Ternary Deep Eutectic Solvents Tasked for Carbon Dioxide Capture

Leonhard L. Sze,[†] Shubha Pandey,[†,‡] Sudhir Ravula,[‡] Siddharth Pandey,[‡,||] Hua Zhao,[§] Gary A. Baker,*,[‡] and Sheila N. Baker*,[†]

[†]Department of Chemical Engineering, University of Missouri-Columbia, Columbia, Missouri 65211, United States
[‡]Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, United States
[§]Department of Chemistry, Savannah State University, Savannah, Georgia 31404, United States
[||]Department of Chemistry, Indian Institute of Technology, Delhi, India

Ⓢ Supporting Information

ABSTRACT: Task-specific ternary deep eutectic solvent (DES) systems comprising choline chloride, glycerol, and one of three different superbases were investigated for their ability to capture and release carbon dioxide on demand. The highest-performing systems were found to capture CO_2 at a capacity of ~10% by weight, equivalent to 2.3–2.4 mmol of CO_2 captured per gram of DES sorbent. Of the superbases studied, 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) gave the best overall performance in terms of CO_2 capture capacity, facility of release, and low sorbent cost. Interestingly, we found that only a fraction of the theoretical CO_2 capture potential of the system was utilized, offering potential pathways forward for further design and optimization of superbase-derived DES systems for further improved reversible CO_2 sequestration. Finally, the shear rate-dependent viscosities indicate non-Newtonian behavior which, when coupled to the competitive CO_2 capture performance of these task-specific DESs despite a 1 to 2 orders of magnitude higher viscosity, suggest that the Stokes−Einstein−Debye relation may not be a valid predictor of performance for these structurally and dynamically complex fluids.
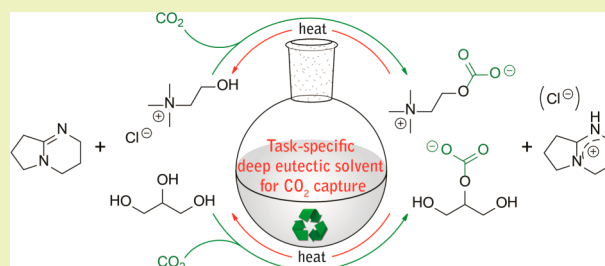
KEYWORDS: Carbon dioxide capture, Deep eutectic solvent, DES, CO_2 sequestration, 1,5-Diazabicyclo[4.3.0]-non-5-ene (DBN)

INTRODUCTION

Carbon dioxide (CO_2) emissions due to anthropogenic activities have continually increased over the past century, gaining worldwide attention due to the negative climate effects of this notorious greenhouse gas. Consequently, developing technologies to efficiently and inexpensively capture CO_2 assumes great importance.[1−4] The current state-of-the art for CO_2 capture in post-combustion power plants is based on the absorption of CO_2 by aqueous monoethanolamine (MEA) solution. However, this technology is expensive to implement and maintain, resulting in high energy penalties for sorbent regeneration. Moreover, amine-based reagents like MEA are corrosive and somewhat volatile, posing a potential threat to humans, animals, and the environment.[5]

In recent years, different methods to improve upon the use of volatile amines have been developed. One such methodology is based upon using ionic liquids (ILs)—organic salts with melting points below 100 °C—for reversible CO_2 capture.[4,6−11] ILs, due to their attractive inherent properties, including low volatility, high thermal stability, nonflammability, and excellent CO_2 solubility, offer several specific advantages over aqueous MEA solutions for carbon capture. Significantly, in contrast with MEA, ILs are nonvolatile and thus do not require condensation during the regeneration (CO_2 release) step. ILs can be designed to serve as physical sorbents for both CO_2 and

SO_2, reducing the heat requirement for regeneration and allowing for an SO_2 polishing step.[12] ILs are particularly well known as physical sorbents for CO_2, with a high CO_2 solubility that may be tuned through appropriate IL cation and anion choice.[13−18] Given their tunability, "task-specific" ionic liquids (TSILs) can also be designed to chemically react with CO_2 by reversibly binding CO_2 through an appended amine group to form a carbamate salt,[19] for example. Another strategy for the covalent capture of CO_2 involves TSILs sporting alcohol functional groups that can be used in conjunction with superbases for reversible CO_2 capture.[20] In previous work, a mixture of the TSIL 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Im$_{21}$OH][Tf$_2$N]) and the superbase 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU) in a 1:1 molar ratio proved capable of rapidly capturing 1.04 mol of CO_2 per mole of DBU at 20 °C, significantly exceeding the typical CO_2 capture capacity of traditional carbamate-forming ILs. Furthermore, this system remained liquid after CO_2 capture, was reversible with nearly quantitative regeneration, and was stable over several iterative capture/regeneration cycles. IL systems, in general, have been shown to capture

0.07−1.13 mol of CO_2 per mole of IL, which equates to 19−112 mg of CO_2 per gram of IL.[7,8] However, there remain several drawbacks to employing ILs for carbon capture, including the complexity and cost of their synthesis on a large scale, frequent use of unsustainable (e.g., fluorinated) components or those not vetted for environmental compatibility, and solvent byproduct wastes generated during their synthesis and purification. While numerous ILs are now available commercially, specialized TSILs best suited for CO_2 separation are typically synthesized in small batches within individual academic laboratories.[4] Besides, there are growing environmental concerns regarding the toxicity and environmental effects of many ILs.[21,22]

An emergent class of solvents related to ILs, deep eutectic solvents (DESs) share many of their favorable characteristics, such as low volatility, nonflammability, and high thermal stability.[23−31] DESs are typically formed from two to three components capable of intermolecular interactions, particularly through hydrogen bonding. In the proper ratio, these components may form a eutectic with a depressed freezing point that lies well below that of the individual components. To describe this new solvent type, Abbot et al. recently coined the term *deep eutectic solvent* and divided DESs into four distinct types. DES types 1 to 3 consist of a quaternary ammonium halide complexed with a metal chloride, a metal chloride hydrate, and a hydrogen bond donor (such as an alcohol), respectively.[32] A type 4 DES consists of a metal salt combined with a hydrogen bond donor.[33] Unlike conventional IL preparation, the synthesis of DESs is very simple and straightforward, typically involving only mixing under mild heating. In fact, DES synthesis is 100% atom efficient, solventless, and requires no further purification steps, simplifying scale up. Equally important, most DESs can be made from biodegradable components whose toxicology is well characterized and may even include the use of vitamins and metabolites.

Due to their many similarities with ILs, CO_2 solubility within DESs has been recently studied.[34−37] Zou and co-workers investigated CO_2 solubility as a function of temperature (313.15−333.15 K) and pressure (0.85−12.52 MPa) within choline chloride (ChCl) + urea DESs, where the mole ratio of ChCl to urea was either 1:1.5, 1:2, or 1:2.5. The highest CO_2 solubility at each temperature and pressure condition was found for the 1:2 ChCl:urea DES (the so-called reline system) and correlates with this molar ratio having the lowest melting point. In each DES studied, the CO_2 solubility increased with increasing pressure and decreased with increasing temperature, suggestive of physical sorption. The dissolved CO_2 mole fraction in the liquid phase ranged from a low value of 0.032 for 1:2.5 ChCl:urea at 333.15 K and 1.08 MPa to a high of 0.309 for the 1:2 ChCl:urea DES system at 313.15 K and 12.5 MPa. We note that these CO_2 solubilities fall well below the CO_2 solubility for imidazolium-based ILs under similar conditions, although they are on the order of the CO_2 solubility observed for ammonium-based ILs.[13] Francisco et al. reported CO_2 solubilities even lower for the 2:1 lactic acid:ChCl DES at similar temperatures and pressures.[34] In contrast, Leron and Li studied CO_2 solubility within ChCl:glycerol and ChCl:ethylene glycol DESs and reported encouraging CO_2 solubilities comparable to imidazolium ILs.[35,36] In all of these studies, CO_2 absorption was predominantly physical in nature, and additional studies are needed to determine how CO_2 absorption depends on the free volume and/or the strength of intermolecular and intramolecular interactions, as well as to what extent CO_2 solubility can be tuned within a DES.

Despite recent efforts investigating CO_2 solubility within DESs, we are aware of no prior study reporting on a task-specific DES system specifically designed for the chemical capture (chemisorption) of CO_2. Toward this, we report on the first task-specific DES system capable of chemically binding CO_2 reversibly and with high capacity. Our DES-based system consists of choline chloride (ChCl), glycerol (Gly), and a superbase (SB) component. The SB serves to deprotonate the alcohol groups of ChCl and Gly, resulting in putative alkoxide anions capable of reacting with CO_2 to reversibly form alkylcarbonate salts under ambient conditions. The generalized reaction scheme summarizing this CO_2 capture strategy is depicted in Figure 1. The effects of employing different SBs and
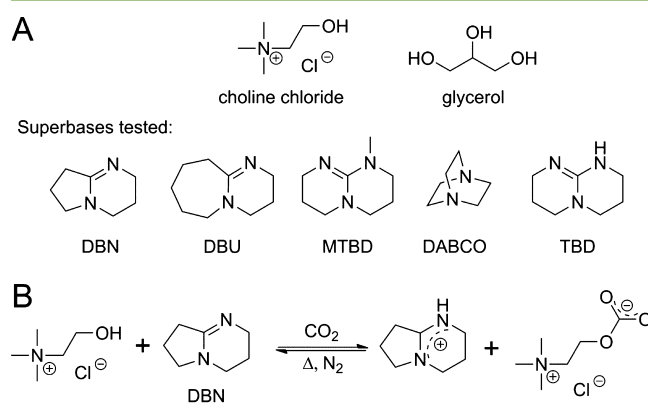

Figure 1. (A) Structures of the DES components used in this study: choline chloride, glycerol, and various superbases considered in our investigation. (B) Proposed reaction scheme for superbase-promoted CO_2 capture using a task-specific DES. In this scheme, choline chloride and the superbase DBN are shown for illustration; however, a similar reaction is believed to be operative for the other superbases as well as for CO_2 binding to the multiple alcohol functionalities of glycerol. Notably, the chemically captured CO_2 can be facilely released upon gentle heating at 60 °C under nitrogen.

the impact of DES component mole fractions on CO_2 capture capacity, absorption rate, reversibility, and the effectiveness of the system over many cycles were evaluated and are discussed herein.

■ EXPERIMENTAL METHOD

Synthesis of DES Systems. Choline chloride (ChCl), glycerol (Gly), 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (TBD), and sodium hydroxide were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. In order to prepare our ternary DES mixtures, a binary mixture of ChCl and Gly was first prepared by combining ChCl and Gly in the appropriate molar ratio under vigorous stirring at 80 °C. Stirring was continued for 1 h before allowing the mixture to cool naturally to room temperature. The resulting solutions were clear and homogeneous. The binary ChCl:Gly DES mixture was further dried overnight at 50 °C under vacuum. The ChCl:Gly:SB ternary DES was subsequently prepared by heating the dried ChCl:Gly binary DES to 50 °C followed by addition of the appropriate mass of the desired SB while stirring. The final mixture (a ternary DES) was then stirred for an additional 30 min after which it was allowed to cool to ambient temperature. At this point, the DES was ready for use. It is important to note that no purification step

was required and no solvents were employed in the preparation of this ternary ChCl:Gly:SB DES.

CO$_2$ Capture and Release Experiments. CO$_2$ capture experiments were performed under ambient conditions by bubbling CO$_2$ (99.9% grade, Airgas) at a rate of 50 mL min^{-1} using a mass flow controller (Aalborg Instruments and Controls, Inc.) into a known initial mass of a ternary DES while stirring. The weight of the DES was monitored over time to determine the mass of CO$_2$ captured. After CO$_2$ capture, the reversibility of the process was investigated by heating the ternary DES system containing chemically bound ("captured") CO$_2$ to 60 °C and bubbling nitrogen (ultrahigh purity, Airgas) into the mixture at a rate of 50 mL min^{-1} using a mass flow controller; during the desorption step, the system was open to the atmosphere. The mass loss for the sample was monitored over time corresponding to the release of CO$_2$.

Characterization Experiments. To characterize and confirm CO$_2$ capture, ^{13}C nuclear magnetic resonance (NMR) spectroscopy was performed using a Bruker ARX-300 Ultrashield NMR spectrometer. Fourier-transform infrared spectroscopy (FTIR) measurements were also performed to track CO$_2$ binding and release. All FTIR measurements were performed either on a Nicolet 4700 equipped with a Thermo Smart Performer germanium crystal attenuated total reflectance (ATR) attachment or on a Nicolet Nexus 670. Viscosity measurements were performed using a Brookfield DV III Ultra cone/plate Rheometer (spindle #42) with the temperature controlled by a Fisher Isotemp circulating bath.

■ RESULTS AND DISCUSSION

For our ternary DES systems, we investigated DBN, MTBD, and DBU as prospective superbases in conjunction with a mixture of ChCl and Gly (chemical structures for these species are provided in Figure 1A). The SB in these systems serves to deprotonate the alcohol (hereafter, simply written as "OH") group of ChCl and the multiple OH groups of Gly, which serve as handles for the subsequent chemisorption of CO$_2$. On the basis of our previous work[20] and what is known regarding superbase-promoted binding of CO$_2$ by neutral alcohols, we propose the reaction mechanism provided in Figure 1B. We initially evaluated several additional bases for their ability to promote a ternary DES system, including DABCO, TBD, and sodium hydroxide. However, these three bases resulted in solid or highly viscous gels when combined with the binary ChCl:Gly DES and were thus not considered further for CO$_2$ capture as such physical constraints are well known to hamper subsequent CO$_2$ absorption.[20]

To verify that the observed DES mass increase upon exposure to CO$_2$ can indeed be ascribed to CO$_2$ capture through alkylcarbonate salt formation, ^{13}C NMR and FTIR experiments were conducted immediately prior to and following CO$_2$ bubbling. Comparing the ^{13}C NMR spectra for the representative 1:2:6 ChCl:Gly:DBN system before and after CO$_2$ bubbling reveals the appearance of a new peak near 160 ppm after CO$_2$ exposure. This peak is fully consistent with alkylcarbonate formation after CO$_2$ exposure (Figure S1, Supporting Information). Similarly, the ATR-FTIR spectrum collected for this DES after CO$_2$ exposure contains new peaks in the 1600−1650 and 1300−1350 cm^{-1} windows, features that can be attributed to the asymmetric and symmetric stretches for unidentate-bound CO$_2$ (Figure S2, Supporting Information). Thus, both the ^{13}C NMR and FTIR experiments confirm the presence of chemically bound CO$_2$ within the ternary DES after CO$_2$ exposure.

Having confirmed covalent CO$_2$ binding within our task-specific DES system, we turned our attention to investigating different SBs to determine which would lead to optimal CO$_2$

capture. For these experiments, a molar ratio of 1:2:6 ChCl:Gly:SB was always used to form the ternary DES mixture. As Figure 2 and Table 1 reveal, each of these systems
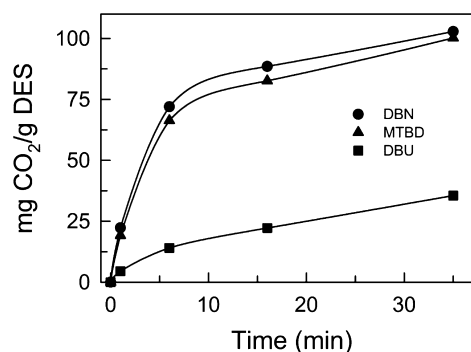

Figure 2. Amount of CO$_2$ captured per gram of DES measured over time for three different task-specific DES systems comprising 1:2:6 ChCl:Gly:SB (SB = DBN, MTBD, or DBU).

proved capable of capturing CO$_2$. After 35 min or so, the amounts of additional CO$_2$ capture became insignificant. The DBN-containing DES performed the best overall on a mass basis (i.e., mg of CO$_2$ captured per gram of DES), but at the 35 min mark, the performance for the MTBD-based DES was essentially equivalent. For the DBN-based DES, 103 mg of CO$_2$ was captured per gram of DES after 35 min compared with 100 mg and 35.5 mg of CO$_2$ capture for the MTBD- and DBU-based DESs, respectively. Given the comparable gravimetric performance, however, more CO$_2$ was captured per mole of SB and per mole of OH groups for the MTBD-containing DES (Table 1). Using these criteria, the superbase MTBD gave the best performance for CO$_2$ capture. In comparison to the other superbases, DBU had a much poorer CO$_2$ capture by all performance criteria.

The variation in performance for the different SBs may be explained on the basis of two main factors: basicity and sterics. Regarding the basicity, the ^{MeCN}p$K_{BH}{}^+$ values are 25.44, 24.33, and 23.89 for MTBD, DBU, and DBN, respectively.[38] So, MTBD should prove only slightly more effective in deprotonating the alcohol groups of ChCl and Gly. This is manifested in the marginally higher CO$_2$ capture ability per mole of OH observed when using MTBD over DBN. Following this argument, however, one would expect DBU to outperform DBN on an OH molar basis. Clearly, this is not the case, however. In light of this, we suggest that the decrease in CO$_2$ capture for DBU compared with DBN arises from DBU's larger bicyclic ring structure (Figure 1), which may sterically interfere with its ability to deprotonate OH groups in close proximity to each other (i.e., the vicinal alcohol groups of glycerol).

As CO$_2$ was added to each ternary DES, changes in the appearance of the various systems were observed. For example, during CO$_2$ addition, the originally transparent DES mixtures generally became cloudy to opaque white (Figure S3, Supporting Information). For all ternary DES systems, the viscosity also increased over time as more CO$_2$ was captured. It is anticipated that such a viscosity increase will negatively affect mass transfer and capture kinetics, hindering further CO$_2$ capture. Within 6 min of CO$_2$ exposure, the MTBD-containing DES was noticeably more viscous, continually becoming more viscous with continued CO$_2$ capture and eventually forming a

Table 1. Summary of CO_2 Capture Capacity for Different Ternary DES Systems[a]

		CO_2 capture figures of merit					
superbase (SB)	DES ratio ChCl:Gly:SB	mg CO_2/g DES	mmol CO_2/g DES	mol CO_2/mol SB	mol CO_2/mol OH	OH groups/DES	CO_2 bound/DES
MTBD	1:2:6	100	2.27	0.47	0.40	7	2.8
DBU	1:2:6	35.5	0.81	0.17	0.14	7	1.0
DBN	1:2:6	103	2.34	0.42	0.36	7	2.5
DBN	1:2:3	96	2.18	0.51	0.22	7	1.5
DBN	1:2:7	105	2.39	0.41	0.41	7	2.9
DBN	1:2:8	103	2.34	0.39	0.44	7	3.1
DBN	1:3:10	104	2.36	0.39	0.39	10	3.9

[a]In practice, 35 min of CO_2 flow proved sufficient to achieve equilibrium.
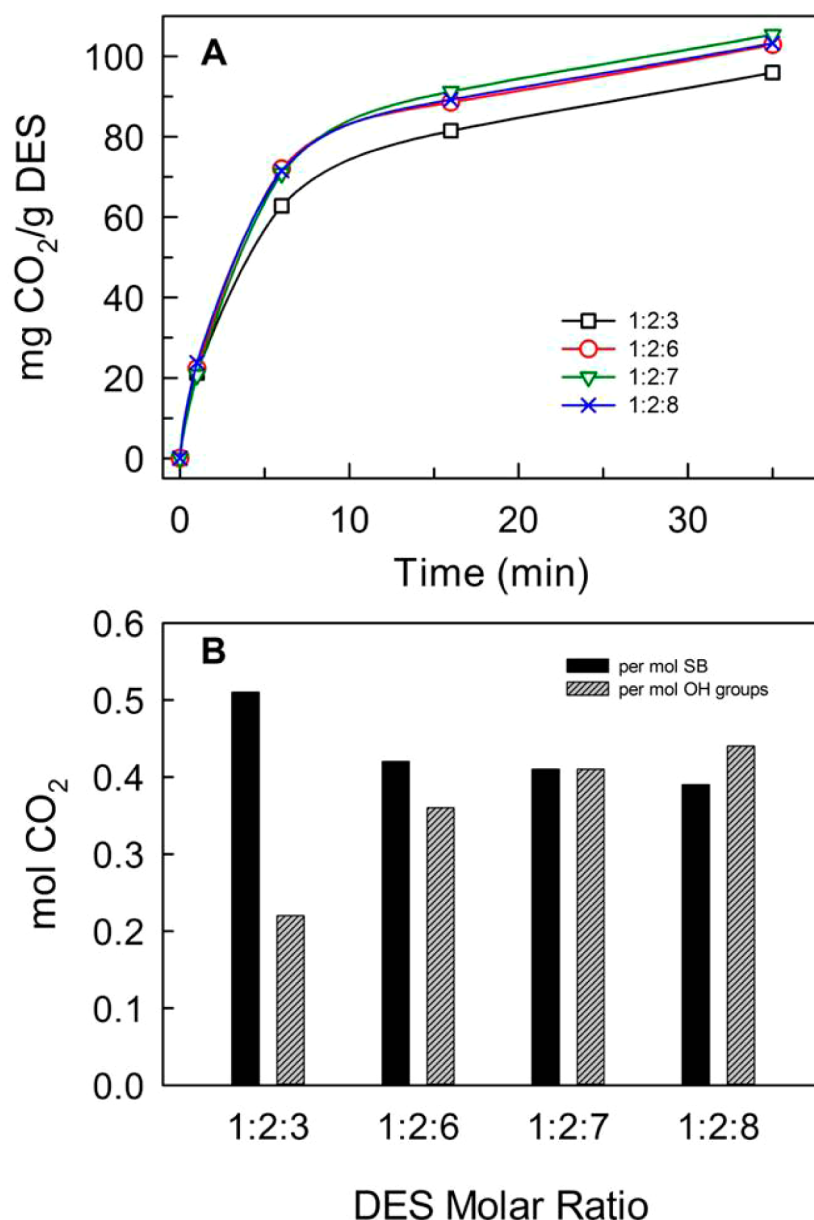

Figure 3. (A) Amount of CO_2 captured per gram of DES as a function of time for 1:2:x molar ratio ChCl:Gly:DBN mixtures (x = 3, 6, 7, or 8). (B) Total amounts of CO_2 captured per mole of DBN and per mole of alcohol (OH) group for the same DES mixtures with increasing relative DBN amounts.

gel. For the DBN-based DES, the viscosity became noticeably greater after 16 min, and upon standing for several hours, the CO_2-containing mixture separated into two phases: a more viscous partially opaque white-hued liquid on the bottom and a less viscous transparent liquid on top (Figure S3, Supporting Information). Comparing the FTIR spectra for the two distinct layers, it was evident that CO_2 was present within the lower viscous phase and largely absent within the upper phase (Figure

S4, Supporting Information). Furthermore, the CO_2 vibrational signature in the more viscous phase disappeared upon releasing the CO_2 during regeneration. In contrast, the DBU-containing DES showed only a slightly noticeable increase in viscosity compared to the other two systems, an observation we assign to the much lower CO_2 capture for this system. Interestingly, this mixture also separated into two phases but with most of the sample being retained in the less viscous upper phase that contained no CO_2.

Although the much higher viscosities observed upon CO_2 binding represent an engineering challenge (and frankly, one also shared with IL systems designed for CO_2 capture), there are likely ways to mitigate this, including dispersion of the DES within highly porous media and onto nanosupports.[39] Another key observation we made is that the viscosity of the DES systems studied typically exhibit non-Newtonian behavior. For example, the experimental viscosities for the 1:2:6 ChCl:Gly:DBN system under ambient conditions ranged from 5450−34,613 cP, depending on the shear rate employed (Figure S5, Supporting Information). Although these viscosities are significantly (1 to 2 orders of magnitude) higher than typical IL viscosities (normally in the 50−1500 cP range),[40,41] the CO_2 capture performance was nonetheless competitive with and better than most known TSIL systems. For instance, the 1:1 $[Im_{21}OH][Tf_2N]$:DBU system discussed earlier showed a CO_2 capture capacity of 7.6 wt %, equivalent to 1.72 mmol/g of sorbent.[20] By comparison, despite the much higher apparent viscosities, our top DES systems showed a CO_2 capture capacity of 10 wt %, corresponding to roughly 2.4 mmol of CO_2 captured per gram of DES sorbent. Additional advantages include the facts that no multi-step synthesis was required (only simple mixing), no solvent wastes were produced during the DES preparation, and the system contains no halogenated species. This result also underscores the complexity of gas transport within IL/DES systems, suggesting that evoking the Stokes−Einstein−Debye (SED) relation may not be the most instructive way to predict which media will yield the greatest CO_2 capture. Both the non-Newtonian behavior and SED validity represent interesting and unresolved issues that merit future inquiry.

Because the DBN-containing DES gave the best performance on a gravimetric basis and represents the least expensive superbase among those studied, further examinations centered solely on the ternary ChCl:Gly:DBN DES system. Our next investigation explored how changes in the molar equivalents of the DBN component of the DES impacted CO_2 capture. For these experiments, we used ternary ChCl:Gly:DBN mixtures consisting of 1:2:x molar ratios, where x equals 3, 6, 7, or 8 (i.e., 0.43, 0.86, 1.00, or 1.14 mol of DBN per OH group, respectively). As shown in Figure 3A, on a mass basis, the 1:2:7 DES captured the greatest amount of CO_2 at 105 mg per gram of DES. The 1:2:6 and 1:2:8 systems behaved similarly, each capturing 103 mg of CO_2 per gram of DES. We note that these values are on par with the higher levels of CO_2 capture reported for TSILs[8] as well as supported amine polymers.[39] As anticipated, the 1:2:3 system captured slightly less: 96 mg of CO_2 per gram of DES. Analyzing the moles of CO_2 captured per DBN and per OH group for each DES composition elucidates the trend that as the relative molar amount of DBN increases the total moles of CO_2 captured per mole of DBN decreases, while the total moles of CO_2 captured per mole of OH group increases (Figure 3B and Table 1). In other words, as more DBN was added, more OH groups could be utilized for

capturing CO_2, but the DBN superbase was utilized more efficiently at lower concentrations. Given that the superbase represents the most expensive component of this task-specific DES, this suggests that 1:2:3 ChCl:Gly:DBN is the most economical choice, while sacrificing little in terms of CO_2 binding capacity.

Because glycerol (Gly) contains more OH groups per molecule (i.e., three as compared to one for choline chloride, ChCl; Figure 1), we increased the relative Gly content of the ternary DES in an effort to increase CO_2 binding capacity on a mass basis. Toward this, the amount of Gly relative to ChCl was increased in the DES mixture while maintaining a constant 1:1 DBN to OH ratio, using 1:2:7 and a 1:3:10 ChCl:Gly:DBN for comparison. The 1:3:10 ChCl:Gly:DBN system was found to capture CO_2 at a slightly faster initial rate, but after 35 min of CO_2 exposure, similar amounts of total CO_2 were captured for both DES mixtures, as shown in Figure 4. The 1:2:7 and 1:3:10
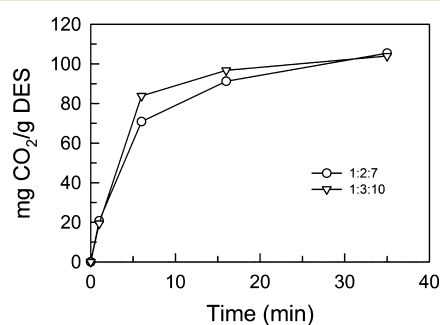
Figure 4. Amount of CO_2 captured per gram of DES over time for ternary DESs consisting of 1:2:7 and 1:3:10 molar ratios of ChCl:Gly:DBN.

ChCl:Gly:DBN mixtures also captured an equivalent 105 versus 104 mg of total CO_2 per gram of DES. This amounts to 0.41 and 0.39 mol of CO_2 captured per mole of OH for 1:2:7 and 1:3:10 ChCl:Gly:DBN, respectively (note that because of the 1:1 DBN to OH ratio in these systems, 0.41 and 0.39 mol of CO_2 were also captured per mole of DBN for 1:2:7 and 1:3:10 ChCl:Gly:DBN as well). From these results, we can see that increasing the relative amount of Gly (relative to ChCl) made little difference and proved to be an ineffective strategy for increasing CO_2 capture efficiency.

The reversibility and performance during capture-and-release cycling was also tested for the representative system 1:2:6 ChCl:Gly:DBN. During each cycle, the amount of CO_2 captured was maximized after 35 min of exposure to a CO_2 flow of 50 mL min^{-1}. The DES could be nearly fully regenerated within 35 min by heating to 60 °C and introducing nitrogen at the same flow rate. Over the course of three cycles, as shown in Figure 5, the CO_2 capture capacity dropped from 103 to 92 to 85 mg of CO_2 per gram of initial DES (i.e., 83% retention of capacity after the third cycle). We note that a similar decay was previously noted for the alcohol-appended $[Im_{21}OH][Tf_2N]$ TSIL coupled with DBU and assigned to slight evaporative losses of the superbase component.[20] Although such evaporative losses are likely to be operative here as well, this drop in capacity during cycling was also due in part to an artifact arising from the manner in which the experiment was performed. That is, in retrospect, very minor losses of DES due to sorption to the glass pipet used to introduce the gas resulted in a small drop in the initial DES mass with each cycle; we estimate this loss to be <1%, however.
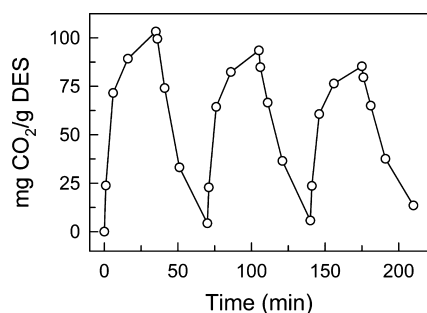
Figure 5. Time profiles showing the reversibility of CO_2 sorption/desorption over three consecutive cycles for 1:2:6 ChCl:Gly:DBN. Although the CO_2 capacity drops noticeably (due in part to an artifact arising from how the experiment was performed; refer to the text for a description), the system shows excellent repeatability for CO_2 capture and on-demand release.

Additional observations made during the cycling experiments are also worthy of mention. As discussed above, after the initial capture of CO_2, a highly viscous lower phase (containing CO_2) and an upper CO_2-absent phase were formed. After regeneration, the mixture again became monophasic but took on a light orange hue (Figure S3, vial C, Supporting Information). After CO_2 was introduced for a second time, two phases were again formed. The bottom phase was a highly viscous opaque-white liquid containing CO_2, and the top phase was now a darker orange liquid free of CO_2 (Figure S3, vial D, Supporting Information), as reconfirmed by ATR-FTIR measurements.

Despite an excellent capability in CO_2 capture and release for ChCl:Gly:SB comparable to that seen with polymer-modified silica particles, there remain limitations preventing the system from achieving its theoretical potential for CO_2 sequestration. One limitation arises from mass-transfer limitations. As we mentioned previously, the already-excessive viscosity of the CO_2-free DES increases substantially and monotonically as CO_2 is captured. According to SED assumptions, this is presumed to slow the CO_2 diffusion rate and kinetics for CO_2 capture. Frankly, from a purely physical perspective, the fact that such excellent and rapid CO_2 uptake, capture, and release features are observed in a DES system possessing viscosities well beyond 5000 cP should be seen as remarkable and invite further study. A second limitation arises purely from the thermodynamics of CO_2 binding. Namely, after deprotonating one OH group on Gly with a superbase, it becomes increasingly less favorable to deprotonate a second and then a third OH group, especially for vicinal anions (i.e., alkoxides, RO^-). And yet, despite these limitations, the capacity for CO_2 capture using the present superbase-containing task-specific DES system shows clear promise, with CO_2 binding capacities up to 2.4 mmol g^{-1}, a value in the range (or above) those found for TSILs and nitrogen-doped carbons.

CONCLUSIONS

After testing the CO_2 capture characteristics for ChCl:Gly:SB DES systems comprising various superbases, we found that the best overall system was the one containing a 1:2:6 ChCl:Gly:DBN molar ratio. This system was found to be capable of capturing 103 mg of CO_2 per gram of sorbent and formed two phases following CO_2 binding. This capture process could also be easily reversed by the application of mild heat under inert gas flow, fully releasing the CO_2. The solvent-

less sorbent was simple to make, involved only straightforward mixing steps, contained no halogens, and was stable over several capture/regeneration cycles. Although some limitations in the system emerged—particularly the excessive non-Newtonian viscosities that presumably limit mass-transfer rates by Stokes–Einstein–Debye considerations—these did not preclude excellent CO_2 capture capacities as high as 2.4 mmol of CO_2 captured per gram of DES sorbent, values surpassing those for most known ionic liquid-based systems. The inability to effectively deprotonate all available alcoholic groups of the DES awaits further elucidation by both experiment and quantum chemical calculations and may hold the key to additional improvements in the efficiency of CO_2 capture for similar task-specific DES systems.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*Phone (573) 882-3691. E-mail: bakershei@missouri.edu.
*Phone (573) 882-1811. E-mail: bakergar@missouri.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) *Emissions of Greenhouse Gases Report*; U.S. Energy Information Administration: Washington, DC, 2009.

(2) Rochelle, G. T. Amine scrubbing for CO_2 capture. *Science* **2009**, *325*, 1652−1654.

(3) McGee, M. Atmospheric CO_2. http://co2now.org/.

(4) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. Advances in CO_2 capture technology−The U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenhouse Gas Control* **2008**, *2*, 9−20.

(5) Shao, R.; Stangeland, A. *Amines Used in CO_2 Capture − Health and Environmental Impacts*; The Bellona Foundation: Oslo, Norway, 2009.

(6) Zhang, L.; Chen, J.; Lv, J. X.; Wang, S. F.; Cui, Y. Progress and development of capture for CO_2 by ionic liquids. *Asian J. Chem.* **2013**, *25*, 2355−2358.

(7) Wang, C.; Luo, X.; Zhu, X.; Cui, G.; Jiang, D. E.; Deng, D.; Li, H.; Dai, S. The strategies for improving carbon dioxide chemisorption by functionalized ionic liquids. *RSC Adv.* **2013**, *3*, 15518−15527.

(8) Zhang, X.; Dong, H.; Zhao, Z.; Zhang, S.; Huang, Y. Carbon capture with ionic liquids: Overview and progress. *Energy Environ. Sci.* **2012**, *5*, 6668−6681.

(9) Hasib-ur-Rahman, M.; Siaj, M.; Larachi, F. Ionic liquids for CO_2 capture—Development and progress. *Chem. Eng. Process.* **2010**, *49*, 313−322.

(10) Huang, J.; Rther, T. Why are ionic liquids attractive for CO_2 absorption? An overview. *Aust. J. Chem.* **2009**, *62*, 298−308.

(11) Baker, S. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. The cybotactic region surrounding fluorescent probes dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate: Effects of temperature and added carbon dioxide. *J. Phys. Chem. B* **2001**, *105*, 9663−9668.

(12) Anderson, J. L.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F. Measurement of SO$_2$ solubility in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 15059−15062.

(13) Torralba-Calleja, E.; Skinner, J.; Gutiérrez-Tauste, D. CO$_2$ capture in ionic liquids: A review of solubilities and experimental methods. *J. Chem.* **2013**, DOI: 10.1155/2013/473584.

(14) Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D. Guide to CO$_2$ separations in imidazolium-based room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2009**, *48*, 2739−2751.

(15) Bara, J. E.; Gabriel, C. J.; Lessmann, S.; Carlisle, T. K.; Finotello, A.; Gin, D. L.; Noble, R. D. Enhanced CO$_2$ separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2007**, *46*, 5380−5386.

(16) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why is CO$_2$ so soluble in imidazolium-based ionic liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.

(17) Shannon, M. S.; Bara, J. E. Properties of alkylimidazoles as solvents for CO$_2$ capture and comparisons to imidazolium-based ionic liquids. *Ind. Eng. Chem. Res.* **2011**, *50*, 8665−8677.

(18) Mejía, I.; Stanley, K.; Canales, R.; Brennecke, J. F. On the high-pressure solubilities of carbon dioxide in several ionic liquids. *J. Chem. Eng. Data* **2013**, *58*, 2642−2653.

(19) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. CO$_2$ capture by a task-specific ionic liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926−927.

(20) Wang, C.; Mahurin, S. M.; Luo, H.; Baker, G. A.; Li, H.; Dai, S. Reversible and robust CO$_2$ capture by equimolar task-specific ionic liquid-superbase mixtures. *Green Chem.* **2010**, *12*, 870−874.

(21) Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123−150.

(22) Ruß, C.; König, B. Low melting mixtures in organic synthesis − An alternative to ionic liquids? *Green Chem.* **2012**, *14*, 2969−2982.

(23) Abbott, A. P.; Harris, R. C.; Ryder, K. S.; D'Agostino, C.; Gladden, L. F.; Mantle, M. D. Glycerol eutectics as sustainable solvent systems. *Green Chem.* **2011**, *13*, 82−90.

(24) Tang, S.; Baker, G. A.; Zhao, H. Ether- and alcohol-functionalized task-specific ionic liquids: Attractive properties and applications. *Chem. Soc. Rev.* **2012**, *41*, 4030−4066.

(25) Zhao, H.; Baker, G. A. Ionic liquids and deep eutectic solvents for biodiesel synthesis: A review. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 3−12.

(26) Francisco, M.; Van Den Bruinhorst, A.; Kroon, M. C. Low-transition-temperature mixtures (LTTMs): A new generation of designer solvents. *Angew. Chem., Int. Ed.* **2013**, *52*, 3074−3085.

(27) Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep eutectic solvents: Syntheses, properties and applications. *Chem. Soc. Rev.* **2012**, *41*, 7108−7146.

(28) Zhang, Y.; Lu, X.; Feng, X.; Shi, Y.; Ji, X. Properties and applications of choline-based deep eutectic solvents. *Prog. Chem.* **2013**, *25*, 881−892.

(29) Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. Deep eutectic solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids. *J. Am. Chem. Soc.* **2004**, *126*, 9142−9147.

(30) Abbott, A. P.; Azam, M.; Ryder, K. S.; Saleem, S. In situ electrochemical digital holographic microscopy; A study of metal electrodeposition in deep eutectic solvents. *Anal. Chem.* **2013**, *85*, 6653−6660.

(31) Wagle, D. V.; Zhao, H.; Baker, G. A. Deep eutectic solvents: Sustainable media for nanoscale and functional materials. *Acc. Chem. Res.* **2014**, DOI: 10.1021/ar5000488.

(32) Abbott, A. P.; Capper, G.; McKenzie, K. J.; Ryder, K. S. Electrodeposition of zinc-tin alloys from deep eutectic solvents based on choline chloride. *J. Electroanal. Chem.* **2007**, *599*, 288−294.

(33) Abbott, A. P.; Barron, J. C.; Ryder, K. S.; Wilson, D. Eutectic-based ionic liquids with metal-containing anions and cations. *Chem.—Eur. J.* **2007**, *13*, 6495−6501.

(34) Francisco, M.; van den Bruinhorst, A.; Zubeir, L. F.; Peters, C. J.; Kroon, M. C. A new low transition temperature mixture (LTTM) formed by choline chloride+lactic acid: Characterization as solvent for CO$_2$ capture. *Fluid Phase Equilib.* **2013**, *340*, 77−84.

(35) Leron, R. B.; Caparanga, A.; Li, M. H. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T = 303.15−343.15 K and moderate pressures. *J. Taiwan Inst. Chem. Eng.* **2013**, DOI: 10.1016/j.jtice.2013.02.005.

(36) Leron, R. B.; Li, M. H. Solubility of carbon dioxide in a choline chloride-ethylene glycol based deep eutectic solvent. *Thermochim. Acta* **2013**, *551*, 14−19.

(37) Li, X.; Hou, M.; Han, B.; Wang, X.; Zou, L. Solubility of CO$_2$ in a choline chloride + urea eutectic mixture. *J. Chem. Eng. Data* **2008**, *53*, 548−550.

(38) *Strong and Hindered Bases in Organic Synthesis*; ChemFiles; Sigma-Aldrich: St. Louis, MO, 2003; Volume 3, No. 1, p 12.

(39) Al-Azzawi, O. M.; Hofmann, C. M.; Baker, G. A.; Baker, S. N. Nanosilica-supported polyethoxyamines as low-cost, reversible carbon dioxide sorbents. *J. Colloid Interface Sci.* **2012**, *385*, 154−159.

(40) Liang, M.; Kaintz, A.; Baker, G. A.; Maroncelli, M. Bimolecular electron transfer in ionic liquids: Are reaction rates anomalously high? *J. Phys. Chem. B* **2012**, *116*, 1370−1384.

(41) Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M. Physical properties of ionic liquids consisting of the 1-butyl-3- methylimidazolium cation with various anions and the bis(trifluoromethylsulfonyl)imide anion with various cations. *J. Phys. Chem. B* **2008**, *112*, 81−92.

2123

dx.doi.org/10.1021/sc5001594 | *ACS Sustainable Chem. Eng.* 2014, 2, 2117−2123