Electronic Supplementary Information

for

Deep Eutectic Solvents as Attractive Media for CO_2 Capture

Tushar J. Trivedi, Ji Hoon Lee, Hyeon Jeong Lee, You Kyeong Jeong, and Jang Wook Choi*

Graduate School of Energy, Environmental Water and Sustainability (EEWS) and Saudi Aramco-KAIST CO_2 Management Center, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

Spectroscopic characterization of deep eutectic solvents (DESs)

Pure [MEA.Cl][EDA]

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm) 5.2 (*s*, -OH, broad), 3.45 (*t*, -HO-CH_2), 2.60 (*t*, -CH_2-NH_3^+), 2.57 (*s*, sharp -CH_2 of EDA); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_C (ppm): 60.98, 41.87, and 40.85; FTIR: (neat) ν_{max}= 839, 948, 1073, 1318, 1460, 1513, 1600, 2139, 2868, 2900, 3338 cm^{-1}; ESI MS: (ESI$^+$) m/z-61.11 $[MEAH]^+$, (ESI$^-$) m/z-255.26 $[Cl(EDA)_3]^-$

[MEA.Cl][EDA] after CO_2 absorption:

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm) 6.51 (*s*, -NH), 5.26 (*s*, -OH, broad), 3.55 (*t*, -HO-CH_2), 3.06 (*t*, -CH_2-NHCOO), 2.846 (*m*, -CH_2-NH_3^+ and –CH_2-NH), 2.74 (*s*, sharp -CH_2 of EDA and -NH_2/-NH),^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_C (ppm) 164.37, 58.20, 41.25, 40.194 and 38.95; FTIR: (neat) ν_{max}= 851, 1015, 1098, 1190, 1320, 1487, 1513, 1600, 2134, 3056, 3342 cm^{-1}; ESI MS: (ESI$^+$) m/z-61.11 $[MEAH]^+$, (ESI$^-$) m/z-283.26 $[Cl(EDA)_3CO_2]^-$

Pure [TEA.Cl][EDA]

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm) 3.69 (*t*, -HO-CH_2-), 2.64 (*t*, -$(CH_2)_3$-NH^+), 2.55 (*s*, sharp -CH_2 of EDA); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_C (ppm): 61.31, 58.21, 44.35; ESI MS: (ESI$^+$) m/z-150.20 $[TEAH]^+$, (ESI$^-$) m/z-255.23 $[Cl(EDA)_3]^-$

[TEA.Cl][EDA] after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm) 3.484 (*t*, -HO-CH_2), 3.071 (*t*, -$(CH_2)_3$-NH^+), 2.819 (*t*, -NH_2-CH_2), 2.747 (*s*, sharp -CH_2 of EDA and -NH_2/-NH), 2.57 (*t*, -CH_2-NHCOO); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_C (ppm) 166.97, 60.97, 58.04, 42.77, 42.28, 41.55; ESI MS: (ESI$^+$) m/z-150.12 $[TEAH]^+$, (ESI$^-$) m/z-283.26 $[Cl(EDA)_3CO_2]^-$

Pure [UE.Cl][EDA]

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm) 2.68 (*s*, sharp -CH_2 of EDA); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_C (ppm): 162.48, 42.67; ESI MS: (ESI$^+$) m/z-61.09 $[UEH]^+$, (ESI$^-$) m/z-255.23 $[Cl(EDA)_3]^-$

[UE.Cl][EDA] after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^oC): δ_H (ppm) 3.027 (*t*, -CH_2-NHCOO), 2.68 (*m*, -CH_2-NH_2 and sharp -CH_2 of EDA); ^{13}C NMR (400 MHz, D_2O, 25 ^oC): δ_C (ppm) 164.46, 161.45, 40.37, 40.24, 40.04; ESI MS: (ESI$^+$) m/z-61.11 $[UEH]^+$, (ESI$^-$) m/z-283.26 $[Cl(EDA)_3CO_2]^-$

Pure [TAE.Cl][EDA]

^{1}H NMR (400 MHz, D_2O, 25 ^oC): δ_H (ppm) 2.712 (*s*, sharp -CH_2 of EDA), 0.92 (*s,* -CH_3); ^{13}C NMR (400 MHz, D_2O, 25 ^oC): δ_C (ppm): 70.88, 41.02, 18.45; ESI MS: (ESI$^+$) m/z-76.18 $[TAEH]^+$, (ESI$^-$) m/z-255.23 $[Cl(EDA)_3]^-$

[TAE.Cl][EDA] after CO_2 absorption:

^{1}H NMR (400 MHz, D_2O, 25 ^oC): δ_H (ppm) 3.09 (*t*, -CH_2NHCOO), 2.78 (*t*, -CH_2-NH_2), 2.72 (*s*, sharp -CH_2 of EDA and -NH_2/-NH), 1.02 (*s,* -CH_3); ^{13}C NMR (400 MHz, D_2O, 25 ^oC): δ_C (ppm) 164.36, 109.88, 40.21, 39.76, 39.13; ESI MS: (ESI$^+$) m/z-76.20 $[TAEH]^+$, (ESI$^-$) m/z-283.26 $[Cl(EDA)_3CO_2]^-$

Heat of Absorption Calculation:

The heat of absorption was calculated based on Van't Hoff equation. For this, equilibrium constants were attained from CO_2 uptakes at series of temperatures.[1, 2] For the general reaction scheme below,

$$2\ DES + CO_2 \leftrightarrow 2DES{\cdot}CO_2$$

Equilibrium constant can be defined as follows:

$$K = \frac{[2DES.CO_2]}{[DES]^2\, P_{CO2}}$$

As all our experiments were carried out at atmospheric pressure, we assume $P_{CO2} = 1$. *K* value at each temperature was then obtained by [DES] and [2DES-CO_2]. The *K* value can be incorporated

with Van't Hoff equation below, from which ΔH can be retrieved from the linear fitting over ln (K) vs. $1/T$ plot.

$$\Delta G = \Delta H - T\Delta S$$

$$-RT\ln(K) = \Delta H - T\Delta S$$

$$\ln(K) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\ln(K) = -\frac{\Delta H}{R}(\frac{1}{T}) + C$$

Corrosion Test:

To measure the corrosiveness of the synthesized DESs and also compare it with that of conventional amine based scrubbing solvents (MEA and EDA), so-called the weight loss technique was employed. In this experiment, a stainless steel piece (~1.75 x 1.15 cm^2) was immersed in a vial (5 mL) containing each of highly concentrated (75 wt%) solvent loaded with 20 wt% CO_2 at 90 ^oC for 10 days. To maintain the constant temperature, an oil bath was used. Before and after the immersion, the weight of each piece was measured. Based on the weight difference, the corrosion penetration rate (CPR) in millimeter per year (mm/y) was calculated using the following formula.[3]

$$\text{Corrosion penetration rate (CPR)} = \frac{KW}{\rho At}$$

where K = rate constant (8.76 x10^4), W = weight loss in g, ρ = density of stainless steel in g/cm^3, t = time of exposure in hours, A = exposed specimen area (cm^2).

Corrosion process

Corrosion is a coupled redox process at an interface of steel surface and corrosive solution (MEA, EDA, and DESs in the current study). The oxidation occurs at the anode via iron dissolution, while the reduction takes place in the solution. The corrosion rate tends to increase with increasing CO_2 loading in the presence of moisture due to the process below producing carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) which can be redox coupled with iron:[3, 4]

Absorption of CO_2:

$$2R\text{-}NH_2 + CO_2 \rightarrow R\text{-}NH_3^+ + RNHCOO^-$$

$$R\text{-}NH_2 + CO_2 + H_2O \rightarrow R\text{-}NH_3^+ + HCO_3^-$$

$$2H_2O + CO_2 \rightarrow H_3O^+ + HCO_3^-$$

$$2H_2O + HCO_3^- \rightarrow H_3O^+ + CO_3^{2-}$$

At the steel surface (oxidation):

$$Fe \rightarrow Fe^{2+} + 2e^-$$

In the solution (reduction):

$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2$$

$$2HCO_3^- + 2e^- \rightarrow 2CO_3^{2-} + H_2$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Formation of corrosion products:

Ferrous hydroxide: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Ferrous carbonate: $Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$

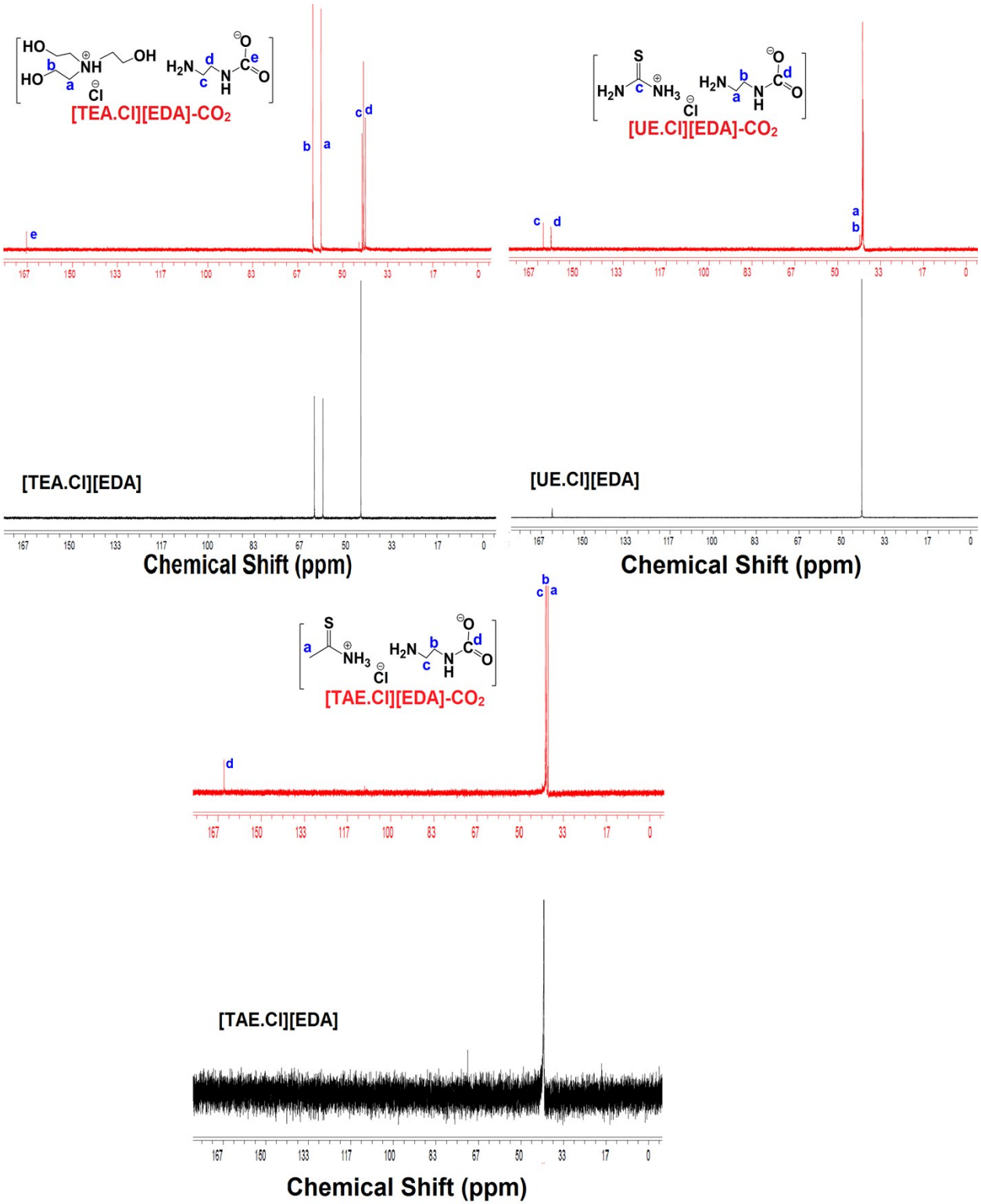

Fig. S1 ^{13}C NMR analyses of various DESs with a molar composition of HBA: HBD=1:3 before (black) and after (red) CO_2 absorption.

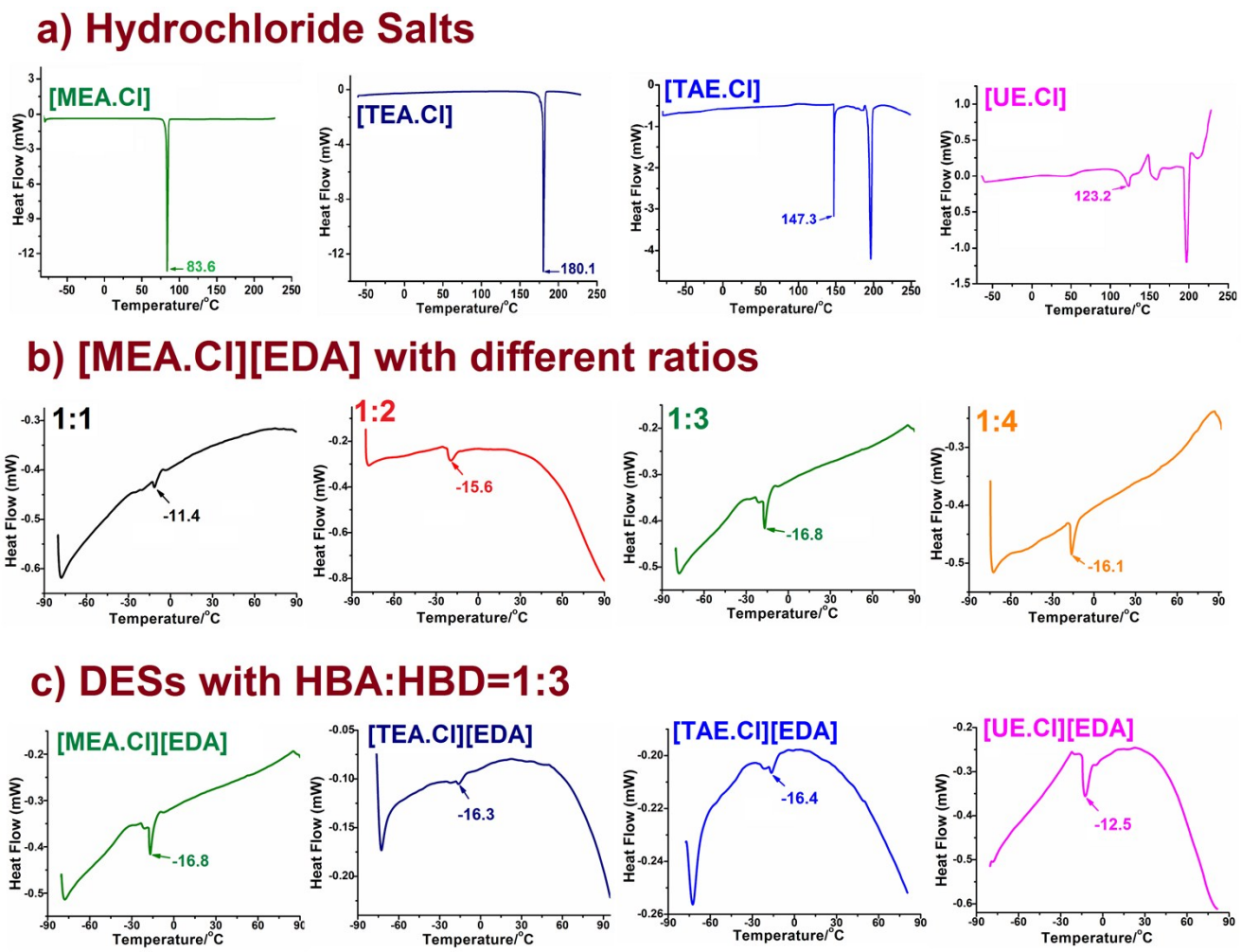

Fig. S2 DSC spectra of (a) Hydrochloride salts; and prepared DESs, (b) [MEA.Cl][EDA] with different molar ratios, and (c) other DESs with HBA:HBD=1:3.

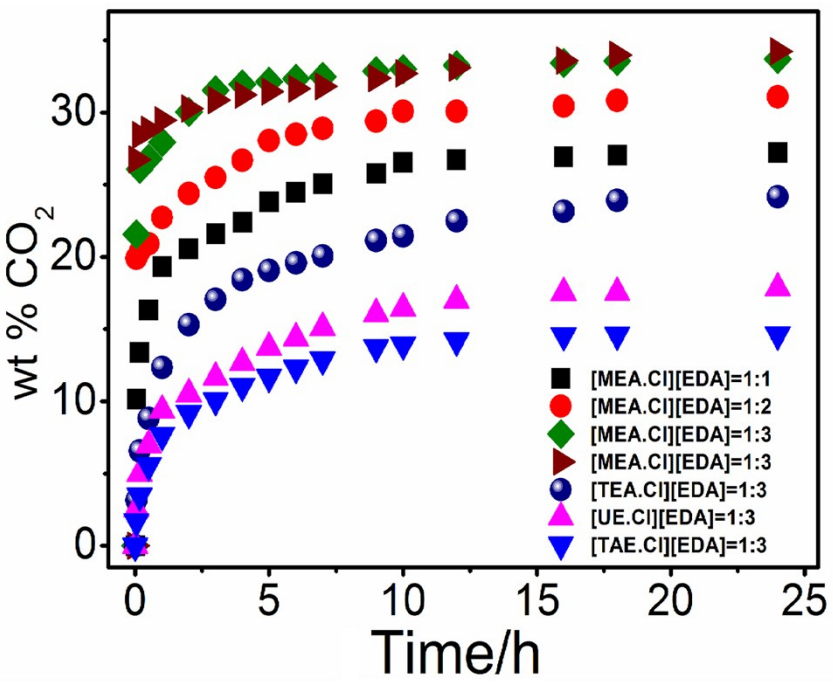

Fig. S3 Time dependent CO_2 absorption capacities of prepared deep eutectic solvents (DESs) at 30^{o}C and atmospheric pressure.

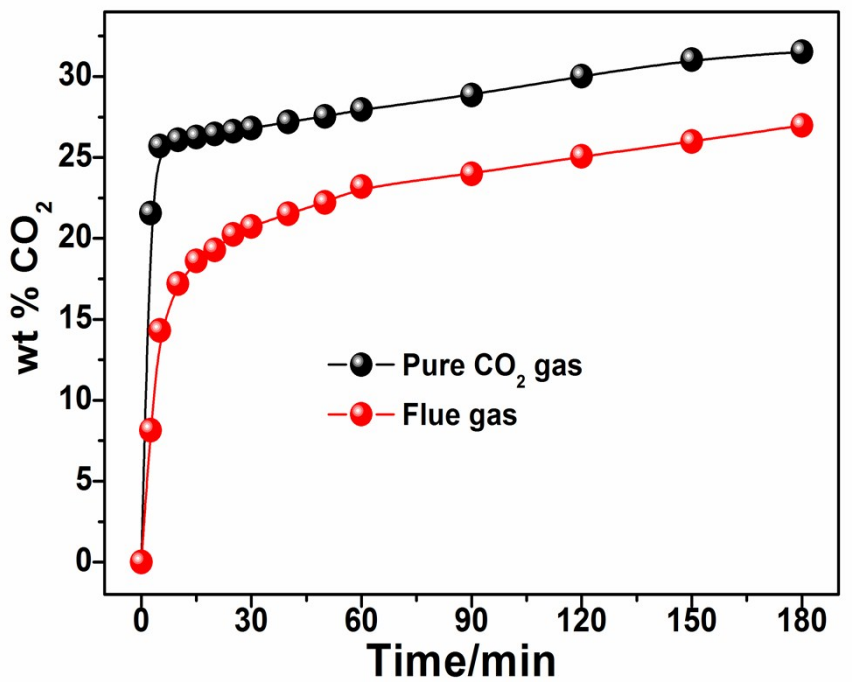

Fig. S4 Comparative CO_2 uptake capacity of [MEA.Cl][EDA]=1:3 with pure CO_2 gas and mixture flue gas (15 wt% CO_2+85 wt% N_2) at 30 ^oC and atmospheric pressure for 3 h.

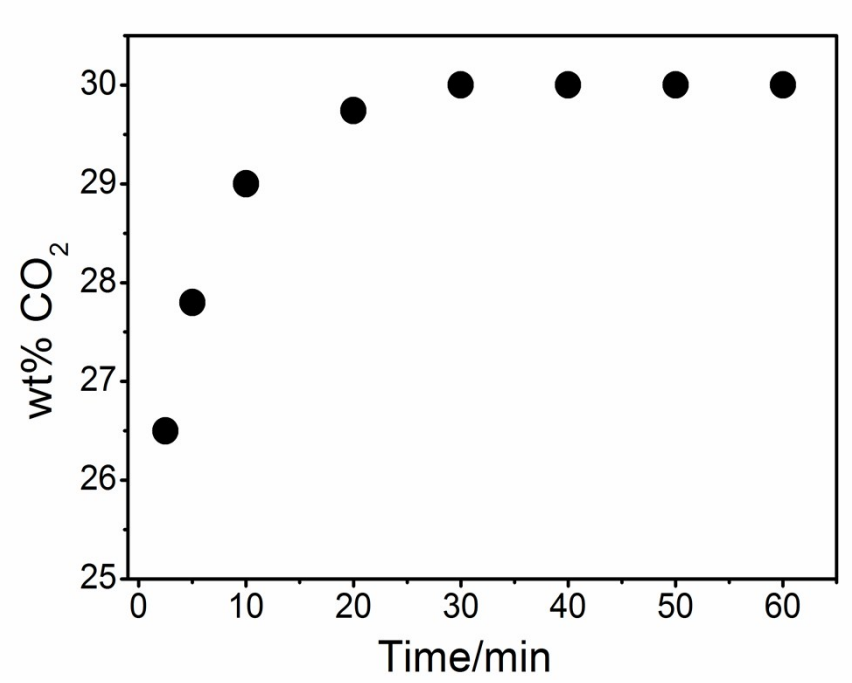

Fig. S5 CO_2 absorption capacities of pure EDA at 30 ^oC and atmospheric pressure.

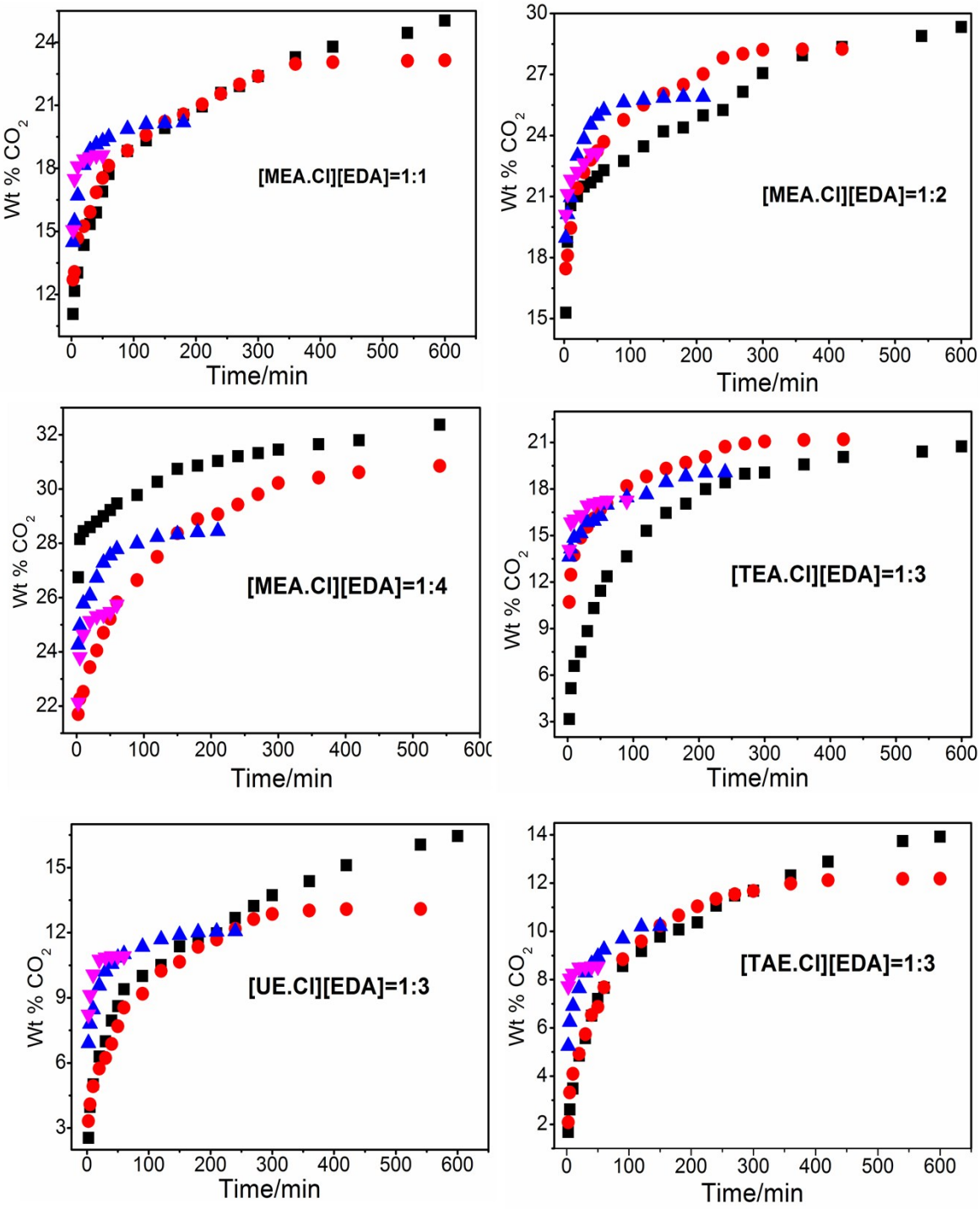

Fig. S6 Time-dependent CO_2 uptakes of synthesized DESs at different temperatures:

■=30 °C, ●=50 °C, ▲=70 °C, ▼=90 °C.

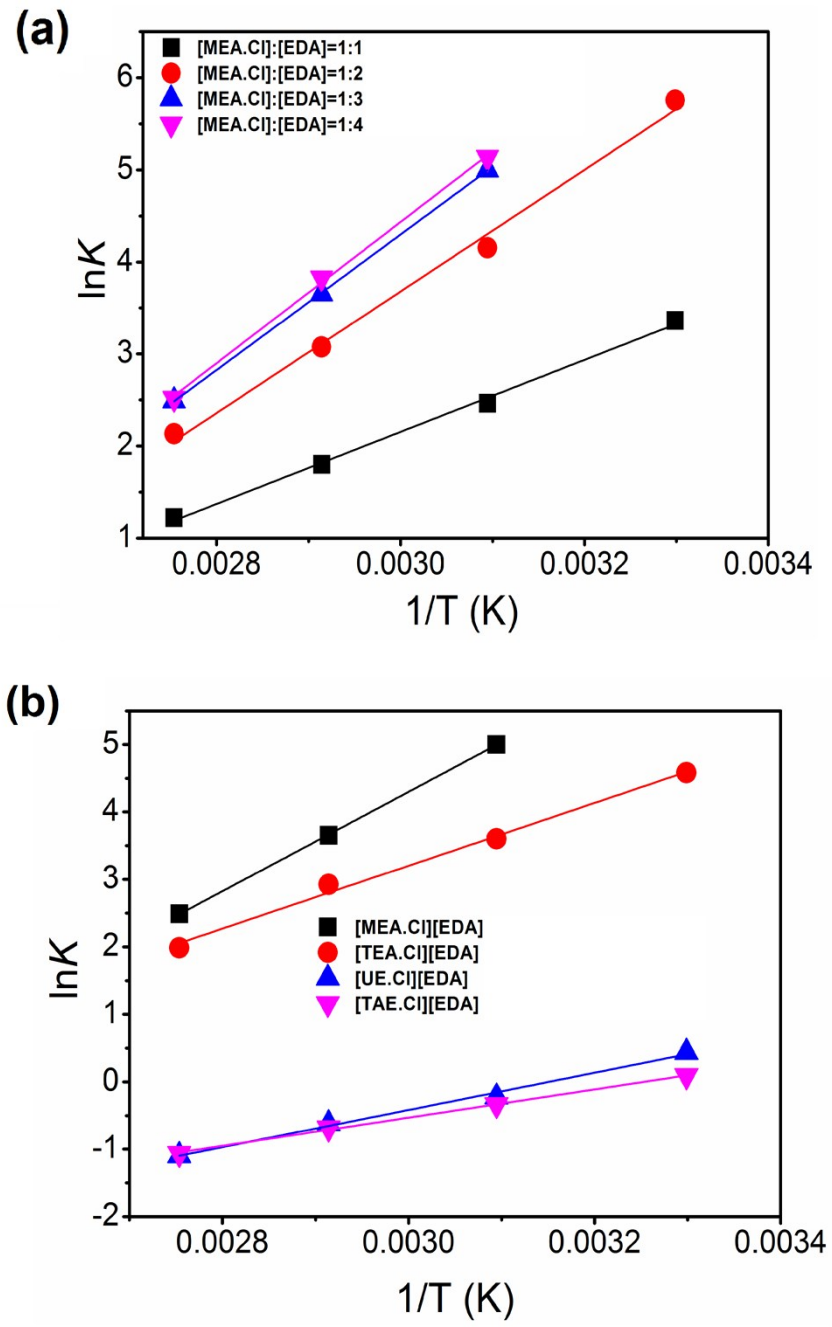

Fig. S7 Van't Hoff plots (ln (*K*) vs. 1/*T*) for CO_2 absorption reaction. (a) [MEA.Cl][EDA] with different molar compositions. (b) Various DESs with different HBAs with a fixed molar composition of HBA:HBD=1:3.

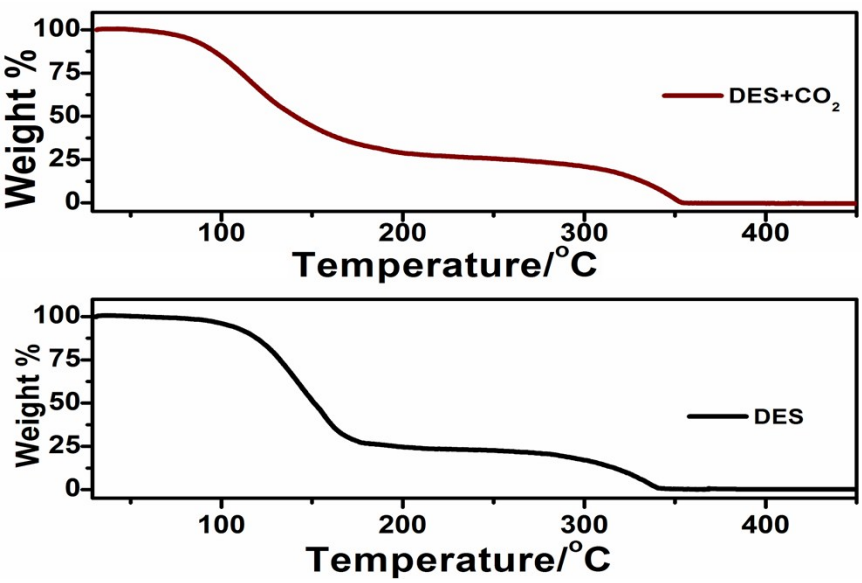

Fig. S8 TGA profiles for [MEA.Cl][EDA]=1:3 for the bare and CO_2-loaded cases: 5 °C min^{-1} scan rate.

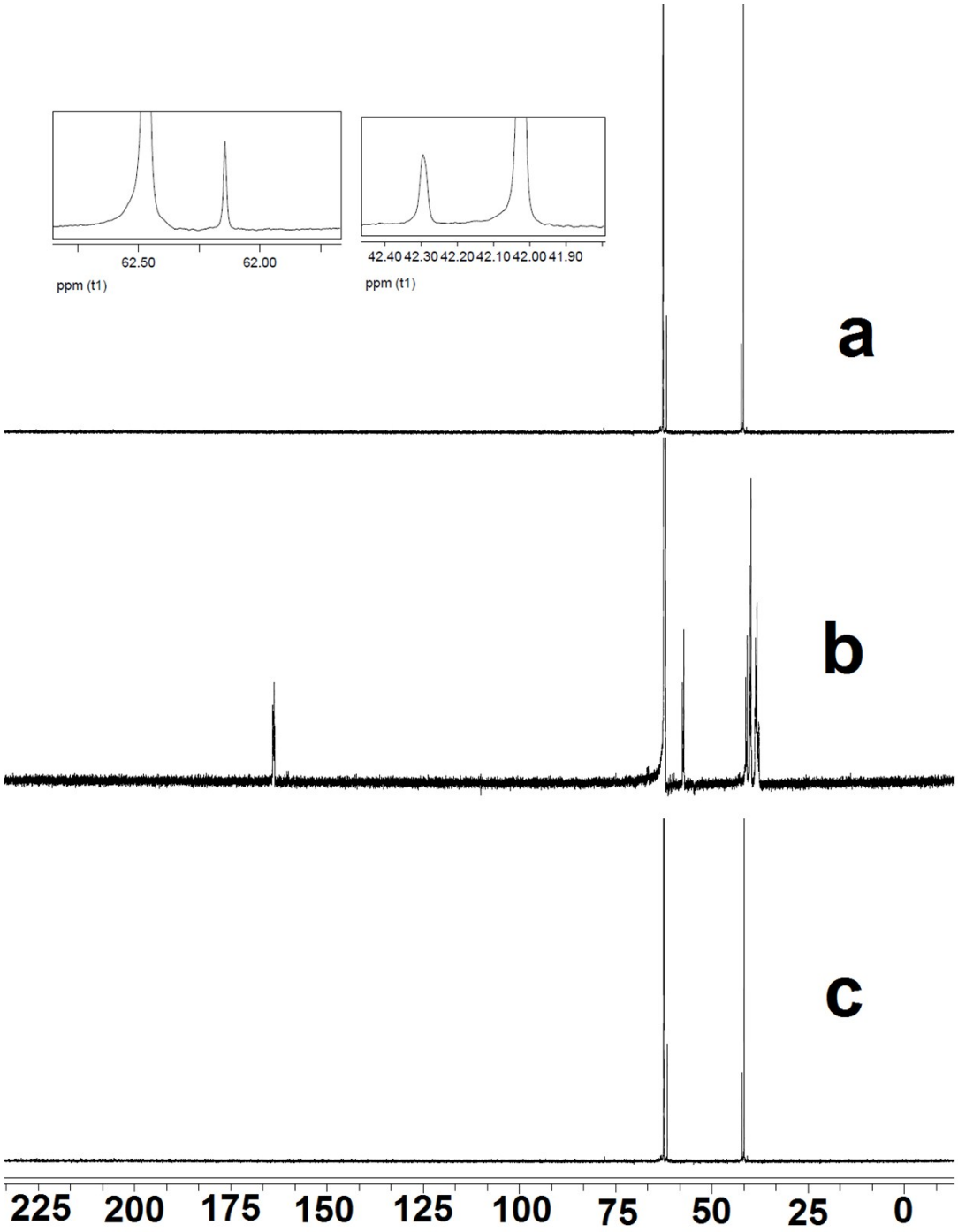

Fig. S9 ^{13}C NMR spectra of 30 wt% [MEA.Cl][EDA]=1:3 in ethylene glycol: a) before CO_2 absorption, b) after CO_2 absorption in the 5th cycle, and c) after CO_2 desorption in the 5th cycle.

Table S1 CO_2 uptake capacities of representative deep eutectic solvents (DESs) in the literatures and present study

No	DESs[a]	Molar weight	Ratio	*T* (°C)	*P* (bar)	CO_2 uptake (in mole)[e]	CO_2 uptake (wt%)	Reference
1.	[ChCl:U]	82.79	1:2.5	40	11.5	0.046	2.35	25
2.	[ChCl:U]	86.58	1:2	40	57.8	0.036	2.00	26
3.	[ChCl:EG]	87.92	1:2	40	61.6	0.022	1.67	27
4.	[ChCl:Gly]	107.93	1:2	30	58.6	0.037	1.87	28
5.	[ChCl:LA]	93.18	1:15	30	35.9	0.099	1.85	29
6.	[ChCl:TEG]	148.06	1:4	25	10	0.042	1.30	31
7.	[ChCl:U]	75.97	1:4	25	10	0.024	1.14	"
8.	[ChCl:EG]	70.68	1:8	25	10	0.026	1.43	"
9.	[ChCl:Gly]	103.97	1:3	25	10	0.045	2.01	"
10	[ChCl:EA]	72.30	1:6	25	10	0.109	7.40	"
11.	[ChCl:DEA]	110.06	1:6	25	10	0.093	4.08	"
12.	[TBA.Br:EA]	98.41	1:6	25	10	0.116	5.91	"
13.	[TBABr:DEA]	136.18	1:6	25	10	0.104	3.73	"
14.	[TBABr:TEA]	192.49	1:3	25	10	0.083	2.07	"
15.	[BTPPCl:Gly]	114.92	1:12	25	10	0.051	2.06	"
16.	[BTPPBr: EA]	115.73	1:12	25	10	0.051	2.01	"
17.	[MTPPBr: EA]	103.38	1:6	25	10	0.144	7.14	"
18.	[MEA.Cl:EDA]	69.46	1:3	30	1	0.502[b]	31.5[b]	Present work
19.	[MEA.Cl:EDA]	69.46	1:3	30	1	0.536[c]	33.7[c]	Present work
20.	[MEA.Cl:EDA]	69.46	1:3	30	1	0.454[d]	28.8[d]	Present work
21.	[TEA.Cl:EDA]	91.49	1:3	30	1	0.354[b]	17.5[b]	Present work
22.	[UE.Cl:EDA]	69.20	1:3	30	1	0.184[b]	11.7[b]	Present work
23.	[TAE.Cl:EDA]	72.97	1:3	30	1	0.168[b]	10.1[b]	Present work

[a][ChCl:U]-Choline chloride:urea; [ChCl:EG]- Choline chloride: ethylene glycol; [ChCl:Gly]- Choline chloride: Glycerol; [ChCl:TEG]- Choline chloride:triethylene glycol; [ChCl:LA]- Choline chloride: lactic acid; [ChCl:MEA]- Choline Chloride: Monoethanolamine; [ChCl:DEA]- Choline chloride: Diethanolamine; [TBA.Br:EA]-Tetra butyl ammonium bromide: ethanolamine; [TBABr:DEA]- Tetra butyl ammonium bromide:Diethanolamine; [TBABr:TEA]- Tetra butyl ammonium bromide:Triethanolamine; [BTPPCl:Gly]-Benzyltriphenylphosphonium chloride: glycerol; [BTPPBr: EA]-n-butyltriphenylphosphonium bromide: Ethanolamine; [MTPPBr: EA]-Methytriphenylphosphonium bromide: Ethanolamine.

[b]CO_2 uptake after 3 h.

[c]CO_2 uptake after 24 h.

[d]CO_2 uptake after 1 h with 10% water.

[e]mol CO_2/mol solvent

Reference

1. J. Ren, L. B. Wu and B. G. Li, *Ind. Eng. Chem. Res.*, 2013, **52**, 8565-8570.
2. X. Y. Luo, F. Ding, W. J. Lin, Y. Q. Qi, H. R. Li and C. M. Wang, *J. Phys. Chem. Lett.*, 2014, **5**, 381-386.
3. Y. Xiang, M. C. Yan, Y. S. Choi, D. Young and S. Nesic, *Int. J. Greenh. Gas. Con.*, 2014, **30**, 125-132.
4. A. Veawab and A. Aroonwilas, *Corros. Sci.*, 2002, **44**, 967-987.