Supporting Information for:

Understanding the potential benefits of tri-amino blended systems for CO_2 capture processes through ^{13}C NMR speciation study and energy cost analysis

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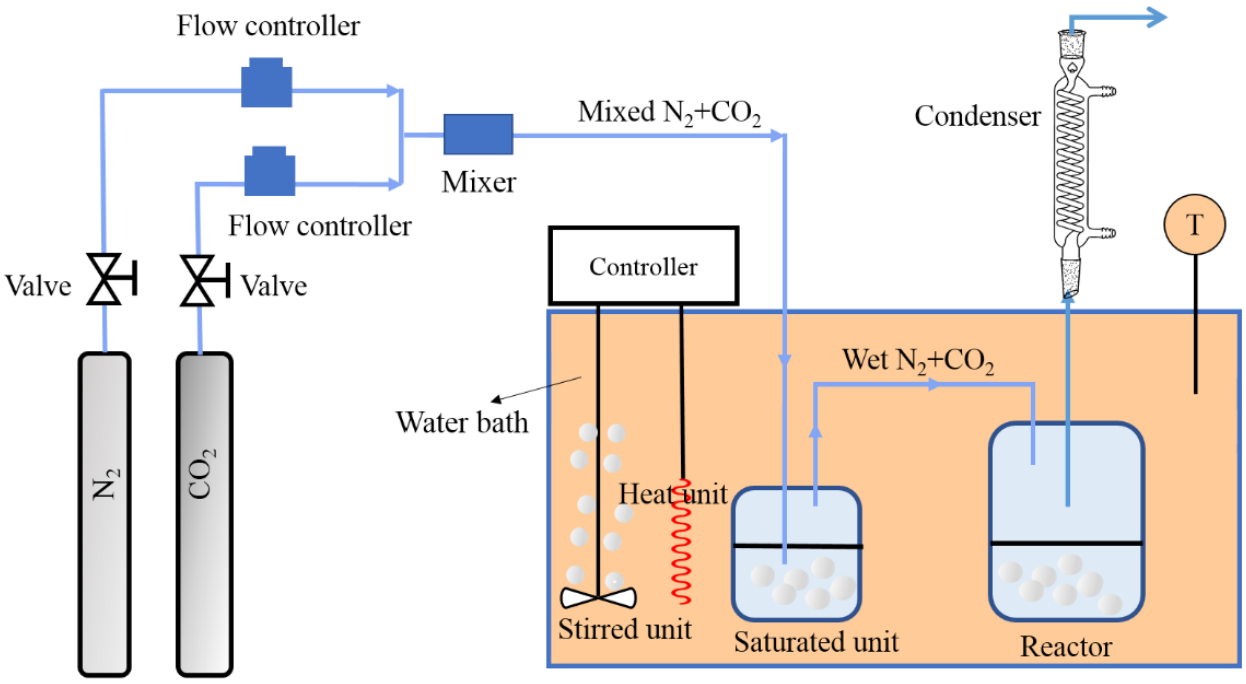

Figure S1. Apparatus used for the determination of the CO_2 solubility at the equilibrium

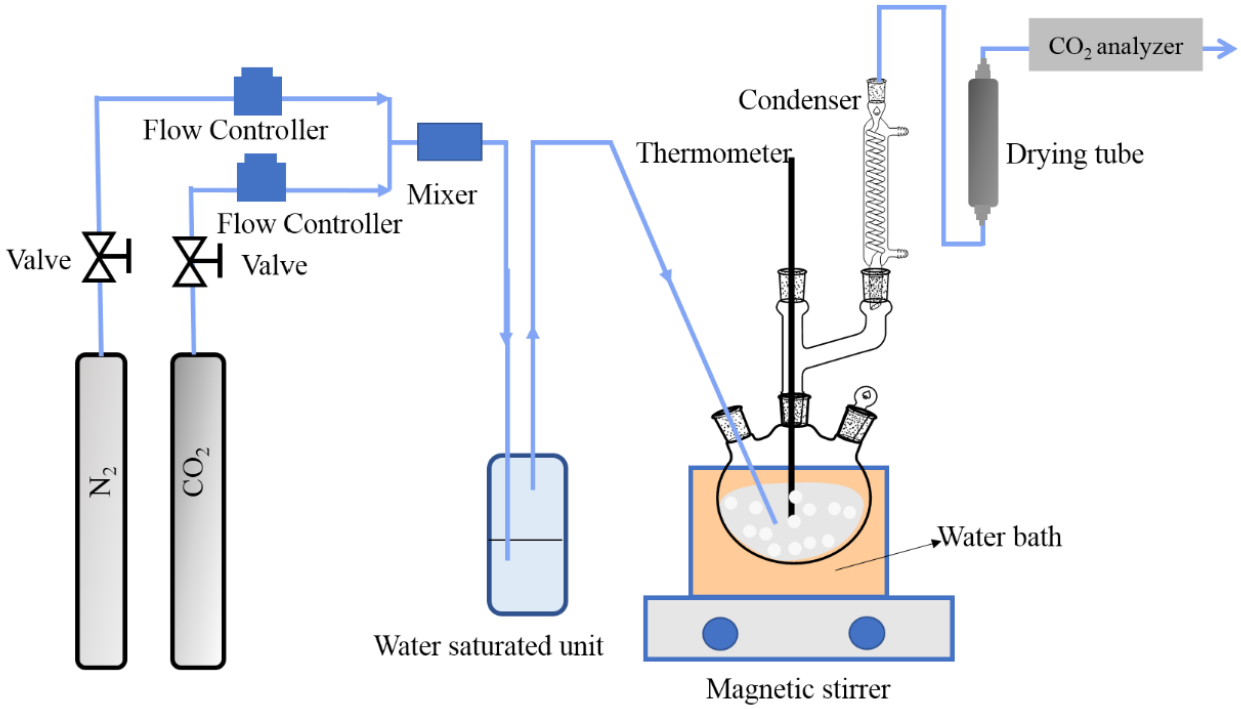

Figure S2. Apparatus used for the determination of the CO_2 loading as a function of time

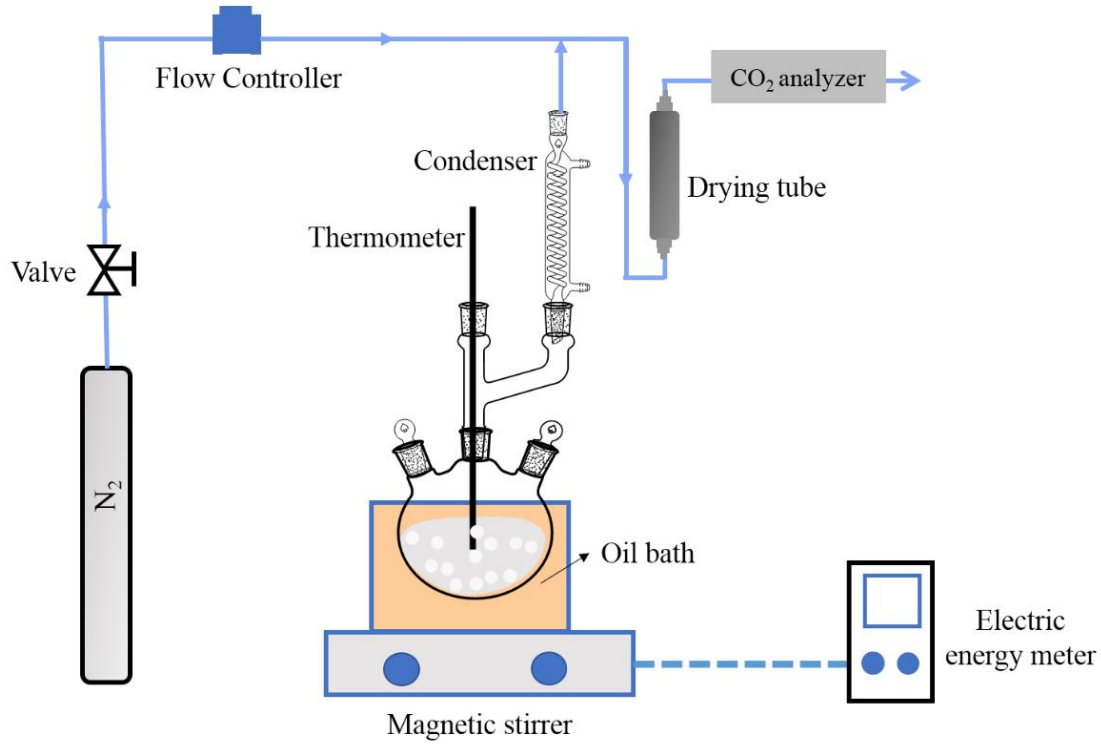

Figure S3. Apparatus used for CO_2 desorption

Table S1. The equilibrium solubility of each blend system at different temperature with various CO_2 partial pressure.

CO_2 partial pressure (kPa)	Equilibrium CO_2 loading (mol CO_2/mol amine)			
	5M MEA	2M MEA-2M MDEA-1M AMP	1M MEA-2M MDEA-2M AMP	2M MEA-1M MDEA-2M AMP
	30°C		35°C	
7.5	0.524	0.398	0.362	0.451
15	0.536	0.492	0.467	0.543
30	0.555	0.544	0.563	0.597
60	0.593	0.599	0.653	0.631
101	0.621	0.647	0.698	0.676
		40°C		
7.5	0.498	0.357	0.344	0.388
15	0.513	0.455	0.453	0.489
30	0.544	0.505	0.549	0.549
60	0.583	0.566	0.609	0.579
101	0.612	0.609	0.672	0.644
		50°C		
7.5	0.475	0.340	0.294	0.404
15	0.489	0.399	0.344	0.449
30	0.512	0.444	0.440	0.502
60	0.529	0.497	0.560	0.554
101	0.545	0.552	0.611	0.598

^{13}C NMR experimental settings and analysis method

^{13}C NMR analysis of the tested solutions was performed with a Bruker Avance III 400 spectrometer, operating at 100.613 MHz. Tetramethylsilane was used as external standard at 0.00 ppm, while CH_3CN was used as internal reference (CH_3, δ = 1.47). A sealed glass capillary containing D_2O (Sigma–Aldrich) was introduced into the NMR tube with the sorbent sample to provide a good signal for deuterium lock. A pulse sequence with proton decoupling and NOE suppression was used to acquire the $^{13}C\{^1H\}$ with the following acquisition parameters: pulse angle = 90.0°, acquisition time = 1.3632 s, delay time = 2–30 s, data points = 65 K, number of scans = 250–500. The relative integration of signals of the $-CH_2-$ carbon atoms containing the same number of attached protons was not affected by an increased acquisition time and/or relaxation delay (up to 60 s). The data were processed by Bruker-Biospin Topspin software.

Normally, the integration of ^{13}C NMR resonances does not grant a reliable quantification of species with carbon atoms in different environments, because the spin–lattice T1 relaxation time strongly depends on the number of protons attached to the carbon atom [S1, S2]. In the species we have been dealing with, i.e. MEA carbamate and free and protonated amine that are fast exchanging on the NMR

scale via proton scrambling, the ^{13}C atoms of the CH_2–CH_2 backbone have a similar chemical environment and the same number of hydrogens directly attached, so that they likely exhibit similar T1, as shown by the similar peak integrals occurred in each CH_2 resonance (estimated error <2%). On the other hand, the ^{13}C atoms of HCO_3^-/CO_3^{2-} pair and of CO_2^- functionality of the MEA carbamate haven't attached hydrogen and show higher relaxation times than those of CH_2 groups, resulting in lower peak intensities. For these reasons the relative amounts of carbamate and freely exchanging free and protonated amine have been confidently determined by NMR integration of the corresponding signals of the CH_2–CH_2 carbons, whose chemical shifts are strongly related to the chemical environment. The feasibility of this procedure was previously tested [S3] by carrying out several ^{13}C NMR spectra on reference solutions prepared by dissolving different molar ratios of accurately weighted amounts free amine, fully protonated amine and amine carbamate in D_2O. Using these standard solutions, we found a quantitative relationship (estimated error <5%) between the relative peak areas of CH_2–CH_2 carbon atoms and the known concentrations of each species. The quantification method is therefore empirically quite reliable, likely reflecting similarities of the relaxation rate for similar carbons in both carbamate and the rapidly exchanging free and protonated amine.

Relative cost of amine solution

The relative cost (RC) of amine solvents has been calculated by considering the initial cost of the prepared amine solution (CP) and the circulation rate (CR_{amine}), while the amine loss due to degradation and vaporization has been neglected. According to the work of Kohl and Nielsen [S4], the lean-amine circulation rate (CR_{amine}, dm^3/min) can be calculated as the rate between the CO_2 flow rate (F_{CO_2}, mol/min) and the CO_2 work capacity, i.e. the amount of CO_2 captured in 1 dm^3 of solution (CC', mol CO_2/dm^3), as reported in Eq. S1.

$$CR_{amine} = \frac{F_{CO_2}}{CC'} \quad \text{(S1)}$$

According to Nwaoha et al. [S5], the circulation rate of an amine solution can be evaluated with equations (S2) and (S3). The ideal gas law (Eq. S2) is employed to calculate the gas flow rate (F_{gas}, mol/min) of the gas mixture feeding the absorber.

$$F_{gas} = \frac{PV_{gas}}{RT} \quad \text{(S2)}$$

where P is 101.3 kPa, V_{gas} is the flow rate of the simulated flue gas for the CO_2 absorption experiment (mL/min), R represents the universal gas constant (8.314 kJ/kmol·K) and T is the CO_2 absorption temperature, corresponding at 313 K (40 °C).

The CO_2 flow rate in the gas mixture (F_{CO_2}) can be calculated with Eq. S3

$$F_{CO_2} = F_{gas} \times x_{CO_2} \quad \text{(S3)}$$

where x_{CO_2} denotes the molar ratio of CO_2 (= 0.15) in the simulated gas mixture.

The costs of the individual amine solvent (CI) were obtained from the supplier's chemical catalog. The initial cost of the prepared amine solution (CP, \$/dm^3) is the sum of the product between the concentration (M) of each amine in an aqueous solution, its corresponding molar mass and its CI, as presented in Eq. (S4)

$$CP = \sum_1^3 (n_i \times m_i \times CI_i) \text{ (i=1, 2, 3)} \quad \text{(S4)}$$

where n_i is the concentration (M) of an amine in the solution, m_i and CI_i are the amine's molar mass in kg/mol and cost in \$/kg, respectively.

Then the relative cost of consumed amine solvent (RC, \$/min) can be calculated using the following Eq. S5.

$$RC = CP \times CR_{amine} \quad \text{(S5)}$$

References:

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[S2] Hook, R.J. An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds. Ind. Eng. Chem. Res. 1997, 36, 1779–1790.

[S3] Barzagli,F.; Mani, F.; Peruzzini, M. A ^{13}C NMR study of the carbon dioxide absorption and desorption equilibria by aqueous 2-aminoethanol and N-methyl-substituted 2-aminoethanol. Energy & Environmental Science 2009, 2, 322-330.

[S4] Kohl, A. L.; Nielsen, R., Gas purification. Elsevier: 1997.

[S5] Nwaoha, C.; Saiwan, C.; Supap, T.; Idem, R.; Tontiwachwuthikul, P.; Rongwong, W.; Al-Marri, M. J.; Benamor, A., Carbon dioxide (CO2) capture performance of aqueous tri-solvent blends containing 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) promoted by diethylenetriamine (DETA). International Journal of Greenhouse Gas Control 2016, 53, 292-304.