

GAS-LIQUID MASS TRANSFER WITH PARALLEL REVERSIBLE REACTIONS—I. ABSORPTION OF CO₂ INTO SOLUTIONS OF STERICALLY HINDERED AMINES

H. BOSCH,[†] G. F. VERSTEEG and W. P. M. VAN SWAAIJ

Department of Chemical Engineering, Twente University, PO Box 217, 7500 AE Enschede, Netherlands

(First received 6 June 1988; accepted in revised form 6 April 1989)

Abstract—A numerical method developed by Versteeg *et al.* (1989, *Chem. Engng Sci.* **44**, 2295–2310; 1990, *Chem. Engng Sci.* **45**, in press) is applied to some specific problems in gas-liquid mass transfer. The experimental results of Chakraborty *et al.* (1986, *Chem. Engng Sci.* **41**, 997–1003) and Zioudas and Dadach (1986, *Chem. Engng Sci.* **41**, 405–408) on the absorption of CO₂ into aqueous solutions of sterically hindered amines are evaluated with the numerical model. It is shown that studying the absorption of CO₂ into aqueous solutions of sterically hindered amines requires a rigorous numerical solution of the differential equations describing the mass transfer instead of analytical and numerical approximations based on a reduction of the number of reactions by neglecting or lumping reactions. It is demonstrated that the absorption rates of CO₂ into sterically hindered amine solutions can be explained in terms of the established reactions of CO₂ in amine solutions alone, and no new reaction paths are necessary to explain the observed behaviour.

1. INTRODUCTION

Many processes involve mass transfer between gas and liquid phases. In some of these processes chemical reactions occur and these may enhance the mass transfer. The description of the phenomenon of mass transfer accompanied by one irreversible reaction has been studied extensively both theoretically and experimentally. Many phenomena observed are very well understood and the results can be found in any book on gas absorption (Astarita, 1967; Danckwerts, 1970) or textbook on chemical reaction engineering (Westertep *et al.*, 1984).

For reversible reactions only a limited number of cases have been studied. Some of the resulting models have been solved analytically and, for a few, analytical approximations were used. Other models were solved numerically. A review of the available solutions has been given by Versteeg *et al.* (1989).

For multiple parallel reactions also some asymptotic models have been solved. In these models only irreversible reactions are considered. Jhaveri (1969) studied the absorption of one gas into a liquid containing two reactants. Analytical solutions for three asymptotic situations were presented: one for two pseudo-first-order reactions, both occurring in the fast reaction regime, a second for two instantaneous second-order reactions and the last for one instantaneous second-order and one fast pseudo-first-order reaction. Additionally he derived an approximate general solution for second-order reactions. Alper (1972) later showed that this last solution was not correct and presented a more general solution (Alper, 1973) derived by means of a linearization technique. Onda *et al.* (1970) used a linearization technique to approximate the solution of the model for absorption of a gas

into a liquid containing any number of reactants with arbitrary kinetics and stoichiometry.

For mass transfer with multiple reversible reactions no analytical solutions of the models are available and the relevant differential equations can only be solved numerically. Some asymptotic solutions for the effect of multiple reactions occurring in the liquid have been presented however. These solutions deal with CO₂ as the absorbing gas. The absorption of CO₂ into mixtures of reactants (e.g. amine-promoted potash solutions) is an industrially important process.

McNeil and Danckwerts (1964), Danckwerts and McNeil (1967a, b) and Shrier and Danckwerts (1969) interpreted their experiments on the absorption of CO₂ into amine solutions and amine-promoted carbonate solutions, respectively, in terms of a mechanism that was later referred to as the "shuttle mechanism". In this mechanism one reaction is considered to be slow compared to mass transfer, and occurring essentially only in the liquid bulk. The other reaction is considered to be very fast with respect to mass transfer, occurring only very near the interface, while the converted fast reacting component is regenerated in the liquid bulk by the reverse reaction. The slow reaction serves as the final chemical sink for CO₂. The overall absorption rate is higher than the absorption rate into a liquid containing only one of the two components in the same concentration. The mechanism will be discussed in more detail by Bosch *et al.* (1989a).

If the spent fast reacting component is not regenerated in the liquid bulk but instantaneously, without intermediate transportation, the mechanism is that of homogeneous catalysis. This homogeneous catalysis mechanism was originally proposed by Roughton and Booth (1938), and was based on the promotion of mass transfer of CO₂ in carbonate solutions by inorganic promoters such as the arsenite ion. Recently this

[†] Author to whom correspondence should be addressed.

mechanism was assumed to hold for the absorption of CO₂ into amine-promoted carbonate solutions by Astarita *et al.* (1981). They considered the reactions of carbonate to be catalyzed by the amine.

Astarita *et al.* (1981) pointed out that both mechanisms (shuttle mechanism and homogeneous catalysis) are extreme cases of the same process (absorption of a gas accompanied by two parallel reactions) and that the reaction rates determine which of the two is more realistic. In most practically important situations neither of the two mechanisms is sufficiently accurate to describe this absorption process.

Application of the numerically solved model presented by Versteeg *et al.* (1989) makes such an extreme case assumption about the mechanism unnecessary, and in the present contribution it is used to describe three specific problems presently under discussion in the literature.

In this part the numerical model is applied to the absorption of CO₂ into aqueous solutions of sterically hindered amines. These amines (Sartori and Savage, 1983) have a very low tendency to form carbamates and therefore do not react directly with CO₂ to the same extent as conventional primary or secondary amines. In this case the reaction of CO₂ with the amine as well as the reaction with water (hydration) is important and therefore it can also be regarded as mass transfer accompanied by multiple reactions. The data on absorption rates presented by Chakraborty *et al.* (1986) and Zioudas and Dadach (1986) will be discussed in view of the results of numerical calculations.

In Part II (Bosch *et al.*, 1989a) the absorption of CO₂ into aqueous mixtures of carbonate and amines will be discussed, and Part III (Bosch *et al.*, 1989b) will be on the absorption of CO₂ into aqueous solutions of mixtures of amines.

2. THEORY OF ABSORPTION OF CO₂ INTO AQUEOUS AMINE SOLUTIONS

In the past, several theoretical approaches to the description of mass transfer in gas-liquid systems have been proposed, of which the film model (Whitman, 1923), the penetration model (von Wroblenski, 1877; Higbie, 1935) and the surface renewal model (Danckwerts, 1951) are most often applied. In the present work mainly the film model will be used because it takes less computational time.

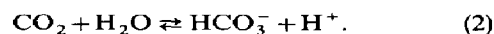
In the film model mass transfer is assumed to take place by molecular diffusion through a stagnant liquid layer of thickness δ . If chemical reactions occur in this layer the differential equations describing the mass transfer process become

$$-\mathbb{D}_n \frac{\partial^2 c_n}{\partial x^2} = \sum_m r_{n,m} \quad (1)$$

for each species n with $r_{n,m}$ being the net volumetric production rate of component n due to reaction m . All reactions in which component n takes part should be

taken into account. For absorption of CO₂ into basic aqueous solutions several reactions occur.

The first reaction to be considered is the hydration of CO₂:



This reaction is very slow (Pinsent *et al.*, 1956) and may usually be neglected compared to the second reaction:



This reaction is fast and can enhance mass transfer even when the concentration of hydroxyl ion is low. As it gives the same products as reaction (2) followed by equilibration of the water dissociation reaction it is often referred to as the hydration of CO₂. The forward reaction can be described by (Pinsent *et al.*, 1956):

$$r = k_{\text{OH}} [\text{CO}_2] [\text{OH}^-] \quad (4)$$

$$\log k_{\text{OH}} = 10.635 - \frac{2895}{T} \quad (5)$$

In carbonate solutions this reaction is assumed to be the only one important for the enhancement of mass transfer.

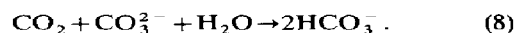
If the concentration of hydroxyl ion is considered to be constant in the mass transfer film (i.e. no depletion of OH⁻ at the interface) and the reaction is considered to be irreversible, the pseudo-first-order solution of mass transfer with chemical reaction is obtained upon integration of eq. (1), which now consists of only one differential equation:

$$E = \frac{Ha}{\tanh Ha} \quad (6)$$

$$Ha = \sqrt{\frac{k_1 \mathbb{D}_{\text{CO}_2}}{k_L^2}} \quad (7)$$

where E is the enhancement factor which is defined as the ratio of the absorption rates with and without chemical reaction. The dimensionless Hatta number, Ha , is defined as the ratio of the maximum amount of transferred component consumed in the mass transfer film and the maximum amount transferred if no chemical reaction occurs and at bulk concentration zero. In this case k_1 is equal to the product of k_{OH} and [OH⁻].

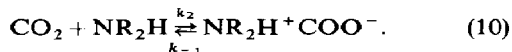
If the hydration reaction is considered to be irreversible and instantaneous with respect to mass transfer CO₂ and OH⁻ cannot coexist, and therefore a reaction plane is formed at some distance from the interface. Now the diffusion of the reactants of the overall reaction (8) to this plane determines the mass transfer rate:



The solution of the model is

$$E = E^\infty = 1 + \frac{\mathbb{D}_{\text{CO}_3^{2-}} [\text{CO}_3^{2-}]_b}{\mathbb{D}_{\text{CO}_2} [\text{CO}_2]_i} \quad (9)$$

Primary and secondary amines also react with CO_2 . The mechanism of these reactions is well understood and was originally presented by Caplow (1968) and reintroduced by Danckwerts (1979). CO_2 reacts with the amine to form an intermediate called a "zwitterion":



The zwitterion can be deprotonated by any base present in the solution producing a carbamate ion and a protonated base according to



Blauwhoff *et al.* (1984) showed that according to this mechanism the forward reaction rate can be described by

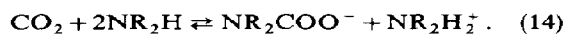
$$r = \frac{k_2[\text{CO}_2][\text{NR}_2\text{H}]}{1 + \frac{k_{-1}}{\sum k_b[\text{B}]}} = \frac{k_2[\text{CO}_2][\text{NR}_2\text{H}]}{1 + \frac{1}{\sum k'_b[\text{B}]}} \quad (12)$$

using the assumption of a pseudo-steady-state condition for the zwitterion concentration.

Depending on the relative magnitudes of the individual reaction rate constants different orders in amine may occur. Values of k'_b for various bases were obtained by Blauwhoff *et al.* (1984) and Versteeg and van Swaaij (1988a). Blauwhoff *et al.* (1984) showed that k'_b increases with the strength of the base. Versteeg and van Swaaij (1988a) showed that the rate constants, k_2 , measured for five amines at three temperatures near ambient conditions are determined by the basicity of the amine and the temperature according to

$$\ln k_2 = 16.26 + pK_a - \frac{7188}{T} \quad (13)$$

In concentrated solutions of amines, the amine is usually the most important base, giving rise to an overall reaction equation of



Tertiary amines cannot react directly with CO_2 like primary and secondary amines because they lack the proton needed in the deprotonation step (11). Despite this, it is observed that aqueous solutions of tertiary amines show considerable reactivity towards CO_2 . Experimental results (Versteeg and van Swaaij, 1988b) indicate that water is essential for this reaction, proceeding according to



The forward reaction rate can be described by

$$r = k_2[\text{NR}_3][\text{CO}_2] \quad (16)$$

Versteeg and van Swaaij (1988b) showed that at 293 K this reaction rate constant is determined by the basicity of the amine and can be calculated according to

$$\ln k_2 = pK_a - 14.24 \quad (17)$$

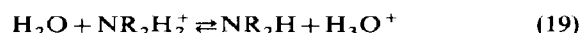
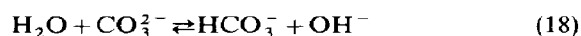
The mechanism of the reaction is not quite clear. Generally it is assumed that it is a kind of amine-catalyzed hydration of CO_2 (Donaldson and Nguyen, 1980).

The reactions of amines in amine solutions are usually much faster than the hydration of $[\text{CO}_2$ reaction (3)]. They can enhance mass transfer and in the analysis of absorption processes the influence of CO_2 hydration is often neglected. This is not always correct and, as will be demonstrated, it can lead to invalid conclusions.

Therefore in studying the absorption of CO_2 into mixtures of amines or of amines and carbonate all the reactions mentioned above and their simultaneous influence on mass transfer should be taken into account. Because no analytical solutions to such mass transfer models can be obtained numerical methods of solution have to be applied. In the present work the film model was used to describe the mass transfer process in order to minimize the required computational time. Detailed information on the numerical technique can be found in Cornelisse *et al.* (1980) and Versteeg *et al.* (1989).

3. REACTION MODEL FOR ABSORPTION OF CO_2 INTO STERICALLY HINDERED AMINE SOLUTIONS

Although it has been suggested (Savage *et al.*, 1984; Chakraborty *et al.*, 1986) that the reaction of CO_2 with hindered amines follows other reaction paths this reaction is considered to be the same as for any primary- or secondary-amine solution here. The reactions occurring are:



The reactions involving only the transfer of a proton [equations (18)–(20)] are regarded to be instantaneous with respect to mass transfer, and are therefore considered to be at equilibrium everywhere:

$$K_p = \frac{[\text{NR}_2\text{H}][\text{H}_3\text{O}^+]}{[\text{NR}_2\text{H}_2^+]} \quad (21)$$

$$K_{c2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} \quad (22)$$

$$K_w = [\text{OH}][\text{H}_3\text{O}^+] \quad (23)$$

In this reaction model eq. (14) seems to imply that all zwitterions are deprotonated by the amine. For the overall effect of this reaction this assumption has no importance because all acid-base pairs are at equilibrium throughout the liquid. In many cases reaction (10) is the rate-limiting step in the reaction of CO_2 with the amine. If the reaction rate of this step is not available it can be estimated with correlation (13).

4. REVIEW OF LITERATURE ABOUT STERICALLY HINDERED AMINES

4.1. General

Relatively few data on sterically hindered amines can be found in the open literature.

Sharma (1965) noticed that steric effects influence the stability of the carbamates formed by reaction (14). In his thesis (Sharma, 1964) he proposed the use of highly branched amines such as AMP (2-amino-2-methylpropanol), for CO₂ absorption because they could show considerable advantages over conventional amines.

Such amines have been called sterically hindered amines only since 1981 (*Chem. Engng News*, 1981). In this note a sterically hindered amine is defined as either a primary amine in which the amino group is attached to a tertiary carbon atom or a secondary amine in which the amino group is attached to either a secondary or a tertiary carbon atom. Examples of this class of chemicals are AMP, 1,8,*p*-methanediamine and 2-piperideneethanol (PE).

These amines were considered to be very attractive for CO₂ removal. They react rather fast but do not form carbamate to a considerable extent, and therefore less amine is consumed per mole of CO₂ absorbed, resulting in a larger loading capacity for CO₂ than that of unhindered amines.

Sartori and Savage (1983) reported on equilibrium and rate experiments with sterically hindered amines. These vapor-liquid equilibrium experiments were executed in an autoclave in which a batch of liquid was allowed to equilibrate with a gas mixture bubbling through it. The sterically hindered amines had higher capacities for CO₂ than unhindered primary and secondary amines.

The absorption rate data were measured in a single sphere absorber. The results showed that whereas absorption rates of conventional amines such as MEA (monoethanolamine), DEA and DIPA, reduce drastically on approaching a liquid loading of $\alpha = 0.5$, sterically hindered amines (AMP, PE) show large absorption rates at even higher loadings. This is an effect of the steric hindrance. Although the reaction rate constants for hindered amines are lower according to Sartori and Savage (1983), the reaction rates are higher at high loadings because more amine is available for reaction, and not fixed as carbamate.

4.2. Absorption of CO₂ into AMP solutions

Chakraborty *et al.* (1986) reported on equilibrium and rate experiments for absorption of CO₂ into AMP solutions at 315 K.

The equilibrium experiments resulted in a value for the protonation constant, K_p , of $3.16 \cdot 10^{-6} \text{ mol m}^{-3}$. The value of the carbamate stability constant, K_c , was found to be lower than $10^{-4} \text{ m}^3 \text{ mol}^{-1}$.

The rate experiments were conducted in a pressure decrease cell. A known amount of amine solution was introduced in a vessel containing an atmosphere of pure CO₂. The liquid in the cell was stirred, and the

pressure and pH were recorded as a function of time. From the independence of the absorption rate on the stirring speed the authors concluded that the absorption occurred in the fast reaction regime. They assumed the reaction to be an amine catalyzed form of the hydration of CO₂, the rate-determining step being the formation of some intermediate by reaction of the amine with CO₂. This reaction was found to be first-order with respect to both reactants (CO₂ and AMP) and the experimental results were interpreted accordingly. They found a value of $10^{-1} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for k_2 . The agreement between this result and that of Savage *et al.* (1984) for amine-promoted carbonate solutions was considered to be good.

Zioudas and Dadach (1986) measured absorption rates of CO₂ and H₂S into solutions of MEA and AMP in a cell containing a stagnant liquid at 298 K. The pressure in the reactor was kept constant by controlled feeding of the absorbing gas. Total amounts of gas absorbed were determined from the pressure decrease in a gas vessel located upstream of the reactor. Amine concentrations of 100, 200 and 300 mol m⁻³ for a partial CO₂ pressure of 100 kPa and partial pressures of 5 and 50 kPa for an amine concentration of 100 mol m⁻³ were used. The results were presented graphically as the total amount of gas absorbed vs time and correlated to the partial pressure of CO₂ and the amine concentration by a power law relation. The differences in behaviour between the two amines were attributed to the steric hindrance in AMP, but no quantitative explanation was given.

5. SIMULATION OF THE EXPERIMENTS BY CHAKRABORTY *ET AL.* (1986)

5.1. Data

Since some of the experimental conditions were not published by the authors, only a limited number of simulations were carried out to see whether the magnitude of the absorption rates observed could be explained. The data used in the simulations are listed in Table 1. The total amine concentration was assumed to be the same as for their equilibrium experiments. A CO₂ partial pressure of 10 kPa was considered. The absorption process was simulated only at a liquid loading of $\alpha = 0.05$. The value of k_L selected is common for stirred cells (Charpentier, 1982).

The value of m is the same as for an MEA solution of the same concentration. For K_p the value given by Chakraborty *et al.* (1986) ($3.16 \cdot 10^{-6} \text{ mol m}^{-3}$) was not used because it seems to be much too high. For other alkanolamines the ratio between the values of K_p at 315 and 298 K is about 2.5. Applying this ratio to the value at 298 K for AMP reported by three different authors (Perrin, 1965) results in a value of $5.1 \cdot 10^{-7} \text{ mol m}^{-3}$ for K_p . For K_c a value of $10^{-5} \text{ m}^3 \text{ mol}^{-1}$, which is 10 times as low as the upper bound given by the authors, was used. The reason for this will be discussed in Section 5.3. For the reaction of CO₂ with AMP the first step in the zwitterion mechanism (10) was assumed to be rate-limiting. This assumption

Table 1. Parameters used in evaluation of experiments by Chakraborty *et al.* (1986)

Parameter	Value	Source
C_{AMP} (mol m ⁻³)	2000	Assumed from Chakraborty <i>et al.</i> (1986)
$C_{CO_2,g}$ (mol m ⁻³)	4.0	Chosen
α	0.05	Chosen
k_L (m s ⁻¹)	10 ⁻⁵	Estimated
m	0.6	From analogy with MEA
k_g (m s ⁻¹)	100	No gas phase resistance
K_{c1} (m ³ mol ⁻¹)	1.64 × 10 ⁴	Chakravarty (1985)
K_{c2} (mol m ⁻³)	6.14 × 10 ⁻⁸	Chakravarty (1985)
K_w (mol ² m ⁻⁶)	3.09 × 10 ⁻⁸	Harned (1958)
K_p (mol m ⁻³)	5.11 × 10 ⁻⁷	Estimated from Perrin (1965)
K_c (m ³ mol ⁻¹)	10 ⁻⁵	Chakraborty <i>et al.</i> (1986)
k_{OH} (m ³ mol ⁻¹ s ⁻¹)	28.1	Pinsent <i>et al.</i> (1956)
k_2 (m ³ mol ⁻¹ s ⁻¹)	7.05	Versteeg and van Swaaij (1988a)
D_{CO_2} (m ² s ⁻¹)	1.4 × 10 ⁻⁹	Estimated
D_{AMP} (m ² s ⁻¹)	0.97 × 10 ⁻⁹	$D = V_b^{-0.6}$
D_{ion} (m ² s ⁻¹)	0.92 × 10 ⁻⁹	V_b from Perry and Chilton (1973)

might not hold in practice, but for the present purpose it is not critical. The rate constant was calculated from correlation (13).

Liquid compositions were calculated by solving the relevant equilibrium equations. Non-idealities in the liquid phase equilibria were not taken into account.

The diffusivity of CO₂ is taken to be the same as in an MEA solution of the same concentration. The other diffusivities were estimated relative to the diffusivity of CO₂ using the proportionality of a Wilke and Chang (1955) type of equation. The diffusivities of all ionic species were taken equal to assure that the solution obeys the charge balance. The value was a weighted average of the diffusivities of the individual ions. Detailed information about the method of weighing can be found in Bosch (1989).

In a stirred cell the penetration model is believed to be more realistic (Versteeg *et al.*, 1987). Because differences are relatively small and in order to minimize the computational time required for the solution, the film model was used in the simulations. Nevertheless to approximate the most important aspect of penetration model solutions the diffusivities of species other than CO₂ were corrected with a square root proportionality [see Bosch (1989)]. For asymptotic cases this approximation is in agreement with the exact solutions of the models. The validity of the approximation was checked against numerical solutions for asymptotic cases. Also the numerical solutions for the penetration model and the corrected film model for an absorption process much like the present one were compared. The corrected film model gave solutions closer to the penetration model than the uncorrected one.

5.2. Results

The parameters chosen resulted in a calculated enhancement factor of 54. From the concentration profiles in Figs 1 and 2 it can be concluded that no simple model can explain the observed behaviour. A large fraction of the enhancement is caused by transportation of CO₂ in the form of carbamate (Fig. 2).

Because the carbamate reverts back to bicarbonate in the liquid bulk, this effect resembles a shuttle mechanism. Due to the production of OH⁻ ions by the amine protonation reaction and the formation of CO₂ by the reversion of reaction (14) the influence of the hydration reaction is increased in comparison to absorption in water. This is a second contribution to the enhancement.

5.3. Discussion

From the value of k_2 calculated by Chakraborty *et al.* (1986) from their results (see Section 4.2) it can be concluded that Ha and therefore the enhancement factor would be about 50 for the conditions of the simulations. This is almost equal to the numerical result.

If the reaction of CO₂ and AMP was pseudo-first-order and irreversible the enhancement factor would be over 400 for the present conditions. This clearly indicates that simple models have a very limited value for the interpretation of absorption rate data in the case of complicated reaction schemes.

From the results in Table 2 (nos 1 and 2) it can be concluded that the value of k_L does influence the absorption rate, but only moderately. A twofold decrease in the value of k_L which can only be achieved by a roughly fourfold decrease in the stirring speed resulted in a decrease of only 33% of the calculated absorption rate. This could explain why Chakraborty *et al.* (1986) found no significant influence of the stirring speed.

Changing the value of the forward reaction rate constant (nos 1, 3 and 4) affects the results only slightly. This indicates that the reaction is at equilibrium everywhere. This conclusion can be confirmed from the calculated concentration profiles (Figs 1 and 2). The present results therefore do not corroborate the validity of eq. (13) for AMP.

Both K_p and K_c showed an influence on the enhancement factor (nos 1, 5 and 6), though much less than proportional. The value of 10⁻⁵ for K_c was chosen because the flux was expected to depend upon

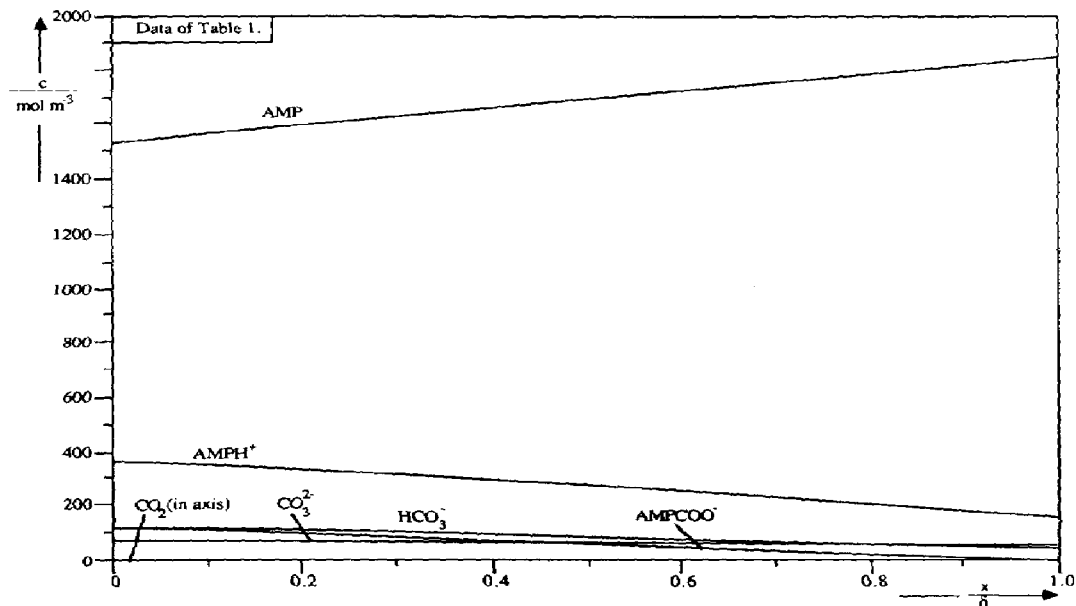


Fig. 1. Calculated concentration profiles for absorption of CO_2 into an aqueous 2000 mol m^{-3} AMP solution at 315 K.

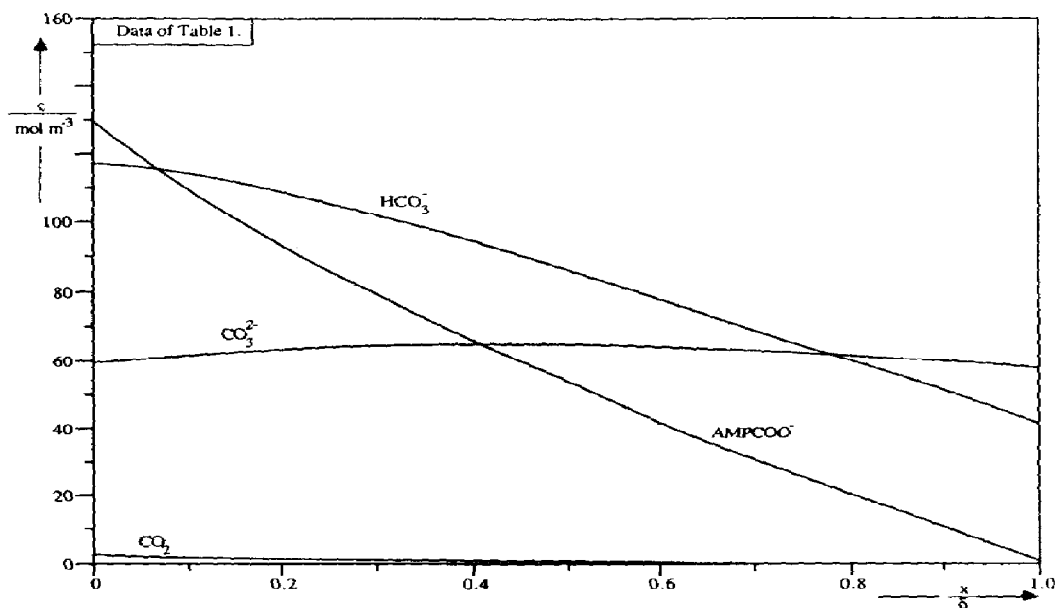


Fig. 2. Calculated concentration profiles for absorption of CO_2 into an aqueous 2000 mol m^{-3} AMP solution at 315 K. Expansion of Fig. 1 for low concentrations.

it, and this was considered to be a low estimate, giving rise to low absorption rates. Multiplying it by 10, making it equal to the upper bound given by Chakraborty *et al.* (1986), only doubles the flux. So its value does not seem to be critical. The influence of K_p is larger, but even with the very high value found by

Chakraborty *et al.* (1986), the flux is only reduced by a factor 2.

The calculated influence of the gas phase concentration of CO_2 is important [eqs (1) and (7)], though much lower than proportional, as would be expected from the mechanism proposed by Chakraborty *et al.*

Table 2. Numerical results for simulation of experiments by Chakraborty *et al.* (1986)

No.	k_L (m s^{-1})	k_2 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	K_c ($\text{m}^3 \text{mol}^{-1}$)	K_p (mol m^{-3})	$C_{\text{CO}_2, \text{g}}$ (mol m^{-3})	E_A	J ($\text{mol m}^{-2} \text{s}^{-1}$)
1	10^{-5}					57.5	1.38×10^{-3}
2	5×10^{-6}	7.05				79.0	9.64×10^{-4}
3		14.1	10^{-5}			58.9	1.41×10^{-3}
4		3.525		5.11×10^{-7}	0.004	55.7	1.33×10^{-3}
5	10^{-5}		10^{-4}			112	2.68×10^{-3}
6		7.05	10^{-5}	3.16×10^{-6}		24.1	5.70×10^{-4}
7				5.11×10^{-7}	0.04	16.7	4.01×10^{-3}

Table 3. Parameters used in evaluation of experiments by Zioudas and Dadach (1986)

Parameter	Value		Source	
	MEA	AMP	MEA	AMP
k_L (m s^{-1})	$1.372 \times 10^{-6} [\text{CO}_2]_i^{0.33}$		Fitted to MEA experiments	
m	0.84		Water at 298 K	
k_p (m s^{-1})	100		No gas phase resistance	
K_{c1} ($\text{m}^3 \text{mol}^{-1}$)	4.73×10^4		Chakravarty (1985)	
K_{c2} (mol m^{-3})	4.65×10^{-8}		Chakravarty (1985)	
K_w ($\text{mol}^2 \text{m}^{-6}$)	9.38×10^{-9}		Harned (1958)	
K_p (mol m^{-3})	3.18×10^{-7}	1.95×10^{-7}	Perrin (1965)	
K_c ($\text{m}^3 \text{mol}^{-1}$)	2.71×10^{-2}	9.03×10^{-6}	Chan and Danckwerts (1981)	
k_{OH} ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	8.42		Pinsent <i>et al.</i> (1956)	
k_2 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	5.92	0	Blauwhoff <i>et al.</i> (1984)	
D_{CO_2} ($\text{m}^2 \text{s}^{-1}$)	1.9×10^{-9}		Water at 298 K	
D_{Am} ($\text{m}^2 \text{s}^{-1}$)	1.51×10^{-9}	1.31×10^{-9}	$D \div V_b^{-0.6}$	
D_{ion} ($\text{m}^2 \text{s}^{-1}$)	1.41×10^{-9}	1.45×10^{-9}	V_b from Perry and Chilton (1973)	

(1986). It is not clear from their paper whether the level of the gas phase concentration was varied sufficiently to check this.

5.4. Conclusion

Chakraborty *et al.* (1986) introduced the concept of homogeneous catalysis to explain the observed absorption behaviour of CO_2 in AMP solutions. The results presented here, however, show that without catalysis of the hydration of CO_2 considerable enhancement is possible in AMP solutions, due to the known reactions of CO_2 with AMP [reaction (14)] and hydroxyl ion [reaction (3)]. The simulations show clearly that the effects of established reactions should be assessed before new catalytic paths are demonstrated.

6. SIMULATION OF THE EXPERIMENTS BY ZILOUDAS AND DADACH (1986)

6.1. Data

The data used for the simulation of the experiments with the numerical film model on the absorption of CO_2 in MEA and AMP by Zioudas and Dadach are listed in Table 3. Because of the low concentrations used by Zioudas and Dadach the value of the physical constants for water were used. In the calculations the carbamate stability constant and the forward reaction rate constant for the reaction of CO_2 and AMP were taken to be very small, simulating no formation of carbamate at all, and therefore the results would give a minimum value for the absorption rate. This is

allowed here because of the low value of the amine concentration compared with the experiments of Chakraborty *et al.* (1986) (see Section 5.1). Numerical results calculated using higher carbamate stabilities and reaction rate constants do not differ very much from the ones presented here.

The values used for k_L were derived in the following way. The diffusion of the amine to the gas-liquid interface is expected to be the rate-limiting step for most of the experiments. For MEA the exponents in the power law fit of the results of Zioudas and Dadach (1986) ($Q = P_{\text{CO}_2}^{0.30} c_{\text{MEA}}^{0.73}$) indicate this kind of behaviour. Also the magnitude of the absorption rate is about 100 times lower than would be expected on the basis of a pseudo-first-order reaction with the rate constant k_2 of Table 3. So in this extreme case the absorption rate is completely diffusion-controlled. This case of a reacting gas diffusing into a stagnant liquid was analyzed by Danckwerts (1950). The absorption rate can be described by

$$Q = a \sqrt{t}. \quad (24)$$

This would mean that no constant absorption rates could be obtained, which is in contradiction with the experimental results. Therefore the liquid cannot be considered completely stagnant during the experiments and some convection must have occurred, presumably Rayleigh convection, caused by density gradients. Because it is possible to calculate absorption rates for a given mass transfer coefficient for the

experiments with MEA, the actual mass transfer coefficients can be estimated. It was found that the mass transfer coefficient increased with increasing MEA concentration and carbon dioxide partial pressure. This can be explained with the proposed cause of the non-stagnancy, because at higher concentrations the density gradients will be larger. Similar to turbulent free convection in heat transfer (Rohsenow *et al.*, 1985) a relation of the form

$$Sh = a(Sc Gr)^{0.33} \quad (25)$$

is used to correlate the mass transfer coefficients for MEA. The Grasshoff number is proportional to the difference between the density at the interface and the density of the liquid bulk. This difference was assumed to be proportional to the total concentration of the absorbed component at the interface multiplied by its molecular weight. The results of Zioudas and Dadach were fitted to this relation, leading to

$$k_L = 3.85 \times 10^{-6} (c_{A,i} M_A)^{0.33} \text{ m s}^{-1}. \quad (26)$$

The interfacial concentrations of carbamate and bicarbonate needed in this equation were obtained by trial and error.

The diffusivities were estimated the same way as in Section 5.1.

In Fig. 3 the results of Zioudas and Dadach are plotted together with the results of the present numerical simulation for MEA. The fit is good, in fact even better than that of the power law relation given by the

authors. In Fig 4 the concentration profiles calculated are plotted. It can be concluded that the reaction can be considered to be instantaneous and irreversible. The analytical solution for this situation should give rather good results. In Table 4 the numerical and analytical enhancement factors are compared with the experimental. The agreement is excellent.

At low partial pressures the simulation overestimates the observed mass transfer rate. This is probably due to the fact that the driving force for Rayleigh convection in this case is not high enough for the characteristic roll cells to develop. Also at these conditions the experiments show a behaviour (convexly curved lines in the Q vs t plot) that comes closer to the one expected for absorption into a truly stagnant liquid. The contact time according to the Higbie penetration model is of the same order of magnitude as the experimental times and therefore the film model is very unrealistic for this case.

The same method was used to simulate the H_2S absorption experiments conducted by Zioudas and Dadach and a satisfactory agreement with the experimental results was found.

6.2. Results for the sterically hindered amine AMP

The results of the simulations can be seen in Fig. 5 together with the experimental results by Zioudas and Dadach for AMP solutions. The concentration profiles are plotted in Fig. 6. The situation is much more complicated than for absorption in MEA solutions.

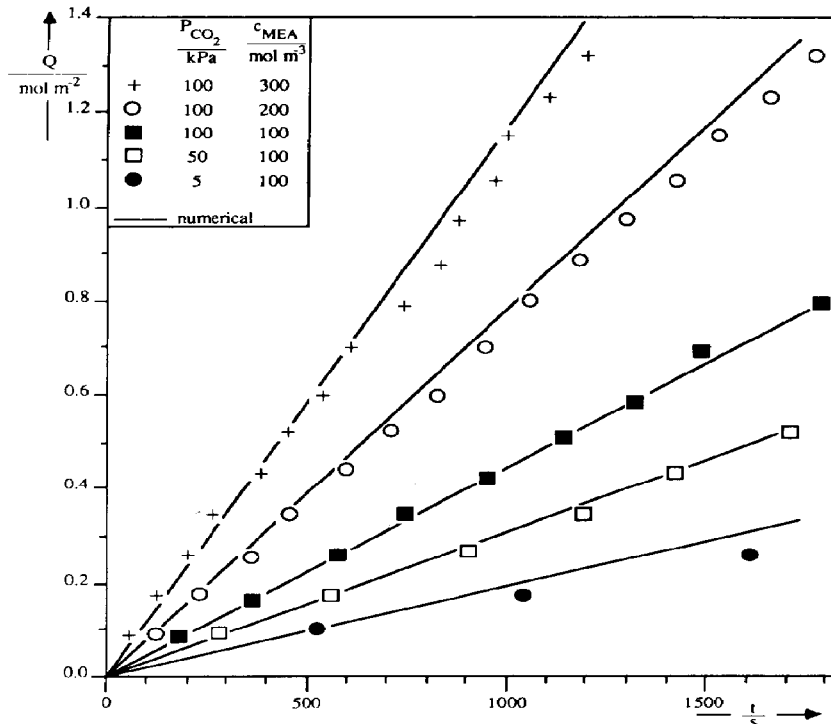


Fig. 3. Experimental results of Zioudas and Dadach (1986) and numerical results for absorption of CO_2 into aqueous MEA solutions at 298 K.

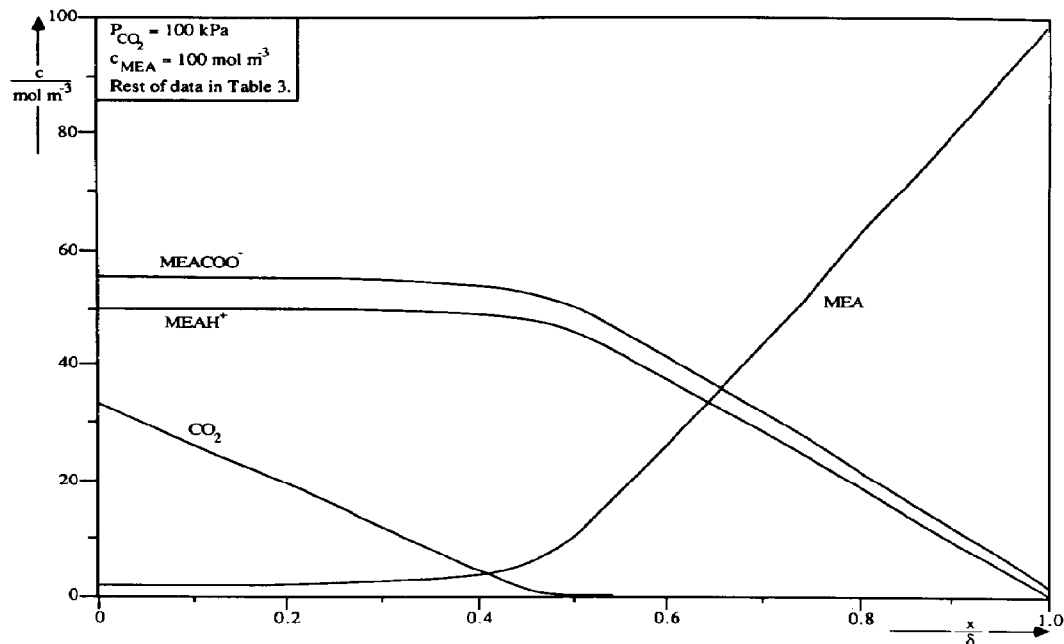


Fig. 4. Calculated concentration profiles for absorption of CO_2 into an aqueous MEA solution at 298 K.

Table 4. Analytical, numerical and experimental (Zioudas and Dadach, 1986) enhancement factors for absorption of CO_2 into aqueous MEA solutions

P_{CO_2} (kPa)	C_{MEA} (mol m^{-3})	$E_{\text{analytical}}$	$E_{\text{numerical}}$	$E_{\text{experimental}}$
5	100	24.6	22.6	20.5
50	100	3.36	3.33	3.35
100	100	2.18	2.19	2.19
100	200	3.36	3.33	3.35
100	300	4.54	4.48	4.48

Again the absorption rate at low partial pressures is overestimated. For higher partial pressures the agreement is good, except for the highest concentration of amine. The influence of the AMP concentration above 200 mol m^{-3} seems to decrease very drastically in the experiments.

6.3. Discussion

Although the reaction rate constant of AMP according to relation (13) was expected to be about as high as that for MEA the absorption rate for AMP is much lower in the fast reaction regime (low CO_2 partial pressures). This is caused by the low carbamate concentration due to the low value of the carbamate stability constant. So at low CO_2 partial pressures, contrary to the experiments of Chakraborty where much higher amine concentrations were used, little enhancement due to this reaction occurs. However, the hydration of CO_2 is fast compared to mass transfer and the molar flux through the interface can be described by

$$\begin{aligned}
 J &= [\text{CO}_2]_i \sqrt{k_{\text{OH}} [\text{OH}^-]_b D_{\text{CO}_2}} \\
 &= [\text{CO}_2]_i \sqrt{k_{\text{OH}} D_{\text{CO}_2} \sqrt{\frac{[\text{AMP}]_b K_w}{K_p}}} \quad (27)
 \end{aligned}$$

under the assumptions of a pseudo-first-order reaction and equilibrium of the acid-base reactions in the bulk of the liquid.

This yields $J = 5.92 \times 10^{-5} [\text{CO}_2]_i [\text{AMP}]_b^{1/4} = 6.29 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ for $P_{\text{CO}_2} = 100 \text{ kPa}$ and $[\text{AMP}]_b = 100 \text{ mol m}^{-3}$. This is about 10 times as high as the observed values. Only for the lowest partial pressures this relation gives reasonable results, so obviously, similarly to MEA, there must be depletion of AMP, as is also indicated by the concentration profiles in Fig. 6.

Knowing this, the experimental results can be explained qualitatively in the following way. At high partial pressures the supply of AMP from the bulk (to neutralize the excess protons) becomes rate-limiting. Only one molecule of AMP is needed per molecule of CO_2 , which means that the absorption rate for AMP

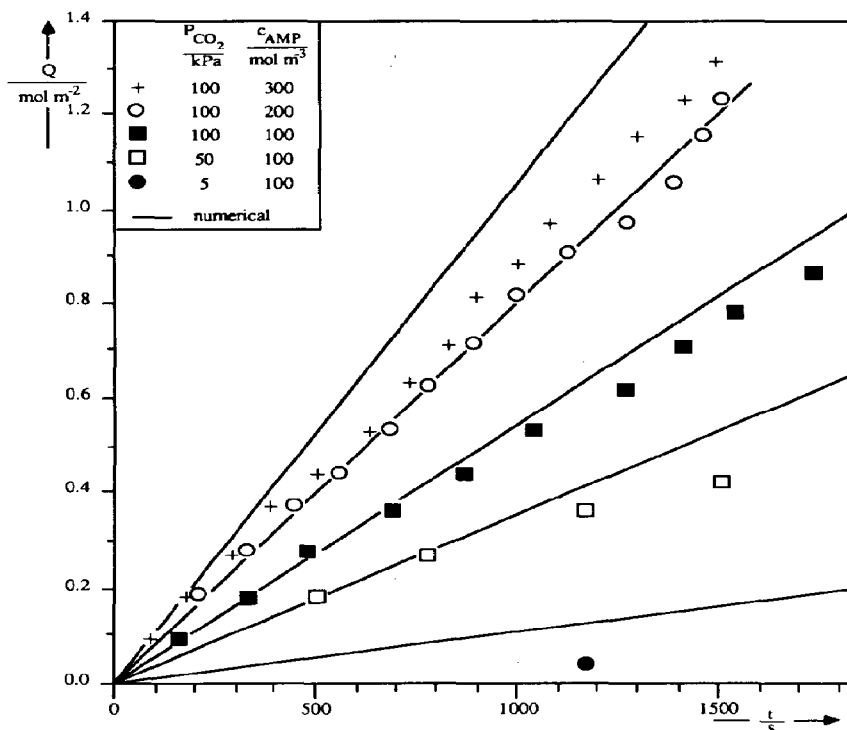


Fig. 5. Experimental results of Zioudas and Dadach (1986) and numerical results for absorption of CO_2 into aqueous AMP solutions at 298 K.

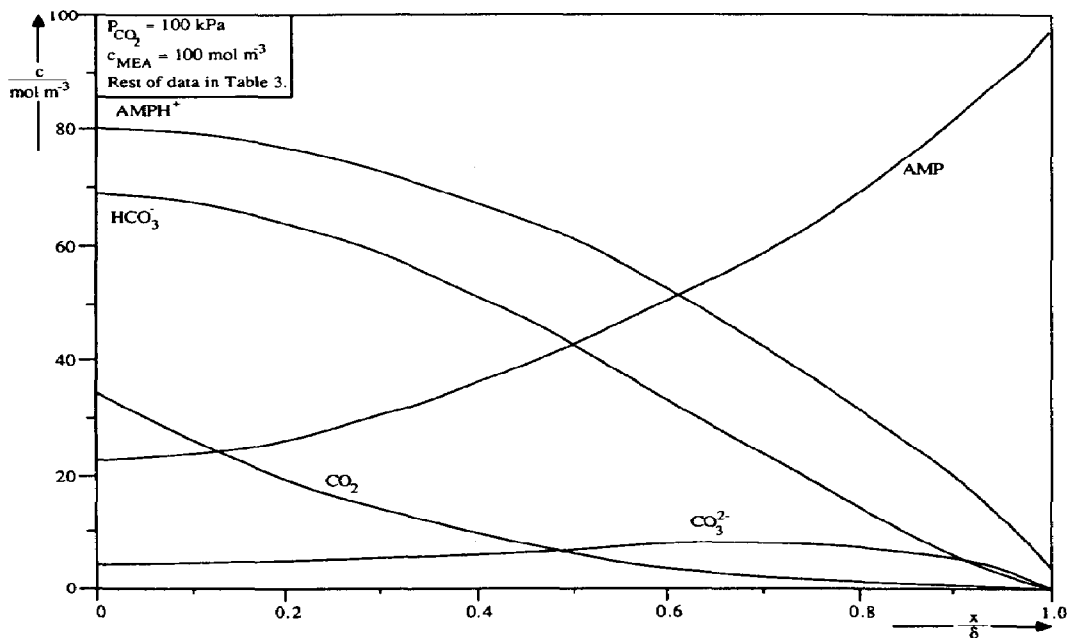


Fig. 6. Calculated concentration profiles for absorption of CO_2 into an aqueous AMP solution at 298 K.

could in principle become about twice as high as that for MEA. The experimental absorption rates in AMP solutions at higher partial pressures are in fact similar to those for MEA solutions, because the absorption

rate for the AMP solution is not completely controlled by AMP diffusion. This can be seen in Fig. 6 where no reaction plane can be identified. If absorption is completely controlled by diffusion all reactions must also

be at equilibrium. This can be checked by equilibrium eq. (28). At the interface the left-hand side of this equation is actually about 8, clearly showing a large deviation from equilibrium:

$$\frac{[\text{HCO}_3^-][\text{AMPH}^+]}{[\text{CO}_2][\text{AMP}]} = \frac{K_w K_{c1}}{K_p} = 2275. \quad (28)$$

6.4. Conclusions

From the simulations it can be concluded that no catalytic effects and not even formation of carbamate are necessary to account for the mass transfer rates observed by Zioudas and Dadach (1986). The hydration of CO_2 in the presence of AMP, which provides the OH^- ions needed for reaction with CO_2 , alone is able to account for the observed behaviour.

7. CONCLUSIONS

In the literature sterically hindered amines are treated as a special class of amines. They show a specific thermodynamical behaviour, and absorption of CO_2 into aqueous solutions is treated in a special way, using the model of homogeneous catalysis of the hydration of CO_2 . In this contribution it was demonstrated that if the effects of well-established reactions are carefully examined no new reaction paths are necessary to explain the observed absorption behaviour of AMP solutions for the available experiments.

For an ultimate decision about what reactions really occur more detailed information than is now available is needed. CO_2 absorption into AMP solutions is presently experimentally studied at our department and will be reported on in the future (Bosch *et al.*, 1989c).

Acknowledgements—These investigations were supported by the National Foundation for Scientific Research, the Dutch Technology Foundation and the Koninklijke/Shell Laboratorium, Amsterdam.

NOTATION

<i>a</i>	constant
A	component transferred from gas phase
B	base
<i>c</i>	concentration, mol m^{-3}
<i>d</i>	characteristic length, m
\mathbb{D}	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
<i>E</i>	enhancement factor
E^∞	enhancement factor for instantaneous reaction
<i>g</i>	gravitational acceleration, m s^{-2}
<i>J</i>	molar absorption flux, $\text{mol m}^{-2} \text{s}^{-1}$
k_b	reaction rate constant for zwitterion deprotonation, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k'_b	k_b/k_{-1} , s^{-1}
k_g	gas phase mass transfer coefficient, m s^{-1}
k_L	liquid phase mass transfer coefficient, m s^{-1}
k_{OH}	reaction rate constant for CO_2 hydration, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$

k_1	first-order reaction rate constant, s^{-1}
k_{-1}	reverse reaction rate constant, s^{-1}
k_2	second-order reaction rate constant, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
K_c	carbamate stability constant $\{K_c = [\text{AmR}_2\text{COO}^-]/([\text{AmR}_2\text{H}][\text{HCO}_3^-])\}$, $\text{m}^3 \text{mol}^{-1}$
K_{c1}	equilibrium constant for CO_2 hydrolysis $\{K_{c1} = [\text{HCO}_3^-]/([\text{OH}^-][\text{CO}_2])\}$, $\text{m}^3 \text{mol}^{-1}$
K_{c2}	bicarbonate dissociation constant $\{K_{c2} = ([\text{CO}_3^{2-}][\text{H}^+])/[\text{HCO}_3^-]\}$, mol m^{-3}
K_p	primary- or secondary-amine protonation constant ($K_p = [\text{AmR}_2\text{H}][\text{H}^+]/[\text{AmR}_2\text{H}_2^+]$), mol m^{-3}
K_w	dissociation constant of water ($K_w = [\text{H}^+][\text{OH}^-]$), $\text{mol}^2 \text{m}^{-6}$
<i>M</i>	molecular weight, kg mol^{-1}
<i>m</i>	distribution coefficient ($m = [\text{CO}_2]_L/[\text{CO}_2]_g$ at equilibrium)
<i>P</i>	pressure, N m^{-2}
<i>Q</i>	total amount of gas absorbed, mol m^{-2}
<i>r</i>	reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$
<i>t</i>	time, s
<i>T</i>	temperature, K
V_b	molecular volume at normal boiling point, $\text{m}^3 \text{mol}^{-1}$
<i>x</i>	spatial coordinate, m

Greek letters

α	liquid loading, mol CO_2 (mol primary absorbent) $^{-1}$
δ	thickness of laminar film, m
ν	kinematic viscosity, $\text{m}^2 \text{s}^{-1}$
ρ	density, kg m^{-3}

Dimensionless groups

<i>Gr</i>	Grasshoff number $\left(\frac{d^3 g \Delta \rho}{v^2 \rho}\right)$
<i>Ha</i>	Hatta number $\left(\sqrt{\frac{k_1 \mathbb{D}}{k_L^2}}\right)$
<i>Sh</i>	Sherwood number $\left(\frac{k_L d}{\mathbb{D}}\right)$
<i>Sc</i>	Schmidt number $\left(\frac{\nu}{\mathbb{D}}\right)$

Amine abbreviations

MEA	monogethanolamine
AMP	2-amino-2-methylpropanol
PE	2-piperidineethanol

Subscripts

<i>b</i>	bulk
<i>g</i>	gas
<i>i</i>	interface
ion	ionic products
<i>L</i>	liquid
<i>n, m</i>	indexes

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