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Combined Effect of Temperature and pK_a on the Kinetics of Absorption of Carbon Dioxide in Aqueous Alkanolamine and Carbonate Solutions with Carbonic Anhydrase

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S Supporting Information

ABSTRACT: In present work the absorption of carbon dioxide in aqueous *N*-methyldiethanolamine, *N,N*-dimethylethanolamine, and triisopropanolamine solutions with and without the enzyme carbonic anhydrase has been studied in a stirred cell reactor at temperatures varying between 278 and 313 K, at an alkanolamine concentration of 1 kmol m⁻³ and carbonic anhydrase concentrations ranging from 0 to 2.4 kg m⁻³, respectively. The experimental data from these experiments have been used to fit the obtained rate constant for the enzymatic CO₂ hydration to the Brønsted relation: $\ln(k) = A(pK_a) + B + C/T$. In addition to the carbon dioxide absorption in the three tertiary alkanolamines, the absorption of carbon dioxide in next three solvents had been studied: 0.3 kmol m⁻³ potassium carbonate, 0.3 kmol m⁻³ sodium carbonate, and 0.2 kmol m⁻³ 2-amino-2-methyl-1-propanol. The kinetics from these solvents are well predicted by the relation fitted to the data of the tertiary amines only.

INTRODUCTION

For postcombustion removal of carbon dioxide from various flue gas streams, technologies based on chemical absorption in aqueous amine solutions are frequently proposed. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied.^{1–3} An example is the mixture of 2-amino-2-methyl-1-propanol (AMP) with piperazine (PZ).⁴ This mixture combines the advantage of PZ, a fast reacting (secondary) diamine, and the lower regeneration temperature of AMP. A disadvantage of this mixture is that PZ is mainly consumed in the top of the absorber during the reactive absorption.⁵ In order to maintain the positive effect over the entire absorber length, a catalyst is preferred.

Carbonic anhydrase (CA) is a very efficient catalyst for the interconversion between CO₂ and HCO₃⁻ in all living organisms.⁶ In the past CA has therefore extensively been investigated primarily from a biochemical point of view.^{7,8} However, more recently the application of CA in CO₂ capture technologies is gaining attention as environmentally benign accelerator.^{9–12}

Penders-van Elk et al. presented the results of kinetic studies of carbonic anhydrase in aqueous alkanolamines^{13–15} and in dilute sodium carbonate solutions at various temperatures.¹⁶ The result of all studies is a Langmuir–Hinshelwood-like equation that describes the observed reaction rate constant as a function of the enzyme concentration. In the present study the impact of both temperature and pK_a value on the absorption rate of carbon dioxide in *N*-methyldiethanolamine (MDEA), *N,N*-dimethylmonoethanolamine (DMMEA), and

triisopropanolamine (TIPA) solutions containing carbonic anhydrase will be presented. Moreover, additional results on the absorption of carbon dioxide in dilute sodium carbonate, dilute potassium carbonate, and aqueous 2-amino-2-methyl-1-propanol (AMP) solutions containing carbonic anhydrase will be presented.

THEORETICAL BACKGROUND

Mass Transfer. The reactive absorption of carbon dioxide in a lean alkanolamine or carbonate solution can be described with

$$J_{\text{CO}_2} = m_{\text{CO}_2} k_L E_{\text{CO}_2} \frac{P_{\text{CO}_2}}{RT} \quad (1)$$

Here the enhancement factor, E_{CO_2} , gives the ratio of the CO₂ flux with reaction and the CO₂ flux without reaction at identical driving forces. The Hatta number, Ha , gives the ratio of the rate of reaction in the liquid film and the rate of diffusion through this liquid film. When the reaction occurs in the so-called pseudo first order regime and $2 < Ha \ll E_{\text{inf}}$, the two numbers equal

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$$E_{\text{CO}_2} = \text{Ha} = \frac{\sqrt{k_1 D_{\text{CO}_2}}}{k_L} \quad (2)$$

E_{inf} is the infinite enhancement factor, which for irreversible reactions is given as¹⁷

$$E_{\text{inf}} = 1 + \frac{D_{\text{Am}} C_{\text{Am}}}{D_{\text{CO}_2} \nu_{\text{Am}}} \frac{RT}{m_{\text{CO}_2} P_{\text{CO}_2}} \quad (3)$$

As the reactions between CO_2 and amines are reversible, the use of eq 3 for the estimation of the infinite enhancement factor is not correct, as this is only valid for irreversible reactions. However, at the conditions studied it can be concluded that the deviations between the infinite enhancement factor for reversible and irreversible reactions respectively are very small.¹⁸ Therefore, the definition for the irreversible infinite enhancement factor was used in the present study.

For more details on determining kinetics from absorption experiments, refer to refs 19 and 20.

Kinetics. When carbon dioxide is exposed to an aqueous solution containing a carbonate or an alkanolamine, the following reactions will occur simultaneously,

with the following overall forward reaction rate,^{21,22}

$$R_{\text{CO}_2} = k_{\text{OH}} C_{\text{OH}} C_{\text{CO}_2} \quad (4)$$

with the following overall forward reaction rate,^{21,23}

$$R_{\text{CO}_2} = k_{\text{H}_2\text{O}} C_{\text{CO}_2} \quad (5)$$

In the case of a primary or secondary alkanolamine solution, carbon dioxide is able to react with the alkanolamine according to a zwitterion mechanism,

The overall forward reaction rate for this mechanism is given by²⁴

$$R_{\text{CO}_2} = -\frac{C_{\text{CO}_2} C_{\text{R}_2\text{NH}}}{\frac{1}{k_{\text{Am}}} + \frac{k_{-\text{Am}}}{k_{\text{Am}}} \sum (k_{\text{b}} C_{\text{B}})} \quad (6)$$

The base, B, can be water, hydroxide, or alkanolamine in lean aqueous solutions. In the case of a fresh aqueous AMP solution, $1/k_{\text{Am}}$ is significantly larger than the second term in denominator, whereby eq 6 reduces to

$$R_{\text{CO}_2} = k_{\text{Am}} C_{\text{Am}} C_{\text{CO}_2} \quad (7)$$

In the case of a tertiary alkanolamine solution carbon dioxide is also able to react with the alkanolamine via base-catalyzed hydrolysis:

Reaction IIIb:

The overall forward reaction rate for this reaction is given by^{25–27}

$$R_{\text{CO}_2} = k_{\text{Am}} C_{\text{Am}} C_{\text{CO}_2} \quad (8)$$

In the absence of mass transfer limitations, the overall forward reaction rate constant of this system becomes

$$k_{\text{OV}} = k_{\text{Am}} C_{\text{Am}} + k_{\text{OH}} C_{\text{OH}} + k_{\text{H}_2\text{O}} \quad (9)$$

In the case of the carbonate solution the first term is neglected since in literature no information is presented that the following reaction might occur:

The second order forward reaction rate constant k_{Am} is dependent on the acid dissociation constant, $\text{p}K_{\text{a}}$, of the amine present in the solution, and the temperature of the solution according to the Brønsted relation:^{26,28,29}

$$\ln(k_{\text{Am}}) = A(\text{p}K_{\text{a}}) + B + \frac{C}{T} \quad (10)$$

The parameters A, B, and C generic for primary and secondary as well as tertiary amines are presented in Table 1.²⁹

Table 1. Parameters of the Brønsted relation (Equation 10) for Primary, Secondary, and Tertiary Amines²⁹

amine	A	B	C
primary/secondary	1.0	16.26	−7188
tertiary	1.3	11.48	−8270

In the presence of the enzyme carbonic anhydrase the reaction mechanism is extended with the cycle of reactions presented in Figure 1.^{6,30}

Figure 1. Reaction mechanism of CO_2 hydration in the presence of the enzyme carbonic anhydrase. The enzyme is represented by E-Zn , where Zn is the catalytic site of the enzyme.

The base, B, used during enzyme regeneration can be the alkanolamine, carbonate, or the bicarbonate ion.³⁰ In the last case, carbon dioxide and water are released as protonated base, BH^+ .

In the presence of the enzyme carbonic anhydrase the CO_2 hydration is the most important reaction during absorption of carbon dioxide into aqueous tertiary alkanolamine or aqueous carbonate solutions. This reaction appeared to be first order in carbon dioxide and first order in water.¹³ When the enzyme carbonic anhydrase is present in the solution, the overall forward reaction rate constant becomes

Figure 2. Schematic drawing of the experimental setup to measure gas absorption in the solvent in time.

$$k_{OV} = k_{OV, \text{without enzyme}} + k_{H_2O}^* C_{H_2O} \quad (11)$$

For all alkanolamines investigated in previous studies, at low enzyme concentration $k_{H_2O}^*$ is linearly dependent on the enzyme concentration, whereas at high enzyme concentrations $k_{H_2O}^*$ becomes constant. This phenomenon is well described with the next Langmuir–Hinshelwood-like correlation:

$$k_{H_2O}^* = \frac{k_3^* C_{\text{Enzyme}}}{1 + k_4^* C_{\text{Enzyme}}} \quad (12)$$

Previous study showed that like k_{Am} the kinetic constants k_3^* and k_4^* are a function of the pK_a value of the amine at 298 K.¹⁴ In the present study, the effect of temperature on the kinetic constants k_3^* and k_4^* and of that on the forward reaction rate, $k_{H_2O}^*$, is investigated for primary and tertiary amines as well as carbonate solutions.

EXPERIMENTAL SECTION

Materials. The purity of the TIPA, DMMEA, AMP, and potassium carbonate, supplied by Acros Organics, was $\geq 98\%$, and the purity of the MDEA, TEA, and sodium carbonate, supplied by Sigma-Aldrich, was 99%. All chemicals were used as supplied. The enzyme used was an evolved form of a tetrameric (4 unit) enzyme (GSH4-043) developed by Codexis. This is the same enzyme as used in ref 16 for the experiments with sodium carbonate. All solutions have been prepared with demineralized water. The carbon dioxide (>99.9%) and nitrous oxide (>99%) used for absorption were obtained from Westfalen Gassen.

Setup. A schematic diagram of the experimental setup used in this study is presented in Figure 2. It consists of two identical stirred reactors in a thermostated water tank, a gas supply unit, and data acquisition instrumentation. Each reactor consists of a glass cylinder with a 10.3 cm internal diameter that is closed with a steel plate at the top and bottom. The total volume of each reactor is approximately 1.4 L, determined accurately. The liquid phase is stirred with a motor, a belt, and four magnetic plates to transmit the rotation from the motor to the stirrer located inside the reactor. The reactors are connected to two gas supply vessels, which can be filled with either CO_2 or N_2O from gas cylinders. Both reactors and one gas supply vessel are equipped with digital pressure transducers and thermocouples.

The measured signals are recorded in a computer through a National Instruments data acquisition system.

Procedure. The measurements of the CO_2 absorption into the aqueous alkanolamine solution in both presence or absence of the enzyme were performed in batch mode with respect to both liquid and gas phase. In a typical experiment approximately 500 mL solution with the desired composition was added to the reactor. The system was evacuated to remove inerts from the solution. Then it was allowed to equilibrate at the desired temperature and the vapor pressure (P_{vap}) was recorded. Also the pressure and temperature in the gas supply vessel were recorded. Then a predetermined amount of CO_2 was fed to the reactor from the gas supply vessel to obtain the desired pressure in the reactor (P_0). Then the stirrer was turned on at such a speed that the horizontal flat gas–liquid interface was maintained. The decrease in total pressure was recorded. By subtraction of the solution's vapor pressure from the total pressure, the partial pressure for CO_2 was obtained. At the end of the experiment the final pressure in the reactor (P_{eq}) and the pressure and temperature in the gas supply vessel were recorded.

The experiments have been performed at several temperatures between 278 and 313 K. For all experiments, the tertiary amine concentration was 1000 mol m^{-3} , the AMP concentration was 200 mol m^{-3} , and the carbonate concentration was 300 mol m^{-3} . The enzyme concentration has been varied between 0 and 2.4 kg m^{-3} .

Overall Forward Reaction Rate Constant. In the case of a pseudo first order reaction, a mass balance over the batchwise operated gas phase for CO_2 in combination with eqs 1 and 2 yields

$$\frac{d \ln P_{CO_2}}{dt} = \frac{\sqrt{k_{OV} D_{CO_2}} A_{GL} m_{CO_2}}{V_G} \quad (13)$$

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

Diffusion Coefficient. Since for most of the alkanolamines used in this study the diffusion coefficient of CO_2 or N_2O into the aqueous amine solution has not been published in literature, the Stokes–Einstein equation has been used to estimate it from the solution's viscosity.³¹

$$D_{\text{CO}_2, \text{Am}} = D_{\text{CO}_2, \text{water}} \left(\frac{\eta_{\text{water}}}{\eta_{\text{Am}}} \right)^{0.8} \quad (14)$$

The diffusion coefficient of CO_2 in water has been calculated using the correlation given by Jamal.³² The viscosity of water has been taken from Perry's Chemical Engineers' Handbook.³³ The viscosity of the MDEA solution has been calculated using the correlation described by Al-Ghawash et al., and the viscosity of the TEA solution has been calculated from the data provided by Maham et al.^{34,35} The viscosity of DMMEA has been measured at the conditions relevant for the present study using the AMVn, Automatic Micro Viscometer, of Anton Paar, while the viscosity of TIPA has been measured using a Stabinger viscometer of Anton Paar. The viscosities of DMMEA and TIPA as determined in this study are well in line with the viscosities found in the literature.^{36–38} All the viscosity data used in the determination of the diffusivity coefficient are presented in Table S2 in the Supporting Information.

Distribution Coefficient. The distribution coefficient of carbon dioxide is estimated using the N_2O analogy:³⁹

$$m_{\text{CO}_2, \text{Am}} = m_{\text{CO}_2, \text{water}} \frac{m_{\text{N}_2\text{O}, \text{Am}}}{m_{\text{N}_2\text{O}, \text{water}}} \quad (15)$$

The distribution coefficients of CO_2 and N_2O in water have been calculated using the correlations given by Jamal.³² All distribution coefficients used in the analyses of the data have been determined experimentally from absorption experiments with N_2O . The distribution coefficient of N_2O in the aqueous alkanolamine solution is calculated as

$$m_{\text{N}_2\text{O}, \text{Am}} = \left(\frac{C_{\text{N}_2\text{O}, \text{L}}}{C_{\text{N}_2\text{O}, \text{G}}} \right)_{\text{eq}} = \frac{P_0 - P_{\text{eq}}}{P_{\text{eq}} - P_{\text{vap}}} \frac{V_{\text{G}}}{V_{\text{L}}} \quad (16)$$

From the same experiment, the liquid side mass transfer coefficient of N_2O , $k_{\text{L}, \text{N}_2\text{O}}$, is obtained. The results of these measurements are presented in Table S3 in the Supporting Information. For the estimation of $k_{\text{L}, \text{CO}_2}$, again the N_2O analogy is used. This k_{L} is required to verify whether the CO_2 absorption has been carried out in the pseudo first order regime, i.e., $2 < \text{Ha} \ll E_{\text{inf}}$.

RESULTS

MDEA. Figure 3 presents the second order rate constant, $k_{\text{Am}} = k_{\text{OV}}/C_{\text{MDEA}}$, for a 1000 mol m^{-3} MDEA solution without enzyme as a function of the temperature.

The results obtained with MDEA solutions in the absence of enzyme are well in line with the relations published by Versteeg and van Swaaij²⁷ and Benamor and Aroua²⁵ and less well in line with the general pK_{a} relation for tertiary amines (eq 10).

The results of the experiments with MDEA at various enzyme concentrations and temperatures are presented in Figure 4. These results show that the forward rate constant increases with the enzyme concentration and with the temperature, respectively.

The kinetic constants, k_3^* and k_4^* , have been determined from the experimental data with help of non linear regression as described in ref 14. The results are presented in Table 2.

DMMEA. Because of its high pK_{a} value DMMEA has been chosen as second alkanolamine. Figure 5 presents the second order rate constant for a 1000 mol m^{-3} DMMEA solution without enzyme as a function of the temperature.

Figure 3. Forward second order reaction rate constant for the reaction of CO_2 with 1000 mol m^{-3} MDEA as a function of the temperature from experiments (circles) and predictions with relations of Versteeg and van Swaaij²⁷ (dash-dot line), Benamor and Aroua²⁵ (dashed line), and eq 10 (dotted line).

Figure 4. Forward reaction rate constant, $k_{\text{H}_2\text{O}}^*$, as a function of the enzyme concentration for aqueous MDEA solutions at four different temperatures.

Table 2. Kinetic Constants k_3^* and k_4^* of Equation 12 with the Standard Error in Parentheses for the Aqueous MDEA Solution with the Enzyme GSH4-043

T (K)	k_3^* ($\text{m}^6 \text{ mol}^{-1} \text{ g}^{-1} \text{ s}^{-1}$)	k_4^* ($\text{m}^3 \text{ kg}^{-1}$)
278	0.043 (0.0047)	0.55 (0.12)
288	0.051 (0.0049)	0.44 (0.096)
298	0.056 (0.0068)	0.37 (0.11)
308	0.066 (0.0028)	0.45 (0.044)

All results obtained with DMMEA solutions in the absence of enzyme are well in line with the correlation published by Littel et al.²⁶ except those at 278 K. In the past, at 278 K a $\ln(k_2)$ of -5.31 has been measured in the same reactor as used in previous studies described in ref 13 and ref 14, which is another but similar reactor as used in the present study. This again is well in line with the correlation published by Littel et al. Therefore, no explanation can be given for the phenomenon observed at 278 K in this study with the present reactor.

The results of the experiments with DMMEA at various enzyme concentrations and temperatures are presented in

Figure 5. Forward second order reaction rate constant for 1000 mol m⁻³ DMMEA as a function of the temperature from experiments (circles) and predictions with the relation of Littel et al.²⁶ (dashed line) and eq 10 (dotted line).

Figure 6. These results show that the forward rate constant increases with the enzyme concentration and with the temperature, respectively.

Figure 6. Forward reaction rate constant, $k_{\text{H}_2\text{O}}^*$, as a function of the enzyme concentration at various temperatures for aqueous 1000 mol m⁻³ DMMEA solution.

With help of nonlinear regression the kinetic constants k_3^* and k_4^* were derived from the experimental data of $k_{\text{H}_2\text{O}}^*$ for each temperature. The results are presented in Table 3.

TEA. Because of its low pK_a value, TEA has been chosen as third alkanolamine. However, as suspected from the results at higher TEA concentrations in combination with the CA mutant

Table 3. Kinetic Constants k_3^* and k_4^* with the Standard Error in Parentheses for the 1000 mol m⁻³ DMMEA Solution with the Enzyme GSH4-043

T (K)	k_3^* (m ⁶ mol ⁻¹ kg ⁻¹ s ⁻¹)	k_4^* (m ³ kg ⁻¹)
278	0.052 (0.059)	0.20 (0.14)
283	0.040 (0.0060)	0.21 (0.11)
298	0.054 (0.0043)	0.21 (0.057)
308	0.062 (0.0030)	0.30 (0.040)
313	0.062 (0.018)	0.28 (0.023)

SX,¹⁴ the tetramer GSH4-043 is not stable in a 1000 mol m⁻³ TEA solution. TEA is not the only alkanolamine that causes deactivation of the enzyme. The same study showed that both human CA II and the CA mutant SX were deactivated by *N,N*-diethylethanolamine (DEMEA).¹⁴

A quick enzyme stability experiment with 1000 mol m⁻³ TEA solution containing 2.4 kg m⁻³ of the enzyme has been done as a verification. Hereto 1 L of the solution was prepared, which was divided in two equal portions and transferred to the reactors. Both reactors were evacuated at the same time. When both solutions were at vapor pressure, a CO₂ absorption experiment was performed in one of the reactors immediately, while in the other reactor the CO₂ absorption experiment was done after a 1 day storage at reaction temperature. The 1 day storage at reaction temperature resulted in a reduction in absorption rate of approximately 25%. To be sure that the results of the experiments are not affected with deactivation, TIPA has been selected instead of TEA as alkanolamine with low pK_a . A quick enzyme stability test showed that the absorption rate is not reduced in a 1000 mol m⁻³ TIPA solution.

TIPA. Figure 7 presents the second order rate constant for a 1000 mol m⁻³ TIPA solution without enzyme as a function of the temperature.

Figure 7. Forward second order reaction rate constant for a 1000 mol m⁻³ TIPA solution as a function of the temperature for experiments (circles) and predictions with eq 10 (dotted line).

The results of the experiments with TIPA at various enzyme concentrations and temperatures are presented in Figure 8. These results show that the forward reaction rate constant increases with increasing enzyme concentration. With respect to the temperature, the forward reaction rate constant of the enzyme catalyzed reaction increases when the temperature is raised from 278 to 288 K and decreases when the temperature is raised from 298 to 308 K. For TIPA solutions with enzyme, there is an optimum temperature between the 288 and 298 K.

With help of nonlinear regression, the kinetic constants k_3^* and k_4^* were derived from the experimental data of $k_{\text{H}_2\text{O}}^*$. The results are presented in Table 4.

AMP. AMP is a sterically hindered alkanolamine with a pK_a value of 9.68 at 298 K. It is known that sterically hindered amines are able to form carbamate but that these carbamates are very unstable.⁴⁰ Figure 9 presents the second order rate constant for a 200 mol m⁻³ AMP solution without enzyme as a

Figure 8. Forward reaction rate constant, $k_{\text{H}_2\text{O}}^*$, as a function of the enzyme concentration at various temperatures for a 1000 mol m^{-3} TIPA solution.

Table 4. Kinetic Constants k_3^* and k_4^* with the Standard Error in Parentheses for the Aqueous TIPA Solution with the Enzyme GSH4-043

T (K)	k_3^* ($\text{m}^6 \text{mol}^{-1} \text{g}^{-1} \text{s}^{-1}$)	k_4^* ($\text{m}^3 \text{kg}^{-1}$)
278	0.027 (0.0014)	0.74 (0.071)
288	0.049 (0.0029)	1.0 (0.098)
298	0.050 (0.0076)	1.3 (0.030)
308	0.042 (0.0097)	1.3 (0.44)

Figure 9. Forward second order reaction rate constant for AMP as a function of the temperature for experiments (circles) and predictions with relations of Alper⁴¹ (gray solid line), Xu et al.⁴² (black dash-dot line), and Ali⁴³ (gray dash-dot line) and eq 10 with the parameters for primary and secondary amines (gray dashed line) and with parameters for tertiary amines (black dashed line) from Table 1.

function of the temperature. Next to the experimental data points, the lines for the pK_a correlations for the primary and secondary amines and for the tertiary amines (eq 10 with the parameters in Table 1) and the lines of relations of Alper,⁴¹ Xu et al.,⁴² and Ali⁴³ are also presented in the same figure. These lines show that the kinetics of AMP are significantly faster than of the tertiary amines. On the other hand due to the sterical hindrance, its kinetics are significantly slower than of primary or

secondary amines. The kinetics for AMP observed during this study are somewhat slower than those presented in literature. An explanation can be the difference in supplier.⁴² However, for the determination of the enzyme enhanced kinetics, it is more important to know the k_{OV} of the uncatalysed reaction for the same batch of AMP than k_2 .

The results of the experiments with AMP at various enzyme concentrations and temperatures are presented in Figure 10. These results show that the forward rate constant increases with the enzyme concentration and temperature.

Figure 10. Forward reaction rate constant, $k_{\text{H}_2\text{O}}^*$, as a function of the enzyme concentration at various temperatures for an aqueous 200 mol m^{-3} AMP solution.

The kinetic constants k_3^* and k_4^* were derived from the experimental data of $k_{\text{H}_2\text{O}}^*$ using nonlinear regression. The results are presented in Table 5.

Table 5. Kinetic Constants k_3^* and k_4^* with the Standard Error in Parentheses for the Aqueous AMP Solution with the Enzyme GSH4-043

T (K)	k_3^* ($\text{m}^6 \text{mol}^{-1} \text{g}^{-1} \text{s}^{-1}$)	k_4^* ($\text{m}^3 \text{kg}^{-1}$)
283	0.039 (0.0046)	0.39 (0.11)
298	0.058 (0.0029)	0.41 (0.049)
313	0.059 (0.0033)	0.30 (0.047)

Carbonate. Unlike MDEA, DMMEA, TIPA, and AMP, carbonates are ions with a high pK_a value. At high carbonate concentrations the ionic strength has a negative influence on the enzyme stability. Therefore, in this study the experiments have been performed with relatively dilute carbonate solutions (300 mol m^{-3}).

Figure 11 presents the second order rate constant for 300 mol m^{-3} sodium carbonate and for 300 mol m^{-3} potassium carbonate solutions without enzymes as a function of the temperature.

The results of the experiments with sodium carbonate at 283 K and with potassium carbonate at 283, 298, and 313 K at various enzyme concentrations are presented in Figure 12. Next to the newly obtained results at 283 K, the left plot also shows the results of sodium carbonate experiments of a previous study¹⁶ with gray markers. These results show that up to a temperature of 313 K the forward rate constant increases with

Figure 11. Experimental forward second order reaction rate constant for 300 mol m⁻³ Na₂CO₃ (triangles) and K₂CO₃ (circles) solutions at various temperatures and predictions with eq 10 with the parameters for tertiary amines from Table 1.

the enzyme concentration and with the temperature, respectively. For sodium carbonate the forward rate constant decreases again when the temperature is increased from 313 to 333 K. At 283, 298, and 313 K, the enzyme showed a somewhat higher $k_{\text{H}_2\text{O}}^*$ in combination with sodium carbonate than with potassium carbonate. No explanation can be given for this observation besides the different batches of the same enzyme that were used.

By use of nonlinear regression, the kinetic constants k_3^* and k_4^* were derived from the experimental data of $k_{\text{H}_2\text{O}}^*$. The results are presented in Table 6.

DISCUSSION

Kinetics without Enzyme. Like tertiary amines, sodium carbonate and potassium carbonate are not able to form carbamates. Therefore, it is not completely surprising that eq 10 predicts not only the second order rate constants for the tertiary amines but also the obtained second order rate constant for the dilute potassium and sodium carbonate solutions in this study very well. Most of the presented rate constants of the tertiary amine solutions and carbonate solutions are predicted with this equation within an error range of 100%, with an average deviation of 50%. The largest deviations are obtained at 278 K for the amines and at 283 K for potassium carbonate.

Table 6. Kinetic Constants k_3^* and k_4^* with the Standard Error in Parentheses for the Aqueous Na₂CO₃ and K₂CO₃ Solution with the Enzyme GSH4-043

solvent	T (K)	k_3^* (m ⁶ mol ⁻¹ g ⁻¹ s ⁻¹)	k_4^* (m ³ kg ⁻¹)
Na ₂ CO ₃	283	0.056 (0.0081)	0.24 (0.11)
K ₂ CO ₃	283	0.048 (0.018)	0.28 (0.30)
	298	0.070 (0.0073)	0.39 (0.10)
	313	0.074 (0.0050)	0.38 (0.062)

From the comparison of the presently obtained kinetic data to the Brønsted relation for tertiary amines (eq 10) presented in Figure 13, it can be concluded that the values for the reaction

Figure 13. Forward second order rate constant, k_2 , as a function of the pK_a value of the reacting component at various temperatures. The lines represent the k_2 predicted with eq 10 and the parameters for tertiary amines from Table 1. The symbols represent the experimental data for k_2 of TEA (○), TIPA (□), MDEA (△), DMMEA (◇), K₂CO₃ (<), and Na₂CO₃ (>).

rate constant calculated with this equation are consequently lower than the experimental values. This may indicate that the amines used in this study were contaminated with traces of faster reacting primary or secondary amines. However, for the determination of the enzyme activity this does not influence the results since, according to eq 11, the overall absorption rates

Figure 12. Forward reaction rate constant, $k_{\text{H}_2\text{O}}^*$, as a function of the enzyme concentration at various temperatures for 300 mol m⁻³ Na₂CO₃ (left) and 300 mol m⁻³ K₂CO₃ (right). The gray symbols in the left plot are experimental results of a previous study.¹⁶

obtained for the experiments with enzyme were corrected for the rates without enzyme.

The fact that the dilute carbonate solutions obey the Brønsted relation derived for the tertiary amines indicates that sodium and potassium carbonates seem to react identically with CO₂, i.e., according to a similar base catalyzed hydrolysis reaction mechanism, as tertiary amines. This single point, however, is no proof that [reaction IIIc](#) actually takes place during the absorption of CO₂ into the carbonate solution. More research is required to verify the exact mechanism.

In this study only dilute solutions of the carbonates have been investigated. For these solutions the influence of the activity on the kinetics is negligible. In the case of more concentrated carbonate solutions, the k_2 calculated with [eq 10](#) needs to be corrected for the activity of the ions.^{44,45}

AMP is a sterically hindered amine. Unlike tertiary amines, sterically hindered amines are able to form carbamates. However, due to the hindrance, these carbamates are not stable. As a result, the kinetics of sterically hindered amines like AMP are significantly faster than those of the tertiary amines. On the other hand due to the sterical hindrance, its kinetics are significantly slower than of primary or secondary amines.

Kinetics with Enzyme. Penders-van Elk et al. showed that at 298 K a Brønsted relation exists between the basic strength of the alkanolamine present in the solution and the rate of the catalytic CO₂ hydration.¹⁴ The results of that study cannot be combined with the results of this study because different enzymes have been used. The relation obtained in previous study underestimates the results obtained with the enzyme used in present study.

In the determination of the relation between the rate constant of the enzyme enhanced CO₂ hydration, the pK_a value of the amine, and the temperature, only the data obtained with the tertiary alkanolamine solutions have been used. As a starting point, the Brønsted relation describing the second order rate constant of the absorption of CO₂ in amine solutions as a function of the liquid temperature and the pK_a value of the amine present in the solvent has been used (see [eq 10](#)).

MDEA. The results of the nonlinear fitting of [eq 10](#) on the experimental data of k_3^* and k_4^* presented in [Table 2](#) are presented in [Table 7](#). The $k_{\text{H}_2\text{O}}^*$ calculated by substituting [eq 10](#)

Table 7. Parameters of Equation 10 with the Standard Error in Parentheses for MDEA in Combination with the Enzyme GSH4-043

	A	B	C
k_3^*	−0.68 (3.7)	2.9 (9.7)	48 (6.4 × 10 ³)
k_4^*	−30 (11)	76 (29)	53 × 10 ³ (19 × 10 ³)

with these fitted parameters into [eq 12](#) predicts the experimental data within a margin of error of 55% with an average deviation of 9.7%. This fit does not seem to be very good; however, the biggest deviations are at the lowest enzyme concentration used in the test. At the higher enzyme concentrations the calculated $k_{\text{H}_2\text{O}}^*$ values fit the experimental data within a margin of error of 25%.

DMMEA. The results of the nonlinear fitting of [eq 10](#) on the experimental data of k_3^* and k_4^* presented in [Table 3](#) are presented in [Table 8](#). The $k_{\text{H}_2\text{O}}^*$ calculated using these fitted equations predicts the experimental data within a margin of error of 50% with an average deviation of 8.6%.

Table 8. Parameters of Equation 10 with the Standard Error in Parentheses for DMMEA in Combination with the Enzyme GSH4-043

	A	B	C
k_3^*	−12 (16)	38 (51)	21 × 10 ³ (29 × 10 ³)
k_4^*	−69 (44)	211 (139)	125 × 10 ³ (80 × 10 ³)

TIPA. The results of the nonlinear fitting of [eq 10](#) on the experimental data of k_3^* and k_4^* presented in [Table 4](#) are presented in [Table 9](#). The $k_{\text{H}_2\text{O}}^*$ calculated using these fitted equations predicts the experimental data within a margin of error of 40% with an average deviation of 7.6%.

Table 9. Parameters of Equation 10 with the Standard Error in Parentheses for TIPA in Combination with the Enzyme GSH4-043

constant	A	B	C
k_3^*	25 (5.0)	−63 (13)	−41 × 10 ³ (7.9 × 10 ³)
k_4^*	9.6 (3.1)	−18 (7.7)	−17 × 10 ³ (4.8 × 10 ³)

The Three Evaluated Tertiary Amines. The parameters A, B, and C fitted with nonlinear regression on the experimental data of the three evaluated tertiary amines, MDEA, DMMEA, and TIPA, are presented in [Table 10](#). The $k_{\text{H}_2\text{O}}^*$ calculated with this

Table 10. Parameters of Equation 10 with the Standard Error in Parentheses for the Fit of MDEA, DMMEA, and TIPA with the Enzyme GSH4-043

constant	A	B	C
k_3^*	0.16 (0.076)	−0.21 (1.1)	−1.2 × 10 ³ (0.33 × 10 ³)
k_4^*	−0.88 (0.16)	1.0 (2.4)	1.7 × 10 ³ (0.71 × 10 ³)

relation fits the measured $k_{\text{H}_2\text{O}}^*$ within a margin of error of 80% with an average deviation of 20%. Again, like with MDEA the largest deviations are at the lowest enzyme concentration used in the experiments. At the higher enzyme concentrations the calculated $k_{\text{H}_2\text{O}}^*$ fits the experimental data within a margin of error of 50%.

The Other Evaluated Solvents. Next to the three tertiary amine solutions, solutions of AMP, Na₂CO₃, and K₂CO₃ have been used in combination with the same enzyme. Although these experimental results were not used in the determination of the parameters in [eq 10](#), their experimental data are compared to the $k_{\text{H}_2\text{O}}^*$ calculated using the parameters given in [Table 10](#) (see [Figure 14](#)). This comparison showed that the $k_{\text{H}_2\text{O}}^*$ measured in the AMP solution can be determined with the Brønsted relation within a margin of error of 92%, with an average deviation of 39%. The largest deviation between the fit and the experimental values is observed at the high enzyme concentrations at 278 K. Leaving these outliers out of consideration, the fit improves to an average deviation of 29% with a maximum deviation of 45%. Given the relative small number of data points and the largest deviation, this should be considered as a good fit; it is almost as good as the fit of the tertiary alkanolamines which were used in the fit.

The experimental data for the two carbonate salts obtained in the temperature range of 278–313 K are predicted with the Brønsted relation within a margin of error of 75%, with an average deviation of 29%. The experimental data obtained with the sodium carbonate solutions at 333 K on the other hand are

Figure 14. Parity plot of all evaluated conditions using eq 10 and the parameters in Table 10. The dashed lines indicate the 50% margin of error.

clearly overestimated when the fit is used. This shows that the derived equation should only be used within the temperature range used in the fit.

CONCLUDING REMARKS

The kinetics of the enzyme catalyzed absorption of CO_2 have been investigated in the temperature range 278–313 K and enzyme concentration in the range 0–2.4 kg m^{-3} . The aqueous solutions of the alkanolamines TIPA, MDEA, DMMEA, and AMP and the salts K_2CO_3 , and Na_2CO_3 cover a pK_a range of 7.62–10.5.

The second order kinetic constants of the three tertiary amines were well predicted with the Brønsted relation presented by Versteeg et al.²⁹ Because the observed kinetic constants for the two carbonate salt solutions were also well predicted with this relation, it may indicate that carbonates react with CO_2 according to the same reaction mechanism as tertiary amines.

The kinetic rate constant of the enzyme catalyzed CO_2 hydration is described with the Langmuir–Hinshelwood-like equation, eq 12. The two kinetics constants, k_3^* and k_4^* , can be well described with the Brønsted relation, eq 10. The parameters A , B , and C obtained from the nonlinear regression on the data of the tertiary amines have been used to estimate the $k_{\text{H}_2\text{O}}^*$ for the aqueous AMP as well as the sodium and potassium carbonate solutions. The observed constants are well reproduced within the same accuracy. The derived equation should only be used within the temperature range 278–313 K. The fact that the relation in ref 14 obtained with the CA mutant SX at 298 K underestimates the rates of present study shows that the derived equation is enzyme dependent.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b02254.

pK_a values of amines and carbonates used in the experiments; viscosity of amines and carbonate solutions used in the experiments; G/L distribution coefficient of

N_2O into the amine and salt solutions used in the experiments (PDF)

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Notes

The authors declare no competing financial interest.

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NOTATION

A	parameter in eq 10
A_{GL}	surface area of G/L interface [m^2]
B	parameter in eq 10
C	parameter in eq 10
C_A	concentration of A [mol m^{-3}]
D_A	diffusion coefficient of A [$\text{m}^2 \text{s}^{-1}$]
E_A	enhancement factor of A [–]
Ha	Hatta number [–]
J_A	flux of A [$\text{mol m}^{-2} \text{s}^{-1}$]
k_1	first order reaction rate constant [s^{-1}]
k_2	second order reaction rate constant [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
k_3^*	kinetic constant in eq 12 [$\text{m}^6 \text{kg}^{-1} \text{mol}^{-1} \text{s}^{-1}$]
k_4^*	kinetic constant in eq 12 [$\text{m}^3 \text{kg}^{-1}$]
k_{Am}	reaction rate constant of reaction of CO_2 with an amine [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
$k_{\text{H}_2\text{O}}$	reaction rate constant of the uncatalysed CO_2 hydration [s^{-1}]
$k_{\text{H}_2\text{O}}^*$	reaction rate constant of the enzyme enhanced CO_2 hydration [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
k_L	liquid side mass transfer coefficient [m s^{-1}]
k_{OH}	reaction rate constant of the CO_2 hydroxylation [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
k_{OV}	overall reaction rate constant [s^{-1}]
m_A	G/L distribution coefficient of A [–]
P	pressure [Pa]
pK_a	acid dissociation value [–]
R	gas constant [$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]
t	time [s]
T	temperature [K]
V	volume [m^3]
η_A	viscosity of A [Pa s]
ν_A	reaction order of A

Subscripts

0	initial
Am	amine
eq	equilibrium
G	gas phase
inf	infinite
L	liquid phase
vap	vapor

Abbreviations

AMP	2-amino-2-methyl-1-propanol
B	base
CA	carbonic anhydrase

DEMEA	<i>N,N</i> -diethylethanolamine
DMMEA	<i>N,N</i> -dimethylethanolamine
EZn	enzyme and its catalytic site
MEA	ethanolamine
MDEA	<i>N</i> -methyldiethanolamine
TEA	triethanolamine
TIPA	triisopropanolamine

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