

## Supporting Information

### Screening study of different amine-based solutions as sorbents for direct CO<sub>2</sub> capture from air

*Francesco Barzagli <sup>†\*</sup>, Claudia Giorgi<sup>‡</sup>, Fabrizio Mani<sup>†</sup>, Maurizio Peruzzini<sup>†</sup>*

<sup>†</sup> National Research Council, ICCOM Institute, via Madonna del Piano 10, 50019 Sesto F.no, Florence, Italy

<sup>‡</sup> University of Florence, Department of Chemistry, via della Lastruccia 3, 50019 Sesto F.no, Florence, Italy

\*Phone number: +39 0555225298; email: [francesco.barzagli@iccom.cnr.it](mailto:francesco.barzagli@iccom.cnr.it)

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## **<sup>13</sup>C NMR experimental settings and procedures**

The <sup>13</sup>C-NMR spectra were acquired with a pulse sequence with proton decoupling and NOE suppression and with the following acquisition parameters: pulse angle = 90.0°, acquisition time = 1.3632 s, delay time = 2-30 s, data points = 65K, number of scans = 250-500. All the data were processed by using Bruker Topspin software. Tetramethylsilane and acetonitrile were used as external standard and internal reference, respectively. A sealed glass capillary containing deuterium water (Aldrich) was inserted inside the NMR tube with the solution sample in order to provide a good signal for deuterium lock.

The relative amounts of carbamate and of the rapidly equilibrating (free amine)/(protonated amine) have been estimated by peak integration for each –CH<sub>2</sub>– resonance: as a matter of fact, increasing the acquisition time and/or the relaxation delay (up to 60 s) does not produce substantial changes in the relative peak areas of the –CH<sub>2</sub>– carbon atoms that contain the same number of attached protons (ref. 35 of the manuscript).

The <sup>13</sup>C atoms of HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and R<sub>1</sub>NH-CO<sub>2</sub><sup>-</sup> (carbamate of the amine) functionalities have no attached hydrogen: they show a longer relaxation time compared to that of –CH<sub>2</sub>– groups, resulting in lower intensity resonances.

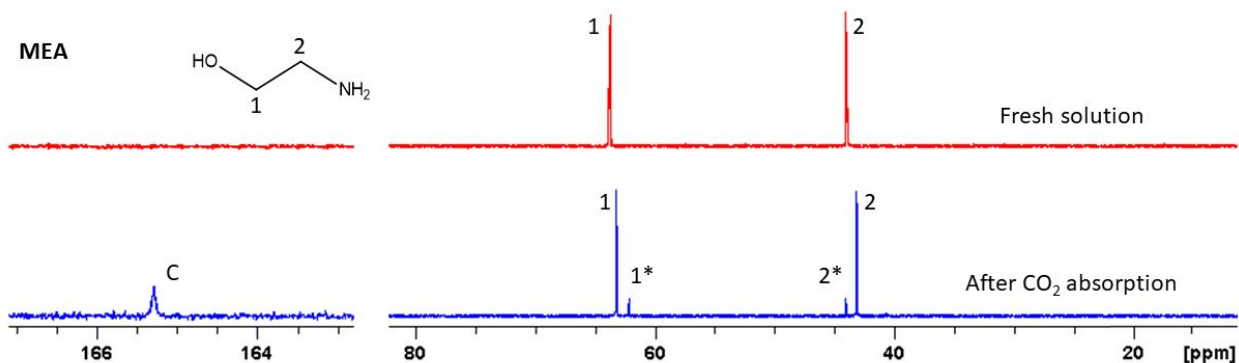
## **Comparison of <sup>13</sup>C NMR spectra before and after CO<sub>2</sub> absorption**

In order to highlight the changes in the NMR spectra of the amine solutions before and after the absorption of CO<sub>2</sub>, the spectra relating to aqueous MEA and aqueous AMP are reported as examples.

In the following spectra, the numbers indicate the carbon atom referred to the both free amine and protonated amine fast exchanging in the NMR scale, assigned as reported in the relative amine structure. Asterisks denote the chemical shifts of carbon backbones of the carbamate of the amine. C indicates the carbonyl atoms of carbamate of the amine, while b/c is referred to the signal of fast exchanging bicarbonate/carbonate ion. The intensity of the signal at about 160 ppm are not in scale.

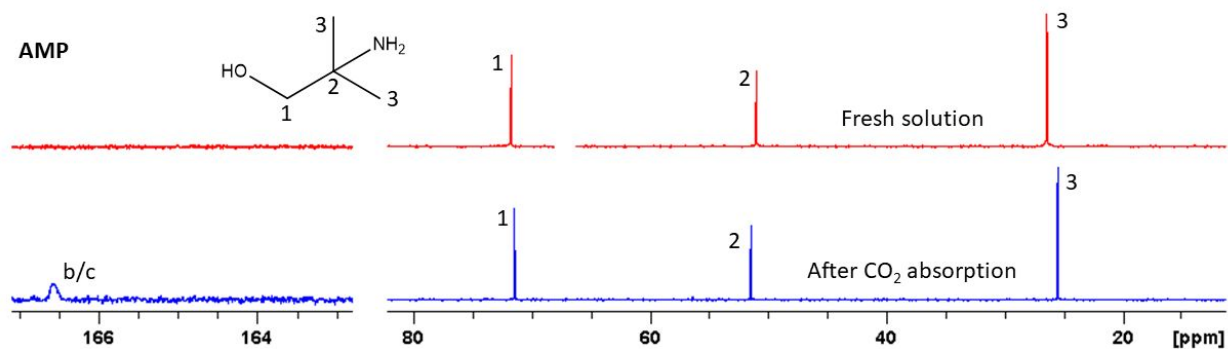
After CO<sub>2</sub> absorption, the spectrum of MEA (fig S1) shows three new peaks (1\*, 2\*, C) with respect to that of the fresh solution, related to the formation of the carbamate of the amine (HOCH<sub>2</sub>CH<sub>2</sub>NHCO<sub>2</sub><sup>-</sup>).

Furthermore, it is also possible to observe a slight variation in the position of peaks 1 and 2, relative to the rapidly equilibrating (free amine)/(protonated amine): after the absorption, the formation of protonated MEA (HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>) causes a signal shift. The greater the amount of protonated amine, the greater the shift with respect to the starting position.

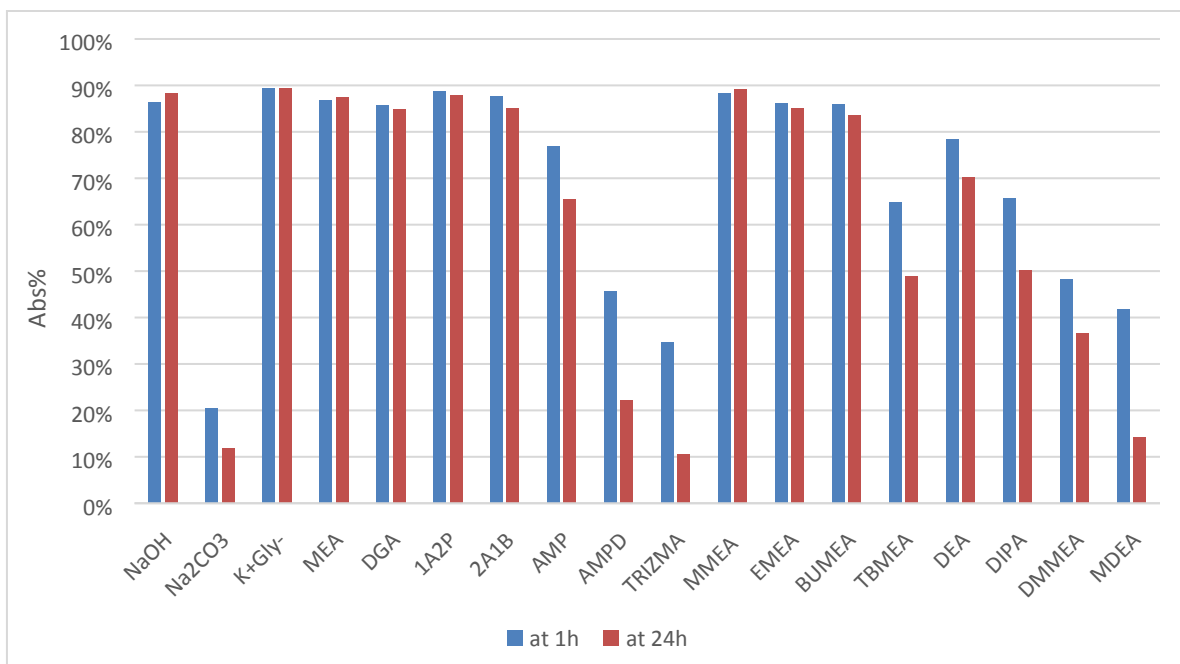


**Figure S1:**  $^{13}\text{C}$  NMR spectra of the aqueous MEA solution before (fresh solution) and after the 24 h of aerial  $\text{CO}_2$  absorption.

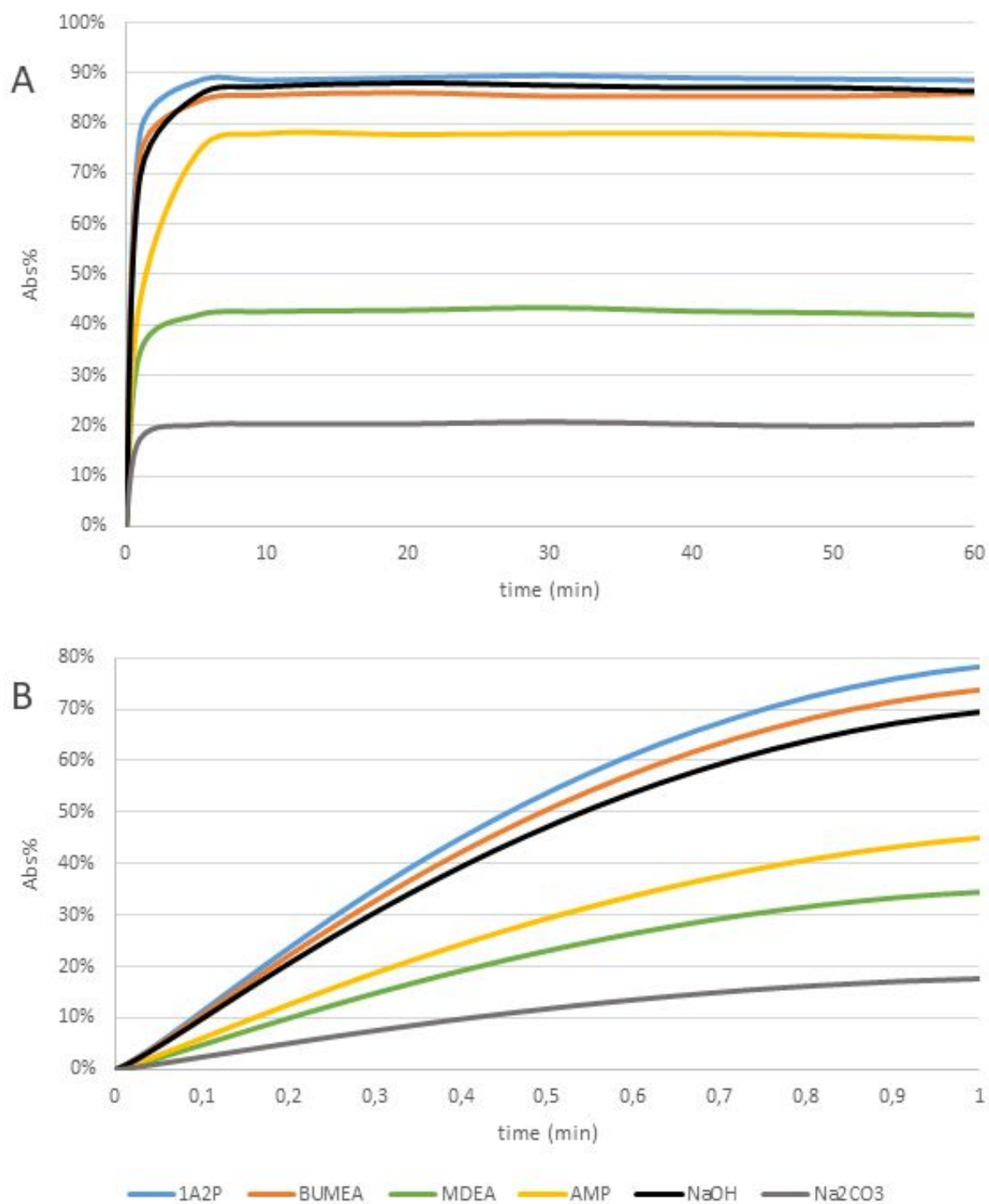
On the other hand, aqueous AMP is unable to form carbamate: after the  $\text{CO}_2$  absorption, the only new signal (b/c) relates to the rapidly equilibrating carbonate/bicarbonate ions ( $\text{CO}_3^{2-}/\text{HCO}_3^-$ ) formed. Also in this case it is possible to observe the shift of the position of the peaks 1, 2 and 3 due to the formation of the protonated AMP species.



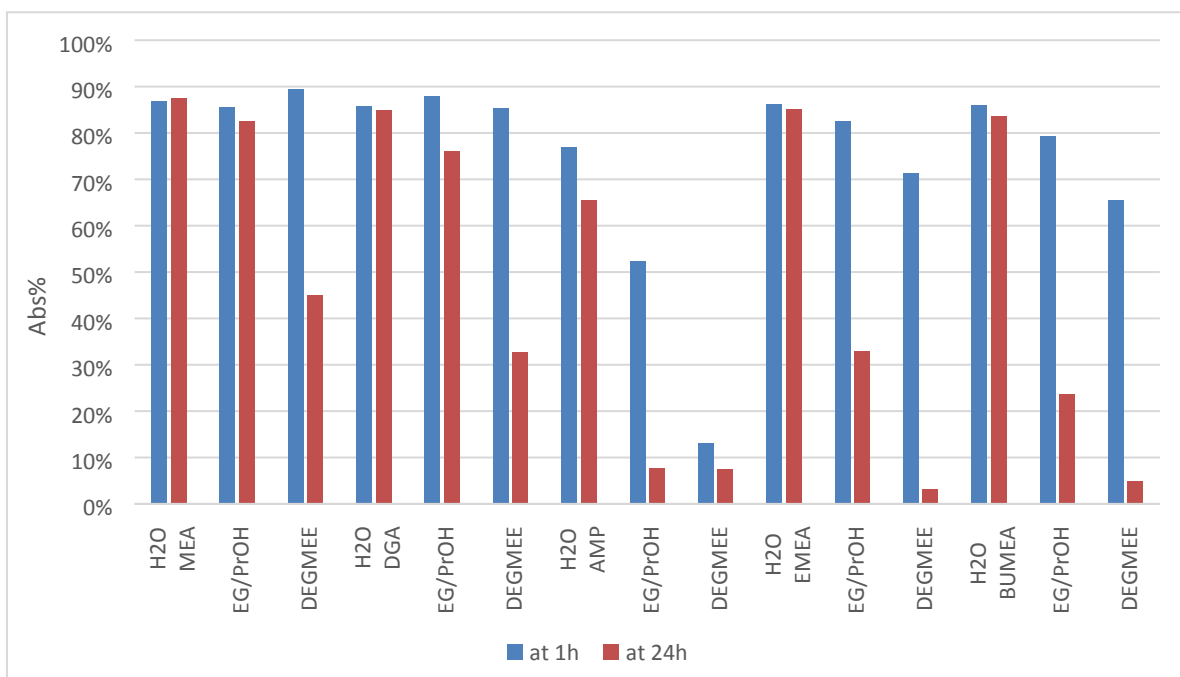
**Figure S2:**  $^{13}\text{C}$  NMR spectra of the aqueous AMP solution before (fresh solution) and after the 24 h of aerial  $\text{CO}_2$  absorption.



**Figure S3.** Actual percentages of the CO<sub>2</sub> absorbed (Abs%) of the tested aqueous amine-based absorbents, measured after 1 and 24 hours. Data taken from Table 2 of the manuscript.



**Figure S4.** (A) Percentage of CO<sub>2</sub> absorbed (Abs%) as a function of time in the first hour of absorption at 25 °C for an aqueous unhindered primary amine (1A2P), an unhindered secondary amine (BUMEA), a tertiary amine (MDEA) a sterically hindered amine (AMP) and for aqueous NaOH and Na<sub>2</sub>CO<sub>3</sub>. (B) Enlargement relative to the first minute of absorption, to highlight the initial CO<sub>2</sub> absorption rate.



**Figure S5.** Actual percentages of CO<sub>2</sub> absorbed (Abs%) of five different amines with three different diluents, measured after 1 and 24 hours. Data taken from Table 3 of the manuscript.