Effect of pKa on the kinetics of carbon dioxide absorption in aqueous alkanolamine solutions containing carbonic anhydrase at 298 K

Nathalie J.M.C. Penders-van Elk a,⇑, Sylvie Fradette b, Geert F. Versteeg c,1

a Procede Gas Treating BV, P.O. Box 328, 7500 AH Enschede, The Netherlands
b CO2 Solutions Inc., 2300 rue Jean-Perrin, Quebec, QC G2C1T9, Canada
c University of Groningen, P.O. Box 72, 9700 AB Groningen, The Netherlands

Highlights
• A Langmuir–Hinshelwood-like equation describes the enzymatic CO2 hydration rate constant.
• The enzymatic CO2 hydration rate increases with increasing pKa value of the amine.
• The enzyme carbonic anhydrase deactivates in diethylethanolamine.
• Brønsted relations exist between the reaction rate constants and the pKa of the amine.

Article info
Article history:
Received 23 April 2014
Received in revised form 1 August 2014
Accepted 2 August 2014
Available online 14 August 2014

Keywords:
Carbon dioxide capture
Carbonic anhydrase
Alkanolamines
Kinetics

ABSTRACT
The absorption of carbon dioxide in various aqueous alkanolamine solutions have been studied with and without carbonic anhydrase respectively in a stirred cell reactor at 298 K. The examined alkanolamines were: N,N-diethylethanolamine (DEMEA), N,N-dimethylethanolamine (DMMEA), monoethanolamine (MEA), triethanolamine (TEA) and tri-isopropanolamine (TIPA). This work confirms that the CO2 hydration is catalysed by the enzyme in presence of alkanolamines. The differences in reaction rate between the tested alkanolamines are attributed to the enzyme regeneration step in the mechanism – that is, an acid base reaction. A Langmuir–Hinshelwood-like equation has been postulated to describe the observed overall rate constant of the enzymatic reaction as a function of the enzyme concentration. The two kinetic constants in the postulated equation both depend exponentially on the pKa value of the alkanolamine present in the solution.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction
Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO2 and H2S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating [1]. An example is the combination of N-methyldiethanolamine (MDEA) and monoethanolamine (MEA) or MDEA and piperazine (PZ) respectively. Here the advantages of MEA or PZ, a fast reacting (primary or secondary) alkanolamine and the lower regeneration energy of MDEA, are combined. However, the main disadvantage is, that MEA and PZ not only act as accelerator but are also consumed during the reactive absorption, and both MEA and PZ form stable carbamates resulting in a high regeneration energy requirement compared to MDEA. In order to maintain the positive effect of the low regeneration energy of MDEA, a real catalyst is preferred above MEA or PZ. On the other hand, better energy performances can also be realised via engineering solutions and modern stripper designs. These methods are usually applicable to all solvents. However, in this paper the focus is on the effect of the solvent characteristics.

The enzyme carbonic anhydrase (CA) is a very efficient catalyst for the interconversion between CO2 and HCO3 [2]. The human CA type II (hCA II) is well known for its large hydration turnover number of approximately 106 s−1 [3] and has been extensively investigated from a biochemical point of view [4,5]. Recently, however, the application of hCA II in CO2 capture technologies has gained attention [6,7].

Penders et al. [8,9] presented the results of a study of carbonic anhydrase in aqueous solutions of MDEA at 298 K. These results...
showed that the enzyme catalysed CO$_2$ hydration is first order in carbon dioxide and first order in water. Moreover, the concentration of MDEA did not affect the enzymatic reaction rate constant. Furthermore, it is known that a proton acceptor is required for enzyme regeneration [10]. In general, the more basic a compound is, the more efficient the abstraction of a proton will be. Therefore it is expected that in enzyme regeneration, the basicity (or pKa value) of the amine will affect the reaction rate.

In this study the effect of several basic compounds, amines, are studied on the observed reaction rates in enzyme catalyzed hydration of CO$_2$. The alkanolamines examined are N,N-diethylethanolamine (DEMEA), N,N-dimethylethanolamine (DMMEA), triethanolamine (TEA), tri-isopropanolamine (TIPA) and monoethanolamine (DEMEA), N,N-dimethylethanolamine (DMMEA), triethanolamine (TEA), tri-isopropanolamine (TIPA) and monoethanolamine (DEMEA), N,N-dimethylethanolamine (DMMEA), triethanolamine (TEA), tri-isopropanolamine (TIPA) and monoethanolamine (DEMEA). With this set of alkanolamines, together with the data available on MDEA, a wide range of pKa and simultaneously a wide range of water concentrations are covered. All experiments were performed at 298 K as the stability of the enzymes is still very good. In future commercial applications higher process temperatures will be encountered but the effect of temperature on kinetics and enzyme stability is not the focus of the present study.

2. Theoretical background

2.1. Mass transfer

The reactive absorption of carbon dioxide in a lean alkanolamine solution can be described as:

\[ J_{CO_2} = m_{CO_2} k_l C_{CO_2} E_{CO_2} \frac{P_{CO_2}}{RT} \]  

(1)

When the reaction occurs in the so-called pseudo first order regime and \( 2 < Ha \ll E_{inf} \), the enhancement factor, \( E_{CO_2} \), equals the Hatta number:

\[ E_{CO_2} = Ha = \frac{\sqrt{k_1 D_{CO_2}}}{k_l} \]  

(2)

where \( E_{inf} \) is the infinite enhancement factor, that for irreversible reactions is defined as [11]:

\[ E_{inf} = 1 + \frac{D_{Am} C_{Am} \frac{RT}{V_{Am} m_{CO_2} P_{CO_2}}} {\sqrt{2 \alpha V_{Am} m_{CO_2} P_{CO_2}}} \]  

(3)

2.2. Kinetics

In aqueous alkanolamine systems carbon dioxide reacts with alkanolamine, hydroxide and water respectively.

Primary (RNH$_2$) or secondary (R$_2$NH) alkanolamines react directly with carbon dioxide forming a carbamate. The reaction mechanism proceeds through the formation of a zwitterion followed by deprotonation by a base [12].

Reaction 1: \( CO_2 + R_2NH \xrightarrow{k_{Am}} R_2N^+HCOO^- \)
\[ R_2N^+HCOO^- + B \xrightarrow{k_b} R_2NCOO^- + BH^+ \]

For this mechanism, the overall forward reaction rate is given by:

\[ R_{CO_2} = - \frac{C_{CO_2} C_{R2NH}}{V_{Am} + \sum (k_b C_b)} \]  

(4)

In lean aqueous solutions, either water, hydroxide or alkanolamine may act as bases. In the case of an aqueous MEA solution, \( 1/k_{Am} \) is significantly larger than the second term in denominator, whereby Eq. (4) reduces to:

\[ R_{CO_2} = k_{Am} C_{Am} C_{CO_2} \]  

(5)
Tertiary alkanolamines (R3N) are not able to react directly with carbon dioxide; they react through base catalysis of the carbon dioxide hydration reaction [13]:

\[ \text{Reaction II : } \text{CO}_2 + \text{R}_3\text{N} + \text{H}_2\text{O} \xrightleftharpoons{\text{k}_{\text{Am}}} \text{HCO}_3^- + \text{R}_3\text{NH}^+ \]

The overall forward reaction rate for this reaction is given by [14–16]:

\[ R_{\text{CO}_2} = k_{\text{Am}}C_{\text{Am}}C_{\text{CO}_2} \quad (6) \]

In basic solutions CO2 reacts with hydroxide [17,18]:

\[ \text{Reaction III : } \text{CO}_2 + \text{OH}^- \xrightleftharpoons{\text{k}_{\text{OH}}} \text{HCO}_3^- \]

with the following overall forward reaction rate:

\[ R_{\text{CO}_2} = k_{\text{OH}}C_{\text{OH}}C_{\text{CO}_2} \quad (7) \]

Also, water reacts with CO2 [17,19]:

\[ \text{Reaction IV : } \text{CO}_2 + 2\text{H}_2\text{O} \xrightleftharpoons{\text{k}_{\text{H}_2\text{O}}} \text{H}_2\text{CO}_3^- + \text{H}_3\text{O}^+ \]

with the following overall forward reaction rate:

\[ R_{\text{CO}_2} = k_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}C_{\text{CO}_2} \quad (8) \]

Since all these reactions occur simultaneously, the overall forward reaction rate of this system becomes:

\[ R_{\text{CO}_2} = k_{\text{Am}}C_{\text{Am}}C_{\text{CO}_2} + k_{\text{OH}}C_{\text{OH}}C_{\text{CO}_2} + k_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}C_{\text{CO}_2} = k_{\text{OV}}C_{\text{CO}_2} \quad (9) \]

where

\[ k_{\text{OV}} = k_{\text{Am}}C_{\text{Am}} + k_{\text{OH}}C_{\text{OH}} + k_{\text{H}_2\text{O}} \quad (10) \]

It has been shown in literature [20] that for aqueous alkanolamine solutions, the contribution of reactions III and IV can be negligible. As a result, Eq. (10) reduces to:

\[ k_{\text{OV}} = k_{\text{Am}}C_{\text{Am}} \quad (11) \]

In the presence of the enzyme carbonic anhydrase the following wheel of reactions is added to the above mentioned reactions:

The base (B) in enzyme regeneration can either be an alkanolamine or even the in Reaction II, III or IV formed bicarbonate ion [21]. In the latter case, carbon dioxide and water are released as protonated base.

The overall forward reaction rate for the enzyme catalysed reaction is [8]:

\[ R_{\text{CO}_2} = k_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}C_{\text{Am}} \quad (12) \]

2.3. pKa

In literature several authors have shown that a Brønsted relation exists between \( k_{\text{Am}} \) and the acid strength, pKa, of the amine [15,22,23]. For primary and secondary amines the correlation is [12]:

\[ \ln (k_{\text{Am}}) = 1.0\text{pKa} + 16.26 - \frac{7188}{T} \quad (13) \]

and for tertiary amines the correlation is [20]:

\[ \ln (k_{\text{Am}}) = 1.3\text{pKa} + 11.48 - \frac{8270}{T} \quad (14) \]

The pKa values of the alkanolamines studied in this work are presented in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Amine</th>
<th>pKa (–)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEMEA</td>
<td>9.75</td>
<td>[24]</td>
</tr>
<tr>
<td>DMMEE</td>
<td>9.22</td>
<td>[24]</td>
</tr>
<tr>
<td>MDEA</td>
<td>8.56</td>
<td>[25]</td>
</tr>
<tr>
<td>MEA</td>
<td>9.45</td>
<td>[24]</td>
</tr>
<tr>
<td>TEA</td>
<td>7.74</td>
<td>[24]</td>
</tr>
<tr>
<td>TIPA</td>
<td>7.82</td>
<td>[25]</td>
</tr>
</tbody>
</table>

3. Experimental

3.1. Set-up

The experiments were carried out in a thermostated stirred cell reactor that was operated with a smooth horizontal gas–liquid interface. The operation was batch wise with respect to the gas and liquid phase. Both the reactor and the gas supply vessels were equipped with PT-100 thermocouples and digital pressure transducers. The stirred cell was equipped with a Druck PTX-520 pressure transducer (range 0–2 bara) and the gas supply vessels were equipped with Druck PTX-520 pressure transducers (range 0–100 bara). The experimental set-up is shown in Fig. 1.

3.2. Materials

The purity of all tested alkanolamines was ≥98%. DEMEA, DMMEA, MEA and TEA were supplied by Sigma-Aldrich, while TIPA was supplied by Acros Organics. All alkanolamines have been used as supplied. The enzyme used was a thermostable variant of the human carbonic anhydrase (5X CA) provided by CO2 Solutions Inc. All solutions have been prepared with demineralised water. The carbon dioxide (99%) and nitrous oxide (>99%) used for absorption, were obtained from Hoekloos.

3.3. Procedure

The experimental procedure has been described in detail by Penders et al. [8]. In the present study, all experiments were performed at 298 K.

3.3.1. Overall forward kinetic rate constant

A carbon dioxide balance over the gas phase in combination with Eqs. (1) and (2) gives for a pseudo first order reaction:

\[ \frac{d\ln P_{\text{CO}_2}}{dt} = \frac{A_{\text{Am}}m_{\text{CO}_2,\text{Am}}V_{\text{G}}}{V_{\text{C}}} \quad (15) \]

A logarithmic plot of the carbon dioxide partial pressure versus time will result in a straight line. From the slope of this line, the overall kinetic rate constant, \( k_{\text{OV}} \), can be determined when the physico-chemical constants \( m_{\text{CO}_2} \) and \( D_{\text{CO}_2} \) are known.
3.3.2. Distribution coefficient

The distribution coefficient of carbon dioxide in the alkanolamine solution, $m_{\text{CO}_2,\text{Am}}$, is estimated using the N$_2$O analogy\[22\]:

$$m_{\text{CO}_2,\text{Am}} = m_{\text{N}_2\text{O, Am}} m_{\text{CO}_2,\text{water}} m_{\text{N}_2\text{O, water}}$$

(16)

The correlation of Versteeg and van Swaaij\[22\] has been used to calculate the ratio of distribution coefficients of CO$_2$ and N$_2$O in water. The physical solubility of N$_2$O in aqueous TIPA has been determined experimentally, whereas the physical solubility of the other alkanolamines has been taken from literature (see Table 2).

### Table 2

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_{\text{Am}}$ (mol m$^{-3}$)</th>
<th>$m_{\text{N}_2\text{O, Am}}$ (–)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEMEA</td>
<td>1000</td>
<td>0.560$^1$</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>0.536$^1$</td>
<td>[27]</td>
</tr>
<tr>
<td>DMMEA</td>
<td>1000</td>
<td>0.582$^1$</td>
<td>[22,27]</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>0.544$^1$</td>
<td>[22,27]</td>
</tr>
<tr>
<td>MEA</td>
<td>100</td>
<td>0.606$^2$</td>
<td>[28]</td>
</tr>
<tr>
<td>TEA</td>
<td>1000</td>
<td>0.567$^1$</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>0.521$^1$</td>
<td>[27]</td>
</tr>
<tr>
<td>TIPA</td>
<td>1000</td>
<td>0.540</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>0.495</td>
<td>This study</td>
</tr>
</tbody>
</table>

$^1$ Interpolated from the experimental data.
$^2$ Calculated with presented equation.

3.3.3. Diffusivity

Since the diffusion coefficient of carbon dioxide, $D_{\text{CO}_2,\text{Am}}$, for most of the tested alkanolamines has yet not been published in literature, it is therefore estimated from the solution's dynamic viscosity, $\eta_{\text{Am}}$, using a modified Stokes–Einstein equation\[22\]:

$$D_{\text{CO}_2,\text{Am}} = D_{\text{CO}_2,\text{water}} \left(\frac{\eta_{\text{water}}}{\eta_{\text{Am}}}\right)^{0.8}$$

(17)

The diffusion coefficient of CO$_2$ in water is calculated using the correlation given by Jamal\[28\]:

$$D_{\text{CO}_2,\text{water}} = 3.7191 \times 10^{-6} \exp\left(-\frac{-2257.9}{T}\right)$$

(18)

The viscosity of water is taken from Perry’s Chemical Engineers’ Handbook\[29\]. The viscosity of TIPA is measured using Ubbelohde viscometers. The viscosity for the other tested alkanolamines has been taken from literature (see Table 3).

### Table 3

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_{\text{Am}}$ (mol m$^{-3}$)</th>
<th>$\eta_{\text{Am}}$ (mPa s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEMEA</td>
<td>1000</td>
<td>1.53$^1$</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>2.77$^1$</td>
<td>[30]</td>
</tr>
<tr>
<td>DMMEA</td>
<td>1000</td>
<td>1.22$^1$</td>
<td>[22,27]</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>1.82$^1$</td>
<td>[22,27]</td>
</tr>
<tr>
<td>MEA</td>
<td>100</td>
<td>0.907$^1$</td>
<td>[31]</td>
</tr>
<tr>
<td>TEA</td>
<td>1000</td>
<td>1.64$^1$</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>2.67$^1$</td>
<td>[31]</td>
</tr>
<tr>
<td>TIPA</td>
<td>1000</td>
<td>2.07</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>5.54</td>
<td>This study</td>
</tr>
</tbody>
</table>

$^1$ Interpolated from the experimental data.

3.3.4. Kinetic rate constant for the enzyme catalysed reaction

The enzymatic rate constant, $k_{H_2O}$, can be determined from the overall kinetic rate constant according to:

$$k_{H_2O} = k_{D\text{V, with enzyme}} - k_{D\text{V, without enzyme}}$$

(19)

4. Results

Previous studies with MDEA\[8,9\] showed that the enzyme catalysed CO$_2$ hydration is first order in carbon dioxide and first order in water respectively. To get a better understanding of the enzyme kinetics with respect to the influence of different alkanolamines, additional experiments were carried out with TEA, TIPA, DMMEA, DEMEA and MEA. The results of these experiments are described in the next subsections.

4.1. TEA

TEA has a lower pKa than MDEA and hence a lower reactivity towards carbon dioxide compared to MDEA. The molecular weight of TEA is higher than that of MDEA, thereby resulting in a larger variation in water concentration.

The TEA concentrations and corresponding water concentrations are presented in Table 4. Also, the second order kinetic rate constants, $k_{Am}$, of the reaction between TEA and CO$_2$ measured in solutions without the enzyme are given in this table.

The forward reaction rate constant, $k_{Am}$, in absence of enzyme, as reported in Table 4, is in line with $k_{Am}$ values published in literature which vary between 2.7 and 3.3·10$^{-3}$ m$^2$ mol$^{-1}$ s$^{-1}$\[20,23,32,33\] and with the $k_{Am}$ of 2.0·10$^{-3}$ m$^2$ mol$^{-1}$ s$^{-1}$ as calculated with Eq. (14). It should be noted that the value of $k_{Am}$ for tertiary amines is very sensitive for the purity of the amine\[12\].
Therefore, in the derivation of \( k'_{\text{H}_2\text{O}} \) from the measured \( k_{\text{OV}} \), the average value of \( k_{\text{Am}} \) (2.4 \( \cdot 10^{-3} \) m\(^3\) mol\(^{-1}\) s\(^{-1}\)) measured in this study was used.

Fig. 2, presenting the \( k_{\text{OV}} \) measured in this study, shows that the enzyme increases the CO\(_2\) absorption rate significantly. In this figure it can be seen that the \( k_{\text{OV}} \) for a 1000 mol m\(^{-3}\) TEA solution with 0.4 kg m\(^{-3}\) enzyme is approximately 250 s\(^{-1}\) which is about 100 times higher than the \( k_{\text{OV}} \) for TEA alone which equals 2.4 s\(^{-1}\) (see Table 4).

Fig. 3 illustrates that \( k'_{\text{H}_2\text{O}} \) increases non-linear with increasing enzyme concentration. At enzyme concentrations \( \geq 0.4 \) kg m\(^{-3}\) the measured \( k'_{\text{H}_2\text{O}} \) in the 2000 mol m\(^{-3}\) solution is lower than in the 1000 mol m\(^{-3}\) solution. For every enzyme concentration tested, the absorption rate of CO\(_2\) into the 4000 mol m\(^{-3}\) solution is substantially lower than that into the 2000 mol m\(^{-3}\) solution. This indicates that TEA has an effect on the activity of the enzyme. At higher TEA concentration it seems that the enzyme is deactivated at such an extent that it affects the experimental results. In order to validate this assumption, experiments were carried out with TEA solutions in which the enzyme was added and stored overnight before the experiment was carried out. It turned out that the remaining enzyme activity was far less than those compared to freshly prepared solutions. Therefore, experiments with the 2000 and 4000 mol m\(^{-3}\) TEA solutions in combination with enzyme have been excluded during the analysis of the results. It is likely that experiments at 1000 mol m\(^{-3}\) TEA are also affected to some extent.

### 4.2. TIPA

The pKa value of TIPA is lower than that of MDEA, and comparable to that of TEA. Hence, the reactivity towards carbon dioxide will be lower than in MDEA. Since the molecular weight of TIPA is larger than that of TEA, the variation in water concentration is not negligible in this set of experiments.

The TIPA concentrations and corresponding water concentrations are presented in Table 5. In addition, the measured second-order kinetic rate constants of the reaction between TIPA and CO\(_2\) in absence of the enzyme, \( k_{\text{Am}} \), are listed in the table. Due to the high viscosity of the aqueous TIPA solutions, only experiments were done with 1000 mol m\(^{-3}\) and 2000 mol m\(^{-3}\) solutions.

The \( k_{\text{Am}} \) as measured during the absorption experiments without enzyme is lower than that calculated with Eq. (14) (i.e. 2.3 \( \cdot 10^{-3} \) mol m\(^{-1}\) s\(^{-1}\)). Unfortunately, no data published in open literature are available for TIPA. As the \( k_{\text{Am}} \) measured with other alkanolamines in this study, e.g. TEA, are in line with literature and with Eq. (14) and this amine was not used in the determination of Eq. (14), it is well possible that due to the bulkiness of the amine the kinetics is slower than with the less hindered amines. In the calculation of \( k'_{\text{H}_2\text{O}} \), the average \( k_{\text{Am}} \) (0.88 \( \cdot 10^{-3} \) m\(^3\) mol\(^{-1}\) s\(^{-1}\)) is used.

The forward reaction rate constants of the enzymatic CO\(_2\) hydration, \( k'_{\text{H}_2\text{O}} \), in aqueous TIPA solutions are presented in Fig. 4. The plot shows that the reaction rate increases with increasing enzyme concentration. At low enzyme concentration there seems to be a linear dependency; however, at enzyme concentrations larger than 0.2 kg m\(^{-3}\) the increase starts to level off. As observed with MDEA [8], in TIPA the measured \( k'_{\text{H}_2\text{O}} \) is independent of the amine concentration. Therefore, it seems justified to conclude that no loss of enzyme activity is observed.

### 4.3. DMMEA

DMMEA is a tertiary alkanolamine with a higher pKa value than MDEA – and hence a higher reactivity towards carbon dioxide.

The DMMEA concentrations, corresponding water concentrations and the second-order kinetic rate constants of the reaction

Table 5

<table>
<thead>
<tr>
<th>C(_{\text{H}_2\text{O}}) (mol m(^{-3}))</th>
<th>C(_{\text{Am}}) (mol m(^{-3}))</th>
<th>( k_{\text{Am}} ) (m(^3) mol(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>45500</td>
<td>(1.0 ( \pm 0.1 )) ( \cdot 10^{-3} )</td>
</tr>
<tr>
<td>2000</td>
<td>35500</td>
<td>(0.79 ( \pm 0.07 )) ( \cdot 10^{-3} )</td>
</tr>
</tbody>
</table>
Fig. 4. Forward reaction rate constant, $k_{H2O}$, as a function of the enzyme concentration for aqueous TIPA solutions.

**Table 6**

<table>
<thead>
<tr>
<th>C_{DEMEA} (mol m$^{-3}$)</th>
<th>C_{H2O} (mol m$^{-3}$)</th>
<th>$k_{Am}$ (m$^3$ mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>50100</td>
<td>(19.1 ± 3.8) · 10$^{-3}$</td>
</tr>
<tr>
<td>2000</td>
<td>45400</td>
<td>(18.6 ± 1.0) · 10$^{-3}$</td>
</tr>
</tbody>
</table>

between DMMEA and CO$_2$ – $k_{Am}$ – as measured in this study, are presented in Table 6. The measured $k_{Am}$ corresponds to that calculated from the relation published by Littel et al. [15], i.e. $17.2 · 10^{-3}$ m$^3$ mol$^{-1}$ s$^{-1}$, and is slightly higher than that calculated from Eq. (14), i.e. $14.0 · 10^{-3}$ m$^3$ mol$^{-1}$ s$^{-1}$.

The measured $k_{Am}$ ($18.9 · 10^{-3}$ m$^3$ mol$^{-1}$ s$^{-1}$) is used in the determination of $k_{H2O}$.

The $k_{H2O}$ derived from the results of the absorption experiments with DMMEA are presented in Fig. 5. This figure shows that $k_{H2O}$ is independent of the DMMEA concentration, therefore it is reasonable to suggest that no enzyme activity loss is observed. Furthermore, Fig. 5 illustrates that $k_{H2O}$ increases with 5X CA concentration. Up to an enzyme concentration of 0.2 kg m$^{-3}$ the increase seems linear.

**Table 7**

<table>
<thead>
<tr>
<th>C_{DEMEA} (mol m$^{-3}$)</th>
<th>C_{H2O} (mol m$^{-3}$)</th>
<th>$k_{Am}$ (m$^3$ mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>52000</td>
<td>(31.5 ± 4.4) · 10$^{-3}$</td>
</tr>
<tr>
<td>1000</td>
<td>48600</td>
<td>(35.6 ± 3.7) · 10$^{-3}$</td>
</tr>
</tbody>
</table>

**4.4. DEMEA**

DEMEA is a tertiary alkanolamine with even a higher pKa than DMMEA – and hence a higher reactivity towards carbon dioxide. The molecular weight of DEMEA is comparable to MDEA.

Table 7 presents the DEMEA concentrations, corresponding water concentrations and the measured second-order kinetic rate constants of the reaction between DEMEA and CO$_2$, $k_{Am}$.

The measured values of $k_{Am}$ are well in line with data published in literature, which varied between 21.3 and $43.4 · 10^{-3}$ m$^3$ mol$^{-1}$ s$^{-1}$ [15,23] and that calculated with Eq. (14), i.e. $27.8 · 10^{-3}$ m$^3$ mol$^{-1}$ s$^{-1}$. In the calculation of $k_{H2O}$, the average of the measured $k_{Am}$ ($33.1 · 10^{-3}$ m$^3$ mol$^{-1}$ s$^{-1}$) is used.

The measured rate constant obtained with aqueous DEMEA are presented in Fig. 6. Comparison of Figs. 5 and 6 shows that although DEMEA has a higher pKa and higher $k_{Am}$, the $k_{H2O}$ is substantially lower than in the DMMEA solutions.

From preliminary experiments with hCA II it was concluded that the enzyme activity decreases in aqueous DEMEA solutions. Stability tests conducted by CO$_2$ Solutions have also confirmed that 5X CA is not stable in aqueous DEMEA. Therefore the results of DEMEA have been excluded from the analysis. In order to have access to data for high pKa, additional experiments with MEA were performed.

**4.5. MEA**

Since MEA is a primary alkanolamine, the reactivity of MEA towards carbon dioxide is substantially higher than any of the tested tertiary alkanolamines. In order to have a significant difference between the overall forward rate constant with and that without enzyme, the MEA concentration used in these tests is much lower than that of the tertiary alkanolamines in previous tests. MEA has a higher pKa-value than DMMEA but, unfortunately, lower than DEMEA. MEA has the lowest molecular weight of the
alkanolamines tested. This, coupled with the low MEA concentration, results in a rather high water concentration. The MEA concentration, corresponding water concentration and the second order kinetic rate constant of the reaction between MEA and carbon dioxide, \( k_{Am} \), as measured are presented in Table 8.

The measured value of \( k_{Am} \) is well in line with that calculated from the relation published by Versteeg et al. [20], i.e. 6.0 m³ mol⁻¹ s⁻¹, and slightly higher than the one calculated from Eq. (13), i.e. 5.0 m³ mol⁻¹ s⁻¹.

Comparison of Figs. 5–7 shows that the \( k_{C3H2O} \) for MEA is higher than for DEMEA and comparable to DMMEA.

5. Discussion

Penders-van Elk et al. [8] showed that the enzyme catalyses the CO₂ hydration, i.e. Reaction IV. This reaction is the same for all tested alkanolamines. For all tested alkanolamines, the dependency between \( k_{C3H2O} \) and the enzyme concentration is linear at low enzyme concentration and that this linear dependency is deviated at higher enzyme concentrations. This observation can be described e.g. with the following Langmuir–Hinshelwood-like equation:

\[
\frac{1}{k_{C3H2O}} = \frac{1}{k_1} \frac{1}{C_{Enzyme}} + \frac{1}{k_2}
\]

Taking the reciprocal of Eq. (20) gives:

\[
\frac{1}{k_{C3H2O}} = \frac{1}{k_1} \frac{1}{C_{Enzyme}} + \frac{1}{k_2}
\]

For the determination of the kinetic constants \( k_1 \) and \( k_2 \), two methods have been used:

1. Eq. (20) in combination with non linear regression.
2. Eq. (21) in combination with linear regression (the Lineweaver–Burk method).

5.1. Non-linear regression

The non-linear regression method used in the present study is the non-linear least squares. For the experimental data of MDEA, this method resulted in following kinetic constants: \( k_1 = 0.040 \text{ m}^3 \text{ mol}^{-1} \text{ kg}^{-1} \text{ s}^{-1} \) with a standard error (SE) of 0.005 and \( k_2 = 1.1 \text{ m}^3 \text{ kg}^{-1} \) with SE = 0.2. The results of the fitting with the non-linear regression method are presented in Fig. 8.

Fig. 8 shows, that at high enzyme concentration the measured \( k_{C3H2O} \) is predicted well, however at low enzyme concentration the measured \( k_{C3H2O} \) is slightly underestimated. The average absolute deviation (AAD) is 13%, calculated from:

<table>
<thead>
<tr>
<th>Amine</th>
<th>Amine</th>
<th>( k_1 (\text{m}^3 \text{ mol}^{-1} \text{ kg}^{-1} \text{ s}^{-1}) )</th>
<th>( k_2 (\text{m}^3 \text{ kg}^{-1}) )</th>
<th>AAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>7.74</td>
<td>0.027 (0.0031)</td>
<td>2.6 (0.52)</td>
<td>7</td>
</tr>
<tr>
<td>TIPA</td>
<td>7.82</td>
<td>0.028 (0.0031)</td>
<td>0.88 (0.26)</td>
<td>12</td>
</tr>
<tr>
<td>MDEA</td>
<td>8.56</td>
<td>0.034 (0.0047)</td>
<td>1.1 (0.25)</td>
<td>13</td>
</tr>
<tr>
<td>DMMEA</td>
<td>9.22</td>
<td>0.058 (0.0022)</td>
<td>0.13 (0.032)</td>
<td>8</td>
</tr>
<tr>
<td>MEA</td>
<td>9.45</td>
<td>0.059 (0.0026)</td>
<td>0.17 (0.029)</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 8

Water concentration and second order rate constant for MEA at tested concentration.

<table>
<thead>
<tr>
<th>( C_{MEA} ) (mol m⁻³)</th>
<th>( C_{H2O} ) (mol m⁻³)</th>
<th>( k_{Am} ) (m³ mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>55000</td>
<td>6.4 ± 1.5</td>
</tr>
</tbody>
</table>

Fig. 7. Forward reaction rate constant, \( k_{H2O} \), as a function of the enzyme concentration for in 100 mol m⁻³ MEA solutions.

Fig. 8. Experimental data of MDEA and the calculated \( k_{H2O} \) (dashed line) versus the 5X CA mutant concentration. The dotted lines in the left plot represent the confidence interval.
Analogously, $k_3$ and $k_4$ have been determined for TEA, TIPA, DMMEA, and MEA. The results for $k_3$ and $k_4$ are presented in Table 9.

5.1.1. Brønsted relationship

Since Reaction IV is the same for all tested alkanolamines, the difference in absorption rate can only be explained by a difference in the regeneration rate of the enzyme. Given that the enzyme regeneration is an acid base reaction, it is likely that a Brønsted relation exists between the forward rate constants, $k_3$ and $k_4$, and the acid strength, $pK_a$, of the alkanolamine. In literature, several authors showed that a Brønsted relation exists between the $k_{Am}$ and $pK_a$ of the amine\[15,22,23,34\] for the uncatalysed CO$_2$ absorption. In Fig. 9, Brønsted plots of $k_3$ (left plot) and $k_4$ (right plot) are shown.

From the Brønsted plot of $k_3$, the relation between the kinetic constant $k_3$ and the $pK_a$ of the alkanolamine in the absorbing solution can be determined from:

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^{n} \frac{|k_{H_2O,calc} - k_{H_2O,exp}|}{k_{H_2O,exp}} \times 100\% \tag{22}$$

Analogously, $k_4$ and $k_3$ have been determined for TEA, TIPA, DMMEA, and MEA. The results for $k_3$ and $k_4$ are presented in Table 9.
and the pKa within 50% as shown in Fig. 13. The average deviation is 8.5 for TEA, TIPA, DMMEA and MEA have been determined. The results for these two sets of data, the rate constants \( k_3 \) and \( k_4 \) obtained with linear regression are plotted as function of the corresponding pKa-value (Fig. 12).

To analyse the Brønsted relations for these two sets of data, the pKa-values, the slopes (1/\( k_4 / k_3 \)) together with their standard errors between parentheses, the derived kinetic constants \( k_3 \) and \( k_4 \) and the deviation of \( k_{H2O} \) as calculated from Eq. (22) for the analysed alkanolamines.

Table 10

<table>
<thead>
<tr>
<th>Amine</th>
<th>pKa</th>
<th>( 1/k_4 ) (mol kg s (^{-6}))</th>
<th>( k_3/k_4 ) (mol s (^{-3}))</th>
<th>( k_3 ) (mol (^6) kg (^{-1}) s (^{-1}))</th>
<th>( k_4 ) (m(^3) kg (^{-1}))</th>
<th>AAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>7.74</td>
<td>25 (3.4)</td>
<td>148 (35)</td>
<td>0.041</td>
<td>6.0</td>
<td>13</td>
</tr>
<tr>
<td>TIPA</td>
<td>7.82</td>
<td>28 (2.4)</td>
<td>51 (25)</td>
<td>0.036</td>
<td>1.8</td>
<td>10</td>
</tr>
<tr>
<td>MDEA</td>
<td>8.56</td>
<td>19 (0.95)</td>
<td>41 (8.5)</td>
<td>0.053</td>
<td>2.2</td>
<td>11</td>
</tr>
<tr>
<td>DMMEA</td>
<td>9.22</td>
<td>15 (0.59)</td>
<td>4.6 (6.4)</td>
<td>0.065</td>
<td>0.30</td>
<td>6</td>
</tr>
<tr>
<td>MEA</td>
<td>9.45</td>
<td>17 (0.43)</td>
<td>3.2 (6.2)</td>
<td>0.060</td>
<td>0.19</td>
<td>2</td>
</tr>
</tbody>
</table>

\[
\ln(k_3) = 0.48 \cdot \text{pKa} - 7.3
\]  \hspace{1cm} (23)

The relation between the kinetic constant \( k_3 \) and the pKa of the alkanolamine in the absorbing solution is given as:

\[
\ln(k_4) = -1.5 \cdot \text{pKa} + 12.2
\]  \hspace{1cm} (24)

Substituting Eqs. (23) and (24) in Eq. (20) fits the presented data for \( k_{H2O} \) within 50% accuracy (see Fig. 10). The average deviation is 19%. This can be considered a good fit with respect to the pKa-range, experimental error inherent to the experimental method and limited number of experiments. Moreover, the results may be (slightly) affected by deactivation of the enzyme to different extents for the various solvents.

5.2. Linear regression

As the combination of \( k_3 \) and \( k_4 \) can vary with the fitting method [35–37], a second method is used. The application of linear regression using Eq. (21) and the data of MDEA resulted in a second set of the kinetic constants \( k_3 \) and \( k_4 \). The results of this fitting are presented in Fig. 11.

Fig. 11 shows, that at low enzyme concentration the measured \( k_{H2O} \) is predicted well, however at high enzyme concentration the measured \( k_{H2O} \) is clearly underestimated. For this set of kinetic constants the average absolute deviation is 11%.

Analogously, \( k_3 \) and \( k_4 \) for TEA, TIPA, DMMEA and MEA have been determined. The results for \( k_3 \) and \( k_4 \) together with the deviation of the fitted \( k_{H2O} \) are presented in Table 10.

To analyse the Brønsted relations for these two sets of data, the rate constants \( k_3 \) and \( k_4 \) obtained with linear regression are plotted as function of the corresponding pKa-value (Fig. 12).

Based on the Brønsted plot for \( k_3 \) presented in the left plot of Fig. 12, the relation between the kinetic constant \( k_3 \) and the pKa of the alkanolamine can be determined from:

\[
\ln(k_3) = 0.31 \cdot \text{pKa} - 5.6
\]  \hspace{1cm} (25)

The relation between the kinetic constant \( k_4 \) and the pKa of the alkanolamine in the absorbing solution is best estimated with:

\[
\ln(k_4) = -1.7 \cdot \text{pKa} + 14.7
\]  \hspace{1cm} (26)

Substitution of Eqs. (25) and (26) in Eq. (20) fit the experimental data for \( k_{H2O} \) within 50% as shown in Fig. 13. The average deviation is 17%.

Both fitting methods resulted in the same conclusion with respect to pKa dependency.
6. Conclusion

This study on the mechanism of enzyme catalysed carbon dioxide absorption into aqueous alkanolamine solutions confirmed that the CO₂ hydration is catalysed by the enzyme. The differences in reaction rates are explained by differences in enzyme regeneration rate in that the enzyme regeneration is an acid-base reaction.

In this study a Langmuir–Hinshelwood-like equation is applied to describe the observed behaviour [9]. At low enzyme concentrations the kinetic constant \( k_{1,CO_2} \) is proportional to the enzyme concentration, whereas at high enzyme concentration this proportionality is deviated. With this equation two kinetic constants are introduced, \( k_1 \) and \( k_2 \). Two methods were used to derive these two kinetic constants from the experimental data, (1) non-linear regression on the unmodified equation and (2) linear regression on the reciprocal of the equation.

The two regression methods resulted in different sets of \( k_1 \) and \( k_2 \) with similar average deviations between model and experiments. It was not possible to have a perfect fit over the whole enzyme concentration range which might be due to the fact that the approximation of the mechanism by a Langmuir–Hinshelwood type of equation is not completely justified. Also it might be possible that the range of enzyme concentrations was too small and also some enzyme deactivation might have occurred to a certain extent. The latter will be more pronounced at low enzyme concentrations.

Finally, it is shown that there exists a Brønsted relation between the kinetic constants \( k_1 \) and \( k_2 \) and the pKa of the absorbing alkanolamine.

7. Final remark

The costs of industrially applied enzymes vary between €25–€100 per kg. From the present study it can be concluded that the enzyme concentrations to be used in commercial application is about 1–2 kg m⁻³ solvent. In the activated MDEA process the piperazine concentration varies between 1 and 10 wt%. The latter value results in the presence of 100 kg piperazine m⁻³ solvent, this equals a costs of about €600. Therefore, at this moment, it is not likely to expect that the costs of enzyme will be a showstopper.

Acknowledgement

This work has been sponsored by the CATO2 program (http://www.co2-cato.org). The authors especially want to thank CATO2 partner E.ON Benelux NV for their support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.cej.2014.08.001.

References