Investigation of the improvement of the CO_2 capture performance of aqueous amine sorbents by switching from dual-amine to trio-amine systems

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ABSTRACT

Mixing amines with different properties is considered a smart strategy for developing efficient aqueous solutions for reversible CO_2 capture. Specifically, dual-amine blends containing the tertiary amine 2-dimethylamino-2-methyl-1-propanol (2DMA2M1P) have proven to be particularly advantageous due to significantly lower regeneration costs compared to conventional sorbents. With the aim of formulating high-efficiency sorbents, in this work we evaluated the improvement in the CO_2 capture performance of such dual-amine blends by adding a further amine to form trio-amine systems: the use of three amines with different characteristics could further emphasize the advantages obtainable during both absorption and desorption. We formulated three new different aqueous solutions prepared by mixing 2DMA2M1P with the reaction rate promoter ethanolamine (MEA) and the absorption capacity promoter 2-amino-2-methyl-1-propanol (AMP) in different molar ratios. For each blend, the CO_2 solubility at equilibrium, the CO_2 absorption rate from a gaseous mixture, the regeneration rate at T = 373 K and the energy requirement for desorption were determined experimentally. In addition, to better understand the capture mechanism, ^{13}C NMR spectroscopy was employed to evaluate the speciation of each blend during the CO_2 absorption. Their CO_2 capture performance was compared with that of the benchmark aqueous MEA and two 2DMA2M1P-based dual-amine mixtures, obtained with the same procedure. As a finding, all formulated trio-amine blends have superior CO_2 equilibrium solubility and desorption performance compared with MEA 5 M. Noteworthy, the comparison with similar dual-amine systems highlighted the role of a suitable third amine in order to obtain enhance both absorption and desorption efficiencies. Among the formulated systems, MEA-2DMA2M1P-AMP (1:2:2) is potentially the most suitable to replace MEA in CO_2 capture processes after a careful cost-benefit analysis on larger scale systems.

1. Introduction

Increasing atmospheric CO_2 levels have been identified as a major cause of observed global warming. The development of strategies and policies to mitigate anthropogenic CO_2 emissions, mainly from fossil fuel-fired power plants, is considered crucial and urgent to tackle climate change [1]. Carbon Capture and Storage (CCS) is currently considered one of the most effective technologies for curbing CO_2 emissions on a large scale; in particular, post-combustion chemical CO_2 capture by aqueous alkanolamines is considered the most feasible approach as it is technically mature and retrofittable to existing plants [2,3]. The advantage of alkanolamines over other sorbents is that they react with CO_2 rapidly and, most importantly, reversibly, allowing their reutilization after thermal regeneration. Among these, ethanolamine (MEA) has been extensively studied for CO_2 absorption from large stationary emission sources over the past decades, and is now considered the benchmark for all CCS processes [4,5]. The MEA process, however, suffers from some serious drawbacks that limit its widespread use on an industrial scale [6–8]. In order to overcome the problems related to the MEA process, new technologies have been proposed in recent years,

based on non-aqueous or biphasic sorbents [9–11], desorption aided by solid acid catalysts [12–14], or as in this study mixing different amines in water [15,16]. Generally, it has been found that a single amine is unlikely to have optimal properties to meet multiple requirements in an integrated CO_2 absorption–desorption system [10,17]. In fact, primary (e.g. MEA) and secondary amines are characterized by fast reaction kinetics with CO_2, but their regeneration involves considerable energy costs due to the stable nature of the carbamates produced. Conversely, sterically hindered amines and tertiary amines generally have a higher loading capacity and can be recycled with lower energy consumption, but their practical application is hampered by slow reaction kinetics [18,19]. Blending different amines is considered a smart strategy to take advantage of each amine and improve the overall sorbent performance [20,21]. In particular, recent studies have shown that mixtures of a primary and a tertiary amine (i.e. dual-amine blends) have a higher CO_2 uptake capacity and lower energy requirement for regeneration than single primary amine, as well as a significantly higher absorption rate than single tertiary amine [22–24]. Among the various tertiary amines tested in these binary mixtures, 2-dimethylamino-2-methyl-1-propanol (2DMA2M1P) has received increasing attention due to its alkalinity, large CO_2 solubility and low heat of CO_2 capture. Several studies have demonstrated the advantageous use of 2DMA2M1P in the design of binary mixtures [25,26]. Recently, our research group also investigated the performance of this tertiary amine combined with several primary and secondary amines (total amine concentration 5 M), namely MEA, 2-amino-2-methyl-1-propanol (AMP), benzylamine (BZA), and diethanolamine (DEA): as a result, all 2DMA2M1P blends showed significantly greater cyclic capacity and lower regeneration heat duty than conventional aqueous MEA. In particular, MEA-2DMA2M1P and AMP-2DMA2M1P blends showed excellent performance in terms of absorption kinetics and energy requirement, respectively [27].

In an attempt to further improve the performance of sorbents based on amine mixtures, several research groups explored the potential of systems with three amines mixed together, generally formulated with a primary amine (reaction rate promoter), a tertiary amine (absorption capacity promoter), and a sterically hindered amine (with intermediate properties) [28–32]: they found that trio-amine blends exhibited greater CO_2 desorption efficiency than conventional aqueous MEA, significantly reducing the total heat duty while maintaining high CO_2 capture efficiency, and required shorter regeneration times than similar dual-amine blends under the same operating conditions.

Based on the excellent performance obtained with 2DMA2M1P-based dual-amine blends and considering the potential improvements achievable with trio-amine mixtures, in the present study we comprehensively analyzed the performance of three aqueous solutions of the three amines MEA, 2DMA2M1P and AMP (mixed in different molar ratios) during bench-scale CO_2 absorption and desorption processes. The CO_2 equilibrium solubility and the CO_2 absorption rate of each trio-amine blend were evaluated at 313 K in batch experiments of CO_2 absorption from gas mixtures with CO_2 partial pressures in the range of 5–60 kPa. In addition, ^{13}C NMR spectroscopy was employed for the identification and quantification of the different species in solution during the capture process, in order to better clarify the reaction mechanism and the role of each amine of the blend in the CO_2 capture reaction [33,34]. Regeneration performance was then evaluated by measuring CO_2 desorption rate and recording energy consumption during desorption experiments conducted at 373 K. The measured CO_2 capture performance was compared to that obtained (using the same methodology) for the reference aqueous MEA and for two 2DMA2M1P-based dual-amine blends, i.e. MEA-2DMA2M1P and AMP-2DMA2M1P, to highlight the potential advantage of trio-amine blends over similar binary systems.

2. Experimental section

2.1. Materials

All the chemicals were reagent grade and were used as received. 2-dimethylamino-2-methyl-1-propanol (2DMA2M1P), ethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP) were purchased from Tokyo Chemical Industry Co., Shanghai Macklin Biochemical Co., and Shanghai Aladdin Industrial Corporation, respectively. CO_2 (99.999%) and N_2 (99.9%) were obtained by Hunan Zhongtai Hongyuan Gas Co., and were used to prepare gas mixtures with the desired CO_2 partial pressure. Two mass flowmeters (Beijing Sevenstar Electronics Co.; accuracy $\pm1.5\%$) were used to control the flow rate and the volumetric composition of the mixtures. Three different ternary amine blends with total amine concentration of 5 M were prepared by mixing different molar ratios of the three amines MEA, 2DMA2M1P and AMP in deionized water. The prepared solutions were 2 M MEA + 2 M 2DMA2M1P + 1 M AMP (2:2:1); 1 M MEA + 2 M 2DMA2M1P + 2 M AMP (1:2:2); 2 M MEA + 1 M 2DMA2M1P + 2 M AMP (2:1:2). In addition, the 5 M MEA aqueous solution was prepared for comparison purposes.

2.2. CO_2 equilibrium solubility experiments

Fig. 1a shows the equipment used to measure CO_2 equilibrium solubilities, i.e., the CO_2 loading value (ratio of moles of captured CO_2 to total moles of amine in solution) at equilibrium for a specific temperature and CO_2 partial pressure (PCO_2). The experiments were carried out at a constant temperature of 313 K, using gas mixtures (CO_2 + N_2) with PCO_2 between 5 and 60 kPa, following a well-established procedure [35,36]. Briefly, the gas mixture with the desired PCO_2 was first saturated with water and then bubbled into the absorber, filled with fresh aqueous amine blend, at a constant flow rate of 500 mL/min. A reflux condenser (cooled at 278 K) was connected to the absorber to reduce the loss of amine and water. After running the absorption reaction for 8 h, the CO_2 loading was determined by titration with 1 M HCl on small aliquots of the solution (2 mL) taken at 1-hour intervals: the system was considered to be at equilibrium when three consecutive titrations gave the same CO_2 loading value.

2.3. CO_2 absorption rate measurement

CO_2 capture experiments were carried out using the instrumentation depicted in Fig. 1b and following a previously described procedure [35,36]. A gas mixture, simulating a typical flue gas (CO_2 + N_2, PCO_2 = 15 kPa, total flow rate = 500 mL/min), was blown into a three-necked flask filled with 200 mL of the absorbent amine solution, immersed into a water bath to maintain the temperature at 313 K, and equipped with a magnetic stirrer (maintained at 100 rpm for the duration of absorption). To limit the loss of solution, a reflux condenser (kept at 278 K) was placed at the top of the flask. The gas leaving the condenser was passed through a H_2SO_4 solution and a P_2O_5 drying tube to avoid entrainment of amine or water to the infrared CO_2 sensor (CozIR-100, GSS Ltd., accuracy $\pm0.01\%$), where the amount of CO_2 in the gas was measured every 10 s, and the CO_2 loading was then calculated [37]. The duration of each experiment was 600 min. The experiment was repeated twice for each sorbent, and the maximum deviation from the mean value of the measured absorbed CO_2 was less than 1%.

2.4. CO_2 desorption experiments

The desorption performance of the sorbent was evaluated according to a well-established procedure [35,36] using the experimental apparatus shown in Fig. 1c. 200 mL of CO_2-loaded amine solution was added to a three-necked flask and heated to 373 K with an oil bath for desorption. The solution was stirred at 900 rpm with a magnetic stirrer during the entire desorption process. A known flow of nitrogen (500 mL/
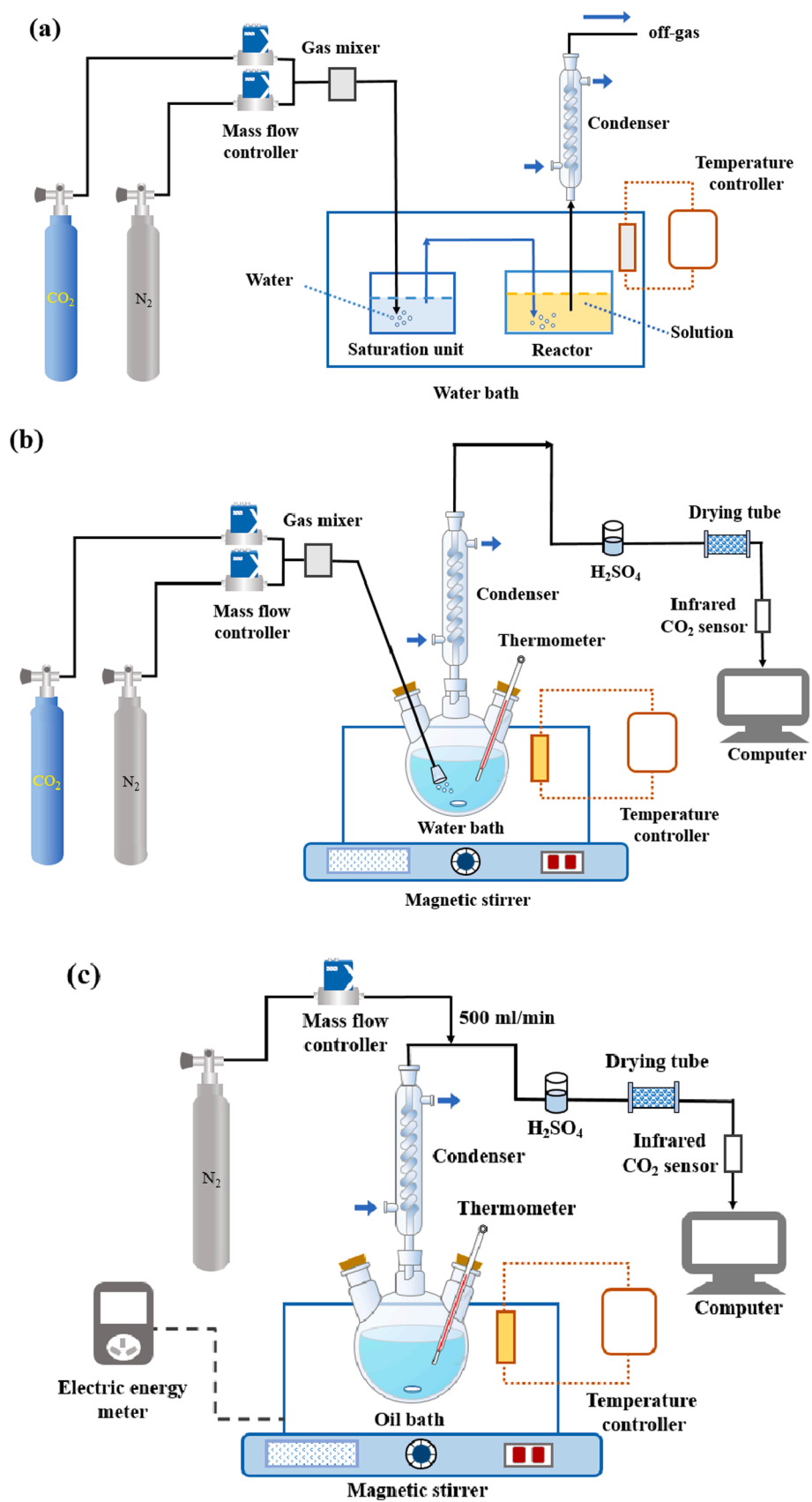
Fig. 1. Simplified representation of the equipment used for (a) CO_2 solubility at equilibrium, (b) CO_2 absorption and (c) CO_2 desorption measurement.

min) was used as a carrier gas to facilitate the release of CO_2 from the sorbent. The resulting gas mixture was cleaned by flowing through a H_2SO_4 solution and a P_2O_5 drying tube. The amount of CO_2 (and subsequently the CO_2 loading) was finally determined with the CozIR-100 infrared CO_2 sensor at 10-second intervals. Following a strategy already adopted by other researchers, the energy cost of the desorption process was measured using a single-phase energy meter (Zhejiang Tepsung Electric Co.; accuracy ±0.001 kW·h) connected directly to the heating system [38–40]: by recording the total electric consumption during the desorption process, the heat of absorption can be calculated, as described in Section 2.6.4. Each desorption experiment was repeated twice; the maximum deviation from the mean value of the measured released CO_2 was less than 1.5%.

2.5 ^{13}C NMR speciation analysis

For each MEA-2DMA2M1P-AMP mixture, a further absorption experiment was performed at T = 295 K to qualitatively and quantitatively analyze the species in solution during the CO_2 capture process. Pure CO_2 was bubbled into 55 mL of solution at a flow rate of 0.344 mol/h. The duration of each experiment was 120 min, during which small aliquots (0.5 mL) were taken and analyzed with a Bruker Avance III 400 spectrometer, operating at 100.613 MHz, following a well-established procedure [41]. Tetramethylsilane and acetonitrile were used as external standard (at 0.00 ppm) and internal reference (CH_3, $\delta = 1.47$), respectively, while the deuterium lock signal was obtained with a sealed glass capillary containing D_2O (Sigma–Aldrich) introduced into the NMR tube. A pulse sequence with proton decoupling and NOE suppression was used to acquire the ^{13}C{^{1}H} with the following acquisition parameters: acquisition time = 1.3632 s, delay time = 2–30 s, pulse angle = 90.0°, scans = 280–320, data points = 65 K. Integration of signals of the —CH_2— structure of MEA allows evaluation of the relative amounts of fast equilibrating (MEA)/(MEAH$^+$) and MEA carbamate (estimated error <2%), while an accurate integration of the signals in the 165–160 ppm range allows good estimation of the relative amount of the species with a carbonyl atom, namely MEA carbamate, the fast-equilibrating HCO_3^-/CO_3^{2-} and alkyl carbonates, if present (estimated error <5%). For each amine in solution, the carbon atoms of the free amine and the protonated amine give a single signal (due to the fast proton exchange between them). However, their relative amounts can be estimated from the position (chemical shift) of their signals after constructing appropriate calibration straight lines [36]: for each single amine, we performed ^{13}C NMR analysis of D_2O standard solutions of pure amine, protonated amine and their 1:1 equimolar mixture (using HCl). Plotting of the chemical shifts of the ^{13}C resonance of the —CH_2OH group provides a calibration straight line. The calibration lines were used to correlate the chemical shift with the relative amount of free and protonated amine. The limiting values found for free amine were: [δ(CH_2OH): MEA = 63.16 ppm; 2DMA2M1P = 67.14 ppm; AMP = 71.35 ppm], while for the protonated amine were: [δ(CH_2OH): MEAH$^+$ = 57.82 ppm; 2DMA2M1PH$^+$ = 64.84 ppm; AMPH$^+$ = 66.60 ppm]. Similarly, the chemical shift of the fast equilibrating HCO_3^-/CO_3^{2-} signal can be used to determine the relative amount of bicarbonate and carbonate ions in solution [42].

2.6. Calculations

2.6.1. CO_2 absorption rate

The CO_2 absorption rate is the amount of CO_2 absorbed per unit of time and volume, defined as in Eq. (1).

$$R_{abs} = \frac{n_{CO2}}{t \times V_{abs}} \tag{1}$$

where R_{abs} is the absorption rate, n_{CO2} is the amount of CO_2 absorbed, t is the absorption time and V_{abs} refers the volume of aqueous amine solution.

2.6.2. Cyclic capacity

The cyclic capacity (CC, mol), obtained from Eq. (2), is the effective quantity of CO_2 desorbed from the sorbent during the regeneration process.

$$CC = (\alpha_{rich} - \alpha_{lean}) \times C \times V \tag{2}$$

where α_{rich} and α_{lean} refer to the CO_2 loading of the loaded and desorbed sorbent, respectively, while C and V refer to the concentration and volume of the sorbent.

2.6.3. Average CO_2 desorption rate

The CO_2 desorption rate is defined as the amount of CO_2 desorbed per unit of time and volume, as given in Eq. (3).

$$R_{des} = \frac{CC}{t \times V_{des}} \tag{3}$$

where R_{des} is the absorption rate, CC is the cyclic capacity, t is the desorption time and V_{des} is the volume of the CO_2-rich amine solution.

2.6.4. Heat duty and relative heat duty

The energy needed to release one mole of CO_2 from the sorbent is called heat duty (H, kJ/molCO_2) and can be calculated as in Eq. (4) from the ratio of the electrical energy consumption (E_{total}, kJ) to the cyclic capacity (CC, mol).

$$H = \frac{E_{total}}{CC} \tag{4}$$

Due to the simplified instrumentation used in our bench-scale tests, the H calculated as in Eq. (4) are usually higher than those reported in other works. To assess the regeneration performance of a sorbent, it is therefore more appropriate to relate the H value found with that of the 5 M aqueous MEA reference (obtained under the same conditions), thus defining the relative heat duty (RH, %), calculated as in Eq. (5):
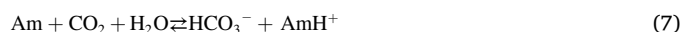
$$RH = \frac{H_i}{H_{MEA}} \cdot 100 \tag{5}$$

where H_i is the heat duty of the sorbent under consideration and H_{MEA} is the heat duty of MEA under the same operating conditions.
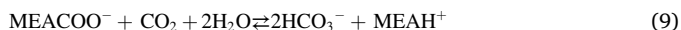
3. Results and discussion

In the present work, we investigated three new sorbents for CO_2 capture, prepared by mixing three amines in different molar ratios, as specified in Section 2.1. In particular, the reaction rate promoter MEA and the absorption capacity promoter AMP were blended with the tertiary amine 2DMA2M1P to form innovative trio-amine blends. Their absorption and desorption efficiencies were determined experimentally and compared with those of the benchmark aqueous MEA 5 M. Furthermore, to assess the potential benefits of switching from dual- to trio-amine systems, their performances were also compared with those of the aqueous blends 2.5 M MEA + 2.5 M 2DMA2M1P (2.5:2.5) and 2.5 AMP + 2.5 M 2DMA2M1P (2.5:2.5) under the same operating conditions [27].

3.1. CO_2 absorption process

The following are the main reactions involved in CO_2 capture by aqueous MEA-2DMA2M1P-AMP systems:

$$MEA + CO_2 + Am \rightleftharpoons MEACOO^- + AmH^+ \tag{6}$$

$$Am + CO_2 + H_2O \rightleftharpoons HCO_3^- + AmH^+ \tag{7}$$

$$HCO_3^- + Am \rightleftarrows CO_3^{2-} + AmH^+ \qquad (8)$$

$$MEACOO^- + CO_2 + 2H_2O \rightleftarrows 2HCO_3^- + MEAH^+ \qquad (9)$$

$$CO_3^{2-} + CO_2 + H_2O \rightleftarrows 2HCO_3^- \qquad (10)$$

$$AmOH + CO_2 + Am \rightleftarrows AmOCOO^- + AmH^+ \qquad (11)$$

Am represents a generic amine (i.e., MEA, AMP or 2DMA2M1P), while AmH^+ refers to the protonated amine (i.e., $MEAH^+$, $2DMA2M1PH^+$ or $AMPH^+$). In these systems, MEA is the only amine capable of forming amine carbamate ($MEACOO^-$): sterically hindered AMP forms an unstable carbamate that hydrolyzes instantly to bicarbonate, whereas tertiary 2DMA2M1P cannot form carbamate because it has no hydrogen atoms bonded to the nitrogen atom [29,43]. For longer absorptions, alkyl carbonates ($AmOCOO^-$) can also be formed from the reaction between the —OH functionality of alkanolamines (highlighted in reaction (11) as AmOH) and CO_2, with the simultaneous protonation of another amine acting as a base [44]. All reported reactions are reversible.

3.1.1. CO2 equilibrium solubility

The CO_2 equilibrium solubility, i.e. the maximum quantity of CO_2 that can be absorbed at a given temperature and PCO_2, is a crucial factor in assessing the suitability of a sorbent for capture processes: a sorbent with a high CO_2 equilibrium solubility is usually very efficient at separating CO_2 from a gas mixture and requires low operating cost, as less CO_2 absorption–desorption cycles are necessary [23,35]. The CO_2 equilibrium solubility was measured for each trio-amine blend at a constant T = 313 K, using gas mixtures with different PCO_2, namely at 5, 7.5, 15, 30 and 60 kPa, as described in Section 2.2; the values obtained are shown in Fig. 2, together with those for MEA 5 M and the binary blends MEA-2DMA2M1P and AMP-2DMA2M1P.

Since the amount of CO_2 molecules in the gas phase at equilibrium is directly related to the CO_2 concentration in the liquid phase [35], CO_2 solubility increased with increasing PCO_2 for all sorbents, (Fig. 2). The dual-blend AMP-2DMA2M1P exhibits higher CO_2 solubilities than all other sorbents at almost all CO_2 partial pressures analyzed, especially for $PCO_2 > 15$ kPa. Besides AMP-2DMA2M1P, the CO_2 equilibrium solubility of the other sorbents follows the order MEA-2DMA2M1P-AMP (1:2:2) > MEA-2DMA2M1P-AMP (2:2:1) $\geq$ MEA-2DMA2M1P (2.5:2.5) > MEA-2DMA2M1P-AMP (2:1:2) > MEA. Trio-amine blends have a CO_2 absorption capacity comparable to that of dual-amine

blends, and in any case higher than MEA 5 M. This trend can be explained by considering that the sterically hindered amine AMP and the tertiary amine 2DMA2M1P react with CO_2 to form mainly bicarbonate, whereas the primary amine MEA forms mainly carbamate: the bicarbonate formation (total amine/CO_2 stoichiometry = 1/1, reaction (7) greatly increases CO_2 solubilization in the sorbent compared to carbamate formation (total amine/CO_2 stoichiometry = 2/1, reaction (6) [33,45].

3.1.2. Evaluation of CO2 absorption rate

A high CO_2 absorption rate is very favorable for improving the efficiency of CO_2 separation from a gas mixture and for reducing the size of the absorber while lowering the capital cost [46]. In order to assess the CO_2 absorption rate of the formulated blends, the CO_2 loading was measured continuously in a 600-minute capture experiment carried out at T = 313 K and PCO_2 = 15 kPa, as explained in Section 2.3. Fig. 3a shows the change in CO_2 loading during the absorption for the three MEA-2DMA2M1P-AMP blends, along with those for 5 M MEA and for the two dual-amine blends. At the beginning of the experiment, the CO_2 loading increases rapidly for almost all solutions, especially for MEA and the two trio-amine blends with a higher MEA concentration, i.e. MEA-2DMA2M1P-AMP (2:2:1) and MEA-2DMA2M1P-AMP (2:1:2), whereas the CO_2 loading increases rather slowly for the dual-amine blend AMP-2DMA2M1P. Between 100 and 200 min, when the sorbent is not yet saturated, the amount of absorbed CO_2 decreases in the order 5 M MEA > MEA-2DMA2M1P-AMP (2:2:1) > MEA-2DMA2M1P-AMP (2:1:2) > MEA-2DMA2M1P-AMP (1:2:2) $\approx$ MEA-2DMA2M1P (2.5:2.5) $\gg$ AMP-2DMA2M1P (2.5:2.5). This trend can be ascribed to the slower reaction kinetics for the formation of bicarbonate and carbonate (reactions (7) and (8)) than for carbamate (reaction (6)); consequently, CO_2 is absorbed more slowly in solutions where the primary amine MEA, known as a reaction rate promoter, is absent or at a lower concentration [47–49]. After about 400 min of absorption, under the experimental conditions used, almost all the sorbents reached the maximum loading: at this point, it appears that the trio-amine blends may have a greater absorption capacity compared to the dual-amine blends, indicating that a smaller absorber can be used with the trio-amine blend to achieve the same absorption efficiency as MEA and the dual-amine blends.

Fig. 3b, which plots the CO_2 absorption rate (calculated using Eq. (1)) as a function of increasing CO_2 loading, further illustrates the different CO_2 uptake behavior of the sorbents. Aqueous MEA, MEA-2DMA2M1P-AMP (2:2:1) and MEA-2DMA2M1P-AMP (2:1:2) maintain high absorption rate values throughout the initial phase of the capture process, with aqueous MEA in particular only starting to decrease significantly at loadings close to 0.4, i.e. close to the final CO_2 equilibrium loading value. MEA has a primary amine group that can react directly with CO_2; a larger amount of MEA in the mixture is favorable to accelerate the rate of absorption. Among the newly formulated trio-amine blends, MEA-2DMA2M1P-AMP (1:2:2) shows the lowest absorption rate value and its trend as a function of loading is quite similar to that of MEA-2DMA2M1P (2.5:2.5), while AMP-2DMA2M1P (2.5:2.5) shows a significantly lower absorption rate than the other sorbents since the beginning of the capture process. The higher absorption rate of trio-amine blends compared to dual-amine systems can be explained by considering the presence of more basic components in the mixture, which can promote the carbamate-zwitterion deprotonation process of MEA and receive the proton from $MEAH^+$. Since AMP has a lower reaction rate with CO_2 than MEA (due to the steric hindrance on amine functionality), the AMP-2DMA2M1P blend shows the lowest absorption rate among the amine sorbents investigated.

3.1.3. 13C NMR speciation study during CO2 capture

The mechanism of the reaction between trio-amine mixtures and CO_2 was studied in detail through ^{13}C NMR spectroscopy, which allows qualitative and quantitative analysis of the species present in solution during the absorption process, as described in Section 2.5. Fig. 4 shows
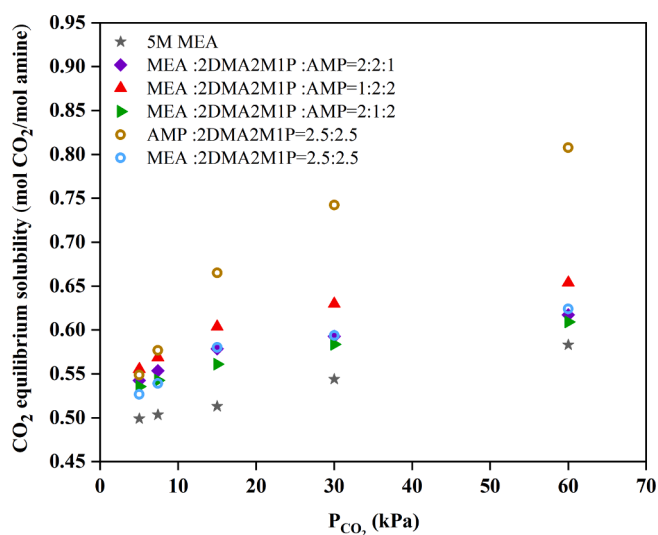

Fig. 2. Equilibrium CO_2 solubility of tested sorbents at T = 313 K, as a function of CO_2 partial pressure (in the range 5–60 kPa).
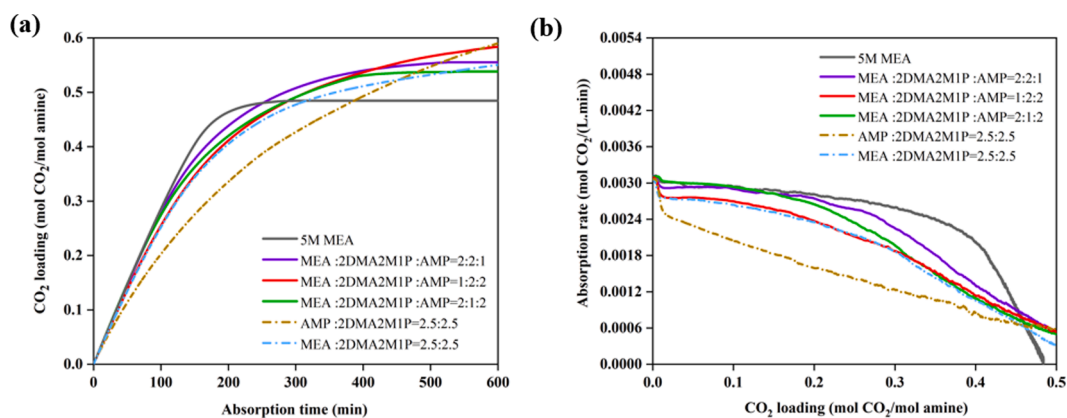
Fig. 3. CO_2 capture performance reported as (a) loading over absorption time and (b) absorption rate over CO_2 loading.

the ^{13}C NMR spectra at increasing loading values (α) for each of the three trio-amine blends: from these, it is possible to follow the evolution of the species in solution as a function of the amount of CO_2 absorbed during the perpetuation of the capture process. Reactions (6) and (11) determine the possible species present in each solution. By observing the carbonyl zone of the spectra shown in Fig. 4a–c (range 160–165 ppm), it is clear that the first signal to appear after the onset of the CO_2 capture reaction is always that due to MEACOO$^-$, confirming the higher kinetics of carbamate formation compared to all other possible products. Then, as CO_2 uptake continues, the signal associated with bicarbonate/carbonate ions (only one peak, due to the fast proton scrambling between the two ions) appears and finally, at high loading values, low intensity signals attributable to alkyl carbonates (which can be formed by any of the alkanolamines used in the blends) also appear. It is worth noting that when the concentration of MEA in the blend is 2 M, MEACOO$^-$ is the most abundant formation product (most intense signal) from the beginning to the end of the capture process. The peaks assigned to the fast exchanging free/protonated amine species, i.e. MEA/MEAH$^+$, 2DMA2M1P/2DMA2M1PH$^+$ and AMP/AMPH$^+$, move towards higher amounts of the protonated species with increasing CO_2 loading. As shown in Fig. 4, the bicarbonate/carbonate (b/c) peak also moves significantly as the capture process progresses and, specifically, shifts towards a lower ppm value, reflecting a predominance of the HCO$_3^-$ ion.

To better understand the speciation variation during the CO_2 capture process, Fig. 5a–c show the trend of the amount of species in solution with increasing CO_2 loading for each trio-amine blend.

At the beginning of the absorption (low CO_2 loading), a similar behavior can be observed in each blend: MEA carbamate increases rapidly and at the same time the protonated species of all amines increase (MEAH$^+$, 2DMA2M1PH$^+$ and AMPH$^+$). Free MEA is the amine that decreases most rapidly, as it is directly involved in the formation of MEACOO$^-$, but it is worth noting that 2DMA2M1P and AMP also participate in this reaction, and indeed their concentrations also decrease, as in reaction (6). In particular, 2DMA2M1P is consumed faster than AMP, due to its higher alkalinity. The formation of bicarbonate and then carbonate (reactions (7) and (8), respectively) begins to be significant at a CO_2 loading above 0.3 when the MEA has an initial concentration of 2 M, and as early as 0.2 when it has an initial concentration of 1 M (Fig. 5b). In fact, in the MEA-2DMA2M1P-AMP (1:2:2) blend, the lower availability of MEA directs the CO_2 capture towards a greater formation of the CO$_3^{2-}$ ion and, most importantly, the HCO$_3^-$ ion, which increases throughout the process and is the most abundant product at the end of the experiment. Conversely, in the other two blends (Fig. 5a and 5c), the most abundant product is MEA carbamate, which increases to a maximum (at CO_2 loading ≈ 0.5) and then begins to decrease slowly, as in reaction (9), with the further production of bicarbonate and the simultaneous increase in the amount of MEAH$^+$ in solution. For all trio-amine blends, the formation of alkyl carbonate

species can also be observed at high loading values (reaction (11)).

The products formed during the CO_2 absorption of have different effects on the subsequent sorbent regeneration; in particular, the relative prevalence of carbamate or bicarbonate has a negative or positive effect on the energy consumption in sorbent regeneration process, respectively [47]. The trends of carbamate and bicarbonate formation obtained in this speciation study for trio-amine blends are shown in Fig. 6 and compared with those previously found for MEA 5 M and dual-amine blends. Obviously, the AMP-2DMA2M1P (2.5:2.5) blend produces much less carbamate than any of the other sorbents studied; this is mainly due to the steric hindrance on the amine functionality of AMP, which makes the AMP carbamate easily decompose to bicarbonate: consequently, the concentration of carbamate is always very low (Fig. 6a), while that of bicarbonate increases rapidly from the start of the experiment (Fig. 6b). In contrast, in all the other sorbents, CO_2 capture occurs with a rapid increase in carbamate as long as the amine is in strong excess (reaction (6)), stoichiometric ratio amine/CO_2 = 2/1: however, when the free amine in solution decreases, CO_2 is captured through the formation of bicarbonate both by direct reaction with water and amine, and by reaction with carbamate, which then decreases (reactions (7) and (9)), respectively, stoichiometric ratio amine/CO_2 = 1/1. In addition, all MEA-2DMA2M1P-AMP trio-blends form less carbamate and more bicarbonate than MEA-2DMA2M1P (2.5:2.5) and 5 M MEA, explainable by the lower initial concentration of MEA. For the same reason, MEA-2DMA2M1P-AMP (1:2:2) produces more HCO$_3^-$ and less MEACOO$^-$ than other two trio-amine blends at the same CO_2 loading.

3.2. CO_2 desorption process

When designing new sorbents for large-scale CO_2 capture, it's vital to determine and optimize the CO_2 desorption performance, as this largely determines the energy cost and hence the feasibility of the process itself. Here, the desorption performances at T = 373 K of the proposed trio-amine blends were measured in terms of cyclic capacity, CO_2 desorption rate and heat duty, following the method reported in Section 2.4. The results have been compared with those obtained for the dual-amine blends and MEA 5 M under the same operating conditions [27]. All the measured desorption performance indicators are summarized in Table 1.

3.2.1. Evaluation of CO_2 desorption rate and cyclic capacity

The quantity of desorbed CO_2 and the decrease in CO_2 loading as a function of desorption time are shown in Fig. 7. After the initial heating period (approx. 10 min), all the sorbents began to release CO_2 until the maximum amount of desorbed CO_2 was reached at about 40–50 min, after which the infrared CO_2 analyzer detected no more CO_2. Under the operating conditions used in our experiments, AMP-2DMA2M1P (2.5:2.5) had the highest value of cyclic capacity, calculated by
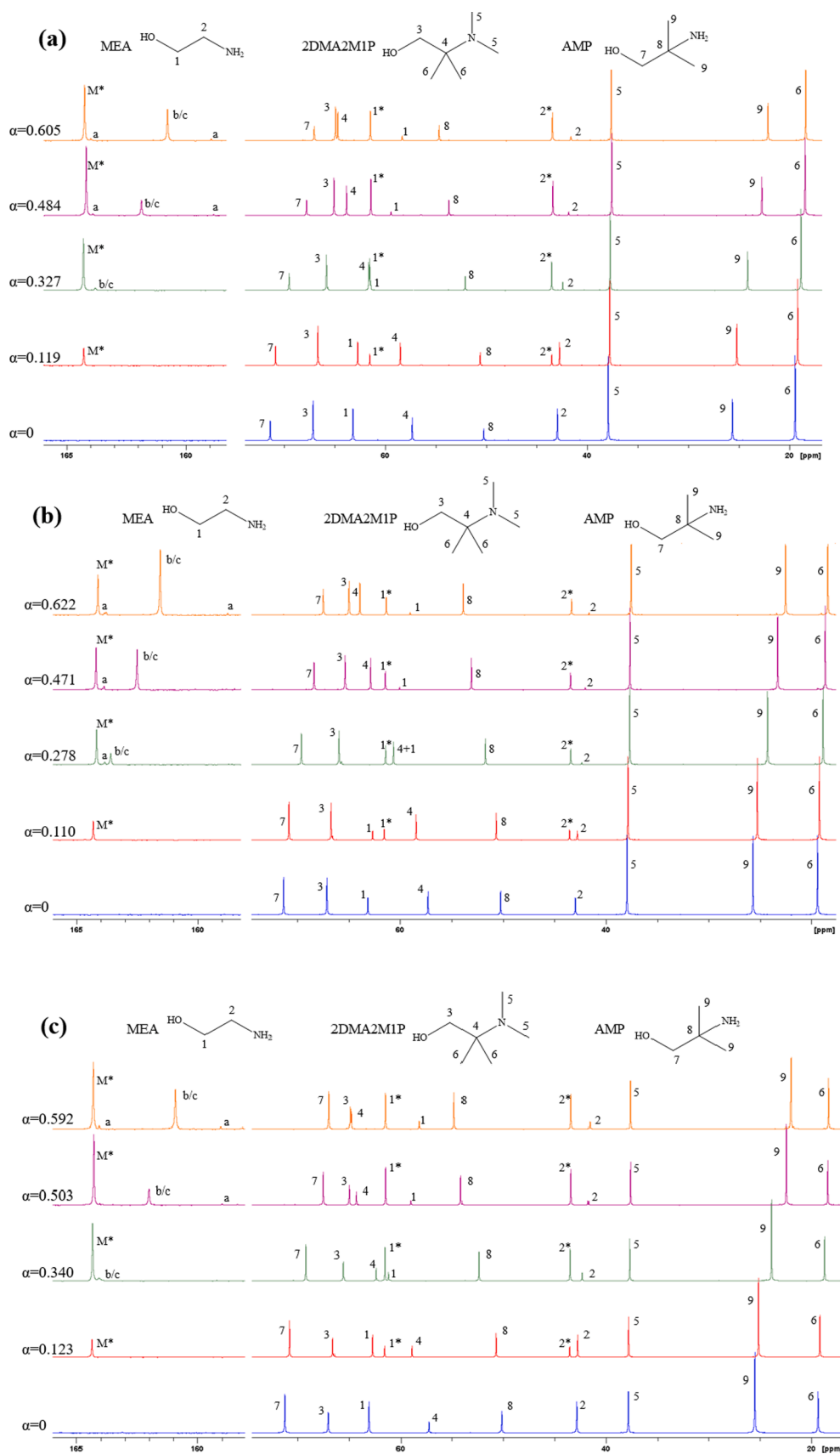
Fig. 4. ^{13}C NMR spectra of (a) MEA-2DMA2M1P-AMP (2:2:1), (b) MEA-2DMA2M1P-AMP (1:2:2) and (c) MEA-2DMA2M1P-AMP (2:1:2) at increasing CO_2 loadings (α). Numbers indicate the carbon atoms of the amine backbones (single signal for both free and protonated amine), while asterisks refer to MEA carbamate. M* is the carbonyl atom of MEA, *b/c* refers to bicarbonate/carbonate, and *a* refers to alkyl carbonates. Signal intensity at 160–165 ppm is not scaled.
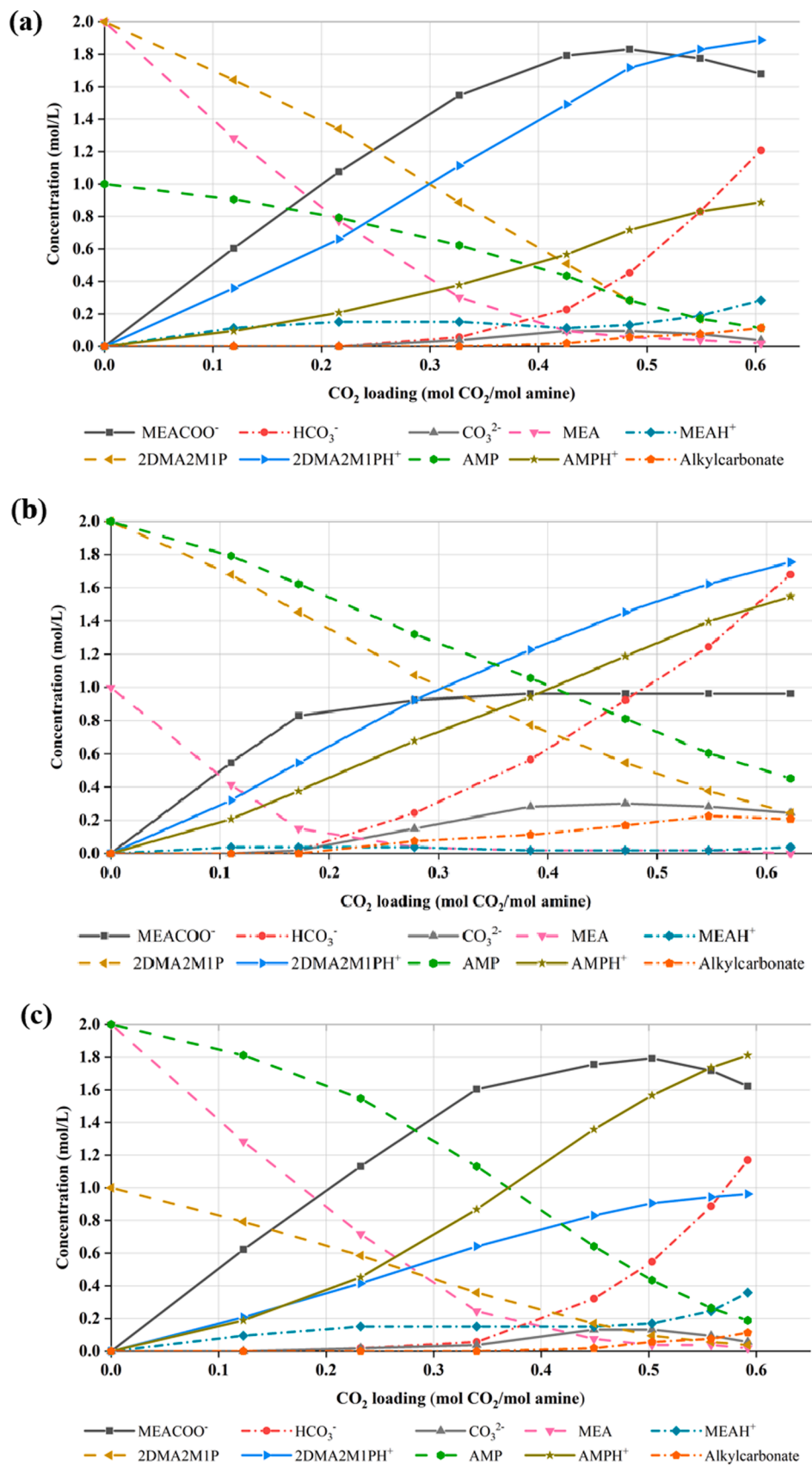
Fig. 5. Speciation as a function of increasing loading for (a) MEA-2DMA2M1P-AMP (2:2:1), (b) MEA-2DMA2M1P-AMP (1:2:2) and (c) MEA-2DMA2M1P-AMP (2:1:2) systems.
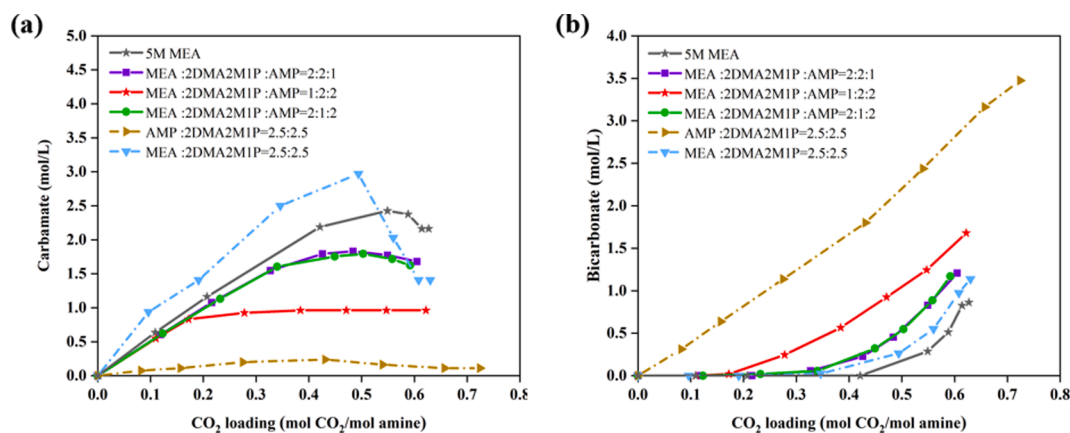
Fig. 6. Amount of (a) carbamate and (b) bicarbonate in each sorbent tested, as a function of CO_2 loading.

Table 1

Measured CO_2 absorption and desorption rates, cyclic capacity (*CC*), heat duty and relative heat duty (*RH*) for aqueous MEA, dual-amine and trio-amine systems.

Amine system	Initial abs. rate (mol/ (L·min))	Average des. rate (mol/ (L·min))	CC (mol)	Heat duty (kJ/mol CO_2)	RH [a] (%)
MEA 5 M	29.91×10^{-4}	31.07×10^{-4}	0.119	1857.55	100
MEA-2DMA2M1P (2.5:2.5)	27.61×10^{-4}	45.55×10^{-4}	0.213	1091.64	58.77
AMP-2DMA2M1P (2.5:2.5)	24.93×10^{-4}	92.52×10^{-4}	0.412	676.35	36.41
MEA-2DMA2M1P-AMP (2:2:1)	29.44×10^{-4}	80.60×10^{-4}	0.279	829.28	44.64
MEA-2DMA2M1P-AMP (1:2:2)	27.94×10^{-4}	104.56×10^{-4}	0.351	680.51	36.64
MEA-2DMA2M1P-AMP (2:1:2)	30.20×10^{-4}	78.35×10^{-4}	0.263	817.91	44.03

[a] Relative to aqueous 5 M MEA.

Equation (2), while MEA-2DMA2M1P-AMP (1:2:2) had the highest CO_2 desorption rate, calculated by Equation (3) (Table 1). All blends released more CO_2 and with higher CO_2 desorption rate than MEA 5 M (Fig. 7a). All the formulated MEA-2DMA2M1P-AMP blends show better desorption performance compared to both MEA 5 M and MEA-2DMA2M1P

(2.5:2.5). In particular, the cyclic capacities of the trio-amine blends were found to be about 2–3 times higher than that of MEA (Table 1). Among them, MEA-2DMA2M1P-AMP (1:2:2) exhibited a higher cyclic capacity (0.351 mol) and CO_2 desorption rate (104.56×10^{-4} mol/ (L·min)) due to its higher amount of HCO_3^-, with respect to MEACOO$^-$, in the loaded solution: in fact, bicarbonate decomposes more efficiently than MEACOO$^-$ at the same temperature [47,50], and its presence in solution promotes the carbamate breakdown [51,52]. Because of the high stability of MEA carbamate and the relatively low amount of HCO_3^-, little CO_2 is desorbed from 5 M MEA (Fig. 7a), and after 50 min the CO_2 loading decreased by only 20% (Fig. 7b). Conversely, solutions of AMP-2DMA2M1P (2.5:2.5) and MEA-2DMA2M1P-AMP (1:2:2) regenerated significantly (60–70%) in a relatively short time at 373 K (Fig. 7b), a very attractive condition when considering their potential use in continuous CO_2 capture systems.

3.2.2. Energy cost of the desorption process

The energy cost for sorbent regeneration has a critical impact on the feasibility of the overall CO_2 capture process [53]. Here, the energy consumption for the regeneration of each sorbent tested was measured during the desorption experiments using a digital energy meter coupled to the heating bath. The recorded energy requirement and the calculated heat duty (Equation (4) are shown in Fig. 8 for all MEA-2DMA2M1P-AMP blends and, for comparison, also for the dual-amine blends and MEA 5 M.

In general, the energy cost (kJ) increases as the CO_2 desorbed increases. As shown in Fig. 8a, for the same energy input, all of the amine mixtures desorb more CO_2 than MEA 5 M. Specifically, as the energy input increases, the amount of CO_2 released decreases in the order MEA-2DMA2M1P-AMP (1:2:2) $\geq$ AMP-2DMA2M1P (2.5:2.5) > MEA-
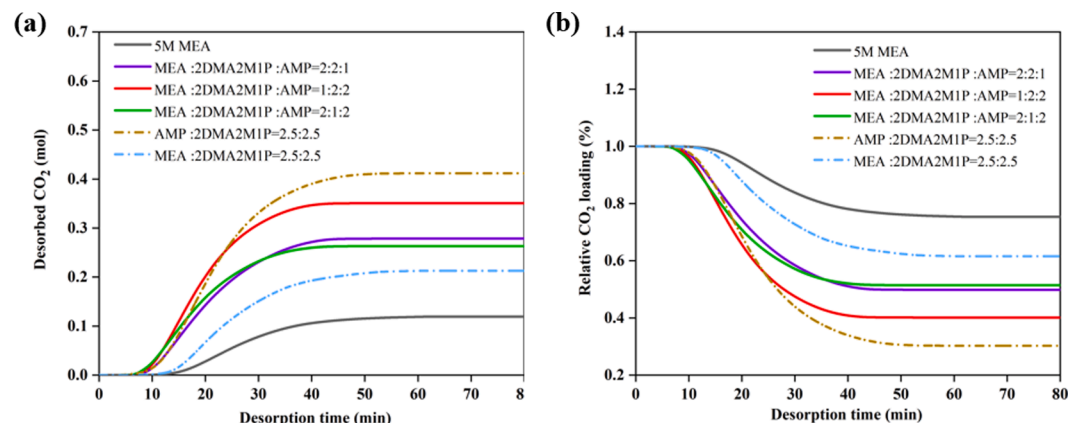

Fig. 7. Amount of CO_2 desorbed (a) and percentage change in CO_2 loading (b) for each sorbent at T = 373 K.

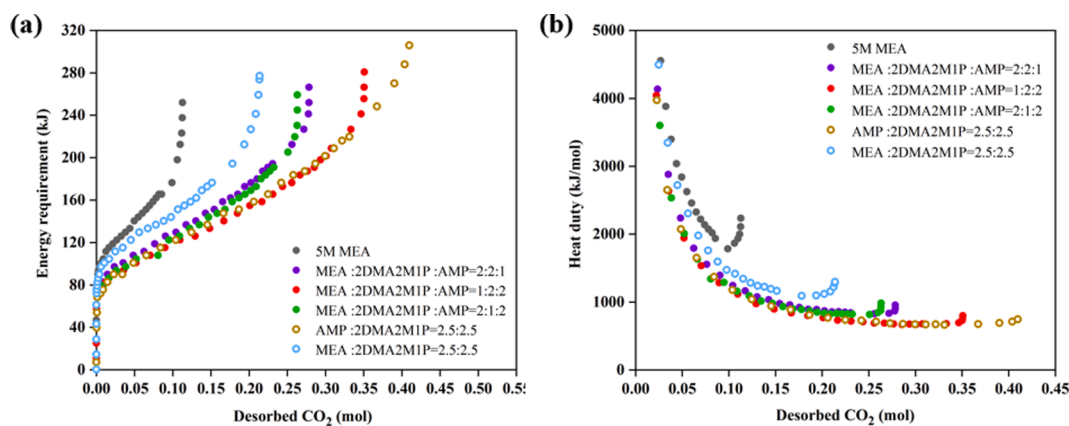**Fig. 8.** Energy consumption (a) and heat duty (b) for the regeneration process of each amine system at T = 373 K.

2DMA2M1P-AMP (2:1:2) ≥ MEA-2DMA2M1P-AMP (2:2:1) > MEA-2DMA2M1P (2.5:2.5) > 5 M MEA: CO_2 is more readily released (low energy consumption) from solutions containing more bicarbonate (low energy required to break the C − O bond) than from solutions containing more of the stable MEA carbamate (high energy required to break the C-N bond) [54–56].

Recently, a new parameter, the Energy Operation Window (EOW), has been proposed for the comparison of the energy requirements of different sorbents during the desorption process [35]. Considering the heat duty versus desorbed CO_2 plot (Fig. 8b), the EOW is defined as the width of the horizontal region for each data series and reflects the ability to desorb CO_2 from a loaded sorbent with a specific amount of energy. In practice, the longer the EOW, the greater the amount of CO_2 desorbed for the same heat duty. Fig. 8b shows that the EOW of MEA-2DMA2M1P-AMP (1:2:2) is like that of AMP-2DMA2M1P (2.5:2.5) and significantly larger compared to that of the other sorbents, which means that the energy required for to regenerate MEA-2DMA2M1P-AMP (1:2:2) is lower than that of any of the other amine blends. It is worth noting that MEA-2DMA2M1P-AMP (2:1:2) and MEA-2DMA2M1P-AMP (2:2:1) have very similar desorption performances: although these are lower than MEA-2DMA2M1P-AMP (1:2:2), they are significantly better than the MEA 5 M and MEA-2DMA2M1P (2.5:2.5) blend.

Since the absolute heat duty values found for the different sorbents are often influenced by the simple bench-scale equipment used (as in

this case), the H values calculated according to Eq. (4) are difficult to compare with those obtained by other laboratories under different conditions. For this reason, it is more useful to normalize the H value found with that obtained for the benchmark 5 M aqueous MEA in the same experimental conditions, thus defining the relative heat duty RH (Eq. (5). The relative heat duties found for the trio-amine blends formulated in this work were then compared with those of other blends reported in the literature [27,29,30,40,57], again using MEA 5 M as a reference (Fig. 9). From this comparison it can be seen that all of the newly formulated trio-amine blends have RH less than half of the benchmark MEA 5 M, and generally have more advantageous regeneration performance than all other reported dual- or trio-amine blends (excluding the AMP-2DMA2M1P mixture). In particular, the MEA-2DMA2M1P-AMP (1:2:2) blend has the lowest total energy requirement and could therefore be considered as a potential replacement for MEA in CCS processes, following experimentation on larger scale systems.

4. Conclusions

In this work, the potential enhancement of CO_2 capture of aqueous amine sorbents by switching from dual-amine to trio-amine blends was evaluated by analyzing the absorption and regeneration performance of ternary aqueous amine systems, formulated by blending the tertiary
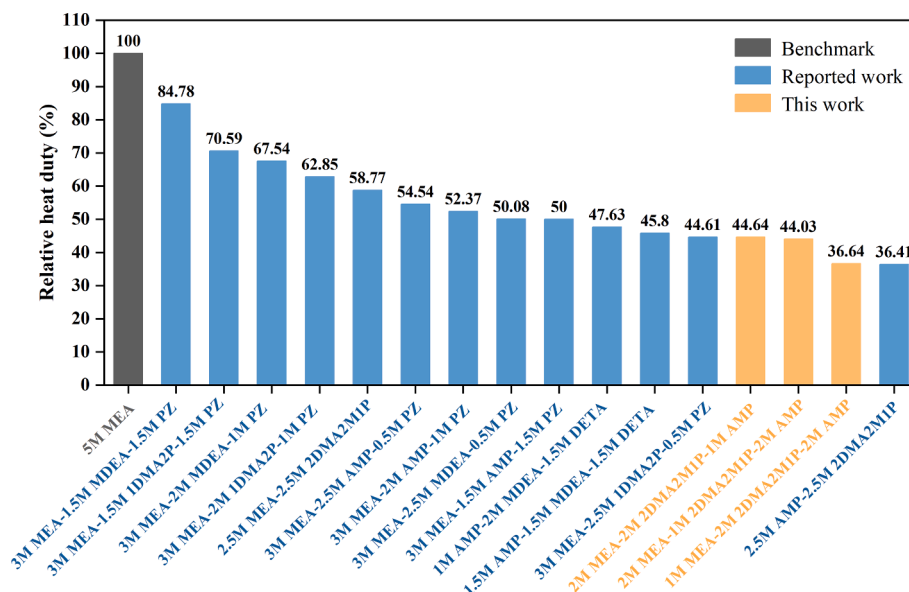

Fig. 9. Relative heat duty (%) of several aqueous amine blends using MEA 5 M as a reference.

amine 2DMA2M1P, the reaction rate promoter MEA and the adsorption capacity promoter AMP. Three solutions with different amine molar ratios, i.e. MEA-2DMA2M1P-AMP (2:2:1), MEA-2DMA2M1P-AMP (2:1:2) and MEA-2DMA2M1P-AMP (1:2:2) were prepared and their performance in CO_2 absorption (at 313 K) and desorption (at 373 K) were determined experimentally. Finally, the results were compared with those obtained under the same operating conditions with aqueous MEA 5 M (reference sorbent for CCS processes) and with two 2DMA2M1P-based binary blends, i.e. MEA-2DMA2M1P (2.5:2.5) and AMP-2DMA2M1P (2.5:2.5). Regarding the CO_2 absorption at 313 K, the trio-amine blends MEA-2DMA2M1P-AMP (2:2:1) and MEA-2DMA2M1P-AMP (2:1:2) showed a CO_2 absorption rate similar to MEA 5 M and higher than the other sorbents tested. On the other hand, the MEA-2DMA2M1P-AMP (1:2:2) blend gave higher CO_2 equilibrium solubility values at all the CO_2 partial pressures tested, only lower than those of the dual-blend AMP-2DMA2M1P. Careful speciation analysis performed by ^{13}C NMR spectroscopy revealed that when the concentration of MEA in the trio-amine blends was 1 M, the most abundant product formed at the end of absorption was bicarbonate, which explains the higher CO_2 solubility values and the lower reaction rate measured. All the trio-amine blends developed have considerably better regenerative properties than MEA-2DMA2M1P (2.5:2.5) and MEA 5 M, due to the easier decomposition of bicarbonate than MEA carbamate. In particular, their cyclic capacities were about 2–3 times higher than MEA 5 M, while their heat duties were 55.36–63.37 % lower.

The results of this work show that all formulated trio-amine blends have superior CO_2 equilibrium solubility and desorption performance compared with MEA 5 M. Comparison with similar dual-amine systems highlights the importance of the addition of a suitable third amine, in order to obtain sorbents that excel during both absorption and desorption. Among the formulated systems, MEA-2DMA2M1P-AMP (1:2:2) has the fastest desorption kinetics, the highest cyclic capacity and the lowest energy demand, and can be considered as a potential replacement of MEA for CCS processes after careful cost-benefit analysis on larger scale systems.

CRediT authorship contribution statement

Rui Zhang: Conceptualization, Writing – original draft, Supervision, Funding acquisition. **Yufan Li:** Writing – original draft, Investigation. **Xinwei He:** Writing – original draft, Investigation. **Yingjie Niu:** Investigation. **Chao'en Li:** Supervision, Funding acquisition. **Mohammad Waleed Amer:** Supervision, Funding acquisition. **Francesco Barzagli:** Methodology, Investigation, Writing – original draft, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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