Electronic supplementary information

Unusual temperature-promoted carbon dioxide capture in deep-eutectic solvents: the synergetic interactions

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1. Synthesis of deep-eutectic solvents

All deep-eutectic solvents were synthesized via a two-step protonation–complexation process. The first step involved protonation of monoethanolamine (MEA) and 1-methylimidazole (MIM) by equimolar amount of 37% hydrochloric acid at 0 ^{o}C. The resulting protic ionic liquid (PIL) was first placed under rotary-evaporator at 60 ^{o}C and later connected to the ultra-high vacuum pump operated at 70 ^{o}C to remove traces of water and other volatile impurities. The second step comprised of complexation of various HBDs with PILs in suitable molar ratio, at 80 ^{o}C for 1 h to yield the desired DESs. The DESs prepared were tested for water content using Karl-Fisher titration (water content > 50 ppm) and kept in air-tight container and placed in desiccator. The synthesized DESs were characterized by ^{1}H- and ^{13}C-NMR spectroscopic methods.

2. Characterization of DESs before and after CO_2 capture

MEA.Cl

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 3.0 (*t*, CH_2-NH_3^+), 3.69 (*t*, CH_2-OH); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 49.2 and 50.8.

HMIM.Cl

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.08, (*s*, N-H), 3.79 (*s*, CH_3-N), 7.29 (*d*, H-C5), 7.30 (*d*, H-C4) and 8.48 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 35.33, 119.9, 122.84 and 135.17.

[MEA.Cl][EDA] = 1:1

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.74 (*s*, CH_2 of EDA), 2.76 (*t*, CH_2-OH) and 3.57 (*t*, CH_2-NH_3^+); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 41.07, 41.96 and 61.37.

[MEA.Cl][EDA] = 1:1 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.75 (*s*, NH_2-CH_2), 2.80 (CH_2-NHCOO), 2.85 (*t*, CH_2-NHCOO), 3.05 (*t*, CH_2-NH_3^+) and 3.55 (*t*, CH_2-OH); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 38.92, 39.60, 40.18, 41.26, 58.09 and 164.35.

[MEA.Cl][EDA] = 1:2

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.68 (*s*, CH_2 of EDA), 2.71 (*t*, CH_2-OH) and 3.55 (*t*, CH_2-NH_3^+); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 41.77, 42.16 and 62.20.

[MEA.Cl][EDA] = 1:2 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 2.71 (*s*, NH_2), 2.76 (CH_2-NHCOO), 2.80 (*t*, CH_2-NHCOO), 3.03 (*t*, CH_2-NH_3^+) and 3.52 (*t*, CH_2-OH); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 39.25, 39.79, 40.18, 41.33, 58.59 and 164.35.

[MEA.Cl][EDA] = 1:3

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.65 (*s*, CH_2 of EDA), 2.69 (*t*, CH_2-OH) and 3.55 (*t*, CH_2-NH_3^+); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 42.12, 42.24 and 62.52.

[MEA.Cl][EDA] = 1:3 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.75 (*s*, NH_2-CH_2), 2.81 (CH_2-NHCOO), 2.85 (*t*, CH_2-NHCOO), 3.07 (*t*, CH_2-NH_3^+) and 3.56 (*t*, CH_2-OH);^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 39.09, 39.72, 40.18, 41.29, 58.40 and 164.39.

[MEA.Cl][EDA] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.64 (*s*, CH_2 of EDA), 2.68 (*t*, CH_2-OH) and 3.54 (*t*, CH_2-NH_3^+); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 42.26 and 62.65.

[MEA.Cl][EDA] = 1:4 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.72 (*s*, NH_2), 2.78 (CH_2-NHCOO), 2.82 (*t*, CH_2-NHCOO), 3.04 (*t*, CH_2-NH_3^+) and 3.53 (*t*, CH_2-OH); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 39.13, 39.73, 40.15, 41.28, 58.45 and 164.36.

[HMIM.Cl][EDA] = 1:1

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.86 (*s*, CH_2-NH_2 of EDA), 3.58 (*s*, N-CH_3), 6.87 (*s*, H-C5), 6.98 (*s*, H-C4) and 7.49 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.02, 39.76, 121.35, 127.36 and 138.47.

[HMIM.Cl][EDA] = 1:1 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.90 (*t*, CH_2-NHCOO), 3.12 (-NH-CH_2), 3.449 (*s*, N-CH_3), 6.83 (*s*, H-C5), 6.91 (*s*, H-C4) and 7.52 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.28, 38.85, 40.24, 121.46, 126.29, 137.88 and 164.41.

[HMIM.Cl][EDA] = 1:2

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.68 (s, CH_2-NH_2 of EDA), 3.57 (*s*, N-CH_3), 6.87 (*s*, H-C5), 6.98 (*s*, H-C4) and 7.48 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.03, 41.50, 121.34, 127.52 and 138.45.

[HMIM.Cl][EDA] = 1:2 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.75 (*t*, CH_2-NHCOO), 2.98 ((-NH-CH_2), 3.33 (*s*, N-CH_3), 6.67 (*s*, H-C5), 6.75 (*s*, H-C4) and 7.32 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.04, 38.57, 38.82, 40.06, 121.25, 126.60, 137.91 and 164.23.

[HMIM.Cl][EDA] = 1:3

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.66 (*s*, CH_2-NH_2 of EDA), 3.60 (*s*, N-CH_3), 6.91 (*s*, H-C5), 7.02 (*s*, H-C4) and 7.52 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.09, 42.0, 121.37, 127.59 and 138.42.

[HMIM.Cl][EDA] = 1:3 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.62 (*s*, CH_2-NH), 2.67(*t*, CH_2-NHCOO), 2.93 (*t*, CH_2-NH), 3.28 (*s*, N-CH_3), 6.61 (*s*, H-C5), 6.70 (*s*, H-C4) and 7.22 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 32.86, 38.94, 39.54, 40.05, 121.12, 127.14, 138.10 and 164.18.

[HMIM.Cl][EDA] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.65 (*s*, CH_2-NH_2 of EDA), 3.61 (*s*, N-CH_3), 6.90 (*s*, H-C5), 7.01 (*s*, H-C4) and 7.51 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.03, 41.91, 121.35, 127.55 and 138.52.

[HMIM.Cl][EDA] = 1:4 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 2.79 (*s*, CH_2-NH), 2.86 (*t*, CH_2-NHCOO), 3.11 (*t*, CH_2-NH), 3.51 (*s*, N-CH_3), 6.81 (*s*, H-C5), 6.91 (*s*, H-C4) and 7.43 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 32.98, 38.99, 39.71, 40.23, 121.30, 127.31, 138.4 and 164.44.

[MEA.Cl][AP] = 1:1

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.71 (*m*, -CH_2- of AP), 2.72 (*t,* CH_2-NH_3^+), 2.82 (*t,* CH_2-NH_2 of AP), 3.55 (*t*, CH_2-OH of AP) and 3.58 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 31.15, 37.35, 42.02, 59.18 and 61.66.

[MEA.Cl][AP] = 1:1 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.41 (*m,* CH_2-$NHCOO^-$), 1.63 (*m*, -CH_2- of AP), 2.84 (*t,* CH_2-NH_3^+), 3.32 (*t*, CH_2-OH of AP), 3.44 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 29.0, 37.14, 41.20, 58.78, 61.17, 161.32 and 164.50.

[MEA.Cl][AP] = 1:2

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.64 (*m*, -CH_2- of AP), 2.65 (*t,* CH_2-NH_3^+ of AP), 2.70 (*t,* CH_2-NH_2), 3.50 (*t*, CH_2-OH of AP) and 3.55 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 32.54, 37.42, 42.24, 59.31 and 62.46.

[MEA.Cl][AP] = 1:2 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.38 (*m,* CH_2-$NHCOO^-$), 1.60 (*m*, -CH_2- of AP), 2.79 (*t,* CH_2-NH_3^+), 3.31 (*t*, CH_2-OH of AP), 3.41 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 29.03, 31.97, 37.08, 58.73, 61.14, 161.57 and 164.52.

[MEA.Cl][AP] = 1:3

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.62 (*m*, -CH_2- of AP), 2.64 (*t,* CH_2-NH_3^+ of AP), 2.67 (*t,* CH_2-NH_2), 3.50 (*t*, CH_2-OH of AP) and 3.55 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 33.03, 37.45, 42.29, 59.36 and 62.66.

[MEA.Cl][AP] = 1:3 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.46 (*m,* CH_2-$NHCOO^-$), 1.68 (*m*, -CH_2- of AP), 2.87 (*t,* CH_2-NH_3^+), 3.41 (*t*, CH_2-OH of AP), 3.49 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 29.07, 32.0, 37.13, 58.79, 59.16 and 164.64.

[MEA.Cl][AP] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.62 (*m*, -CH_2- of AP), 2.64 (*t,* CH_2-NH_3^+ of AP), 2.66 (*t,* CH_2-NH_2), 3.51 (*t*, CH_2-OH of AP) and 3.56 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 33.20, 37.43, 42.28, 59.40 and 62.76.

[MEA.Cl][AP] = 1:4 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.27 (*m,* CH_2-$NHCOO^-$), 1.48 (*m*, -CH_2- of AP), 2.67 (*t,* CH_2-NH_3^+), 3.21 (*t*, CH_2-OH of AP) and 3.29 (*t*, CH_2-OH of MEA.Cl); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 28.95, 31.91, 36.94, 58.59, 58.99 and 164.35.

[HMIM.Cl][AP] = 1:1

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.71 (*m*, -CH_2-), 2.90 (*t,* CH_2-NH_2), 3.48 (*s*, N-CH_3), 3.53 (*t*, CH_2-OH), 6.79 (*s*, H-C5), 6.88 (*s*, H-C4) and 7.40 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 29.36, 32.98, 37.29, 58.91, 121.27, 127.36 and 138.34.

[HMIM.Cl][AP] = 1:1 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.65 (*m*, -CH_2-), 2.84 (*t,* CH_2-$NHCOO^-$), 3.37 (*s*, N-CH_3), 3.44 (*t*, CH_2-OH), 6.70 (*s*, H-C5), 6.79 (*s*, H-C4) and 7.33 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 29.02, 33.0, 37.22, 58.79, 121.22, 127.0, 138.03 and 164.55.

[HMIM.Cl][AP] = 1:2

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.64 (*m*, -CH_2-), 2.73 (*t,* CH_2-NH_2), 3.52 (*s*, N-CH_3), 3.53 (*t*, CH_2-OH), 6.84 (*s*, H-C5), 6.94 (*s*, H-C4) and 7.44 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 31.75, 32.98, 37.36, 59.21, 121.30, 127.49 and 138.43.

[HMIM.Cl][AP] = 1:2 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ_H (ppm): 1.66 (*m*, -CH_2-), 2.85 (*m,* CH_2-$NHCOO^-$), 3.43 (*s*, N-CH_3), 3.47 (*t*, CH_2-OH), 6.74 (*s*, H-C5), 6.84 (*s*, H-C4) and 7.36 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 ^{o}C): δ_c (ppm): 29.07, 32.95, 37.17, 58.79, 121.24, 127.18, 138.22, 161.02 and164.61.

[HMIM.Cl][AP] = 1:3

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.61 (*m*, -CH_2-), 2.66 (*t,* CH_2-NH_2), 3.52 (*s*, N-CH_3), 3.55 (*t*, CH_2-OH), 6.84 (*s*, H-C5), 6.95 (*s*, H-C4) and 7.46 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 32.61, 32.99, 37.40, 59.30, 121.30, 127.51 and 138.41.

[HMIM.Cl][AP] = 1:3 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.59 (*m*, -CH_2-), 2.78 (*m,* CH_2-$NHCOO^-$), 3.36 (*s*, N-CH_3), 3.39 (*t*, CH_2-OH), 6.67 (*s*, H-C5), 6.78 (*s*, H-C4) and 7.30 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 29.05, 32.0, 37.08, 58.72, 121.18, 127.12, 138.12, 161.08 and 164.51.

[HMIM.Cl][AP] = 1:4

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.59 (*m*, -CH_2-), 2.63 (*t,* CH_2-NH_2), 3.52 (*t*, CH_2-OH), 3.56 (*s*, N-CH_3), 6.85 (*s*, H-C5), 6.96 (*s*, H-C4) and 7.47 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 29.03, 33.03, 37.43, 59.34, 121.30, 127.53 and 138.41.

[HMIM.Cl][AP] = 1:4 after CO_2 absorption

^{1}H NMR (400 MHz, D_2O, 25 °C): δ_H (ppm): 1.54 (*m*, -CH_2-), 2.73 (*m,* CH_2-$NHCOO^-$), 3.31 (*s*, N-CH_3), 3.34 (*t*, CH_2-OH), 6.63 (*s*, H-C5), 6.73 (*s*, H-C4) and 7.25 (*s*, H-C2); ^{13}C NMR (400 MHz, D_2O, 25 °C): δ_c (ppm): 29.02, 31.97, 37.01, 58.66, 121.14, 127.07, 138.05, 161.07 and 164.43.

3. CO_2 uptake experiment and capture profile in DESs

The absorption experiments were carried out by bubbling CO_2 gas into a vial containing 3 g of DESs at a flow rate of 50 ml min^{-1} under inert conditions. The vial was weighed at regular intervals to record the differential weight of absorbed CO_2 from which the weight percent of absorbed CO_2 were calculated in the respective DES. The electronic balance used for weighing had an accuracy of ±0.1 mg. Desorption experiments were also performed under inert atmosphere by weighing the vials at regular time intervals.

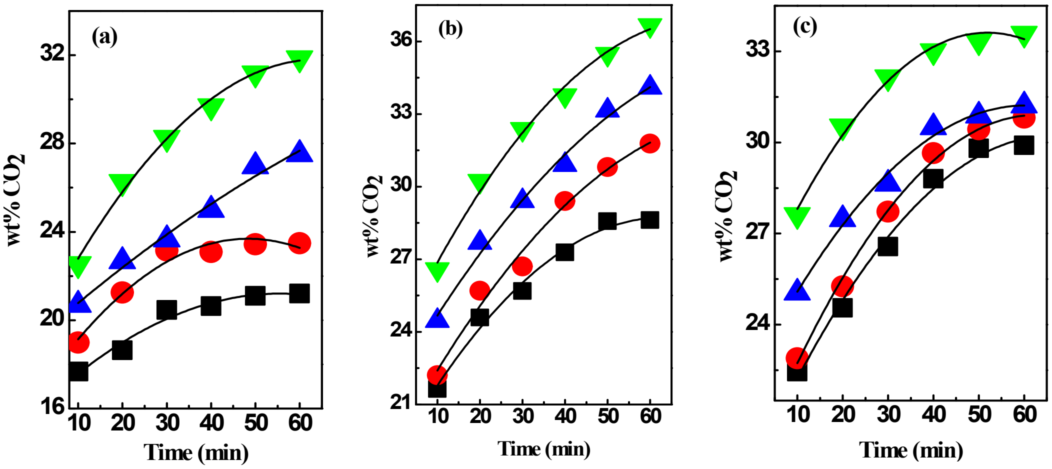


Fig. S1 CO_2 uptake profiles in [MEA.Cl][EDA]-based DESs at (a) 1:2, (b) 1:3 and (c) 1:4 mole at 298K (■), 308K (●), 318K (▲) and 328K (▼).

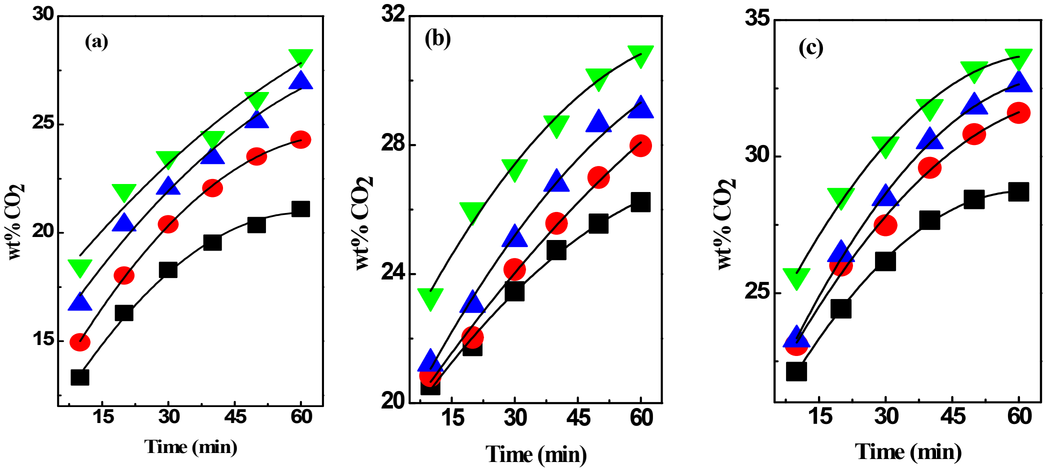


Fig. S2 CO_2 uptake profiles in [HMIM.Cl][EDA]-based DESs at (a) 1:2, (b) 1:3 and (c) 1:4 mole at 298K (■), 308K (●), 318K (▲) and 328K (▼).

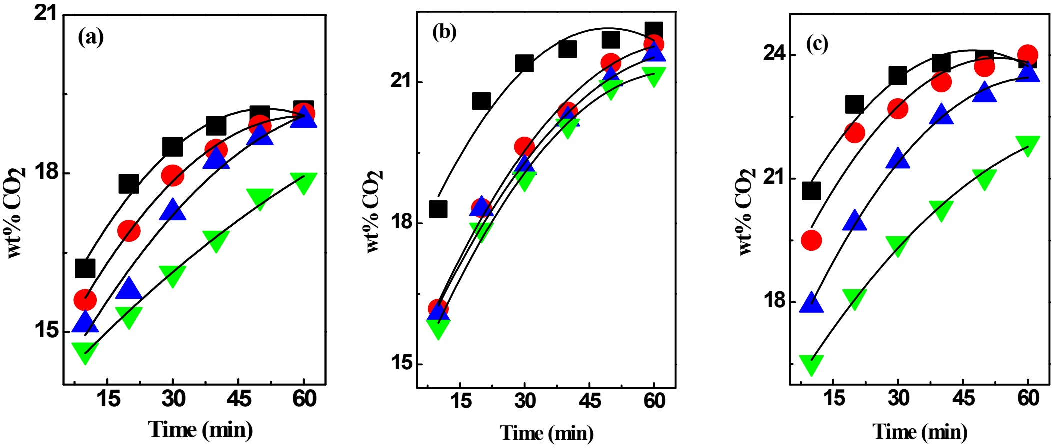


Fig. S3 CO_2 uptake profiles in [MEA.Cl][AP]-based DESs at (a) 1:2, (b) 1:3 and (c) 1:4 mole at 298K (■), 308K (●), 318K (▲) and 328K (▼).

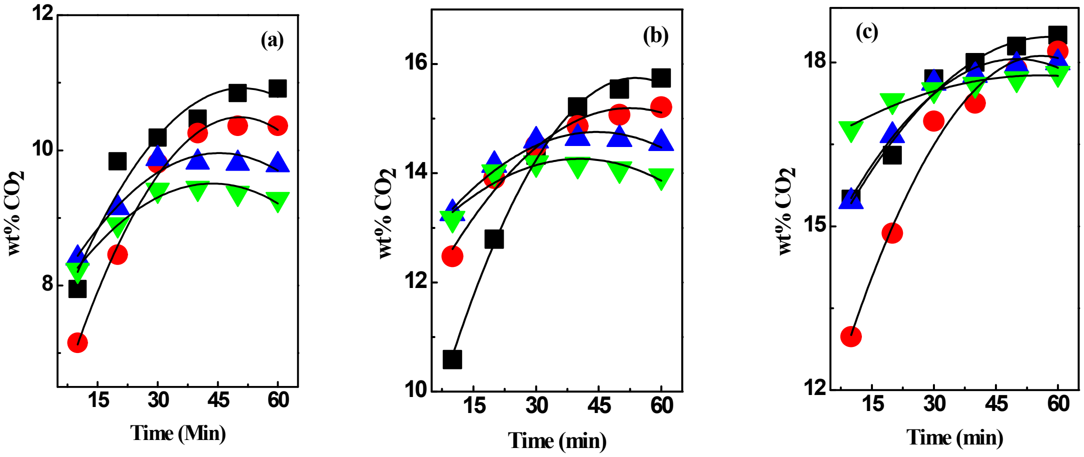


Fig. S4 CO_2 uptake profiles in [HMIM.Cl][AP]-based DESs at (a) 1:2, (b) 1:3 and (c) 1:4 mole at 298K (■), 308K (●), 318K (▲) and 328K (▼).

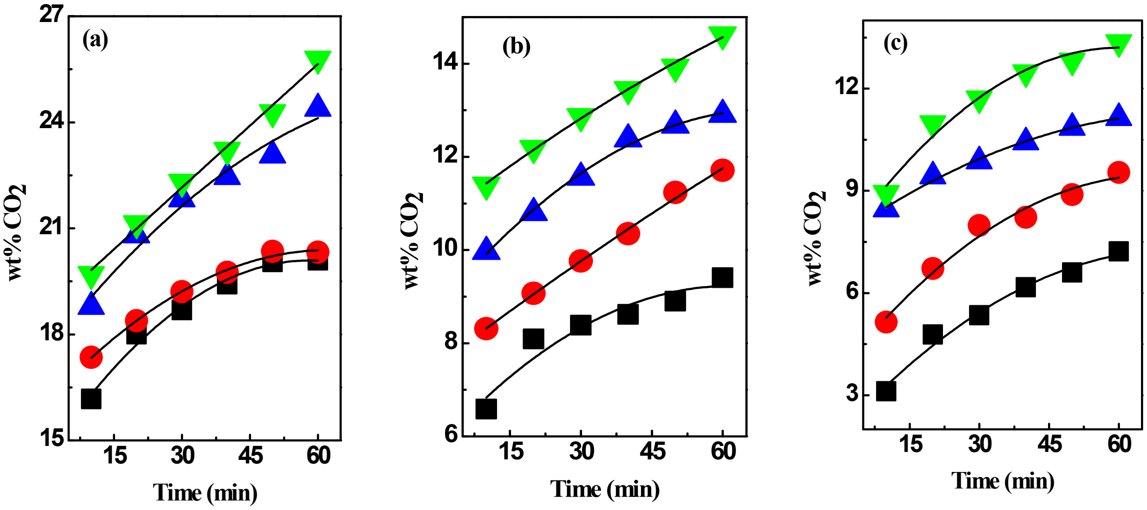


Fig. S5 CO_2 uptake profiles in (a) [MEA.Cl][DETA], (b) [MEA.Cl][TEPA] and (c) [MEA.Cl][PEHA] at 1:4 mole at 298K (■), 308K (●), 318K (▲) and 328K (▼).

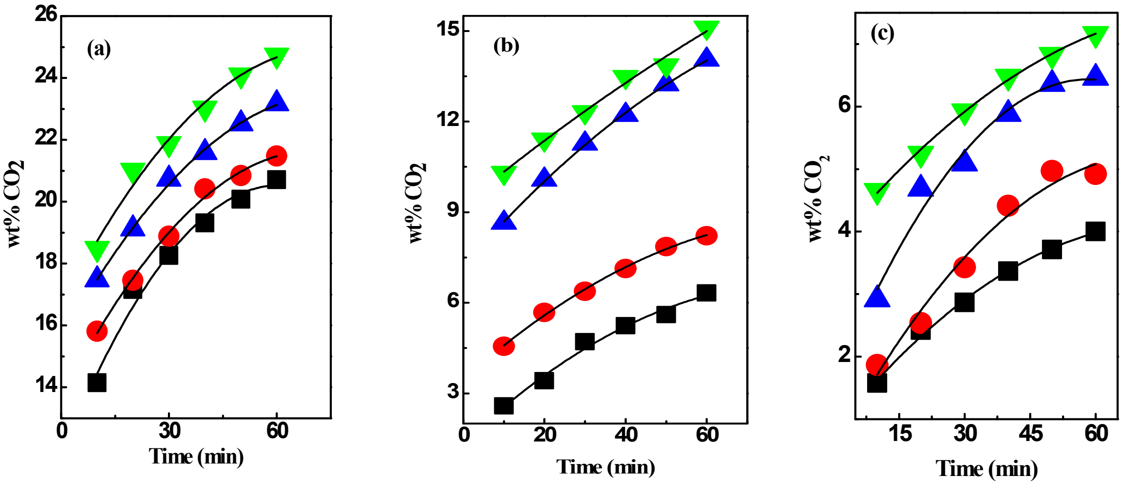


Fig. S6 CO_2 uptake profiles in (a) [MEA.Cl][DETA], (b) [MEA.Cl][TEPA] and (c) [MEA.Cl][PEHA] at 1:4 mole at 298K (■), 308K (●), 318K (▲) and 328K (▼).

3. Determination of activation energy of viscous flow ($E_{a,\eta}$)

The activation energy of viscous flow ($E_{a,\eta}$) in DESs was determined from the temperature dependent viscosity data using Arrhenius-type equation.

$$ln\eta = ln\eta_0 - \frac{Ea}{RT} \quad (1)$$

The activation energy of viscous flow was obtained from the slope of fit using equation 1.

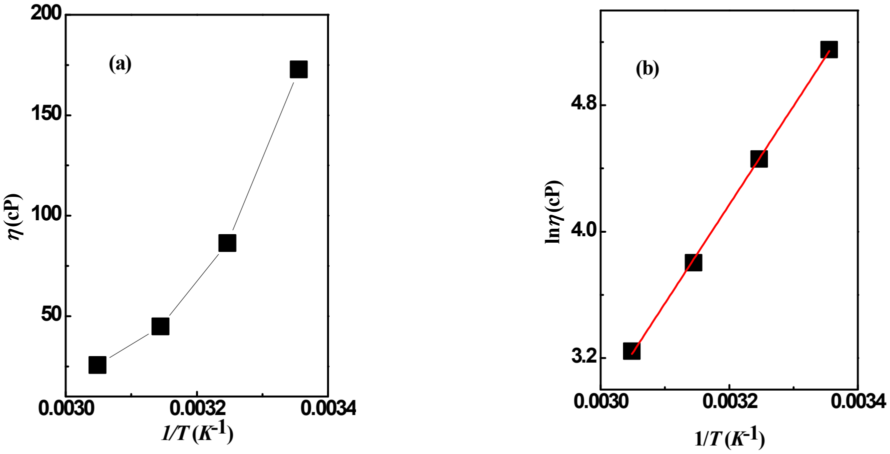


Fig. S7 Plot of (a) η vs $1/T$ and (b) lnη vs $1/T$ in a typical DES for the calculation of activation energy of viscous flow ($E_{a,\eta}$).

Table S1. Thermodynamic parameters, activation energy of viscous flow and polarity parameters in [DETA]-, [TEPA]- and [PEHA]-based DESs.

DESs	$E_{a,\eta}$ (kJ.mol^{-1})	△H^0 (kcal.mol^{-1})	△S^0 (J.K^{-1}.mol^{-1})	$E_T(30)$ (kcal.mol^{-1})	α	β
[MEA.Cl][DETA] = 1:4	53.0	8.8	3.4	50.9	0.512	0.900
[MEA.Cl][TEPA] = 1:4	54.8	9.2	3.3	50.7	0.553	0.917
[MEA.Cl][PEHA] = 1:4	61.2	14.2	5.5	50.1	0.565	0.955
[HMIM.Cl][DETA] = 1:4	43.5	14.9	5.1	50.7	0.512	0.855
[HMIM.Cl][TEPA] = 1:4	56.1	15.3	5.7	50.5	0.542	0.917
[HMIM.Cl][PEHA] = 1:4	60.6	15.9	5.8	50.2	0.655	1.119

4. Determination of thermodynamic parameters

The standard enthalpy and entropy change ($\triangle H^0$ and $\triangle S^0$) were obtained using the van't Hoff equation.

$$\Delta G^0 = -RTlnK_{eq} \tag{2}$$

At a given temperature, ΔG^0 depends on $\triangle H^0$ and $\triangle S^0$ by the relation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

Thus,

$$lnK_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{4}$$

The equilibrium constant (K_{eq}) during the CO_2 capture was obtained by following equilibria,

$$2DES + CO_2 \leftrightarrow 2DES\text{-}CO_2$$

$$K_{eq} = \frac{[2DES.CO_2]}{[DES]^2 p_{CO2}}$$

(5)

At atmospheric pressure $p_{CO2} = 1$.

The $\triangle H^0$ and $\triangle S^0$ was obtained from the slope and intercept, respectively by using equation 4

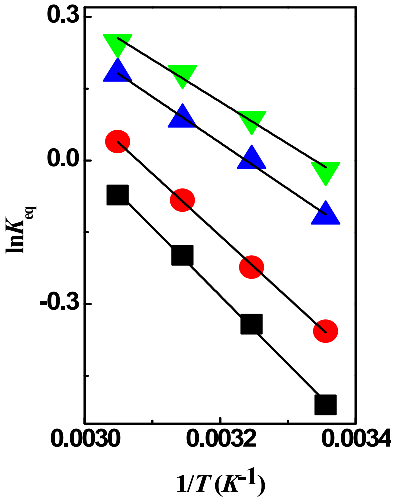


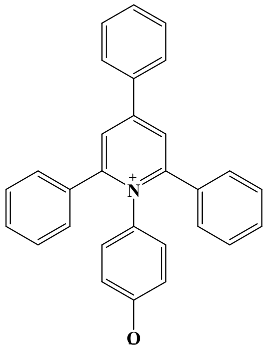
Fig S8. A typical lnK vs 1/*T* plot in DES.

6. Determination of Kamlet-Taft parameters

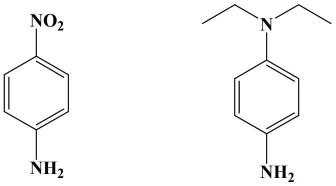
The Kamlet-Taft parameters were determined by using the UV−visible spectroscopic method described in the literature.[1] The longest wavelength intramolecular charge transfer spectra of Reichardt's dye (30), *N,N*-diethyl-4-nitroaniline (DENA) and 4-nitroaniline (NA) dissolved in 1 mL of a DES was recorded. The polarity and Kamlet−Taft parameters of DESs were calculated by using following empirical equations.

Table S2 Empirical equation to determine the E_T^N and Kamlet-Taft parameters.

Polarity parameters	**Empirical equations**
Electronic transition energy (E_T^N)	$E_T(30)\ (\text{kcal mol}^{-1}) = hc\nu_{max} = 28591/\lambda_{max\,(\text{nm})} = 2.8591\,\nu_{max}$ where λ_{max} is the maximum wavelength of lowest energy band of Reichardt's dye (1)
Polarity index (π^*)	$\nu_{(3)\,max} = 27.52 - 3.182\pi^*$
Hydrogen bond donor acidity (α)	$\alpha = [E_T(30) - 14.6(\pi^* - 0.23) - 30.31]/16.5$
Hydrogen bond acceptor basicity (β)	$\nu_{(2)max} = 1.035\nu_{(3)max} - 2.8\beta + 2.64$ where $\nu_{(2)max}$ and $\nu_{(3)max}$ are the maximum wave number of the 4-nitroaniline (probe 2) and *N,N*-diethyl-4-nitroaniline (probe 3), respectively.



2,6-diphenyl-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate (1)



4-nitroaniline (2) ***N,N*-diethyl-4-nitroaniline (3)**

Fig. S9 Structure of the solvatochromic probe molecules.

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[1] S. K. Shukla, N. D. Khupse, and A. Kumar, *Phys. Chem. Chem. Phys.* 2012, **14**, 2754−2761.