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# Kinetics of absorption of carbon dioxide in aqueous MDEA solutions with carbonic anhydrase at 298 K

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ABSTRACT

In present work the absorption of carbon dioxide in aqueous N-methyldiethanolamine (MDEA) solutions with and without the enzyme carbonic anhydrase has been studied in a stirred cell at 298 K, with MDEA concentrations ranging from 0.5 to 4 kmol $m^{-3}$ and carbonic anhydrase concentrations ranging from 0 to 2275 g $m^{-3}$, respectively. The obtained experimental results show that carbonic anhydrase significantly enhances the absorption of carbon dioxide in aqueous MDEA solution. When the enzyme is present in the absorption solution, MDEA concentration does not materially influence on the absorption rate. Therefore, the enzyme does not enhance the reaction of $CO_2$ with MDEA, since the rate of this reaction is a function of the MDEA concentration. Rather, the enzyme enhances the reaction of carbon dioxide with water. In the presence of enzyme this reaction is not only first order in $CO_2$, but also first order in water. Thus, carbonic anhydrase may provide a solution for the efficient capture of carbon dioxide from flue gases by significantly increasing the kinetics of its absorption in MDEA, a tertiary amine which requires less energy for regeneration than monoethanolamine (MEA), the current industry benchmark.



## 1. Introduction

Reactive absorption of carbon dioxide from process gas streams has been an important part of many industrial processes for decades. The conventional technology to capture $CO_2$ on a large scale is an absorption–desorption process, in which (aqueous) solutions of alkanolamines are frequently used as solvents. Different alkanolamines can be used:

- primary amines such as monoethanolamine (MEA);
- secondary amines such as diethanolamine (DEA);
- tertiary amines such as N-methyldiethanolamine (MDEA);

The reaction mechanisms between primary/secondary and tertiary amines with $CO_2$ are different. The reaction between $CO_2$ and primary/secondary amines is significantly faster than the reaction between $CO_2$ and tertiary amines (Versteeg et al., 1996). As a result of the faster reaction, the absorption column has smaller dimensions when primary/secondary amines are used. However, advantage of tertiary amines is that the regeneration energy is significantly lower than the regeneration energy of primary and secondary amines (Carson et al., 2000). As a result of the lower regeneration energy of tertiary amines, the costs for stripping are stated to be lower. An ideal solution would be a combination of fast absorption and low regeneration energy – such as activated tertiary amine solutions (Derks et al., 2006).

At present, the addition of small amounts of a (fast reacting) activator to such a solution is finding more and more application in the bulk removal of carbon dioxide. Well-known activators are amines, such as piperazine. Other chemical additives can also be employed such as hypochlorite. A new approach is to utilise a biocatalyst, the enzyme carbonic anhydrase.

Carbonic anhydrase (CA) is a powerful biocatalyst that accelerates the transformation of carbon dioxide to bicarbonate ion. CA is among others found in the blood of humans and other mammals, and facilitates the transfer of $CO_2$ during respiration. Genetic modification of this enzyme makes it possible to use it in combination with aqueous alkanolamine solutions within an industrial environment, like flue gas treatment (Davy, 2009).

In the present study, the results of the determination of the effect of carbonic anhydrase (CA) on the absorption rate of carbon dioxide into aqueous MDEA solutions are described.

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**Nomenclature**

| | |
|---|---|
| $A_{GL}$ | surface area of G/L interface ($m^2$) |
| $C_A$ | concentration of A ($mol\,m^{-3}$) |
| $D_A$ | diffusion coefficient of A ($m^2 s^{-1}$) |
| $E_A$ | enhancement factor of A |
| $J_A$ | flux of A ($mol\,m^{-2}\,s^{-1}$) |
| $k_1$ | first order reaction rate constant ($s^{-1}$) |
| $k_2$ | second order reaction rate constant ($m^3\,mol^{-1}\,s^{-1}$) |
| $k_L$ | liquid side mass transfer coefficient ($m\,s^{-1}$) |
| $k_{OV}$ | overall reaction rate constant ($s^{-1}$) |
| $m_A$ | G/L distribution coefficient of A |
| $P$ | pressure (Pa) |
| $R$ | gas constant ($8.314\,J\,mol^{-1}K^{-1}$) |
| $R_A$ | reaction rate of A ($mol\,m^{-3}s^{-1}$) |
| $T$ | temperature (K) |
| $V$ | volume ($m^3$) |
| $\nu_A$ | reaction order of A |

*Subscripts*

| | |
|---|---|
| 0 | initial |
| Am | amine |
| eq | equilibrium |
| G | gas phase |
| inf | infinite |
| L | liquid phase |
| vap | vapour |

## 2. Kinetics

When carbon dioxide is absorbed in an aqueous solution containing a tertiary alkanolamine, following three reactions occur simultaneously:

- Reaction I – with tertiary alkanolamine (Versteeg and van Swaaij, 1988a; Littel et al., 1990; Benamor and Aroua, 2007)

$$CO_2 + R_3N + H_2O \rightleftharpoons HCO_3^- + R_3NH^+$$

- Reaction II – with hydroxide ion (Pinsent et al., 1956; Pohorecki and Moniuk, 1988)

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

- Reaction III – with water (Pinsent et al., 1956; Kern, 1960)

$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

The overall forward reaction rate constant, $k_{OV}$, is determined by the contributions of each of these three reactions, whose kinetic rate expression is usually given as follows:

- Reaction I:

$$R_{CO_2,I} = k_{Am} C_{Am} C_{CO_2} = k'_{Am} C_{CO_2} \quad (1)$$

- Reaction II:

$$R_{CO_2,II} = k_{OH} C_{OH^-} C_{CO_2} = k'_{OH} C_{CO_2} \quad (2)$$

- Reaction III:

$$R_{CO_2,III} = k_{H_2O} C_{CO_2} = k'_{H_2O} C_{CO_2} \quad (3)$$

In the absence of any mass transfer limitations, the overall forward pseudo-first order reaction rate constant is defined as the sum of these rates divided by the concentration of carbon dioxide.

$$k_{OV} = k'_{Am} + k'_{OH} + k'_{H_2O} \quad (4)$$

The forward reaction rate constants of the three reactions as reported in literature are listed in Table 1.

Table 1 illustrates that in a $2\,kmol\,m^{-3}$ MDEA solution the contribution of reaction III can be neglected based on the reaction rate constant. The pH of a lean $2\,kmol\,m^{-3}$ MDEA solution is approximately 11.4, giving a hydroxide ion concentration of $0.00286\,kmol\,m^{-3}$, however, as soon as the solution is slightly loaded the hydroxide ion concentration quickly decreases. Therefore, after initial loading, the contribution of reaction II can also be neglected. As a result the overall forward reaction rate for the absorption of carbon dioxide into an aqueous tertiary alkanolamine solution is fully determined by the rate of reaction I, and therefore $k_{OV} \approx k'_{Am}$.

### 2.1. Carbonic anhydrase

Carbonic anhydrase, a very efficient catalyst that enhances the reversible reaction of $CO_2$ to $HCO_3^-$, was first identified in 1933 in red blood cells (Dodgson, 1991). Carbonic anhydrase is not just a single enzyme form, but a broad group of zinc metallo-proteins (enzymes) that exists in three genetically unrelated families of isoforms (α, β and γ) (Chegwidden and Carter, 2000). Carbonic anhydrases are present in almost all living organisms, from animals, to plants, algae and bacteria (Chegwidden and Carter, 2000; Lindskog, 1997). At least 14 genetically distinct α-CA isozymes have been identified in human beings. These isozymes have different tissue distributions and intracellular locations. The human variant CA II, located in red blood cells, is the most studied and has the largest catalytic turnover number (Kalifah and Silverman, 1991). It plays a major role in respiration and the blood acid–base balance (Chegwidden and Carter, 2000). In literature, for the catalysed reaction of $CO_2$ hydration, a mechanism for CA has been proposed (Lindskog and Silverman, 2000). Above pH 7 the dominant reaction mechanism of carbonic anhydrase with carbon dioxide can be described with:

- Reaction IV – $CO_2$–$HCO_3^-$ interconversion

$$CO_2 + EZnOH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EZnOH^-CO_2 \rightleftharpoons EZnHCO_3^-$$

$$EZnHCO_3^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EZnH_2O + HCO_3^-$$

- Reaction V – enzyme regeneration

$$EZnH_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H^+EZnOH^-$$

$$H^+EZnOH^- + B \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} EZnOH^- + BH^+$$

At low buffer concentrations (<10 mM), the intermolecular proton transfer, i.e. the second step of reaction V, is rate limiting, while at high buffer concentration, the intra molecular proton transfer, i.e. the first step of reaction V, is rate limiting (Kalifah and Silverman, 1991). Since water is a very weak base and therefore a poor proton

**Table 1**
Forward kinetic rate constants as defined in Eq. (4) in a 2 kmol m$^{-3}$ MDEA solution at 298 K.

| Reaction | 2nd order rate constant ($m^3 mol^{-1} s^{-1}$) | | 1st order rate constant ($s^{-1}$) | | Reference |
|---|---|---|---|---|---|
| $CO_2$ +MDEA | $k_{Am}$ | 0.0052 | $k'_{Am}$ | 10.4 | Littel et al. (1990) |
| | | 0.0070 | | 14.0 | Benamor and Aroua (2007) |
| $CO_2$ +$OH^-$ | $k_{OH}$ | 8.35 | $k'_{OH}$ | 23.8 | Pinsent et al. (1956), Pohorecki and Moniuk (1988) |
| $CO_2$ +$H_2O$ | | | $k'_{H_2O}$ | 0.026 | Pinsent et al. (1956) |

acceptor and $OH^-$ is not abundant at the pH at which the enzyme functions best, a dilute buffer solution is usually used as proton acceptor in kinetic experiments. In the present study the dilute buffer solution (millimolar range) is replaced by a more concentrated alkanolamine solution with concentrations up to 4 M and a corresponding pH-range of 11–11.6.

Larachi (2010) showed that $CO_2$ hydration by hCA II is best described by a random pseudo quad quad iso ping pong catalytic (1-transitory complex) mechanism. In that mechanism, the first transitory complex ($EZnOH^- CO_2 \rightleftharpoons EZnHCO_3^-$) is left out of consideration and the intermolecular $H^+$ transport (2nd part of reaction V) is extended with an additional parallel reaction:

- Reaction Vb – enzyme regeneration

$$H^+EZnOH^- + HCO_3^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} CO_2 + H_2O + EZnOH^-$$

The reaction mechanism of catalytic $CO_2$ hydration as described above, results in Fig. 1.

This mechanism results in a very complex and long kinetic rate expression and therefore is referred to Larachi (2010). The aim of this work is to identify which reaction rate constant, $k_{Am}$, $k_{OH}$ or $k_{H_2O}$, is enhanced by carbonic anhydrase during enzyme catalysed absorption of carbon dioxide into an aqueous MDEA solution.

## 3. Mass transfer

The absorption of a gas A into a liquid is generally described by Westerterp et al. (1984):

$$J_A = \frac{C_{A,G} - C_{A,L}/m_A}{1/k_G + 1/m_A k_L E_A} \quad (5)$$

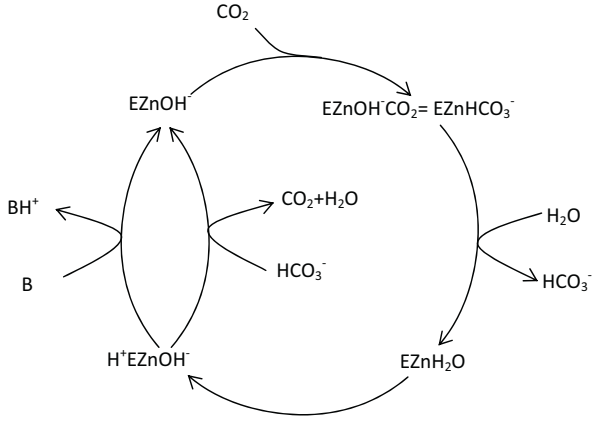


**Fig. 1.** Reaction mechanism of catalytic $CO_2$ hydration by carbonic anhydrase.

For a system consisting of a pure gas and assuming ideal gas behaviour and a freshly prepared and therefore lean liquid ($C_{A,L}$ = 0), Eq. (5) can be simplified to:

$$J_A = m_A k_L E_A \frac{P_A}{RT} \quad (6)$$

The chemical enhancement factor, $E_A$, is a function of the so-called Hatta number. When the absorption occurs in the first order regime and $Ha > 2$, the enhancement factor equals the Hatta number:

$$E_A = Ha = \frac{\sqrt{k_1 D_A}}{k_L} \quad (7)$$

For reactions different from the simple first-order reaction, the process can be considered in the pseudo first order regime when next criterion is fulfilled:

$$2 < Ha \ll E_{inf} \quad (8)$$

where $E_{inf}$ is the infinite enhancement factor. For irreversible reactions the infinite enhancement factor is defined as (van Swaaij and Versteeg, 1992):

$$E_{inf} = 1 + \frac{D_{Am}}{D_A}\frac{C_{Am}}{\nu_{Am}}\frac{RT}{m_A P_A} \quad (9)$$

## 4. Experimental

All absorption experiments were performed in a thermostatted stirred cell type reactor operated with a smooth and horizontal gas–liquid interface. The reactor was connected to two gas supply vessels filled with carbon dioxide (99.9%, Hoekloos) or nitrous oxide (>99%, Hoekloos) from gas cylinders. Both the reactor and gas supply vessels were equipped with digital pressure transducers and PT-100 thermocouples. The measured signals were recorded in a computer. The pressure transducer connected to the stirred cell was a Druck PTX-520 pressure transducer (range 0–2 bars) and the gas supply vessels were equipped with Druck PTX-520 pressure transducers (range 0–100 bars). A schematic drawing of the experimental set-up is shown in Fig. 2.

In a typical experiment an MDEA solution with desired concentration was prepared by dissolving a known amount of MDEA (99%, Aldrich) in a known amount water together with a known amount of enzyme solution (human carbonic anhydrase (hCA II) or a thermostable variant of hCA II ('5X' mutant, $CO_2$ Solutions).

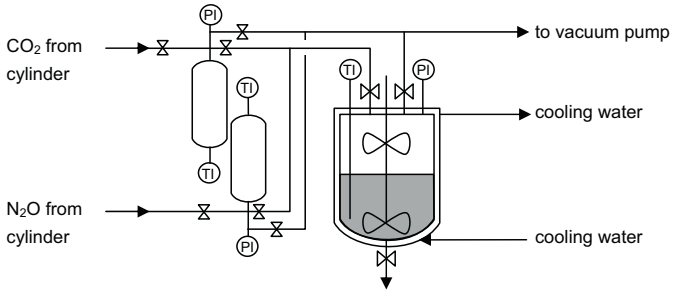


**Fig. 2.** Schematic drawing of the experimental set-up.

Approximately 500 ml of the solution was transferred to the reactor, where inerts were removed by applying vacuum for a short time. Next, the solution was allowed to equilibrate at 298 K before its vapour pressure ($P_{vap}$) was recorded.

### 4.1. Physical absorption

A predefined amount of $N_2O$ was fed to the reactor from the gas bomb. The stirrer in the reactor was switched on, while a flat gas–liquid interface was maintained in the reactor. The stirrer speed was adjusted to 100 rpm. The absorption rate was studied by measuring the pressure decrease as a function of time. After a certain time the stirrer speed was increased to approximately 1000 rpm to reach the equilibrium pressure ($P_{eq}$) in the gas phase. The final temperature and pressure in the gas supply bomb was noted. From the initial and final conditions ($T$ and $P$) in the gas supply system, the amount of gas added to the reactor was calculated.

A mass balance over the gas and liquid phase for $N_2O$ in combination with Eq. (5) yields:

$$\frac{d\ln(P - P_{eq})}{dt} = -\frac{k_L A_{GL}(m_{N_2O}V_L + V_G)}{V_L V_G} \tag{10}$$

The $N_2O$ partial pressure in the reactor was calculated by subtracting the lean liquid's vapour pressure, determined explicitly at the beginning of the experiment, from the recorded total pressure in the reactor.

The liquid side mass transfer coefficient, $k_L$, is determined from the straight line with a constant slope yielded by plotting the ln-term on the left hand of Eq. (10) versus time. The distribution coefficient of $N_2O$ in aqueous MDEA can be calculated from the same experiment by:

$$m_{N_2O} = \left(\frac{C_{N_2O,L}}{C_{N_2O,G}}\right)_{eq} = \frac{P_0 - P_{eq}}{P_{eq} - P_{vap}}\frac{V_G}{V_L} \tag{11}$$

### 4.2. Reactive absorption

The method for the reactive absorption is analogous to the method for physical absorption, only now the gas is $CO_2$ instead of $N_2O$.

A mass balance over the gas phase for $CO_2$ in combination with Eqs. (6) and (7) and obeying Eq. (8) yields:

$$\frac{d\ln P_{CO_2}}{dt} = -\frac{\sqrt{k_{OV}D_{CO_2}}A_{GL}m_{CO_2}}{V_G} \tag{12}$$

The $CO_2$ partial pressure in the reactor was calculated by subtracting the lean liquid's vapour pressure from the recorded total pressure in the reactor.

Typically, a plot of the natural logarithm of the carbon dioxide partial pressure versus time will yield a straight line with a constant slope, from which the overall kinetic rate constant, $k_{OV}$, can be determined, once the required physico-chemical constants are known.

The diffusion coefficient of carbon dioxide in the solution is calculated with the $N_2O$ analogy from the diffusion coefficient of $N_2O$ in the solution taken from Versteeg and van Swaaij (1988b), and the diffusion coefficients of $CO_2$ and $N_2O$ in water were calculated using the correlations given by Jamal (2002).

$$D_{CO_2,Am} = D_{CO_2,water}\frac{D_{N_2O,Am}}{D_{N_2O,water}} \tag{13}$$

The distribution coefficient of carbon dioxide is estimated using the $N_2O$ analogy:

$$m_{CO_2,Am} = m_{CO_2,water}\frac{m_{N_2O,Am}}{m_{N_2O,water}} \tag{14}$$

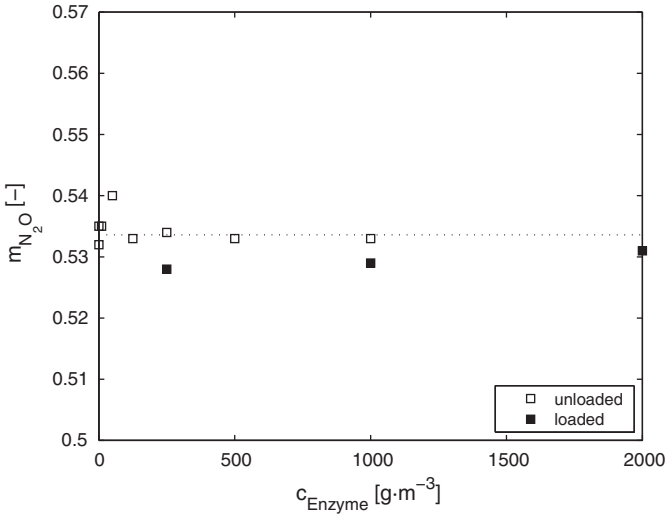


**Fig. 3.** Physical solubility of $N_2O$ in 2 kmol m$^{-3}$ MDEA solution with varying enzyme concentration at 298 K.

The distribution coefficients of $CO_2$ and $N_2O$ in water were calculated using the correlations given by Jamal (2002). The physical solubility of $N_2O$ in aqueous MDEA was experimentally determined for experimental conditions relevant for the present study as described above.

## 5. Results and discussion

### 5.1. Distribution coefficient

To determine the influence of carbonic anhydrase on the physical solubility of nitrous oxide in aqueous MDEA solutions, measurements with and without carbonic anhydrase were performed. Two series of experiments were carried out at 298 K, MDEA concentration of 2 kmol m$^{-3}$ and enzyme concentrations ranging from 0 to 1000 g m$^{-3}$ for freshly prepared solutions and solutions with a $CO_2$-loading of 0.01 mol mol$^{-1}$. The experimental results are presented in Fig. 3. From the experimental data shown in Fig. 3, it can be concluded that, within the experimental accuracy, the physical solubility of nitrous oxide is not influenced by the presence of carbonic anhydrase.

The obtained distribution coefficient is well in line with data found in literature. Mandal et al. (2004) reported a distribution coefficient for $N_2O$ in 2 kmol m$^{-3}$ MDEA of 0.537. Versteeg and van Swaaij (1988b) have derived a polynomial function to calculate the distribution coefficient for various concentrations at 298 K that resulted in a distribution coefficient of 0.549 for a 2 kmol m$^{-3}$ MDEA solution.

### 5.2. Liquid side mass transfer coefficient

Next to the distribution coefficient, the liquid side mass transfer coefficient ($k_L$) is determined for the same set of experiments. The experimental data in Fig. 4 show that for a fresh aqueous MDEA solution the enzyme concentration has some influence on $k_L$; initially $k_L$ decreases and then increases with increasing enzyme concentration. This phenomenon was also observed by others in the case of surfactants or oil-in-water emulsions (Yoshida et al., 1970; van der Meer et al., 1992). However, as soon as the solution is slightly pre-loaded with $CO_2$ (0.01 mol mol$^{-1}$ < $CO_2$-loading <0.05 mol mol$^{-1}$) the presence of enzyme has no influence on $k_L$.

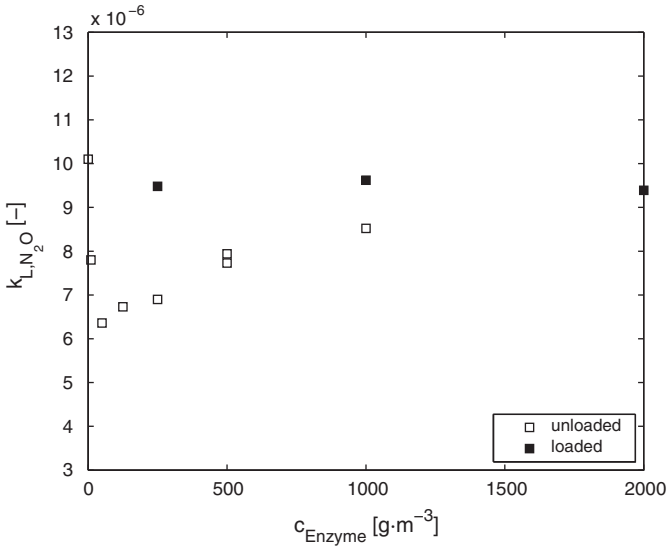


**Fig. 4.** Liquid side mass transfer coefficient of $N_2O$ in 2 kmol m$^{-3}$ MDEA solution with varying enzyme concentration and $CO_2$ loading at 298 K.

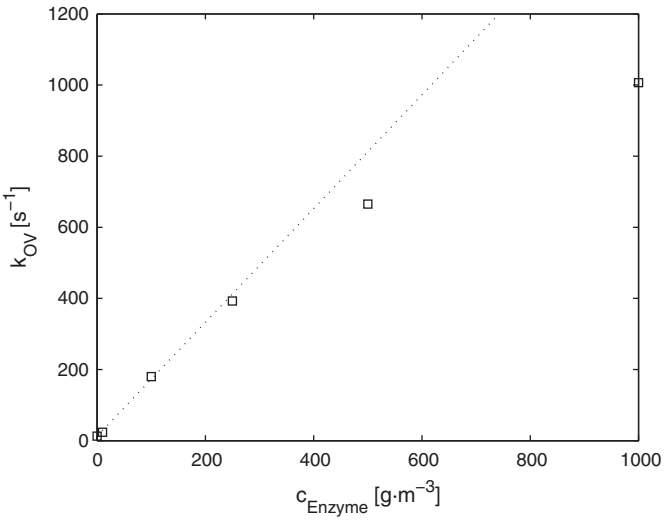


**Fig. 6.** The overall reaction rate constant as function of the enzyme concentration in combination with 2 kmol m$^{-3}$ MDEA at 298 K.

### 5.3. Absorption without enzyme

In order to validate the obtained overall reaction rate constants from experiments without enzyme, the results obtained in this study are compared to data from literature. Most correlations in literature are for the second order reaction rate constant for the amine. By multiplying this constant with the amine concentration as used in the experiment, the corresponding second order overall reaction rate constant is obtained. The correlations of Littel et al. (1990) and Benamor and Aroua (2007) are used to verify the present results. From the data presented in Fig. 5 it can be concluded that the results of this study are well in line with data found in literature.

### 5.4. Absorption with hCA II

The results of the $CO_2$ absorption rate experiments in 2 kmol m$^{-3}$ MDEA with hCA II are presented in Fig. 6. The overall reaction rate constant ($k_{OV}$) is given as a function of the enzyme concentration. From the experimental data, it can be concluded that the overall reaction rate increases significantly with the addition of enzyme, and that the rate increases with an increase in the enzyme concentration. This is in line with results presented by Alper and Deckwer (1980), who used, amongst others, dilute phosphate buffers as proton acceptors. At low enzyme concentration, there appears to be a linear relationship between $k_{OV}$ and the enzyme concentration, which is deviated at higher enzyme concentrations.

Next, the effect of the amine concentration at a given, constant enzyme concentration is studied. The results of these experiments are presented in Fig. 7.

From these results, it can be concluded that the amine concentration has a negligible influence on the obtained overall reaction rate constant as shown in Fig. 8 for aqueous MDEA solutions and hCA II. Therefore, it is unlikely that the enzyme enhances the reaction rate constant of reaction I, $k'_{Am}$, as this constant is linearly dependent on the MDEA concentration (see Eq. (1)).

$$k_{OV} = k_{Am}C_{Am} + k_{OH}C_{OH} + k'_{H_2O} \quad (15)$$

Apparently, MDEA mainly acts as proton acceptor during the regeneration of the enzyme (reaction V). From these results, it can

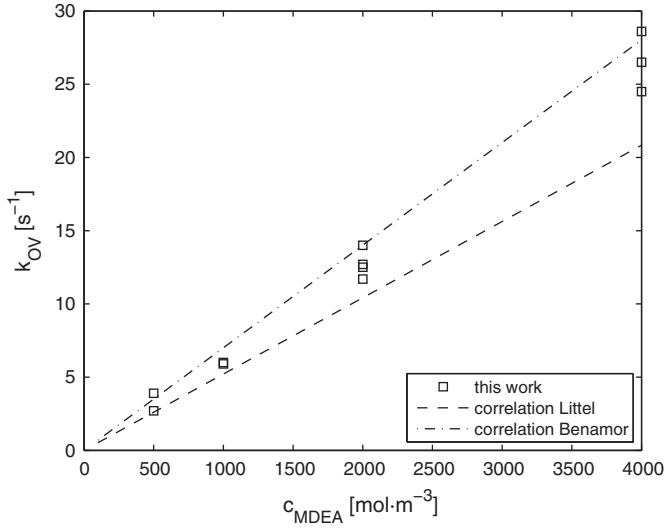


**Fig. 5.** The overall forward reaction rate constant at varying MDEA concentration in the absence of enzyme at 298 K.

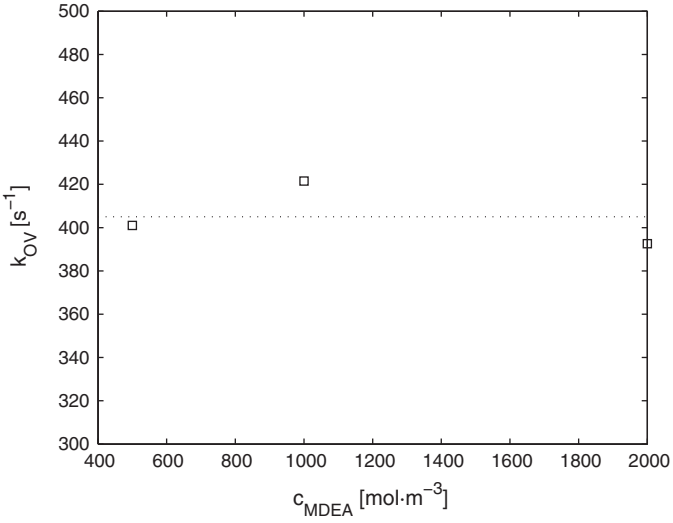


**Fig. 7.** The overall reaction rate constant as function of the MDEA concentration in combination with 250 g m$^{-3}$ hCA II at 298 K.

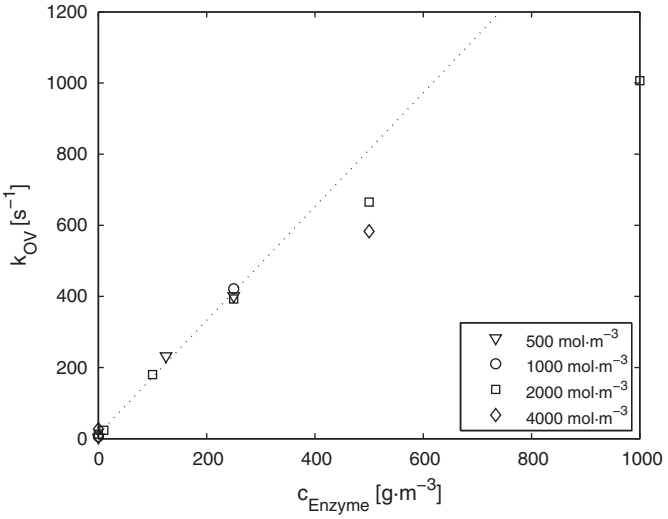


**Fig. 8.** The overall reaction rate constant as function of the hCA II concentration at various MDEA concentrations at 298 K.

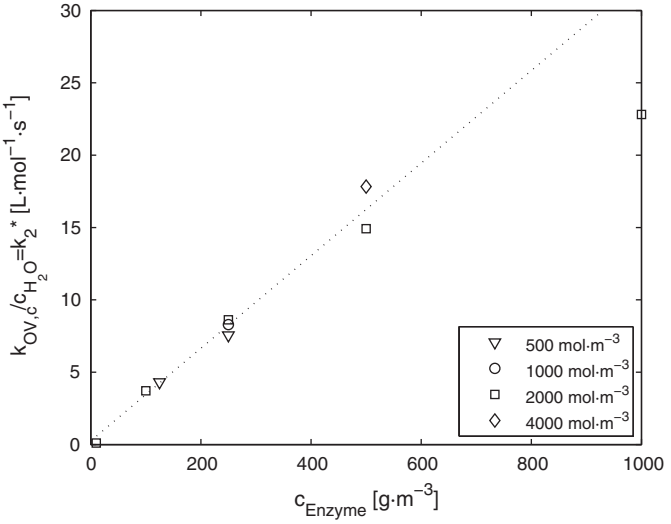


**Fig. 10.** Reaction rate constant $k_2^* = k_{OV,c}/C_{H_2O}$, as function of the hCA II concentration at various MDEA concentrations at 298 K.

be concluded that the intermolecular $H^+$ transport is not rate determining since the rate of this reaction is also dependent on the MDEA concentration.

Therefore, it seems justified to conclude that reactions I and III occur in parallel and that the effect of the presence of the enzyme is taking place via reaction III. The experimentally determined values of $k_{OV}$ are corrected for reaction I via:

$$k_{OV,c} = k_{OV} - k_{Am}C_{Am} \tag{16}$$

where $k_{Am}$ is derived from Fig. 5 for the results obtained in this study, resulting in $k_{Am} = 0.0064 \pm 0.00064\ m^3 mol^{-1} s^{-1}$.

In Fig. 9 the corrected values of $k_{OV}$, i.e. $k_{OV,c}$, are presented for the experiments with hCA II.

These results show that the differences between the various MDEA concentrations are more accentuated; at higher MDEA concentrations, the corrected overall reaction rate constant is lower. On the other hand, it is generally known that with increasing MDEA concentrations, the water concentration decreases. It seems that the reaction has a certain order in water. To eliminate the water concentration from the corrected overall forward reaction rate constant, $k_{OV,c}$ is divided by the water concentration:

$$k_2^* = \frac{k_{OV,c}}{C_{H_2O}} \tag{17}$$

Fig. 10 shows the with Eq. (17) calculated values of $k_2^*$ for the experiments with hCA II.

Fig. 10 shows that the reaction is first order in water. Therefore, the enzyme catalysed absorption of carbon dioxide in aqueous MDEA is first order in $CO_2$ and first order in water for enzyme concentrations lower than 500 g m$^{-3}$. At higher enzyme concentrations, experiments were performed with only one or two MDEA concentrations. Therefore, on basis of these experiments it is not justified to extend this statement to higher enzyme concentrations.

### 5.5. Absorption with 5X CA mutant

The results of the absorption rate experiments of carbon dioxide in 2 kmol m$^{-3}$ MDEA with the 5X CA mutant are presented in Fig. 11. The reaction rate constant $k_2^*$ is given as a function of the enzyme

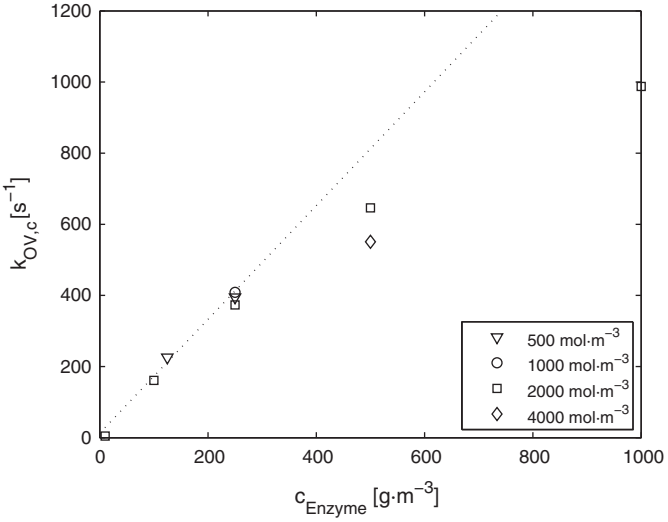


**Fig. 9.** The corrected overall reaction rate constant, $k_{OV,c} = k_{OV} - k_{Am}C_{Am}$, as function of the hCA II concentration at various MDEA concentrations at 298 K.

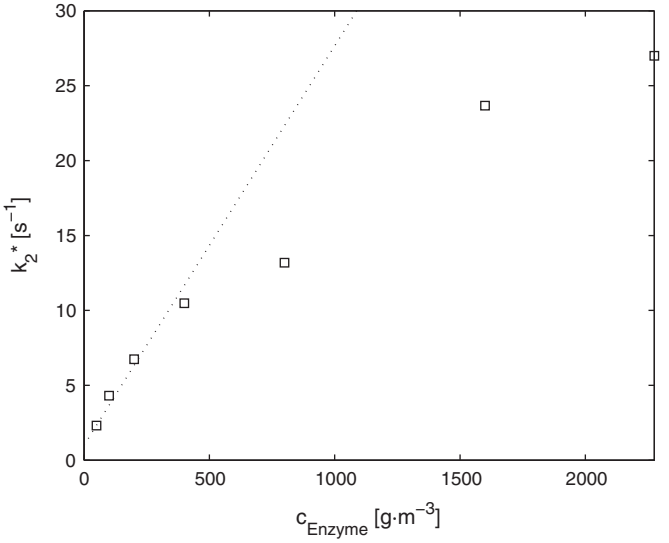


**Fig. 11.** $k_2^*$ as function of the 5X CA mutant concentration in combination with 2 kmol m$^{-3}$ MDEA at 298 K.

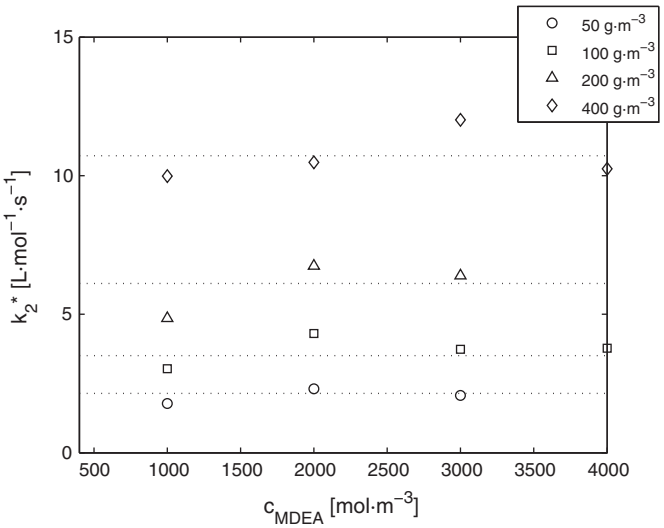


**Fig. 12.** $k_2^*$ as function of the MDEA concentration in combination with 5X CA at 298 K.

concentration. From the experimental data shown in Fig. 11, it can be concluded that the values of $k_2^*$ obtained with 5X CA mutant also increases with increasing enzyme concentration. The activity of the 5X CA seems to be nearly identical to that of hCA II at low enzyme concentrations (directly proportional relationship), however, the deviation from this dependency for the 5X CA begins at lower enzyme concentrations.

When the reaction rate constant $k_2^*$ is presented as a function of the MDEA concentration as shown in Fig. 12, it can be concluded that the MDEA concentration hardly has any influence on the obtained value of $k_2^*$ at a given, constant enzyme concentration. This is in line with the results obtained with hCA II. The statement that enzyme catalysed carbon dioxide absorption into aqueous MDEA is first order in water, is confirmed by the results presented in Figs. 12 and 13, even at enzyme concentrations higher than 500 g m$^{-3}$.

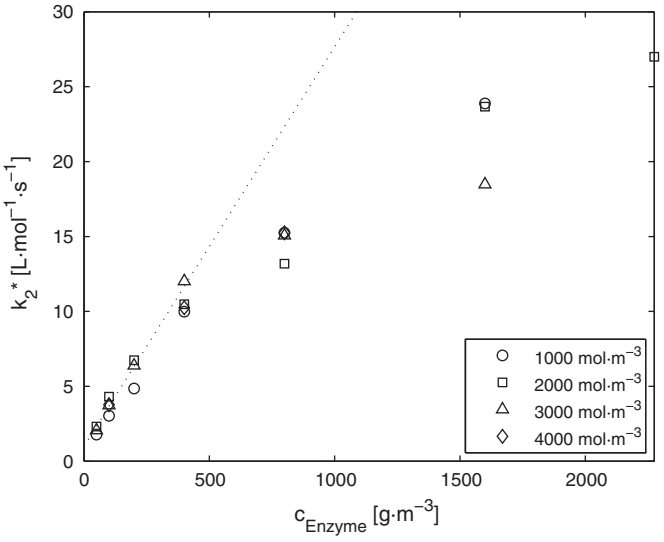


**Fig. 13.** $k_2^*$ as function of the 5X CA concentration in the presence of various MDEA concentrations at 298 K.

## 6. Concluding remarks

These initial studies on the mechanism of enzyme catalysed carbon dioxide absorption into aqueous tertiary alkanolamines showed that the enzyme does not catalyse reaction I, the reaction between $CO_2$ and tertiary alkanolamine, since the overall reaction rate constant is not influenced by the amine concentration. The amine mainly acts as proton acceptor during the regeneration of the enzyme (reaction V). Besides, this study also showed that reactions I and III, $CO_2$ hydrogenation, occur parallel, enzyme enhances reaction III and that reaction III is not only 1st order in $CO_2$, but also 1st order in $H_2O$.

The enzyme carbonic anhydrase significantly increases kinetics of the absorption of carbon dioxide in aqueous MDEA solutions. The absorption rate obtained with a 2000 mol m$^{-3}$ MDEA solution containing 0.25 kg m$^{-3}$ enzyme is comparable with the rate obtained with a mixture of 4000 mol m$^{-3}$ MDEA and 500 or 600 mol m$^{-3}$ piperazine (Bishnoi and Rochelle, 2002; Derks, 2006); only the capacity of the enzymatic solution is less because of the lower amine concentration. Thus, the combination of CA with aqueous MDEA may provide a solution for the efficient capture of carbon dioxide from e.g. flue gases, since MDEA requires less energy for regeneration than MEA, the current industry benchmark.

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