(Supporting Information)

CO_2 capture in alkanolamine-RTIL blends via carbamate crystallization: route to efficient regeneration

Muhammad Hasib-ur-Rahman[†] *and Faïçal Larachi**[†]

[†]Department of Chemical Engineering, Laval University, Québec, QC G1V 0A6, Canada. Fax: (418) 656-5993; Tel: (418) 656-3566;

E-mail (Faïçal Larachi): Faical.Larachi@gch.ulaval.ca

E-mail (Muhammad Hasib-ur-Rahman): muhammad.hasib-ur-rahman.1@ulaval.ca

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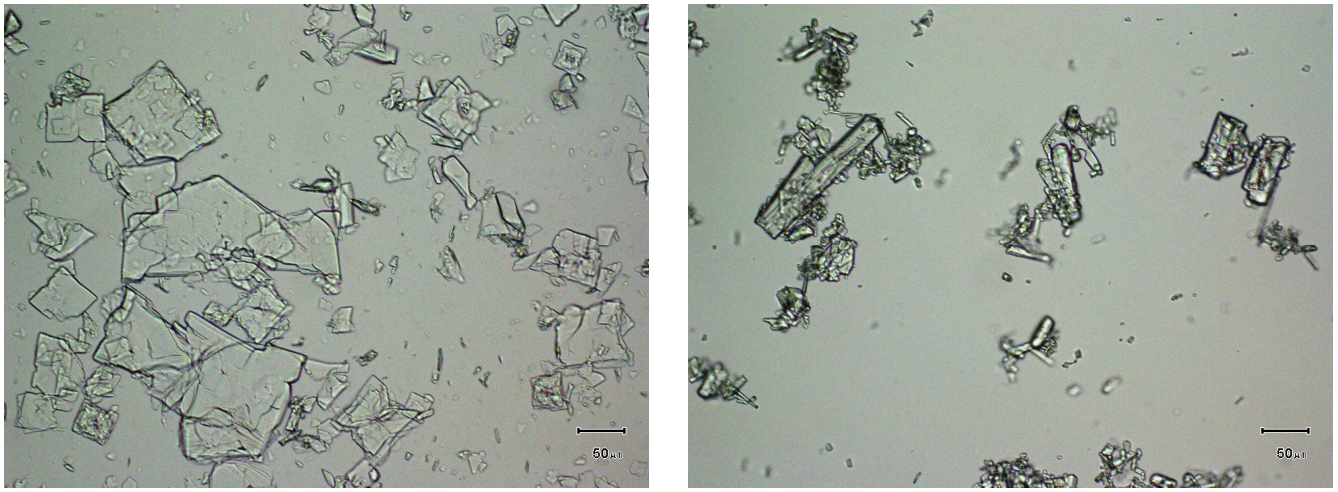
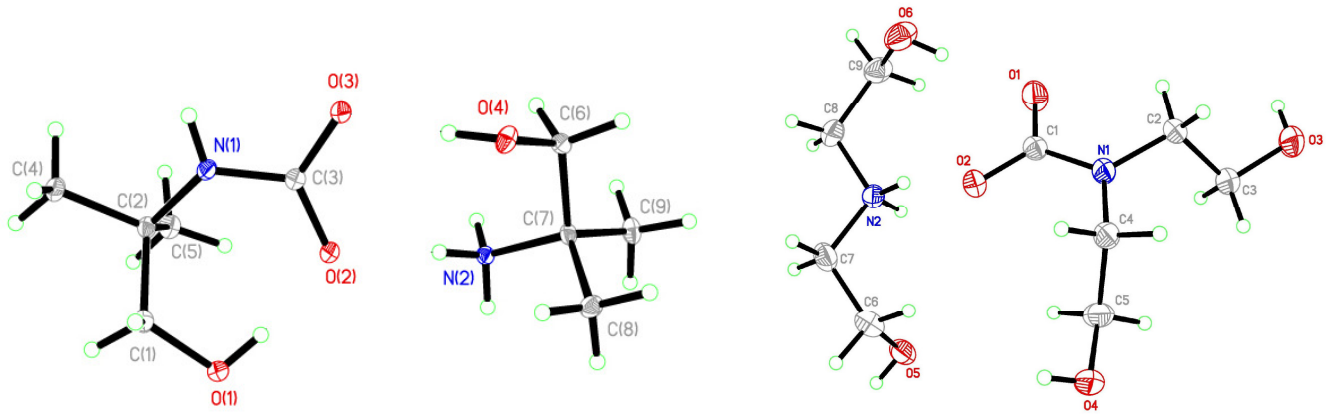
Single crystal X-ray diffraction studies:

To obtain carbamate crystals, CO_2 was bubbled in respective amine-RTIL (AMP-[hmim][Tf_2N] and DEA-[hmim][Tf_2N]) blends. Supernatant crystals were separated from the RTIL and washed thoroughly with acetone. The crystals were then dried and stored at room temperature for characterization.



(a) **(b)**

Figure S1. Carbamate crystals in RTIL medium, as seen under optical microscope: **a)** AMP-carbamate; **b)** DEA-carbamate.



(a) $C_9H_{22}N_2O_4$ (AMP-Carbamate) **(b)** $C_9H_{22}N_2O_6$ (DEA-Carbamate)

Figure S2. Structural units: a) AMP-carbamate; b) DEA-carbamate [reproduced with permission from (s8)].

Crystal structure determination:

Crystallographic data measurements were made at 100 K on a Bruker APEX II area detector diffractometer equipped with a source of CuKα monochromatic radiation (λ = 1.54178 Å). APEX 2 and SAINT programs were used for retrieving cell parameters and data collection.[s1-s2] Absorption corrections were performed using SADABS.[s3] The structure was solved and refined by full-matrix least-squares against F^2 using SHELXS-97 and SHELXL-97 programs.[s4-s6] Refinement of all non-hydrogen atoms was done anisotropically. The hydrogen atoms were placed at geometrically idealized positions using a riding model. Further experimental details are provided in Tables S1-S2, and as CIF report. Crystal structure data for AMP-carbamate has also been reported previously by Jo et al., 2010.[s7] Single crystal X-ray diffraction analysis of DEA-carbamate has been discussed in our previous work.[s8]

Table S1. Crystal data and structure refinement for AMP-carbamate

Empirical formula	$C_9H_{22}N_2O_4$
Formula weight	222.29
Temperature	100K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.02881(12) Å α = 90°
	b = 9.88517(19) Å β = 97.8757(8)°
	c = 20.4701(4) Å γ = 90°
Volume	1208.43(4)Å^3
Z	4
Density (calculated)	1.222 g/cm^3
Absorption coefficient	0.790 mm^{-1}
F(000)	488
Crystal size	0.12 x 0.08 x 0.04 mm
Theta range for data collection	4.36 to 70.86°
Index ranges	$-6\leq h\leq 7$, $-12\leq k\leq 12$, $-25\leq l\leq 24$
Reflections collected	23054
Independent reflections	2270 [R_{int} = 0.025]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2270 / 0 / 164
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R_1 = 0.0328, wR_2 = 0.0864
R indices (all data)	R_1 = 0.0336, wR_2 = 0.0872

Table S2. Bond lengths and angles for $C_9H_{22}N_2O_4$ (AMP-carbamate).

Bond lengths [Å]			
O(1)-C(1)	1.4322(12)	C(2)-C(4)	1.5338(14)
O(2)-C(3)	1.2800(13)	O(4)-C(6)	1.4129(13)
O(3)-C(3)	1.2688(13)	N(2)-C(7)	1.5022(12)
N(1)-C(3)	1.3625(13)	C(6)-C(7)	1.5306(14)
N(1)-C(2)	1.4785(13)	C(7)-C(8)	1.5220(14)
C(1)-C(2)	1.5343(15)	C(7)-C(9)	1.5227(14)
C(2)-C(5)	1.5288(14)		
Bond angles [°]			
C(3)-N(1)-C(2)	127.14(9)	O(3)-C(3)-N(1)	117.45(9)
O(1)-C(1)-C(2)	115.03(8)	O(2)-C(3)-N(1)	120.08(9)
N(1)-C(2)-C(5)	110.59(9)	O(4)-C(6)-C(7)	113.41(8)
N(1)-C(2)-C(4)	105.89(8)	N(2)-C(7)-C(8)	107.96(8)
C(5)-C(2)-C(4)	110.06(9)	N(2)-C(7)-C(9)	107.96(8)
N(1)-C(2)-C(1)	112.45(8)	C(8)-C(7)-C(9)	111.61(9)
C(5)-C(2)-C(1)	111.37(9)	N(2)-C(7)-C(6)	108.25(8)
C(4)-C(2)-C(1)	106.24(9)	C(8)-C(7)-C(6)	111.43(9)
O(3)-C(3)-O(2)	122.45(9)	C(9)-C(7)-C(6)	109.51(9)

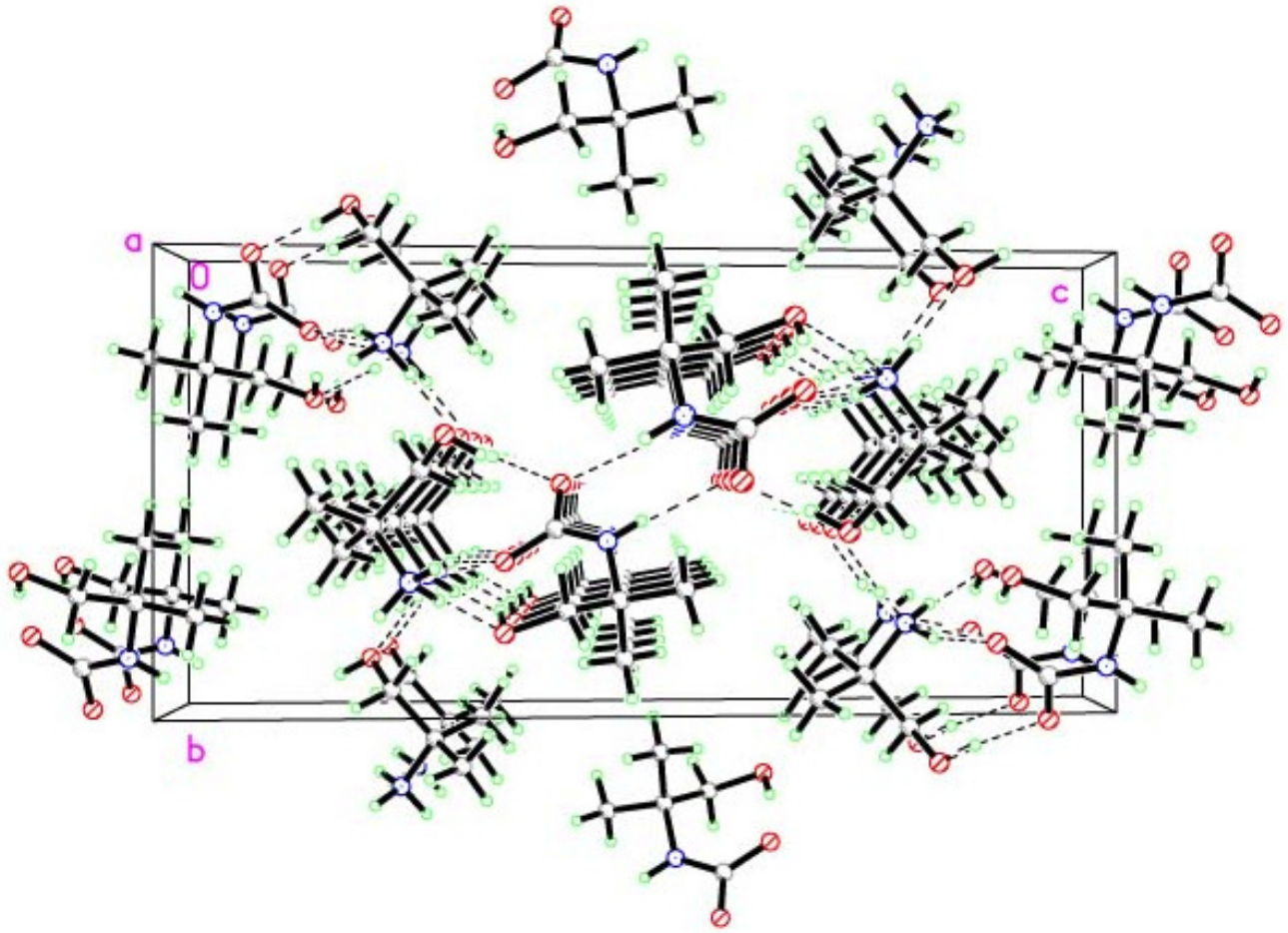


Figure S3. Packing diagram of $C_9H_{22}N_2O_4$ compound (AMP-carbamate).

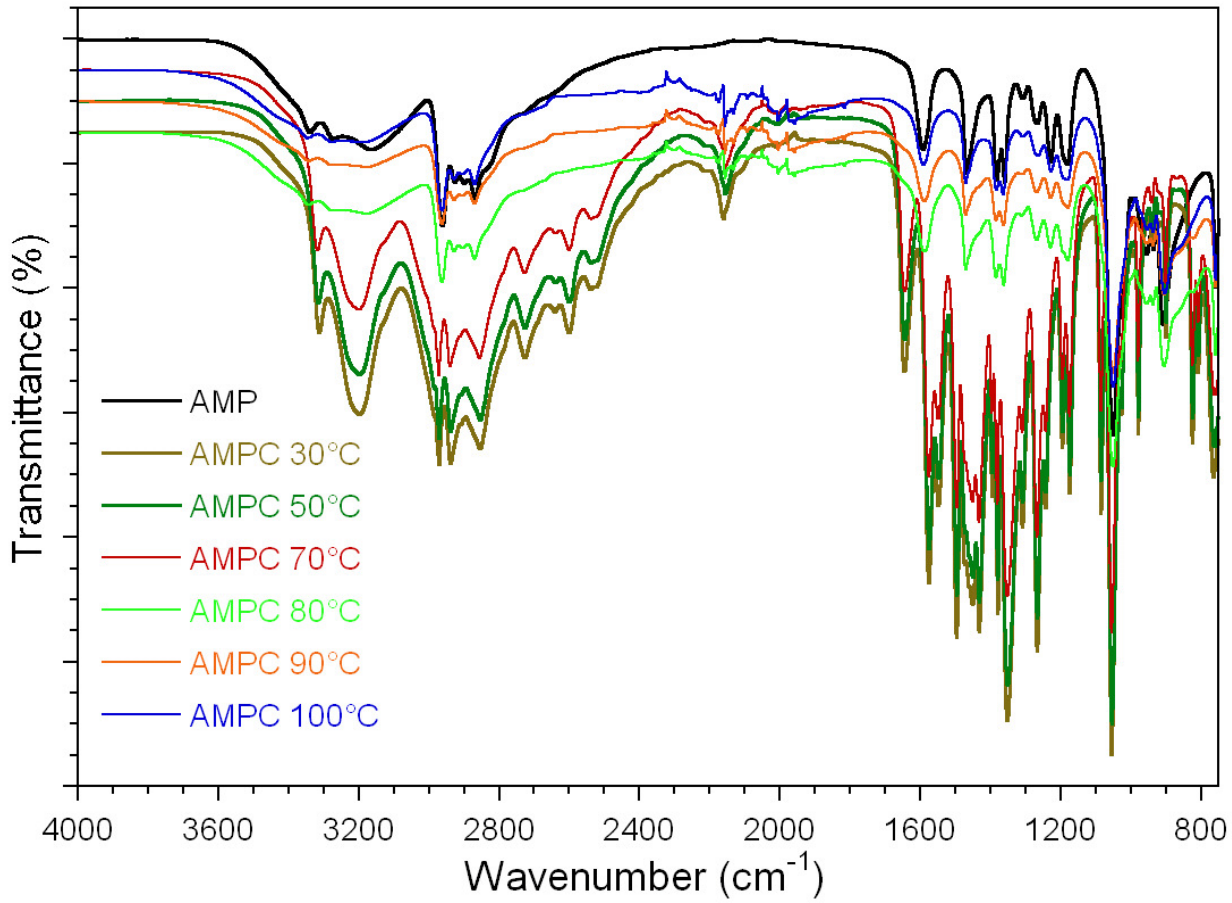


Figure S4. FTIR spectrum of AMP-carbamate in the temperature range of 30-100 °C (regenerated AMP appeared in spectra taken at 80 °C and above).

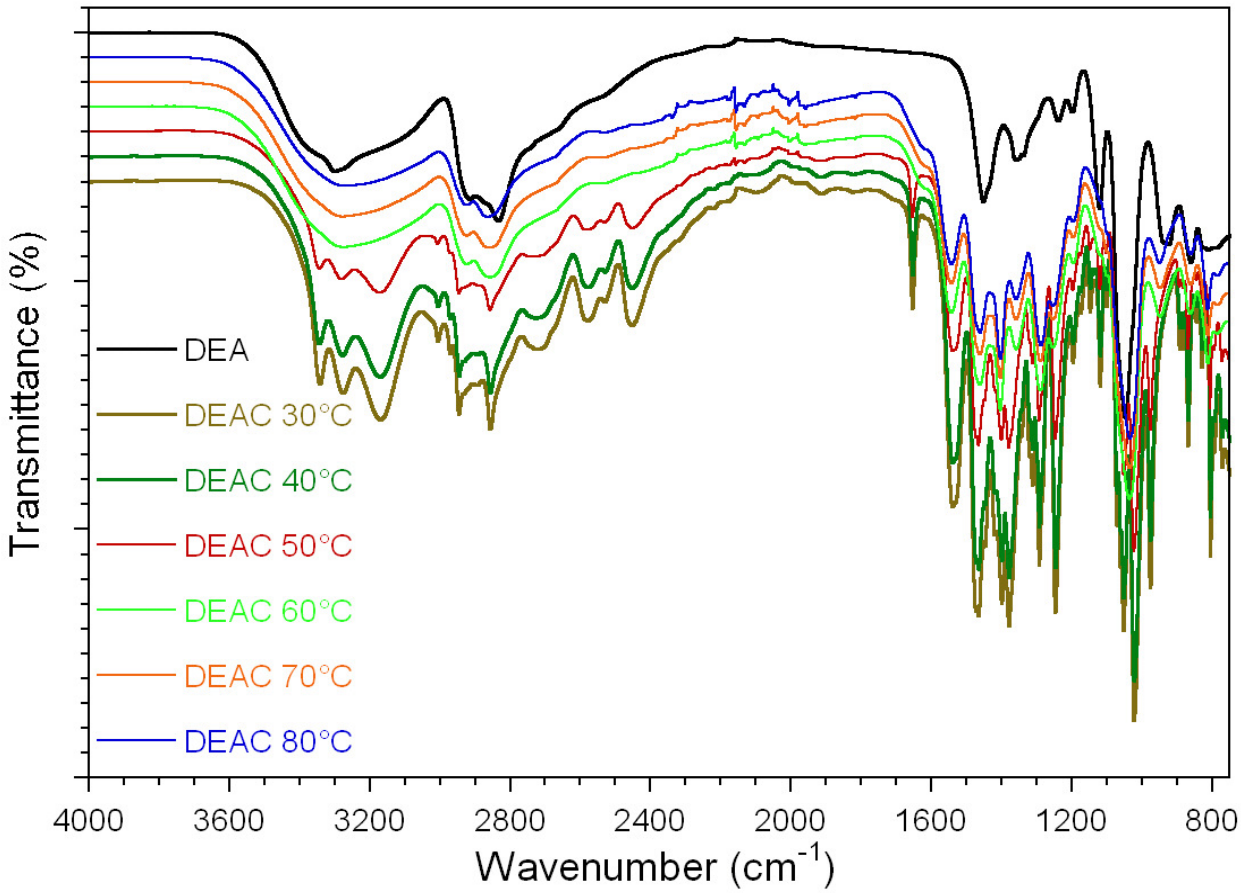


Figure S5. FTIR spectrum of DEA-carbamate in the temperature range of 30-80 °C (regenerated DEA appeared above 50 °C).

References:

(s1) APEX2, *Bruker Molecular Analysis Research Tool*. Bruker AXS Inc., Madison, WI, **2009**.

(s2) SAINT, Release 7.34A; *Integration Software for Single Crystal Data*. Bruker AXS Inc., Madison, WI, **2006**.

(s3) Sheldrick, G.M. SADABS; *Bruker Area Detector Absorption Corrections*. Bruker AXS Inc., Madison, WI, **2008**.

(s4) Sheldrick, G.M. *Acta Crystallogr.* **2008**, A64, 112-122.

(s5) SHELXTL, version 6.12; Bruker Analytical X-ray Systems Inc., Madison, WI, **2001**.

(s6) XPREP, Version 2008/2; *X-Ray Data Preparation and Reciprocal Space Exploration Program*. Bruker AXS Inc., Madison, WI, **2008**.

(s7) Jo, E.; Jhon, Y.H.; Choi, S.B.; Shim, J.-G.; Kim, J.-H.; Lee, J.H.; Lee, I.-Y.; Jang, K.-R.; Kim, J. Crystal structure and electronic properties of 2-amino-2-methyl-1-propanol (AMP) carbamate. *Chem. Commun.* **2010**, 46, 9158-9160.

(s8) Hasib-ur-Rahman, M.; Siaj, M.; Larachi, F. CO_2 capture in alkanolamine/room-temperature ionic liquid emulsions: A viable approach with carbamate crystallization and curbed corrosion behavior. *Int. J. Greenh. Gas Control* **2012**, 6, 246-252.