configurations and processes, which we later highlight in section 3.

2.3.1. Nonaqueous Organic Amine Blends. Solutions of aqueous primary and secondary alkanolamines such as MEA or diethanolamine (DEA) constitute the most mature technology for chemisorption of CO_2 from point sources such as flue gas from power plants (Figure 2).[5] These alkanolamines have rapid CO_2 absorption kinetics to form carbamates at low partial pressures.[16] Deployment of these aqueous alkanolamines to market is limited by their high regeneration temperature (>120 °C), high steel corrosion, and high solvent evaporative losses. These problems can be addressed by lowering the regeneration temperature below 100 °C. One way to achieve this is to eliminate the water cosolvent, which partly contributes to the high regeneration temperature because its heat capacity is twice that of organic solvents.

The first water-lean aqueous organic amine blends took the conventional aqueous amines and replaced water with an organic cosolvent. These first solvents were initially developed to enhance physical solubility of CO_2 in tertiary alkanolamines such as *N*- MDEA in methanol,[17] TEA in alcohols,[18] and diethanolamine (DEA) in ethylene glycol (EG).[19] These solvent blends were studied for high pressure CO_2 capture for natural gas cleanup. Lee et al. studied CO_2 solubility for chemically binding amine MEA in EG and poly(ethylene glycol) (PEG) with a small quantity of water.[20,21] Addition of physical sorbent cosolvents to aqueous MEA was found to increase CO_2 solubility and capacity, though it should be noted that the use of volatile organic solvents to dissolve the CO_2 carrier is impractical for industrial use.

More recent advancements by several research groups have led to the development of nonaqueous amine solvents. For example, Kim et al. developed a nonaqueous solvents system comprising sterically hindered amines 2-[(1,1-dimethylethyl)amino]ethanol (TBAE) and 1-[(1,1-dimethylethyl)amino]-2-propanol (TBAP).[16,22−24] These amines reversibly bind CO_2 by nucleophilic attack of the electrophilic carbon in which the alcohol forms an ammonium alkylcarbonate zwitterion, which can be regenerated at lower temperature than aqueous MEA and DEA (Figure 3).[16] The zwitterionic carbonate formed in this reaction is a solid, and therefore TBAE and TBAP are dissolved in organic solvents such as ethylene glycol or methanol.

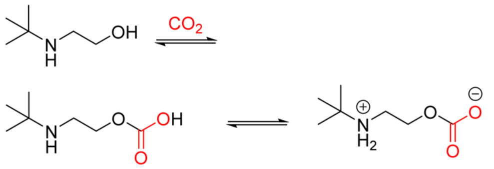

Figure 3. Reaction of TBAE with CO_2 to form zwitterionic ammonium carbonate.

Barzagli et al. also reported a sterically hindered amine solvent system consisting of AMP/PZ in a solution of ethyl glycol monomethyl ether (EGME) and 15 wt % water.[25] These solvents were designed based on the hypothesis that a sterically hindered primary amine will form a weaker, less stable carbamate or carbamic acid that will be regenerated at lower temperature (80−90 °C). Another nonaqueous solvent system developed by Mani et al. comprises AMP blended with other alkanolamines such as DEA, MDEA, MMEA, and diisopropanolamine (DIPA), in organic cosolvents such as ethylene glycol, 1,2-propanediol, methanol, or ethanol.[26,27] These solvents were continuously circulated in a closed cycle at a temperature between those of the absorber (20 °C) and desorber (65−80 °C), demonstrating 73−96% CO_2 absorption efficiency at equilibrium. Mani's group also developed a single amine system consisting of sterically hindered secondary amines like dipropylamine (DPRA), *N*-ethylbutylamine (EBUA), dibutylamine (DBUA), and dioctylamine (DOCA) that showed promise in this class of materials.[28] The CO_2 binding mode for materials is the conventional carbamate mechanism; however, significant amounts of zwitterionic carbonate species can form, resulting in a loading capacity greater than 50 mol %, and the viscosity of the CO_2-rich material is low (<30 cP). A recent advancement by Barzagli et al. demonstrated that alkanolamines such as 2-(isopropylamino)ethanol (IPMEA), 2-(methylamino)ethanol (MMEA), 2-(ethylamino)ethanol (EMEA), 2-(benzylamino)ethanol (BZMEA), and 2-(butylamino)ethanol (BUMEA) can bind

CO_2 to form liquid carbamate salts.[29] These single-component solvents do not require organic or aqueous diluents since they are liquid in CO_2-free or CO_2-rich states at the experimental temperatures.

Chen et al. reported recently that a solution of ethylmonoethanolamine (EMEA) in a tertiary alkanolamine cosolvent such as diethylethanolamine (DEEA) or MDEA results in a CO_2 capture formulation with increased equilibrium solubility and high cyclic capture capacity compared to using triethylene glycol (TEG) or diethylene glycol (DEG) cosolvents.[30−32] This is the first example where tertiary alkanolamines are used as cosolvents for CO_2 capture. Although tertiary amines cannot bind CO_2 chemically, Chen's team showed that DEEA participates in chemical absorption by abstracting protons from an EMEA carbamic acid intermediate. Chen and co-workers also observed that using tertiary amine DEEA in nonaqueous solvent results in better performance than using alcohols and glycols.[30]

2.3.2. Aminosilicones. Perry et al. developed aminosilicone solvents that contain both physisorbing and chemisorbing components in one molecule to improve the CO_2 capture capacity per molecule.[33,34] A CO_2-philic siloxane backbone is combined with CO_2-reactive amino groups, resulting in aminosilicone solvents known as GAP-0 and GAP-1 (Figure 4). These solvents capture CO_2 with nearly quantitative yields, forming solids or becoming highly viscous; thus, TEG 50% was added as cosolvent. This solvent resulted in CO_2 capture greater than 100% of theoretical capacity relative to amine content due to the combination of both physisorption and chemisorption. These solvents were shown to be thermally stable by recycling several times without loss of activity.

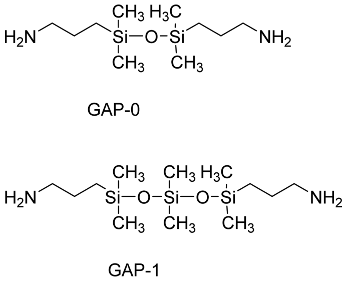

Figure 4. GAP-0 and GAP-1 aminosilicones.

The viscosities of aminosilicones in TEG cosolvent increase with CO_2 loading; for example, the viscosity of GAP-0 in TEG is ~1300 cP at 40 °C.[33] This increase in viscosity is attributed to formation of a hydrogen-bonding network between the carbamate and TEG cosolvent. Another potential challenge identified for TEG-containing solvents is their hygroscopic nature, which will lead to accumulation of water in the system, posing a process-engineering challenge. Using tertiary alkanolamines such as *N*,*N*-diisopropylethylamine (DIPEA), diethylpropanolamine (DEPA), DEA, and MDEA as cosolvents, Perry et al. addressed these challenges.[34] These tertiary amino alcohol cosolvents for aminosilicones improve CO_2 capture efficiency; in some cases, significant increases compared to equivalent loading using TEG were achieved. This is attributed to secondary CO_2 binding by the alkanolamines. Additionally, viscosity of this formulation was lower at a given CO_2 loading than with the TEG system. Aminosilicones containing secondary amines functionalized with electron-donating groups (RO−, R_2N, $ROCH_2−$) had CO_2 uptake capacity higher than theoretical maximum and formed low-viscosity carbamate salts due to charge solvation (Figure 5).[35] Primary aminosiloxanes have high heats of CO_2 absorption, with typical values in excess of 2500 kJ/kg of CO_2; for example, the heat of absorption of GAP-0 is 2554 kJ/kg of CO_2, while that of GAP-1 is 2558 kJ/kg of CO_2.[36] Solvents with high heats of CO_2 absorption require additional cooling in the absorber in order to keep the temperature from rising and maintain high capture efficiency. Furthermore, materials possessing high heats of absorption would lead to higher parasitic energy load during desorption.[35] Secondary aminosilicones had lower heats of CO_2 absorption than primary amine-based aminosilicones like GAP-0; for example, compounds with unbranched alkyl groups have heats of CO_2 absorption in the range 2100−2200 kJ/kg of CO_2, while those for materials with branched or cyclic R groups are in the range of 2000−2100 kJ/kg of CO_2.[35] The most promising aminosilicones comprise materials possessing ether functionality; they showed low viscosities with high CO_2 uptake with heats of absorption in the optimal thermodynamic range.

2.3.3. Switchable Carbamates. Switchable carbamates are a class of nonaqueous amine-based solvents first developed by Eckert and Liotta for CO_2 capture.[37] These amines are also referred to as "reversible ionic liquids" (RILs) since they bind CO_2 reversibly via standard carbamate mechanism, forming ionic liquids (Figure 6). In this solvent system, two anhydrous primary or secondary amines are used: one equivalent of amine acts as the nucleophile attacking CO_2 and making a carbamic acid, and a second amine acts as a proton scavenger, forming a carbamate ionic liquid (Figure 6, top).

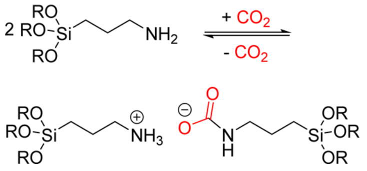

Figure 6. First carbamate-derived RILs.[38]

The first formulations of reversible carbamate are siloxylated ethylamines (Figure 6).[38] Trimethoxy- and triethoxysilylpropylamine were found to bind CO_2, forming the corresponding carbamate ionic liquids 3-(trimethoxysilyl)-propylammonium 3-(trimethoxysilyl)-propylcarbamate (TMSAC) and 3-(triethoxysilyl)-propylammonium 3-(triethoxysilyl)propylcarbamate (TESAC).[38] Just like other nonaqueous carbamates, these carbamates release CO_2 readily when subjected to thermal heating or a nitrogen sparge, which is not viable in a workable process. The CO_2 uptake capacities for these solvents were 13 wt

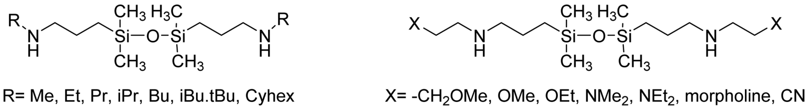

Figure 5. Functionalized aminosilicones.

% for TMSAC and 9 wt % for TESAC at 1 atm of CO_2, with complete CO_2 release demonstrated at 88 and 125 °C, respectively.[38] These first formulations of siloxylated ethanolamines had excellent CO_2 capture capacity and low regeneration temperature and were liquids at full CO_2 loading but suffered from lack of chemical durability due to hydrolysis of the labile Si−O bond. To address this problem, Eckert and Liotta developed new derivatives based on trialkylsilylpropylamines (Figure 7).[39,40] At approximately the same time, Jessop demonstrated that low-volatility alkyldiamines can also be used in RILs without the need for heteroatoms such as silicon (Figure 7b).[41] These diamines formed zwitterionic carbamate ionic liquids with 28 wt % CO_2, though the chemistry is limited by the high vapor pressure of the diamine.[41]

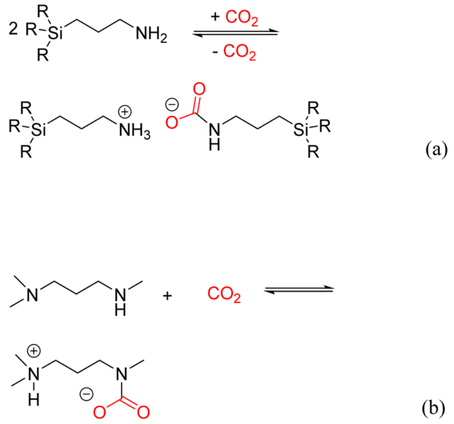

Figure 7. Reactions of (a) trialkylsilylpropylamines and (b) alkyldiamine with CO_2.[40]

Rohan et al.[42] demonstrated CO_2 capture application of four silylamines: 3-(aminopropyl)trimethoxysilane (TMSA), 3-(aminopropyl)triethoxysilane (TESA), 3-(aminopropyl)-triethylsilane (TEtSA), and 3-(aminopropyl)tripropylsilane (TPSA). Their CO_2 uptake followed the conventional carbamate stoichiometry of 0.5 mol of CO_2 per mole of amine, though higher absorption occurred than expected, which could be attributed to either physical absorption of CO_2 or formation of a carbamic acid, resulting in stoichiometry greater than 2:1.[43] The CO_2 uptake capacity was 0.6 mol of CO_2 per mole of amine, although testing was not under flue gas conditions (25 °C and 1 atm CO_2). All four silylamines had binding enthalpies between −81 and −92 kJ/mol CO_2,[42] which are close to the range identified by Mathias. All four liquids exhibited large increases in viscosity with CO_2 uptake; however, the viscosities were at or below 1300 cP at full loading at 40 °C.[42] Eckert and Liotta suggested that viscosity can be maintained below 300 cP if the CO_2 uptake is kept below 70% conversion at 40 °C (Figure 8). The molecular-level interactions that occur around this transition point remain unknown, though the transition point appears in all switchable or reversible ionic liquid formulations; see below.

Eckert and Liotta tested 13 additional silylamines for CO_2 capture, which demonstrated comparable performance to the initial four formulations.[37] CO_2 uptake ranged from 0.33 to 0.63 mol CO_2 per mole amine at 1 atm CO_2 and 25 °C, with TEtSA and 2-methyl-3-(triethylsilyl)propylamine (*β*Me-TEtSA) both absorbing 0.60 mol CO_2 per mole amine at 40 °C and 1 atm CO_2 (Figure 9). Binding enthalpies were also comparable to prior formulations, ranging from as low as −21 kJ/mol for trans-2-methyl-4-(tripropylsilyl)butyl-2-amine (trans-*α*,*α* DMe-TPSA) to as high as −152 kJ/mol for 4-(aminobutyl)triethylsilane (TEtSBA).

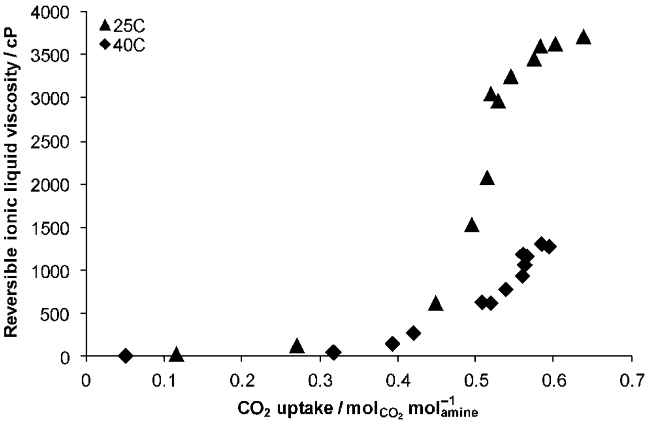

Figure 8. Viscosity versus CO_2 uptake for TPSA at 25 and 40 °C.[37]

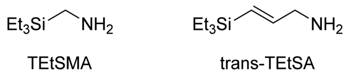

Figure 9. TEtSMA and *trans*-TEtSA derivatives for CO_2 separations.[37]

The two silylamines with the best CO_2 capture capacity were 1-(aminomethyl) triethylsilane (TEtSMA) and *trans*-TEtSA (Figure 9).[37] TEtSMA and *trans*-TEtSA had heats of reaction of −76 and −85 kJ/mol, respectively, with CO_2-rich solvent viscosities at 40 °C of 625 and 362 cP, respectively.[37] These two derivatives show promise due to their relatively low CO_2-rich solvent viscosities compared to those of the CO_2-binding organic liquid (CO_2BOL) alkanolguanidine formulations, and their CO_2 binding enthalpies lie within the desired range identified by Mathias.[13] It should be noted that these materials are still being tested at the laboratory scale; data is needed at a meaningful scale in a continuous flow to assess their performance at scale.

Lail et al. have developed improved RILs known as "nonaqueous solvents" (NASs). These solvents consist of hydrophobic, sterically hindered, carbamate-forming amines (which have low water solubility) in combination with unspecified amounts of low-vapor-pressure organic diluent to produce NASs that exhibited minimized foaming, reduced viscosity, and reduced water accumulation. NAS chemistry enables phase separation of the CO_2-reactive solvent from water; while not a truly classical RILs application by definition (due to the use of diluents), we highlight the testing of the NASs here as it is the first example of RIL-like chemistry with comprehensive property analysis and testing in a continuous flow at a meaningful scale to assess process viability.[44]

Similar to all nonaqueous amine derivatives, NASs have lower regeneration temperatures than water-based solvents, allowing for the use of lower-quality heat to regenerate the solvent, which improves process efficiency. NASs have achieved CO_2 partial pressures up to 200 kPa at 90 °C in the stripper; in comparison, 30 wt % MEA requires heating to or above 120 °C.[44,45] NAS heats of absorption are −70 to −75 kJ/mol CO_2 at 40 °C, but they decrease to 55−70 kJ/mol of CO_2 at a stripping temperature of 90 °C,[44] almost completely within the preferred range indicated by Mathias.[8,9] The viscosities of CO_2 rich NASs were between 2.5 and 38 cP, which are orders of magnitude lower than those of other organic solvents presented in this review.[44] The low viscosities of NASs were achieved by the use of diluents, and nearly all of the solvents presented in this review can achieve comparable viscosity reduction if diluents are added. It should be noted that diluents are likely to be volatile, requiring treatment systems to prevent fugitive emissions. Further, the addition of diluents may complicate phase chemistry and remove or diminish unique phase and thermodynamic behavior; thus, this viscosity reduction strategy is unlikely to be used universally across solvent platforms.

The exact formulation of the NAS has not been disclosed, but the promising results from this study indicate that RIL-like carbamate chemistry has potential for improving the efficiency of CO_2 capture processes.

2.3.4. Amines with Superbase Promoters.

Primary amines combined with a strong nonnucleophilic base as a secondary component have been shown to have enhanced CO_2 capture efficiency with capture ratios greater than 1:1 on a molar basis (CO_2 per primary amine group) (Figure 10).[46] The reaction mechanism is analogous to that of conventional amine chemistry, where the amino group binds CO_2 to yield a carbamate product with subsequent proton transfer to the stronger base (Figure 10). The second, stronger base enables independent fine-tuning of amine nucleophilicity and Brønsted basicity, providing an opportunity to optimize the overall reaction kinetics and thermodynamics.[46] Due to the increases in viscosity or solid formation in the CO_2-rich form, these materials were dissolved cosolvents such as toluene, sulfolane, and dimethyl sulfoxide (DMSO). The CO_2 capture capacity of this formulation was shown to be greater than 130 mol % per primary amine base. A solvent system consisting of ethoxyethylamine (EEA) and tetramethylguanidine (TMG) was shown to have a high CO_2 capture capacity at ∼65 and 90 °C, which makes these materials amenable to elevated temperature CO_2 capture applications.

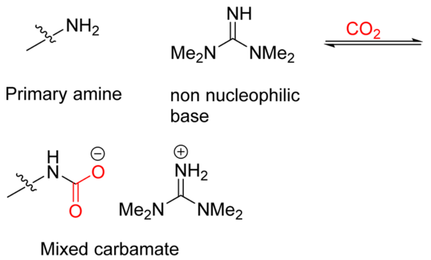

Figure 10. Reaction of primary amines with CO_2 in the presence of a strong nonnucleophilic base.

Kortunov et al. have extended this solvent system to nucleophilic polyamines with nonnucleophilic strong bases (Figure 11).[47,48] A solution of these amines in DMSO has been shown to bind CO_2 to form high density carbamate ions whose negative charge can be balanced by ammonium counterions or guanidinium from the strong base. This combination has yielded a less viscous formulation compared to the polyamines alone; thus, neat liquid sorbent can be used for CO_2 capture, but for practical application, a cosolvent is required.[47] These materials have a unique property: they can bind CO_2 at elevated temperatures (between 45 and 90 °C) and have even greater CO_2 uptake capacity at lower temperatures. These materials can be applied to flue gas streams without the need to cool the gas. CO_2 stripping temperature was determined to be 120 °C in a thermal regeneration cycle, or lower if aided by vacuum or nitrogen gas.[47]

2.3.5. Amino Acids in Organic Solvents.

Task-specific or functionalized ionic liquids were first reported by Davis et al.[49] in 2002; 1-propylamide-3-butyl imidazoliumtetrafluoroborate ([apbim][BF4]) was tethered to an amino group to enable reaction with CO_2 under a conventional carbamate mechanism. Subsequent to Davis's seminal work, numerous task-specific ionic liquid solvents have been developed and extensively reviewed.[4,50,51] This section focuses on a subset of task-specific ionic liquids with an amino acid anion.

Amino acids have been shown to be efficient CO_2 capture materials due to their intrinsic basicity, high water solubility, thermal stability, excellent CO_2 selectivity, biodegradability, and commercial availability. Sartori et al. reported the first use of sterically hindered, monosubstituted amino acids as promoters in aqueous alkali carbonate CO_2 scrubbers.[52,53] Subsequent to this seminal work, Jansen et al. developed a solvent system comprising a mixture of amino acids and amino acid salts for CO_2 capture.[54] Significant progress has been made in the development of aqueous amino acid solvents for CO_2 capture;[55−57] however, that work is not the focus of this section. Nonaqueous amino acid salts with bulky N-substituents have been shown to have a high CO_2 capacity with stoichiometric CO_2 binding in PEG solution.[58] This high CO_2 uptake capacity for sterically hindered amino acid salts is attributed to the formation of the carbamic acid rather than the carbamate in aqueous analogs (Figure 12). The unsubstituted sodium glycinate salt captured CO_2 via formation of ammonium carbamate with a 2:1 stoichiometry. The carbamic acid adduct has low regeneration

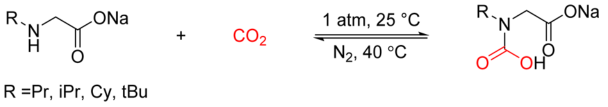

Figure 12. CO_2 capture via carbamic acid using an amino acid salt.

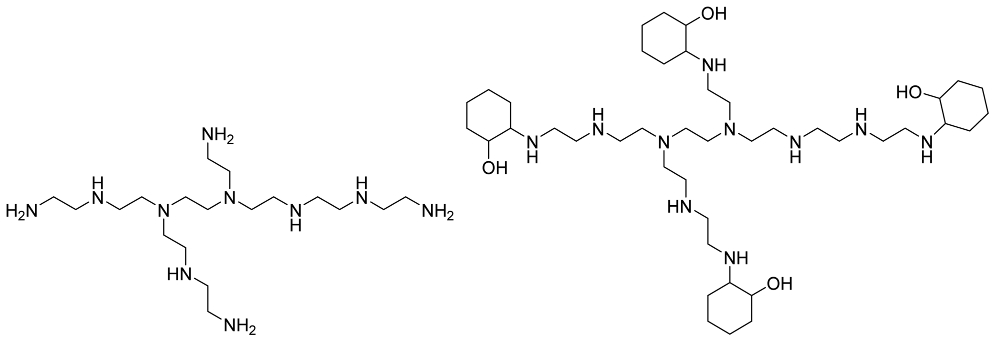

Figure 11. Polyamine bases for CO_2 capture.

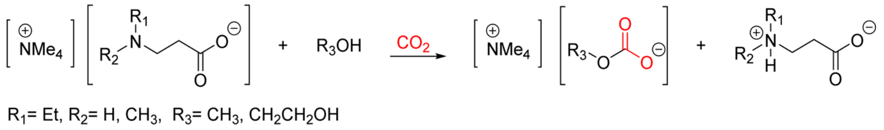

Figure 13. Reaction of CO_2 with TMAAs to form alkylcarbonates.

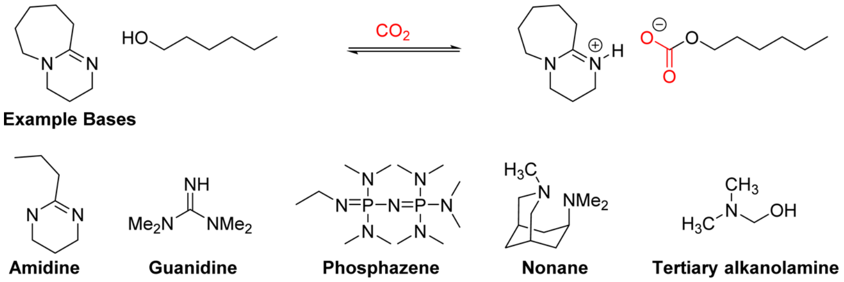

Figure 14. Bases that form stable alkylcarbonate ionic liquids (amidines, guanidines, phosphazenes, nonanes, and tertiary alkanolamines).

temperature, releasing CO_2 at 40 °C with N_2 bubbling, or thermally at 90 °C. Cations of the salts capable of coordinating polar solvents like PEG were found to enhance CO_2 capacity.

Gurkan et al. reported analogous carbamic acid binding mechanisms in phosphonium prolinate and methioninate ionic liquids.[59] In this system, steric hindrance is believed to stabilize the carbamic acid by introducing a bulky cationic species. Dai et al. developed a simplified amino acid solvent system that can stabilize the formed carbonic acid via intramolecular hydrogen bond.[60] In Dai's formulation, crown ethers were added to amino acids to solvate the alkali metal cations, thus enabling hydrogen bonding between the carboxylate anion and the carbamic acid hydrogen. An example is potassium prolinate with 18-crown-6 in PEG-bound CO_2 in a 1:1 ratio; the product released CO_2 at 50 °C with N_2 bubbling. Following this work, Kim et al. reported a 1:1 CO_2 capture stoichiometry using tetramethylammonium-based amino acid (TMAA) salts via the formation of alkyl carbonate (Figure 13).[61] In this system, the amino acid salt enables the reaction of alcohol with CO_2 by facilitating the deprotonation and also stabilization of the incipient alkyl carbonate. Similar transformations will be presented in the section on CO_2BOLs, in which a strong base such as a guanidine combines with alcohols to produce alkylcarbonates. Recently, Firaha et al. performed a detailed analysis of chemical absorption of CO_2 in amino acid ionic liquids using first-principles calculations.[62] This study found that the mechanism of CO_2 absorption in amino acid ionic liquids, for example, 1-ethyl-3-methyl-imidazolium glycinate ([C_2C_1Im][Gly]), involves the formation of a gylcinate-CO_2 adduct followed by proton abstraction by the amino or the carboxylate group. The composition of the equilibrium mixture contained the carbamate glycinate zwitterion and carbamic acid. The equilibrium between carbamic acid and carbamate was mostly shifted toward the carbamic acid in the amino acid ionic liquids evaluated.

2.3.6. Alkylcarbonates. Heldebrant et al. were the first to evaluate the viability of alkylcarbonate-derived switchable ionic liquids[63] in postcombustion CO_2-capture application under the name CO_2−Binding Organic Liquids (CO_2BOLs).[64] CO_2BOLs were the first alkylcarbonate solvents consisting of a non-nucleophilic amidine or guanidine superbase and an alcohol that reversibly capture CO_2, with the CO_2 carried being liquid alkylcarbonate salts. The CO_2 capture process operates on simple acid/base chemistry, where CO_2 and the alcohol make an alkylcarbonic acid, which subsequently protonates the base component. This binding mechanism is different from that of the nucleophilic primary and secondary amines described above, in which an amine reacts directly with CO_2 to form a carbonic acid, which then protonates a second equivalent of base. The thermodynamic strength of CO_2 capture by CO_2BOLs can be assumed to be a heat of protonation between alkylcarbonic acid and the base. Heldebrant et al. had shown that alkylcarbonate formation can only occur in the presence of superbases such as amidines and guanidines or even phosphazenes (Figure 14) possessing dissociation constants (pKas) in acetonitrile greater than 18.3, while less basic tertiary amines with an alcohol or tertiary alkanolamines cannot be protonated by the weak alkylcarbonic acids made when CO_2 inserts into alcohols.[65]

Lo et al. have recently developed and calculated the basicity of new, stronger superbases for CO_2 capture in combination with alcohols via the alkylcarbonate binding mechanism.[66] These organic superbases were appended to a substituted 3-methyl-3-azabicyclo[3.3.1]nonane molecular framework (Figure 15).[66] These derivatives have two basic sites, enabling the potential for two moles of CO_2 captured per mole of alkalinity.

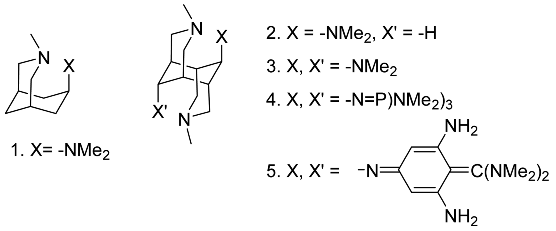

Figure 15. Superbases derived from 3-methyl-3-azabicyclo[3.3.1]-nonane.[66]

The first-generation CO_2BOLs comprised separate bases and alcohol molecules that had high boiling points, but their vapor pressures were too high for practical CO_2 capture applications due to potentially extensive evaporative losses.[64] Koech and Heldebrant mitigated evaporative losses by combining the alcohol and base components into a single molecule. Single-component liquid alkanolguanidine derivatives were made by chemically functionalizing a TMG base core with linear alcohols.[41] Subsequently, Kim et al. reported three alkanolamidines derived from DBU, also known as hydroxylated amidines (HAMs).[67] These materials were crystalline solids with melting points above 116 °C. Both single-component alkanolamidines and alkanolguanidines capture CO_2 through an alkylcarbonate binding mechanism like the dual-component molecules, albeit now as zwitterionic solids and liquids, respectively. Alkanolguanidines and alkanolamidines are less volatile than dual-component systems, but these initial derivatives had poor CO_2 uptake due to reduced mass transfer that was attributed to either solid-state CO_2 capture (alkanolamidines) or large viscosity increases upon CO_2 capture (alkanolguanidines). The exponential increase in viscosity with CO_2 uptake made the first alkanolguanidine liquids too viscous for CO_2 to diffuse through during CO_2 sparging.[41] In most cases, the viscosity of these derivatives increased to thousands of centipoise at full saturation of CO_2, and other derivatives turned to glass or solidified, severely limiting their CO_2 uptake capacity.

Koech et al. significantly reduced the viscosity of the CO_2-rich liquids in an alkanolguanidine derivative[68] based on a guanidinium core from a conventional ionic liquid first presented by Davis et al.[49] and Dai et al.[69] This new CO_2BOL, (1-((1,3-dimethylimidazolidin-2-ylidene)amino)propan-2-ol), also known as IPADM-BOL, had viscosity nearly an order of magnitude lower than previous single-component derivatives, capping out at 3000 cP at 10 wt % CO_2 loading.[70] Koech also showed that viscosity increase as a function of CO_2 uptake by all CO_2BOL derivatives follows a nonlinear trajectory, similarly to RILs described above. It is interesting that the deviation for RILs and CO_2BOLs appears to occur at or above ~70% of the derivative's reported maximum CO_2 uptake capacity (Figure 8 and Figure 16).[68] Similarly to the RILs, this finding suggests that viscosity can be controlled, or at least kept to an workable level, by limiting the CO_2 loading on the CO_2BOL derivatives.

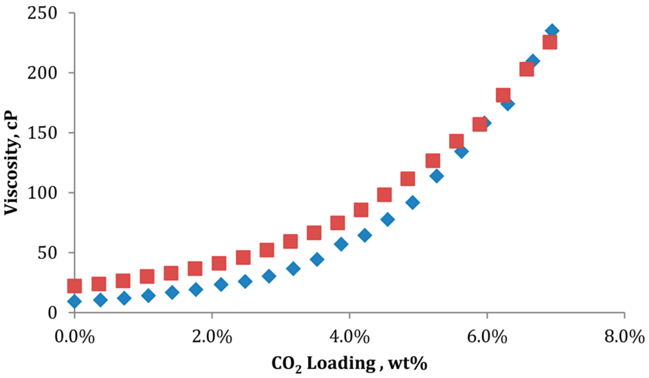

Figure 16. Nonlinear viscosity increase with CO_2 loading at 40 °C for anhydrous IPADM-BOL (blue ◆) and with 5 wt % (red ■).[68]

Lee et al. demonstrated that poor mass transfer of CO_2 by the solid HAMs could be mitigated through increasing the surface area by impregnating five mesoporous silicas with two HAMs derivatives.[71] The HAM-impregnated silica (while not a liquid) was akin to a filter for CO_2 separations, offering the ability to control the release of CO_2 by varying the temperature between room temperature and 60 °C under a flow of N_2 gas. Reduced activity was observed after five cycles of CO_2 uptake and release, indicating some deactivation of the material over time. Carrera et al. recently reported dual-component switchable ionic liquids featuring abundant biodegradable saccharides such as D-mannose, D-glucose, *β*-cyclodextrin, and mannitol in combination with superbases like TMG and DBU.[72,73] These solvent systems bind CO_2 by forming alkylcarbonates, just like CO_2BOLs. High CO_2 uptake capacity was observed; for example, a formulation of D-mannose:DBU in a ratio of (1:0.62) bound 13.9 wt % CO_2, indicating that 3.3 of the 5 alcohol groups in the sugar were converted to carbonates. The solvent viscosity increases with uptake capacity, and in some cases, solids are formed. In order to manage the viscosity further, the authors added more superbase.

2.3.7. N-Heterocyclic Azoles. Imidazoles are a class of heterocyclic compounds ubiquitous in many important biological compounds and possess a basic nitrogen center, which acts as a Brønsted base. Several imidazole compounds have been used as precursors for the synthesis of imidazolium-based ionic liquids used in postcombustion CO_2 capture. The potential use of imidazoles as CO_2 capture reagents was explored by Bara and co-workers;[74] they performed a comprehensive study of alkyl imidazoles as CO_2 capture solvents. The imidazole-derived ionic liquids were found to be more viscous than their alkyl-imidazole counterparts by an order of magnitude, and the transformation of imidazoles to the ionic liquid did not enhance the solubility of CO_2. As discussed earlier, viscosity translates directly to operational costs, so lower viscosity of imidazoles would be desirable. To this end, Bara and co-workers studied a mixture of 1-butylimidazole and MEA, which showed a CO_2 capture capacity that exceeded the stoichiometric limitation of 2:1 MEA. The reaction mechanisms shown in Figure 17 were proposed to account for this unusual result for the combined solvent system.

In order improve the CO_2 uptake capacity of imidazole-based solvents, Bara et al. evaluated the effect of side chains in 1-*n*-alkylimidazoles.[75] This study showed that different derivatives of 1-*n*-alkylimidazoles and 1-methylimidazole gave the highest CO_2 selectivity and solubility. To further refine their strategy to identify potential CO_2 capture solvent systems, Bara's group used COSMOtherm software to estimate the thermophysical properties of a series of 1-alkylimidazoles.[76] Their findings showed that COSMOtherm can be a reliable screening tool to identify efficient solvent systems for CO_2 capture. Recently, Venkatra-

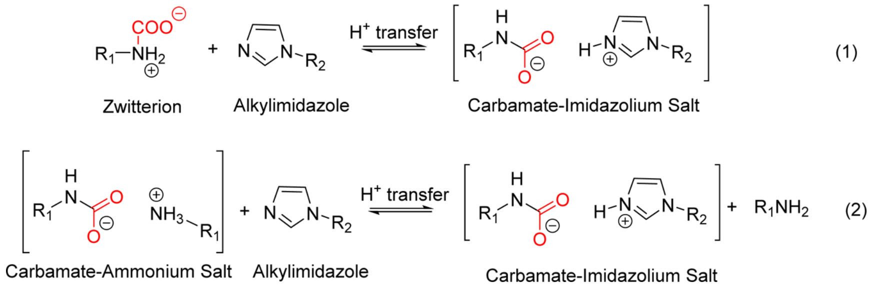

Figure 17. Potential mechanistic routes for CO_2 capture in a system of alkyl imidazoles and amine via carbamate-imidazolium salt.[74]

man et al. developed an evolutionary de novo design of novel imidazole-based compounds for CO_2 capture.[77] Using a quantitative structure property relationship (QSPR) model of molecular structure descriptors, they are able to calculate semiempirical pK_a's of imidazole compounds relative to experimental values. The QSPR model also took into consideration other important material properties such as density, viscosity, vapor pressure, and biodegradability, thus making sure that the high-pK_a structures identified have acceptable values for these properties. Bara and co-workers have extended the scope of CO_2 capture solvents to benzimidazoles and synthesized a series of 1-*n*-alkylimidazoles with variable chain lengths.[78] Alkylbenzimidazoles had a viscosity higher than alkylimidazoles and had 10−30% lower CO_2 capture capacity. The increase in viscosities of the alkylbenzimidazoles was attributed to the presence of a fused ring system in the molecular structure, which can facilitate $\pi-\pi$ stacking. Garist et al. discovered that addition of an ether for every third methylene group in the side chains of imidazoles (1-butylimdazole and 1-(2-methoxyethyl)-imidazole) reduced the vapor pressure by 50−75%.[79] The presence of this ether motif was also shown to improve CO_2 selectivity.

N-heterocyclic carbenes (NHCs) are another class of azole compounds that have been reported to capture stoichiometric amounts of CO_2 reversibly in solution to form CO_2 coordination complexes, for example, imidazolium carboxylates. Kuhn et al. reported the synthesis of the first NHC-carboxylate by the reaction of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene with CO_2. In this transformation, carbene attacks the electrophilic carbon of CO_2 to form zwitterionic carboxylate.[80] Rogers and co-workers reported an efficient synthesis of the NHC−CO_2 complex (1,3-dimethylimidazolium-2-carboxylate) by the reaction of imidazole with dimethylcarbonate (DMC).[81] The imidazole ring is *N*-alkylated by DMC, and then proton abstraction by the methyl carbonate anion generates a carbene intermediate, which subsequently attacks CO_2 to generate the zwitterionic species (Figure 18).

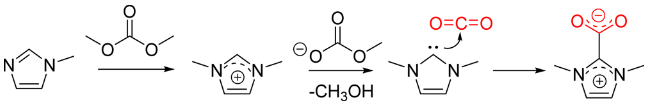

Figure 18. Mechanistic proposal for the reaction of imidazole with DMC via carbene intermediate.[81]

Louie et al. evaluated the stability of a series of imidazolium carboxylates using crossover experiments and thermogravimetric analysis in order to design efficient materials for CO_2 capture.[82] It was observed from this study that the formation of imidazolium carboxylates is reversible and the adduct stability followed the order *i*-PrImCO_2 > IMesCO_2 > IPrCO_2. Subsequent to this work, Louie's group performed a detailed study examining factors affecting the decarboxylation of imidazolium carboxylates.[82] This study showed that the rate of decarboxylation increases as the steric hindrance of *N*-alkyl substituent increases, a clear indication that the steric environment affects the decarboxylation rate. Moreover, they found that an increase in the basicity of an imidazolium ring leads to stabilization of the imidazolium carboxylate complex, which substantiates the concept that the presence of extra electron density in the ring makes it less susceptible to decarboxylation. Ganguly et al. have performed a comprehensive computational analysis to predict an efficient CO_2 capture solvent system comprising carbenes (cyclic or acyclic) and alkylcarbonic acids.[83] In accordance with their study, steric and electronic factors affect the mode of CO_2 capture in carbenes (i.e., either direct CO_2 zwitterionic adduct formation or propylcarbonate salt formation). Inspired by the detection of NHC frameworks as solid-state CO_2 capture agents,[84] Ashfeld's group explored the scope of anionic N-heterocyclic dicarbene systems in CO_2 capture.[85] Site-specific CO_2 binding was observed where the C4 carbene underwent carboxylation and the C2 carbene center behaved as a spectator; this presented an alternative front for investigating efficient CO_2 capture materials. A large variety of imidazoles and NHC variants explored by several research groups as an alternative class of CO_2 capture solvents have been presented here. However, efforts to find an optimum carbon capture and sequestration reagent are a work in progress, which is unsurprising due to the early stage of development of this class of CO_2 capture solvents.

Brennecke and co-workers developed another class of N-heterocyclic azole solvents comprising aprotic heterocyclic anion (AHA) ILs aimed at eliminating the hydrogen-bonding network in order to lower viscosity.[86−88] AHA ILs are ionic liquids consisting of an alkyl-phosphonium cation and an AHA such as indazolide, imidazolide, pyrrolide, pyrazolide, or triazolide.[86−88] These anions react with a stoichiometric amount of CO_2 to form carbamate ILs. This class of materials has no hydrogen-bonding ability, which eliminates hydrogen-bonding networks typical of regular ILs; thus, the solvents exhibit no viscosity increase with CO_2 loading. A recent study conducted on several AHA ILs with varying substituents on the pyrrolide anion showed that these ILs could be functionalized to tune the binding energy of CO_2.[88] One initial limitation of the AHA solvent class is the propensity of the negatively charged anion to be a strong Brønsted base and react with water and CO_2 to form solid bicarbonate rather than the desired AHA carboxylate. Brennecke recently demonstrated increased water tolerance of AHA ILs with the [P2222][BnIm] formulation (in the absence of CO_2) compared to other AHA anions,[88] illustrating the potential for viable operation of these materials in hydrated flue gas streams (Figure 19). However, the cost of the solvents and low enthalpy of binding may limit their practical application in CO_2 capture processes.

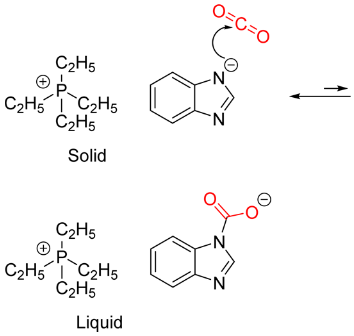

Figure 19. Reaction of [P2222][BnIm] with CO_2.[89]

2.3.8. Hybrid Systems.

With volatility of liquids being a critical parameter of solvent viability, some research strategies have been devised that immobilize the solvent to reduce volatility. One such strategy led to the development of liquidlike nanoparticle organic hybrid materials (NOHMs), a novel CO_2 solvent class with appealing chemical and physical properties. Specifically, they have enhanced thermal stability, negligible volatility, and easy tunability, making NOHMs attractive candidates for CO_2 capture applications.

NOHMs were first developed by Park and co-workers in 2011. They synthesized liquid NOHMs using silica nanoparticles from commercially available starting materials as cores (Figure 20).[90]

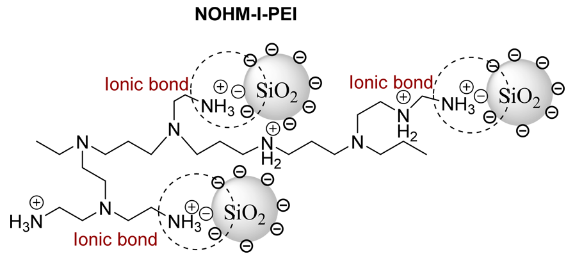

Figure 20. Structure of NOHM-I-PEI (no linker, canopy consists of polyethylenimine).[90]

The NOHMs contained surface-modified nanoparticles attached to an oligomeric or polymeric canopy via ionic or covalent bonds. NOHMs have high selectivity toward CO_2 over O_2, N_2, and N_2O, and promising recyclability was demonstrated in CO_2 over multiple cycles. In order to explore the scope of NOHMs in CO_2 capture application, Park et al. used attenuated total reflectance Fourier transform infrared spectroscopy to investigate the swelling behaviors and CO_2 capture capacities of NOHMs, for example, NOHM-I-PE2070 at variable temperatures and pressures.[91] The polymeric canopy material of NOHM-I-PE2070 without CO_2 reactive groups (such as amines) showed less swelling and enhanced (or comparable) CO_2 uptake capacity compared to Jeffamine M-2070 (polyetheramine polymer). Their study on the effect of canopy conformation and of grafting density on the CO_2 capture ability of NOHMs demonstrated the role of entropic effects on CO_2 sorption behavior.[92] To mitigate the high viscosity inherent to NOHMs, Park and co-workers directed their attention to reducing the bulk of inert material (i.e., the inorganic core in NOHMs). By doing so, they discovered liquidlike NOHMs based on polyhedral oligomeric silsesquioxane, also known as the smallest silica nanoparticle.[93] These hybrid nanomaterials had improved thermal stability compared to the parent polymer, and the viscosity was similar to those reported in the literature for ILs. Bai et al. have expanded on this work by designing and synthesizing a series of liquidlike polyhedral oligomeric silsesquioxane derivatives (liquid-Ds), in order to study the effect of structural modifications on CO_2 capture capacity of these materials.[94] This study found that CO_2 capacity of liquid-Ds is affected by their structure including bonding type, flowability, molecular weight, and amine functionality. Higher N−H content increased chemical absorption, while smaller molecular size promoted physical adsorption. Qu et al. recently evaluated the structure and rheological properties of NOHMs and developed novel NOHMs with surfaces of multiwalled nanotube cores functionalized with Jeffamine M-2070 or M-1000.[95] These materials exhibited excellent CO_2 capture capacity and low regeneration energy, adding a new tool to the classical inventory of CO_2 capture technology.

Feldmann's group have identified an inorganic−organic hybrid nanomaterial with high CO_2 uptake capacity.[96] They synthesized magnesium aminoethyl phosphonate [Mg(AEP)-(H_2O)] nanomaterial with lower specific weight, greater surface area, molar quantities of base (amino group), and less-toxic components. This new material exhibited a great potential to replace alkylamine absorbents, as it showed enhanced CO_2:N_2 selectivity (at ≥20 bar) and high CO_2 uptake capacity (152 mg/g at 110 bar). More recently, Zurmühl et al. prepared hollow ZrO_2 nanospheres via gelatin-stabilized microemulsions.[97] The ZrO_2 nanospheres were shown to reversibly capture CO_2 with uptake capacity of CO_2 of 96 mg/g at 80 bar, with low N_2 uptake (17 mg/g at 80 bar), making these hollow nanospheres also potential candidates for CO_2−N_2 separation. Certainly, hybrid systems have exhibited the desirable properties of a CO_2 sorption process, but further modification of the current formulations is required to design an efficient and robust system for their industrial application.

3. UNIQUE PROPERTIES THAT CAN BE EXPLOITED FOR EFFICIENCY GAINS

Water-based solvents have similar thermodynamic and physical properties because the properties are dominated by those of water as the carrier fluid. Water-lean solvents, however, entail distinctive physical and thermodynamic properties because each solvent is unique and not dominated by water as a cosolvent. As consequence, physical properties, such as physical state (e.g., solid, liquid), contact angle, wettability, viscosity, and volatility, and thermodynamic properties, such as thermal conductance and solvation free energy, differ substantially from water-based and other water-lean solvents. In some cases, these properties can be detrimental to CO_2 capture performance (e.g., higher viscosity and lower thermal conductance). Conversely, these properties can be exploited to improve process performance (e.g., lower specific heat and higher physical solubility of CO_2). We focus here on identifying how the unique properties of water-lean solvents could be exploited to promote efficiency gains in full-scale CO_2 capture processes. We limit the discussion in this section to water-lean solvents that have been validated at a scale large enough to make full-scale process projections.

3.1. Faster-Than-Expected CO_2 Mass Transfer

Water-lean solvents were initially believed to have poor mass transfer and require large and costly absorbers due to their high viscosities. This concept stems from the fact that the flow of CO_2 in coal-fired power plant exhaust is held constant, and the rate of mass transfer of CO_2 dictates the size of infrastructure, which ultimately dictates the cost. Skeptics often point to the high viscosities of water-lean solvents as a barrier to an energetic or economical process, though new research is showing that this may not be the case.

Mathias et al. were the first to show that water-lean solvents demonstrate unexpected kinetic behavior. Two kinetic anomalies were observed when CO_2BOL solvents were tested on a wetted-wall apparatus.[70] First-generation (DBU and 1-hexanol at 35, 45, and 55 °C) and second-generation (IPADM-2-BOL) CO_2BOL solvents (40, 60, 80, and 100 °C) were tested at varied CO_2 loadings.[70] In this study, the measured liquid film mass transfer coefficients for both solvents (k'_g) were found to be comparable to those of water-based MEA and PZ solvents, when plotted against a comparable driving force (Figure 21).[70] This finding was unexpected because aqueous solvents are an order of magnitude less viscous than the CO_2BOLs. The higher-than-expected mass transfer is a welcome finding, indicating that water-lean solvents may not require absorbers that are significantly larger (and costlier) than those for water-based solvents.

Mathias discovered a second kinetic anomaly in the study: k'_g was found to have an inverse temperature dependence (Figure 22). This unexpected behavior was linked to the higher physical solubility of CO_2 in organic liquids than its solubility in water.[70]

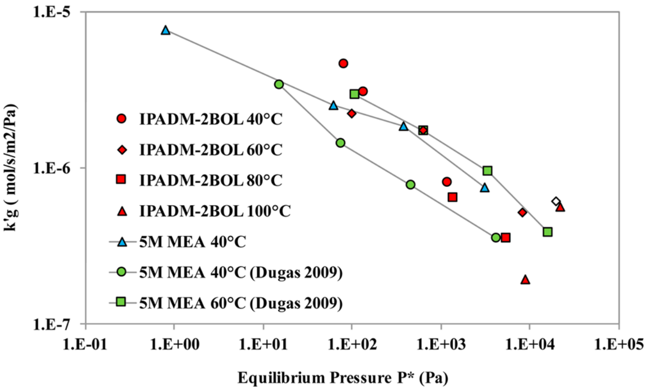

Figure 21. Comparison of k'_g values of IPADM-2-BOL and aqueous 5 M MEA.[70]

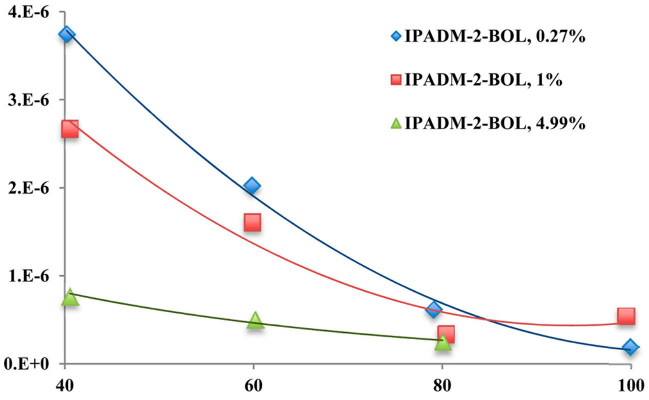

Figure 22. Comparison of k'_g values of IPADM-2-BOL at three CO_2 loadings as a function of temperature.[70]

This finding indicates that while water-lean solvents are designed to operate on chemical fixation of CO_2, they are operating (at least initially) like physical solvents, where a high CO_2 concentration can be achieved to drive the liquid-stage kinetics of CO_2 binding.[98−100] Whyatt et al. confirmed the higher CO_2 solubility in water-lean solvents by measuring the k'_g values for N_2O in a first-generation (DBU, 1-hexanol) CO_2BOL solvent.[101] The k'_g values were found to be higher than that of 5 M aqueous MEA under comparable conditions, matching the measured Henry's coefficients for N_2O in organic liquids.[101] Unsurprisingly, these behaviors have not been observed in water-based solvents due to the negligible solubility of CO_2 in water. It should be noted that although two CO_2BOL solvents have been tested using a wetted-wall apparatus, other water-lean solvents are expected to exhibit similar behavior.

This unique mass-transfer behavior of water-lean solvents can be exploited to improve both the economics and efficiency of CO_2 capture processes. An inverse temperature dependence and higher-than-expected mass transfer could enable new configurations of water-lean solvents that water-based solvents could not utilize. One can envision chemically based solvents being configured to run like physical solvents, where incoming flue gas and solvent would be cooled well below 40 °C to promote a high degree of physical dissolution of CO_2, which would then drive the liquid-stage kinetics. At lower temperatures, a higher rate of CO_2 flux would allow use of smaller absorber units, which would require less capital investment. Further, cooling the flue gas below 40 °C would promote condensation of more water from the gas stream, reducing the amount of water accumulation during operation, and thus the reboiler duty.[13,102] It should be noted that the smaller absorber and reboiler duty would be at the expense of either increased consumption of cooling water or use of a small refrigeration unit. Heldebrant and team have shown that small refrigeration units are not cost prohibitive and that the energetics of such a process can be favorable when establishing a water balance.[13,102] The unique kinetic behavior of water-lean solvents opens new doors for process configurations that are more economical and more energy efficient, though we caution that these observations have currently been limited to the CO_2BOL solvent class. Other water-lean solvents are expected to behave similarly, though more data is required before such kinetic behavior would be considered constant across all water-lean solvent platforms.

3.2. Phase Changes

Most CO_2 capture materials are designed to retain the same physical state before and after reaction with CO_2. However, liquid amines almost always form solid carbamate or bicarbonate salts, and in some cases, gases or solids become liquids after exposure to CO_2. In this review, we have focused on water-lean solvents, highlighting the fact that cosolvents are often considered a necessity for a workable solvent-based process. One might consider a phase change problematic, though in some cases, physical property changes can be utilized to reduce the energy penalty of sorbent regeneration. Recently, many groups have developed CO_2-capture systems that take advantage of phase transformations to concentrate the CO_2-rich material in the form of either a solid or a separate liquid phase. The objective of such systems is to achieve energy efficiency by thermally regenerating only CO_2-rich material instead of the entire material

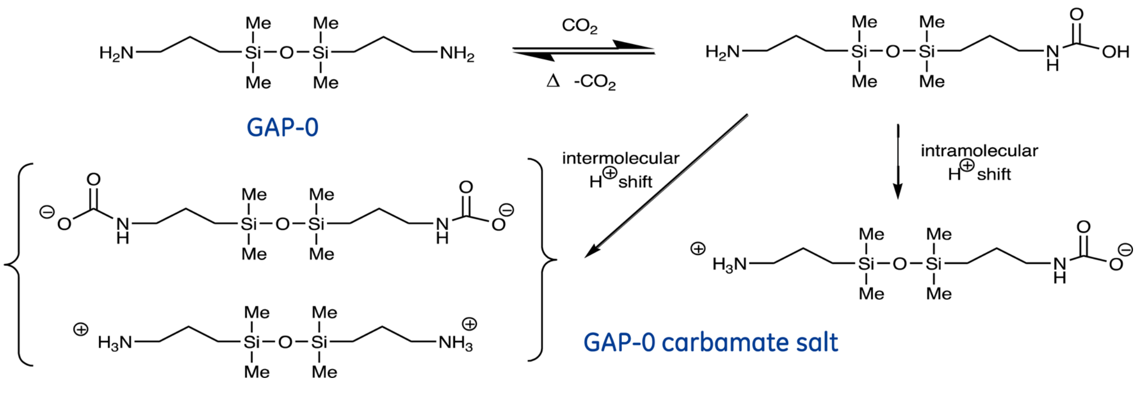

Figure 23. GAP-0 solvent system. Reproduced from ref 36. Copyright 2012 American Chemical Society.

inventory. Solvents that are designed around this principle are driven by potential energy savings with respect to thermal regeneration: the less material there is to heat, the less energy is required to strip it of CO_2. Consider that reducing the amount of material sent to a reboiler by half could potentially halve the reboiler duty, but also pumping costs as well. This subsection describes examples of novel phase-change materials that have been developed for CO_2 capture.

3.2.1. Liquid−Solid Phase Transitions. Perry et al. were the first to develop such a system, using nonvolatile liquid amines that form solid carbamate salts after CO_2 uptake.[34,36,103] Perry et al. used spray nozzles to spray a fine mist of a liquid aminosilicone that reacted with CO_2 to form carbamate salt powder.[36] Their solvent includes 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, called GAP-0 (Figure 23); it has a CO_2 capacity of up to 18 wt % (95% of theoretical value) and a heat of reaction of ∼2500−2600 kJ/kg of CO_2 reacted. This is 30% higher than that of MEA in water (∼1900 kJ/kg CO_2).[36] The GAP-0 solvent reacts with CO_2 at 45 °C, forming a solid carbamate that can be regenerated at temperatures as high as 160 °C. This high enthalpy of reaction with CO_2 can be exploited to create substantial partial pressures of CO_2 during thermal regeneration, achieving pressures up to 9 bar at 160 °C, but regeneration is projected to occur at 6 bar (Figure 24). These regeneration pressures are far higher than those used with water-based formulations and other organic systems, which are typically done at 1.2 bar. The high pressures of CO_2 generated in the stripper have potential to reduce the mechanical compression required to pressurize CO_2 (to over 2000 psi) for sequestration, which increases efficiency.[36]

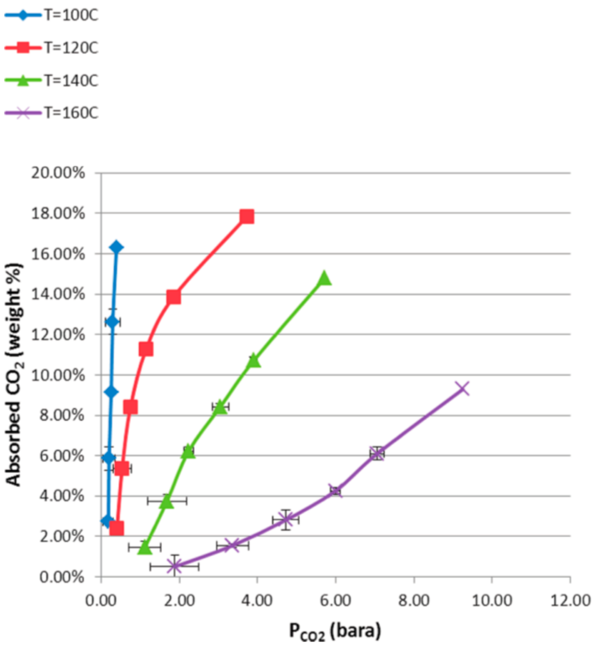

Figure 24. Isotherms of GAP-0 carbamates. Reproduced with permission from ref 36. Copyright 2012 American Chemical Society.

Phase-changing GAP-0 solvent was shown to be energetically feasible but very sensitive to moisture, which made the solid carbamate a sticky semisolid. Perry and team addressed this problem by developing less moisture-sensitive variants for the phase-change process.[104] Aminosilicones bis(aminopropyl) tetramethyldisiloxanes (GPO) and derivatives cyclocarbosiloxanes and dialkyldiamines were synthesized and tested by Perry and team (Figure 25) The aminosilicone 2,2-dihexylpropane-1,3-diamine tested with wet CO_2 resulted in a weight gain of 22.8%, equivalent to 125% of theoretical capacity. There was no evidence of bicarbonate formation or other CO_2 binding modes, indicating that the carbamate was intact and water had been absorbed into the powder. This result demonstrated water tolerance for the second-generation aminosilicones. All new formulations were found to be less thermally stable in air at 150 °C than GAP-0. The lower thermal stability suggests a trade-off between water tolerance and durability; stabilizers would be required to increase solvent lifetime.[104]

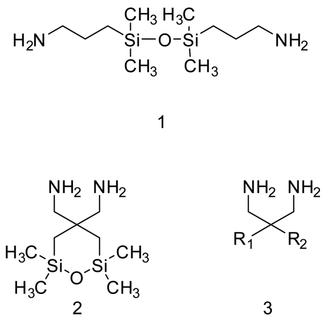

Figure 25. Three classes of less moisture-sensitive materials used for phase-change chemistry.[104]

The GAP-0 phase-change process consists of a rotating spray nozzle that atomizes a liquid aminosilicone into microdroplets, which reacts with the CO_2 in flue gas to form the GAP-0 carbamate solid (Figure 26).[104] This carbamate powder is accumulated at the bottom of the absorber by vortexing; a mechanical device is used to move this solid to the stripper, where CO_2 is thermally released under pressures >1.2 atm. The CO_2-lean aminosilicone liquid is pumped back to the spray nozzle, and the process is repeated. Here, there is no cosolvent, and the phase change from liquid to solid enables only CO_2-rich

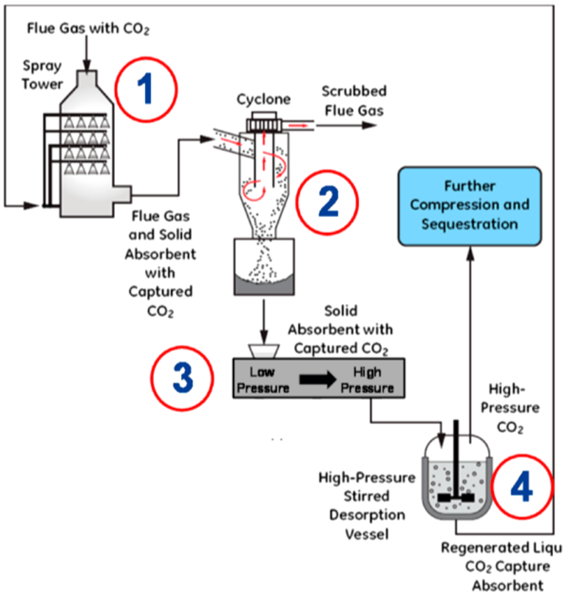

Figure 26. General process configuration of liquid−solid phase-change process. Reproduced from ref 104. Copyright 2013 American Chemical Society.

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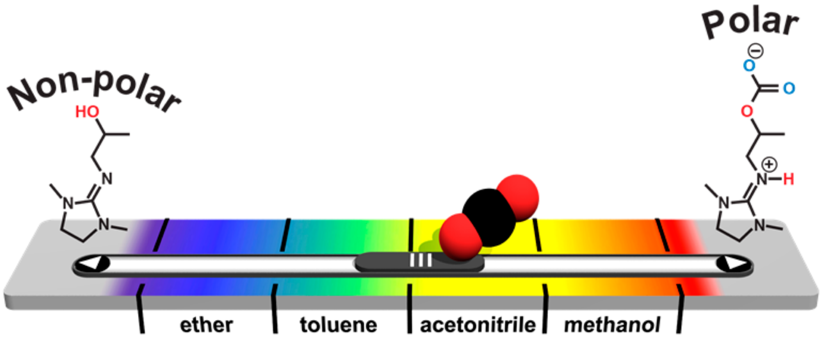

Figure 27. Conceptual polarity “switch” of IPADM-2-BOL with CO_2 loading (polarity scale of Nile-red indicator dye).[13]

material to be sent to the stripper, thereby promoting significant energy savings.

GE projects that applying the phase-change process of Perry et al. to CO_2 capture from a power plant could result in a reduction to 16%[36] of the energy penalty attributed to removal of 90% of the CO_2, which is nearly half that of the 30% energy penalty for the National Energy Technology Laboratory (NETL) case 10 amine baseline.[2] Like a majority of the water-lean systems, the phase-change process benefits result from reduced energy penalties associated with water vaporization, higher stripper pressure that reduces the sensible heat and the compression energy of the solvent, and regeneration of a concentrated CO_2 carrier. It should be noted that the numbers reported by GE are near the minimum work identified by Rochelle (109 kWh/tonne CO_2)[105] removed and are likely the result of a first-of-a-kind assessment made on optimiztic assumptions of performance. Still, GE’s phase-change process using the GAP-0 solvent shows promise for CO_2 capture as one of the more mature water-lean phase-change systems, though it is likely that the level of estimated performance in real-world application may be less than that predicted.

A new, but less-mature phase-change solvent system comprising 1,2-ethanediamine (EDA) with PEG cosolvent that binds CO_2 to form solid products known as CO_2 storage material (CO_2SM) was recently reported by Zhao and co-workers.[106] The EDA-PEG solvent system captured almost 1 mol equiv of CO_2; the resulting solid CO_2SM can be regenerated at 105 °C and has been shown to be stable over multiple cycles. Due to the excellent water stability of CO_2SM, it has been shown to have potential use as fast-acting fertilizer for enhanced plant growth.[106]

Phase-change solvents we have discussed so far have been focused on water-lean solvents, but it is worth noting that a water-based phase-change solvent was recently reported by Wang et al. that uses an amino acid salt solvent in water.[107] In this solvent system, a liquid containing a nontoxic, low vapor pressure, natural amino acid salt in water binds CO_2 to form a solid carbamate and bicarbonate mixture which phase separates to CO_2-lean and CO_2-rich phases. The CO_2-lean phase contains about 10% CO_2, and the CO_2-rich phase consists mainly of bicarbonate species and contains 90% CO_2. The two phases have been separated and the CO_2-rich phase regenerated at 120 °C.

3.2.2. Solid–Liquid Phase Changes. Brennecke et al. have developed a creative approach for phase-change ionic liquids (PCILs) derived from their AHAs that were described in subsection 2.3.7 (Figure 19). PCILs use a phase-change concept that is in the direction opposite to that of GE’s GAP solvents. The PCILs are designed to convert from solid to liquid during CO_2 uptake (Figure 19).[89] This system has a unique advantage, since when a liquid is converted to a solid during CO_2 absorption, the heat of fusion (ΔH_{fus}) (the energy released during freezing) is released; this heat can be used to provide a part of the heat required for the endothermic CO_2 stripping process. Brennecke reports that the heats of fusion for the four PCIL materials ranged from −3.8 to −19.9 kJ/mol, which are large fractions of the heats of reaction with CO_2 of −44 to −52 kJ/mol. The low heats of reaction may be problematic as they lie outside the preferred binding range identified by Mathias.[102,103]

From a processing perspective, there are many advantages. The phase change could absorb sufficient energy to offset the heat of reaction with CO_2, minimizing a temperature bulge during CO_2 absorption inside the absorber column. Similarly, in the reverse reaction, the endothermic melting of the solid can help offset the heat of exothermic binding with CO_2 during absorption. It is unclear, however, how a liquid-to-solid phase transition would be handled in a stripper in a working process.

The prospects of this technology are enticing, though it should be noted that these claims are based on laboratory-scale results and have yet to be tested at a meaningful scale or in continuous operation.[89]

3.2.3. Gas–Liquid Phase Transitions. Another type of phase-change process that could be used for CO_2 capture involves the conversion of a gas to liquid during CO_2 uptake. The “distillable ionic liquid” dimethylammonium carbamate, or DIMCARB, was the first example of a material to undergo such a process.[108−110] Gaseous dimethylamine reacts with gaseous CO_2 to form a liquid dimethylammonium dimethylcarbamate salt ($[Me_2NH_2][O_2CNMe_2]$), with CO_2 capture capacity of 33% by weight. DIMCARB is structurally similar to the switchable carbamate chemistry described in subsection 2.3.3, although DIMCARB’s CO_2-lean form is gaseous. It is unlikely that a gas-to-liquid phase transition could work in a real-world process because the high vapor pressure of dimethylamine would result in unacceptable fugitive emissions. Further, the propensity of gaseous dimethylamine and CO_2 to recombine in the top of the stripper would render this (or comparable technologies) useless for CO_2 capture applications.

3.3. Changing Free Energy of Solvation

Heldebrant and team demonstrated that efficiency could be gained by changing the free energy of solvation of the CO_2-containing ions in solution.[13] This phenomenon is unique to the switchable and reversible ionic liquids that the CO_2BOL, RIL, and NAS solvent platforms are based upon. As described earlier in section 2, switchable ionic liquids undergo a polarity change during the conversion between the CO_2-lean and CO_2-rich forms of the liquid.[41,63] This phenomenon cannot happen in other water-based or water-lean solvents that have a cosolvent (i.e., water or glycerol) used to dissolve the CO_2 carrier. Further, conventional or task-specific ionic liquids cannot undergo changes in polarity because they are always ionic whether CO_2 is chemically bound or not.

Heldebrant and team were the first to demonstrate that changes in a solvent's polarity could aid in the release of CO_2 from a water-lean capture solvent.[13] They defined this phenomenon as a polarity swing assisted regeneration (PSAR), which was first demonstrated on their H_2S-binding organic liquids (H_2SBOLs) solvent platform.[111] The PSAR was demonstrated by adding a chemically inert nonpolar "anti-solvent" to decrease the polarity of the CO_2BOL by making a CO_2BOL antisolvent mixture and thus favoring CO_2 release.[13] Heldebrant reports that PSAR occurs by changes in the Gibbs free energy of solvation of the CO_2-containing ions in the solvent.[13] Conceptually, CO_2-lean forms of the CO_2BOL favor nonpolar solvents, while CO_2-rich forms of the CO_2BOL favor a polar solvent. Introduction of an antisolvent destabilizes the CO_2-rich form of the CO_2BOL, favoring the CO_2-lean form, and in turn, shifts the equilibrium of CO_2 binding to the left in Figure 27.[13] The PSAR can be used to either release more CO_2 at a given temperature or establish a higher release pressure of CO_2 at that given temperature.[13] Heldebrant reports that the PSAR is an equilibrium-controlled process, where the presence of anti-solvent changes the equilibrium to favor a lower CO_2 loading than in the absence of antisolvent. This was demonstrated by dosing different amounts of antisolvent (0.5 to 3 mol equiv) to CO_2BOL, showing different regeneration temperatures that were reduced by as much as 73 °C.[13] The theoretical limit for PSAR is believed to be 65 °C, based on miscibility between the IPADM-2-BOL and hexadecane antisolvent used in that study, though this limit has yet to be experimentally validated. The primary advantages of PSAR are that lower regeneration temperatures may reduce thermal degradation and evaporative losses of the solvent.

Mathias concluded that there were also promising gains for efficiency when PSAR was employed, albeit at the expense of high capital costs.[102] Mathias et al. modeled the CO_2BOL/PSAR process based on continuous flow data of IPADM-2-BOL with hexadecane as an antisolvent. The primary advantage of the PSAR was the observed 73 °C drop in reboiler temperature required to regenerate the solvent, which enabled the use of intermediate pressure steam put through a let-down turbine to make power and use of the rejected heat from that turbine to regenerate the CO_2BOL solvent. Mathias showed that the use of lower pressure steam increased the efficiency of the CO_2BOL process, reducing parasitic loads to 19%, with a theoretical minimum of 17%,[102] one-third lower than the NETL Case 10 amine baseline of 30%.[2] Additionally, the PSAR process was projected to recoup 87 MW of lost power compared to the NETL Case 10 amine baseline. If a 65 °C regeneration could be realized, this could translate to a recuperation of up to 102 MW of lost power compared to the NETL Case 10 baseline.[13,102]

The PSAR process was configured (Figure 28) like the NETL Case 10 amine baseline, albeit with the addition of an antisolvent circulation loop (pumps and coalescing system), of which all are commercially available infrastructure. While attractive from an efficiency standpoint, the process is severely limited by the high intrinsic viscosity of CO_2BOL fluids, and the process is projected to be too costly for commercialization until less viscous derivatives can be made.

We conclude this section by highlighting that the unique thermodynamic and physical properties of water-lean solvents can be used to provide efficiency gains by very different means. Higher-than-expected mass transfer, inverse temperature mass transfer relationships, phase changes, and controlling solvation free energies all provide unique strategies to improve process efficiency. We note that, looking forward, few of these methodologies have been tested at a meaningful scale or continuously. In the coming years, it is believed that more rigorous testing will validate these behaviors, and other unique physical and thermodynamic properties will be discovered.

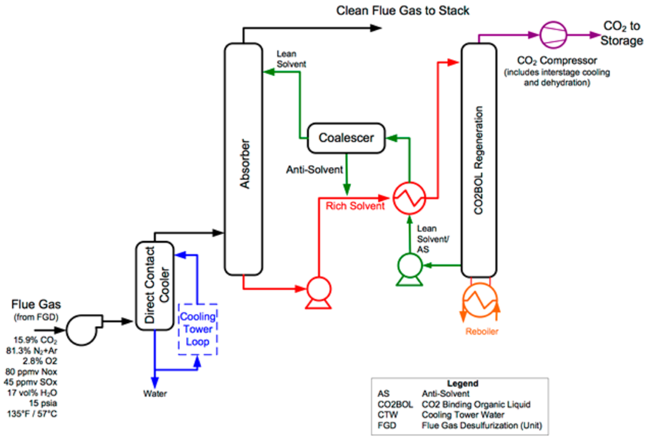

Figure 28. Conceptual CO_2BOL PSAR process flow diagram. Reproduced with permission from ref 13. Copyright 2013 Royal Society of Chemistry.

4. MOLECULAR-LEVEL INSIGHTS

Understanding solvent molecular-level interactions is critical to the development and optimization of water-lean solvents. Unlike aqueous amines or conventional ionic liquids that have been studied extensively, water-lean solvents described above have yet to be studied in such detail. As a consequence, little is known about how CO_2 diffuses in and out of these fluids, how CO_2 is binding in solution, or how the CO_2 binding results in structural changes in the fluid structure, including conversion from nonionic to ionic, and the dynamic evolution of equilibria among these species. Solvent developers are flying blind, so to speak, in that there is a substantial knowledge gap on how water-lean solvents operate or how these behaviors described in section 3 manifest. As such, research groups have begun to delve into molecular-level understandings of water-lean solvents and their behavior to provide such knowledge to the research community. This section highlights the efforts of these pioneers in solvent modeling.

4.1. Linking Structure to Function through Molecular Theory

Despite the proposed efficiency of water-lean solvents, the overall fundamental processes of CO_2 capture are not well-understood, in particular the kinetics of the CO_2 uptake process, which is greatly affected by conditions of temperature, pressure, and the composition of the liquid phase. This complexity arises from the fact that CO_2 uptake involves the CO_2 solvation into the liquid, diffusion, and chemical binding by the solvent. Similarly to other water-lean solvents,[112] in the two-component ionic liquids, CO_2 binding does not alter the charge states of the solvent, but in the case of single-component organic binding liquids, a charged zwitterionic species is initially formed upon CO_2 binding. The result is the development of a highly heterogeneous phase whose structure is poorly understood and affects solvent viscosity. These different processes also reflect different rates that also need to be understood to accelerate these technologies. Most commonly, calorimetric, heat capacity, boiling point, density, and viscosity measurements are performed, but these can hardly provide any real insights into the mechanistic details, solvent composition, or speciation. Nuclear magnetic resonance (NMR) measurements tend to provide more information on specific species present in the bulk, but they cannot give the broader picture either. There is a scarcity of experimental data on the extended liquid structure that could also help validate molecular models but also explain the unique physical and thermodynamic behavior of water-lean solvents as outlined in section 3. Modern molecular theory is poised to address the issues of complex solvent structure, heterogeneity, phase transitions, and unique transport phenomena. Nonetheless, computational studies addressing these concerns are extremely demanding in terms of methodologies and are only now beginning to respond to these challenges in a quantitative manner.[113−115]

Recent advances in computer architectures, algorithms, and computational tools have placed atomistic simulations on the same footing as other characterization techniques that can provide structural, thermodynamic, kinetic, and mass/heat transport information at the molecular or extended structure level. Often, simulation is the only way to access this type of information in a timely and cost-effective manner. A number of methods are used for modeling CO_2 capture solvent systems, depending on what type of information is needed. Density functional theory (DFT) based electronic structure methods are definitely at the top of the list because they can provide information about the reactivity and molecular structures. Because DFT allows for reliable and economic representation of these complicated systems, one can even access properties of the liquid state such as local intermolecular interactions and solution phase reactivity. The large number of available functionals and literature data also allow for the correct treatment of short/long interactions that are crucial for more accurate representation of the solvent structure. In addition, DFT methods when combined with molecular dynamics techniques[116] (AIMD) and enhanced sampling for free energy calculations (Blue Moon,[117] metadynamics[118]) are essential in following reactivity and extracting free energies and entropy contributions to the various steps of CO_2 absorption. We expect that correct representation of these quantities is critical for the understanding of the overall process, including diffusion, CO_2 release, and solvent regeneration.

Given the long length and time scales involved (nm/ns), transport properties and extended liquid structures require alternate approaches because such system sizes and scales are beyond the reach of modern AIMD. However, DFT-based calculations can be efficiently parametrized in the form of a wide variety of classical potentials that can give reliable representation of intermolecular interactions in the liquid phase. In this respect, classical molecular dynamics (CMD) and Monte Carlo (MC) approaches have provided insights into extended structures, CO_2 transport, solvent volatility, extended structure, and viscosity.[119,120] Nevertheless, classical simulations cannot describe nor follow reactivity and dynamic evolution of the reactive species, and they should be used in conjunction with other methods that will provide a measure of reactivity.

Given the deficiencies identified throughout this review, there is an import role for theory to play, not just in rationalizing observations but also in developing mitigation strategies for the most critical bottlenecks. With the ability of theory and simulation to represent these systems quantitatively across many scales, it is possible to relate a given bulk macroscopic problem directly to the underlying molecular interactions. However, simulating properties of massive libraries of compounds by brute force is undesirable and highly impractical. Instead, a quantitative structure−property relation (QSPR) approach should, in principle, allow for a more tractable screening of libraries by associating a molecular descriptor that correlates to it. Such an approach is far more strategic and imparts insights that contribute to a more fundamental knowledge pertinent to these technologies. These molecular descriptors are identified through simulation and can be used to pick targets with improved properties either for more aggressive simulation or for synthesis and testing. In this respect, theory is used as a tool for prediction or characterization.

In this context, we outline the progress of simulation in three main areas: molecular structure and reactivity, extended solution structure and transport, and molecular development. We present a brief summary of the growing literature on water-lean solvents and illustrate the critical issues with recent findings on single-component solvents. Each section concludes with an outlook that highlights important issues.

4.1.1. Molecular Structure and Reactivity. The CO_2 capture/release process in nonaqueous solvents is a chemical conversion that involves minimally two distinct steps, as is schematically outlined in Figure 29.

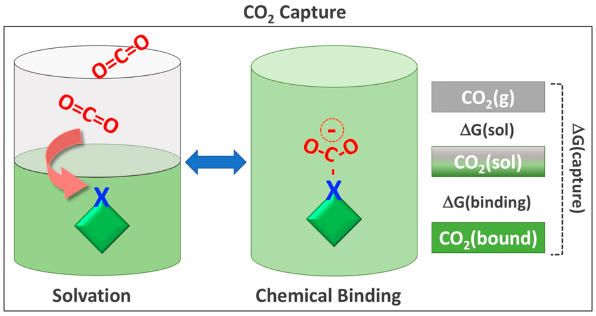

Figure 29. Schematic representation of the overall CO_2 capture process.

The process starts with CO_2 solubilization into the organic liquid and follows with chemical binding of CO_2 on the solvent. In water-lean solvents, reactivity of CO_2 in the liquid leads to the formation of alkylcarbonates, carbamates, or azoline carboxylates, and other acid/base reactions like proton transfer or dehydration. The capture free energy for this process includes both these quantities:

$$\Delta G(\text{capture}) = \Delta G(\text{solvation}) + \Delta G(\text{binding}) \tag{1}$$

In these systems, the binding itself needs to be low enough to push equilibrium toward capture at low T (ΔG(binding) ∼ 10−20 kJ/mol at $T \sim 40$ °C) and release also at relatively low temperature ($T < 100$ °C). Hence, prediction needs to account not only for the enthalpic changes that are easily obtainable with DFT to within a few kJ/mol, but also for the entropic ones, that, as explained below, are more difficult to obtain.[70]

Predicting the free energetics of these processes has been a challenge for theory, because the solute is surrounded by, and interacting with, many neighboring molecules with no particular structure. The solvated CO_2 is in equilibrium with CO_2 in the gas phase and the chemically bound CO_2, resulting in complex multicomponent media. These processes give rise to nonideal behavior of a statistical nature that the simple liquid phase

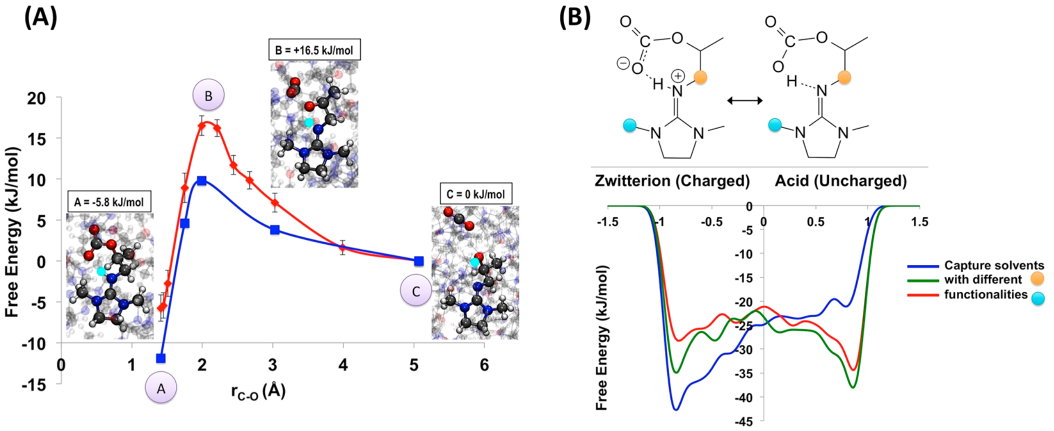

Figure 30. CO_2 chemical binding in prototypical CO_2BOL solvents (A). Deliberate molecular modifications of solvent molecules can be used to shift the chemical (acid/base) equilibrium of the solvent species (B). The cyan group is CH_3 for the blue and green lines, and CF_3 for the red, while the orange group represents CH_2 in the blue and red lines, and O in the green.

models fail to capture.[121] For instance, physical solvation of CO_2 has been examined in the context of continuum models,[122] where CO_2 is embedded in a polarizable continuum and a solvation free energy can be extracted.[123,124] Although continuum solvation models, like COSMOtherm,[125,126] can be very useful for predicting properties of solvents and mixtures and have been used to predict properties of ionic liquids,[76,127,128] these models are best-suited for homogeneous liquids of constant composition and low ionic strength. Using continuum models to predict properties in CO_2BOLs, and other water-lean solvents whose dielectric and ionic strength change with loading, should be done with care and in conjunction with the chemical equilibria. A more rigorous approach is to employ grand canonical ensemble/MC methods[129] where one directly computes solvation free energy by balancing the chemical potential between a gas phase CO_2 box and a solvent phase box via insertion moves. Nonetheless, this approach is appropriate as long as CO_2 does not react with the solvent molecules. Hence, our ability to quantitatively predict ΔG(solvation) remains a challenge except for solvents that only physically adsorb CO_2. Here we note that recent progress in reactive MC simulations, collectively referred to as RxMC,[130−138] show much promise at a lower cost compared to AIMD. However, these methods are also subject to the availability of interatomic potentials.

DFT methods can typically estimate reaction energies such as CO_2 binding to an alcohol or amine to form alkylcarbonates or carbamates and other acid/base side reactions within a few kJ/mol.[121] Combined with continuum models, we can extract reasonable relative energetics because the systematic errors between products and reactants often cancel, as long as no charged species form.[139] On the other hand, transition states are problematic, particularly when the reaction involves two species coming together and merging their solvation spheres. Ab initio molecular dynamics methods have been very useful in modeling CO_2 sorption and acid/base chemistry in both amine[121] and guanidium[124] based solvents. However, the limited statistics and small simulation boxes make estimates of free energies and transition states of reactions a forefront challenge we are just beginning to address. With amines being the prototypical industrial solvent for CO_2 capture, and alcohol-based solvents represented by CO_2BOLs (see section 2), theoretical estimates show that at least three types of species can be found in equilibrium: (i) solvated CO_2 and unreacted solvent molecules; (ii) alkyl carbamates/carbonates ($RNCO_2^-$/$ROCO_2^-$) with protonated amines as counterions;[140,141] and (iii) carbamic[43,142]/carbonic acids.

The points listed above can be best illustrated by the recent work of Cantu et al.,[124] on the tuning of chemical equilibria in CO_2BOLs, by deliberate modification of the molecular structure, as summarized in Figure 30.

This work examines the CO_2 chemical binding by means of Blue Moon ensemble AIMD simulation, resulting in rigorous estimates of the enthalpy and free energy of CO_2 binding in single-component CO_2BOLs (Figure 30A). In addition, the acid/base equilibrium for proton transfer is discussed on the basis of metadynamics simulations (Figure 30B) that show how this equilibrium can be shifted through molecular structure modifications. This realization led to the novel idea of neutral capture via formation of alkylcarbonic acid or carbamic acid, as opposed to their charged alkylcarbonate or carbamate counterparts. The overall effect of such a modification gives rise to multiple coupled equilibria consisting of solvated CO_2, unreacted solvent, CO_2-bound zwitterionic species, and CO_2-bound neutral species.

As will be discussed in the next subsection, the population of charged and neutral species affects the structure and transport properties of the CO_2-loaded liquid. Hence calculating equilibria (and transition states) in the liquid is mandatory for understanding uptake and speciation under operating conditions. To do so quantitatively is a great challenge due to the variation of species formed in a dynamic fashion as more CO_2 is adsorbed into the liquid. Formation of charged species changes the solvent polarity, and we minimally need to understand how the equilibria change as a function of solvent dielectric, entropic factors, and transition. Such insights can be used to further improve or completely remove bottlenecks associated with deployment of these technologies, for example, viscosity reduction, lower regeneration temperatures, low-cost scale-up, chemical degradation, solvent volatility, and durability, to name a few. In the following section, we will discuss how theory is used to mitigate the viscosity problems in some water-lean solvents.

4.1.2. Extended Liquid Structure and Transport.

Despite years of solvent synthesis and testing, until recently very little has been known regarding extended solvent structure and how this affects viscosity, CO_2 diffusion, and other bulk properties.[124,143−148] In this section, we outline recent progress toward predicting speciation and structure and connect them to observed macroscopic phenomena described in section 3.

Molecular interactions, liquid structure, and mass and heat transport can be explored by means of larger scale CMD simulations. These methods have been successfully used to analyze and describe the structure and transport properties of task-specific ionic liquids,[143−146,148,149] single-component solvents such as CO_2BOLs,[124,147] as well as monoethanolamine.[139] As discussed above, a proper solvent model system contains many species: CO_2, solvent, carbonate/carbamate-bound CO_2, and potentially their acid forms, in addition to additives like tetraethlyene glycol or water. All these species can influence both the extended structure and the transport properties, which makes quantitative modeling of these systems challenging. Current MD work reveals that the actual extended structure of the liquid is far from ideal or uniform, as illustrated in Figure 31.

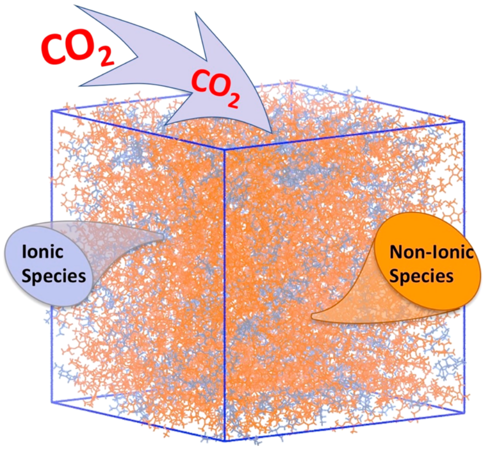

Figure 31. Molecular dynamics simulations reveal complex and nonuniform liquid structure, as a result of the variety of species present.

This arises because chemical speciation is strongly affected by CO_2 loading, particularly for switchable ionic solvents, such as CO_2BOLs (see section 2), RILs,[150] or the aminosilicone complexes of GE,[34] because they contain both ionic species and neutral organic species. Moreover, the populations and aggregation of these species change as CO_2 is adsorbed/desorbed. When establishing trends in transport as a function of CO_2 exposure, one needs to account for speciation as well. This situation arises from the tendency of ionic species to cluster, forming domains where ionic species are in high concentration and domains where they are absent. The size and shape of these domains fluctuate in time and change as a function of CO_2 loading, chemical equilibria, or addition of other species such as water. It is likely these disparate domains (CO_2-lean vs CO_2-rich) within the fluid account for the higher-than-expected mass transfer of CO_2 described in section 3. It is possible that the less-polar CO_2-lean regions in the fluid would provide favorable dissolution of CO_2 in the fluid, establishing diffusion pathways for CO_2 to freely move in and out.

Transport properties such as viscosity, thermal conductivity, heat capacity, and diffusion of CO_2 are all relevant to solvent design and need to be considered to achieve the implementation of water-lean solvent systems. These properties can be directly modeled through molecular dynamics simulations.[151,152] Most challenging of these are viscosity and thermal conductivity, which can be most accurately estimated via a Green−Kubo formalism,[151,153] which requires long trajectories to obtain reasonable estimates, or via a linear response approach, which can provide faster estimates but suffers from difficulty when the requisite relaxation times of the liquid phase are slow compared to the MD time scale. Despite these challenges, transport has been successfully modeled for solvent systems of both task-specific ionic liquids and single-component CO_2BOLs.

To illustrate these points, we consider the shear viscosity of the IPADM-2-BOL system.[124] Figure 32 shows a very good agreement of the computed viscosity with experimental data[70] as a function of CO_2 loading.

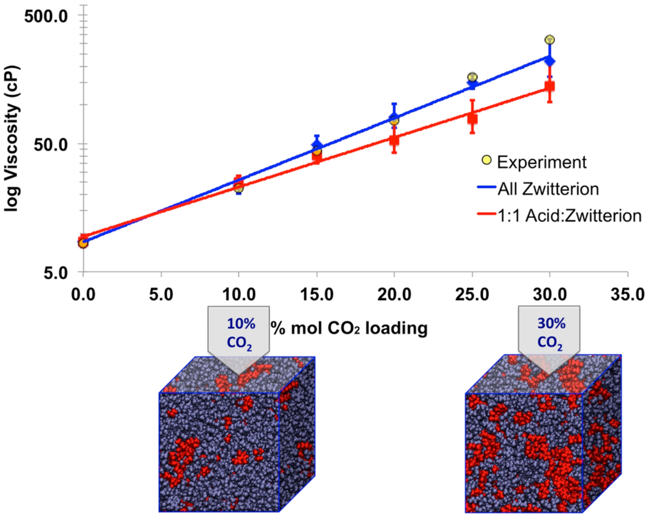

Figure 32. Validation and verification of the computational protocol for the estimation of the viscosity from classical molecular dynamics simulations (blue line) compared to experimentally measured viscosities (yellow points). The red line shows the viscosity reduction with tuning of the chemical equilibrium. The two snapshots at the bottom show the increasing inhomogeneity with CO_2 loading (red aggregates).

The choice of compound is relatively simple because the chemical equilibrium results in almost 100% of the adsorbed CO_2 existing as alkylcarbonate zwitterion. Clearly, both zwitterionic and neutral species need to be included to model the extended liquid structure. Finally, the snapshots from two loadings (low and intermediate) clearly show the increasing inhomogeneity in the system as more CO_2 is absorbed and bound. The zwitterions (in red) tend to cluster in domains with dimensions of approximately a few nanometers. The classical MD simulations can faithfully reproduce the measured viscosities of these complexes, particularly the exponential variation of viscosity with CO_2 loading. This has allowed for the identification of nearest neighbor intermolecular "salt bridges" or intermolecular hydrogen bonding to be the major drivers of viscosity in both task-specific ionic liquids[154] and CO_2BOLs complexes. Subsequent efforts to design solvents that minimize these contacts will be further discussed below.

In the particular case of IPADM-2-BOL, the equilibrium as shown in Figure 30 is mostly shifted toward the charged species (zwitterion). The red line in Figure 32 represents the hypothetical case of the same system being at a 1:1 equilibrium between zwitterion and acid forms of the CO_2-loaded system. This points out the significant drop in viscosity (∼30−50% or more at the higher loadings) when the chemical equilibrium shift is taken into account. This has led to the conjecture that an appreciable viscosity reduction, while not altering the CO_2 storage capacity, may be obtainable if one were to design a CO_2 capture solvent where the acid/base equilibrium lies toward a large percentage of O−COOH or N−COOH species. In other words, the viscosity bottleneck can potentially be surmounted by nonionic CO_2 capture solvent systems. This may also enable lower regeneration temperatures, as indicated by simulations.[124,147]

The computational machinery for studying the extended structure and transport properties is quite mature and well-suited to the problems at hand. The real complexity arises in accurate identification of the types and relative populations of species as well as their spatial distributions. This can have immense impact on transport, and necessitates large system models (thousands of molecules, $>10^5$ atoms) with simulation times ranging from 10–1000 ns. The challenge, then, is a multiscale one where quantum chemical information is needed to reliably represent the species complexity prior to attempting to evaluate transport properties. In an effort similar to the Materials Genome Initiative (MGI), we address the challenge of connecting molecular structure information and chemical equilibria to macroscopic properties in a rigorous fashion as opposed to a phenomenological one. In the following section, we describe the computational protocol for the construction of reduced-order models.

4.1.3. Molecular Design and Quantitative Structure Property Relationships.

The ultimate goal of the theoretical/computational study of water-lean CO_2 solvent systems is not to strictly rationalize or reproduce experimental findings. Rather, one would prefer to use theory as a tool to identify key principles that allow one to make predictions that will enable the design of the next generation of solvents. This is a tall order given the complexity alluded to above and is not necessarily possible simply through large-scale computational screening, nor is it desirable.

A far more efficient and desirable approach is to build QSPRs and link, via correlation, desired properties to molecular descriptors, which can be evaluated solely on the basis of single-molecule calculations. This can reduce the effort of screening large synthetic libraries to hours or days rather than months of brute force simulations and/or synthesis and testing. A fruitful strategy for realizing this includes the following key steps: (i) identify the key property that needs optimization, and generate a theoretical data set based on a list of potential target molecules. This can be best achieved by taking a subset of compounds, simulating that property with existing theories to the highest degree possible, and validating the findings with respect to experimental measurements whenever possible. (ii) By careful analysis of the above data set, identify the molecular descriptor that most strongly correlates with the desired property. (iii) Construct a screening library of target compounds, including new ones that were not included in the training set. At this point, it is prudent to factor in species that obey already well-established constraints, usually associated with synthesis and scale-up processes, for example, low volatility, ease of synthesis, and low cost of scale-up. This allows one to carry learning from one set of experiments/property on to the next. (iv) Build a simple reduced order model (ROM) that expresses the desired property in terms of the descriptor(s) and can evaluate the entire target library using the lowest level of molecular theory possible. (v) Use the most likely candidates identified by the ROM for validation either by the use of higher levels of theory, or via synthesis and testing. (vi) Revise and repeat the cycle as needed until the model is refined to the accuracy needed and a large subset of compounds is identified, allowing for additional screening based on other constraints.

This approach has had some limited but impactful success in water-lean CO_2 solvents, most notably in screening compounds for CO_2 binding energies[147,155] and viscosities.[147,154]

To illustrate the above protocol, we consider the recently published work by Cantu et al.,[147] on the construction of a ROM for single-component CO_2BOL solvents that binds CO_2 almost exclusively in the form of a zwitterionic carbonate. By analysis of molecular dynamics simulations of a trial set of ~20 molecules, it was observed that there was a correlation between viscosity, η, and the percentage of CO_2-bound molecules with internal hydrogen bonding (within the same molecule), P_{int}, with a functional form

$$\eta = c_1 \ln(1/P_{int}) \exp(c_2 L) \tag{2}$$

These internal hydrogen bonds are symptomatic of complexes that are not involved in strong electrostatic interactions with their neighbors and, hence, have less affinity for the ionic domains within the heterogeneous liquid structure. Combining this correlation with the exponential dependence of η on CO_2 loading, it was found that with knowledge of P_{int} alone, one could estimate the viscosity with a correlation factor < 95%; see Figure 33.

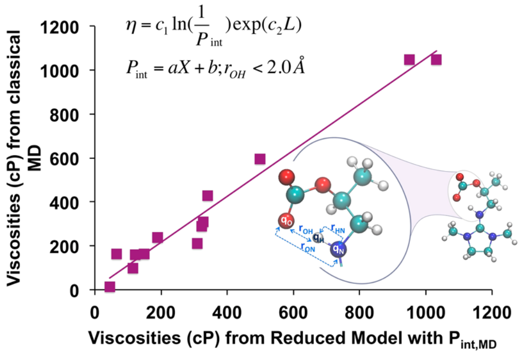

Figure 33. Viscosity correlation obtained through a ROM for single compound CO_2BOLs. The ROM allows for quick screening of compounds, once the P_{int} is identified from single-molecule DFT calculations.[148]

This work clearly demonstrates that theory can reliably be used to identify critical molecular-level descriptors that control viscosity. While the initial validation came from estimation of P_{int} from classical MD simulation, the desired outcome is to be able to predict this quantity solely from single-molecule quantum chemical calculations. Cantu et al.,[147] described how this quantity can be estimated from electrostatic energy terms within the H-bonding interaction. The estimated P_{int} and viscosity were obtained with a slightly reduced accuracy, ~90%, but at an appreciably lower computational cost and time. Nevertheless, this analysis provides a direct link between a simple way to evaluate molecular parameters and a bulk liquid property. Precisely this level of quantitative insights is needed for a screening protocol of large compound libraries with simple molecular calculations. Subsequent synthetic efforts, combined with large-scale classical MD simulations and viscosity measurements, validated the results and produced a modified zwitterionic complex with ~30% lower viscosity than IPADM-2-BOL at 25% CO_2 loading.[147]

In closing, this section highlights that the QSPR approach requires a strong knowledge of chemistry as well as the requisite skills in quantum chemical calculations and the statistical

Table 1. Water Tolerance, Loading, And Testing Scale of Multiple Water-Lean Solvents

solvent	CO_2-binding mechanism	projected water tolerance	steady-state water load (wt %)	scale tested	reference
CO_2BOL (IPADM-2-BOL)	alkylcarbonate	moderate	5	bench	102
NAS (unknown)	carbamate	high	unknown	bench	44
reversible ionic liquid	carbamate	high	unknown	bench	42
aminosilicones (GAP-1/TEG)	carbamate	high	<10	slipstream	34,103
concentrated amine (BUMEA)	carbamate	high	unknown	lab	29
phase-change aminosilicones	carbamate	high	N/A	bench	104
ION (unknown)	unknown	high	unknown	slipstream	157
AHA ILs	AHA-carbonate	poor	not yet tested	lab	86,87
phase-change AHA ILs	AHA-carbonate	some	not yet tested	lab	88

mechanics of complex liquids. This approach has led to appreciable progress in identifying solvent behavior in a short time but requires the integrated, concurrent input of experts from many fields to obtain critical insights. Theoretical advancements coupled with novel instrumentation and chemistries need to be developed from the ground up and in parallel for a tightly integrated effort that will overcome the current implementation of known bottlenecks identified in this section. There is a clear need for large multidisciplinary research teams working in concert to continue to make significant advances in solvent design and performance within the coming decade.

5. UNCERTAINTIES

With many knowns of water-lean solvents described above, we turn our focus here to the unknowns surrounding water-lean solvents and opportunities for further advancement of the field. We synopsize here the lifetime and durability of water-lean formulations and assess the ambiguities required for a workable process.

5.1. Water Tolerance

Water management is critical to water-lean solvent performance because lower water content equates to reduced reboiler duty.[13,44,111] The challenge in designing a solvent to operate in the absence of water is that flue gas contains roughly 10% water,[2] and water-lean solvents tend to be hygroscopic. Without water management strategies, all water-lean solvents will accumulate water during use, thus defeating the advantage of running water-lean solvents in the first place. Exacerbating this problem is the fact that dehumidification systems like Drizo are energy intensive and costly, both of which would increase capital and operational expenditures. Further, it is not known whether all water-lean formulations have appreciable water tolerance because water interacts with each solvent differently. Each solvent formulation is distinct, and water may have adverse effects on one solvent but not on another. In some formulations, water can potentially cause hydrolysis and chemically degrade the solvent.[68] In others, water can protonate the basic (CO_2 binding) moiety, thus deactivating the solvent.[86−88] Fortunately, there has been a significant amount of research in the field demonstrating water tolerances and water management strategies for multiple formulations and binding mechanisms.

Water can directly influence the selectivity of CO_2 binding in certain solvents. Amine-based systems tend to favor the carbamate binding mechanism of CO_2,[34,37,39−44,103,156] while the alcohol-based chemistries of CO_2BOLs tend to fluctuate between alkylcarbonate and the more thermodynamically stable bicarbonate.[13] An initial concern for water-lean solvents was that, regardless of formulation or binding mechanism, the precipitation of a solid carbamate or bicarbonate salt would introduce significant processing challenges and reduce performance. CO_2BOLs were the most likely to suffer from bicarbonate precipitation because the amidine and guanidine bases in CO_2BOLs are known to form solid bicarbonate salts, which are favored because alcohols in CO_2BOLs are less acidic and nucleophilic than water.[13]

Heldebrant was the first to demonstrate binding competition between water and the alcohol with CO_2 in CO_2BOLs, demonstrating an equilibrium that slightly favored bicarbonate formation.[13] Heldebrant concluded that bicarbonate formation could be retarded as long as the alcohol concentration was higher than that of water.[13] Koech later showed that bicarbonate salts could remain dissolved in solution and would carry through to the stripper without precipitation.[68] Koech's alkanolguanidine could dissolve 50% bicarbonate in solution without any observed precipitation, making a vast improvement in water tolerance compared to first-generation derivatives.[68] Similarly, Eckert and Liotta demonstrated that concentrated siloxated amines and siloxylamines were able to remain liquid in the presence of water.[37−40,42,43] Comparable observations were reported by Jessop, who demonstrated water tolerance for concentrated primary, secondary, and diamine systems.[41,63] Perry et al. also demonstrated that aminosilicones have a significant water tolerance of over 10 wt %, though it should be noted that this solvent system utilizes TEG as a cosolvent.[34,103] Conversely, Perry and team have shown that 100% concentrated aminosilicones can form a dry carbamate powder even in the presence of water in their phase-change embodiment as described earlier.[110] On the other hand, Brennecke's AHA-based ionic liquids were initially found to be water reactive: the basic anion would directly deprotonate water and neutralize the AHA CO_2 capture agent.[86,87] Brennecke has recently shown new AHA derivatives that display a higher water tolerance, indicating that even water-reactive solvents can operate in the presence of water.[88] It is clear that while water tolerance is solvent-specific, nearly all formulations could operate with some level of water present.

Lail et al. demonstrated not only water tolerance but also water management, by phase-separating their CO_2-rich solvent from water using the switchable polarity of their NAS. The phase separation from water is beneficial because the CO_2-rich phase will achieve low steady-state loading of water, in turn preventing dilution of the NAS, which enables lower reboiler duties.[44] Lail and his team first demonstrated this principle using hydrophobic amidines and/or guanidines paired with an alcohol or amine. Here, the CO_2-rich solution was found to phase-separate from water, leaving a concentrated CO_2-rich solution.[44] Lail and team later used fluorinated alcohols to further promote the phase separation from water, though it should be noted that the potential environmental impact and high cost and weight of the perfluorinated material are not likely to be viable in a workable process.

A second example of a unique phase separation from water was recently reported by Wang et al. that uses an amino acid salt solvent in water to precipitate a solid CO_2 carrier.[107] In this solvent system, a liquid containing a nontoxic, low vapor pressure, natural amino acid salt in water binds CO_2 to form a solid carbamate and bicarbonate mixture which phase separates to CO_2-lean and CO_2-rich phases. The CO_2-lean phase contains about 10% CO_2, and the CO_2-rich phase consists mainly of bicarbonate species and contains 90% CO_2. The two phases have been separated, and the CO_2-rich phase regenerated at 120 °C, though this has been demonstrated only at the laboratory scale.

There are recent reports of steady-state water loadings being achieved in multiple solvent systems across multiple scales, which we highlight in Table 1. Mathias et al. modeled the IPADM-2-BOL formulation in Aspen Plus based on continuous-flow laboratory-scale data, reporting that a steady-state concentration of water could be maintained by condensing water upstream of the absorber while also elevating the reboiler temperature as needed.[13,102] Mathias modeled 2.5, 5, and 7.5 wt % water loads, finding that the 5 wt % water load was projected to be the most energy efficient loading of water, which was validated by bench-scale continuous flow testing of a 2 slpm inlet gas saturated with water at 14.9% CO_2 and 40 °C, with the solvent preloaded to 5 wt % water.[102] Similarly, Lail et al. reported a steady-state water loading in one NAS formulation in bench-scale testing, though it should be noted that the exact composition of the solvent remains unknown.[44] The NAS was run on a continuous flow absorber/desorber reactor being fed with an inlet gas of nitrogen with 13.3% CO_2, saturated with 5.65% water at 35 °C. Steady accumulation of water in the solvent was observed until 60 h on stream, after which a steady-state water loading is claimed to have been reached.[44] Lail and team report that steady state was verified by performing a mass balance of water in the system, though the exact water loading was not specified. The water balance for this specific NAS was achieved similarly to the CO_2BOL case or water-based amines, where the majority of water leaves with the treated gas stream with a properly configured reboiler. Mani et al. recently reported steady-state CO_2 flux for BUMEA in the presence of moisture on a small benchtop apparatus.[29] They claim steady state was achieved for 36 h with no loss in efficiency, though the temperature in the stripper and the steady-state water loading in the solution were not reported. ION Engineering recently completed 1100 h of steady-state water loading during slipstream testing at the National Carbon Capture Center (NC^3),[157] though the solvent composition and binding mechanism are unknown, and to our knowledge those results have yet to be published.

Water was considered an impediment to water-lean solvents, but in certain cases water may actually benefit CO_2 capture by water-lean solvents. Mathias et al. modeled the performance of the IPADM-2-BOL CO_2BOL derivative, reporting that the presence of water reduced the solvent circulation rate compared to a purely anhydrous case due to stronger CO_2 fixation in solution.[13] Stronger complexation was thought to occur by a combination of bicarbonate formation or by charge solvation of the CO_2 carrier through stronger hydrogen bonding.[13] Mathias also highlighted the fact that the presence of water vapor in the stripper could aid in the release of CO_2 as it does in aqueous systems, by reducing the partial pressure of CO_2 over the liquid during CO_2 stripping.[13,102] Further, organic liquids have lower thermal conductivities than water, requiring larger cross-exchangers than their aqueous counterparts.[102] The presence of some water could recoup some thermal conductivity loss of water-lean solvents, enabling more rapid heat exchange in the cross-exchanger than a completely anhydrous solvent could. It should be noted that this is purely speculative, and we have yet to find any modeling studies of this in the literature.

Ultimately, these results from laboratory scale through slipstream indicate the majority of water-lean solvents have an appreciable water tolerance, and in some cases water may actually benefit performance of water-lean solvents. The seminal work of Mathias, Mani, Lail, and ION Engineering indicates that costly dehumidification may not be required for water-lean solvents and that some level of water loading is needed to achieve acceptable performance. Ultimately, the work summarized here dismisses the misconception that water-lean solvents could not but also should not operate in the presence of water.

5.2. Foaming

Foaming during operation is a critical challenge for CO_2 capture technologies; foaming leads to poor process performance and is often observed in water-based amine solvents.[158] Foaming greatly affects capture efficiency via column flooding, potential loss of solvent due to foam carryover, incomplete regeneration of the solvent, and variations in column pressure. Unsurprisingly, a majority of water-based solvents require the addition of control measures, such as mechanical filtration, solution reclamation, or antifoam additives.[158] Antifoam additives are not desirable because they do not remove contaminants from the solvent or permanently prevent foaming.[159−162] Naturally, foaming tendency has been studied for aqueous amines, as they are closer to deployment, though there are limited studies of foaming in water-lean solvents.

Lail et al. were the first to study the foaming tendencies of a water-lean solvent. The foaming potential of a NAS derivative was tested and compared against a solution of 30 wt % MEA/water for comparison.[44] Testing was performed according to a testing method, ASTM D1881-73. No foaming was observed with the NAS solvent during testing, which was in contrast to visible foaming and volume expansion with the CO_2-rich MEA solution under testing conditions at 40 and 80 °C.[44] Lail and team concluded that their NAS formulation's "reasonable" viscosity, low surface tension, and high density were beneficial properties to prevent foaming.

Similarly, Mani and team also saw no evidence of foaming of solvent-free alkanolamines. Mani and team studied continuous absorption (50 °C) and desorption (100−120 °C) of CO_2 using neat BUMEA with water-saturated flue gas using a custom apparatus with glass columns.[29] Continuous testing of BUMEA lasted for 24−26 h until a steady state was achieved. Mani saw no visual evidence of foaming in the absorber or stripper columns, indicating that water-lean alkanolamines may have antifoaming tendencies, in direct contrast to aqueous alkanolamines, which tend to foam.

The lack of foaming with the NAS and solvent-free alkanolamines is encouraging; many water-lean solvents are likely to have similar surface tensions and densities. It should be noted that the foaming tests described above were performed at the bench scale on simulated flue gas and that foaming may occur in larger scale testing, though there are no published reports of foaming with CO_2BOLs, ION Engineering's solvent, or GE's GAP solvent. Nonetheless, it is promising that water-lean solvents may be less likely to foam than their aqueous counterparts.

5.3. Corrosivity

The corrosivity of CO_2 capture fluids is a major area of concern for safety, process durability, and costing. Costs of steel alloys vary significantly, with stainless steel adding significant costs over carbon steel. The primary cause of corrosion of steel is carbonic acid, produced by the reaction between water and CO_2.[163] Because they are all water-based, all aqueous amines require high-cost stainless steel to minimize corrosion and degradation of process infrastructure.[2] A less corrosive capture solvent might yield significant cost savings for technologies using lesser grade steels.

Water-lean solvents were initially thought to be less corrosive than water-based solvents, primarily due to the lower water content that would translate to reduced carbonic acid concentration and thus lower corrosion potential. Further, some amines and amidines have been shown to act as corrosion inhibitors, suggesting that water-lean solvents might be less corrosive than their aqueous counterparts.[164]

The first (to our knowledge only) reported corrosion testing on a water-lean solvent was performed on the $[P_{66614}]$[2CNPYL] azoline ionic liquid[165] from Maginn et al. Corrosion testing was performed on a small scale using linear polarization resistance (LPR) and potentiodynamic scans (PDs) on carbon steel (1018-CS) and stainless steel (304L-SS) at varied conditions (25 and 150 °C, CO_2-free and CO_2-loaded). In this study, both carbon steel and stainless steel exhibited excellent corrosion resistance (corrosion rates of 0.1 milli-inch per year), suggesting that carbon steel could be used in process infrastructure (e.g., absorber columns and packing). In this study, they predicted that the use of cheaper alloys of steel could save $11.2 MM in capital costs (to an estimated 550 MW coal-fired power plant). It should be noted that these corrosion tests were performed at the laboratory scale in controlled conditions on a limited time scale, and that extended corrosion testing is needed to validate true corrosivity. Nonetheless, these initial corrosion tests are encouraging for other water-lean solvents.

The only extended corrosion testing performed to date with a meaningful length of time on stream was performed by ION Engineering at NC^3 in 2015.[157] ION's team studied the corrosion potential of carbon steel and 304, 304L, and 316L steels in their stripper column for over 1100 h on stream (Figure 34). The carbon steel (top right) showed significant corrosion, while the 304, 304L, and 316 stainless all showed minimal corrosion. Key dissolved impurities were chromium, nickel, silicon, and iron. ION reports that their water-lean solvent showed better corrosion resistance and less dissolved metal ion content than MEA under comparable testing conditions. It is encouraging that ION's solvent shows minimal corrosion at a meaningful scale over 1100 h of testing, suggesting potential for other water-lean solvents to behave similarly.

Figure 34. Steel coupons from ION's regenerator after 1100 h of testing.[157]

5.4. Cost of Solvents

It is a given that water-lean solvents will cost more than aqueous amines. The simple fact that water-lean systems are concentrated organics and water-based solvents contain significant fractions of water cannot be disputed. Further, the majority of solvents discussed here are composed of designer molecules that were made by the researchers who designed them. Scale-up costing is an imprecise science, and there are no guidelines or rules to project costs at scale, so costing is often subjective. Until candidate formulations make it through slipstream testing, the exact cost of each formulation cannot be identified. We emphasize that the energy performance of candidate solvent systems is more critical than cost, as costs can decrease as production scale increases and with market competition by manufacturers of the chemicals that compose the solvents.

One neglected component of manufacturing solvents for CO_2 capture is whether the world has enough chemical production capacity to make these chemicals at scale. Consider the fact that a single 550 MW subcritical coal-fired power plant using MEA is projected to circulate over 4000000 kg/h of solvent, not including solvent makeup rates.[2] With hundreds of coal-fired power plants in the United States alone, the amount of solvent needed for CO_2 capture is discouraging. Bara was the first to ask this question, pondering whether or not the world had enough chemical production capacity to make even the simplest alkanolamine (MEA) for CO_2 capture if every power plant used it.[15] Bara's analysis of the capacity to synthesize alkanolamines such as MEA, PZ, or other hindered amines suggests capacity is limited at best, and any viable capture solvent would skyrocket into the world's Top 50 commodity chemicals.[15] Aside from NH_3, MEA is the cheapest and simplest molecule for CO_2 capture. Bara concludes that MEA is likely the only CO_2 capture chemical for which production may be scalable because its primary components, NH_3 and ethylene oxide, both fall in the Top 50 commodity chemicals. Bara highlights that the production viability of advanced amines such as PZ or hindered amines such as KS-1 or AMP is not yet clear because their components are not yet scaled, and there may not be markets for their byproducts.[15] It should be noted that the majority of solvents described in this review are specialty chemicals; they are all relatively simple molecules containing C, N, O, and H and should be somewhat easy (though not necessarily cheap) to synthesize. Ultimately, the cost outlook for the molecules of water-lean solvents should be taken with a grain of salt because solvent cost may be irrelevant if there is not enough capacity to manufacture at scale.

5.5. Material Durability and Lifetime: SO_x, NO_x, Oxidative Degradation, Toxicity, and Fugitive Emissions

This section covers what is known and what is not known regarding chemical tolerance and environmental impact of these solvents. There is little information regarding the durability and environmental impact of water-lean solvents, primarily because water-lean solvents are at early stages of development. As such, for many of the solvents, chemical tolerance to SO_x and NO_x, potential fugitive emissions, and projected toxicity have rarely

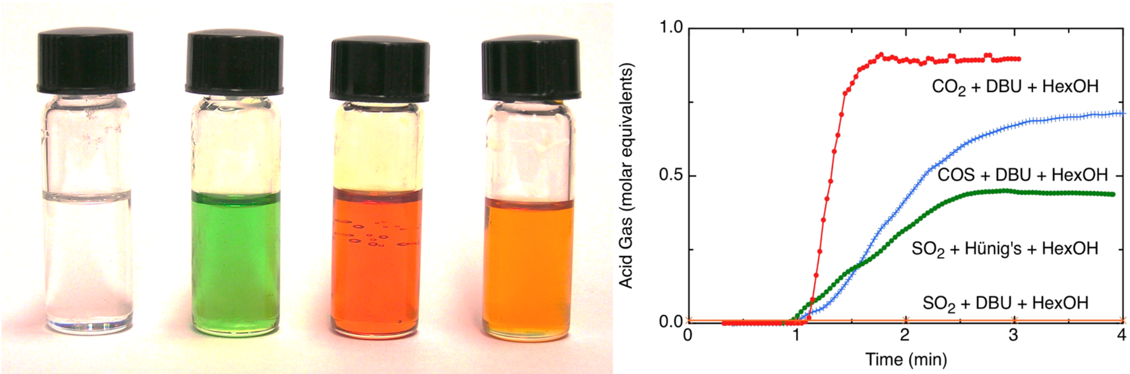

Figure 35. (Left) DBU:1-hexanol mixture chemically reacted with CO_2, COS, CS_2, or SO_2. (Right) Removal of CO_2 and COS from DBU and 1-hexanol, removal of SO_2 from Hünig's base and 1-hexanol at 140 °C. Heating begins at 1 min.[168]

been studied. Happily, there are studies showing chemical tolerance and in some cases reversible binding of sulfur analogues (e.g., COS, CS_2, and SO_2), though we know of no reported studies with NO_x.

5.5.1. Sulfur Oxides.

The chemical tolerance of water-lean solvents to SO_x was expected to be comparable to that of water-based amines because similar functional groups are used to complex with CO_2, albeit in the absence of water. The chemical fixation of COS, CS_2, and SO_2 were expected because all three are electrophilic acid gases like CO_2, susceptible to nucleophilic attack on the gas's central atom by either a nucleophilic nitrogen (amines, imidazoles), or oxygen (CO_2BOLs). Reversibility was not guaranteed because sulfur analogues tend to form heat-stable salts in water-based solvents, with the exception of hindered or tertiary amines such as Shell's aqueous Cansolv solvent[166] or aqueous solutions of aniline.[167] Sulfur chemical fixation is irreversible because sulfur-containing gases are more electrophilic (i.e., more acidic than CO_2). The pK_a values of the acidic forms of sulfur gases in solution (e.g., sulfurous acid) are orders of magnitude higher than that of CO_2 (carbonic acid) and form much stronger acid:base pairs in solution.[65] Another difference between water-lean and water-based solvents is the solvation of H^+ in solution, potentially changing the pK_a of not only the acid (CO_2, SO_2) but also the conjugate acids of the bases used in CO_2 capture. Different pK_a values of the base and acids in organics compared to water promote ambiguity of reversible chemical fixation of sulfur-containing acid gases.

Heldebrant was the first to demonstrate chemical tolerance of chemistry inherent to the CO_2BOL solvent class to electrophilic sulfur gases.[168] Heldebrant demonstrated that nonnucleophilic amidine or guanidine bases in CO_2BOL solvents (when paired with an alcohol) showed strong chemical binding of electrophilic acid gases SO_2, COS, and CS_2 through the alcohol moiety, making alkylsulfite ($ROSO_2^-$), alkylthiocarbonate ($ROCSO^-$), and alkylxanthate ($ROCS_2^-$) ionic liquids, respectively (Figure 35, left).[168] Zheng et al. also showed that diazabicyclo-[5.4.0]-undec-7-ene (DBU) paired with ethanol or hexanol chemically fixated CS_2 as alkylxanthate ionic liquids.[169] Heldebrant et al. also showed that COS and CS_2 could be thermally released from amidine or guanidine and alcohol blends (Figure 35, right), though amidinium or guanidinium alkylsulfite ($ROSO_2^-$) salts were thermally stable and SO_2 could not be released even up to 180 °C (Figure 35, right).[168] The reversibility of COS and CS_2 was attributed to COS and CS_2 producing weaker thiocarbonic or alkylxanthanthanic acids, respectively, compared to the strong alkylsulfurous acids made with SO_2. Interestingly, Li and team showed that a solid polymeric (1,1,3,3-tetramethylguanidine acrylate) (PTMGA) ionic liquid could reversibly bind SO_2 through the nonnucleophilic guanidine's imminium nitrogen.[170] SO_2 loading in PTMGA was found to be as high as 0.3 g/g polymer, with SO_2 able to be released at 140 °C. It should be noted that the guanidine in PTMGA is protonated (i.e., neutralized), unlike the free amidine or guanidines used in CO_2BOLs, likely contributing to the reversibility of this system.

Amine systems have also been shown to be reversible with SO_2. Heldebrant demonstrated that less basic tertiary amines[168] or tertiary alkanolamines[171] could form thermally reversible (at 140 °C) trialkylammonium alkylsulfite ($ROSO_2^-$) ionic liquids in the absence of water. The release of SO_2 is due in part to the decreased basicity of tertiary amines compared to the amidines or guanidines used for complexing CO_2 and COS (Figure 35, right). Kim and Lee presented similar observations of reversible binding of SO_2 with anhydrous nitrile-functionalized tertiary alkanolamines.[172] In their system, *N*,*N*-dibutyl-*N*-ethanol amine (DBEA) reversibly fixated SO_2 as an alkylsulfite salt, with SO_2 release requiring >120 °C.[172] Han and team also presented reversible SO_2 complexation using anhydrous nonvolatile polymeric tertiary alkanolamines.[173] Kim and Lee were among the first to demonstrate reversible SO_2 binding in the presence of water with diamine-anchored Merrifield resins.[174] The reversibility is notable, as bisulfite (HSO_3^-) salts have historically been heat-stable salts for most water-based 1° and 2° aqueous amines. It should be noted that the tertiary alkanolamines of Heldebrant and Kim and Lee were specifically designed for SO_2 capture because the tertiary amines are basic enough to capture CO_2 in the absence of water. These studies are highlighted here to demonstrate the chemical tolerance and potential reversibility of water-lean amines with SO_2.

Wu and Hu demonstrated the first example of reversible binding of SO_2 by imidazoles. 1,1′-[oxybis(2,1-ethanediyloxy-2,1-ethanediyl)]bis(imidazole) and *N*-dodecylimidazole were tested and isotherms made for SO_2 uptake.[186] Analogously, Bara et al. demonstrated chemical binding of SO_2 with different imidazoles, making a plethora of colored ionic liquids and solids. Bara showed complexation of SO_2 with varied imidazole derivatives, following a 1:1 chemical absorption mechanism with heats of reaction between −35 and −42 kJ mol^{-1}.[175] It should be noted that in Bara's work, the relatively low enthalpy of binding between imidazoles and SO_2 would indicate that SO_2 could be thermally released, though there is no mention of SO_2 release from the imidazoles that were tested.[175]

Table 2. Performance Projections for Notable Water-Lean Solvents versus NETL Reference Case 10 for MEA (550 MWe Subcritical Pulverized Coal Power Plant)[a]

	NETL Case 10[2] – MEA capture	GAP-1/TEG[33,34]	NAS[44,180]	CO_2BOL/PSAR[13,102]	ION[179]
estimated reboiler duty (Btu/lb CO_2)	1520	not reported	735	1107 (870[b])	1090[c]
net plant efficiency (HHV)	25.4%	30%	32.5%[d]	27.5% (29.5%[b])	not reported
cost per tonne CO_2 captured (USD)	60	50	47[e]	63 (39[b])	39–45

[a] Performance CO_2 capture estimates based on NETL Reference Case 9: net power plant efficiency equal to 36.8%, higher heating value (HHV). [b] Aspen Plus projections based on a theoretical assumption of 20 cP maximum CO_2BOL viscosity and equilibrium behavior for IPADM-2-BOL and has not been experimentally validated.[26] [c] Design case using ProTreat simulation model. [d] Range given for NAS-1–NAS-4 formulations. [e] NAS-3 formulation on Case 12 using Aspen ENRTL-SR model (3.6 bar stripper pressure).

Dai et al. also demonstrated chemical tolerance and reversible binding of SO_2 for azole-based solvents, albeit on an ionic liquid platform.[176] Dai and team reported that tetrazole $[P_{66614}][Tetz]$ and imidazole $[P_{66614}][Im]$ tetraalkylphosphonium ionic liquids could reversibly bind SO_2.[176] The tetrazole derivative showed an impressive 28 cycles of SO_2 binding and release (80 °C, N_2 flow, 30 min) with no reported loss in activity.[176] Dai indicates the tetrazole and imidazole derivatives strongly bind SO_2 chemically, with calculated binding enthalpies of −89.3 and −124.6 kJ/mol, respectively. Similar results were presented by Li and team with tetraalkylphosphonium or imidazolium tetrazolate ionic liquids.[177] Here, these tetrazolate ionic liquids demonstrated repeated SO_2 binding and release (80 °C, 60 mL/min N_2) for six cycles with no observed loss in activity.

Park et al. were the first to study the impacts of SO_2 on the NOHM class of materials. Park and team exposed NOHM-I-HPE (HPE = high polyetheramine content) materials to dilute N_2/SO_2 gas blends, mimicking the average and worst-case SO_2 concentrations expected in flue gas, 200 and 3010 ppm, respectively.[178] In this study, minimal SO_2 uptake was observed from the 200 ppm stream, while significant SO_2 absorption (0.1 mmol of SO_2/g NOHM-I-HPE) was observed from the more concentrated 3010 ppm stream. Absorption of SO_2 was found to proceed by either physical or weakly chemical binding to the ethereal oxygen groups in the polymer canopy, indicating good reversibility. Park and team reported no evidence of polymer dissociation from the core, indicating strong chemical tolerance in the presence of SO_2 for the ionic-bond tethered NOHMs. Durability of NOHMs was confirmed by running over 100 thermal cycles of capture and release at 120 °C.[178]

5.5.2. NO_x, HCl, and Oxidative Degradation.

There are still unknowns regarding the fate of other acid impurities such as NO_x and HCl. HCl is likely to form heat-stable salts that could be reclaimed and regenerated with methodologies such as ion-exchange resins, while reactions with NO_x are less clear. NO_x most likely would form heat-stable solids that could be reclaimed and regenerated via ion exchange. It remains possible that NO_x would react with solvents to generate nitrosamines that may or may not be carcinogenic. It also remains feasible (though less likely) that formation of NO_x salts may be thermally reversible. Also, the majority of water-lean solvents will undergo some level of oxidative degradation due to repeated stripping in the presence of O_2 at high temperatures, though to our knowledge there are no published studies for any solvent. The lower reboiler temperatures of water-lean systems may reduce the rate of degradation compared to water-based solvents, though formal studies are required to substantiate the degree of oxidative degradation.

It is promising that some formulations of water-lean solvents can chemically fixate, with some formulations able to thermally release SO_2 and other acid gas impurities. The majority of water-lean solvent formulations operate on similar chemical binding principles, thus they are likely to have similar tolerance for SO_2. We close this section emphasizing that there are many positive signs that water-lean solvents are at least comparable to their aqueous counterparts, and it remains possible that water-lean solvents will have better performance, though more work is needed to substantiate these claims.

5.5.3. Evaporative Losses and Toxicity.

As mentioned in section 2, fugitive emissions are an area of concern for water-lean solvents, for economic and environmental impact. It is a given that emissions controls will be required for water-lean solvents, to keep costs and environmental impact low. To our knowledge, there are no peer-reviewed estimates of fugitive emissions or studies of toxicity and environmental impact of water-lean solvents. The lack of toxicity studies is not surprising, since the majority of solvents are custom molecules that are still being tested at the laboratory or bench scale. It should be noted that the majority of these solvents are nonhalogenated and comprised of organic amines with mostly C, O, N, H atoms that would have a relative volatility and toxicity comparable to that of amines currently used in aqueous formulations.

Complete eco-toxicity studies for water-lean solvents and any potential degradation products that would arise over time are needed to ensure safe operation over time. The potential long-term effects of an acute exposure (immediate or delayed effects) or the effects of a chronic exposure (over weeks or months) in situations where there is continued release of chemicals to the environment need to be considered. Further, there is no information regarding the environmental distribution, persistence, and fate of these chemicals. Thus, we conclude that evaporative losses and environmental impact remain unknown but a potential area of concern.

6. OPPORTUNITIES

Building off the unknowns highlighted in section 4, we briefly highlight areas of study that are needed to continue the advancement of water-lean solvents. Here, we assess the viability of thermodynamic models: film theories that are used to model process performance. Further, we quickly delve into potential new configurations and concepts that could continue the enhancement of solvent performance.

6.1. Performance Projections of Notable Water-Lean Formulations

Implementation of CO_2 capture infrastructure at a coal-fired power plant adds a significant load to the power plant that reduces net power plant efficiency and power output. For example, implementation of the NETL Case 10 amine baseline infrastructure is projected to add a 30% parasitic load to a coal-fired power plant.[2] This load arises in part from the high reboiler duty associated with releasing CO_2 from an aqueous amine solvent at ∼120 °C and the duty associated with boiling and condensing water.[2] It has been speculated that water-lean solvents would have a lower reboiler duty due to lower heat capacities. It is also believed that lower regeneration temperatures (<100 °C) of water-lean solvents would enable the use of lower grade heat (i.e., lower pressure steam) to regenerate the solvent, reducing the parasitic load on the plant.[13,33,34,44,179]

Four notable water-lean solvents have been subjected to rigorous testing at a meaningful (>3 L) scale over dozens of hours of continuous flow to enable process performance projections. The four solvents listed in Table 2 represent all three CO_2 binding mechanisms. The carbamates are represented by the aminosilicone/TEG blends[33,34] along with the NAS hydrophobic amine blends,[44] with alkylcarbonate chemistry represented by the CO_2BOL solvent class,[13] while azoline-carboxylates are represented by ION solvent.[179] Table 2 provides relevant process data and energy projections for each solvent in comparison to the NETL Case 10 amine baseline. All four solvents in Table 2 show significant reductions in reboiler duty from the NETL Case 10 baseline (1520 Btu/lb CO_2), ranging from 735 to 1107 Btu/lb CO_2. The lower reboiler duties are primarily due to the lower water content and lower specific heat of the organic formulations. The combination of lower reboiler duties and regeneration temperatures below 100 °C enable higher plant efficiencies, resulting in a 2.1−7.1% increase in net plant efficiency over the NETL Case 10 baseline. Costs per tonne of CO_2 captured also are projected to be substantially lower than the \$60/tonne CO_2 for the Case 10 baseline, with costs ranging between \$39/tonne CO_2 and \$63/tonne CO_2. It should be noted that all of these notable solvents are projected to have significant increases in net plant efficiency and substantial reductions in costs per tonne of CO_2, which is remarkable for first-of-a-kind formulations and configurations. There is potential for more significant efficiency gains with process infrastructure designed and optimized for the physical and thermodynamic properties of these water-lean solvents.

6.2. Modeling Solvent Performance

The projections of process performance and costing for the four solvents listed in Table 2 are encouraging but may be misleading because they are modeled using conventional water-based models and process infrastructure used for water-based solvents. We emphasize that the modeling guidelines and process performance projections above treated each solvent as a drop-in solvent using water-based amine infrastructure to enable comparisons to the Case 10 baseline,[2] though the models used to project performance themselves have been under question.[181] Wilcox was the first to postulate that aqueous film theories may not be correctly modeling mass transfer of CO_2 into and out of ionic liquids.[181,182] Similarly, Mathias questions whether the free energy of solvation of the CO_2-rich ions that comprise CO_2 capture solvents are adequately accounted for.[13] It is unclear whether the thermodynamic or process models account for the changes in physical and thermodynamic properties of water-lean solvents such as film thickness, surface tension, and contact angle.

Thermodynamic models in Aspen Plus have been shown to be highly sensitive to inputs into the system, and any errors can greatly overstate or underestimate solvent performance. Mathias highlighted that speciation of CO_2 in solution (i.e., complexation or solvation) and the electrolyte activity coefficients are critical parameters needed for thermodynamic models.[13] Mathias reported reasonable fits for CO_2BOL solvents using the ElecNRTL-RK model in Aspen Plus, as it employs the Redlich−Kwong equation of state to describe the vapor phase and Chen's electrolyte activity-coefficient model.[13] The ElecNRTL-RK model may provide reasonable fits of the CO_2BOL solvent platform, though it remains unclear whether models like this account for complex water-lean solvents such as CO_2BOL's heterogeneous molecular solvent structure,[124,183] complex mixtures of amines or imidazoles with water, or mixtures of amines, water, and hydrophobic diluents of NASs.[44,179,180]

6.3. Configurations

We speculate that greenfield designs would be designed to exploit the unique physical and thermodynamic properties of water-lean solvents, thus opening new doors for transformative CO_2 capture processes. As we have highlighted in this review, properties such as mass transfer, heat exchange, surface tension, and contact angle all differ from water-based systems, and the designs of absorbers, heat exchangers, and strippers are clean sheets with respect to optimized process configurations.

The first example of potentially new configurations to exploit water-lean solvents would be changing absorber design and the way absorbers are operated. Direct-contact conventional packed or trayed columns are often used in absorbers for water-based solvents, though conventional designs may not be optimal for water-lean solvents. Alternative column designs such as high-G columns and indirect hollow-fiber or sheet membrane contactors may be more efficient for viscous water-lean solvents.[184] Absorber operation can also be altered. As discussed in section 2, some water-lean solvents have shown faster absorption at lower absorption temperatures, suggesting an absorber could be configured to operate like those of notable physical solvents such as Rectisol, Selexol, and Fluor Solv. An absorber configured to run at <40 °C may provide faster CO_2 uptake, enabling a smaller and cheaper absorber. Another benefit from a lower absorption temperature would be condensation of water from the incoming flue gas, further reducing the water content and subsequent reboiler duty of the water-lean solvent.[13] The trade-off for a cooled absorber column would be balancing the efficiency and cost benefits against the refrigeration costs and the tolerance of higher viscosity of the capture solvent.

Column packing is another area where new designs may provide further routes to increased efficiency. Water-based solvents have column packing that is uniform throughout the column because the physical properties of the fluid (water) remain relatively unchanged with CO_2 loading. However, the physical properties of water-lean solvents in the absence of a cosolvent change with CO_2 loading. These properties include, but are not limited to, surface tension, contact angle, thermal conductivity, density, polarity, and viscosity. Gradual changes in the packing shape and composition in columns could be matched to the physical properties of the fluid at a given stage in absorber or stripper columns to optimize contact angle or wettability as the fluid changes. Similarly, core−shell encapsulation of solvent has been proposed to offer improvements in surface area that may increase the CO_2 uptake rate of viscous solvents.[185] Heat exchangers could also be designed around similar principles, where the exchanger could have different dimensions and construction for the hot CO_2-lean or colder CO_2-rich fluid. Ultimately, there is potential for more efficient, exotic designs, and concepts of CO_2 capture infrastructure that are unavailable for water-based solvents.

7. OUTLOOK

In this review, we addressed misconceptions from advocates and skeptics alike, separating what is known and what is not known regarding the implementation of water-lean solvents for postcombustion CO_2 capture. We concede that the debate on the viability of organic solvents for CO_2 will likely continue until these solvents are implemented at scale. Water-lean solvents are able to use conventional infrastructure and have acceptable water tolerance and faster CO_2 mass transfer than their aqueous counterparts albeit at the expense of higher solvent costs and higher intrinsic viscosities. Chemical durability is expected to be comparable to that of aqueous formulations because both fluid classes comprise the same chemical functional groups. However, we note continued work is needed on the uncertainties and unknowns regarding solvent performance and durability. Further, the potential long-term effects of an acute or chronic exposure as well as environmental distribution, lifetime, and fate of these chemicals and their degradation products needs to be studied before any implementation can occur.

Molecular-level interactions within solvents are just being discovered, and new methodologies are being developed to rapidly predict material properties. Such simulations are providing critical insight into the unique thermodynamic and physical properties of water-lean solvents, how to control them, and how they can be exploited for efficiency gains. It is unclear whether similar molecular structural changes affect performance of all water-lean solvents similarly, though we boldly predict that most water-lean solvents will operate on similar principles, just as the majority of water-based solvents do.

Notable water-lean solvents have been tested at the bench or slipstream scale for flue gas applications. Lower reboiler duties and higher-than-expected mass transfer have been observed, albeit at the expense of an intrinsic viscosity increase (for some but not all solvents) that will have to be addressed. In either case, notable solvents continue to progress through larger scale testing and the forthcoming results will continue to advance the larger field of gas separations. We emphasize that the technologies presented here have been targeted for postcombustion separations, but they are not and should not be limited to just flue gas applications. There are other large-scale gas streams that require efficient removal of CO_2, such as natural gas, biogas, or precombustion sources, where similar design and performance criteria could apply. Ultimately, this review spoke to the advancements of water-lean solvents under the understanding that flue gas is only one such embodiment of these technologies.

We caution that the promising performance projections highlighted in Table 2 should include caveats regarding unknowns of model accuracy on water-lean physical and thermodynamic properties and modeling of what are likely unoptimized process configurations. Currently, water-based models have been used to predict performance of unoptimized water-lean solvents, indicating that water-lean solvents may be considerably more efficient than their aqueous brethren at the expense of higher capital costs. It may not be fair to base performance of water-lean systems on aqueous solvent infrastructure, but an apples-to-apples comparison is needed as a starting point. We anticipate that new configurations and process designs may further improve efficiency and cost of these first-of-a-kind solvents. The recent advancements and progress by the notable research teams identified herein indicate potential for these solvent systems to be tested for large-scale CO_2 separations in the coming years. Ultimately, we conclude that the outlook is promising for water-lean solvents and that they might be a "solution" for postcombustion CO_2 capture.

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