ACS Sustainable Chemistry & Engineering

pubs.acs.org/journal/ascecg

Research Article

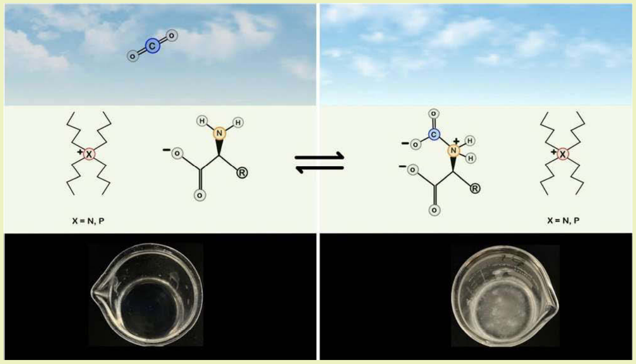
Direct Air Capture of CO_2 via Ionic Liquids Derived from “Waste” Amino Acids

Elizabeth A. Recker, Matthew Green, Mohammad Soltani, Daniel H. Paull, Gregory J. McManus, James H. Davis, Jr,* and Arsalan Mirjafari*

Cite This: https://doi.org/10.1021/acssuschemeng.2c02883

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Direct capture of CO_2 from anthropogenic emissions is an imperative societal task as the concentration of global atmospheric CO_2 continues to increase drastically. The long-term goal of negative emission requires methods to remove carbon directly from the atmosphere, oceanwater, and nonpoint sources. Ionic liquids (ILs) have had a pivotal impact on finding and implementing innovative solutions that enable a more sustainable future. Here, we report the first example of an IL-enabled approach for direct CO_2 capture from the atmosphere on a laboratory scale. These de novo bioderived materials represent an ideal milieu for direct carbon capture applications because of their nonvolatility and a priori low toxicity. Easily prepared liquid salts based on a mixture of three common amino acids, valine, leucine, and isoleucine, were found to be effective sorbents for ready and reversible CO_2 sequestration from air despite its very low concentration. Collectively known as branched-chain amino acid, they are commonly derived from biowaste products, for example, feathers, fur, and even human hair. Therefore, the resultant ILs from the “waste” amino acids provide an exciting prospect in terms of CO_2 transformation and waste utilization. We provided valuable design insights for engineering structure−property relationships in amino acid-based ILs. The impact of moisture on the absorption characteristics and capacity was evaluated in ambient conditions. We postulate that the high capture efficiency and stability of these ILs make them superior to present amine- and alkali-assisted approaches for the direct air capture of CO_2 as a scalable process.

KEYWORDS: *direct air capture, sustainable materials, ionic liquids, CO_2 removal, carbon capture*

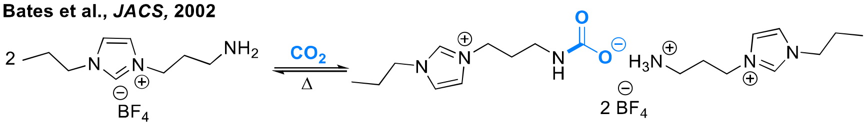
INTRODUCTION

As documented by the Intergovernmental Panel on Climate Change (IPCC), the atmospheric concentration of carbon dioxide has drastically increased from ca. 280 ppm to more than 412 ppm from solely anthropogenic carbon emissions.[1] This phenomenon has already led to unprecedented growth in global temperatures and amplification of the risk of destructive climate disasters[2] and spread of infectious diseases (e.g. cholera, malaria, COVID-19).[3,4] It has been suggested that the CO_2 concentration must be reduced 45% by 2030 to prevent “*rapid and far reaching*” changes to the earth.[5] The CO_2 removal technologies from point sources (i.e. flue gases from coal burning power plants, cement factories, and fermentation plants), which often contain higher CO_2 concentrations (∼10%), have been the primary focus of carbon capture and sequestration approaches.[6] However, practical and economical technologies are needed to capture CO_2 from small distributed sources, viz., cars, home heating, and cooking. That is, capturing CO_2 from air[7] and oceanwater[8] plays a vital role in achieving the net-zero emission goals.

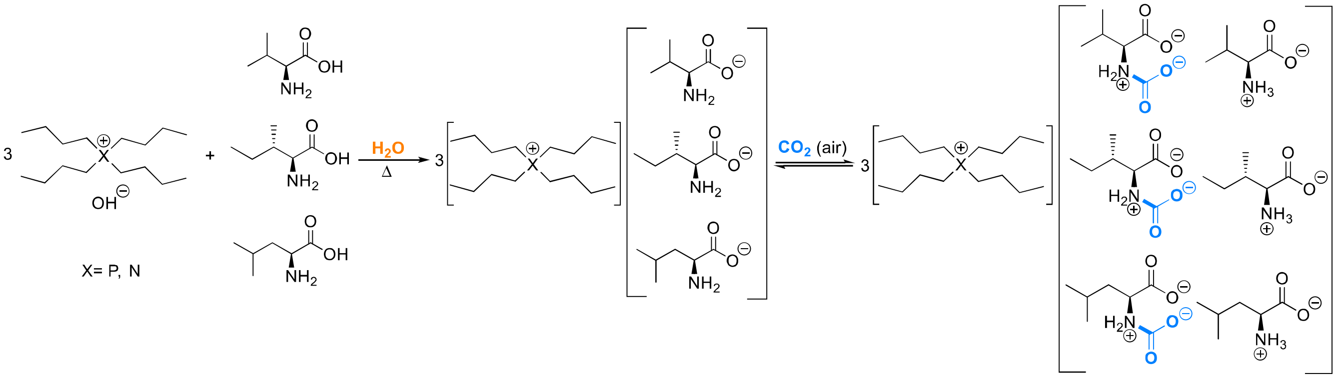
Direct Air Capture (DAC) has attracted momentous attention by offering a practical solution for CO_2 uptake from ambient air on the scale required to fulfill the Paris Agreement.[9] This concept was first introduced by Lackner, aiming to reduce emissions from nonpoint sources and ideally stabilize atmospheric CO_2 levels by closing the carbon cycle and permanently sequestering the captured CO_2.[5] Since then, the potential impact of DAC on climate crisis mitigation has been well described in the recent literature.[10−15] To achieve these goals, DAC technologies must overcome a number of economic and technical hurdles. First, the high thermodynamic barrier due to the low concentration of CO_2 in air (i.e. 412 ppm) mandates that DAC sorbents bind CO_2 effectively and selectively against other atmospheric components, particularly

Received: May 14, 2022
Revised: August 16, 2022

Scheme 1. First Reported Task-Specific IL Designed for CO_2 Capture[25]



Scheme 2. Preparation of Two Amino Acid-derived ILs via Neutralization and the Subsequent Chemisorption of CO_2[a]



[a]The anion is a 2:1:1 mixture of leucine, valine, and isoleucine, respectively.

water as it is usually 10−100 times more abundant in the atmosphere than CO_2. Second, because DAC sorbents need to be produced on a massive scale, the energy and material cost of moving great quantities of air through an absorbing structure are other limiting factors.[16] DAC is still an viable option for carbon sequestration, costing ca. \$100/ton of CO_2 sequestered.[17] Recently, Brethomé et al. reported a cost-effective DAC approach using aqueous solutions of glycine and sarcosine amino acids.[18] The disadvantages of this system are the energy requirement for evaporation of a large amount of water and a poor air−liquid interfacial area relative to the volume of the amino acid sorbent.

With nearly two decades of extensive development, ionic liquids (ILs) are unequivocally versatile materials for carbon sequestration, indicated by a large number of publications focused on technical surveys of IL−CO_2 research.[19−23] ILs have immense possibility in this regard because of their low vapor pressure, chemical stability, and tunability, providing an alternative to currently deployed amines such as monoethanolamine (MEA), a volatile, toxic, and corrosive compound. The key challenges associated with amine scrubbing are the formation of nitrosamines and amine loss, which increase the cost of CO_2 capture and can pose serious health and environmental hazards.[24,25] Exciting IL-enabled approaches/technologies for the chemisorption of CO_2 were introduced by Bates et al.[26] in 2002, as shown in Scheme 1. Since then, the IL systems for carbon capture have evolved substantially in effectiveness and scope, employing naturally occurring amino acids as elements of task-specific ILs for reversible CO_2 capture and have repeatedly been the subject of related studies by our groups[27,28] and others.[29−33] However, despite the wealth of literature, to the best of our knowledge, the development of an IL-enabled DAC strategy has remained limited to only one report.[34]

We previously noted that strategically placed side-chain branching poses a substantial depressive effect on the melting point (T_m) values of ILs in which they are incorporated.[35−37] Encouraged by these results, we speculated that using a mixture of hydrophobic amino acids as the basis for our anions might provide a workable degree of fluidity (viz. reducing melting point and viscosity) on the part of the IL, thus improving the efficiency of the resulting salts to chemisorb CO_2 from air. Thus, systematic evaluation of key components such as the type and ratio of amino acids as well as the selection of cationic backbones led to the discovery of an IL platform that could achieve the DAC objectives. In order to develop an effective, but as likely as possible to be biologically innocuous DAC system, we herein disclose an economical and energy efficient IL-driven strategy for small-scale direct air capture of CO_2, involving a mixture of three branched-chain amino acids (BCAAs) as the environmentally friendly and readily available capturing agents (a 2). These ILs are able to reversibly absorb CO_2 under mild conditions in repeated cycles, presenting promising candidates for negative emission technologies from dilute sources such as atmosphere. Furthermore, the structure−toxicity relationships studies demonstrated that ILs with bioderived anions (e.g. amino acids) and tetrabutylammonium cations with short aliphatic tails (≤C4) are less (eco)toxic toward many strains.[38,39] However, tetrabutylphosphonium ILs exhibit a higher toxicity toward cells/organisms belonging to several trophic levels, which certainly must be considered when assessing these materials for industrial-scale applications.

Compared to the status quo, these ILs offer many advantages such as amine-level reactivity toward CO_2, very low volatility, and high chemical stability, as well as excellent kinetics and good reversibility while utilizing inexpensive and readily available starting materials. Strikingly, mixtures of these three amino acids are produced on very large scales industrially, directly from the processing of keratin that is rich in amino acids and peptides. The keratin, in turn, is sourced from hard-to-degrade biowaste such as feathers, fur, and even human hair, resulting in millions of tons of waste produced each year worldwide.[40] *Consequently, their use in the present application is conceptually tantamount to using one waste product to capture another.*

■ RESULTS AND DISCUSSION

As an extension of our previous studies (vide supra), here, we describe the development of de novo amino acid-derived ILs with a priori low toxicity for direct air capture of CO_2 at ambient conditions. These materials were simply prepared from the neutralization of a mixture of three BCAAs with tetra-*n*-butylphosphonium hydroxide, $[P_{4444}][OH]$, or tetra-*n*-butylammonium hydroxide, $[N_{4444}][OH]$, at various pH conditions (Scheme 2). Their structures were characterized via ^1H, ^{13}C and ^{31}P NMR, and mass spectroscopy. As discussed above, the IL products are composed of a mixture of three BCAAs: leucine (Leu), valine (Val), and isoleucine (Ile) in a 2:1:1 molar ratio, paired with $[N_{4444}]^+$ or $[P_{4444}]^+$ cations. Both organic salts remained as free-flowing liquids at room temperature. Water was selected as the solvent for its biocompatibility and high boiling point. We observed that the ILs with the BCAAs have radically lower T_m and viscosity values than their single amino acid analogs while demonstrating tunability and specific reactivity toward CO_2.

To test the validity of our hypothesis, the thermophysical properties and water content of the new IL products were evaluated. Measured by thermogravimetric analysis (TGA), the thermal decomposition temperature and water content of $[N_{4444}][BCAAs]$ are 156.1 °C and 18.1%, respectively, and those of $[P_{4444}][BCAAs]$ are 260.7 °C and 6.1%, respectively. The ILs showed no visible phase transitions from ordered solids to isotropic liquids (viz. melting point or crystallization), as evidenced by the lack of endothermic/exothermic peaks in the differential scanning calorimetry (DSC) curves, reflecting the broad liquid range associated with the ILs. In fact, this is not an unusual phenomenon for ILs because upon cooling, viscous glassy liquids are formed that resist recrystallization.[41]

Along with T_m, viscosity, a key parameter affecting mass transfer and diffusion, is another fluid characteristic of the ILs in which lower values are favorable for CO_2 capture. Accordingly, the dynamic viscosity, kinetic viscosity, and density of the ILs were measured over the temperature at the range of 20−80 °C at 1 atm (see the SI, Figure S1). The results indicate a viscosity decrease compared to common amino acid ILs with similar structures. For instance, measured $\Delta\eta$ at 65 °C for the $[N_{4444}][BCAAs]$ versus $[N_{4444}][Val]$, $[N_{4444}][Leu]$, and $[N_{4444}][Ile]$ are 103.5, 104.4, and 131.5 mPa s, respectively.[42] In light of this consideration, it seemed worthwhile to employ these ILs to serve as readily made materials with discrete structural differences for DAC. This premise proved to be well-grounded.

The BCAA ILs captured CO_2 initially through the formation of a carbamate intermediate that eventually transitioned into a carbonate/bicarbonate capture mode. During the initial hours of the ambient air exposure, these absorbents effectively scrubbed quantitative amounts of CO_2 from the atmosphere, despite its low concentration. A qualitative ^{13}C NMR study of $[N_{4444}][BCAAs]$ and $[P_{4444}][BCAAs]$ after CO_2 exposure indicates the formation of carbamates when the amount of CO_2 present is <0.5 equiv compared to the IL. For the initial CO_2 uptake performance studies, we prepared various salts containing tetra-*n*-butylammonium and tetra-*n*-butylphosphonium cations with C_1−C_4 side chains and various BCAAs. For the sake of comparison, we made six salts, each with only one of the selected BCAAs, as the anion and measured the overall uptake capacity and uptake kinetics of the salts with individual and mixed BCAAs for a period of three days. Each of the salts participated in absorption, indicated by the formation of carbamate peaks ∼161 ppm in the ^{13}C NMR spectra. We observed significant differences in weight, and gravimetrical measurements were used to quantify the uptake capacity when exposed to ambient air at 1 atm (vide infra). Qualitatively, only two aforementioned ILs with the BCAAs anion exhibited visual cues of CO_2 absorption by transitioning to white solids (Figure 1).

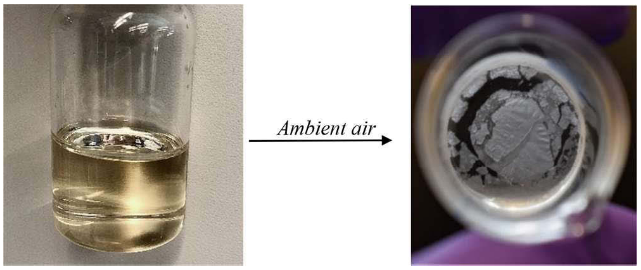


Figure 1. Solidification of the $[P_{4444}][BCAAs]$ before (left) and after (right) ambient air exposure.

The ^{13}C NMR results indicate that CO_2 is captured in a carbamate form, manifested by peaks characteristic of CO_2-adduct anions at 163.8−182.6 ppm, congruent with our previous observations.[28] Following the labeling convention used in our previous work, the numericals represent carboxyl/carboxylate of the amino acids, and "double prime" peaks represent BCAA-carbamate species (Figures 2, S2, and S3). For comparison, the spectra of the pure ILs prior to CO_2 loading are also shown. During the carbon capture, these signals slightly shift in the upfield direction, which is attributed to a pH swing associated with the absorption of CO_2. As CO_2 loading progresses, each peak associated with the BCAAs considerably shifts upfield, ultimately stabilizing on Day 3. Unsurprisingly, during the initial exposure, carbamates are frequently formed, but as transitory species. Because various products can be formed as a function of the extent of CO_2 exposure, we studied prolonged CO_2 exposure, which eventually led to the formation of carbonate/bicarbonate (Day 30) as the predominant capture mode. Higher humidity levels also contributed to the formation of this species as we found that it occurred much more rapidly under wet versus dry conditions (see the SI for a detailed experimental procedure as to how dry conditions were achieved for CO_2 capture experiments). The absorption of CO_2 with $[N_{4444}][BCAAs]$ and $[P_{4444}][BCAAs]$ was further confirmed by FTIR spectroscopy at 25 °C, displaying characteristic peaks of dissolved CO_2 at 2380−2400 cm^{-1} (see the SI, Figure S4).

We measured the overall uptake capacity of the ILs and due to the large differences in weight, gravimetrical measurement was chosen in order to quantify the uptake capacity. A comparison to MEA, a common industrial CO_2 scrubber, was also made to assess the ability of this primary amine to absorb CO_2 in low atmospheric concentration. The surface area of the ILs exposed to ambient air reflects the rate and capacity at which it can absorb CO_2. To maximize the gas/liquid contact area, the ILs were dissolved in dry dichloromethane and dispersed onto a filter paper (it is noteworthy that dichloromethane has no CO_2 uptake capacity and low boiling point, leading to quick evaporation). The molar uptake of CO_2 per mole of IL during the 3 h exposure period approaches 0.5, the theoretical maximum for CO_2 sequestration as carbamate salts

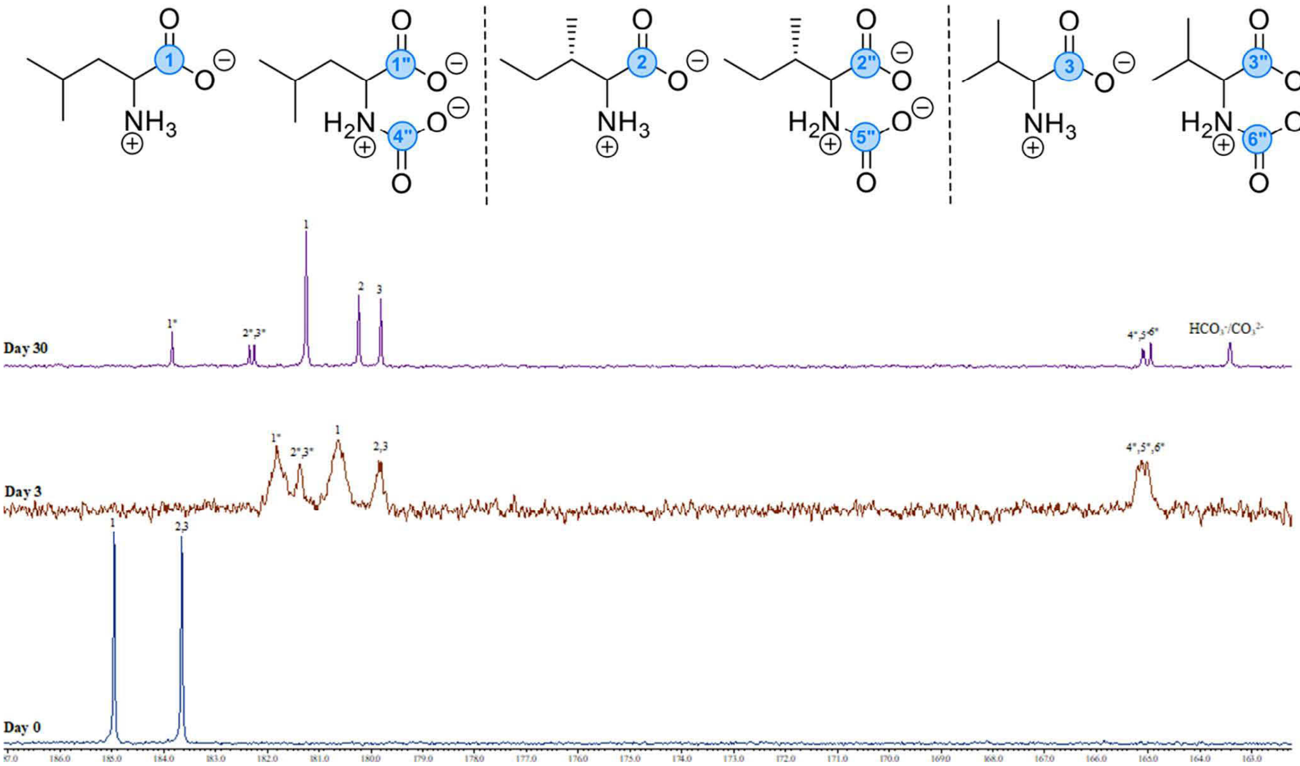


Figure 2. ^{13}C NMR spectra of the $[N_{4444}]$[BCAAs] in various stages of CO_2 exposure to ambient air. The spectra emphasized the downfield area where the carbamate peaks appear.

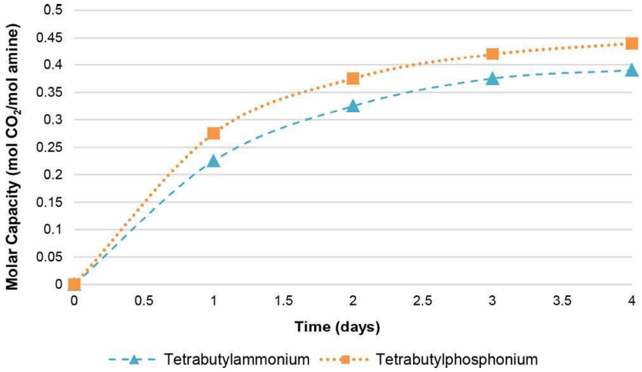


Figure 3. Molar CO_2 uptake capacity of the ILs over a four-day period.

(Figure 3). The mass changes of the ILs and MEA were also compared and despite the substantial decrease in the overall mass of MEA (due to its high volatility), the overall mass of ILs increased (see the SI, Figure S5).

The variation in the molar capacity between the individual and mixed BCAAs is different, perhaps due to higher fluidity of ILs with the mixed BCAAs anion (see the SI, Table S1), convincing us to employ the ILs with the mixed BCAAs anion for this study. $[P_{4444}]$[Val], $[P_{4444}]$[Leu], and $[P_{4444}]$[Ile] were made of the individual components of the commercial variety and subsequently exposed to the ambient air for a period of three days. These salts are high viscous waxes at room temperature, but they participated in absorption, as shown in the carbamate peak at 163−165 ppm in the ^{13}C NMR spectra. The variations in mass increase between the individual BCAAs and the mixed BCAAs were low as shown in Table S1.

For repeated, long-term use, ideally, the ILs should be able to undergo several adsorption/desorption cycles without noticeable loss in absorption capacity. The process of CO_2 uptake is reversible, CO_2 being extruded from the IL upon heating for 2.5 h under vacuum. CO_2 was released from the isolated carbamate solids under relatively mild conditions between 70 and 120 °C. The recovered ILs were repeatedly recycled for CO_2 uptake (five cycles) with no observed loss of efficiency, confirmed by ^{13}C NMR Spectroscopy.

CONCLUSIONS

Direct capture of CO_2 from air offers a useful approach in the global carbon removal technological landscape, offsetting carbon emissions from a nonspecific sector. There is a pressing need to advance the development of technologies for DAC of CO_2, as a result of which, this has been a rapidly expanding field of research in recent years. This technology looks quite "seductive"[43] on paper, but there are numerous challenges associated with implementation of DAC technology, primarily due to its high cost.

Easy to make IL materials based on a mixture three branched-chain amino acids (valine, leucine, and isoleucine) were found to have significant capacity for the repeated capture of CO_2 directly from air under wet conditions, despite the low atmospheric concentration. These BCAAs are commonly derived from biowaste products such as feathers, fur, and even human hair that could be therefore ideally suited for coupling CO_2 capture with treatment of organic waste. The reported ILs successfully captured CO_2 in 1 CO_2: 2 IL mol ratio, initially through the formation of carbamate intermediates that eventually transitioned into carbonate/bicarbonate species. The duration of the transition was shown to be partially a function of the humidity in the ambient air.

We conducted systematic structure−property relationship studies for precise tuning of the ILs for DAC performance. Their regenerative capability was also determined in a short series of absorption/desorption cycles. At this juncture, we developed new concept materials that combine the best attributes of liquid and solid sorbents while being energy-efficient and cost-effective for DAC research. This flexibility allows us to create a range of different ILs for various practical applications. These amino acid-derived liquid sorbents offer a greener alternative to the common DAC sorbents such as amines and aqueous alkali. It is worth mentioning that further testing of the complete life cycle of these compounds is necessary to fully understand their potential and the full extent of the environmental effect of the individual components of the system.

In this study, we have largely focused on the DAC capabilities of this system because of its uniquely suited properties compared to other ILs for the CO_2 capture technologies proposed up to this point. Moreover, we predict that the versatility and robustness of our proposed system is well-suited for a wide range of applications even beyond carbon capture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c02883.

> Synthesis and characterizations of the amino acid-based ILs: ^1H, ^{13}C and ^{31}P NMR, MS, and IR spectroscopy; DSC and TGA thermographs; dynamic viscosity, kinetic viscosity, and density; structural characterizations of ILs after CO_2 capture via ^1H and ^{13}C NMR spectroscopy; and CO_2 capture and IL regeneration procedures (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

James H. Davis, Jr − *Department of Chemistry, University of South Alabama, Mobile, Alabama 36688, United States;* orcid.org/0000-0001-9573-3597; Phone: +1-251-460-7427; Email: jdavis@southalabama.edu

Arsalan Mirjafari − *Department of Chemistry, State University of New York at Oswego, Oswego, New York 13126, United States;* orcid.org/0000-0002-5502-0602; Phone: +1-315-312-4301; Email: arsalan.mirjafari@oswego.edu

Authors

Elizabeth A. Recker − *Department of Chemistry and Physics, Florida Gulf Coast University, Fort Myers, Florida 33965, United States*

Matthew Green − *Department of Chemistry, University of South Alabama, Mobile, Alabama 36688, United States*

Mohammad Soltani − *Department of Chemistry, University of South Alabama, Mobile, Alabama 36688, United States*

Daniel H. Paull − *Department of Chemistry and Physics, Florida Gulf Coast University, Fort Myers, Florida 33965, United States;* orcid.org/0000-0003-4033-5326

Gregory J. McManus − *Department of Chemistry and Physics, Florida Gulf Coast University, Fort Myers, Florida 33965, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.2c02883

Author Contributions

The manuscript was written through contributions of all authors. They contributed to conceptualization, original draft preparation, review, and editing. Funding acquisition was done by A.M. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. CHE−1952846. A.M. and G.J.M. gratefully acknowledge the generous support from the Southwest Florida Community Foundation, Inc., DBA Collaboratory as well as the contributions of Reef Gingell, Caroline Lee, and Cassidy Marino to this project. A.M. thanks Grace Anderson, Jessica Miceli, and Anusha Malik for their assistance through the review process.

■ DEDICATION

This article is dedicated to the memory of Prof. Robert (Bob) Grubbs, the 2005 Nobel Laureate in Chemistry (1942−2021), for his groundbreaking contributions to green chemistry.

■ REFERENCES

(1) Friedlingstein, P.; O'Sullivan, M.; Jones, M. W.; Andrew, R. M.; Hauck, J.; Olsen, A.; Peters, G. P.; Peters, W.; Pongratz, J.; Sitch, S.; Le Quéré, C.; Canadell, J. G.; Ciais, P.; Jackson, R. B.; Alin, S.; Aragão, L. E. O. C.; Arneth, A.; Arora, V.; Bates, N. R.; Becker, M.; Benoit-Cattin, A.; Bittig, H. C.; Bopp, L.; Bultan, S.; Chandra, N.; Chevallier, F.; Chini, L. P.; Evans, W.; Florentie, L.; Forster, P. M.; Gasser, T.; Gehlen, M.; Gilfillan, D.; Gkritzalis, T.; Gregor, L.; Gruber, N.; Harris, I.; Hartung, K.; Haverd, V.; Houghton, R. A.; Ilyina, T.; Jain, A. K.; Joetzjer, E.; Kadono, K.; Kato, E.; Kitidis, V.; Korsbakken, J. I.; Landschützer, P.; Lefèvre, N.; Lenton, A.; Lienert, S.; Liu, Z.; Lombardozzi, D.; Marland, G.; Metzl, N.; Munro, D. R.; Nabel, J. E. M. S.; Nakaoka, S.-I.; Niwa, Y.; O'Brien, K.; Ono, T.; Palmer, P. I.; Pierrot, D.; Poulter, B.; Resplandy, L.; Robertson, E.; Rödenbeck, C.; Schwinger, J.; Séférian, R.; Skjelvan, I.; Smith, A. J. P.; Sutton, A. J.; Tanhua, T.; Tans, P. P.; Tian, H.; Tilbrook, B.; van der Werf, G.; Vuichard, N.; Walker, A. P.; Wanninkhof, R.; Watson, A. J.; Willis, D.; Wiltshire, A. J.; Yuan, W.; Yue, X.; Zaehle, S. Global Carbon Budget 2020. *Earth Syst. Sci. Data* **2020**, *12*, 3269−3340.

(2) Peters, G. P.; Andrew, R. M.; Canadell, J. G.; Friedlingstein, P.; Jackson, R. B.; Korsbakken, J. I.; Le Quéré, C.; Peregon, A. Carbon Dioxide Emissions Continue to Grow amidst Slowly Emerging Climate Policies. *Nat. Clim. Change* **2020**, *10*, 3−6.

(3) Rohr, J. R.; Cohen, J. M. Understanding How Temperature Shifts Could Impact Infectious Disease. *PLoS Biol.* **2020**, *18*, No. e3000938.

(4) Rodó, X.; San-José, A.; Kirchgatter, K.; López, L. Changing Climate and the COVID-19 Pandemic: More than Just Heads or Tails. *Nat. Med.* **2021**, *27*, 576−579.

(5) Lackner, K. S. A Guide to CO^2 Sequestration. *Science* **2003**, *300*, 1677−1678.

(6) Bui, M.; Adjiman, C. S.; Bardow, A.; Anthony, E. J.; Boston, A.; Brown, S.; Fennell, P. S.; Fuss, S.; Galindo, A.; Hackett, L. A. Carbon capture and storage (CCS): the way forward. *Energy Environ. Sci.* **2018**, *11*, 1062−1176.

(7) Keith, D. W.; Ha-Duong, M.; Stolaroff, J. K. Climate Strategy with CO_2 Capture from the Air. *Clim. Change* **2006**, *74*, 17−45.

(8) Digdaya, I. A.; Sullivan, I.; Lin, M.; Han, L.; Cheng, W.-H.; Atwater, H. A.; Xiang, C. A Direct Coupled Electrochemical System for Capture and Conversion of CO_2 from Oceanwater. *Nat. Commun.* **2020**, *11*, 4412.

(9) Keith, D. W.; Holmes, G.; St. Angelo, D.; Heidel, K. A Process for Capturing CO_2 from the Atmosphere. *Joule* **2018**, *2*, 1573−1594.

(10) Goeppert, A.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R. Carbon Dioxide Capture from the Air Using a Polyamine Based Regenerable Solid Adsorbent. *J. Am. Chem. Soc.* **2011**, *133*, 20164−20167.

(11) Lackner, K. S. The Thermodynamics of Direct Air Capture of Carbon Dioxide. *Energy* **2013**, *50*, 38−46.

(12) Smith, W. A.; Burdyny, T.; Vermaas, D. A.; Geerlings, H. Pathways to Industrial-Scale Fuel Out of Thin Air from CO_2 Electrolysis. *Joule* **2019**, *3*, 1822−1834.

(13) Shi, X.; Xiao, H.; Azarabadi, H.; Song, J.; Wu, X.; Chen, X.; Lackner, K. S. Sorbents for the Direct Capture of CO_2 from Ambient Air. *Angew. Chem., Int. Ed.* **2020**, *59*, 6984−7006.

(14) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO_2 from Ambient Air. *Chem. Rev.* **2016**, *116*, 11840−11876.

(15) Azarabadi, H.; Lackner, K. S. Postcombustion Capture or Direct Air Capture in Decarbonizing US Natural Gas Power? *Environ. Sci. Technol.* **2020**, *54*, 5102−5111.

(16) Fasihi, M.; Efimova, O.; Breyer, C. Techno-Economic Assessment of CO_2 Direct Air Capture Plants. *J. Cleaner Prod.* **2019**, *224*, 957−980.

(17) Lackner, K. S.; Azarabadi, H. Buying down the Cost of Direct Air Capture. *Ind. Eng. Chem. Res.* **2021**, *60*, 8196−8208.

(18) Brethomé, F. M.; Williams, N. J.; Seipp, C. A.; Kidder, M. K.; Custelcean, R. Direct Air Capture of CO_2 via Aqueous-Phase Absorption and Crystalline-Phase Release Using Concentrated Solar Power. *Nat. Energy* **2018**, *3*, 553−559.

(19) Ramdin, M.; de Loos, T. W.; Vlugt, T. J. H. State-of-the-Art of CO_2 Capture with Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 8149−8177.

(20) Zeng, S.; Zhang, X.; Bai, L.; Zhang, X.; Wang, H.; Wang, J.; Bao, D.; Li, M.; Liu, X.; Zhang, S. Ionic-Liquid-Based CO_2 Capture Systems: Structure, Interaction and Process. *Chem. Rev.* **2017**, *117*, 9625−9673.

(21) Mota-Martinez, M. T.; Brandl, P.; Hallett, J. P.; Dowell, N. M. Challenges and Opportunities for the Utilisation of Ionic Liquids as Solvents for CO_2 Capture. *Mol. Syst. Des. Eng.* **2018**, *3*, 560−571.

(22) Chen, Y.; Mu, T. Conversion of CO_2 to Value-Added Products Mediated by Ionic Liquids. *Green Chem.* **2019**, *21*, 2544−2574.

(23) Cuéllar-Franca, R. M.; García-Gutiérrez, P.; Hallett, J. P.; Dowell, N. M. A Life Cycle Approach to Solvent Design: Challenges and Opportunities for Ionic Liquids − Application to CO_2 Capture. *React. Chem. Eng.* **2021**, *6*, 258−278.

(24) Dutcher, B.; Fan, M.; Russell, A. G. Amine-Based CO_2 Capture Technology Development from the Beginning of 2013—A Review. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2137−2148.

(25) Wang, Y.; Song, L.; Ma, K.; Liu, C.; Tang, S.; Yan, Z.; Yue, H.; Liang, B. An Integrated Absorption−Mineralization Process for CO_2 Capture and Sequestration: Reaction Mechanism, Recycling Stability, and Energy Evaluation. *ACS Sustainable Chem. Eng.* **2021**, *9*, 16577−16587.

(26) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO_2 Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926−927.

(27) Soutullo, M. D.; Odom, C. I.; Wicker, B. F.; Henderson, C. N.; Stenson, A. C.; Davis, J. H. Reversible CO_2 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.

(28) McDonald, J. L.; Sykora, R. E.; Hixon, P.; Mirjafari, A.; Davis, J. H. Impact of Water on CO_2 Capture by Amino Acid Ionic Liquids. *Environ. Chem. Lett.* **2014**, *12*, 201−208.

(29) Balsamo, M.; Erto, A.; Lancia, A.; Totarella, G.; Montagnaro, F.; Turco, R. Post-Combustion CO_2 Capture: On the Potentiality of Amino Acid Ionic Liquid as Modifying Agent of Mesoporous Solids. *Fuel* **2018**, *218*, 155−161.

(30) Bhattacharyya, S.; Shah, F. U. Ether Functionalized Choline Tethered Amino Acid Ionic Liquids for Enhanced CO_2 Capture. *ACS Sustainable Chem. Eng.* **2016**, *4*, 5441−5449.

(31) Sang Sefidi, V.; Luis, P. Advanced Amino Acid-Based Technologies for CO_2 Capture: A Review. *Ind. Eng. Chem. Res.* **2019**, *58*, 20181−20194.

(32) Huang, Z.; Karami, D.; Mahinpey, N. Study on the Efficiency of Multiple Amino Groups in Ionic Liquids on Their Sorbents Performance for Low-Temperature CO_2 Capture. *Chem. Eng. Res. Des.* **2021**, *167*, 198−206.

(33) Min, Z.; Li, Z.; Wang, H.; Xuan, X.; Zhao, Y.; Wang, J. How Does the Moisture Affect CO_2 Absorption by a Glycinate Ionic Liquid? *ACS Sustainable Chem. Eng.* **2021**, *9*, 853−862.

(34) Wang, T.; Hou, C.; Ge, K.; Lackner, K. S.; Shi, X.; Liu, J.; Fang, M.; Luo, Z. Spontaneous Cooling Absorption of CO_2 by a Polymeric Ionic Liquid for Direct Air Capture. *J. Phys. Chem. Lett.* **2017**, *8*, 3986−3990.

(35) Mirjafari, A.; O'Brien, R. A.; West, K. N.; Davis, J. H. Synthesis of New Lipid-Inspired Ionic Liquids by Thiol-Ene Chemistry: Profound Solvent Effect on Reaction Pathway. *Chem. − Eur. J.* **2014**, *20*, 7576−7580.

(36) Mirjafari, A. Ionic Liquid Syntheses via Click Chemistry: Expeditious Routes toward Versatile Functional Materials. *Chem. Commun.* **2018**, *54*, 2944−2961.

(37) Siegel, D. J.; Anderson, G. I.; Cyr, N.; Lambrecht, D. S.; Zeller, M.; Hillesheim, P. C.; Mirjafari, A. Molecular Design Principles of Ionic Liquids with a Sulfonyl Fluoride Moiety. *New J. Chem.* **2021**, *45*, 2443−2452.

(38) Ferlin, N.; Courty, M.; Gatard, S.; Spulak, M.; Quilty, B.; Beadham, I.; Ghavre, M.; Haiß, A.; Kümmerer, K.; Gathergood, N.; Bouquillon, S. Biomass Derived Ionic Liquids: Synthesis from Natural Organic Acids, Characterization, Toxicity, Biodegradation and Use as Solvents for Catalytic Hydrogenation Processes. *Tetrahedron* **2013**, *69*, 6150−6161.

(39) Egorova, K. S.; Ananikov, V. P. Toxicity of Ionic Liquids: Eco(Cyto)Activity as Complicated, but Unavoidable Parameter for Task-Specific Optimization. *ChemSusChem* **2014**, *7*, 336−360.

(40) Peng, Z.; Mao, X.; Zhang, J.; Du, G.; Chen, J. Biotransformation of Keratin Waste to Amino Acids and Active Peptides Based on Cell-Free Catalysis. *Biotechnol. Biofuels* **2020**, *13*, 61.

(41) Siegel, D. J.; Anderson, G. I.; Paul, L. M.; Seibert, P. J.; Hillesheim, P. C.; Sheng, Y.; Zeller, M.; Taubert, A.; Werner, P.; Balischewski, C.; Michael, S. F.; Mirjafari, A. Design Principles of Lipid-like Ionic Liquids for Gene Delivery. *ACS Appl. Bio Mater.* **2021**, *4*, 4737−4743.

(42) Ossowicz, P.; Klebeko, J.; Roman, B.; Janus, E.; Rozwadowski, Z. The Relationship between the Structure and Properties of Amino Acid Ionic Liquids. *Molecules* **2019**, *24*, 3252.

(43) Ranjan, M.; Herzog, H. J. Feasibility of Air Capture. *Energy Procedia* **2011**, *4*, 2869−2876.

https://doi.org/10.1021/acssuschemeng.2c02883