

Supporting Information for

Room-Temperature Ionic Liquid – Amine

Solutions: Tunable Solvents for Efficient and

Reversible Capture of CO₂

Dean Camper, Jason E. Bara, Douglas L. Gin, Richard D. Noble**

Department of Chemical & Biological Engineering,
University of Colorado at Boulder, Boulder, Colorado 80309

Email: jason.bara@colorado.edu, nobler@colorado.edu

Materials and General Procedures

All syntheses and manipulations were performed in air. All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI), with the exception of lithium bis(trifluoromethane)sulfonamide (LiTf_2N), which was obtained from 3M (St. Paul, MN). All chemicals were obtained in the highest purity grade possible from these suppliers, and were used as received. CO_2 (instrument grade, minimum purity 99.99%) was purchased from Air Gas (Radnor, PA).

Instrumentation

^1H NMR and ^{13}C data were obtained using a Varian INOVA 400 Spectrometer (400 MHz). FT-IR data were obtained using a Matteson Satellite. Water content (ppm) in **2a** and **2b** was determined using a Mettler Toledo DL32 Karl Fischer coulometer. A Thermolyne MaxiMix Plus vibrating mixer was used for homogenizing RTIL-amine solutions. The stainless steel cell used in CO_2 uptake experiments was fabricated by Dragan Mejjic in the machine shop in the Department of Chemical & Biological Engineering at CU-Boulder. Pressure sensors (PX303) were purchased from Omega. Automated data acquisition was performed using LabView (National Instruments) interfaced through a custom system designed by Dana Hauschulz in the electronic shop in the Department of Chemical & Biological Engineering at CU-Boulder.

Production of RTILs **2a** & **2b**

*Synthesis of 1-hexyl-3-methylimidazolium bis(trifluoromethane)sulfonamide (**2a**):*

1-Methylimidazole (103.50 g, 1.2605 mol) was dissolved in CH_3CN (500 mL) in a 1-L round-bottom flask. 1-Bromohexane (228.98 g, 1.3872 mol) was then added, and the reaction

mixture heated at reflux for 16 h. The reaction was then stopped, the solvent removed by rotary evaporation, and Et₂O (300 mL) added, resulting in the formation of two phases. The denser, oily phase was stirred in Et₂O for several hours at ambient temperature. Both phases were then poured into deionized H₂O (1 L), and the aqueous phase was then separated from the Et₂O phase. The aqueous phase was washed with EtOAc (3 x 500 mL) and then collected in a 2-L round-bottom flask. LiTf₂N (398.21 g, 1.3871 mol) was added to the aqueous phase, and an oily phase immediately separated. The mixture was subsequently vigorously stirred for 24 h to ensure thorough mixing in this large vessel. After this time, the oily phase was extracted into CH₂Cl₂ (750 mL) and washed with deionized H₂O (4 x 500 mL). The fifth aqueous washing was exposed to AgNO₃, to confirm that residual bromide anion was no longer present via the lack of AgBr precipitate formation. The organic phase was then dried over anhydrous MgSO₄, treated with activated carbon, and filtered through a plug of basic Al₂O₃. The solvent was then removed by rotary evaporation, and the final product was dried while stirring at 65 °C under dynamic vacuum (< 1 torr) for 16 h. The product **2a** was obtained as a clear, pale yellow oil. Yield: 464.05 g (82%). The water content in the product was found to be 217 ppm by Karl- Fischer titration. ¹H NMR data were consistent with published values for **2a**.¹

Synthesis of 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethane)sulfonimide (2b).

1-Methylimidazole (77.63 g, 0.9454 mol) was dissolved in CH₃CN (200 mL) in a 1-L round-bottom flask. 2-Chloroethanol (114.12 g, 1.4174 mol) was then added, and the reaction stirred at reflux for 72 h. After this time, the reaction was stopped, and the solvent removed via rotary evaporation. Et₂O (500 mL) was then added, resulting in the formation of two phases. The mixture was then placed in a freezer at -10 °C. Upon cooling for several hours, colorless

crystals formed. These crystals were then collected, washed with Et₂O (1 L), and dried at ambient temperature under dynamic vacuum (< 1 torr) overnight, yielding 124.35 g (81%) of 1-(2-hydroxyethyl)-3-methylimidazolium chloride. The 1-(2-hydroxyethyl)-3-methylimidazolium chloride (50.00 g, 0.3110 mol) was then dissolved in deionized H₂O (300 mL), to which LiTf₂N (89.28 g, 0.3110 mol) was added to immediately form a separated oily phase. The reaction was then stirred overnight at ambient temperature, after which the oily phase was extracted with EtOAc (500 mL) and washed with deionized H₂O (4 x 250 mL). The absence of chloride anion was confirmed through addition of AgNO₃ to the fourth aqueous washing, without any AgCl precipitate formation. The organic phase was then dried over anhydrous MgSO₄, treated with activated carbon, and filtered through a plug of basic Al₂O₃. The solvent was removed via rotary evaporation, and the product dried under dynamic vacuum (< 1 torr) while stirring at 65 °C overnight to produce **2b** as a clear, colorless oil. Yield: 60.58 g (48%). The water content in the product was found to be 225 ppm by Karl-Fischer titration. ¹H NMR data were consistent with published values for **2b**.²

General Procedure for the Formulation of RTIL-amine Solutions

50:50 (Mol:mol) solutions of RTILs with amines were prepared for comparison with amine-functionalized TSILs, which contain one 1° amine group per ion pair.³ RTIL **2a** (10.00 g, 22.35 mmol) was mixed with MEA (1.365 g, 22.35 mmol) in a 20-mL glass vial. The vial was sealed and the liquids were held on a vibrating mixer, typically for < 10 s, until a homogeneous solution was achieved. This procedure was repeated for **2b**-MEA and **2b**-DEA.

Notes on Preparing RTIL-amine Mixtures with > 50 mol% Amine Content

RTILs **2a** and **2b** are miscible with MEA in all proportions. Solutions containing > 50 mol % MEA content were prepared in the same manner as those with 50 mol % content, as outlined above. No phase separation was observed for any mixture with >50 mol% of MEA. Similarly, **2b** was miscible with DEA, and solutions of **2b**-DEA with > 50 mol% DEA were also prepared. MEA is typically dissolved in water at 30 wt% (~5 mol/L) in industrial processes.⁴ These concentrations can be achieved in RTIL-amine solutions.

CO₂ Capture Experiments

CO₂ uptake experiments in RTIL-amine solutions were performed using a dual-volume, dual-transducer apparatus described in a previous work.⁵ A summary of the operation is included below.

An aliquot of RTIL-amine solution of known mass and volume was sealed in a stainless steel cell of known volume. The cell was heated to 40 °C and purged under dynamic vacuum (< 10 torr) for a short time to remove any residual air from the system. CO₂ was then introduced at ~ 1 atm. As the CO₂ reacted with the amines, the pressure in the cell was observed to decay and was recorded electronically as a function of time. The difference between the initial and final CO₂ pressures was converted into moles of CO₂ reacted with amine using the ideal gas equation (Equation S1). Complexation and decomplexation of CO₂ from amines were performed at 40 °C and 100 °C, respectively, so as to make direct comparisons with the data for aqueous amine solutions in Reference 4, wherein Chapter 9, especially pages 217-218, is a very useful resource relating to CO₂ capture.⁴

$$n_{CO_2} = \frac{\Delta PV}{RT} \quad (S1)$$

Example Data for CO₂ Capture and Release with Equimolar 2a-MEA Solutions

Figure S1 is an example of the pressure decay of CO₂ in an equimolar solution of 2a-MEA.

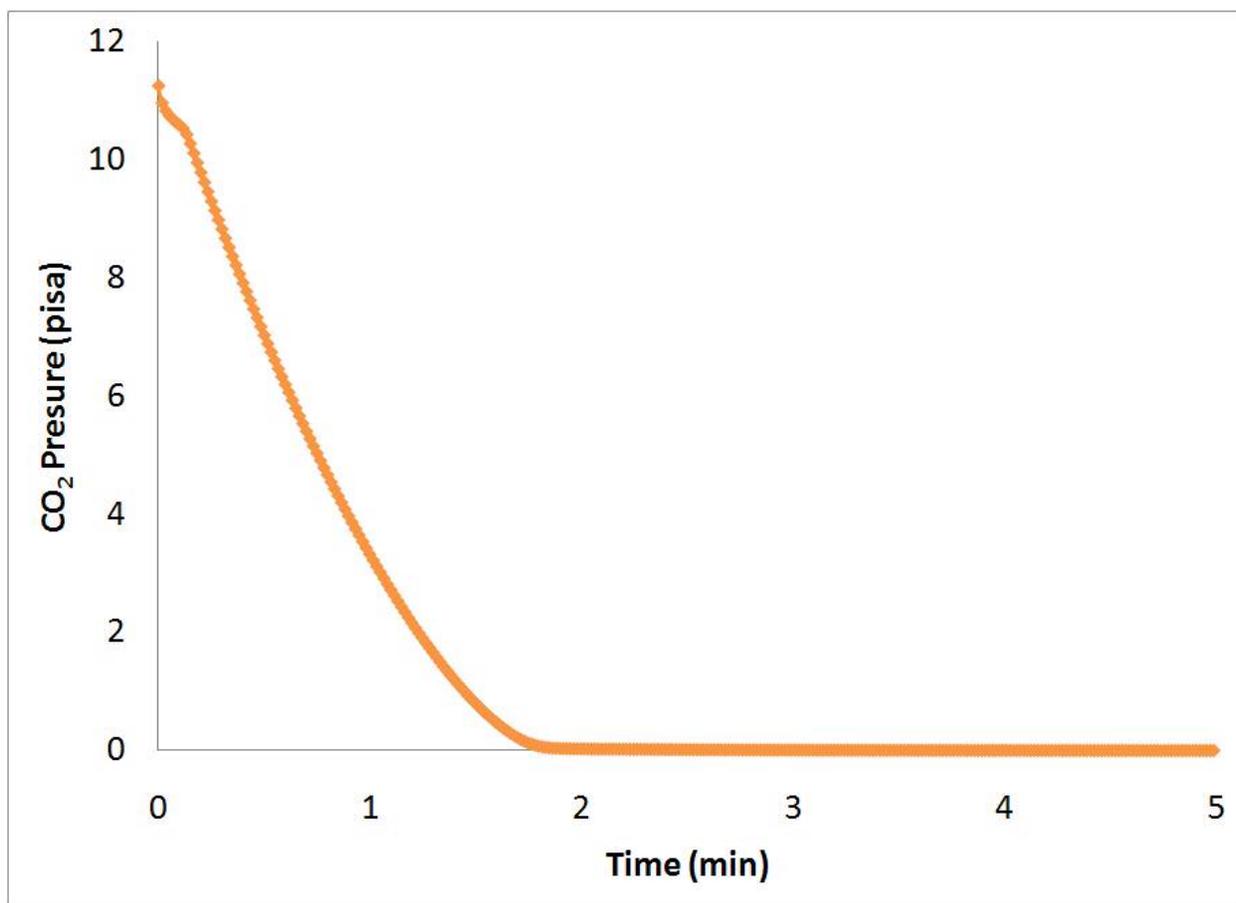


Figure S1: Example of CO₂ pressure data for uptake in an equimolar 2a-MEA solution.

Figure S1 also shows that the CO₂ concentration in the gas feed can be rapidly reduced and effectively brought to zero using an equimolar 2a-MEA solution. These solutions can be rapidly stirred to increase reaction rate, unlike TSILs.³ The final pressure of CO₂ in Figure S1 is

0 ± 0.015 psia, where 0.015 psia is the accuracy of the pressure sensor used. The complete reaction of CO_2 was favored by MEA-carbamate precipitating from the RTIL solutions. As the final pressure is near 0.00 psia, there is no CO_2 dissolved in the RTIL after the reaction with MEA is complete. The chemical absorption (reaction with MEA) is much more favorable than the physical absorption (dissolution into RTIL, based on partial pressure of CO_2).

Figure S2 shows the rate of conversion of CO_2 to MEA-carbamate salt of this system, since the initial moles of amine in solution are known.

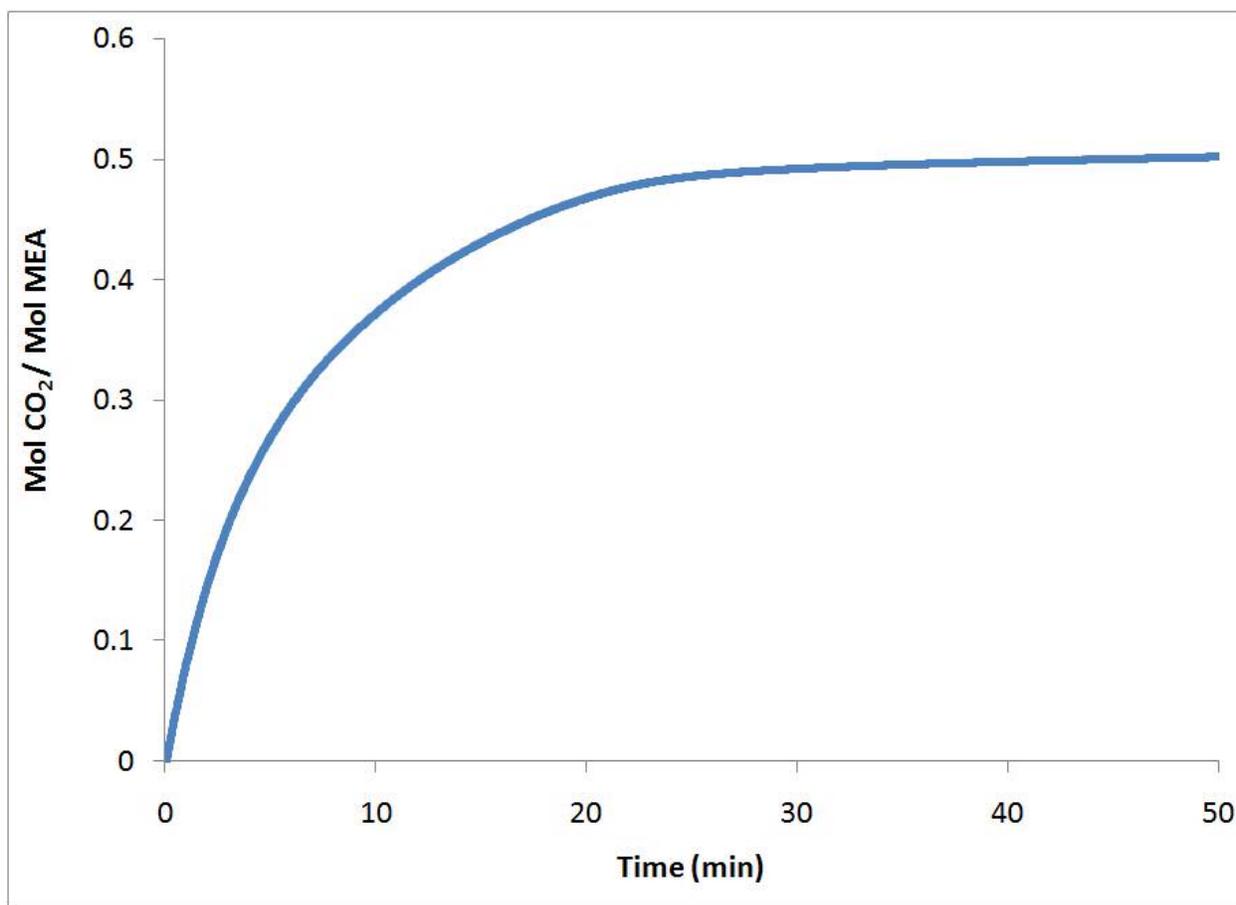


Figure S2: Example graph of CO_2 conversion to MEA-carbamate as a function of time.

CO₂ was decomplexed from MEA-carbamate by increasing the temperature to from 40 °C to 100 °C and reducing the pressure from 605 torr (11.7 psia) to 279 torr (5.4 psia), which favors the release of CO₂ and reformation of neutral MEA (Scheme 1). Figure S3 shows the rate of CO₂ release from MEA-carbamate in **2a**. Upon reducing the system pressure, to remove some CO₂ from the cell volume, the ratio of CO₂ to amines was reduced from 0.395 to 0.350 within 2 minutes. The initial value of 0.395 is less than the 0.500 that was achieved from complete capture at 40 °C. This is a consequence of heating from 40 °C to 100 °C, as some CO₂ had already been released.⁴

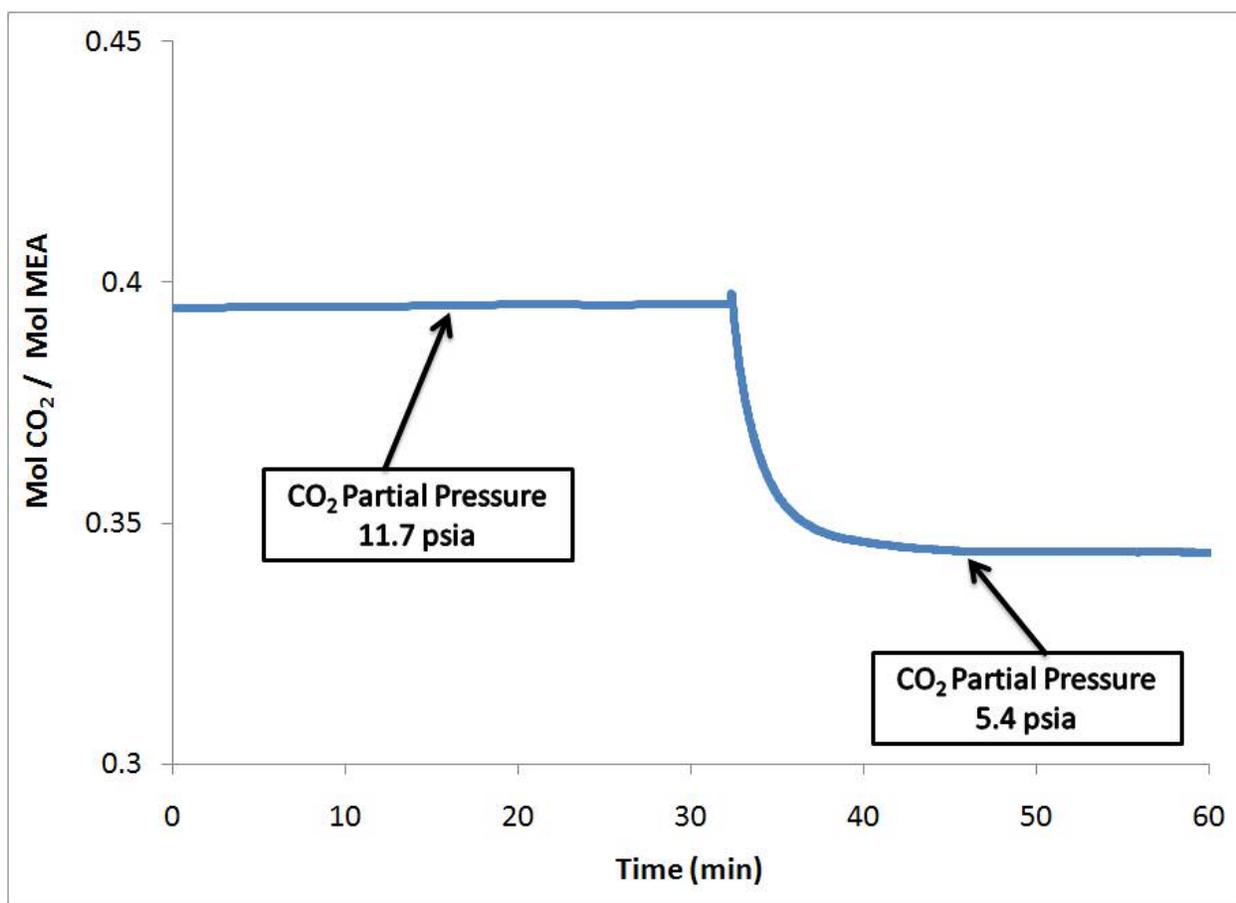


Figure S3: Plot of the release of CO₂ from MEA-carbamate in **2a** at 100 °C and under reduced pressure as a function of time.

Example Data for CO₂ Capture and Release with Equimolar 2b-DEA Solutions

CO₂ reacts with DEA in **2b** with CO₂ at low pressure to loading levels similar to what can be achieved in aqueous solutions (see Figure 3 in the main manuscript). However, DEA-carbamate (Figure S4) is a weaker CO₂-adduct than MEA-carbamate, thus the moles of CO₂ captured by DEA are less than 1:2 at the equilibrium pressure of 30.4 torr (0.588 psia).⁴ An equilibrium pressure of ~155 torr (3 psia) is required to achieve a 1:2 ratio of CO₂:DEA.⁴

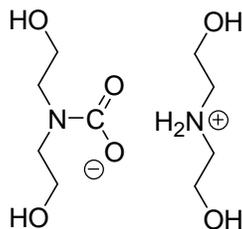


Figure S4: DEA-carbamate formed by reaction of 2 moles of DEA with 1 mole of CO₂.

An added benefit of the **2b**-DEA solutions is that increasing the partial pressure of CO₂, even at elevated temperatures, resulted in increased uptake of CO₂ by equimolar **2b**-DEA solutions (Figure S5). The molar ratio of CO₂ to DEA increased from 0.093 to 0.165 with increasing CO₂ partial pressure from 248 torr (4.8 psia) to 708 torr (13.7 psia) at 100 °C. Although aqueous amine solutions are near their boiling points at this temperature, RTILs are effectively non-volatile at 100 °C.

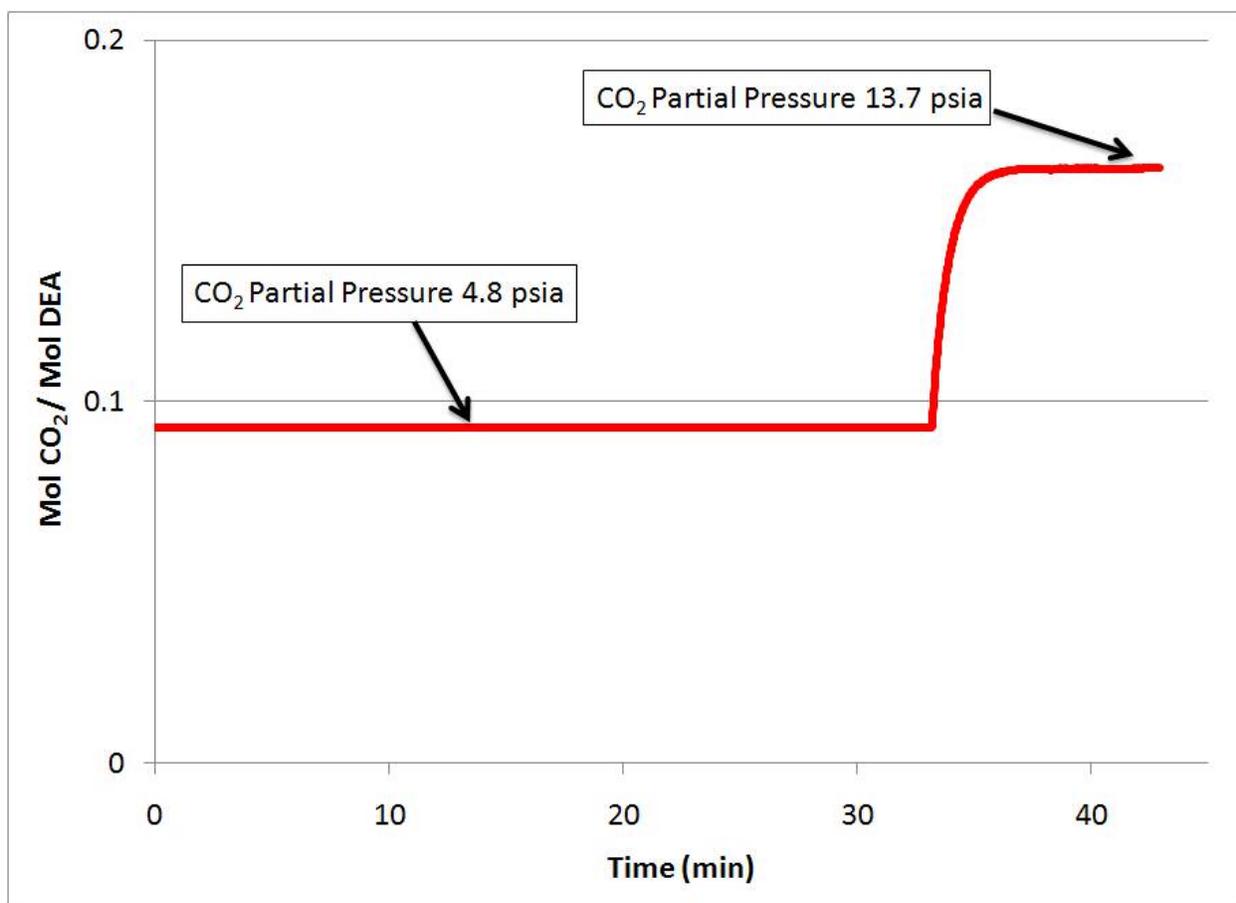


Figure S5: Plot of increased CO₂ uptake in **2b**-DEA at 100°C with increasing pressure of CO₂.

Notes on the Advantages of RTILs over Water in Industrial Amine-based CO₂ Scrubbing

Figure S6 is a schematic of a typical aqueous amine gas treatment unit.⁶ The advantages of RTIL-amine solutions can be realized in several ways with minimal modifications. The simplest approach may be to replace water with an RTIL or a mixture of RTILs and/or normal co-solvents. Also, since RTILs have approximately one-half the heat capacity of water on volume basis there is an immediate energy savings from the heating and cooling of the solution between the absorber and regenerator. Also, as RTILs have a negligible vapor pressure there would be essentially no losses of the RTIL due to vaporization. Another benefit of the negligible vapor pressure of the RTIL is that if a sweep gas is needed (in typical aqueous amine solutions

water vapor is the sweep gas), a more energy efficient method could be implemented. A very interesting feature of these RTIL-MEA solutions is that while MEA is soluble in imidazolium-based RTILs, MEA-carbamate is not. This allows for the possibility of separating out the precipitated carbamate for direct regeneration (to MEA and CO₂) without consuming energy to heat a large volume of RTIL solvent to the temperatures required to decomplex CO₂.

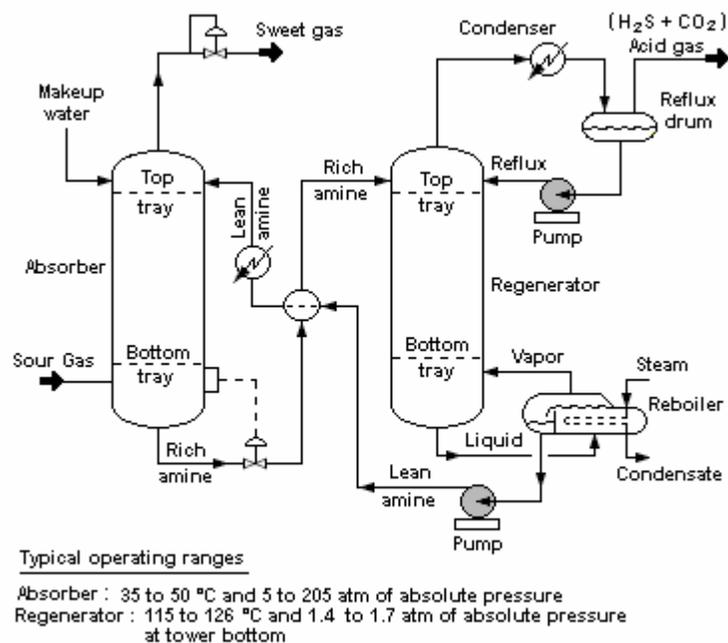


Figure S6: Typical aqueous amine treatment process schematic.⁶

NMR and FT-IR Spectra

The following spectra are available in a separate file:

¹H NMR for:

2a

2b

equimolar **2a**-MEA prior to CO₂ exposure

equimolar **2b**-DEA prior to CO₂ exposure

2a-rich phase after CO₂ exposure

MEA-carbamate rich precipitate

2b-DEA after CO₂ exposure

Stack plot of **2b**-DEA before and after CO₂ exposure

¹³C NMR for:

MEA-carbamate rich precipitate

2b-DEA after CO₂ exposure

FT-IR for:

2a

2b

equimolar **2a**-MEA prior to CO₂ exposure

equimolar **2b**-DEA prior to CO₂ exposure

2a-rich phase after CO₂ exposure

MEA-carbamate rich precipitate

2b-DEA after CO₂ exposure

References for Supporting Information:

- (1) ¹H NMR data for **2a**: Baba, K.; Ono, H.; Itoh, E.; Itoh, S.; Noda, K.; Usui, T.; Ishihara, K.; Inamo, M.; Takagi, H. D.; Asano, T. *Chem-Eur. J.* **2006**, *12*, 5328.
- (2) ¹H NMR data for **2b**: Shimojo, K.; Kamiya, N.; Tani, F.; Naganawa, H.; Naruta, Y.; Goto, M. *Anal. Chem.* **2006**, *78*, 7735.
- (3) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 926.
- (4) Astarita, G.; Savage, D. W.; Bisio, A. *Gas treating with Chemical Solvents*; John Wiley & Sons: New York, 1983.
- (5) Bara, J. E.; Gabriel, C. J.; Lessmann, S.; Carlisle, T. K.; Finotello, Alexia; Gin, D. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **2007**, *46*, 5380.
- (6) Image source: http://en.wikipedia.org/wiki/Amine_gas_treating. Copyright 2006 Mbeychok. Permission to reproduce granted under the terms of the GNU Free Documentation License.