

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231667338>

Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO₂ Capture

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · DECEMBER 2010

Impact Factor: 7.46 · DOI: 10.1021/jz101533k

CITATIONS

100

READS

231

13 AUTHORS, INCLUDING:



Edward J Maginn

University of Notre Dame

204 PUBLICATIONS 9,468 CITATIONS

SEE PROFILE



William F Schneider

University of Notre Dame

205 PUBLICATIONS 4,388 CITATIONS

SEE PROFILE

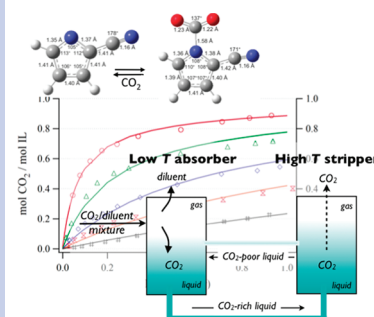
Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO₂ Capture

B. Gurkan,[†] B. F. Goodrich,[†] E. M. Mindrup,[†] L. E. Ficke,[†] M. Massel,[†] S. Seo,[†] T. P. Senftle,[†] H. Wu,[†] M. F. Glaser,[†] J. K. Shah,[†] E. J. Maginn,^{*,†} J. F. Brennecke,^{*,†} and W. F. Schneider^{*,†,‡}

[†]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States, and [‡]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

ABSTRACT The discovery of materials that combine selectively, controllably, and reversibly with CO₂ is a key challenge for realizing practical carbon capture from flue gas and other point sources. We report the design of ionic liquids (ILs) with properties tailored to this CO₂ separation problem. Atomistic simulations predict that suitably substituted aprotic heterocyclic anions, or “AHAs,” bind CO₂ with energies that can be controlled over a wide range suitable to gas separations. Further, unlike all previously known CO₂-binding ILs, the AHA IL viscosity is predicted to be insensitive to CO₂. Spectroscopic, temperature-dependent absorption, rheological, and calorimetric measurements on trihexyl(tetradecyl)-phosphonium 2-cyanopyrrolide ([P₆₆₆₁₄][2-CNpyr]) show CO₂ uptakes close to prediction as well as insignificant changes in viscosity in the presence of CO₂. A pyrazolide-based AHA IL behaves qualitatively similarly but with weaker binding energy. The results demonstrate the intrinsic design advantages of ILs as a platform for CO₂ separations.

SECTION Atmospheric, Environmental and Green Chemistry



The atmospheric concentration of CO₂ has increased unabated since the dawn of the industrial revolution, due primarily to CO₂ emissions from the combustion of fossil fuels, and this growing carbon burden has significant implications for the global climate.¹ While the development of a carbon-neutral energy infrastructure is the long-term solution to this problem, the increasing world demand for energy and the ready availability of fossil fuels—in particular coal—make it highly likely that fossil fuel combustion will continue to be a substantial fraction of the energy portfolio for the foreseeable future.² In this environment, alternative approaches to managing CO₂ emissions become essential.³

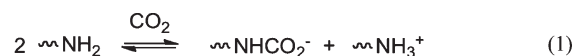
For coal-fired power plants and other point source emitters, postcombustion carbon capture is the most straightforward and promising route to limiting CO₂ release, but practical carbon capture depends on the discovery of energy-efficient means of separating CO₂ from the other gaseous components of a flue gas.⁴ For example, a typical 500 MW coal-fired power plant produces on the order of 22 kmol s⁻¹ of flue gas containing ~15% CO₂ in N₂, O₂, H₂O and other trace gases at near ambient temperature and pressure.⁵ Separating CO₂ from this stream is estimated to consume more than 30% of the power of the plant using presently available amine absorption technologies, far above the theoretical minimum work of separation.⁵

In absorption-based separations, CO₂ selectively dissolves into a liquid-phase absorbent from the flue gas mixture; a CO₂-enriched stream is subsequently recovered either by vacuum or thermal desorption. Figure 1 illustrates schematically how the pressure- and temperature-dependent solubility of CO₂ in an absorbing liquid can be exploited to effect a separation. The

energy cost to drive this cycle is closely tied to CO₂-absorbent equilibria, as embodied in the CO₂–liquid isotherms, and means to control these isotherms are thus highly desirable.

In addition to the properties specific to the CO₂-absorbent solubility, the ideal liquid will absorb CO₂ rapidly and reversibly and will have physical characteristics (high thermal stability, low volatility, low viscosity, low heat capacity) well suited to the separation process. Ionic liquids (ILs)—low-melting and virtually nonvolatile salts of bulky cations and anions—are an ideal platform for developing absorbents with these characteristics.^{6–9} An essentially limitless number of ILs can be envisioned, and the challenge is to navigate this very large design space to identify optimal materials. We report here a molecular-simulation-driven design of new IL classes specifically tailored to the CO₂ separation problem.

Common ILs are intrinsically selective for CO₂ over O₂ and N₂, but the physical solubility of CO₂ is modest and insufficient for flue-gas separations.¹⁰ The most common approach to separating CO₂ from dilute gas streams involves selective and reversible reaction with aqueous amines:⁵



Initial attempts to increase the capacity of ILs for CO₂ involved tethering primary amine functionality to the IL

Received Date: November 11, 2010

Accepted Date: November 29, 2010

Published on Web Date: December 03, 2010

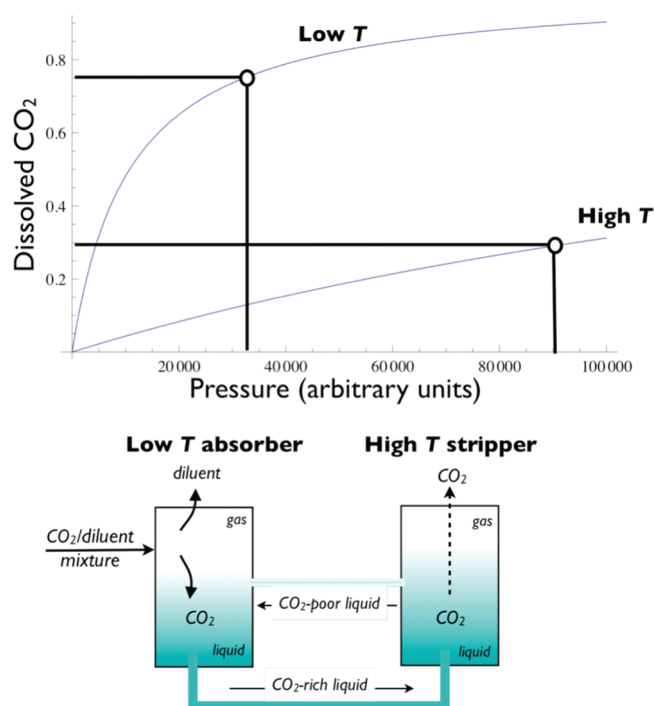


Figure 1. Absorption-based gas separation. Top: Isotherms relate partial pressure, temperature, and equilibrium concentration in an absorbing liquid that reacts selectively with CO₂. Bottom: In a temperature-swing separation, the gas mixture is contacted with a cool, CO₂-poor liquid, and the CO₂ selectively dissolves into the liquid phase up to a concentration dictated by the solubility isotherm; the diluent gases do not dissolve substantially in the absorbent and are emitted to the atmosphere. Raising the temperature of the CO₂-laden liquid lowers the CO₂ solubility, and gas desorbs down to a concentration consistent with the higher temperature isotherm. The desorbed CO₂ is captured for subsequent sequestration.

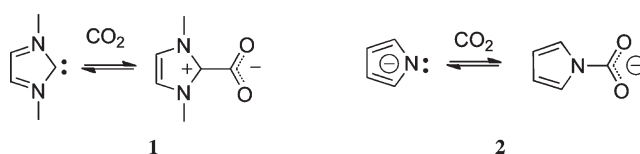
cation.^{11–15} These functionalized ILs do indeed combine stoichiometrically and reversibly with CO₂ in a 2 amine:1 CO₂ proportion, but with large and generally undesirable increases in the liquid viscosity. Our atomistic molecular dynamics (MD) simulations trace this large viscosity increase to the formation of a pervasive salt bridge network connecting product carbamate and ammonium species.¹⁶ Computed ion rotational relaxation times increase by 2–3 orders of magnitude, translational dynamics are greatly reduced, and radial distribution functions show the formation of a gel-like network.¹⁶ We have recently shown that the stoichiometry of reaction between IL and CO₂ can be increased to nearly 1:1 simply by tethering the primary amine to the IL anion rather than the cation,^{17,18} effectively doubling the molar efficiency of the separation:



Nonetheless, the viscosity changes remain, and systematic improvement of these materials remains illusive.

These attempts to create chemically selective ILs fail to take advantage of the intrinsic nucleophilicity of the anion functionality. We reasoned that, by integrating the anion and CO₂ reaction functions, we could create a more atom-efficient

absorbent material. Further, to eliminate the viscosity changes, the ideal reaction should not create acidic protons. Most common IL anions (BF₄[−], NO₃[−], etc.) are too weakly nucleophilic to combine directly with CO₂. However, *N*-heterocyclic carbenes (**1**) have been reported to reversibly form carboxylate adducts with CO₂,¹⁹ suggesting that the isoelectronic *N*-heterocyclic anions might be capable of the same chemistry:



Further, the pyrrolide (**2**) is effectively a tertiary amine, eliminating protons from the CO₂ capture chemistry. To our knowledge, these pyrrolide-based ILs and their reactions with CO₂ are unknown.

To test this idea, we first used molecular electronic structure calculations at the *G3* level²⁰ to compute the structure and energetics of the pyrrolide and its CO₂ reaction product (details in the Supporting Information). The pyrrolide anion itself is planar and aromatic.²¹ As shown in Figure 2a, it is calculated to combine with CO₂ through the N center to form a carbamate anion analogous to the carbene carboxylate. The planarity of the carbamate product and 39 kJ mol^{−1} rotational energy barrier are both indicative of π conjugation that extends across the N–C bond.²² The −109 kJ mol^{−1} computed 298 K reaction enthalpy indicates strong affinity for CO₂—greater than that, for instance, of the aqueous amines.²³ Further, the evident σ and π electronic communication between CO₂ and pyrrolide suggests that the ring–CO₂ bond energy should be sensitive to ring substitutions. We explored a large number of substituted pyrroles and found a strong effect on binding energies arising from a combination of inductive, π conjugation, and steric effects. The cyano-substituted compounds are representative: 3-substituted cyanopyrrolide (Figure 2b) forms a similar carbamate with CO₂ but with reaction enthalpy increased by 39 kJ mol^{−1}; substitution in the 2 position introduces steric interference between N and CO₂ that raises the reaction enthalpy 21 kJ mol^{−1} further, to −49 kJ mol^{−1}. These results suggest a much wider range of tunability of the reaction enthalpy than is generally possible with the aqueous amines. Further, these absorption energies are in a window well suited to separations, between those normally associated with physically dissolved (−12 kJ mol^{−1})¹⁰ and chemically bound (−80 kJ mol^{−1}) CO₂.²³

To probe the viscosity of the pyrrolide-based IL in combination with CO₂, MD simulations were carried out for an IL comprised of 2-cyanopyrrolide anions paired with tetrabutylphosphonium cations. A classical force field for the unreacted and reacted form of the anion (Figure 2c) was developed using a combination of electronic structure calculations and parameters from the generalized Amber force field.²⁴ MD simulations were carried out for the neat unreacted IL and for mixtures representing 25–100% extent of reaction. In contrast to the primary-amine-containing IL,¹⁶ the simulations show that the ion translational and rotational dynamics are

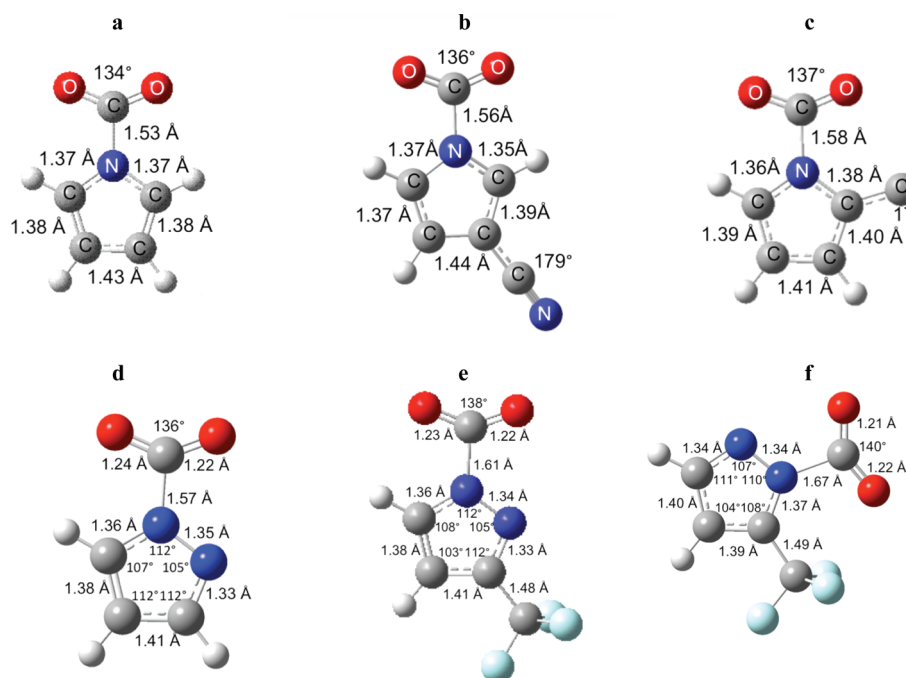


Figure 2. Computed products of CO_2 reaction with aprotic heterocyclic anions (AHAs). G3-level geometry optimizations show that CO_2 binds to pyrrolide N-heteroatom a. CO_2 binds with slightly modified geometry and decreased binding energy upon cyano substitution in the 3- (b) or 2- (c) positions on the pyrrolide ring. Binding at a pyrazolide anion d is calculated to be about 30 kJ mol^{-1} weaker than the pyrrolide. CF_3 -substitution on the pyrazolide creates two inequivalent CO_2 binding sites, with the 1,3 substitution pattern e calculated to be 27 kJ mol^{-1} more strongly bound than the 1,2 pattern f.

essentially insensitive to reaction with CO_2 . For example, the simulations predict the bulky phosphonium cation and cyanopyrrolide anion in the unreacted IL to have a rotational time constants of 1.4 and 0.5 ns, respectively, at 333 K. Converting 100% of the anions to the CO_2 -reacted form increases the cation rotational time constant to 1.7 ns while leaving the anion rotational dynamics virtually unchanged. The liquid structure in unreacted and CO_2 -reacted states are also very similar; hydrogen bonding analysis and pair distribution functions show little change between the two. These simulations strongly suggest that the viscosity of pyrrolide-based ILs will be insensitive to reaction with CO_2 .

On the basis of these findings, we synthesized trihexyl-(tetradecyl)phosphonium 2-cyanopyrrolide ($[\text{P}_{66614}][2\text{-CNpyr}]$) by condensation of the phosphonium hydroxide with the protonated 2-cyanopyrrole and subsequent drying. Details can be found in the Supporting Information. We chose an asymmetric phosphonium cation rather than the tetrabutyl version used in the simulations to increase the likelihood that the IL would be liquid at room temperature. The product is, in fact, a stable room-temperature IL; NMR analysis (see Supporting Information) confirms its chemical identity. We exposed this IL at 22°C to CO_2 gas in an in situ infrared spectrometer (Figure 3); results clearly indicate the formation of a chemically bound carbonate at lower pressure and additional physically absorbed CO_2 at higher pressures. Upon application of vacuum, the carbamate asymmetric stretch disappears, and the original spectrum is restored. These results are all consistent with a 1:1 and reversible reaction between $[2\text{-CNpyr}]^-$ and CO_2 .

As shown in Figure 4a, the viscosity of $[\text{P}_{66614}][2\text{-CNpyr}]$ before exposure to CO_2 is less than 100 cP at typical flue-gas temperatures (approximately 50°C) and, as expected, decreases with increasing temperature. More remarkably, the viscosity measured under 1 bar of CO_2 atmosphere is nearly identical to the unreacted form. This behavior stands in stark contrast to all previously reported CO_2 -complexing ILs.^{13,15,25} $[\text{P}_{66614}][\text{Isoleucinate}]$, a primary amine-functionalized IL, is representative: its viscosity increases over 200-fold when exposed to 1 bar of CO_2 ,²⁵ to a level much too large for the material to be useful in a liquid absorber/stripper such as the one shown in Figure 1. In fact, previous efforts to apply reactive ILs for CO_2 capture have focused on fixing the ILs to a solid support.^{12,13} $[\text{P}_{66614}][2\text{-CNpyr}]$ is the first reported IL with both CO_2 affinity and flow characteristics suitable for flue gas CO_2 separations.

Isotherms measured at temperatures from 22 to 100°C are shown in Figure 4b. The steep initial slopes reflect chemical reaction between CO_2 and the IL; gradual slopes at higher pressure reflect the contributions of weaker physical absorption. The uptake approaches 1 mol CO_2 per mole $[\text{P}_{66614}][2\text{-CNpyr}]$ at the highest pressures and lowest temperatures shown, consistent with a 1:1 reaction stoichiometry. At higher pressures (see Supporting Information) the uptake goes above 1 mol CO_2 per mole of IL due to the continued increase in CO_2 physical solubility with increasing pressure. A sample of $[\text{P}_{66614}][2\text{-CNpyr}]$ that was saturated with approximately 6.3 wt % water did not show any diminished capacity per mole of $[\text{P}_{66614}][2\text{-CNpyr}]$ at 22°C . Moreover, the chemical shifts of the protons on the cyanopyrrolide anion when

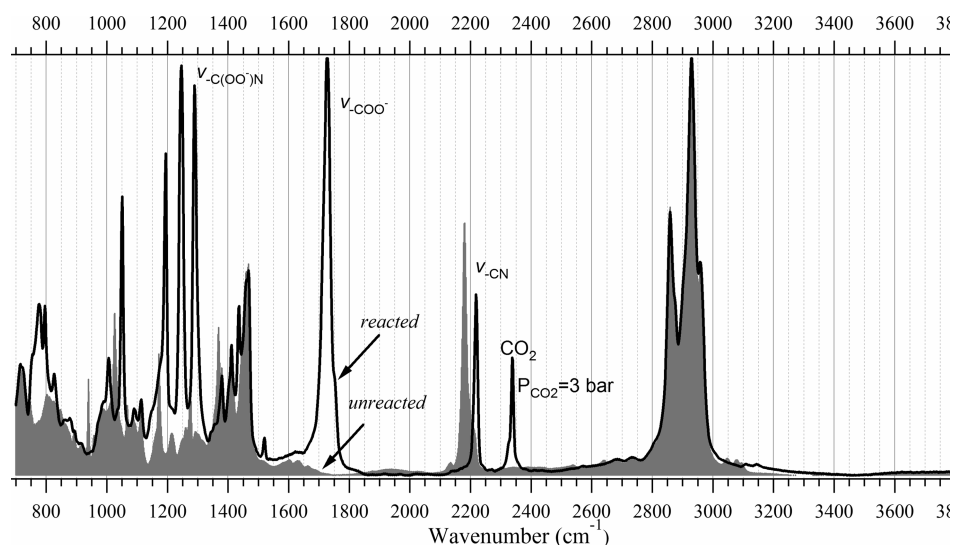
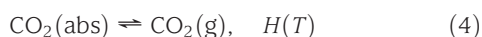


Figure 3. Infrared analysis of 2-CNpyr IL reaction with CO₂. Solid plot shows vibrational spectrum of unreacted [P₆₆₆₁₄][2-CNpyr] at 22 °C. The unreacted compound has a feature at 2183 cm⁻¹ characteristic of the cyano group. After exposure to 1 bar CO₂ (line plot), the cyano band shifts to 2220 cm⁻¹ and prominent features appear at 1728 and 1521 cm⁻¹, indicative of the -NCOO⁻ stretches. These observed features are in excellent agreement with those predicted from the computations for the carbamate (see Supporting Information). At higher CO₂ pressures (> 1 bar), a band due to physically dissolved CO₂ appears between 2370 and 2300 cm⁻¹.

complexed with CO₂ were the same both with and without water present (see Supporting Information), suggesting similar reaction chemistry between the IL and the CO₂ in the presence of water.

A model that incorporates both the stoichiometric reaction and physical uptake nicely fits the isotherm data:



Total CO₂ uptake on a mole ratio basis ($z = n_{\text{CO}_2}/n_{\text{IL}_0}$) is expressed as:

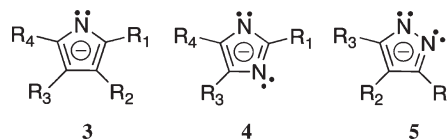
$$z = \frac{P_{\text{CO}_2}/H}{1 - P_{\text{CO}_2}/H} + \frac{k_1 P_{\text{CO}_2} C_3}{1 + k_1 P_{\text{CO}_2}} \quad (5)$$

where P_{CO_2} is the CO₂ pressure in bar, H is Henry's law constant in bar, k_1 is the reaction equilibrium constant, and C_3 is a measure of the reaction site density. We found it convenient to fix the Henry law constant by applying Beer's law to the physical absorption IR band. These values were determined at 22, 40, and 55 °C, and extrapolated to higher temperatures from the linear plot of $\ln H$ versus $1/T$ (K) (Figure 4c). The contribution from the physical dissolution is very small, never reaching more than 3 % of the total uptake.

Reaction enthalpies and entropies can be determined from the temperature-dependence of the equilibrium constants, and the graph for the enthalpies is shown in Figure 4c. The close linearity of the van't Hoff plots lends credence to the model. The -10 kJ mol^{-1} physical uptake enthalpy is consistent with that observed for nonreacting ILs; the chemical reaction enthalpy and entropy referenced to gas-phase CO₂ are found to be -43 kJ mol^{-1} and $-130 \text{ J mol}^{-1} \text{ K}^{-1}$. The latter reflects the nearly complete loss of translational entropy associated with chemical complexation to the IL anion via reaction 3.

Differential calorimetry¹⁷ gives a reaction enthalpy of -53 kJ mol^{-1} , further corroborating the isotherm-derived thermodynamics. The calorimetry depends on the total amount of CO₂ uptake at a given temperature and pressure, which we take from the measured isotherms; we estimate the associated uncertainty to be $\pm 5 \text{ kJ mol}^{-1}$. These two independent measurements are thus in good agreement with one another and with the G3-computed reaction energy for the gas-phase anion (-49 kJ mol^{-1}), and are much less exothermic than the -80 kJ mol^{-1} observed for [P₆₆₆₁₄][Prolinate] with the same method.¹⁷ The very close agreement between the experimental liquid measurements and computed gas-phase reaction enthalpy can be understood by noting that the two differ by the difference in solvation enthalpies of the reactant and product anions (Figure 5), a quantity that is expected to be small for these rather large anions.

[P₆₆₆₁₄][2-CNpyr] thus has both physical and chemical properties superior to any previously reported chemically functionalized ILs for CO₂ separations. This general approach is not limited to the substituted pyrrolides (3): one can reasonably expect similar chemistry for imidazolides (4), pyrazolides (5), or any of many other aprotic heterocyclic anions, or AHAs:



As demonstration of the generality of the approach, we prepared and characterized 3-(trifluoromethyl)pyrazolide ([P₆₆₆₁₄][3-CF₃pyra]) following a similar protocol. Figure 4d compares absorption isotherms of [P₆₆₆₁₄][3-CF₃pyra] with [P₆₆₆₁₄][2-CNpyr] at 22 °C. The two ILs exhibit similar CO₂ uptakes, although the [P₆₆₆₁₄][2-CNpyr] capacity is slightly

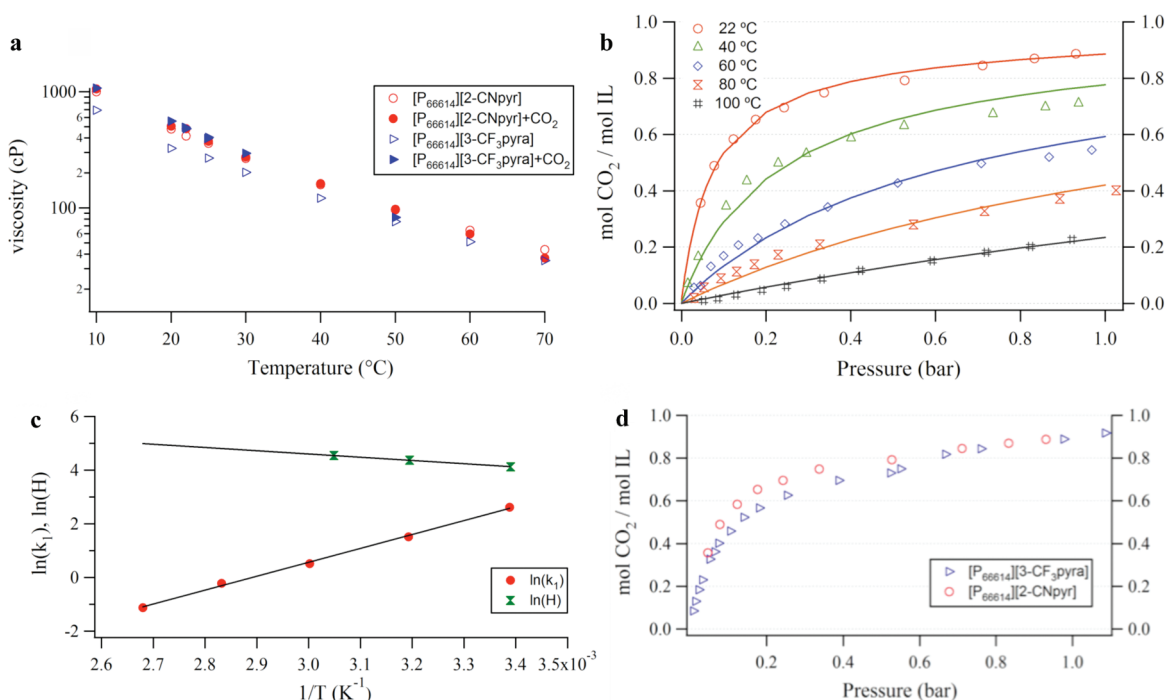


Figure 4. Observed CO₂-uptakes in AHA ILs. (a) Viscosities of [P₆₆₆₁₄][2-CNpyr] and [P₆₆₆₁₄][3-CF₃pyra] are nearly unchanged before and after reaction with CO₂. Viscosities are measured in a closed rheometer under either N₂ or CO₂ (reacted samples). Reacted samples are withdrawn from uptake measurements performed at 22 °C and 1 bar of CO₂. (b) CO₂ uptake capacity of [P₆₆₆₁₄][2-CNpyr] measured in a closed, stirred, variable temperature volumetric absorption cell. Lines indicate fits to a Langmuir-type isotherm model. (c) van't Hoff plots of fitted Henry's law and equilibrium constants for CO₂ with [P₆₆₆₁₄][2-CNpyr]. (d) Comparison of 22 °C absorption isotherms shows [P₆₆₆₁₄][3-CF₃pyra] exhibits slightly lower uptake than [P₆₆₆₁₄][2-CNpyr]. Measurements performed in room-temperature volumetric uptake apparatus.

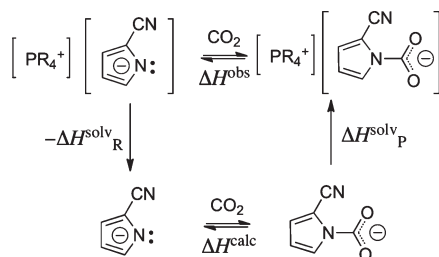


Figure 5. Thermodynamic cycle relating liquid- and gas-phase reaction enthalpies. Experimentally observed absorption enthalpies ΔH^{obs} are related to calculated gas-phase enthalpies ΔH^{calc} by ion solvation and desolvation steps, ΔH^{solv}. While the absolute solvation enthalpies are large, differences between reactant and product solvation are small. Test calculations with implicit solvent or explicit counter cations estimate ΔH^{solv}_P - ΔH^{solv}_R at approximately -5 kJ mol⁻¹.

greater than that of [P₆₆₆₁₄][3-CF₃pyra] at pressures below about 0.75 bar. This difference is consistent with a slightly more positive [P₆₆₆₁₄][3-CF₃pyra] reaction enthalpy with CO₂, measured calorimetrically to be -46 kJ mol⁻¹. The Langmuir-type isotherm model used to fit the [P₆₆₆₁₄][2-CNpyr] data does an equally good job of representing the [P₆₆₆₁₄][3-CF₃pyra] data. Like [P₆₆₆₁₄][2-CNpyr], [P₆₆₆₁₄][3-CF₃pyra] shows no measurable increase in viscosity when fully complexed with CO₂ at 1 bar pressure (Figure 4a).

The [3-CF₃pyra]⁻ anion offers two distinct CO₂ binding sites. The 1,3-substituted product (Figure 2e) is more stable and forms with a 298 K G3 reaction enthalpy of -54 kJ mol⁻¹,

while the more sterically congested 2,3-substituted product (Figure 2f) binds a more modest -28 kJ mol⁻¹. Both likely contribute to the observed uptake and account for the net weaker absorption energy than observed with [2-CNpyr].

In summary, we have used a computational molecular design approach to identify a new class of ILs based on the AHAs, which experiments show to react stoichiometrically and reversibly with CO₂ and to not suffer the large viscosity increases that have plagued previous attempts to create CO₂-complexing ILs. The AHA platform provides a number of chemical handles for tuning CO₂ binding. The results are a promising step forward in the search for energy-optimal carbon capture materials.

SUPPORTING INFORMATION AVAILABLE Complete description of electronic structure simulations, molecular dynamics simulations, synthesis, characterization, and capacity measurement results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: ed@nd.edu (E.J.M.); jfb@nd.edu (J.F.B.); wschneider@nd.edu (W.F.S.).

ACKNOWLEDGMENT This material is based upon work supported by the Department of Energy under Award Number DE-FC-07NT43091.

REFERENCES

- (1) Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K. B.; Tignor, M.; Miller, H. L. *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007*; Cambridge University Press: Cambridge, U.K., 2007.
- (2) *Annual Energy Outlook 2010*; Department of Energy/EIA: Washington, DC, 2010.
- (3) White, C. M.; Strazisar, B. R.; Granite, E. J.; Hoffman, J. S.; Pennline, H. W. Separation and Capture of CO₂ from Large Stationary Sources and Sequestration in Geological Formations—Coalbeds and Deep Saline Aquifers. *J. Air Waste Manage. Assoc.* **2003**, *53*, 645–715.
- (4) Herzog, H. J. What Future for Carbon Capture and Sequestration? *Environ. Sci. Technol.* **2001**, *35*, 148A–153A.
- (5) Rochelle, G. T. Amine Scrubbing for CO₂ Capture. *Science* **2009**, *325*, 1652–1654.
- (6) Sheldon, R. A. Green Solvents for Sustainable Organic Synthesis: State of the Art. *Green Chem.* **2005**, *7*, 267–278.
- (7) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water. *J. Phys. Chem. B* **2001**, *105*, 10942–10949.
- (8) Baltus, R. E.; Counce, R. M.; Culbertson, B. H.; Luo, H.; DePaoli, D. W.; Dai, S.; Duckworth, D. C. Examination of the Potential of Ionic Liquids for Gas Separations. *Sep. Sci. Technol.* **2005**, *40*, 525–541.
- (9) Huang, J.; Rüther, T. Why are Ionic Liquids Attractive for CO₂ Absorption? An Overview. *Aust. J. Chem.* **2009**, *62*, 298–308.
- (10) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.
- (11) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO₂ Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
- (12) Ohno, H.; Fukumoto, K. Amino Acid Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1122–1129.
- (13) Zhang, J.; Zhang, S.; Dong, K.; Zhang, Y.; Shen, Y.; Lv, X. Supported Absorption of CO₂ by Tetrabutylphosphonium Amino Acid Ionic Liquids. *Chem.—Eur. J.* **2006**, *12*, 4021–4026.
- (14) Soutullo, M. D.; Odom, C. I.; Wicker, B. F.; Henderson, C. N.; Stenson, A. C.; Davis, J. H. Reversible CO₂ Capture by Unexpected Plastic-, Resin-, and Gel-like Ionic Soft Materials Discovered during the Combi-Click Generation of a TSIL Library. *Chem. Mater.* **2007**, *19*, 3581–3583.
- (15) Zhang, Y. Q.; Zhang, S. J.; Lu, X. M.; Zhou, Q.; Fan, W.; Zhang, X. P. Dual Amino-Functionalised Phosphonium Ionic Liquids for CO₂ Capture. *Chem.—Eur. J.* **2009**, *15*, 3003–3011.
- (16) Gutowski, K. E.; Maginn, E. J. Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for the Dramatic Increase in Viscosity upon Complexation with CO₂ from Molecular Simulation. *J. Am. Chem. Soc.* **2008**, *130*, 14690–14704.
- (17) Gurkan, B. E.; de la Fuente, J.; Mindrup, E. M.; Ficke, L. E.; Goodrich, B. F.; Price, E. A.; Schneider, W. F.; Brennecke, J. F. Equimolar CO₂ Absorption by Anion-Functionalized Ionic Liquids. *J. Am. Chem. Soc.* **2010**, *132*, 2116–2117.
- (18) Mindrup, E. M.; Schneider, W. F. Computational Comparison of Tethering Strategies for Amine Functionalized Ionic Liquids. In *Ionic Liquids: From Knowledge to Application*; Seddon, K., Rogers, R., Plechkova, N., Eds.; American Chemical Society: Washington, DC, 2010; pp 419–430.
- (19) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. Reversible Carboxylation of *N*-Heterocyclic Carbenes. *Chem. Commun.* **2004**, *1*, 112–113.
- (20) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. Gaussian-3 (G3) Theory for Molecules Containing First and Second Row Atoms. *J. Chem. Phys.* **1998**, *109*, 7764.
- (21) da Silva, G.; Moore, E. E.; Bozzelli, J. W. Quantum Chemical Study of the Structure and Thermochemistry of the Five-Membered Nitrogen-Containing Heterocycles and Their Anions and Radicals. *J. Phys. Chem. A* **2006**, *110*, 13979–13988.
- (22) Mindrup, E. M.; Schneider, W. F. Computational Comparison of Substituted Amine Reactions with CO₂. *ChemSusChem* **2010**, *3*, 931–938.
- (23) McCann, N.; Maeder, M.; Attalla, M. Simulation of Enthalpy and Capacity of CO₂ Absorption by Aqueous Amine Systems. *Ind. Eng. Chem. Res.* **2008**, *47*, 2002–2009.
- (24) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General AMBER Force Field. *J. Comput. Chem.* **2004**, *25*, 1157–1174.
- (25) Goodrich, B. F.; de la Fuente, J.; Zadigian, D. J.; Price, E. A.; Huang, Y.; Gurkan, B. E.; Brennecke, J. F. Experimental Measurements of Amine-Functionalized Anion-Tethered Ionic Liquids with Carbon Dioxide. *Ind. Eng. Chem. Res.*, DOI: 10.1021/ie101688a.