

# Enzyme-assisted CO<sub>2</sub> absorption in aqueous amino acid ionic liquid amine blends

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## ABSTRACT

The influence of carbonic anhydrase (CA) on the CO<sub>2</sub> absorption rate and CO<sub>2</sub> load in aqueous blends of the amino acid ionic liquid pentaethylenehexamine proline (PEHAp) and methyl diethanolamine (MDEA) was investigated and compared to aqueous monoethanolamine (MEA) solutions. The aim was to identify blends with good enzyme compatibility, several fold higher absorption rates than MDEA and superior desorption potential compared to MEA. The blend of 5% PEHAp and 20% MDEA gave a solvent with approximately 5-fold higher initial absorption rate than MDEA and a 2-fold higher regeneration compared to MEA. Experiments in a small pilot absorption rig resulted in a mass transfer coefficient (KGa) of 0.48, 4.6 and 15 mol (m<sup>3</sup> s mol fraction)<sup>-1</sup> for 25% MDEA, 5% PEHAp 20% MDEA and 25% MEA, respectively. CA could maintain approximately 70% of its initial activity after 2 h incubation in PEHAp MDEA blends. Integration of CA with amine-based absorption resulted in a 31.7% increase in mass of absorbed CO<sub>2</sub> compared to the respective non-enzymatic reaction at the optimal solvent: CA ratio and CA load. Combining novel blends and CA can offer a good compromise between capital and operating costs for conventional amine scrubbers, which could outperform MEA-based systems.

**KEYWORDS** amines, amino acid, carbonic anhydrase, CO<sub>2</sub> capture, ionic liquid, proline, pentaethylenehexamine, methyl diethanolamine

## INTRODUCTION

Chemical absorption by aqueous amine systems is one of the most mature post combustion techniques applicable to large CO<sub>2</sub> point emissions, such as the process industry.<sup>1</sup> Apart from scrubbing flue gases, CO<sub>2</sub> absorption is also important for the upgrading of biogas or natural gas.<sup>2</sup> In a typical CO<sub>2</sub> capture process, the CO<sub>2</sub>-rich gas enters the absorption column from the bottom and contacts the lean CO<sub>2</sub> absorbing solvent, which enters from the top, in a counter-current flow. Subsequently, the CO<sub>2</sub>-rich solvent is pumped through a stripping column, where the solvent is thermally regenerated, and then pumped back to the absorber for another cycle of absorption. During the regeneration process, a pure CO<sub>2</sub> stream can be taken out at the top of the column and can be compressed for transportation and storage.<sup>3</sup> Conventional carbon capture techniques are considered expensive and energy intensive and, like in all processes, it is desired to minimize capital and operating costs. Naturally, the solvent has a major impact on the process. Generally, fast absorption kinetics translates to small equipment size and a relatively low capital cost. On the other hand, faster reaction kinetics are connected to higher heat of reaction and so the regeneration temperature in the desorber must be high, leading to steam requirements that can make up to 90% of the total operational costs.<sup>4</sup> Other important factors for solvent development are the load capacity, CO<sub>2</sub> specificity, corrosion properties and solvent degradation rate due to the high temperatures and the presence of SO<sub>2</sub>, NO<sub>2</sub> and O<sub>2</sub> in several flue gases.<sup>5,6</sup> Ultimately, it remains a challenging task to optimize a CO<sub>2</sub> capture solvent for a specific application, where the end result is a compromise between the solvent's absorption and desorption properties.

Since the development of the conventional amine scrubber in the 1930s, numerous amine blends have been screened for the optimum compromise, where aqueous solutions of the primary amine

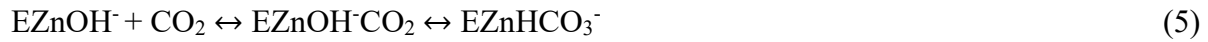
monoethanolamine (MEA) remains the industry standard.<sup>1</sup> However, the high absorption rates for MEA are linked to a high reactivity that, in turn, results in regeneration temperatures of 120-140°C and steam consumption equivalent to between 3.24-4.20 GJ/ton.<sup>7</sup> Primary and secondary amines form carbamates (equations 1-2) and have relative low loading capacity at around 0.5 mol CO<sub>2</sub> mol<sup>-1</sup> amine. In water solutions, the carbamates can also decompose into HCO<sub>3</sub><sup>-</sup> (equation 3) and, in such cases, the amine may bind another CO<sub>2</sub> molecule.<sup>8</sup> Tertiary amines, such as methyldiethanolamine (MDEA), produce bicarbonate (equation 4) and have a loading capacity of 1 mol CO<sub>2</sub> mol<sup>-1</sup> amine. Although they require lower regeneration temperatures, they suffer from significantly lower absorption rates.<sup>9</sup> Polyamines such as diethylenediamine (DETA), triethylenetetramine (TETA) and pentaethylenehexamine (PEHA) are known to display high loading capacities and display absorption rates faster or comparable with MEA. However, as they require similar regeneration temperatures, they still make the process highly energy intensive, which in turn promotes corrosion, solvent degradation and heat loss. Good corrosion properties have been identified by certain amines, such as the designer amine with cyclic structure 4-amino-1-propyl-piperidine.<sup>10</sup>



Where R<sub>2</sub> is a hydrogen for primary amines and B base



Catalysts are an interesting avenue for CO<sub>2</sub> capture as they can improve the absorption rates without compromising the desorption properties.<sup>11</sup> Carbonic anhydrase (CA) is one of the fastest enzymes known catalyzing the hydration of CO<sub>2</sub> (equations 5-8), which is the rate-determining step of the reactive absorption of CO<sub>2</sub> for MDEA.



Where E is the enzyme CA and Zn is the metal ion at the active site of CA.

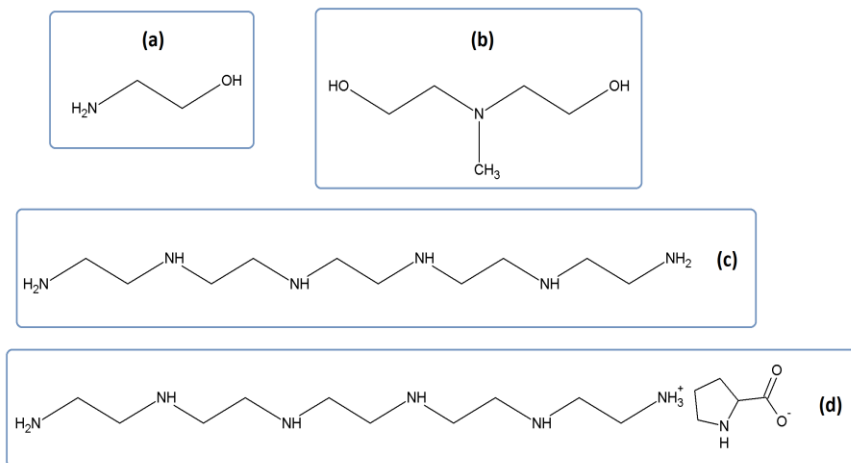
The addition of CA in the solvent could increase the absorption rates by exploiting the ability of CA to convert CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> very quickly, and thus keeping the concentration gradient between the gas and liquid phases; that is the driving force for CO<sub>2</sub> dissolution.<sup>12</sup> Bovine CA has been reported to enhance both the CO<sub>2</sub> absorption rate and loading capacity in low concentrations of alkanolamines (5-10%) including MEA, diethanolamine (DEA), aminomethyl propanol (AMP) and MDEA.<sup>13</sup> However, enzyme catalysts have not been assumed to tolerate exposure to the high temperatures and the alkaline environment of amine-based capture and desorption processes. Yet, an engineered CA from *Desulfovibrio vulgaris* (DvCA8.0) was shown to have exceptional properties for CO<sub>2</sub> absorption at high temperatures in MDEA.<sup>14,15</sup>

Comparatively, little work has been done on the integration of CA to amine systems other than MDEA, most likely due to the poor performance of CA in reactive highly alkaline amine

solutions, such as MEA. Ionic liquids, which are basically molten salts with tunable properties, have gained attention as CO<sub>2</sub> sorbents, as the regeneration energies can be significantly lower compared to alkanolamines. However, many ionic liquids are expensive, viscous and usually display considerably lower CO<sub>2</sub> absorption rates compared to alkanolamines. Blending amines and ionic liquids in aqueous solutions have shown promising results coupling advantages of both sorbents.<sup>16</sup> Introducing the amino functional group in ILs by the use of an amino acid generates so called amino acid ILs (AAILs) which, when blended with MDEA, have shown increased CO<sub>2</sub> absorption rates<sup>8</sup>. Switchable ILs (SILs) are a new class that have been shown as promising and high-capacity solvents for CO<sub>2</sub> absorption.<sup>17</sup> Besides their high CO<sub>2</sub> capturing efficiency, another advantage of SILs is their simple synthesis methods and their proven compatibility with enzymes.<sup>18</sup>

In the current study, we propose to use a mix between an AAIL (PEHA proline, PEHAp) and a tertiary amine (MDEA) in order to promote enzyme stability and reach higher absorption rates than MDEA, achieving at the same time advanced desorption properties compared to MEA. In this ternary blend, the tertiary amine would partly function as a proton acceptor from the zwitterion to allow the fast primary and secondary amines to react with CO<sub>2</sub>. In addition, it promotes better desorption properties for the solvent, since tertiary amines only form bicarbonate with CO<sub>2</sub>, which upon heating, decomposes back to CO<sub>2</sub> easier than carbamates. In order to promote high absorption rates and loading capacity, PEHA was selected as the cation component and proline as the anion of the AAIL. Proline was assumed to take a protective role for the enzyme with its hydrophobic character. Furthermore, it was reasoned that the desorption properties of proline would be superior to other amino acids, such as lysine. Proline carries only a secondary amine, which has shown moderate absorption rates compared to lysine that carries a

primary amine.<sup>19</sup> The amines MEA, MDEA and PEHA and the AAIL PEHAp are depicted in Figure 1.



**Figure 1.** Structure of the amines MEA (a) MDEA (b) PEHA (c) and the AAIL PEHAp (d) prepared by neutralizing PEHA with proline at a 1:1 molar ratio.

## EXPERIMENTAL

**Chemicals.** MEA (synthesis grade), PEHA (technical grade), MDEA (technical grade), L-proline,  $\text{KHCO}_3$ , phenolphthalein and other chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA).

**Preparation of the ionic liquid and blends.** The aqueous solution of the ionic liquid PEHAp was prepared by neutralizing PEHA with proline, at a 1:1 molar ratio to ensure protonation of the primary amine, followed by addition of appropriate amount of water and overnight stirring. Structural characterization was done by NMR spectroscopy performed in  $\text{D}_2\text{O}$  with a Bruker Avance 600 MHz instrument (Billerica, MA, USA) (SI Figure S1 and S2). The obtained data were further processed with the TopSpin 3.2 software. As one equivalent acid was used for the preparation, it is expected that the primary amine is protonated (Figure 1).

PEHAp MDEA blends were produced by adding MDEA in appropriate amount of PEHAp and diluting with water to reach desired concentration. For 1 kg of the blend 5% PEHAp 20% MDEA, 33.435 g of PEHA were dissolved in 250 g of distilled water and neutralized with 16.565 g of proline during stirring. Subsequently, 200 g of MDEA were mixed with 250 g of water and then were added to the aqueous ionic liquid solution. Finally, 250 g of distilled water was added to reach 1 kg of solution. The molecular weight (MW) of PEHAp was calculated by summing the molecular weights of respective components. In the each blend, the amount of amine was calculated by summing the total amount of amines. For 1 kg of 5% PEHAp (MW  $347.5 \text{ g mol}^{-1}$ ) 20% MDEA ( $119.16 \text{ g mol}^{-1}$ ), there were  $(50/347.5+200/119.16)=1.82$  moles amines.



**Measurement of viscosity and density.** The viscosity and density measurements were made on a Lovis 2000 ME Microviscometer (Anton Paar GmbH, Graz, Austria). Measurements were done in triplicates, where the standard deviation was less than 1%.

**Protein and enzyme assays.** The protein concentration was determined with the BCA Kit (Millipore, Burlington, MA, USA). The CA activity was determined according to Alvizo *et al.*<sup>14</sup> Briefly, 195  $\mu\text{L}$  of a fresh 300 mM  $\text{KHCO}_3$  buffer (pH 8.1), containing 1.25 % v/v of 1% w/v phenolphthalein in 70% v/v ethanol, was mixed with 5  $\mu\text{L}$  whole cell lysate. The increase in absorbance at 550 nm was monitored on a plate reader (SpectraMax® M2, Molecular Devices, San Jose, CA, USA) for 20 min at room temperature with shaking before each measurement. The enzymatic sample was diluted if required so that there was a linear relationship between the enzyme concentration and the rate. The enzymatic rate was calculated according to equation (9):

$$r = D \cdot \frac{\Delta A_{\text{sample}} - \Delta A_{\text{control}}}{\Delta t} \quad (9)$$

where D the dilution factor,  $\Delta A_{\text{sample}}$  the change in absorbance at 550 nm over time for the enzymatic sample,  $\Delta A_{\text{control}}$  the change in absorbance at 550 nm over time for the control and  $\Delta t$  the reaction time.

**CA expression and recovery of the whole cell lysate.** The nucleotide sequence of the thermostable variant DvCA8.0 originating from *Desulfovibrio vulgaris*<sup>14</sup> incorporated with a polyhistidine tag (6xHis-tag) was inserted between the NdeI and XhoI restriction sites of the pET22b(+) vector. The gene synthesis and cloning was performed by GenScript (Piscataway, NJ,

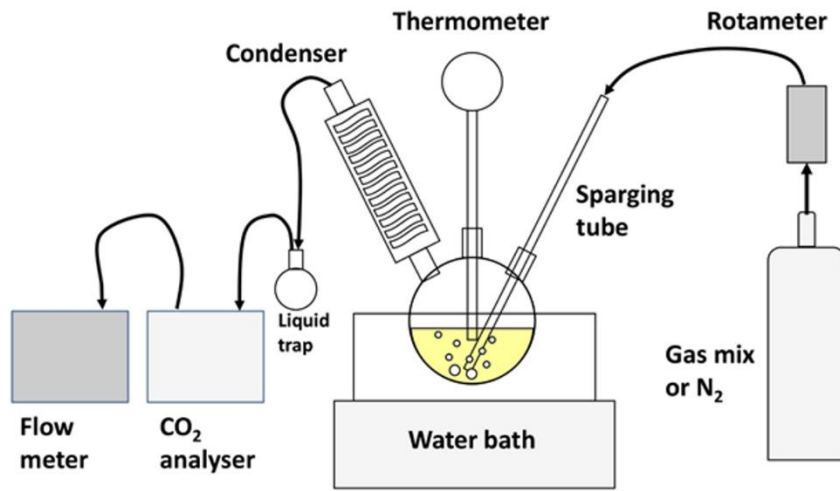
USA). The vector was subsequently transformed to *Escherichia coli* BL21(DE3) and stock cultures were stored. For the production of CA, 500  $\mu\text{L}$  of stock transformed *E. coli* BL21 (DE3) culture cells were inoculated in 50 mL Luria-Bertani preculture medium containing 100  $\mu\text{g mL}^{-1}$  ampicillin, following overnight incubation at 37°C and 180 rpm. 1% v/v of pre-culture was added in auto-inducing lactose medium (ZYP-5052 without trace elements), containing 100  $\mu\text{g mL}^{-1}$  ampicillin. The cultures were grown at 32°C and 180 rpm for 24 h. The harvested culture was centrifuged at 8000 rpm for 5 min and the supernatant was collected and discarded, as no CA activity was detected. The cells from 1 L culture were re-suspended in 200 mL 1:1 v/v Tris-HCl 0.1 M pH 8.0: NaOH 0.2 M. Then, they were lysed by a laboratory homogenizer (SPX, Crawley, United Kingdom) applying 3 cycles at 700 bar. The cell debris were removed by centrifugation at 8000 rpm for 5 min and the supernatant (whole cell lysate) was collected and filtrated to 0.2  $\mu\text{m}$  using a pressurized filtration system (Sterlitech, Kent, WA, USA). Last, the lysate was ultra-filtrated using a tangential flow filtration system (Millipore, Burlington, MA, USA; MWCO 10 kDa) until desired concentration. Expressions were verified by SDS-PAGE and the CA activity assay. Non-transformed *E. coli* BL21(DE3) culture was prepared and used as negative control. An amount of lysate was subjected to His-Tagged purification using a TALON IMAC resin (Takara Bio, Gothenburg, Sweden) and an Äkta purification system (GE Healthcare Life Sciences, Uppsala, Sweden). The fractions were subjected to SDS-PAGE and analyzed for protein concentration and CA activity, in order to determine the CA content in the whole cell lysate (135 $\pm$ 15.4 mg CA per 1 g protein).

**Thermal and solvent stability of CA.** The thermal stability of CA was assessed by incubation of whole cell lysate in a temperature-controlled water bath (25-100°C) for 2 h. The solvent

stability of CA was determined by adding 6  $\mu\text{L}$  lysate in 400  $\mu\text{L}$  25% w/w amine and by incubating for 2 h at room temperature. Non-transformed *E. coli* BL21 (DE3) lysate was used as negative control. The residual activity (%) was calculated comparing the enzymatic rate after incubation with the initial enzymatic rate, expressed as a percentage. All reactions were carried out in duplicate.

**CO<sub>2</sub> absorption and desorption experiments.** Reactions were performed using 100 mL solvent in a 250 mL three neck round bottom flask. The absorption was performed at atmospheric pressure and 40 °C using a premixed gas containing 20% CO<sub>2</sub> and 80% N<sub>2</sub> (technical grade, AGA, Luleå, Sweden) at a flow rate of 700 mL min<sup>-1</sup>. In the case of enzyme-assisted absorption, whole cell lysate of desired concentration was added at different solvent: enzyme ratios together with 10  $\mu\text{L}$  antifoam 204 in order to prevent excessive foaming. Before starting the absorption experiments, the solvent in the reactor was weighed and heated to 40 °C in a water bath with a specified accuracy of 0.5 °C (Grant Instruments Ltd, Cambridge, UK). The calibration of a CO<sub>2</sub> analyzer (Geotech G110, Geotechnical Instruments (UK) Ltd, Warwickshire, England) was checked with calibration gases (AGA, 3% CO<sub>2</sub>: 10% O<sub>2</sub>: 87% N<sub>2</sub>, 7% CO<sub>2</sub>: 18% O<sub>2</sub>: 75% N<sub>2</sub> and 20% CO<sub>2</sub>: 80% N<sub>2</sub>) and the flow rate of the premixed absorption gas was then set at 700 mL min<sup>-1</sup>, as verified by a flowmeter (ADM2000, Agilent technologies, Santa Clara, SA, USA). The experiments were started by directing the gas into the solvent by steel tube (ID=1mm) with a valve. The CO<sub>2</sub> concentration and flow rate at the output of the reactor was measured with the flow meter and the CO<sub>2</sub> analyzer. For the absorption, the experiments were stopped when the % CO<sub>2</sub> in the exhaust gas was 90% of the inlet concentration. At the end of reaction, the solvent in the flask was weighed in order to determine gravimetrically the mass of absorbed CO<sub>2</sub>. Prior to

desorption, the tubing and the head space of the reactor with the rich solvent were purged until no CO<sub>2</sub> remained, as measured by the CO<sub>2</sub> analyser. The reactor was then heated to 80 °C in a water bath and the experiments started with the initiation of N<sub>2</sub> sparging (technical grade, AGA, Luleå, Sweden) through the steel tube with a flow rate of 200 mL min<sup>-1</sup>. The outlet flow rate and % CO<sub>2</sub> was measured until the % CO<sub>2</sub> in the outlet was 1%. All experiments were carried out in duplicate. The experimental set-up is presented in Figure 2.



**Figure 2.** Principle set-up of the CO<sub>2</sub> absorption and desorption equipment.

The absorption rate, desorption rate and load capacities were calculated according to Luo et al.<sup>20</sup>

The absorption and desorption rates (mol s<sup>-1</sup>) at any given time,  $Q_{CO_2}$ , were calculated according to equation (10),

$$Q_{CO_2} = \left( n_{CO_2}^{In} - \frac{X_{CO_2}^{Out} n_{N_2}}{(1 - X_{CO_2}^{Out})} \right) \quad (10)$$

where  $n_{N_2}$  and  $n_{CO_2}^{In}$  the molar flow rates of N<sub>2</sub> and CO<sub>2</sub> into the solution respectively and  $X_{CO_2}^{Out}$  the molar fraction of CO<sub>2</sub> out of the solution.

The absorption and desorption rates ( $\text{mol L}^{-1} \text{s}^{-1}$ ) were subsequently calculated according to equation (11),

$$r_{CO_2} = \frac{Q_{CO_2}}{V_L} \quad (11)$$

where  $V_L$  the volume of the solution.

$Q_{CO_2}$  was logged with time,  $t$ , and the accumulated moles of  $CO_2$  absorbed by the liquid,  $N_{CO_2}$ , was calculated according to equation (12),

$$N_{CO_2} = \int_0^t Q_{CO_2} dt \quad (12)$$

The  $CO_2$  load,  $N$ , at a particular time point could then be calculated according to equation (13) in  $\text{mol L}^{-1}$  or equation (14) in  $\text{mol mol}^{-1}$  amine

$$N_{mol/L} = \frac{N_{CO_2}}{V_L} \quad (13)$$

$$N_{mol/mol \text{ amine}} = \frac{N_{CO_2}}{N_{amine}} \quad (14)$$

Where  $N_{amine}$  the amount of amine (mol) in solution.

The percent increase in absorbed  $CO_2$  for the enzyme catalyzed reactions,  $\Delta CO_2\%$ , were calculated according to equation (15),

$$\Delta CO_2(\%) = 100 \cdot \frac{m_{CO_2,E} - m_{CO_2,C}}{m_{CO_2,C}} \quad (15)$$

Where  $m_{CO_2,E}$  the mass of absorbed  $CO_2$  during enzyme-catalyzed reaction and  $m_{CO_2,C}$  the mass of absorbed  $CO_2$  during the respective non-enzymatic reaction.

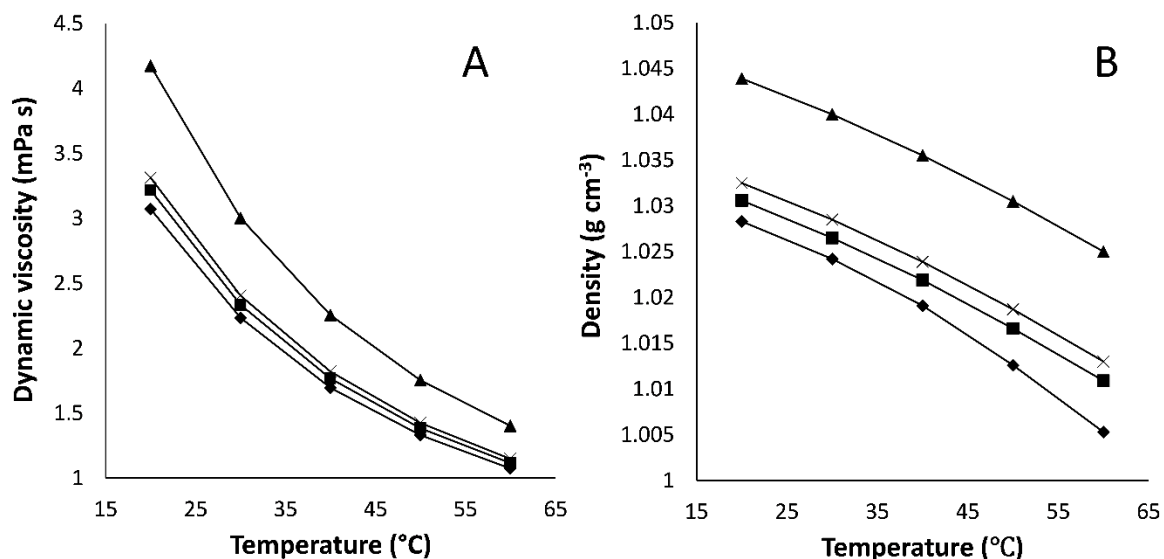
**Scaled-up CO<sub>2</sub> absorption on a packed bed column.** Scaled-up demonstration experiments were performed in a 1 m packed bed absorption rig CHE 626 (HFT Global Ltd, Derbyshire, UK) at 20°C for selected solvents, at a fixed gas flow rate of 65 L min<sup>-1</sup>, containing 8 % CO<sub>2</sub> and 92% N<sub>2</sub>. The liquid flow rate was 0.58 L min<sup>-1</sup>. The inlet and outlet CO<sub>2</sub> concentration was recorded with a CO<sub>2</sub> analyzer. The overall volumetric mass transfer coefficient, KG<sub>a</sub>, was calculated for dilute conditions (CO<sub>2</sub> < 10%) according to equation (16), assuming ideal gas behavior in the vapor phase, which is derived from a general mass balance over a packed absorption column,

$$KG_a = \frac{PN}{AZ} \left( \frac{\ln\left(\frac{P_i}{P_o}\right)}{(P_i - P_o)} \right) \quad (16)$$

Where P=total pressure in the column (atm), P<sub>i</sub>=partial pressure of CO<sub>2</sub> in the inlet stream (atm), P<sub>o</sub>=partial pressure of CO<sub>2</sub> in the outlet stream (atm), A=cross-sectional area of the column (m<sup>2</sup>), N= gram moles CO<sub>2</sub> absorbed s<sup>-1</sup>, Z=height of packing (m).

## RESULTS AND DISCUSSION

**Viscosity, density and pH of the AAIL amine blends.** The viscosities and densities of PEHAp MDEA blends as a function of time were analyzed (Figure 3A and 3B).



**Figure 3.** Viscosities (A) and densities (B) as a function of time for selected blends. ▲ = 25% PEHAp, × = 10% PEHAp 15% MDEA, ■ = 7.5% PEHAp 17.5% MDEA, ◆ = 5% PEHAp 20% MDEA.

In general, the viscosities and densities were water like due to the high water activity, which promotes hydration of the involved species and decreases their interactions. The data are consistent with similar reported blends.<sup>21</sup> The water-like behavior of the solvents can facilitate their direct use in conventional amine scrubbers. Increasing the temperature naturally weakens the intermolecular bonds, leading to increased fluidity and decreased density. The higher viscosity and density of the 25% PEHAp solution could be related to intermolecular hydrogen bonding with higher strength between water and PEHA compared to intra- and intermolecular hydrogen bonding in PEHA.<sup>22</sup> The 25% PEHA solution displayed a viscosity of 5.6 mPa·s at

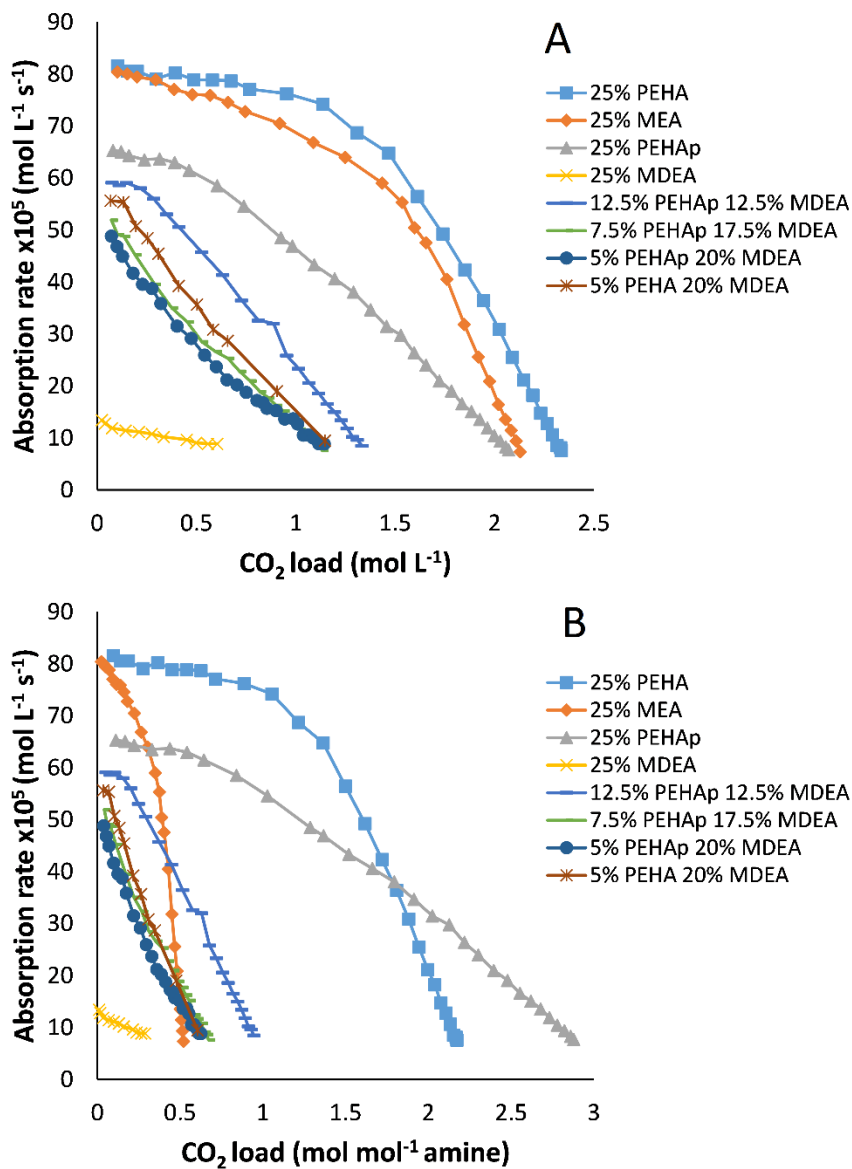
20°C (data not shown) which can be compared to 4.2 mPa·s for 25% PEHAp. As the fraction of MDEA increased, the viscosity decreased reaching 3.1 and 1.1 at 20°C and 60°C respectively for the 5% PEHAp 20% MDEA blend, which is consistent with literature values for aqueous 25% MDEA solutions.<sup>23</sup> The viscosity of 25% MEA at 30°C falls between 2.1-1.5 mPa·s that is slightly lower than the 5% PEHAp 20% MDEA blend<sup>23</sup>. The pH values of all PEHAp MDEA blends were similar to 25% PEHAp. In comparison, 25% PEHA and 25% MEA had higher pH values, equal to 12.14 and 12.22, respectively (Table 1).

**Table 1.** Initial pH value of amines and AAIL amine blends.

Composition	25% MEA	25% PEHA	25% MDEA	25% PEHAp	5% PEHAp 20% MDEA	7.5% PEHAp 17.5% MDEA	12.5% PEHAp 12.5% MDEA
pH	12.22	12.14	11.35	10.58	10.62	10.59	10.55

**Absorption rate versus CO<sub>2</sub> load.** The absorption rates of different PEHAp MDEA blends versus the CO<sub>2</sub> load are presented in Figure 4. 25% MEA, PEHA, PEHAp and MDEA were also used as reference for comparison of their absorption properties with the investigated PEHAp MDEA blends.





**Figure 4.** Absorption rate versus  $\text{CO}_2$  load of different amines and AAIL amine blends. The load is presented in  $\text{mol L}^{-1}$  in (A) and  $\text{mol mol}^{-1}$  amine in (B).

It can generally be observed that the initial absorption rates for 25% PEHA and 25% MEA are the highest, where PEHA displayed the highest overall absorption rate. In contrast to the other solutions, the 25% PEHA and MEA solutions also maintained a high absorption rate over a larger  $\text{CO}_2$  load ( $\text{mol L}^{-1}$ ) interval, which is consistent with the availability of a high number of

strong primary and secondary amines per unit volume (Figure 4A). The results confirm other reports where it was shown that 30% PEHA displayed faster absorption rates and higher loads compared to a 30% MEA solution.<sup>22</sup> Other aqueous polyamine solutions such as tetraethylenepentamine (TEPA) has also shown higher absorption rates compared to MEA<sup>24</sup>. The third highest absorption rate was observed for 25% PEHAp. The absorption rate declined in proportion to the amount of MDEA that was blended into the solvent, where 25% MDEA displayed the lowest absorption rate. Compared to the 25% PEHA and MEA solutions, there was a noticeable drop in the absorption rate for the 25% PEHAp solution. This can be expected due to the neutralization of one of the primary amines of PEHA by the carboxylic acid group of proline and the associated drop in pH from about 12.1 to 10.6. Generally, the viscosity can strongly influence the mass transfer in the solvents but in this case, 25% PEHAp displayed lower viscosity compared to 25% PEHA (Figure 3). Thus, it is not considered responsible for the sharp drop in absorption rate for 25% PEHAp compared to 25% PEHA. It can also be noted that the pH values of 25% PEHAp, 25% MDEA and the PEHAp MDEA blends are similar (between 10.5-11.4, Table 1) so pH is not likely to influence the initial absorption rate much for these solvents, but rather do the available primary and secondary amine groups.

Blending 5% PEHAp and 20% MDEA increased the initial absorption rates almost 5-fold, whereas blending 12.5% PEHAp and 12.5% MDEA increased the absorption rate about 6-fold compared to 25% MDEA. Hence, the largest positive effect compared to 25% MDEA is given by the first 5% PEHAp in the blends, as the increase of PEHAp concentration in the blend does not promote an increase in the initial absorption rate in a linear manner. The introduction of the very reactive primary and secondary amines from PEHA and proline in combination with excess of MDEA, acting as a proton acceptor for the rate determining steps in carbamate formation,

may promote the large improvement in absorption rate compared to the 25% MDEA solution.

The more modest improvements in the absorption rates with further addition of PEHAp may be related to the increasing viscosities with higher amounts of PEHAp and the fact that a larger fraction of the primary and secondary amines must act as proton acceptors themselves during carbamate formation.

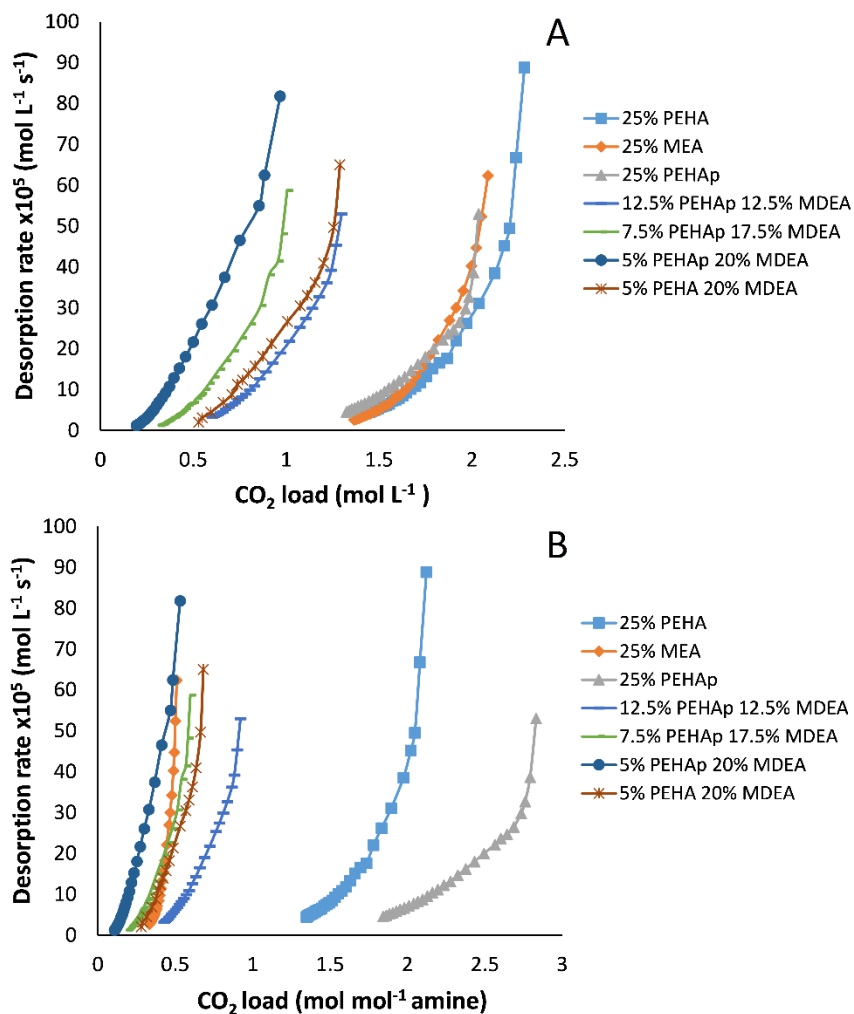
On a mol L<sup>-1</sup> basis, the maximum load was highest for the 25% PEHA solution at 2.3 mol L<sup>-1</sup> closely followed by 25% MEA and 25% PEHAp at 2.13 and 2.1 mol L<sup>-1</sup> respectively. The capacities for the blends ranged between 1.1 and 1.4 mol L<sup>-1</sup> with a gradual increase as more PEHAp was added (Figure 4A). The load for 25% MEA was about 0.54 mol CO<sub>2</sub> mol<sup>-1</sup> amine and consistent with other studies on aqueous MEA solutions.<sup>25</sup> In water solutions, the capacity is generally slightly higher than 0.5 mol CO<sub>2</sub> mol<sup>-1</sup> (theoretical value) as water and OH<sup>-</sup> can act as base as well. The 25% PEHA solution displayed a load of 2.3 mol CO<sub>2</sub> mol<sup>-1</sup> amine under the prevailing conditions reflecting that several of its amine groups react with CO<sub>2</sub> (Figure 4B). This value is consistent with another study under similar conditions where a load of about 2.46 mol CO<sub>2</sub> mol<sup>-1</sup> amine for a 30% aqueous PEHA solution was reported.<sup>22</sup> With two primary and four secondary amine sites, PEHA could theoretically be expected to bind 3 mol CO<sub>2</sub> mol<sup>-1</sup> amine assuming that no other reactions occur. The 25% PEHAp solution displayed a higher capacity (2.88 mol CO<sub>2</sub> mol<sup>-1</sup> amine) than 25% PEHA (2.46 mol CO<sub>2</sub> mol<sup>-1</sup> amine) even though one of the nitrogen atom got protonated. This is due to the fact that the proline anion is also contributing in the chemisorption of CO<sub>2</sub>.<sup>26</sup> The blends displayed intermediate values between about 1 mol mol<sup>-1</sup> amine for 12.5% PEHAp 12.5% MDEA and 0.6 mol mol<sup>-1</sup> amine for the 5% PEHAp 20% MDEA solution. The obtained results are similar to a recent study that employed the diamine trans-1,4-diaminocyclohexane as a bicarbonate formation rate promoter in MDEA-

based CO<sub>2</sub> capture. The blend (0.5 M diamine 3.0 M MDEA) showed CO<sub>2</sub> loading of 0.576 mol CO<sub>2</sub> mol<sup>-1</sup> amine.<sup>27</sup>

**Desorption rates versus CO<sub>2</sub> load.** Depending on whether the CO<sub>2</sub> load is given in mol L<sup>-1</sup> (Figure 5A) or mol mol<sup>-1</sup> amine (Figure 5B), the desorption profile looks different for some solvents, particularly for MEA, which has a small molecular weight. However, the desorption rates generally dropped fast with decreasing CO<sub>2</sub> loads and displayed a more gradual decrease as the lean loading, i.e. the remaining load after desorption, was approached. The initial high desorption rate is most likely related to the amount of bicarbonate which is highest at the maximum load and decomposes more easily to CO<sub>2</sub> compared to the decomposition of the carbamates and their respective amines.<sup>22</sup> On a mol L<sup>-1</sup> basis, the lean loading for the 25% PEHA, 25% MEA and 25% PEHAp solutions were between at 1.2-1.4 mol L<sup>-1</sup> indicating the stability of the carbamates formed with the primary and secondary amines involved (Figure 5A). Despite that the 25% PEHA solution had the highest absorption rate, it displayed a slightly lower lean load compared to 25% MEA and a similar lean load as 25% PEHAp. This suggests destabilization of the inner secondary amine groups of PEHA in combination with the high initial pH, resulting also in a larger amount of bicarbonate formed compared to 25% PEHAp. Although 25% MEA should have similar amounts of bicarbonate after absorption, it cannot benefit from such destabilization of internal carbamates. On a mol mol<sup>-1</sup> amine basis, 25% PEHAp had the highest lean load (1.75 mol mol<sup>-1</sup> amine) followed by 25% PEHA (1.18 mol mol<sup>-1</sup> amine) (Figure 5B). The unexpectedly lower initial desorption rates for the 25% PEHAp solution compared to 25% PEHA may be related to non-specific interaction between the ionic character of the AAIL and CO<sub>2</sub> and possibly a stabilization of the formed carbamates. Stabilization of carbamates from reversible ionic liquids have been reported.<sup>28</sup> Although 25% MEA forms stable

carbamates, it had a lower lean load when expressed per mol mol<sup>-1</sup> amine compared to 25% PEHA and 25% PEHAp, due to its small molecular weight and only one primary amine group (Figure 5B). The blend 5% PEHAp 20% MDEA had lowest lean load, equal to 0.21 mol L<sup>-1</sup> or 0.13 mol mol<sup>-1</sup> amine (Figure 5A and 5B, respectively) that increased by increasing the concentration of PEHAp in the blend. Interestingly, its initial absorption rate was higher compared to 5% PEHA 20% MDEA indicating that the potential stabilization of formed carbamates due to interaction between the ionic character of the AAIL and CO<sub>2</sub> is not strong when MDEA is present in the blend.

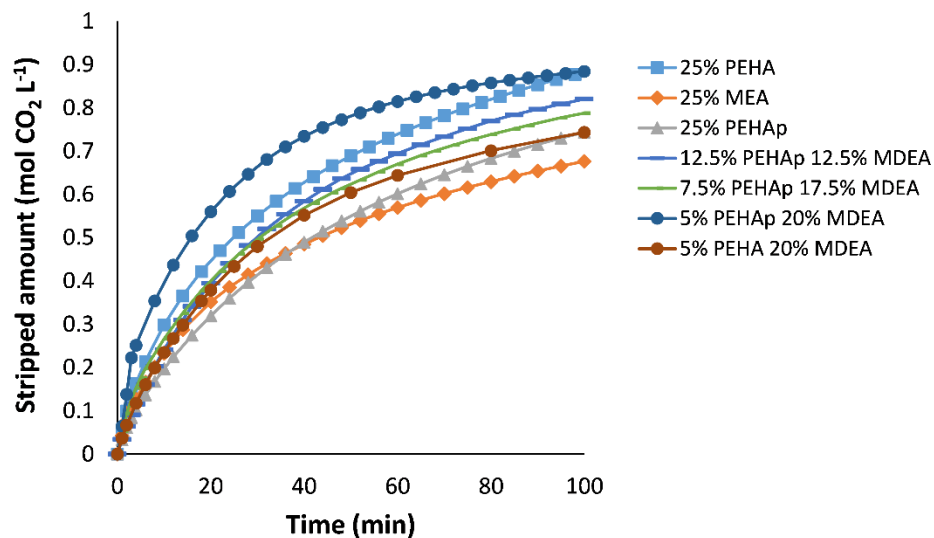
As expected, the 5% PEHAp 20% MDEA blend displayed the highest desorption rate being the most promising tested blend (Figure 6). At the first 40 min, the desorbed amount of CO<sub>2</sub> was clearly highest for 5% PEHAp 20% MDEA, thus for a given processing rate of CO<sub>2</sub>, the operational costs could potentially be the lowest using this solvent. However, if full regeneration conditions are used, i.e. higher temperature, the concentration would have to be increased to match the mol L<sup>-1</sup> capacity for 25% MEA or 25% PEHA. The 5% PEHA (i.e without proline) 20% MDEA blend did not have as good desorption properties as 5% PEHAp 20% MDEA, which could be attributed to the fact that none of its primary amines are neutralized. As MDEA was replaced with more PEHAp in a blend, the desorption rates decreased and lean loadings increased. Hence, the proline part seemed to have a key role in maintaining a good absorption capacity and desorption potential. As previously mentioned, the proline anion contributes in the chemical absorption of CO<sub>2</sub> resulting in good capacity. In the case of desorption, the carbamate formed with proline anion might be able to decompose fully and easier at 80°C, requiring lower desorption energy and resulting in good desorption, too.



**Figure 5.** Desorption rate versus CO<sub>2</sub> load of different amines and AAIL amine blends. The load is presented in mol L<sup>-1</sup> in (A) and mol mol<sup>-1</sup> amine in (B).

The % regeneration increased as more PEHAp was replaced by MDEA, which is consistent with the lower desorption energy requirements for MDEA related to more bicarbonate formation during absorption. For the PEHAp MDEA blends, the % regeneration was roughly proportional to the fraction of MDEA present. A summary of the absorption and desorption performance of all tested amines and AAIL blends is presented in Table 2. The blend 5% PEHAp 20% MDEA

was selected as the most promising solvent, as it combines competitive absorption rates, 5-fold higher than 25% MDEA, (Figure 4) with the best % regeneration, 2-fold higher than MEA (Figure 6). The superior desorption suggest that the blend should have considerable lower regeneration energy per ton CO<sub>2</sub> absorbed compared to MEA.



**Figure 6.** Amount of stripped CO<sub>2</sub> per reaction volume versus time for different amines and AAIL amine blends.

**Table 2.** Summary of the performance of different amine and AAIL blends during absorption (40°C) and desorption (80°C).

Composition	Load after absorption		Load after desorption		Released CO <sub>2</sub>		CO <sub>2</sub> regeneration (%)
	(mol L <sup>-1</sup> )	(mol amine) mol <sup>-1</sup>	(mol L <sup>-1</sup> )	(mol amine) mol <sup>-1</sup>	(mol L <sup>-1</sup> )	(mol amine) mol <sup>-1</sup>	
<b>25% MEA</b>	2.12±0.14	0.52±0.004	1.37±0.01	0.34±0.001	0.75±0.02	0.18±0.01	35.4±0.7
<b>25% PEHA</b>	2.20±0.18	2.04±0.16	1.27±0.11	1.18±0.10	0.93±0.10	0.87±0.1	42.3±2.8
<b>25% PEHAp</b>	2.1±0.01	2.89±0.02	1.26±0.03	1.75±0.04	0.82±0.04	1.14±0.05	39.6±1.7
<b>12.5%PEHAp</b>	1.35±0.02	0.96±0.02	0.54±0.05	0.38±0.04	0.81±0.07	0.58±0.05	60.1±4.2
<b>12.5% MDEA</b>							
<b>7.5% PEHAp</b>	1.22±0.12	0.72±0.07	0.36±0.06	0.21±0.04	0.86±0.06	0.51±0.04	70.8±2.1
<b>17.5% MDEA</b>							
<b>5% PEHAp</b>	1.13±0.03	0.62±0.02	0.21±0.03	0.12±0.01	0.92±0.01	0.50±0.004	81.1±1.6
<b>20% MDEA</b>							
<b>25% MDEA</b>	0.92±0.05	0.44±0.02	N/A	N/A	N/A	N/A	N/A
<b>5% PEHA</b>	1.29±0.04	0.68±0.02	0.51±0.02	0.27±0.01	0.79±0.02	0.42±0.01	60.5 ±0.30
<b>20% MDEA</b>							

N/A: not assessed.

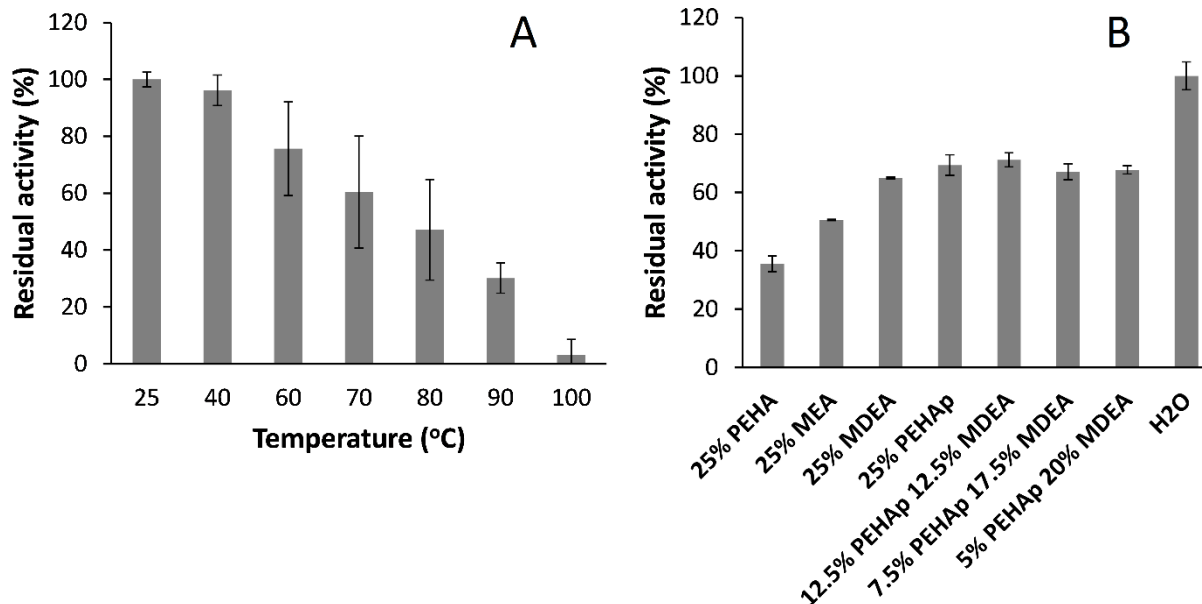


**Scaled-up CO<sub>2</sub> absorption on a packed bed column.** In order to compare the most promising blend with MDEA and MEA under more realistic conditions, the overall volumetric mass transfer coefficients, KGa, were determined using a packed bed absorption column (Table 3). Here, the 5% PEHAp 20% MDEA blend displayed a 9.6 times higher KGa than 25% MDEA which could save capital costs compared to MDEA-based plants.

**Table 3.** KGa for selected solvents under the same condition.

Solvent	KGa (mol· (m <sup>3</sup> s mol fraction) <sup>-1</sup> )
25% MEA	15
25% MDEA	0.48
5% PEHAp 20% MDEA	4.6

**Thermal and solvent stability of CA.** As a first step for the integration of CA with chemical absorption, it was desired to confirm the compatibility of the enzyme with the developed solvent blend and with relative temperatures. Thus, the residual activity of CA was determined after challenge of lysate to different temperatures (25-100°C) and to the different amines and AAIL blends (Figure 7).



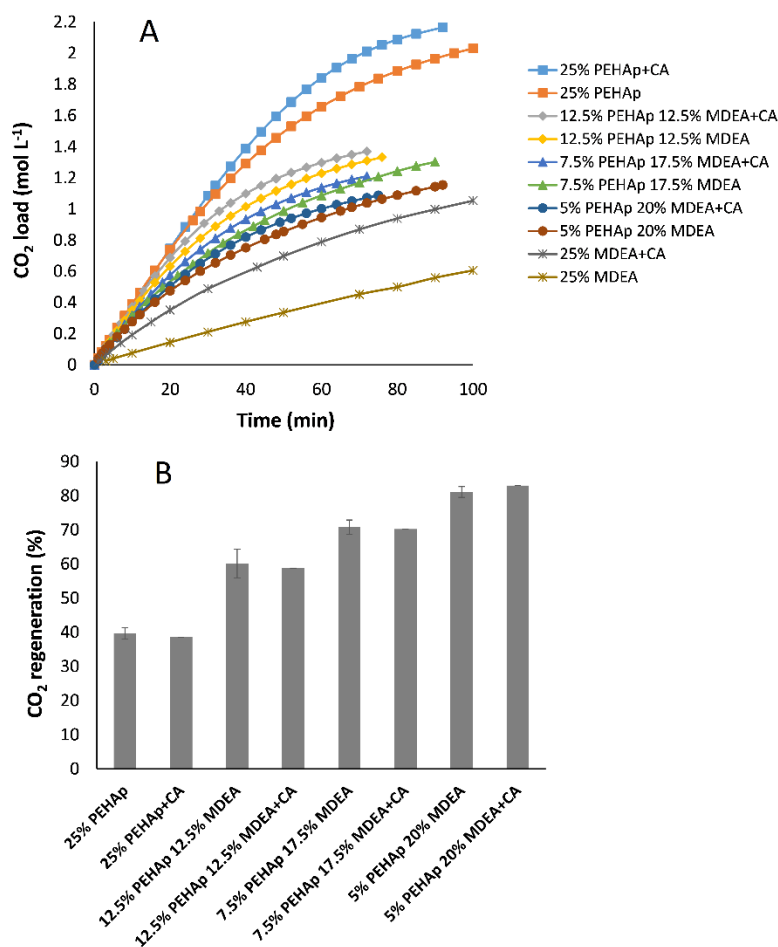
**Figure 7.** Residual activity of CA after 2 h incubation of whole cell lysate at different temperatures (A) and with different solvents (100:1.5 v/v solvent: enzyme) at room temperature (B). The bars represent the standard deviation between duplicate runs.

Between 60 and 90°C, the residual activity decreased linearly while above 90°C it dropped sharply to inactivation. CA could maintained 76% of its activity at 60°C and 47% at 80°C, after 2 h of incubation (Figure 7A). According to previous report, the enzyme could retain 40% of its activity after being challenged at 50°C and was completely inactivated at 60°C, after 14 weeks in 4.2 M MDEA (50% w/w).<sup>14</sup> Based on our findings, the enzyme is not likely to survive for long times in a typical MEA-based stripping column where the re-boiler temperatures often are between 120-140°C. However, could the desorption temperature be lower or the enzyme be immobilized in the absorption column, where the temperatures typically are between 40-60°C, it is likely to endure for longer periods.

As presented in Figure 7B, incubation in different amines for 2 h revealed that CA could maintain approximately 70% of its activity in all tested PEHAp MDEA blends and 25% PEHAp (pH 10.55-10.62). Incubation in 25% MDEA (pH 11.35) resulted in 65% residual activity, while in 25% MEA (pH 12.22) and 25% PEHA (12.14) resulted in 51% and 35% residual activity, respectively. Although the MEA and PEHA solutions had similar pH, the activity after incubation in PEHA was significantly reduced. This indicates that the enzyme inactivation in 25% PEHA can be attributed to the harsh nature of the solvent and not the pH. The protective role of proline by neutralization of one the primary amine in PEHA was validated as the enzyme was much more stable in 25% PEHAp compared to 25% PEHA.

**Effect of CA on the CO<sub>2</sub> absorption/desorption in amine and AAIL blends.** The influence of CA on the CO<sub>2</sub> absorption employing different blends was studied at fixed enzyme load (Figure 8A). It was generally confirmed that the enzyme improved the absorption rate. The rate increase was the highest for 25% MDEA, reflecting that the enzyme acts on the rate limiting step for CO<sub>2</sub> hydration by MDEA and that the respective non-enzymatic MDEA absorption reaction is slow. This slow reaction rate of MDEA leaves room for a large improvement because there is no development of mass transfer limitation phenomena. When PEHAp was present in the blends, the fast primary and secondary amines groups could take a similar role to the enzyme and MDEA could, to a large extent, function as a proton acceptor. The observed effect of the enzyme in PEHAp MDEA blends was not as high as in MDEA, possibly because mass transfer limitations may come into play. The enzyme worked rather well in 25% PEHAp, particularly at the later phase of absorption, after 30 min of reaction, reflecting its ability to hydrate CO<sub>2</sub> and maintain a stronger driving force for mass transfer. After the end of absorption, the blends were

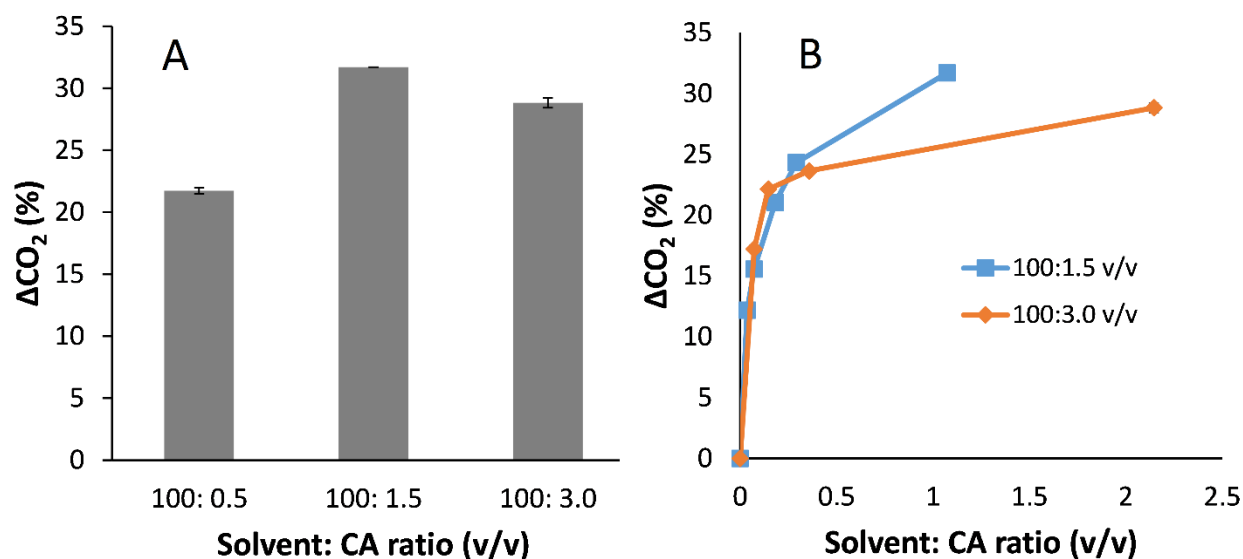
subjected to desorption at 80°C. It was observed that the regeneration of solvent was not affected by the presence of enzyme in the solvent blends (Figure 8B). This was expected as CA catalyzes the hydration of CO<sub>2</sub>, forming bicarbonate that destabilizes easily and decomposes to CO<sub>2</sub> at low temperatures such as 80°C. Moreover, it was confirmed that possible impurities present in the whole cell lysate did not affect the desorption efficiency of the solvent.



**Figure 8.** CO<sub>2</sub> load versus time during CA-assisted absorption in amine and AAIL amine blends (A). Effect of CA on solvent regeneration (B). The solvent: CA ratio was 100:1.5 v/v and the protein load was 0.3 g/L reaction volume. The bars represent the standard deviation between duplicate runs.

**Effect of solvent: CA ratio and CA load on the absorption.** The effect of the solvent: CA ratio was investigated in the most promising AAIL amine blend, 5% PEHAp 20% MDEA. Initially, lysate of fixed stock concentration was added at different ratios in the blend (Figure 9A). It was observed that a 10% increase in the mass of absorbed CO<sub>2</sub> compared to the non-enzymatic reaction by increasing the lysate volume from 0.5 to 1 mL. In contrast, increasing the lysate volume from 1.5 to 3 mL caused a small reduction in the absorbed CO<sub>2</sub>, from 31.7% to 28.8%. The lack of improvement in CO<sub>2</sub> absorption could be attributed to the introduction of higher amount of water, particles and other cells components in the reaction mixture.

To assess the combined effect of solvent: CA ratio and CA load in the CO<sub>2</sub> absorption, lysate of different concentrations was introduced in the blend at different ratios (100: 1.5 v/v and 100: 3.0 v/v) (Figure 9B). It was observed that up to 0.02 g L<sup>-1</sup> protein load, the increase in the amount of absorbed CO<sub>2</sub> compared to the non-enzymatic reaction was not affected by the solvent: CA ratio. For given high protein loads above 0.5 g L<sup>-1</sup>, the introduction of higher lysate volume affected negatively the absorption performance. Thus, it was concluded that the negative effect is attributed to the increase of impurities in the reaction mixture. The optimal conditions for enzyme-assisted absorption were determined as 100: 1.5 v/v solvent CA: ratio and 1 g L<sup>-1</sup> protein load, offering a 31.7% increase in the amount of absorbed CO<sub>2</sub> compared to the non-enzymatic respective reaction.



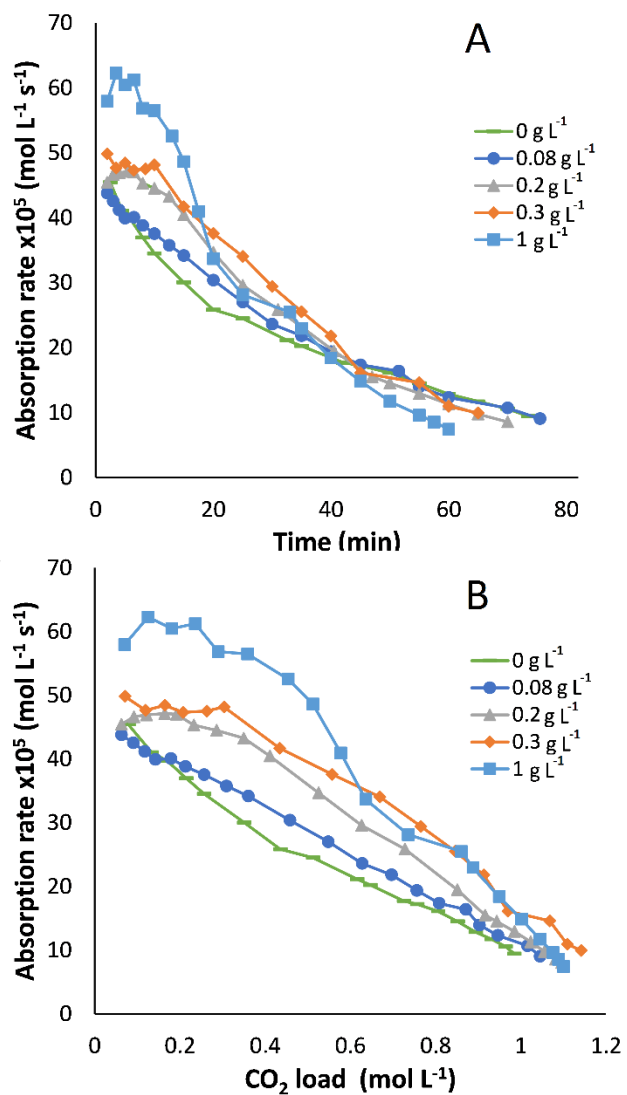
**Figure 9.** Effect of solvent: CA ratio (A) and protein load (B) on the mass of absorbed  $\text{CO}_2$ . Absorption was carried out in 5% PEHAp 20% MDEA. The bars represent the standard deviation between duplicate runs.

Investigating the effect of protein load on the absorption rate at fixed solvent: CA ratio (100: 1.5 v/v), a 1.4-fold increase in the initial reaction rate was observed, compared to the non-enzymatic reaction (Figure 10A). The enzymatic reaction was fastest during the first 25 min at optimal conditions, while all enzyme-catalyzed reactions converged to a  $\text{CO}_2$  load of approximately 1.1 mol  $\text{L}^{-1}$  (Figure 10B). Except for the increase in the absorbed  $\text{CO}_2$  the benefits of employing CA include enhanced absorptions rates and reduced operation times. In our case, at optimal protein load the enzyme-assisted reaction was concluded at only 60 min compared the non-catalyzed reaction that lasted 80 min (Figure 10A).

The apparent kinetic constant ( $k_{\text{app}}$ ) was 2-fold higher for the CA-catalyzed reaction at optimal conditions, compared to the non-enzymatic reaction. Vinoba *et al.*<sup>13</sup> reported almost a 3-fold increase in the  $k_{\text{app}}$  constant adding bovine CA in 5% w/w MDEA, among other tested solvents.

The lower rate in our study could be attributed potentially to limited enzyme stability at significantly higher amine concentrations (25% w/w). Nevertheless, there are limited reports for CA-assisted absorption in amines other than MDEA, while little focus has been put on optimization of the absorption parameters with focus on the biocatalyst<sup>29-30</sup>.

In our study, the initial absorption rate of enzyme-assisted absorption performed in the ternary blend of 5% PEHAp, 20% MDEA and enzyme, was approximately 6 times higher than the one of the respective chemical absorption performed with 25% MDEA (Figure 4A). The obtained results are comparable with other studies related to enzyme-assisted absorption in MDEA-based systems. Gladis *et al.*<sup>14</sup> have demonstrated that addition of 0.2% w/v CA offered a 5 times enhancement of mass transfer in 30% MDEA at 40°C. Immobilized CA on metal–organic frameworks (MOFs) was applied for the enhancement chemical absorption in 1 M MDEA, resulting in a 2.5-6 times increase in the absorption rate depending on the enzyme load.<sup>31</sup> Application of catalyst mimicking CA in 30% MDEA increased absorption efficiency by 10%.<sup>32</sup>



**Figure 10.** Absorption rate at different protein loads ( $\text{g L}^{-1}$  reaction volume) versus time (A) and versus CO<sub>2</sub> load (B). Absorption was carried out in 5% PEHAp 20% MDEA at fixed solvent: CA ratio (100:1.5 v/v).



## CONCLUSIONS

In conclusion, polyamine/amino acid ionic liquids in combination with tertiary amines are a good alternative solvent to conventional amine scrubbers for CO<sub>2</sub> capture from liquid streams. In this study, the blend 5% PEHAp 20% MDEA offered approximately 5-fold higher initial absorption rate compared to MDEA and 2-fold higher regeneration compared to MEA. Addition of a thermostable CA (DvCA8.0) in the blend offered a further increase in the absorption rates and did not affect the solvent desorption properties. Enzyme-assisted absorption resulted a 31.7% increase in mass of absorbed CO<sub>2</sub> was observed compared to the non-enzymatic reaction. Combined with the good desorption properties of the developed solvent, integration of CA in chemical absorption could result in short operating times and reduced energy, factors directly related to operating cost. This approach highlights the potential for application of greener and more sustainable bioprocesses for CO<sub>2</sub> sequestration. However, it remains to be studied whether the cost to incorporate a process involving an enzyme and an amino acid is economically viable compared to the conventional one, and thus be projected on a large scale.

## **Supporting information**

<sup>1</sup>H NMR spectra of pentaethylenehexamine proline (PEHAp) and pentaethylenehexamine (PEHA) (Figure S1)

<sup>13</sup>C NMR spectra of pentaethylenehexamine proline (PEHAp) and pentaethylenehexamine (PEHA) (Figure S2)

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### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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#### ABBREVIATIONS

AMP, aminomethyl propanol; CA, carbonic anhydrase; CCS, carbon capture and storage; DEA, diethanolamine; DETA, diethylenetriamine; MDEA, methyl diethanolamine; MEA, monoethanolamine; PEHA, pentaethylenehexamine; PEHAp, pentaethylenehexamine proline; TETA, triethylenetetramine.

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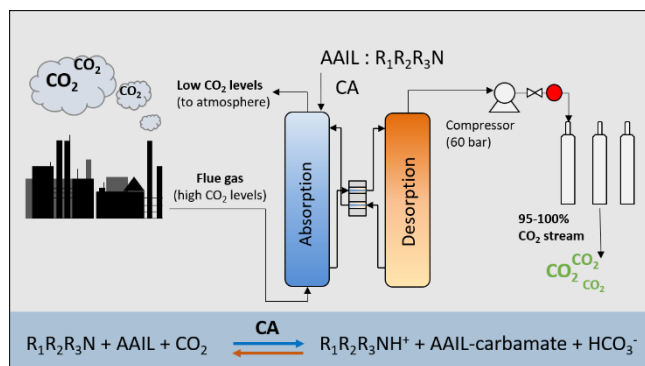
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Enzyme-assisted CO<sub>2</sub> absorption by amine amino acid ionic liquid blends was investigated to enhance absorption rates and regeneration efficiency compared to conventional CO<sub>2</sub> scrubbing systems