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

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Abstract

Aqueous blends of the three amines 2-aminoethanol (MEA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) were tested as sorbents for CO_2 capture processes. We formulated three different blends with the same overall amine concentration (5M) but with different amine molar ratio, namely blend-1 (2M MEA+2M MDEA+1M AMP), blend-2 (1M MEA+2M MDEA+2M AMP) and blend-3 (2M MEA+1M MDEA+2M AMP). Their CO_2 absorption and desorption performances were investigated in batch experiments in terms of CO_2 equilibrium solubility, CO_2 absorption at 40 °C and CO_2 desorption at 100 °C as a function of time, and energy consumption during the regeneration process. The results were compared to those obtained under the same operating conditions with 5M aqueous MEA, the benchmark sorbent for CO_2 absorption processes. The effect of the different amino composition on the CO_2 capture mechanism was evaluated by identifying and quantifying the species formed during the capture process through an accurate ^{13}C NMR speciation study. The results obtained showed that all formulated sorbents have higher desorption performance and require less energy for regeneration than conventional aqueous MEA, confirming that blending different alkanolamines has the potential to improve CO_2 capture. In particular, blend-2 can be regarded as a promising sorbent for implementation in commercial systems, as it performed a desorption rate up to 5 times higher than conventional aqueous MEA, combined with a significantly lower relative heat duty for regeneration (41.5%) and lower operating costs for CO_2 capture.

Keywords

CO_2 capture • alkanolamine • regeneration heat duty • ^{13}C NMR speciation • amine carbamates • ternary amine system

1. Introduction

The chemical capture of carbon dioxide (CO_2) from industrial flue gases by liquid amine solutions is considered one of the most effective techniques to lower CO_2 emissions into the atmosphere, and its rapid development is deemed crucial to curb global warming and related climate changes [1–4]. Aqueous alkanolamine solutions are capable to efficiently absorb CO_2 from a gas mixture, and can be reused several times because they can be thermally regenerated. In particular, aqueous solution of 2-aminoethanol (MEA) has been extensively investigated and tested in post combustion CO_2 capture systems, and today is regarded as the benchmark for all CCS (carbon capture and storage) processes [5–7]. Unfortunately, the use of aqueous MEA entails some severe drawbacks that limit the wide application of this technology: in particular, the large amount of energy required to regenerate the sorbent through the decomposition of the stable carbamate formed during CO_2 capture (at temperatures around 120-140 °C) accounts for approximatively 70% of the total operating costs, and need to be lowered to approach the commercial viability [8–11].

In an effort to improve the conventional aqueous MEA in terms of CO_2 absorption efficiency and regeneration heat requirement, new techniques have recently been proposed, such as the use of solid catalysts to improve desorption [12–15], together with the development of a large number of innovative sorbents, such as water-lean sorbents [16–19] or, as in this work, blended aqueous alkanolamines [20].

Blending different alkanolamines can effectively combine the advantages of individual alkanolamines, resulting in sorbents with brilliant CO_2 capture performance compared to aqueous MEA under similar operating conditions [21]. Generally, aqueous solutions of individual primary or secondary alkanolamines react rapidly with CO_2, but requires high temperature (and consequently high energy) for regeneration, due to the high stability of the formed carbamates; differently, tertiary or sterically hindered alkanolamines have high CO_2 absorption capacity and need a low energy consumption for regeneration, but with an unfavorable low reaction rate [22,23]. A large number of studies have shown that an aqueous blended system, usually formed by a primary (or a secondary) amine mixed with a tertiary (or a sterically hindered) amine, can exhibit a faster reaction rate with CO_2 than the single tertiary (or sterically hindered) amine, and can require less energy for regeneration than the single primary (or secondary) amine [24–27]. In particular, the primary (or secondary) amine promotes the reaction rate and the mass transfer, while the tertiary (or sterically hindered) amine acts as a base (proton acceptor) and enhances the desorption efficiency [28]. As a further improvement, more recently a lot of attention has been paid to blended ternary amine systems, formed by mixing three amines generally chosen between MEA, piperazine (PZ), 2-amino-2-methyl-1-propanol (AMP), N-methyldiethanolamine (MDEA) or diethylenetriamine (DETA): results reported by several research groups, such as Zhang et al. [29], Nwaoha et al. [21,30] and Liu et al. [31] suggest that these blends greatly increased the efficiency of the CO_2 desorption process, significantly reducing the total heat duty compared to conventional aqueous MEA. Liu's research team also found that a sorbent with three amines blended (MEA, MDEA and AMP) required a shorter time for the desorption compared to a similar solution with two amines blended (MEA and MDEA) under the same operating conditions [31].

Although the reported studies show the potential advantage of using blends of three amines for CCS processes, it has not yet been clarified how the individual amines in these systems interact with each other and with CO_2 during capture and regeneration processes: a better understanding of the reaction mechanisms could help to define general criteria for the formulation of new and even more efficient sorbents. In an attempt to fill this gap, in the present experimental work we thoroughly investigated three novel aqueous solutions of mixed MEA, MDEA and AMP as sorbents for CO_2 capture processes, and their absorption and desorption performances were correlated with an accurate speciation study, in order to understand the effect of the different sorbent composition on the CO_2 capture mechanism. The primary amine MEA has been blended with MDEA (a tertiary amine) and with the sterically hindered amine AMP in three different molar ratios, namely 2/2/1, 1/2/2 and 2/1/2, keeping constant the total amine concentration at 5M. The three different resulting blends were tested for CO_2 absorption from a gas mixture in batch experiments, in order to determine their CO_2 capture as a function of time (at T = 40 °C and P_{CO_2} = 15 kPa) and the CO_2 equilibrium solubility at different temperatures and CO_2 partial pressure. With the aim of understanding how the different composition of the sorbent affects the CO_2 capture mechanism, we investigated the variation over time of the different species in solution during the CO_2 capture process through an accurate ^{13}C NMR speciation study [32,33]. Moreover, the desorption properties of the three blends were evaluated measuring the CO_2 released from the solution as a function of time and by recording the energy consumption during the regeneration process (at T = 100 °C). All the results were compared with those obtained by using the benchmark 5M aqueous MEA solution under the same operating conditions. Finally, the potential energy savings for regeneration and the potential lowering of operating costs during the use of the three blends with respect to MEA were assessed. The improved desorption performance and lower energy demand penalty observed for all the blends compared to aqueous MEA confirm that aqueous blended ternary amine systems can be considered as promising sorbents for CO_2 capture processes, and in particular the blend MEA 1M + MDEA 2M + AMP 2M can be regarded as an effective alternative to conventional sorbents in CCS systems.

2. Experimental section

2.1. Materials

The alkanolamines 2-aminoethanol (MEA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) were of analytical grade (Sigma-Aldrich) and were used without further purification to prepare a 5M aqueous MEA solution and three different aqueous amine blends (namely blend-1, blend-2 and blend-3) with different percentage of each amine but with the same total concentration of 5M. The detailed formulations of the three blends are reported in Table 1. Gas mixtures with different percentages of pure CO_2 and N_2 were prepared to evaluate the capture performance of the tested solutions. The gas flow rates and volumetric compositions were controlled with two mass flow controllers (Beijing Sevenstar Electronics Co., Ltd., China;

accuracy = ±1.5%). The concentration of CO_2 in the gas mixture was measured with a COZIR-100 CO_2 infrared sensor (GSS Ltd., UK; accuracy = ±0.01%).

Table 1. Amine composition of the tested 5M aqueous blends.

name	Amine concentration (M)		
	MEA	MDEA	AMP
blend-1	2	2	1
blend-2	1	2	2
blend-3	2	1	2

2.2. CO_2 equilibrium solubility

The CO_2 equilibrium solubility is defined as the measured CO_2 loading value (mol CO_2 absorbed/mol amine) at the equilibrium for a given temperature and with a specific CO_2 partial pressure. Several values of CO_2 solubility at the equilibrium in aqueous MEA and in all the blends were determined at various temperatures (between 30 and 50 °C) and CO_2 partial pressures (between 7.5 and 101 kPa) with the apparatus depicted in Figure S1 in Supporting Information, following a previously used procedure [34]. The desired CO_2 partial pressure was obtained by mixing together pure N_2 and CO_2. The gas mixture was water saturated and continuously bubbled inside the fresh amine solution, kept in a flask maintained at the desired temperature with a thermostatic bath. The flask was equipped with a condenser kept at 0 °C, in order to avoid any amines and water loss. Each experiment lasted 9 hours, to ensure the reaction system reach the equilibrium. The CO_2 equilibrium solubility (i.e., the CO_2 loading) was measured by titration, using an aqueous solution of HCl (1M) [35]. For the final CO_2 loading determination, at least three titrations were performed with the interval of 30 minutes. When three consecutive titration measurements provide the same value of CO_2 solubility, the process is considered at equilibrium at the corresponding experimental conditions, and the last value obtained is considered the CO_2 solubility at equilibrium.

2.3. CO_2 absorption over time

The CO_2 loading (mol CO_2 absorbed /mol amine) over time for the different blends and for the reference 5M aqueous MEA was evaluated with the apparatus reported in Figure S2 in Supporting Information, with a previously described procedure [34]. Briefly, a volume of 200 mL of the tested absorbent was placed into a three-necked flask and maintained at T = 40 °C by means of a thermostatic water bath. A gas mixture (CO_2 partial pressure = 15 kPa) was bubbled inside the sorbent at the gas flow rate of 600 mL/min (90 mL/min CO_2 + 510 mL/min N_2). The CO_2 concentration of the gas mixture exiting from the condenser was continuously recorded with the CO_2 infrared analyzer. The CO_2 loading over time was evaluated by integrating the recorded CO_2 absorption profiles [36]. Each experiment lasted at least 800 consecutive minutes and ended when the measured CO_2 concentration in the outlet gas stream did not change over time.

2.4. CO_2 desorption over time

After the CO_2 saturation at 40 °C with the gas mixture (CO_2 = 15 kPa), aqueous MEA and the three different blends were desorbed with an apparatus similar to that of the absorption experiments (depicted in Figure S3 in Supporting Information), with a well-established procedure [34,37]. The flask containing the CO_2-loaded solutions was immersed into an oil bath coated with insulation cotton, kept at the constant temperature of 100 °C, under magnetic stirring at 900 rpm. The CO_2 exiting from the desorber was mixed with pure N_2 with a constant flow rate of 500 mL/min. The CO_2 concentration in the resulting gas mixture was continuously recorded with the CO_2 infrared analyzer, and the CO_2 loading over time was evaluated. The choice of this desorption temperature (100 °C) allows to better evaluate the different desorption performances of the examined sorbents: in fact, under the industrial operating temperatures (120-140 °C), the desorption rate would be high for all the solutions and differences would not be appreciable. A similar strategy has been used in previous works and by other authors [29,38]: in this way it is possible to identify the sorbents capable of better desorbing with a lower need for energy. As in other studies in the literature, the cumulative consumption of electric energy during the regeneration process was recorder with an electric meter (Zhejiang Tepsung Electric Meter Co., Ltd. China; accuracy = ± 0.001 kW·h) connected to the oil bath [39–41].

2.5. ^{13}C NMR analysis

An accurate qualitative and quantitative ^{13}C NMR analysis of the carbonated species formed in all the MEA/MDEA/AMP blends was performed during the CO_2 capture process, following a well-established procedure [42]. In Supporting Information are reported details of the ^{13}C NMR experimental settings and of analysis methods. The integration of the peaks of the carbon atoms of the $–CH_2–$ and –CH– backbone of each amine allows to evaluate the relative amounts of fast equilibrating (free amine)/(protonated amine) and amine carbamate. Knowing the initial amount of amine, it is possible to obtain the concentration of each related species. The carbonyl carbon atom of MEA carbamate and those of the fast-equilibrating HCO_3^-/CO_3^{2-} system are not directly bonded to H atoms: as a consequence, they have a longer relaxation time compared to $CH_3–$, $–CH_2–$ and –CH– carbon atoms, resulting in lower signal intensity. Notwithstanding, an accurate integration of their peaks (in the range 165–160 ppm) can provide a good estimation of their relative quantities.

As reported in previous studies, the chemical shift (ppm) of the unique signal of the fast-equilibrating (free amine)/(protonated amine) of the ^{13}C atom of the -CH_2OH group is directly correlated to the concentration of these two species, and their relative amounts can be evaluated [43,44]. Here is the procedure: for each individual amine, we carried out ^{13}C NMR analysis of D_2O standard solutions of neat amine, protonated amine and their 1:1 equimolar blend. Plotting of the chemical shifts of the ^{13}C resonance of the -CH_2OH group provides a calibration straight line. The calibration line, for each amine, was used to correlate the chemical shift found with the relative percentage of free and protonated amine. The limiting values found for free amine were: [$\delta(\boldsymbol{C}H_2OH)$: MEA=63.04 ppm; MDEA=58.44 ppm; AMP=71.25 ppm], while for the protonated amine were: [$\delta(\boldsymbol{C}H_2OH)$:

MEA=57.13 ppm; MDEA=54.69 ppm; AMP=65.91 ppm]. With an analogous procedure, the relative quantity of bicarbonate and carbonate ions in solution was evaluated from the chemical shift of the fast equilibrating HCO_3^-/CO_3^{2-} signal, as already described in a previous work [45].

2.6. Calculations

The difference between the amount of CO_2 present in solution after absorption and after desorption represents the amount (mol) of CO_2 desorbed, and it is calculated with Eq. (1).

$$CO_2des = (\alpha_r - \alpha_l) \times C \times V \quad (1)$$

where α_r is the loading of CO_2-rich solvent, α_l represents the loading of CO_2-lean solvent after regeneration, C (M) is the concentration and V (dm^3) is the volume of the sorbent.

The heat duty (H , kJ/molCO_2) for the sorbent regeneration has been calculated with Eq. (2) [38,46].

$$H = \frac{E_{des}}{CO_2des} \quad (2)$$

where E_{des} is the energy consumption (kJ) for desorption. With the apparatus used in this work for the regeneration process, the energy consumption is the electric consumption recorded with the digital electric meter.

Due to the simplified instrumentation used in our laboratory, we have found that H values calculated as in Eq. (2) were generally much higher than the actual heat duty. Therefore, in order to compare the regeneration performance of the different sorbents, we used the relative heat duty (H_R, %), calculated as in Eq. (3):

$$H_R = \frac{H_b}{H_{MEA}} \cdot 100 \quad (3)$$

where H_b denotes the heat duty for the desorption of a blended amine system and H_{MEA} is the heat duty of the benchmark 5M aqueous MEA in the same operating conditions.

The Desorption Parameter (DP) has been recently proposed [34] as a useful parameter to evaluate and compare the energy efficiency of different sorbent at the same stripping conditions. DP is calculated taking into account the amount of CO_2 desorbed (CO_2des) and the average desorption rate (r_{dv}), as in Eq. (4):

$$DP = CO_2des \times r_{dv} \quad (4)$$

where r_{dv} (mol/(dm^3·min)) is calculated following Eq. (5):

$$r_{dv} = \frac{CO_2des}{time \cdot V} \quad (5)$$

Finally, the relative cost (RC, $/min) of the tested amine sorbents has been evaluated as in Eq. (6):

$$RC = CP \times CR_{amine} \quad (6)$$

where CP ($/$dm^3$) is the initial cost of the prepared amine solution and CR_{amine} (dm^3/min) is the circulation rate. Details on the calculation of CP and CR_{amine}, together with the complete procedure for assessing the relative cost of the amine solutions, can be found in Supporting Information.

3. Results and Discussion

3.1. Chemical equilibria in solutions and CO_2 solubility at the equilibrium

In this work we formulated three different aqueous blends of MEA, MDEA and AMP, with different amine molar ratio but with the same total amine concentration (5M), as reported in Table 1. We investigated their absorption-desorption performance and compared them with those of 5M aqueous MEA, the reference absorbent for CCS processes, in the same operating conditions.

When formulating new absorbents for CO_2 capture processes, a paramount parameter to consider is the CO_2 equilibrium solubility in the solution, defined as the CO_2 loading (i.e., the ratio between the amount of captured CO_2 and the total amount of amine in solution) at the equilibrium, for a given temperature and with a specific CO_2 partial pressure. As reported in literature, higher values of CO_2 solubility at the equilibrium are usually related to higher efficiency in the CO_2 separation from a gas mixture and to lower operating costs, since fewer CO_2 absorption-desorption cycles are required [26,34]. Following the procedure reported in section 2.2, here we measured the CO_2 equilibrium solubility for 5M aqueous MEA and for the three MEA/MDEA/AMP blends, at the temperature of 30, 35, 40 and 50 °C and with different CO_2 partial pressure in the gas mixture, namely at 7.5, 15, 30, 60 and 101 kPa. All the measured CO_2 solubility values at the equilibrium, reported as CO_2 loading values, are summarized in Table S1 in Supporting Information.

Figure 1a reports the values of CO_2 solubility at the equilibrium for aqueous MEA and for the three blends at 40 °C. As a general result, the solubility increases for all solutions as the CO_2 partial pressure increases: in fact, the greater the number of free CO_2 molecules in the gas phase, the greater the concentration of CO_2 in the liquid phase when the system reaches the equilibrium [34]. As shown, aqueous MEA provides the highest values at low CO_2 partial pressure (7.5-30 kPa); on the contrary, at high partial pressure of CO_2 (60-101 kPa), the highest values were obtained with blend-2 (MEA 1M + MDEA 2M + AMP 2M), which is the solution containing the lowest amount of MEA among those tested. Furthermore, as shown in Figure 1b (here for blend-2, but the same trend was observed for all the other blends) the equilibrium solubilities decrease with increasing temperature, since the reactions between the amines and CO_2 are exothermic.

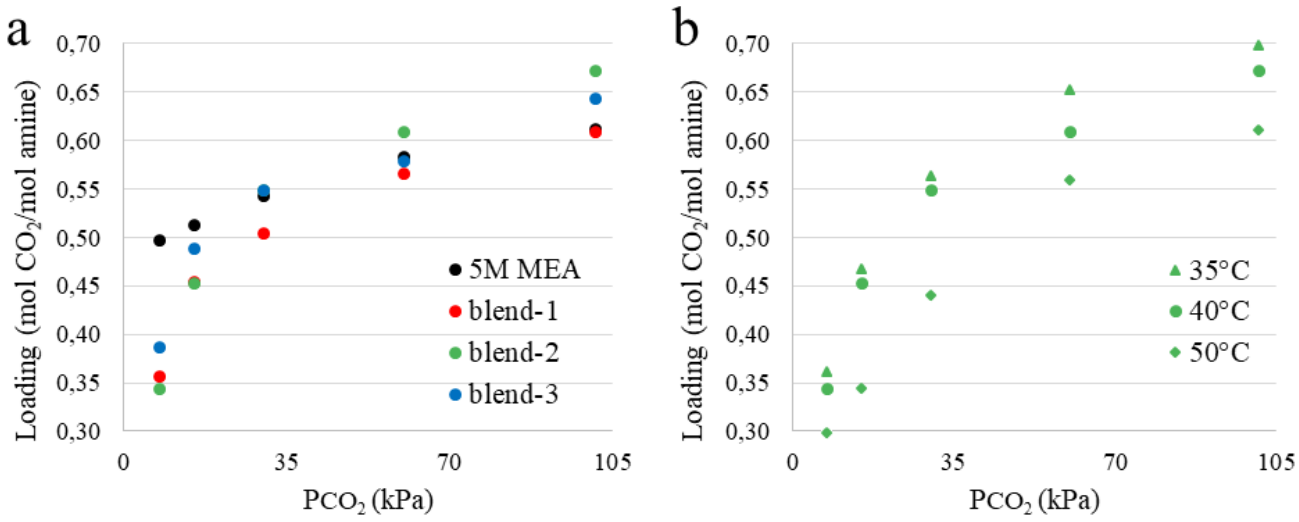

Figure 1. CO_2 solubility at the equilibrium as a function of the P_{CO_2} (a) for MEA, blend-1, blend-2 and blend-3 at 40°C, and (b) for blend-2 at 35, 40 and 50 °C.

With the aim of better understanding the reaction mechanism between the blends and CO_2, and the intermolecular interactions between the different amines during the capture process, samples of solution were collected during the absorption experiments, and the carbonated species present in the three different MEA/MDEA/AMP/CO_2/H_2O systems were qualitatively and quantitatively determined by ^{13}C NMR analysis. When CO_2 reacts with an aqueous blend of MEA, MDEA and AMP, the products formed in solution are MEA carbamate ($MEACO_2^-$), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and the protonated species $MEAH^+$, $MDEAH^+$ and $AMPH^+$ [29,47,48]. MDEA cannot form carbamate due to the lack of H atoms on its tertiary amine functionality, while the carbamate of AMP is unstable due to the steric hindrance near the amine functionality and quickly hydrolyzes to bicarbonate [21,49].

In Figure 2 is reported the variation of the concentration of the different species present in solution during the CO_2 absorption, as a function of the increasing loading, for all the formulated blends at 40 °C and at the CO_2 partial pressure of 101 kPa. A careful analysis of Figure 2 allows to understand the reaction mechanism between the amines and CO_2 in the different solutions, as reported below.

As evident from the ^{13}C NMR analysis, at the beginning of the capture process (loading 0-0.14) CO_2 quickly reacts with the solution to form MEA carbamate ($MEACO_2^-$). The formation of the protonated species for all the amines in the blend since the beginning (Figure 2) indicates that also MDEA and AMP are involved in the production of $MEACO_2^-$, according to Eq. (7), where Am indicates MEA, MDEA or AMP, and AmH^+ indicates $MEAH^+$, $MDEAH^+$ or $AMPH^+$:

$$MEA + Am + CO_2 \rightleftarrows MEACO_2^- + AmH^+ \quad (7)$$

It is worth noting that even in the case of blend-2, where MEA is in a lower concentration than the other amines, $MEACO_2^-$ is the most abundant product formed, confirming its high reaction kinetics and the involvement of other amines in its production.

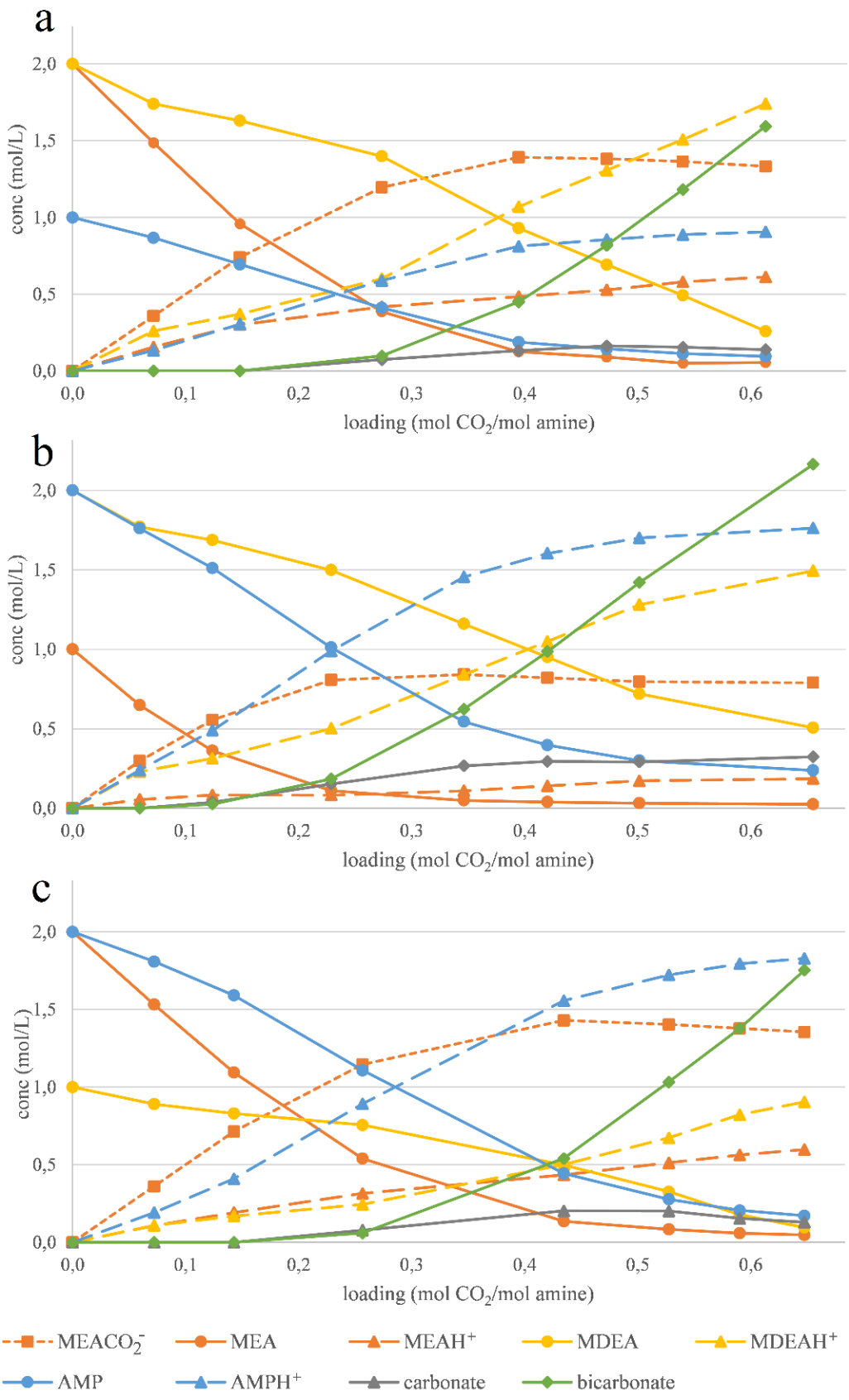

Figure 2. Speciation, reported as the concentration of each species in solution, as a function of the increasing loading (T = 40 °C; P_{CO_2} = 101 kPa) for (a) blend-1, (b) blend-2 and (c) blend-3.

As the absorption continues (loading 0.14-0.44), the amount of $MEACO_2^-$ formed increases (albeit with a lower production rate) and, at the same time, the reaction also produces carbonate and, to a greater extent, bicarbonate, according to Eq. (8) and (9):

$$Am + CO_2 + H_2O \rightleftarrows HCO_3^- + AmH^+ \quad (8)$$

$$HCO_3^- + Am \rightleftarrows CO_3^{2-} + AmH^+ \quad (9)$$

The production of bicarbonate is more evident in blend-2, where AMP and MDEA, which cannot form their own carbamate, are in greater concentration than in MEA.

When most of the starting amine are consumed, and unreacted amines in solution become scarce (loading 0.44-0.65), CO_2 can also react with the previously formed $MEACO_2^-$, as shown in Eq. (10):

$$MEACO_2^- + CO_2 + 2H_2O \rightleftarrows 2HCO_3^- + MEAH^+ \quad (10)$$

consequently, the amount of HCO_3^- increases sharply, while the $MEACO_2^-$ begins to decrease slowly. Additional bicarbonate could also be formed by the reaction of CO_2 with carbonate:

$$CO_2 + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^- \quad (11)$$

Although this reaction is less favored given the scarce presence of CO_3^{2-} in solution, from the carbonate trend in blend-1 and blend-3 it is possible to appreciate a slight decrease in concentration in this step.

For all the tested blends, bicarbonate is the most abundant carbonated species in solution at the equilibrium. Blend-2, with the higher MDEA and AMP concentration, forms a greater amount of bicarbonate (Figure 2b) than the other blends, and consequently has the highest loading values at high CO_2 partial pressures (Figure 1a). Moreover, the comparison of speciation in blend-1 and blend-3 (Figures 2a and 2c) reveals that, despite an equal amount of MEA (and a similar amount of MEA carbamate formed), blend-3 forms a considerably larger amount of bicarbonate, presumably due to the higher alkalinity of AMP compared to MDEA, which is reflected in a higher loading value at P_{CO_2} = 101 kPa (Figure 1a).

To better appreciate the variation of the speciation during the absorption experiment, Figure 3 reports the ^{13}C NMR spectra of the carbonyl atoms (range 160-165 ppm) and of the carbon atoms of the $-CH_2OH$ unit for each amine (range 55-72 ppm) in blend-3, as a function of the increasing amount of absorbed CO_2 (increasing loading). As clear from Figure 3, the fast equilibrating (free amine)/(protonated amine) signals, indicated with M, D and A for MEA, MDEA and AMP, respectively, move to high fields (lower ppm values) as the loading increases, to chemical shift values corresponding to higher percentages of protonated amines with respect to free amines. Moreover, the intensity of the MEA/$MEAH^+$ signal (M) significantly decreases at increasing loading, as the amount of the formed MEA carbamate (M*) increases. Finally, the intensity of the signal of the fast exchanging HCO_3^-/CO_3^{2-} (b/c) increased during the absorption and moved to high field, to chemical shift values corresponding to higher amounts of HCO_3^- [45].

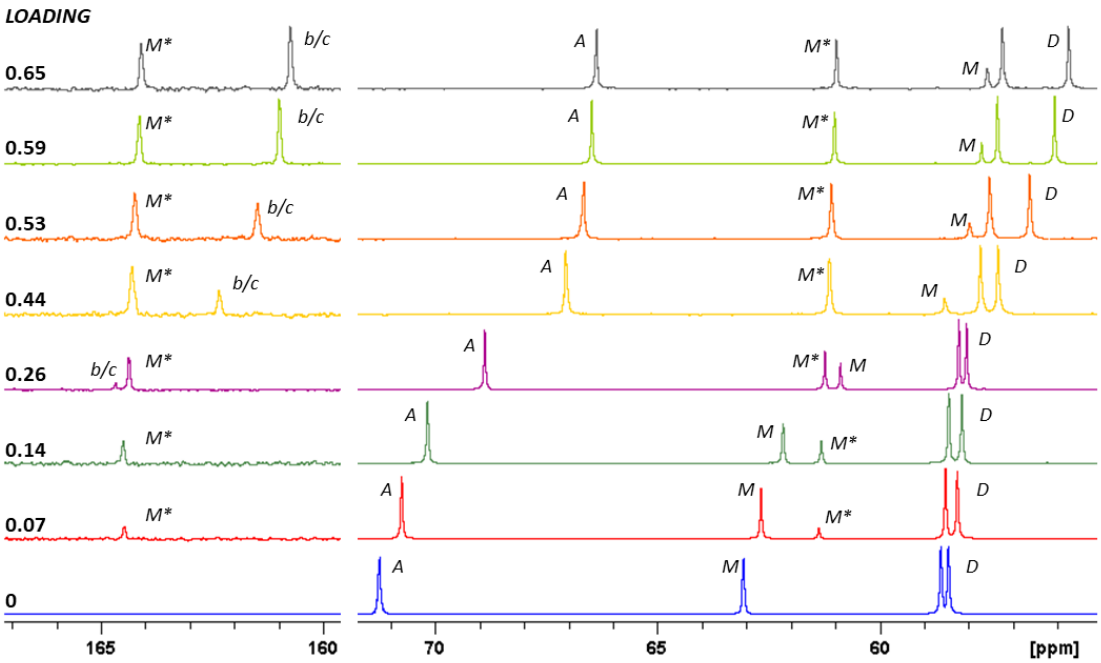

Figure 3. Variation of the ^{13}C NMR spectra of blend-3 as a function of the absorbed CO_2 (loading), at T = 40 °C and P_{CO_2} = 101 kPa. The spectra relate to the carbonyl atoms (range 160-165 ppm) and to the C atoms of the -CH_2OH unit for each amine (range 55-72 ppm). M, D, A denotes the signal of the fast equilibrating (free amine)/(protonated amine) for MEA, MDEA and AMP, respectively. M* indicates MEA carbamate, while b/c indicates the bicarbonate/carbonate ion.

3.2. CO_2 absorption and desorption

In order to evaluate the potential advantages of the three blends with respect to conventional MEA in CO_2 capture processes from flue gases (usually containing about 12-15% CO_2), we studied their absorption performance with a gas mixture with CO_2 partial pressure of 15 kPa, and the subsequent regeneration at higher temperature. The absorption experiments were performed at 40 °C as described in section 2.3, and the resulting trends of CO_2 loading as a function of the absorption time are reported for all the tested sorbents in Figure 4.

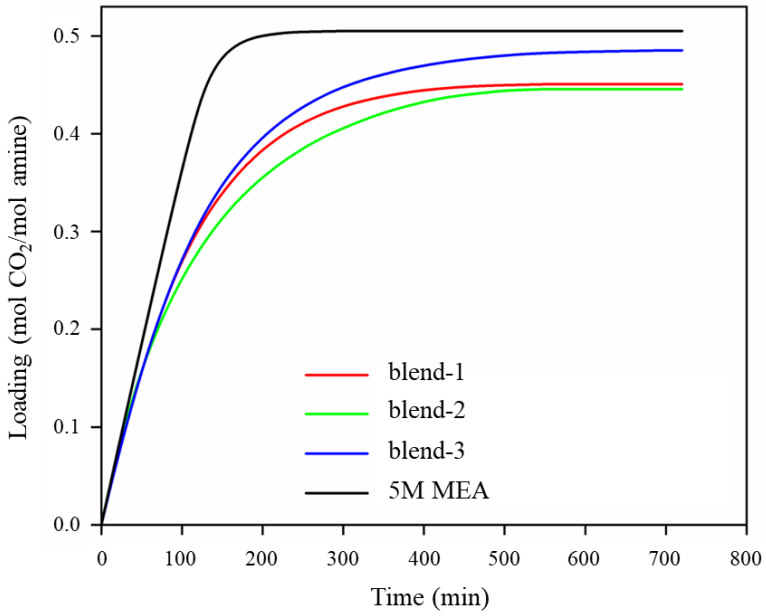

Figure 4. CO_2 loading as a function of the absorption time for each tested sorbent (T = 40 °C; P_{CO_2} = 15 kPa).

The CO_2 loading capacity increases significantly at the beginning of the experiment for all tested blends and for the 5M aqueous MEA reference solution. After 50 minutes, the loading increases more rapidly as a function of the concentration of MEA in solution, following the order MEA > blend-3 > blend-1 > blend-2. This is because the formation of the carbamate (Eq. 7) is kinetically favored with respect to carbonate and bicarbonate formation (Eq. 8 and 9), and consequently CO_2 is absorbed more rapidly where more MEA is present [48,50,51]. Blend-1 and blend-3 have the same concentration of MEA (2M), but blend-3 reacts faster because of the higher reaction kinetics with CO_2 of the sterically hindered AMP compared to a tertiary amine (MDEA) [21,26]. Due to its lower MEA concentration (1M), blend-2 reacts with CO_2 to produce mainly bicarbonate, and for this reason its reaction rate is the lowest among the tested solutions.

After the absorption step, the CO_2-loaded amine solutions were regenerated at 100 °C with the procedure described in section 2.4, and their desorption performances were measured in terms of CO_2 desorbed and variation of the CO_2 loading of the solution as a function of time, as reported in Figure 5a and 5b, respectively. As shown in Figure 5a, after 10-15 minutes of heating, all tested sorbents release CO_2 rapidly, reaching the maximum amount of desorbed CO_2 in about 50 minutes. All the MEA/MDEA/AMP blends desorb more CO_2, and consequently have better desorption performance, than aqueous MEA, following the order blend-2 > blend-1 > blend-3 > MEA. At the temperature of 100 °C, only a small amount of CO_2 is released from the MEA solution (Figure 5a), due to the high stability of the MEA carbamate formed during the absorption. Conversely, blend-2 contains mainly bicarbonate, which is decomposed more efficiently than $MEACO_2^-$ at the same temperature [52,53]. Furthermore, a higher presence of HCO_3^- ions in solution increase the decomposition rate of MEA carbamate [53–55]. As a final result, the amount of desorbed CO_2 in blend-2 is much greater (Figure 5a) compared to the other sorbents and regenerates almost completely (Figure 5b), a paramount condition for its utilization in continuous absorption/desorption cycles.

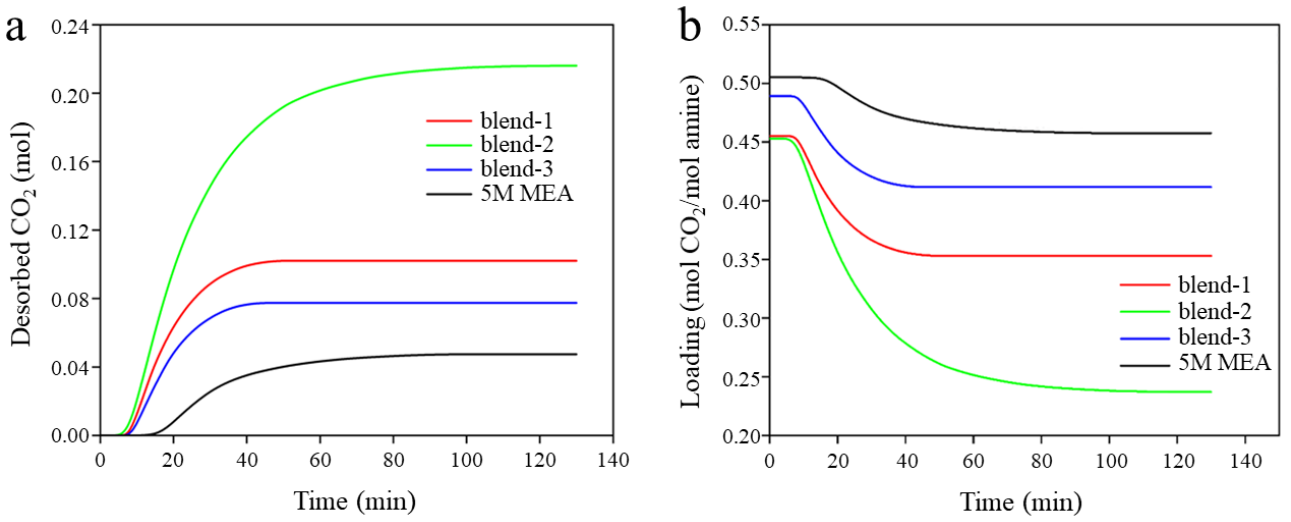

Figure 5. (a) Amount of desorbed CO_2 (mol) and (b) variation of the CO_2 loading as a function of the desorption time for each sorbent tested.

3.3. Evaluation of the energy consumption for sorbent regeneration

The amount of energy required for CO_2 desorption has a decisive impact on the economic cost of the entire capture process [56,57]. The formulation of sorbents with low energy demand for their regeneration is of primary importance to approach the CO_2 capture technology to commercial viability. In this work, we recorded with a digital meter (connected to the heating oil bath) the cumulative energy consumption during the sorbent regeneration. Figure 6a shows the correlation between the energy input for each desorption experiment and the amount of CO_2 desorbed (CO_2des, mol).

As clear from Figure 6a, the overall energy consumption for all sorbents increases with the amount of desorbed CO_2: in particular, at the beginning of desorption (low CO_2des values), a low energy input is enough to release CO_2 from the CO_2-loaded solutions, especially for the solutions where the prevailing species is bicarbonate, which requires low energy to desorb CO_2 by breaking C−O bonds [58]. For increasing amount of desorbed CO_2, the energy input for the CO_2 release increases drastically, mainly due to the higher energy needed to break C−N bond in MEA carbamate. Figure 6a also shows that in our experimental conditions, for energy input higher than 150 kJ, all the formulated blends desorb a higher amount of CO_2 compared to 5M aqueous MEA. It's noteworthy that, with the same energy consumption, blend-2 desorbs a significantly greater amount of CO_2 compared to the other blends and, to a greater extent, to aqueous MEA. This last consideration is even more evident from Figure 6b, where the heat duty (calculated as in Eq. 2) is reported as a function of the desorbed CO_2 (CO_2des) for all the solutions: the energy consumption to desorb one mole of CO_2 follows the order blend-2 < blend-1 < blend-3 < MEA. From these results, blend-2 has the highest energy efficiency in the regeneration process compared to the other blends and to the conventional aqueous MEA.

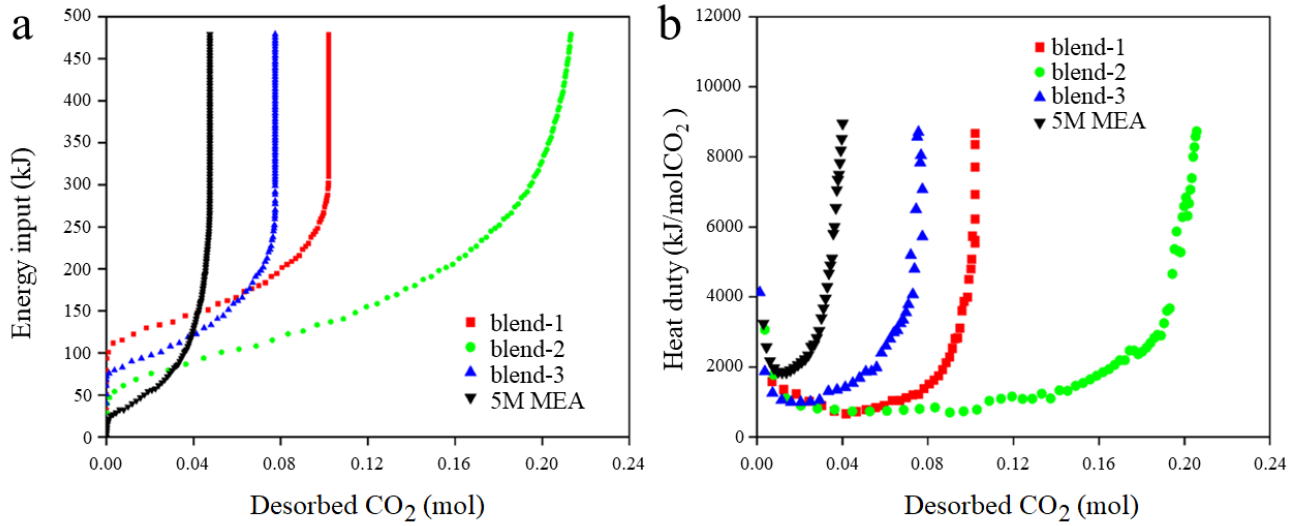

Figure 6. (a) Total energy input and (b) heat duty as a function of the amount of desorbed CO_2 for blends and aqueous MEA (P_{CO_2} = 15 kPa; T abs = 40 °C; T des = 100 °C).

The desorption performances of the different sorbents have been evaluated by calculating the average CO_2 desorption rate (Eq.5), the amount of desorbed CO_2 (Eq.1) and the heat duty (Eq.2) after 50 minutes of regeneration, when all the solutions have desorbed the corresponding maximum amount of CO_2 (Figure 5). The obtained results have been summarized in Table 2.

Table 2. Average desorption rate, amount of desorbed CO_2, heat duty and relative heat duty calculated for the tested blends, after 50 minutes of sorbent regeneration.

Amine system	Average desorption rate (mol/ (dm^3· min))	Desorbed CO_2 (mol)	Heat duty (kJ/molCO_2)	Relative Heat duty (%)
MEA	$0.86 \cdot 10^{-3}$	0.043	3621.05	100%
blend-1	$2.04 \cdot 10^{-3}$	0.102	3034.70	83.8%
blend-2	$3.84 \cdot 10^{-3}$	0.192	1500.78	41.5%
blend-3	$1.55 \cdot 10^{-3}$	0.077	3578.16	98.8%

It should be noted that the absolute values of the heat duties obtained are much higher than those usually reported in the literature, relating to industrial operating conditions. This is because simplified laboratory instrumentation, whit high electricity consumption, was used for their determination. Furthermore, CO_2 desorption rate at the temperature used here (100 °C) is lower than that at the temperature used for industrial applications (120-140 °C), with a consequent increase in the heat duty value. Therefore, the calculated absolute values of energy costs must be considered only for purposes of comparison between them, as they are obtained under the same operating conditions. In order to have a more realistic comparison between the energy consumption of the different sorbents, we calculated the relative heat duty (Eq.3), tacking the 5M aqueous MEA as the reference. From the found values (reported in Table 2), the formulated blended ternary amine systems show better desorption performance compared to the benchmark MEA in the same operating condition, and in

particular blend-2 has the faster average desorption rate, the lower heat duty and desorbs the greater amount of CO_2 compared to the other sorbents. Blend-2 requires a significative lower amount of energy for regeneration than the other sorbents, and in particular 58.5% lower than MEA. The greater amount of bicarbonate with respect to carbamate in the solution to be regenerated is therefore decisive to decrease the amount of energy required for the desorption process.

In a recent work [34] Zhang et al. proposed and validated an innovative parameter, called Desorption Parameter (DP) and calculated by multiplying the amount of desorbed CO_2 with the average desorption rate (Eq. 4), to assess the energy efficiency of a sorbent, as an alternative to the accurate calculation of the energy requirements. The higher the DP, the higher the energy efficiency. Here, the Desorption Parameter for all the tested sorbents has been calculated and reported in Figure 7, together with the computed relative heat duty.

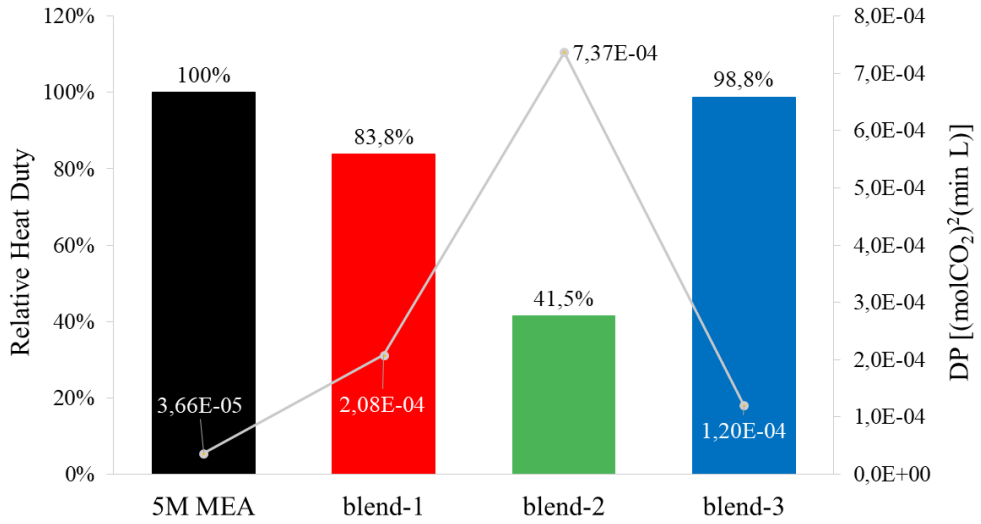

Figure 7. Relative heat duty of the different blends compared to aqueous MEA, and its relationship with the desorption parameter (DP).

Figure 7 clearly shows that a high DP corresponds to a low heat duty and that the trend of the DP values is strictly correlated to the trend of the relative heat duty values, confirming that the Desorption Parameter can be used in fast sorbent screening processes to quickly estimate the energy efficiency of a solution without the direct measurement of the heat cost. According to the results obtained, the energy efficiency follows the order blend-2 > blend-1 > blend-3 > MEA, and blend-2 is clearly the most promising for implementation in CO_2 capture processes.

3.4. Relative cost of amine solution

It has been estimated that about 10% of the operating costs of an amine-based capture process are due to the cost of the amine solution [59]. In this work we evaluated the relative cost (RC) of all the tested sorbents with a simplified calculation that takes into account the initial cost of the prepared amine solution (CP) and its

circulation rate (CR_{amine}), as reported in Eq.6. In addition, the cost analysis of each tested amine system was also performed based on the work of Hu et al. [41]. The values calculated for the initial cost of aqueous MEA, blend-1, blend-2 and blend-3 were 22.32, 49.93, 42.50 and 34.54 \$/dm^3, respectively. The complete procedure for assessing the CP and subsequently the RC of the amine solutions can be found in Supporting Information. The results obtained for the relative cost (\$/min), reported in Figure 8, show that all the blended ternary amine systems have a lower relative cost than MEA; even in this circumstance, the advantage of using blend-2 is truly remarkable, with a much lower RC, less than half, compared to all the other sorbents tested, and in particular 57.7% lower than aqueous MEA.

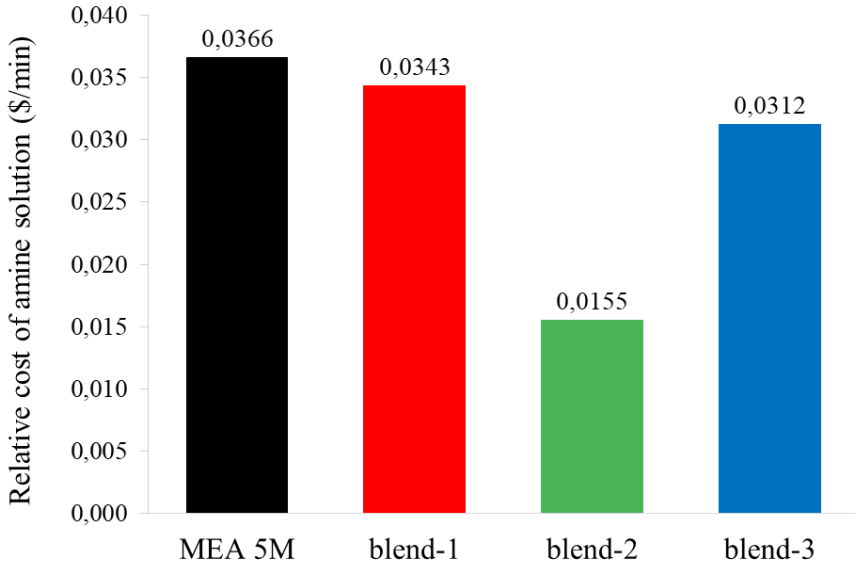

Figure 8. Relative cost (\$/min) of the different sorbent used.

4. Conclusions

With the aim of better understanding the potential benefits of blended ternary amine systems for CO_2 capture, and identifying general criteria for the formulation of innovative sorbents for effective and economically sustainable CCS processes, we investigated the absorption and desorption performance of three different aqueous MEA/MDEA/AMP blends, namely blend-1 (5M, 2/2/1), blend-2 (5M, 1/2/2) and blend-3 (5M, 2/1/2). Their CO_2 solubility at the equilibrium, CO_2 absorption (at 40 °C) and CO_2 desorption (at 100 °C) as a function of time, and their energy consumption during the regeneration process, were measured and compared to those of 5M aqueous MEA, the reference sorbent for all CCS processes, under the same operating conditions. Moreover, their capture performances were correlated with an accurate ^{13}C NMR speciation study, in order to obtain information on the reaction mechanisms involved. The experimental results showed that all the tested blends have slightly lower reaction rate than aqueous MEA: in fact, the greater the amount of MDEA and AMP in solution, the greater the CO_2 captured as bicarbonate, with a lower reaction rate compared to the formation

of MEA carbamate. On the other hand, bicarbonate decomposes much more easily than MEA carbamate (and moreover, the presence of HCO_3^- ions in solution increase the decomposition rate of MEA carbamate), and consequently all blends showed significantly better desorption performance compared to aqueous MEA, resulting in higher overall energy efficiency, following the order: blend-2> blend-1> blend-3> MEA. As a general result, in a blended ternary amine system, the presence of a tertiary amine (such as MDEA) has a decisive impact on the regeneration efficiency, while a sterically hindered primary amine (such as AMP) also contributes to maintain high absorption values, similar to those of aqueous MEA alone. Between the tested sorbents, blend-2 showed a desorption rate up to 5 times higher, a 58.5% lower heat duty and a 57.6% lower relative cost compared to 5M aqueous MEA. By virtue of these performances, aqueous MEA 1M + MDEA 2M + AMP 2M solution could be considered as a potential alternative to conventional CCS sorbents, after a careful experimentation in pilot scale plants to assess actual costs and benefits, before its implementation in commercial systems.

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