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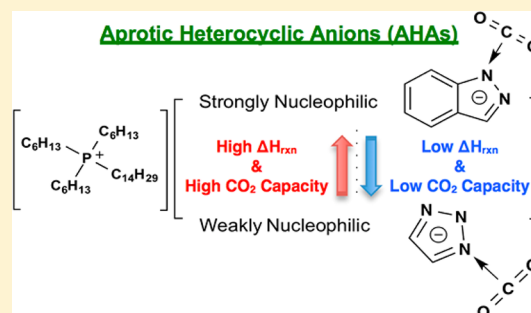
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Chemically Tunable Ionic Liquids with Aprotic Heterocyclic Anion (AHA) for CO₂ CaptureSamuel Seo,[†] Mauricio Quiroz-Guzman,[†] M. Aruni DeSilva,[†] Tae Bum Lee,[†] Yong Huang,[†] Brett F. Goodrich,[‡] William F. Schneider,^{†,‡} and Joan F. Brennecke^{*,†}[†]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States[‡]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

S Supporting Information

ABSTRACT: Ionic liquids (ILs) with aprotic heterocyclic anions, or AHAs, can bind CO₂ with reaction enthalpies that are suitable for gas separations and without suffering large viscosity increases. In the present work, we have synthesized ILs bearing an alkyl-phosphonium cation with indazolide, imidazolide, pyrrolide, pyrazolide and triazolide-based anions that span a wide range of predicted reaction enthalpies with CO₂. Each AHA-based IL was characterized by NMR spectroscopy and their physical properties (viscosity, glass transition, and thermal decomposition temperature) determined. In addition, the influence of substituent groups on the reaction enthalpy was investigated by measuring the CO₂ solubility in each IL at pressures between 0 and 1 bar at 22 °C using a volumetric method. The isotherm-derived enthalpies range between −37 and −54 kJ mol^{−1} of CO₂, and these values are in good agreement with computed enthalpies of gas-phase IL-CO₂ reaction products from molecular electronic structure calculations. The AHA ILs show no substantial increase in viscosity when fully saturated with CO₂ at 1 bar. Phase splitting and compositional analysis of one of the IL/H₂O and IL/H₂O/CO₂ systems conclude that protonation of the 2-cyanopyrrolide anion is improbable, and this result was confirmed by the equimolar CO₂ absorption in the presence of water. Taking advantage of the tunable binding energy and absence of viscosity increase after the reaction with CO₂, AHA ILs are promising candidates for efficient and environmental-friendly absorbents in postcombustion CO₂ capture.



■ INTRODUCTION

While the demand for renewable, clean sources of energy is increasing, fossil fuels and natural gas will continue to be the primary fuel and chemical feedstock sources for the foreseeable future. This will continue to contribute to the accumulation of carbon dioxide (CO₂) in the atmosphere, which raises serious environmental concerns about the impact of CO₂ on the global climate. Emission of CO₂ from coal-burning power plants is a major anthropogenic source of greenhouse gases,¹ and one of the most effective solutions to significantly reduce the level of CO₂ emissions is CO₂ mitigation by postcombustion carbon capture. Using conventional technology, CO₂ would be selectively absorbed from the flue gas into a solvent and subsequently released by stripping at an elevated temperature. Currently available technology would adopt volatile organic compounds (VOCs), primarily aqueous solutions of monoethanolamine (MEA) or other amines, to chemically trap CO₂ by forming ammonium carbamate in postcombustion CO₂ capture units.^{2–4} Although aqueous MEA solutions show high reactivity, low cost, and good absorption capacity, researchers continue to work on developing a replacement to overcome the drawbacks of aqueous amines, such as corrosion, oxidative degradation, and solvent loss due to evaporation, which eventually contribute to increased environmental pollution as well as extra cost of operation through solvent replacement.⁵

Another challenge is the large energy requirements associated with aqueous amine technology. Due to a large enthalpy associated with the MEA-CO₂ reaction, as well as the presence of large amounts of water, approximately 30% of the energy generated from the power plant would have to be diverted to the CO₂ capture process; this translates into a substantial increase in the cost of electricity.^{6–8}

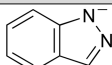
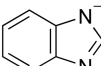
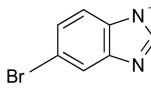
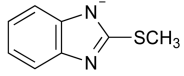
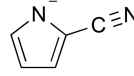
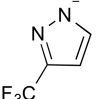
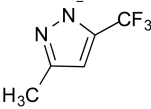


Within this context, ionic liquids (ILs) are a promising class of potential CO₂ absorbents, especially considering their unique properties.^{9,10} Negligible vapor pressure, high thermal stability, and nonflammability make them an excellent choice for absorbents, while the chemical tunability of ILs offers limitless opportunities to design ILs with desirable characteristics suitable for CO₂ capture.^{11–13} Furthermore, ILs do not require water as a diluent or carrier, and a substantial energy improvement is projected over technologies that employ aqueous amines. More than a decade ago, we reported that CO₂ is highly soluble in imidazolium-based ILs and the selectivity over other common gases is high.^{14,15} Although the physical solubility of CO₂ in ILs can be improved by fluorinating or increasing the alkyl chain length on the anion

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Table 1. Structure, Abbreviation, and Full Name of Anions Studied^a

structure	abbreviation	full name
	[Inda] [−]	Indazolid
	[BnIm] [−]	Benzimidazolid
	[6-BrBnIm] [−]	6-bromo-benzimidazolid
	[2-SCH ₃ BnIm] [−]	2-methylthio-benzimidazolid
	[2-CNPyrr] [−]	2-cyano-pyrrolide
	[3-CF ₃ Pyra] [−]	3-trifluoromethyl-pyrazolid
	[3-CH ₃ -5-CF ₃ Pyra] [−]	3-methyl-5-trifluoromethyl-pyrazolid
	[3-Triaz] [−]	1,2,3-triazolid
	[4-Triaz] [−]	1,2,4-triazolid

^aEach anion is paired with a [P₆₆₆₁₄]⁺ cation.

or cation components,^{16–19} Henry's law constants are still too large and, therefore, chemical absorption is necessary for any practical CO₂ capture from flue gas, where the CO₂ partial pressure is typically around 0.15 bar. Taking the lead from the conventional aqueous amine technology, Bates et al. first proposed task-specific ionic liquids (TSILs) that have a pendant amine group tethered to a propyl chain on a dialkylimidazolium cation, which, by forming carbamate and ammonium ions, achieved a stoichiometry of one CO₂ to two amines under ambient conditions.²⁰ While chemical absorption of CO₂ by these TSILs is significantly higher than is achievable by physical absorption, and is comparable on a molar basis to that observed for primary and secondary amines, the 1:2 stoichiometry is still atom inefficient. Zhang and co-workers reported that CO₂ capacity could be increased up to one CO₂ per one IL ion pair by adding reactive amino groups to both the cation and the anion.²¹ On the other hand, theoretical and experimental studies by Gurkan et al. showed that the equimolar uptake can be simply achieved when the amine functionality is tethered to the anionic component rather than the cation.²² Computational methods attributed the doubling of capacity to the absence of deprotonation of the product carbamic acid, since the dianion that would be formed is highly unstable.²³ In studies with amino acid-based ILs that exhibit equimolar CO₂ uptake, a precipitous increase in viscosity after CO₂ absorption made any practical application of those particular ILs for postcombustion CO₂ capture quite challenging.^{21,24–26} Subsequent molecular simulations in analogous systems by Gutowski et al. concluded that the

dramatic viscosity increase is attributable to the formation of a strong, pervasive hydrogen-bonded network.²⁷ More recently, Wang et al. suggested protic ILs based on superbases that are capable of equimolar CO₂ absorption under ambient conditions.²⁸ In an attempt at lowering the CO₂ binding energy, they have proposed a strategy to tune the reaction enthalpy of CO₂ utilizing anions with various basicity²⁹ and investigated the effect of electron-withdrawing and electron-donating substituents on phenolic ILs in a subsequent study.³⁰

In 2010, Gurkan et al. proposed a solution for eliminating the viscosity problem.³¹ Taking the lead from carboxylation of N-heterocyclic carbenes,³² ILs with aprotic heterocyclic anions (AHAs) have been developed to react stoichiometrically and reversibly with CO₂, without suffering the viscosity increases. AHA ILs offer improved structural features over their amino-functionalized predecessors; the formation of hydrogen bonding interactions between IL-CO₂ complexes is frustrated by minimizing the number of freely available hydrogens on the anion, and the heterocyclic platform can provide countless possibilities for chemical functionalization for CO₂ binding.³¹

In this paper, we present a strategy to tune the enthalpy of CO₂ absorption by incorporation of electron-withdrawing and steric hindering substituents on the AHA-based ILs. Taking advantage of their trait as “designer solvents”, nine different AHA ILs with a phosphonium-based cation were synthesized and their physical properties determined. The anions in this study were chosen to represent a wide variety of AHAs that have different enthalpies of reaction with CO₂. For these ILs, the cation has only a negligible effect on CO₂ absorption, but

has a large impact on physical properties such as viscosity.^{33,34} Unsymmetrical and bulky alkyl chains on the phosphorus increase the likelihood that the AHA ILs remain liquid at room temperature. CO₂ equilibrium isotherms are measured experimentally to better understand the capacity and strength of chemical reaction between each AHA IL and CO₂. Based on the CO₂ solubility data, the enthalpy of reaction for each IL was estimated and compared with the values obtained from molecular electronic structure calculations at the G4 level.³⁵ We also show that the viscosity remains virtually unchanged upon reaction with CO₂. The viscosities of CO₂-saturated ILs are compared with those of the pure ILs at temperatures between 10 and 70 °C.

An essential component in the evaluation of ILs for CO₂ separations is the effect of water naturally present in a postcombustion flue gas: ILs are generally hygroscopic and expected to easily and rapidly absorb water from flue gas. Water can affect the physical properties of ILs,³⁶ and has the potential to interfere with the CO₂ absorption chemistry.²⁵ In fact, CO₂ solubility in ILs of amino acid anions is reduced when wet, due to reprotonation of the anion in the presence of water.^{25,37} Stevanovic et al. combined experimental data with molecular simulation to investigate the effect of water on 1-alkyl-3-methylimidazolium acetate and concluded that water both reduces the extent of chemical reaction and hinders CO₂ physical solubility.³⁸ In contrast, Ren et al. demonstrated that 7 wt % water in the flue gas stream had no significant impact on the absorption of SO₂ in 1,1,3,3-tetramethylguanidinium lactate,³⁹ and a similar results were reported for azole-based ILs used for SO₂ capture.⁴⁰ We include here a discussion of the effect of water on CO₂ absorption by the AHA ILs.

EXPERIMENTAL METHODS

Materials and Synthesis. Structures and abbreviations of all the ILs synthesized in this study are listed in Table 1. Most heterocyclic precursors including indazole (98% purity), 6-bromo-benzimidazole (97%), 2-methylthio-benzimidazole (97%), 3-trifluoromethyl-pyrazole (99%), 3-methyl-5-trifluoromethyl-pyrazole (99%), 1H-1,2,3-triazole (99%), and 1H-1,2,4-triazole (99%) were purchased from Sigma-Aldrich, except for benzimidazole and pyrrole-2-carbonitrile (purchased from Alfa-Aesar), and used without further purification. ILs were prepared by a two-step synthesis protocol. First, trihexyl(tetradecyl)phosphonium hydroxide ([P₆₆₁₄][OH]) was prepared by stepwise ion exchange of trihexyl(tetradecyl)phosphonium bromide, [P₆₆₁₄][Br] (97% purity, Sigma-Aldrich), with SBR LG NC(OH) ion-exchange resin or Amberlite IRN78 (Sigma-Aldrich) in methanol (ACS grade, Fischer Scientific). Subsequently, an acid–base reaction was carried out between [P₆₆₁₄][OH] and equimolar amount of corresponding heterocyclic precursor to yield the desired IL. Methanol was removed under reduced pressure then other volatiles, including the water byproduct, were removed by further drying at 60 °C under reduced pressure for approximately a week. The water content was measured using a Brinkman 831 Karl Fischer coulometer, and all ILs contained less than 0.1% by weight (or 1000 ppm), except for the cases when water was intentionally added to the samples. The water was deionized using a Milli-Q water filtration system (Millipore). The structure and purity of the ILs were evaluated by ¹H NMR (Varian INOVA-500) and ³¹P NMR (Varian INOVA-300) spectroscopy (details in the Supporting Information) and thermal gravimetric analysis. In addition, the bromide

content was determined using a DIONEX DX-500 Ion Chromatograph and the concentration was below 20 ppm in all ILs.

Decomposition Temperature Measurements. The thermal stability of the ILs was studied using a Mettler-Toledo thermal gravimetric analyzer (TGA), model TGA/SDTA 851e/SF/1100, under either nitrogen or air. We report the onset temperature (T_{onset}), which is the intersection of the baseline weight, from either the beginning of the experiment or after the drying step, and the tangent of the weight versus temperature curve as decomposition occurs.⁴¹ The samples were placed in a 40 μ L aluminum crucible and heated at a rate of 10 °C min⁻¹, except for being dried in situ at 110 °C for 45 min. Manually determining the tangent point imparts an uncertainty of ± 2 °C in T_{onset} .

Glass Transition Temperature and Heat Capacity Measurements. Glass transition temperature (T_g) and heat capacity (C_p) were measured with a Mettler-Toledo differential scanning calorimeter (DSC), model DSC822°. Mettler-Toledo STARe software version 9.10 was used to analyze the data. T_g is defined as the midpoint of a small heat capacity change upon heating from the amorphous glass state to a liquid state.⁴² DSC measurements have an accuracy of ± 0.3 °C when a standard solution is evaluated, but the presence of trace impurities increases the estimated uncertainty to ± 1 °C. The heat capacity was determined relative to a sapphire (α -alumina) sample, as described by Fredlake et al.⁴¹ The estimated uncertainty of these measurements is on the order of $\pm 5\%$.

Density Measurements. Densities were measured using a DMA 4500 Anton Paar oscillating U-tube densitometer at temperatures between 10 and 60 °C under atmospheric pressure. The temperature was controlled internally by two integrated Pt-100 platinum thermometers with an uncertainty of ± 0.01 °C. The uncertainty in the density measurements is $\pm 5 \times 10^{-5}$ g cm⁻³, but is approximately $\pm 1 \times 10^{-3}$ when taking the purity of the ILs (97–99%) into account.

Viscosity Measurements. Two separate rheometers were used for viscosity measurements in this study. The first was a Brookfield DV-III Ultra rheometer with a 40 mm cone-and-plate spindle with an uncertainty of $\pm 5\%$. A TC-602 bath thermostat with a Brookfield temperature controller unit was used to control the temperature with a precision of ± 0.1 °C and a range of 10 to 70 °C. The second rheometer was an ATS Rheosystems Viscoanalyzer with an ETC-3 Joule-Thomson effect temperature cell allowing for a temperature range of -10 to $+400$ °C. It was equipped with a 20 mm cone-and-plate spindle, which allowed for a shear stress range of 7.1×10^{-6} to 7.1×10^3 Pa. Measured viscosities have an uncertainty of $\pm 5\%$ above 100 cP and $\pm 10\%$ between 50 cP and 100 cP.

Small quantities of water have been shown to have a large impact on the viscosity.^{25,43} To minimize water uptake during the experiments, neat samples were studied under a nitrogen environment (Praxair grade 4.8, 99.998%, H₂O < 3 ppm) and CO₂ saturated samples under a CO₂ environment (Praxair, 99.99% purity). As the sample was briefly exposed to the atmosphere during sample loading, the water content was measured before and after viscosity measurements. None of the ILs gained more than 3000 ppm water in this process.

CO₂ Solubility Measurements. The CO₂ solubility at room temperature (22 ± 1 °C) was determined using a volumetric method. Approximately 2 g of pure IL sample were added to a calibrated stirred vessel (closed system, 127 mL for setup A and 253 mL for setup B) under a nitrogen environment

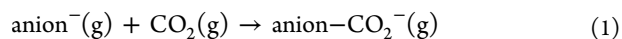
to minimize the absorption of atmospheric moisture and CO₂. Using the density of each IL (available in the Supporting Information), the volume displaced by the liquid sample has been subtracted from the total calibrated volume of the vessel. The water content was measured prior to and after the measurements; the readings were below 800 ppm in all samples. The vessel was initially evacuated to a pressure of less than 5×10^{-3} bar. Then CO₂ (Praxair, 99.995% purity) was introduced into the vessel by briefly opening the valve that is connected to a calibrated reservoir (177 mL) with a known pressure of CO₂. The pressure and temperature in both the vessel and the reservoir were recorded prior to and after the addition of CO₂. The amount of CO₂ that entered the stirred vessel was calculated from the pressure drop in the reservoir and verified by the pressure increase in the vessel. When mechanical stirring was activated to mix the IL, the pressure in the vessel started to drop, confirming absorption of CO₂ by the sample. The pressure in the stirred vessel was recorded until it remained constant for a minimum of 6 h when the vapor–liquid system was considered to be at equilibrium. Using the Lee-Kesler correlation,⁴⁴ the amount of CO₂ absorbed by the sample was determined from the total pressure drop in the stirred vessel after the addition of CO₂. This procedure was repeated until the equilibrium pressure was near 1 bar. The water content in the samples after CO₂ solubility measurements were slightly higher than the initial values, but still below 1500 ppm.

Characterization of Water–IL and Water–IL–CO₂ Systems. [P₆₆₆₁₄][2-CNPyrr] + water and [P₆₆₆₁₄][2-CNPyrr] + water + CO₂ systems were investigated by ¹H NMR spectroscopy in order to determine whether reprotonation of the anion takes place, as has been reported for amino acid-based ILs.³⁷ [P₆₆₆₁₄][2-CNPyrr] is one of our most thoroughly investigated AHA ILs and was studied here as an example. Investigations of the effect of water and CO₂ on the reaction chemistry with the other ILs presented here are currently underway. [P₆₆₆₁₄][2-CNPyrr] (0.9987 g, 1.737 mmol) and deionized water (1.0357 g, 57.51 mmol) were weighed into a scintillation vial with a stir bar. The mixture was stirred vigorously for 35 min. The resulting brownish emulsion was allowed to settle at room temperature until phase splitting was observed. This resulted in a bottom milky layer (aqueous layer) and a top brownish layer (IL rich layer). The cloudiness in the aqueous phase suggests that the separation may not be complete, but there was no brownish color in the aqueous phase, which would be indicative of [P₆₆₆₁₄][2-CNPyrr]. Nonetheless, both phases were sampled for ¹H NMR analysis. Subsequently, CO₂ at ambient temperature and pressure was bubbled into the IL–H₂O mixture for 30 min with vigorous stirring. After ceasing bubbling and stirring, the system was, once again, allowed to phase split, and each layer was sampled for ¹H NMR analysis. NMR spectra from all the aqueous layers were recorded in D₂O and those of the IL rich layers in DMSO-*d*₆. Additionally, CO₂ was bubbled into neat [P₆₆₆₁₄][2-CNpyrr] (1.0317 g, 1.7944 mmol) for 30 min and its NMR spectrum recorded in D₂O and DMSO-*d*₆ as control experiments.

The effect of prolonged exposure of a [P₆₆₆₁₄][2-CNPyrr] + H₂O mixture to CO₂ was also studied. [P₆₆₆₁₄][2-CNpyrr] (0.4592 g, 0.7987 mmol) and deionized water (1.3959 g, 77.50 mmol) was weighed into a test tube with a stir bar. Then CO₂ at ambient temperature and pressure was bubbled into the IL/H₂O mixture for 12 h with vigorous stirring, then 1 mL of water was added four different times to make up for the water that

evaporated due to the continuous flow of CO₂. The resulting emulsion was allowed to settle at room temperature until phase splitting was observed. Sampling was performed for ¹H NMR analysis as previously described.

Computational Methods. We computed optimized geometries of CO₂, the AHA anions, and anion–CO₂ complexes at the B3LYP/GTbas3 level using the Gaussian 09 package.⁴⁵ The harmonic vibrational spectra of all species were confirmed to contain only real modes. Energies of all species were determined at the G4 composite level.⁴⁶ We calculated 298 K reaction enthalpies ($\Delta H^\circ(298)$) for reaction 1



by combining the G4 electronic energy with zero-point and finite temperature corrections based on the B3LYP/GTbas3 frequencies.

RESULTS AND DISCUSSION

Glass Transition and Thermal Decomposition Temperatures and Heat Capacities. Table 2 shows that the glass

Table 2. Decomposition Temperatures (T_{onset}), Glass Transition Temperatures (T_g), and Heat Capacities (C_p) of [P₆₆₆₁₄][AHA] ILs

ILs	T_{onset} (°C)		T_g (°C)	MW (g mol ^{−1})	C_p (J mol ^{−1} °C ^{−1})	
	N ₂	air			25 °C	50 °C
[P ₆₆₆₁₄][Inda]	296	281	−74	600.98	1109	1158
[P ₆₆₆₁₄][BnIm]	314	285	−68	600.98	1160	1242
[P ₆₆₆₁₄][6-BrBnIm]	327	314	−71	679.88	1211	1259
[P ₆₆₆₁₄][2-SCH ₃ BnIm]	319	314	−69	647.08	1285	1380
[P ₆₆₆₁₄][2-CNPyrr]	316	303	−76	574.95	1195	1241
[P ₆₆₆₁₄][3-CF ₃ Pyra]	260	253	−78	618.92	1163	1218
[P ₆₆₆₁₄][3-CH ₃ -5-CF ₃ Pyra]	260	239	−69	632.95	1224	1286
[P ₆₆₆₁₄][3-Triaz]	328	326	−70	551.91	1116	1156
[P ₆₆₆₁₄][4-Triaz]	320	319	−70	551.91	1064	1110

transition temperatures (T_g) of [P₆₆₆₁₄][AHA] ILs vary from −79 to −68 °C, which are comparable to those of amino acid-based anions paired with a [P₆₆₆₁₄]⁺ cation.^{25,26} Generally, ILs with long alkyl chains on the cation frustrate crystallization and form a glass at low temperatures rather than exhibiting freezing or melting transitions. Similar anions paired with phosphonium cations with shorter and more symmetric alkyl chains such as 3-(aminopropyl)tributylphosphonium, [aP₄₄₄₃]⁺, or tetrabutylphosphonium, [P₄₄₄₄]⁺, tend to have higher T_g values.^{13,21}

Decomposition temperatures (T_{onset}) of the AHA ILs under N₂ and air are also listed in Table 2. All the ILs examined in this study had T_{onset} above 250 °C under nitrogen and were observed to decrease in the following order: [3-Triaz][−] > [6-BrBnIm][−] > [4-Triaz][−] > [2-SCH₃BnIm][−] > [2-CNPyrr][−] > [BnIm][−] > [Inda][−] > [3-CF₃Pyra][−] = [3-CH₃-5-CF₃Pyra][−]. In general, [P₆₆₆₁₄]⁺ is a thermally stable cation yet T_{onset} is also highly dependent on the choice of the pairing anion. In this regard, T_{onset} can be as high as 420 °C when paired with less nucleophilic anions such as bis-dicarbollylcobalt(III).⁴⁷ [P₆₆₆₁₄]⁺ cations paired with pyrazolide-based AHAs, such as [3-CF₃Pyra][−] or [3-CH₃-5-CF₃Pyra][−], had relatively lower decomposition temperatures compared to other AHAs. On the

other hand, benzimidazole, pyrrolide and triazolidine-based ILs exhibited superior thermal stability. The presence of air slightly decreased decomposition temperatures in most cases and this should be taken into serious consideration if one plans to operate ILs under air at high temperature.

The heat capacities of ILs were measured between 25 and 65 °C. The values at 25 and 50 °C are shown in Table 2 and the linear correlations of C_p as a function of temperature are provided in the Supporting Information. Heat capacity depends on the number of translational, vibrational, and rotational energy storage modes and increases roughly linearly with increasing molar mass for compounds with similar structures (see Figure S2 in the Supporting Information).

CO₂ Solubility. The CO₂ solubility in each of seven newly synthesized AHA ILs was measured at pressures between 0 and 1 bar at room temperature. In Figure 1, the vapor–liquid

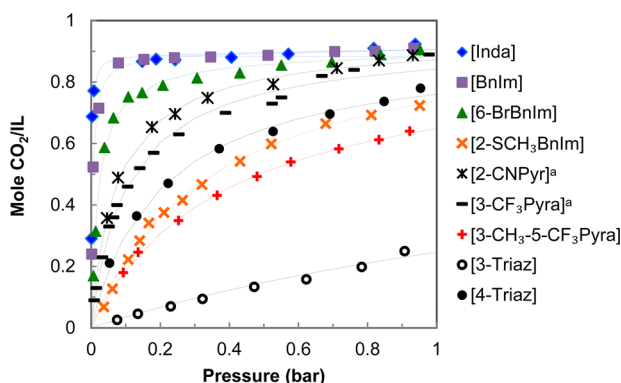


Figure 1. CO₂ capacity of [P₆₆₆₁₄][AHA] ILs at 22 °C. “From Gurkan et al.³¹”

equilibrium isotherms are plotted in mole ratio of CO₂ per IL as a function of CO₂ partial pressure. CO₂ solubilities in two AHAs, [P₆₆₆₁₄][2-CNPyra] and [P₆₆₆₁₄][3-CF₃Pyra], which have been reported previously,³¹ are plotted as well. The uncertainty in the CO₂ uptake measurements is approximately ± 0.02 mol CO₂/IL, which is approximately the size of the symbols in Figure 1.

Each anion of the ILs listed in Figure 1 is a tertiary amine incorporated into a heterocyclic ring. Therefore, each mole of IL (or each AHA) has the ability to bind to one mole of CO₂ via Lewis acid–base interaction to form a stable carbamate ion, as described in Scheme 1. The isotherms in Figure 1 show that CO₂ capacity approaches the 1:1 stoichiometry expected from theoretical arguments.^{31,48} The AHAs that do not reach 1 mol of CO₂ per mole of IL have smaller magnitude reaction enthalpies with CO₂ and may require higher CO₂ partial pressures to be fully saturated. Alternatively, failure to achieve stoichiometric uptake may arise from deactivation of amide groups via unknown mechanism at high CO₂ loadings. According to the quantitative ³¹P NMR analysis (details in

the Supporting Information), the phosphine oxide impurity content in the ILs is no higher than 3 wt %. Wang et al.²⁹ reported the CO₂ solubility in [P₆₆₆₁₄][Inda] to be 0.98 mol CO₂/IL under 1 bar of CO₂, which is slightly higher than the 0.92 mol CO₂/IL at 0.94 bar obtained in this study. In addition, they reported 0.95 mol CO₂/IL at 1 bar for [P₆₆₆₁₄][4-Triaz], which is significantly different than 0.78 mol CO₂/IL at 0.95 bar. The higher value reported by Wang et al.²⁹ may be due to water uptake during the course of the experiment. Water can have a significant effect on CO₂ uptake by AHA ILs, as will be discussed.

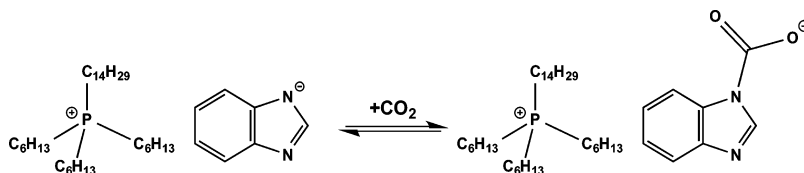
The anions in this study were chosen to represent a wide variety of AHAs that exhibit different chemical affinity toward CO₂, and the variation is confirmed by the isotherms with distinct slopes and CO₂ capacity, as shown in Figure 1. The sharpness in the slope of the CO₂ absorption isotherm corresponds to the strength of chemical binding or reaction enthalpy between CO₂ and the anion, the correlation of which will be discussed quantitatively below. The chemical reaction between [Inda][−] or [BnIm][−] with CO₂ is nearly complete around 0.025 bar and subsequent small increases at higher pressures likely reflect the contribution of physical CO₂ absorption into the liquid phase. It is evident that the chemical complexation is responsible for the vast majority of the uptake and the contribution from physical solubility is insignificant at pressures below 1 bar. Three ILs, those with [2-SCH₃BnIm][−], [3-CF₃Pyra][−], and [3-Triaz][−] anions, had much lower CO₂ capacity than the theoretical maximum value (unity), only reaching approximately 0.7, 0.6, and 0.3 mol CO₂/IL under 1 bar CO₂, respectively. Relatively weak driving force for the reaction of CO₂ with these AHAs presumably left a significant fraction of unreacted ILs even at 1 bar. [P₆₆₆₁₄][3-Triaz] exhibited the lowest CO₂ solubility among the AHAs, but it is clear that its capacity is still superior to ILs that only physically absorb CO₂.¹⁶

To quantitatively describe both chemical and physical absorption in the AHA ILs, the equilibrium points are fitted with a “deactivated model” proposed by Goodrich et al.²⁶ This model assumes that only one reaction takes place and not all of the amide functional group may be available for CO₂ binding.

$$Z = \frac{P_{\text{CO}_2}/H}{1 - P_{\text{CO}_2}/H} + \frac{K_{\text{eq}}P_{\text{CO}_2}C_3}{1 + K_{\text{eq}}P_{\text{CO}_2}} \quad (2)$$

where Z is the molar ratio of CO₂ to IL, P_{CO_2} is the CO₂ pressure in bar, H is the Henry’s law constant in bar, K_{eq} is the reaction equilibrium constant, and C_3 represents the molar ratio of active IL to the total IL. The Henry’s law constants (H) represent the physical solubility in each IL, but the estimation of Henry’s law constant is not reliable at this pressure range since the amount of physically dissolved CO₂ into ILs is insignificant (typically less than 2% of the total absorption). Henry’s law constants for CO₂ in ILs at room temperature typically range from 30 to 200 bar,^{18,19,49–51} and Gurkan et al.

Scheme 1. Complexation Mechanism of CO₂ with [P₆₆₆₁₄][BnIm]



reported a value of 62 bar for $[P_{66614}][2\text{-CNPyrr}]$ at 22 °C.³¹ Since the bulky $[P_{66614}]^+$ cation is largely responsible for the free volume of ILs (and, consequently, the Henry's law constants) and the free volume variation resulting from the type of anion is expected to be small, the Henry's law constant has been fixed at 62 bar during the fitting process. In fact, the value of the Henry's law constant has no appreciable effect on the rest of parameters or the visual quality of the fit. The other two parameters, K_{eq} and C_3 , were fit to the experimental CO_2 solubility data for each IL at room temperature using a Levenberg–Marquardt algorithm and are available in Table 3.

Table 3. Computed AHA– CO_2 Reaction Enthalpies and Fit Parameters for “Deactivated” Isotherm Model (eq 2)^a

anion	ΔH_{rxn} (kJ mol ^{−1})		K_{eq} (unitless)	C_3 (unitless)
	experimental	computational		
[Inda] [−]	−54	−61	680	0.89
[BnIm] [−]	−52	−65	207	0.90
[6-BrBnIm] [−]	−48	−55	46	0.89
[2-SCH ₃ BnIm] [−]	−41	−48	2.9	0.96
[2-CNPyrr] [−]	−45	−48	14	0.92
[3-CF ₃ Pyra] [−]	−44	−53	9.7	0.91
[3-CH ₃ -5-CF ₃ Pyra] [−]	−41	−50	2.7	0.87
[3-Triaz] [−]	−37	−52	0.54	0.66
[4-Triaz] [−]	−42	−63	5.0	0.89

^aHenry's law constants were fixed at 62 bar.

The model provides a good representation of the data for all of the systems as indicated by dashed lines in Figure 1. Most AHAs yield C_3 values of approximately 0.9, except for [3-Triaz], which showed exceptionally weak interaction with CO_2 and therefore had C_3 of only 0.66.

In a previous report by Gurkan et al., both enthalpy and entropy of CO_2 binding reaction for $[P_{66614}][2\text{-CNPyrr}]$ were determined experimentally by probing the temperature-dependence of the equilibrium constants.³¹ Since other AHA ILs lend themselves to a similar reaction mechanism with CO_2 (amine lone pair forms an N–C bond with CO_2 via Lewis acid–base reaction, as confirmed by NMR and IR spectroscopy, see Scheme 1), in this work the standard entropy of reaction (ΔS°) between each AHA IL and gas-phase CO_2 is assumed to be comparable to that of $[P_{66614}][2\text{-CNPyrr}]$: $-130 \text{ J mol}^{-1} \text{ K}^{-1}$.³¹ We believe this is reasonable because the entropy change for the absorption is dominated by entropy loss of the CO_2 molecule upon transforming from an ideal-gas like state to the absorbed state in the liquid phase⁵² and most liquid CO_2 absorbents show very similar entropy changes at the standard conditions.⁵³ The entropies of reaction have been estimated using temperature-dependent data from triazolide and pyrazolide-based AHA ILs⁵⁴ and all were consistent within $\pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$. Knowing standard entropy and equilibrium constants enables us to estimate the enthalpy of reaction for each AHA at constant temperature employing basic thermodynamic relations ($\Delta G^\circ = -RT \ln(K_{eq}) = \Delta H^\circ - T\Delta S^\circ$). A summary of the calculated enthalpy of reaction for each IL is listed in Table 3. The estimated values range between -37 and -54 kJ mol^{-1} . The reaction enthalpies of all of the AHA ILs with CO_2 are substantially less exothermic than that of MEA, the enthalpy of which can be as high as -85 kJ mol^{-1} at 40 °C.⁵⁵ The superior molar CO_2 capacity of the AHAs combined

with the lower molar enthalpy could potentially reduce the energy requirement for solvent regeneration compared to commercial aqueous amine processes.

Quantum chemical computations have proved invaluable in understanding and characterizing chemically reactive IL– CO_2 systems.^{27,31,48,56–58} Because the differential solubility of the unreacted and reacted anions is small,³¹ gas-phase reaction energies have generally shown themselves to be good predictors of CO_2 solubility in reactive ILs.⁴⁶ We computed the structures of the unreacted and CO_2 -reacted anions in Table 1 at the G4 level of theory. The aromatic anions are uniformly planar. We separately tested CO_2 binding at each distinct N center. As shown in Figure S4, and consistent with all previous reports, CO_2 binds bent and coplanar with the aromatic ring to form a carbamate; equilibrium N–C distances range from 1.53 to 1.68 Å and O–C–O angles range from 135° to 141°. We computed reaction energies using the G4 composite method and corrected to 298 K enthalpies using the computed B3LYP/GTbas3 vibrational spectra and standard ideal gas statistical mechanical models. In general, reaction enthalpies differ systematically by approximately -2 kJ mol^{-1} from 0 K reaction energies. Results for $[2\text{-CNPyrr}]^{\cdot-}$ are consistent with those reported previously.³¹ On anions that present more than one potential reactive site, reaction is predicted to be more exothermic at the nitrogen center adjacent to the fewest nearest neighbor ring nitrogen and at centers less hindered by bulky neighbor functional groups (see Figure S4).

Table 3 compares computed enthalpies for the most stable binding site with those extracted from the room temperature isotherms and standard entropy assumption. Overall, the computations provide excellent directional predictions of observed reactivity. The G4 enthalpies systematically predict reactions to be more exothermic than inferred from the isotherms. For the majority of the anions this difference is -7 to -9 kJ mol^{-1} . The difference is a larger -13 kJ mol^{-1} for $[\text{BnIm}]^{\cdot-}$; here the product carbamate may be more poorly solvated (have a less negative solvation enthalpy) than the reactant due to the reduction in anion symmetry accompanying reaction. Test calculations show that, in anions that present more than one reaction site, reaction with one CO_2 deactivates the ring for further reaction.⁵⁹ Such multisite absorption effects are unlikely to account for these differences.

Even more substantial differences between experiment and computation are found for the smallest anions, $[3\text{-Triaz}]^{\cdot-}$ (-15 kJ mol^{-1}) and $[4\text{-Triaz}]^{\cdot-}$ (-21 kJ mol^{-1}). Similar arguments about differences in solvation enthalpies may account for some of this exaggeration of reactivity. Note that triazolides have three nitrogens that could bind with CO_2 . Lee et al., for instance, found evidence in two-dimensional nuclear Overhauser effect (NOE) NMR for association between weakly basic $[\text{Tf}_2\text{N}]^{\cdot-}$ anions and the acidic hydrogen atoms on $[\text{P}_{2228}]^+$ tail groups in a $[\text{P}_{2228}][\text{Tf}_2\text{N}]$ IL.⁶⁰ We expect intermolecular interactions to be even more prominent as anions become smaller and more basic. Moreover, the three nitrogens in the triazolides are susceptible to hydrogen-bonding interactions with the alpha hydrogens on the tetra-alkylphosphonium cations. The small size of the triazolide anions could result in “trapping” of the anion by the long alkyl chains on the cation, reducing the reactivity of the anion with CO_2 . In this context, Gohndrone et al. recently discovered that at elevated temperatures some AHA anions can abstract the acidic α -hydrogen atoms of a phosphonium cation to produce an ylide at temperatures above ambient.⁶¹ While ylide formation is

relatively insignificant at room temperature, strong anion–cation interactions could manifest themselves in diminished CO₂ binding energies. In extreme cases, intermolecular interactions could direct some or all of the CO₂ to the less exothermic reaction site, decreasing the observed enthalpy. Clearly, models that explicitly capture bulk solvation in the unreacted and reacted materials are necessary to fully explain differences between computation and experiment.

One of the main advantages of ILs over conventional absorbents is that ILs with various functionalized groups or substituents can offer remarkable variations in binding energies. While there are other basic anions that can chemically bind with CO₂ (e.g., acetates, [CH₃CO₂][−]),^{62–65} they offer limited chemical tunability. Utilizing the heterocyclic platform, we proposed a strategy to tune the reactivity of the interaction site in ILs by substituents that are capable of modifying both steric hindrances and electronic interactions. The electron-withdrawing group on the heterocyclic ring delocalizes the electron density around the ring, reducing the basicity of the nucleophilic nitrogen(s). Previous studies have also shown that electron-donating groups can change the reactivity of amines with CO₂.³⁰ The Dai research group has correlated IL–CO₂ reaction energy and CO₂ solubility with the corresponding Bronsted basicity (pK_a) of the anion.^{29,30} Teague et al. also showed that interaction energy may be tuned across a range from reactive to nonreactive (or physical) interactions using a series of oxygen-containing Lewis base anions.⁶⁶ More accurate G3 calculations indicated that reaction enthalpy for pyrrolide anion is expected to decrease from −109 to −49 kJ mol^{−1} simply by appending an electron-withdrawing cyano group on the C-2 position of the pyrrolide ring.³¹ The position of the substituent also has a significant effect, as a cyano (CN[−]) substituent on the 3 position should only moderately decrease the enthalpy to −70 kJ mol^{−1}.³¹ This is consistent with observations by Wang et al., that placing identical substituent on different positions on phenolate results in a noticeably different reaction strength.³⁰ Similar trends can be seen in the experimental results presented in this study. The parent [BnIm][−] anion provides the strongest reaction with CO₂ compared to its substituted-counterparts, such as [6-BrBnIm][−] and [2-SCH₃BnIm][−]. In addition to this, it is evident that the methylthio group adjacent to the nitrogen atoms in benzimidazolide had a much more dominant effect on the reactivity compared to [6-BrBnIm][−], in which a bromide atom is appended at a distance from the reactive sites. An analogous trend can also be observed for the pyrazolide-based AHAs.

The target with absorbents used in postcombustion CO₂ capture is to form fairly strong chemical complexes such that the carrying capacity even at low partial pressure of CO₂ is relatively high yet the energy requirements to regenerate the sorbent are not tremendous. The CO₂ solubility results show how AHAs can be chemically tuned to successfully achieve molar capacities superior to aqueous amine solutions, yet with significantly reduced enthalpy of absorption, and, thus, lower regeneration energy requirements. In this respect, Figure 2 compares the CO₂ solubility in AHAs at CO₂ partial pressure of 0.15 bar at 22 °C, which is a typical concentration of CO₂ in flue gas. It is evident that the molar uptake of CO₂ in AHAs is significant even at this low partial pressure and that more than half of the AHA ILs in this study exceeded the molar uptake of 0.5 (the maximum molar capacity achievable by MEA). The CO₂ capacity correlates well with the absolute values of reaction enthalpy (see Table 3), as more basic anions can

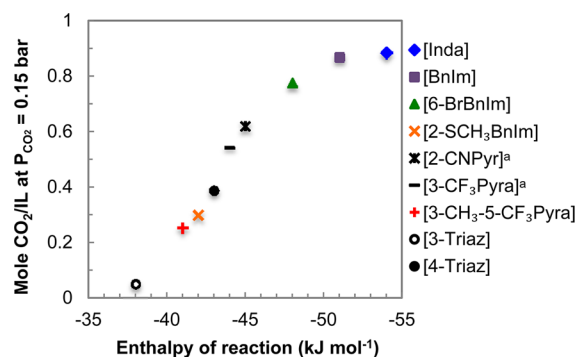


Figure 2. Solubility of CO₂ in [P₆₆₆₁₄][AHA] at CO₂ partial pressure of 0.15 bar, as a function of enthalpy derived from the isotherms. ^aFrom Gurkan et al.³¹

effectively capture CO₂ at this pressure range. The solubility will be slightly less at typical absorber temperatures (40–50 °C); nonetheless, two of the most basic AHAs ([Inda][−] and [BnIm][−]) should reach close to their theoretical equimolar ratio even at these temperatures.

The absorption/desorption recycling of an absorbent is an essential property that is directly associated with the operating cost of gas separation, as it establishes the frequency of the sorbent replacement.⁶⁷ Using [P₆₆₆₁₄][2-CNPyr], we confirmed the stability of CO₂ absorption during multiple absorption–desorption cycles. The results for three absorption–desorption cycles are shown in Figure 3. It is evident that CO₂ was fully

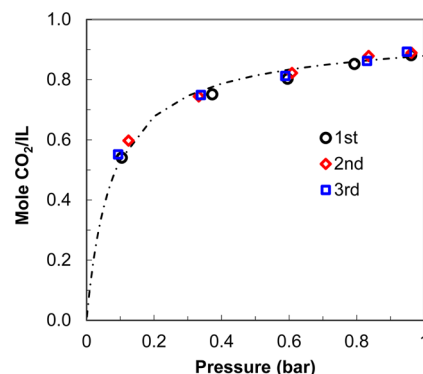


Figure 3. Three absorption/desorption cycles of [P₆₆₆₁₄][2-CNPyr]: 1st (circles), 2nd (diamonds), and 3rd (squares) cycle. Absorption of CO₂ was performed at 22 °C, and desorption was carried out at 80 °C under a N₂ atmosphere for 60 min.

desorbed under N₂ gas at 80 °C and that the reaction between [P₆₆₆₁₄][2-CNPyr] is completely reversible for at least 3 cycles. Based on these results, we do not expect any significant capacity degradation for operation between room temperature and 80 °C.

Viscosity. Viscosity measurements of both pure and CO₂-saturated ILs were performed at temperatures ranging from 10 to 70 °C under 1 bar of N₂ and CO₂ gas, respectively. Figure 4 summarizes the viscosity of neat AHA ILs as a function of temperature in logarithmic scale. The temperature dependence of the viscosity is described by the empirical Vogel–Fulcher–Tamman (VFT) model and the fitting parameters are available in the Supporting Information. The viscosity of neat AHA ILs decreased in the order [6-BrBnIm][−] > [BnIm][−] > [2-SCH₃BnIm][−] > [4-Triaz][−] > [3-Triaz][−] > [3-CH₃-5-CF₃Pyr][−].

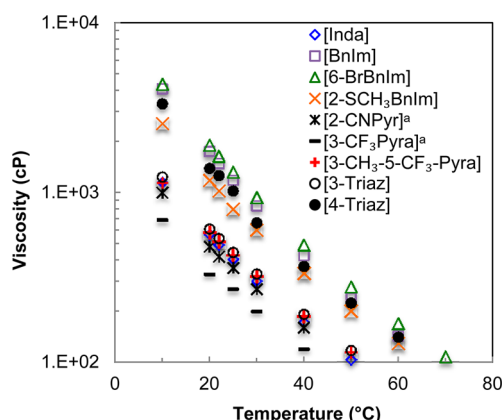


Figure 4. Viscosity of AHA ILs as a function of temperature. ^aFrom Gurkan et al.³¹

> [Inda][−] > [2-CNPyra][−] > [3-CF₃Pyra][−]. Although the viscosity can be as high as 1635 cP ([P₆₆₆₁₄][6-BrBnIm]) at room temperature, it decreases exponentially with increasing temperature and the viscosities of all AHA ILs in this study are below 300 cP at 50 °C. AHAs with one 5-membered heterocyclic ring exhibited lower viscosity compared to the AHAs with polycyclic systems. The bulkiness and added molecular weight of the polycyclic systems contributes to increased viscosity, which is a trend prominent in the field of polymers.⁶⁸

Figure 5 compares the viscosity of seven newly synthesized AHA ILs (plus [P₆₆₆₁₄][2-CNPyra] and [P₆₆₆₁₄][3-CF₃Pyra])³¹

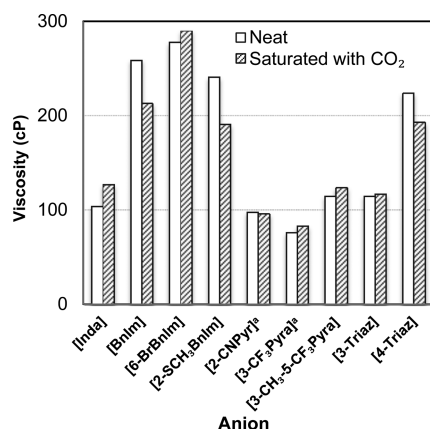


Figure 5. Viscosity of AHA ILs at typical flue gas temperature, 50 °C: before (white) and after (gray) CO₂ absorption. ^aFrom Gurkan et al.³¹

before and after CO₂ absorption. A temperature of 50 °C is chosen to represent the typical flue gas temperature from coal-burning power plants after the desulfurization unit. The AHA ILs in this study did not exhibit any significant viscosity increase after they were fully saturated with CO₂, as reported previously for other ILs with AHAs.³¹ Slight differences in the viscosities of the neat and CO₂-saturated samples are likely due to small variations in the water content. Note that the samples that were saturated with CO₂ at room temperature were then cooled for the first viscosity measurement at 10 °C, and then heated to 70 °C. Upon heating, some of the CO₂ will desorb so the actual CO₂ loading will slightly decrease with increasing temperature above 22 °C. While ILs with amine-functionality on the anion that have been published previously successfully achieved

equimolar absorption of CO₂, such ILs appeared to be impractical for CO₂ capture application due to dramatic increases in viscosity upon addition of CO₂.^{21,25,26} Gutowski et al. attributed the large viscosity increase to the formation of pervasive salt bridge hydrogen-bonded networks connecting product carbamate and ammonium species.²⁷ The key to eliminating large viscosity increases while maintaining equal molar capacity of CO₂ was to constrain the amine functionality in a ring structure. An aprotic ring structure translates to a reduced number of free hydrogens that are amenable for the aforementioned hydrogen-bonding network. Wu et al.⁵⁸ have recently performed molecular dynamics simulations to probe the viscosity of the pyrrolide-based IL in combination with CO₂ and concluded that the ion translational and rotational dynamics are essentially insensitive to the reaction with CO₂ and that there is only infinitesimal change in hydrogen-bonding between the unreacted and reacted IL. Such observation is entirely consistent with the experimental results.

Effect of Water. Among the phosphonium AHAs examined so far, we believe [P₆₆₆₁₄][2-CNPyra] is a possible candidate IL for CO₂ capture due to its high CO₂ capacity (0.92 mol CO₂/IL under 1 bar CO₂ at room temperature), moderate reaction enthalpy (−45 kJ mol^{−1}, calorimetry), excellent reversibility (Figure 3), relatively low viscosity (<100 cP at 50 °C) and good thermal stability (*T*_{onset} > 300 °C).³¹ In addition, recent studies show that [P₆₆₆₁₄][2-CNPyra] has superior reaction rates with CO₂ over [P₆₆₆₁₄][3-CF₃Pyra] or even aqueous amines and that CO₂ absorption by [P₆₆₆₁₄][2-CNPyra] takes place virtually instantaneously under absorber and desorber conditions.⁶⁹ Hence, investigations with water have been performed for [P₆₆₆₁₄][2-CNPyra] and [P₆₆₆₁₄][2-CNPyra] saturated with CO₂.

Initially, the solubility of water in the IL was determined by adding deionized water to [P₆₆₆₁₄][2-CNPyra] until a liquid–liquid phase split occurred. The solubility of water in the IL was roughly 5 wt %, or a mole fraction of 0.6, at 22 °C. Then, a series of water–IL mixtures below the saturation limit (<5 wt %) were prepared by adding deionized water to [P₆₆₆₁₄][2-CNPyra], and then the CO₂ solubility in each mixture was measured (see Figure 6). Previously, we have reported that the presence of water in trihexyl(tetradecyl)phosphonium proline ([P₆₆₆₁₄][Pro]) reduced its CO₂ molar capacity,²⁵ presumably due to reprotonation of the anion.³⁷ In contrast, the solubility of CO₂ in [P₆₆₆₁₄][2-CNPyra] increased slightly and the slope of the isotherm was altered significantly in the presence of water.

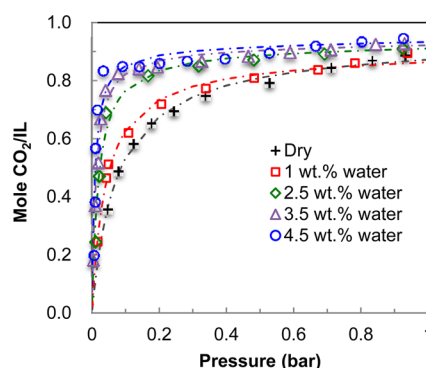
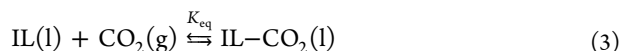


Figure 6. CO₂ capacity of [P₆₆₆₁₄][2-CNPyra] at 22 °C: pure (squares),³¹ with 1 wt % water (pluses), with 2.4 wt % water (diamonds), with 3.5 wt % water (triangles), and with 4.5 wt % water (circles).

Phenolate ILs also demonstrate a modest increase in CO₂ capacity with the addition of water,³⁰ but such dramatic change in the shape of the isotherm has not been reported previously. Wang et al. attributed the increase in CO₂ solubility for phenolate IL + water systems to bicarbonate formation.³⁰ While bicarbonate formation from CO₂ and water is conceivable, the amount of bicarbonate formed is not expected to be prevalent enough at such low partial pressures of CO₂ to substantiate the results displayed in Figure 6. Another possible explanation for enhanced CO₂ solubility could be changes in the activity of the IL-CO₂ complex upon addition of water. The reaction between the IL and the CO₂ to form an IL-CO₂ complex can be described by an equilibrium constant:



$$K_{\text{eq}} = \frac{a_{\text{IL-CO}_2}}{a_{\text{IL}}a_{\text{CO}_2}} = \frac{x_{\text{IL-CO}_2}\gamma_{\text{IL-CO}_2}}{(x_{\text{IL}}\gamma_{\text{IL}})(\phi_{\text{CO}_2}P_{\text{CO}_2})} \quad (4)$$

where a is activity, x is the mole fraction of each species, and γ is the activity coefficient, which accounts for the nonideality of the liquid phase. The fugacity coefficient, ϕ , accounts for the nonideality of the gas phase, but it is close to unity when the pressure is not sufficiently high (as is the case here). If the liquid phase is assumed to behave ideally such that activity coefficients for both IL and IL-CO₂ complex are unity ($\gamma_{\text{IL}} = \gamma_{\text{IL-CO}_2} = 1$), then the equilibrium conversion to IL-CO₂ complex, is essentially determined by the fugacity or partial pressure of CO₂ ($\phi_{\text{CO}_2}P_{\text{CO}_2} \approx P_{\text{CO}_2}$). If the liquid phase is actually nonideal (γ_{IL} and $\gamma_{\text{IL-CO}_2} \neq 1$), on the other hand, the mole fraction of IL-CO₂ ($x_{\text{IL-CO}_2}$) could change dramatically to compensate for changes in γ_{IL} and $\gamma_{\text{IL-CO}_2}$ at a given temperature (and equilibrium constant) when water is added. This argument is the same as mentioned earlier in the discussion of the quantum chemical calculations of reaction enthalpy; the solvation energy of the anion-CO₂ complex may be different than that of the anion. In this case, the differences are most evident in the interaction of the anion and the anion-CO₂ complex with water. Specifically, molecular simulations have discovered that small amounts of water strongly solvate the CO₂ reacted [2-CNPyr][−] anion by forming hydrogen bonds with the COO[−] group and that water has much stronger associations with the reacted anion compared to those of the unreacted one.⁵⁸ Hence, the presence of water in the liquid mixture would likely lower $\gamma_{\text{IL-CO}_2}$, more than γ_{IL} , which would increase the amount of the CO₂-IL complex present in order to maintain phase and reaction equilibrium. Further investigation of these possibilities is in progress. The CO₂ saturated [P₆₆₆₁₄][2-CNPyr]·H₂O mixture was regenerated by purging with nitrogen gas at 80 °C, and both ¹H NMR spectra and the CO₂ uptake isotherm (available in the Supporting Information) confirmed that the IL-CO₂ reaction in the presence of water is fully reversible.

The effect of water on the viscosity of both pure IL and IL-CO₂ complex is demonstrated in Figure 7. When 3 wt % of deionized water was added to pure [P₆₆₆₁₄][2-CNPyr], the viscosity at room temperature was reduced almost 2-fold, which is consistent with the trends displayed by previously studied ILs.^{25,36,43} The solvating water molecules appear to reduce the electrostatic attractions between the ions so that the overall cohesive energy of the system is lowered.³⁶ However, once the sample with water was exposed to 1 bar of CO₂, the viscosity increased dramatically (diamonds in Figure 7). The increase in

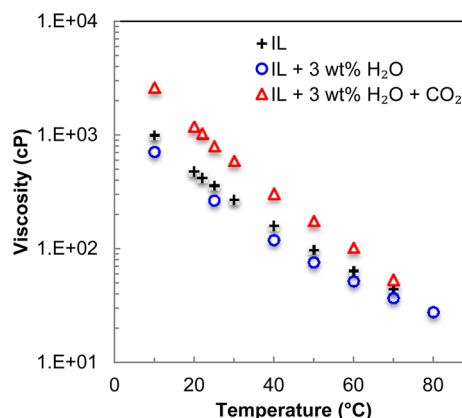


Figure 7. Viscosity of [P₆₆₆₁₄][2-CNPyr] as a function of temperature: pure IL (crosses),³¹ IL with 3 wt % water (circles), and IL with 3 wt % water after CO₂ absorption (triangles).

viscosity after CO₂ absorption in wet [P₆₆₆₁₄][2-CNPyr] could be due to formation of a pervasive network of hydrogen bonding bridges between the carbamate product and water molecules. We believe the water is providing the hydrogen-bonding that we eliminated with the choice of AHA anions. Additional water after equimolar ratio of water to IL eventually decreases the viscosity. This interesting behavior is under further investigation.

Not only does the presence of water in the IL phase significantly affect physical properties like viscosity, it has a potential to make a considerable impact on the CO₂ capture chemistry. As mentioned above, it has been reported that the CO₂ capacity of [P₆₆₆₁₄][Pro] suffered from the protonation of the anion when water was present, eventually inactivating the anion's ability to bind with CO₂.^{25,37} The CO₂ capacity of [P₆₆₆₁₄][2-CNPyr] increases with added water, which is in contrast to the CO₂ capacity of [P₆₆₆₁₄][Pro], which decreases with increasing water concentration. Nonetheless, in order to examine the possibility of deprotonation of [P₆₆₆₁₄][2-CNPyr] in the presence of water, the IL was mixed with an excess of water at room temperature so that two-phase liquid-liquid equilibrium (LLE) existed and the phases sampled for analysis. This was repeated after having saturated the system with CO₂ at room temperature and 1 bar CO₂. NMR analysis was conducted by comparing the ¹H NMR spectra of the pure [P₆₆₆₁₄][2-CNPyr], the neutral protonated-heterocyclic anion (2-cyanopyrrole), the dry IL after saturation with CO₂, the IL-rich phase from the IL/water LLE experiment, and the IL-rich phase from the IL/water/CO₂ LLE experiment (details in the Supporting Information). Dilution in the NMR solvents did not appear to change the species present. Guided by the differences in chemical shifts that are characteristic to each species in each part of these processes and by the integrals that provide the relative numbers of chemically distinct hydrogens of each species, it was possible to conclude that [P₆₆₆₁₄][2-CNPyr] did not undergo protonation at the anionic heterocyclic moiety while mixed only with water nor when mixed with water and saturated with CO₂. This was corroborated by comparing the ¹H NMR chemical shifts of the protonated-heterocyclic anion with the chemical shifts of aqueous phase after splitting. Thus, we conclude that at the conditions investigated [P₆₆₆₁₄][2-CNPyr] does not suffer from the anion reprotonation in the presence of water and CO₂, which has plagued amino acid based ILs.^{25,37}

■ CONCLUDING REMARKS

The ideal CO₂ sorbent for postcombustion capture process should involve a simple and reversible reaction with chemical handles that introduce tunability into the strength of binding, while the viscosity remains unchanged. In this context, aprotic heterocyclic anions, or AHAs, offer a highly versatile and tunable platform for the development of postcombustion CO₂ capture media. In this work, a series of AHAs paired with a phosphonium-based cation were investigated as potential absorbents for CO₂ capture from postcombustion flue gas. These ILs showed a low glass transition temperatures in the range of −68 to −79 °C and high thermal decomposition temperatures in the range of 260 to 327 °C under a nitrogen atmosphere. A significant part of the operating cost is the energy required in the regeneration step so the ability to control the binding energy between the AHA ILs and CO₂ has been investigated. The IL-CO₂ equilibrium at pressures between 0 and 1 bar suggests a much wider range of tunability of binding energy than is generally possible with conventional aqueous amines. The viscosity was insensitive to reaction with CO₂, which is in stark contrast to most task-specific ILs that have been investigated for CO₂ capture previously. The presence of water in [P₆₆₆₁₄][2-CNPyrr] did not seem to be problematic since its CO₂ capacity remained high (close to a 1:1 molar ratio) in the presence of water, and no reprotonation of the anion was observed, as determined by NMR spectroscopy. While the ability to tune the enthalpy of binding of AHA ILs with CO₂ suggests options to reduce the energy demand for CO₂ capture, challenges still remain in understanding the effect of water on the viscosity of IL-CO₂ complexes.

■ ASSOCIATED CONTENT

■ Supporting Information

Details on the NMR characterization for each IL synthesized along with the compositional analysis of the [P₆₆₆₁₄][2-CNPyrr]/H₂O and [P₆₆₆₁₄][2-CNPyrr]/H₂O/CO₂ systems. All density, viscosity, and CO₂ uptake data are available in tabular form. In addition, optimized geometries of the anion-CO₂ complexes from electronic structure calculations are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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