

ON THE KINETICS BETWEEN CO₂ AND ALKANOLAMINES BOTH IN AQUEOUS AND NON-AQUEOUS SOLUTIONS—I. PRIMARY AND SECONDARY AMINES

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Abstract—The reaction between CO₂ and primary and secondary alkanolamines (DEA and DIPA) has been studied both in aqueous and non-aqueous solutions (ethanol and *n*-butanol) at various temperatures. Reaction kinetics have been established by chemically enhanced mass transfer of CO₂ into the various solutions. The experiments were performed in a stirred vessel operated with a horizontal interface which appeared to the eye to be completely smooth. The reaction can be described with the zwitterion-mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979). Literature data on the reaction rates can be correlated fairly well with this mechanism. As all amines react with CO₂ in a reversible way, and the mass transfer models used for the interpretation of the experimental data neglect this reversibility and take only the forward reaction rate into account, the influence of the reversibility is studied. With the aid of numerical mass transfer models (Versteeg *et al.*, 1987b,c) the experimental method with its underlying assumptions have been verified and the applicability and the limits of this method were determined. Special attention has been paid to the influence of small amounts of impurities (amines) on the measured mass transfer rates. A Brønsted relationship exists between the second-order rate constant, k_2 , for the formation of the zwitterion and the acid dissociation constant of the alkanolamine.

1. INTRODUCTION

In the extensive field of gas treating, alkanolamines have become one of the most important classes of chemicals for the removal of the acidic components H₂S and CO₂. Well known and industrially important amines are: monoethanolamine (MEA), diethanolamine (DEA) and diisopropanolamine (DIPA) (Kohl and Riesenfeld, 1979). Usually gas treating processes are operated with aqueous amine solutions but solvents consisting of a mixture of water and a non-aqueous solvent, e.g. sulfolane in the Shell-Sulfinol process, are also frequently used.

In many cases the removal of only H₂S is required whereas CO₂ should preferably remain in the treated gas. In these cases selective absorption of H₂S may lower capital and operating costs of the treating process drastically (Blauwhoff *et al.*, 1985). Selective removal of H₂S is achieved among others by the reduction of the reaction rate between CO₂ and the alkanolamine. Therefore a complete understanding of the reaction mechanism is necessary to select amines suitable for the selective removal of H₂S. The reaction rate between H₂S and alkanolamines can be regarded to be infinitely fast with respect to mass transfer as it involves only a proton transfer (Danckwerts and Sharma, 1966), however, this assumption may be invalid in case non-polar solvents are used because in these solvents H₂S is almost unionized.

In the last decade a large number of articles on the reaction between CO₂ and alkanolamines in aqueous solutions have been published which were recently reviewed by Blauwhoff *et al.* (1984). In spite of the amount of investigations considerable discrepancies

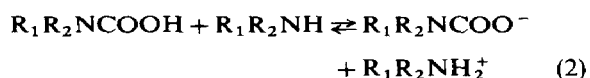
appear in the results of the various authors. The results will be briefly summarized here.

Only for MEA a general agreement exists on the reaction order and the value of the reaction rate constant. This agreement is remarkable because various techniques have been used, e.g. the rapid-mixing method, wetted wall, stopped flow technique, tracer-diffusion method and continuously stirred vessel (Blauwhoff *et al.*, 1984). Another extensively studied amine is DEA. For this amine there is no general agreement on reaction order and value of kinetic constant (Blauwhoff *et al.*, 1984). The same conclusion holds for DIPA (Blauwhoff *et al.*, 1984; Savage and Kim, 1985). For these secondary amines the reaction mechanism according to Danckwerts (1979) is widely supported however.

In the present study additional experiments for the verification of the proposed mechanism for primary and secondary alkanolamines are presented.

2. THE REACTION MECHANISM

The overall forward reaction between CO₂ and alkanolamines has usually been represented as:

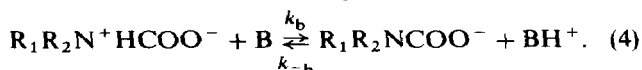
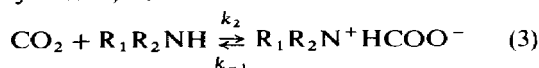


the first step being bimolecular, second-order and rate determining, while the second step was supposed to take place *instantaneously*. However, this reaction scheme is a crude simplification for the process that actually occurs in practice. As mentioned before, only for aqueous MEA solutions good agreement exists on

the overall reaction order and reaction rate constant (Blauwhoff *et al.*, 1984). For the two secondary amines DEA and DIPA the issue of the reaction order is still under discussion. Several authors reported overall second order kinetics (Sada *et al.*, 1967; Barth *et al.*, 1983; Blanc and Demarais, 1984; Savage and Kim, 1985), or overall third order kinetics (van Krevelen and Hofstijzer, 1948; Nunge and Gill, 1963; Hikita *et al.*, 1977a; Alvarez-Fuster *et al.*, 1980). Blauwhoff *et al.*, (1984) and Laddha and Danckwerts (1981) reported an overall reaction order varying between two and three with the amine concentration. All the publications mentioned above were based on the results of experiments carried out in aqueous solutions.

Alvarez-Fuster *et al.* (1981), however, reported of experiments conducted in non-aqueous solutions. They found that the overall reaction order for both MEA and DEA in the solvents ethanol and ethylene-glycol had a value of three. From these results it can be concluded that the reaction order for MEA shifted from two to three by changing the solvent from water to ethanol or ethyleneglycol. Therefore the mechanism of the reaction between CO₂ and alkanolamines is even for MEA not as simple and straightforward as suggested by the reaction equations (1) and (2).

Danckwerts (1979) reintroduced a mechanism proposed originally by Caplow (1968) which describes the reaction between CO₂ and alkanolamines via the formation of a zwitterion followed by the removal of a proton by a base, B:



For this mechanism the overall forward reaction rate equation can be derived with the assumption of quasi-steady state condition for the zwitterion concentration:

$$r = \frac{k_2 [\text{CO}_2] [\text{R}_1\text{R}_2\text{NH}]}{1 + \frac{k_{-1}}{\sum k_b [\text{B}]}} \quad \text{mol.m}^{-3}.\text{s}^{-1} \quad (5)$$

where $\sum k_b [\text{B}]$ is the contribution to the removal of the proton by all bases present in the solution. In lean aqueous solutions the species water, OH⁻ ions and the amine act as bases whereas for non-aqueous solvents usually only the amine can be regarded as a base.

For two asymptotic situations eq. (5) may be simplified resulting in:

1. The second term in the denominator is $\ll 1$. This

results in simple second-order kinetics, as for instance is found experimentally for aqueous MEA solutions:

$$r = k_2 [\text{CO}_2] [\text{R}_1\text{R}_2\text{NH}] \quad \text{mol.m}^{-3}.\text{s}^{-1} \quad (5a)$$

2. The second term in the denominator is $\gg 1$. This results in a more complex expression for the kinetics:

$$r = k_2 [\text{CO}_2] [\text{R}_1\text{R}_2\text{NH}] (\sum k_b [\text{B}]) / k_{-1} \quad \text{mol.m}^{-3}.\text{s}^{-1} \quad (5b)$$

As can be concluded from eq. (5b) it is possible that the overall reaction order is three. In the transition region between the two asymptotic cases the overall reaction order changes between two and three (Blauwhoff *et al.*, 1984; Laddha and Danckwerts, 1981). Therefore the reaction mechanism proposed by Danckwerts (1979) covers the shifting reaction orders for the reaction between CO₂ and different primary and secondary alkanolamines.

2.1. MEA

For aqueous MEA solutions the overall reaction order has a value of two and the partial order in the amine is equal to one. This corresponds with asymptotic case 1 and indicates that the deprotonation of the zwitterion by the bases present in the solution is very fast compared to the rate of the reverse reaction to CO₂ and amine. However, by changing the solvent the overall reaction order and the partial reaction order in the amine also changes. Sada *et al.* (1985) investigated the reaction between CO₂ and MEA at 303 K in water, methanol, ethanol and 2-propanol solutions respectively and found a gradual change of the partial reaction order in MEA from 1 to 1.90, the overall reaction order changing from 2 to 2.90. Alvarez-Fuster *et al.* (1981) reported that the reaction order in MEA was 2 at 293 K for both the solvents ethanol and ethylene-glycol, however, due to the interpretation method applied this author was not able to detect reaction orders different from whole numbers. Both results can be explained with the zwitterion-mechanism if the rate of the deprotonation step decreases relative to the rate of the reverse reaction, indicating that the zwitterion is less stable and that the solvent is not able to produce the zwitterion in a complete ionic form, i.e. the value of k_{-1} will increase relative to $\sum k_b [\text{B}]$ and the overall reaction order will gradually change from 2 up to 3. In Table 1 the results for the reaction between CO₂ and MEA in non-aqueous solvents are summarized.

Table 1. Literature data on the reaction between CO₂ and MEA in non-aqueous solvents

Investigators	Solvent	Temperature (K)	k_2 (m ³ .mol ⁻¹ .s ⁻¹)	$k_2.k_b/k_{-1}$ (m ⁶ .mol ⁻² .s ⁻¹)
Alvarez-Fuster <i>et al.</i> (1981)	ethanol	293	—	2.87×10^{-3}
	ethyleneglycol	293	—	8.17×10^{-3}
Sada <i>et al.</i> (1985)	methanol	303	8.33	6.49×10^{-3}
	ethanol	303	8.33	2.91×10^{-3}
	2-propanol	303	8.33	2.28×10^{-3}

2.2. DEA

For aqueous DEA solutions the overall reaction order varied from 2 to 3. Blauwhoff *et al.* (1984) interpreted all results published according to the zwitterion mechanism and considered all bases present in the solution (H₂O, OH⁻ and amine) to contribute to the removal of the proton of the zwitterion. The contributions of H₂O and OH⁻ were usually neglected by other authors. By this approach their kinetic model was also able to obtain a good agreement with the results of Jensen *et al.* (1954) and Jørgensen (1956). Barth *et al.* (1984) re-examined his results and concluded that the Blauwhoff approach was the closest to his results with respect to both reaction order and reaction rate constant. In spite of this good agreement a discrepancy still remains between the Blauwhoff approach and the results of Hikita *et al.* (1977a).

Also for DEA Sada *et al.* (1985) studied the influence of the nature of the solvent on the reaction at 303 K. The reaction order in amine was measured with water, methanol, ethanol and 2-propanol solutions and changed from 1.42 to 2, the overall reaction order changing from 2.42 up to 3. For ethanol and ethylene-glycol Alvarez-Fuster *et al.* (1981) found a second order in amine at 293 K. These changes in reaction order can also be explained with the zwitterion-mechanism in a similar way as for MEA. However, the overall reaction order for aqueous solutions also differs from 2, which can be explained from the fact that DEA is a much weaker base than MEA which results in a less stable zwitterion and therefore in a relative higher value of k_{-1} . Also steric hindrance may

contribute to a lower rate of deprotonation of the zwitterion as the ability to reach and remove the proton of the zwitterion is less easy resulting also in lower values of k_b . In Table 2 the results for the reaction between CO₂ and DEA in non-aqueous solvents are summarized.

2.3. Conclusion

The observed reaction orders between CO₂ and alkanolamines in various solutions can be explained and described with the zwitterion-mechanism and most of the apparent discrepancies can be explained by this mechanism. However, the deviation of the results of a few studies (Hikita *et al.*, 1977a; Barth *et al.*, 1984) still remains unsatisfactorily. In order to evaluate the zwitterion-mechanism in more detail, additional experiments have been carried out in this study over a wider range of conditions and solvents. The reaction of CO₂ and DEA has been studied for the solvents ethanol and *n*-butanol at 293 K. Furthermore the temperature influence on the reaction of CO₂ and DIPA has been studied. For aqueous DEA-solutions at 298 K the kinetic data have been re-examined because of new data on the physico-chemical properties (Versteeg and van Swaaij, 1987; Versteeg, 1986).

3. EXPERIMENTAL

The experiments were carried out in a stirred vessel with a smooth gas-liquid interface and were operated batchwise with respect to both liquid and gas phases. The experimental set-up used is identical to that of Blauwhoff *et al.* (1984) and is shown in Fig. 1.

Table 2. Literature data on the reaction between CO₂ and DEA in non-aqueous solvents

Investigators	Solvent	Temperature (K)	k_2 (m ³ .mol ⁻¹ .s ⁻¹)	$k_2 \cdot k_b / k_{-1}$ (m ⁶ .mol ⁻² .s ⁻¹)
Alvarez-Fuster <i>et al.</i> (1981)	ethanol	293	—	0.133×10^{-3}
	ethyleneglycol	293	—	0.304×10^{-3}
Sada <i>et al.</i> (1985)	methanol	303	0.34	0.340×10^{-3}
	ethanol	303	0.29	0.200×10^{-3}
	2-propanol	303	0.24	0.180×10^{-3}

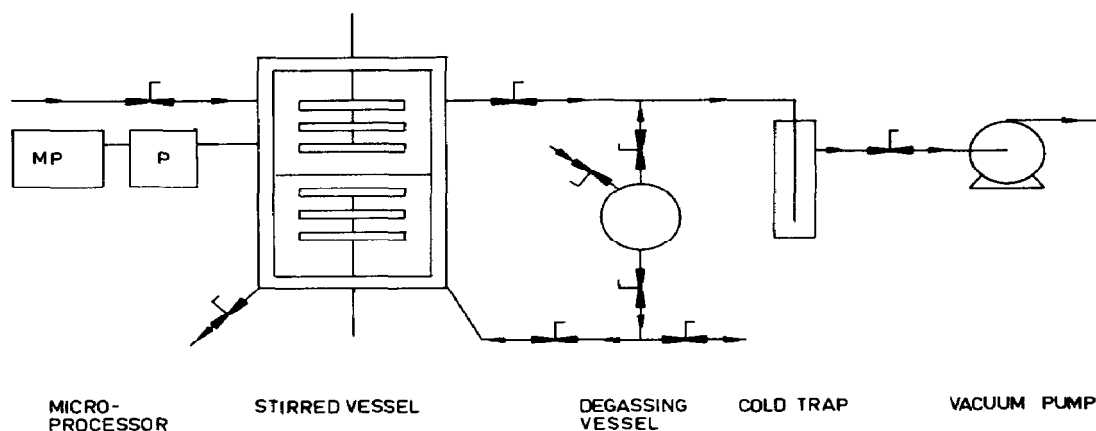


Fig. 1. Experimental set-up.

However, for the original set-up the pressure decrease was recorded by a mercury pressure indicator and in the present set-up with a pressure transducer. This transducer was connected to a micro-computer which calculated directly the overall reaction rate constant, k_{ov} , after the equilibrium pressure at the end of the experiment was reached. A detailed description of the experimental procedure is given by Blauwhoff *et al.* (1984).

During each experiment the pressure decrease due to the absorption of pure CO_2 was recorded and the reaction kinetics could be obtained if the following conditions were satisfied:

$$2 < Ha \ll E_{\text{CO}_2,i} \quad (6)$$

with:

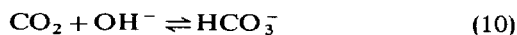
$$Ha = \frac{\sqrt{k_{ov} D_{\text{CO}_2}}}{k_1} \quad (7)$$

$$E_{\text{CO}_2,i} = \sqrt{\frac{D_{\text{CO}_2}}{D_{\text{Am}}}} + \sqrt{\frac{D_{\text{Am}}[\text{Am}] \cdot R \cdot T}{D_{\text{CO}_2} \gamma_{\text{Am}} \cdot P_{\text{CO}_2}}} \quad (8)$$

If condition (6) is fulfilled, the reaction can be regarded as pseudo first order and the CO_2 -absorption rate is then described by:

$$J_{\text{CO}_2} \cdot A = \sqrt{k_{ov} D_{\text{CO}_2}} m_{\text{CO}_2} P_{\text{CO}_2} A / RT \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \quad (9)$$

In aqueous amine solutions the pseudo first order overall reaction rate constant, k_{ov} , comprises the contributions of the following reactions:



with the following relation for the overall forward reaction rate constant

$$k_{ov} = (k_{\text{OH}^-})' \cdot [\text{OH}^-] + (k_{\text{H}_2\text{O}})' + k_{\text{app}} \text{ s}^{-1} \quad (13)$$

The value of $(k_{\text{OH}^-})'$ can be calculated according to McLachlan and Danckwerts (1972), the value of $(k_{\text{H}_2\text{O}})'$ can be calculated according to Pinsent *et al.* (1956) and k_{app} is the pseudo first order reaction constant for the reaction between CO_2 and the alkanolamine.

As CO_2 reacts with the alkanolamine it is not possible to determine the solubility and diffusivity directly, therefore the properties must be estimated from the corresponding data of more or less similar non-reacting gases. In view of the similarities with regard to configuration, molecular volume and electronic structure, N_2O is often used as non-reacting gas to estimate the properties of CO_2 . In the present study the solubility and diffusivity of CO_2 in both aqueous and non-aqueous amine solutions were determined by means of the CO_2 - N_2O analogy (Laddha *et al.*, 1981; Versteeg and van Swaaij, 1987).

The actual $P_{\text{CO}_2,t}$ in the reactor can be calculated

according to the following relation:

$$P_{\text{CO}_2,t} = P_{\text{tot},t} - P_{\text{eq},t} - P_{\text{solvent}} - P_{\text{inert}} \quad (14)$$

where P_{tot} is the total pressure in the system, P_{solvent} the vapour pressure above the unloaded amine solution, P_{inert} the pressure due to impurities in the gas phase and P_{eq} is the equilibrium pressure of the unconverted CO_2 in the liquid, due to CO_2 -alkanolamine equilibrium. The value of P_{eq} is influenced by the total amine conversion and therefore P_{eq} changes during the experiment. For aqueous amine solutions and low amine conversions P_{eq} can be neglected compared to $(P_{\text{solvent}} + P_{\text{inert}})$ but for non-aqueous solutions P_{eq} can have substantial values.

The assumption of pseudo first order kinetics and therefore the use of eq. (9) for the description of the molarflux is valid only for irreversible chemical reactions. However, if the equilibrium constant of reaction (12) is sufficiently high and the amine conversion is very low the use of eq. (9) is allowed. In case of low equilibrium constants or high amine conversions this assumption may not always be valid and has to be checked by a model which describes the phenomenon mass transfer followed by a reversible chemical reaction (Versteeg *et al.*, 1988b).

The purity of all amines was $\geq 98\%$ and were used as supplied. In order to check the influence of contaminants (fast reacting primary and secondary amines) on the reaction rate, the measured molfluxes were compared with calculated molfluxes according to the numerical multi-component model (Versteeg *et al.*, 1987b).

4. RESULTS

4.1. DEA-ethanol

In the present investigation, the reaction between CO_2 and DEA in ethanol has been studied at 293 K. The reaction rate expression according to the zwitterion mechanism for non-aqueous solvents, e.g. ethanol, is simplified to:

$$r = \frac{k_2 [\text{CO}_2] [\text{R}_1 \text{R}_2 \text{NH}]}{1 + \frac{k_{-1}}{k_b [\text{B}]}} \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \quad (15)$$

as the amine is the only base left for the deprotonation of the zwitterion. Therefore the reaction order in amine can have values changing from 1 up to 2.

In Table 3 the values of the term $m\sqrt{D}$ of CO_2 in ethanol and N_2O in both ethanol and DEA in ethanol solutions are presented. The results of the absorption experiments are presented in Fig. 2. From Fig. 2 it can be concluded that the reaction order in amine gradually changes from about 2 (low amine concentrations) to a value of about 1.5 (high amine concentrations) which is well in line with the zwitterion mechanism. If the zwitterion mechanism is valid and eq. (15) holds, a plot of $[\text{DEA}]/k_{\text{app}}$ against $1/[\text{DEA}]$ should yield a straight line with slope $k_{-1}/k_2 k_b$ and intercept $1/k_2$. Such a plot is shown in Fig. 3. Linear regression leads to $k_2 = 0.215 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $k_2 k_b / k_{-1} = 0.150$

Table 3. $m\sqrt{D}$ for N₂O and CO₂ in DEA-ethanol solutions

[DEA] (mol.m ⁻³)	Gas	Temperature (K)	$m\sqrt{D} \times 10^3$ (m.s ^{-1/2})	Reference
0	CO ₂	293	0.137	our result
0	CO ₂	293	0.164	Alvarez-Fuster <i>et al.</i> (1981)
0	CO ₂	298	0.143	Takeuchi <i>et al.</i> (1975)
0	CO ₂	298	0.156	Takahahi <i>et al.</i> (1982)
0	CO ₂	298	0.166	Tang and Himmelblau (1965)
0	CO ₂	303	0.171	Sada <i>et al.</i> (1985)
0	N ₂ O	293	0.144	our result
490	N ₂ O	293	0.126	our result
927	N ₂ O	293	0.112	our result
1096	N ₂ O	293	0.113	our result
1319	N ₂ O	293	0.112	our result
1640	N ₂ O	293	0.103	our result
1930	N ₂ O	293	0.100	our result
2287	N ₂ O	293	0.088	our result
2599	N ₂ O	293	0.082	our result
2937	N ₂ O	293	0.082	our result

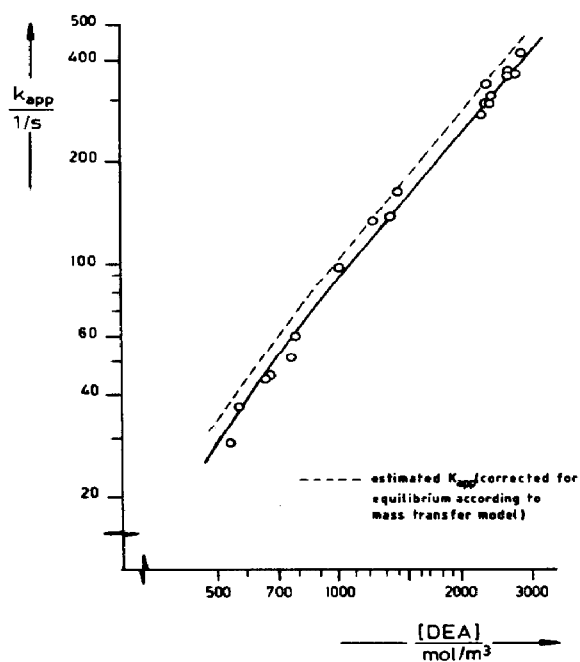


Fig. 2. Experimental results for DEA-ethanol at 293 K.

$\times 10^{-3} \text{ m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$. It can therefore be concluded that the reaction between DEA and CO₂ in ethanol can be described satisfactorily with the zwitterion mechanism. The agreement on the reaction order found in amine with Alvarez-Fuster *et al.* (1981) and Sada *et al.* (1985), with values 2.0 and 1.74 respectively, is good. After calculation of the absorption rates according to the values for the reaction rate constants in Table 2, it can be concluded that the results of Alvarez-Fuster *et al.* (1981) and the present results at 293 K are comparable up to an amine concentration of about 400 mol.m⁻³. However, for amine concentrations above 750 mol.m⁻³ the results of Alvarez-Fuster *et al.* (1981) are even much higher than the results of Sada

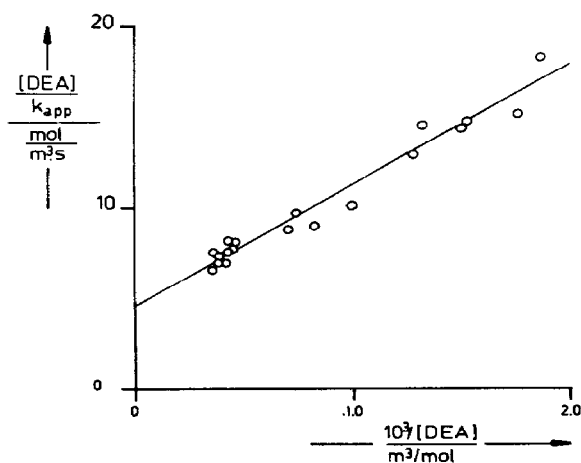


Fig. 3. The zwitterion mechanism plot for DEA-ethanol at 293 K.

et al. (1985) at 303 K. These discrepancies in the calculated absorption rates at higher amine concentrations can not be explained from differences in the physico-chemical data used for the interpretation of the absorption experiments as can be concluded from Table 3. A likely explanation for these differences in absorption rates at higher amine concentrations could be the occurrence of interfacial turbulence due to the formation of ionic reaction products close to the gas-liquid interface. The absorption rate can then increase either by differences in density or by differences in surface tension. This effect was visually observed for our experiments but only at high amine concentrations and relative large values of P_{CO_2} ($> \sim 7 \text{ kPa}$). A similar effect may possibly have affected the results of Alvarez-Fuster *et al.* (1981) resulting in too high observed rate constants (their values of P_{CO_2} were between 4.1 kPa and 11.1 kPa). For the present investigation the experiments carried out with large values of P_{CO_2} were not used for

determining the reaction rate constants. However, this does not imply that the influence of these eddies was completely excluded.

For the interpretation of the absorption experiments it was assumed that the experiments could be described as gas absorption into a liquid followed by an irreversible pseudo first order reaction. However, the actual reaction is not irreversible and therefore the influence of its reversibility and the CO_2 -liquid load (or amine conversion) on the mass transfer rate has to be checked. Therefore molflux calculations were used according to a numerical model for mass transfer with an equilibrium reaction (Versteeg *et al.*, 1988b).

The enhancement factor for the equilibrium reaction was calculated for a low and a high amine concentration and the other conditions, P_{CO_2} and CO_2 -liquid concentration, used for the calculations were the extreme values of the experiments. It should be realized that the results of this verification are not completely reliable because data on the reverse reaction are not available and therefore have been derived from the definition that at equilibrium the overall reaction rate is equal to zero:

$$r = 0 = \bar{r} - \bar{r} \quad (16)$$

and both forward and reverse reaction rate expressions have been derived from the following equation:

$$K_{\text{eq}} = \frac{\bar{k}}{\bar{k}} = \frac{[\text{AmCOO}^-][\text{AmH}^+]}{[\text{CO}_2][\text{Am}]^2} \quad (17)$$

resulting in:

$$\begin{aligned} \bar{r} &= k_3 [\text{Am}]^2 [\text{CO}_2] \quad \text{and} \\ \bar{r} &= k_2 [\text{AmCOO}^-][\text{AmH}^+]. \end{aligned} \quad (18)$$

The reaction rate expression obtained in this way should be used carefully as it may only be valid for the actual process close to equilibrium. An exact verification therefore is only possible if the reverse reaction rate is determined. Also the diffusivities of the various components have to be estimated. The diffusivity of

CO_2 was measured experimentally with a laminar film reactor. The diffusivity of the amine has been calculated according to Versteeg and van Swaaij (1987) and the values of the diffusivities of the ionic products have been taken equal in order to assure overall electro-neutrality and were given the same value as the component (amine) with the lowest diffusivity:

$$D_{\text{Am}} = D_{\text{AmCOO}^-} = D_{\text{AmH}^+} \quad (19)$$

In Fig. 4 the enhancement factor for the pseudo first order irreversible reaction is plotted together with the enhancement factor for the equilibrium reaction as a function of the Ha -number. Plots like Fig. 4 have been used to select the experiments which can be used for the calculation of the reaction rates. From this figure it can be concluded that only the experiments carried out at a low P_{CO_2} and with a low amine conversion can be used for the correct determination of the reaction rate constants because for these experiments the assumption of pseudo first order irreversible reaction is virtually fulfilled. At low amine concentrations the Ha -number has the lowest allowable value for calculating reaction rates with respect to both reversibility and the fast reaction condition ($Ha > 2$).

Figure 4 can also be used to estimate the errors due to reversibility and in Fig. 2 the estimated pseudo first order reaction rate constant corrected for reversibility according to the numerical model is also plotted. However, it is not possible to calculate the reaction rate constant exactly with this model because the reverse reaction was not studied and may actually have less effect than suggested in Fig. 2.

4.2. DEA-*n*-butanol

Experiments were also carried out for the system CO_2 -DEA-*n*-butanol at 293 K. In Table 4 the physico-chemical data for the system DEA-*n*-butanol are presented. From the results presented in Fig. 5 it can be concluded that the reaction order in amine is

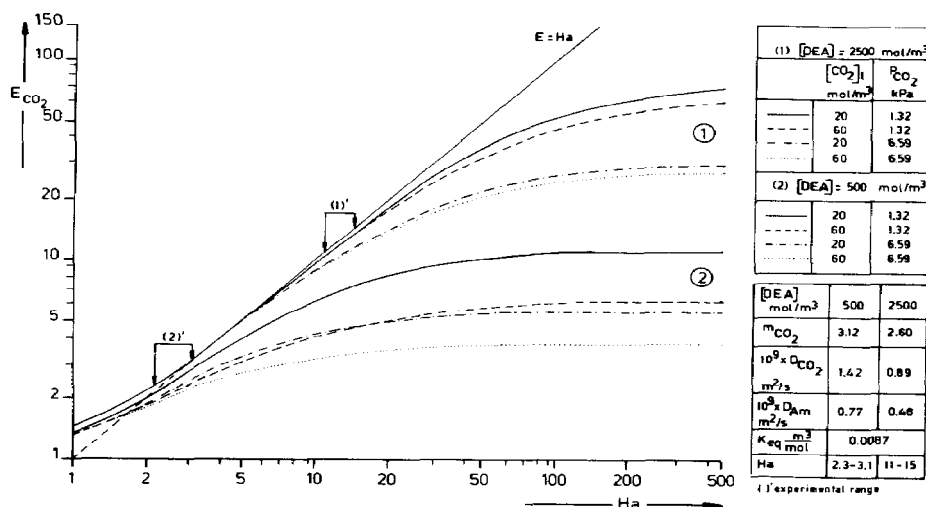
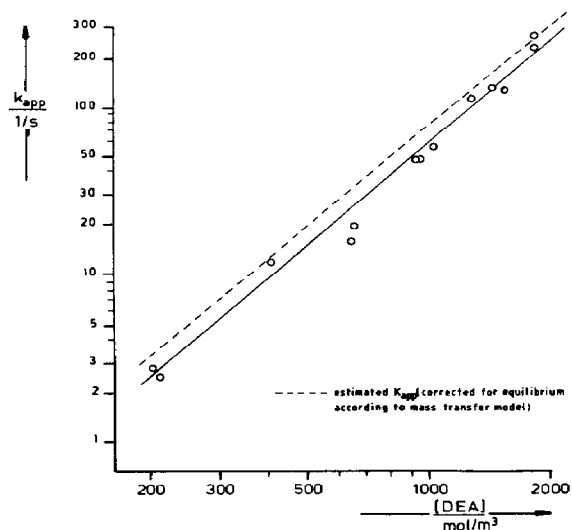


Fig. 4. Enhancement factor vs. Ha -number for DEA-ethanol at 293 K.

Table 4. $m\sqrt{D}$ for N₂O and CO₂ in DEA-*n*-butanol solutions at 293 K (our measurements)

[DEA] (mol.m ⁻³)	Gas	$m\sqrt{D} \times 10^3$ (m.s ^{-1/2})
0	CO ₂	0.082
0	N ₂ O	0.144
400	N ₂ O	0.117
750	N ₂ O	0.108
1130	N ₂ O	0.092
1400	N ₂ O	0.091
1950	N ₂ O	0.088

Fig. 5. Experimental results for DEA-*n*-butanol at 293 K.

constant for all the amine concentrations and equal to 2. The reaction rate, with $k_2 k_b / k_{-1} = 59 \times 10^{-6} \text{ m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$, is clearly lower than the reaction rate for the system CO₂-ethanol. This can be explained as the stability of the zwitterion decreases if

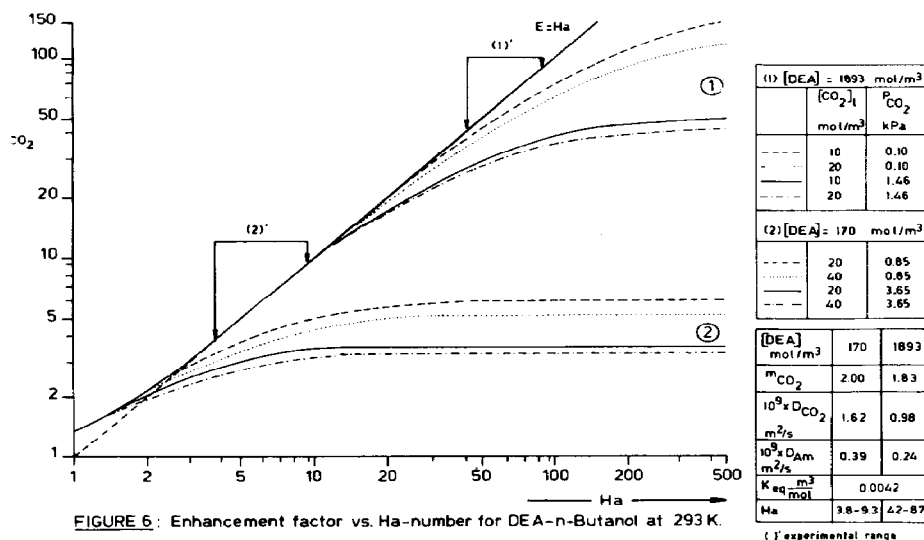
the solvent is changed from ethanol to *n*-butanol resulting in a relatively higher value of k_{-1} .

In Fig. 6 the enhancement factor, calculated according to the procedure mentioned before, is plotted for the irreversible and reversible reaction respectively, as a function of the *Ha*-number. From this figure it can be concluded that it was not possible to fulfil the criteria of a pseudo first order irreversible reaction. Therefore the experimentally determined reaction rate constant can be considered only as a first approximation and that it is impossible to obtain purely kinetic data for the forward reaction from absorption experiments at 293 K. In Fig. 5 the estimated pseudo first order reaction rate constant corrected for the reversibility according to the numerical model is also plotted. Overall it can be concluded that for the correct determination of the kinetics of a reversible reaction by means of mass transfer experiments the assumption of pseudo first order irreversible reaction always should be checked for the experimental conditions used. This is possible with the aid of a mass transfer model according to Onda *et al.* (1970) and Versteeg *et al.* (1988b).

4.3. DIPA-H₂O

In the present work the kinetics of the reaction between CO₂ and aqueous DIPA solutions was studied at 293, 298, 308, 318 and 333 K.

The experiments were evaluated according to Blauwhoff *et al.* (1984) using the zwitterion mechanism and regarding the amine, H₂O and OH⁻ as species which are able to deprotonate the zwitterion. From the interpretation of the results it could be concluded that it was not possible to determine accurately the contribution of the OH⁻ ions to the deprotonation of the zwitterion because this contribution was always less than 10%. According to the results from Blauwhoff *et al.* (1984), the pseudo first order reaction rate constant for the actual composition of the amine solution and

FIGURE 6: Enhancement factor vs. *Ha*-number for DEA-*n*-Butanol at 293 K.Fig. 6. Enhancement factor vs. *Ha*-number for DEA-*n*-butanol at 293 K.

the reaction rate constant for $[\text{OH}^-] = 0$ were calculated and the difference between these calculated reaction rates is less than 10% at amine conversions above 1%. It was also concluded from the experiments that it is difficult with the experimental technique used to measure absorption rates for systems with amine conversions below 1% and that it therefore was impossible to determine the reaction rate constant for the deprotonation of the zwitterion by means of the OH^- ion accurately. However, for industrial processes the amine conversion is nearly always larger than 1% and therefore it is allowed to simplify the reaction rate expression without significant loss of accuracy. The experiments were evaluated with only two species relevant to the rate of deprotonation of the zwitterion: amine and H_2O .

The results of the experiments at 293 K and 298 K are presented in Table 5. The fitted values of the kinetic constants are calculated with an optimization technique (maximum likelihood principle) (Klaus, 1981) and are presented in Table 6. The influence of reversibility on the mass transfer rate is checked with a mass transfer model. In Fig. 7 the enhancement factor is plotted as a function of the Ha -number for both irreversible and reversible reaction at 293 K. From Fig. 7 it can be concluded that it is possible to determine reaction rate constants at 293 K from mass transfer experiments. The same conclusion holds for the experiments carried out at 298 K. The results of Blauwhoff *et al.* (1984) agree extremely well with the present results at 298 K.

For the other temperatures the reversibility has a pronounced effect on the measured absorption rates (at 333 K the measured enhancement factors are of the same order as the enhancement factors at 298 K). The influence of reversibility has been estimated with the mass transfer model and it could be concluded that this influence was always larger than 10% and that the assumption of irreversible pseudo first order could not be fulfilled. Therefore it was not possible to obtain purely kinetic data for reaction (12) at higher temperatures. In Fig. 8 the enhancement factor is plotted as a function of the Ha -number for both irreversible and reversible reaction at 333 K. The kinetic constants used for the simulation are extrapolated with the aid of the results presented in Table 6.

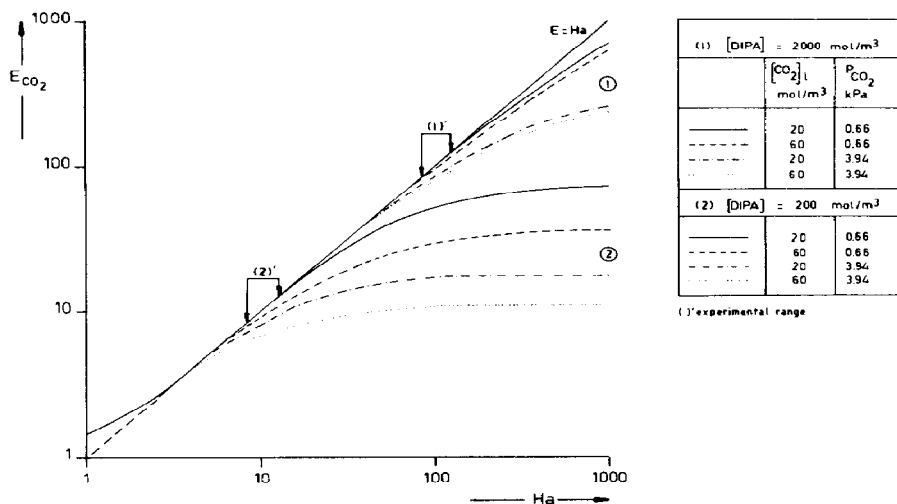
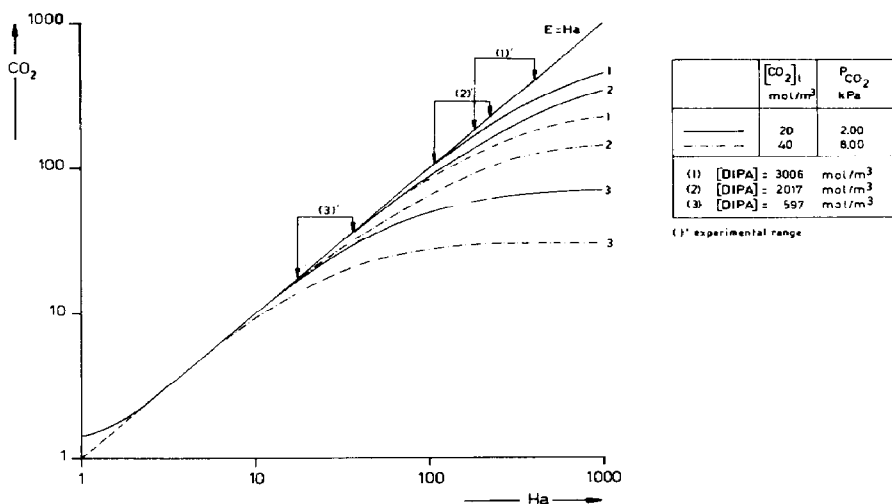
As the amine purity used was only 98% wt, and could not be improved by means of vacuum distillation, the influence of contaminants on the absorption rate has been checked by means of the model proposed by Versteeg *et al.* (1988c). In this simulations it was

Table 5. Experimental results for the system DIPA-water

[DIPA] (mol.m ⁻³)	[H ₂ O] (mol.m ⁻³)	[OH ⁻] (mol.m ⁻³)	T (K)	k _{app} (1/s)
228	53500	0.050	293	17.1
237	53400	0.048	293	17.7
257	53460	0.099	293	21.1
263	53200	0.058	293	23.2
295	53300	0.115	293	27.4
335	52390	0.066	293	36.3
409	52380	0.143	293	48.7
426	52000	0.084	293	40.7
508	51400	0.101	293	55.2
547	51500	0.199	293	66.8
560	51500	0.263	293	68.9
732	49820	0.137	293	113
780	49410	0.134	293	122
782	49810	0.278	293	140
790	49500	0.159	293	144
863	49100	0.189	293	141
906	48700	0.187	293	150
969	48600	0.393	293	176
972	48600	0.416	293	159
1413	45200	0.304	293	375
1469	45100	0.584	293	384
1486	44550	0.260	293	391
1492	44880	0.493	293	406
1510	44770	0.511	293	388
1686	43240	0.307	293	540
1913	41800	0.389	293	541
1976	41600	0.739	293	649
1995	41500	0.818	293	624
2464	37700	0.385	293	921
2484	38100	0.970	293	1010
2492	38100	1.042	293	867
2552	37190	0.448	293	1098
2620	37110	0.876	293	1027
2707	36060	0.445	293	1117
2769	35680	0.447	293	1190
2880	35440	1.488	293	1205
2966	34320	0.513	293	1286
200	53400	0.037	298	16.1
215	53500	0.053	298	18.6
274	53300	0.116	298	26.7
275	53300	0.122	298	30.4
497	51600	0.129	298	63.4
506	51400	0.112	298	74.9
540	51400	0.208	298	77.5
543	51500	0.274	298	71.6
909	48300	0.147	298	202
911	48900	0.427	298	164
947	48600	0.364	298	218
1880	41600	0.320	298	669
2300	39000	0.538	298	857
2310	38700	0.427	298	865
2380	38600	0.718	298	1045
3050	33900	0.925	298	1730
3080	33900	1.101	298	1723
3880	28100	1.080	298	2414
3960	28000	1.273	298	2453

Table 6. Fitted values of kinetic constants for the system DIPA-water

T (K)	k ₂ (m ³ .mol ⁻¹ .s ⁻¹)	k ₂ .k _{H₂O} /k ₋₁ (m ⁶ .mol ⁻² .s ⁻¹)	k ₂ .k _{Am} /k ₋₁ (m ⁶ .mol ⁻² .s ⁻¹)	Reference
293	2.09	0.75 × 10 ⁻⁶	0.180 × 10 ⁻³	our results
298	2.70	0.84 × 10 ⁻⁶	0.198 × 10 ⁻³	our results
298	2.44	0.60 × 10 ⁻⁶	0.175 × 10 ⁻³	Blauwhoff <i>et al.</i> (1984)

Fig. 7. Enhancement factor vs. Ha -number for DIPA-H₂O at 293 K.Fig. 8. Enhancement factor vs. Ha -number for DIPA-H₂O at 333 K.

assumed that the contaminant was 2% wt mono-isopropanolamine (MIPA), a component which is likely to be formed during the production of DIPA. Enhancement factors are calculated for the systems with the pure amine and the amine mixture respectively as function of the CO₂ liquid load.

In Fig. 9 the results at 293 K of these simulations are presented. From Fig. 9 it can be concluded that for the experimental conditions used the influence of contaminants was always less than 10%. In practice the influence is far less as the largest part of the contaminants is water and therefore the purity of the amine is greater than 98% wt (e.g. see Table 7 for the composition of methyldiethanolamine). The influence of contaminants on the reaction rate measured is small and therefore this influence on the determination of the kinetics of the reaction between DIPA and CO₂ can be neglected.

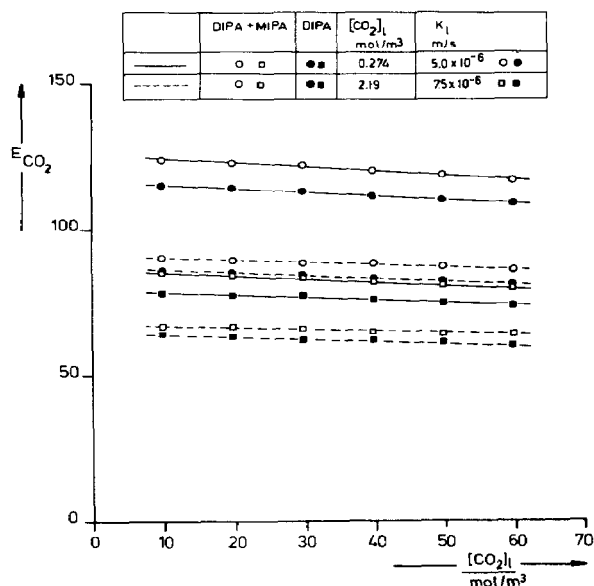
The influence of temperature on the forward reaction between CO₂ and DIPA can only be determined at low temperatures (< 298 K) because for these conditions the reversibility of the absorption reaction can be neglected (see Table 8 for the equilibrium constant of reaction 12). It may be possible to determine the reverse reaction at high temperatures ($T > 373$ K) where possibly the reversibility of the forward reaction can be neglected, which has to be verified with the mass transfer model. For application in practice, in the temperature area where both forward and reverse reaction affect the reaction rate, the absorption rates should therefore be calculated with the aid of a mass transfer model (Versteeg *et al.*, 1988b) and the pure kinetic data.

4.4. DEA-H₂O

For the system DEA-water at 298 K only Sada *et al.*

Table 7. Primary and secondary amine contaminants in MDEA before and after vacuum distillation

Contaminants	Vacuum distillation	
	before	after
Monoethanolamine	< 10 mg/kg	< 10 mg/kg
Diethanolamine	350 mg/kg	310 mg/kg
Methylmonoethanolamine	360 mg/kg	220 mg/kg

Fig. 9. Influence of contaminants on the enhancement factor for CO₂-2500 mol/m³ amine-H₂O at 293 K.Table 8. Equilibrium constant of reaction (12) for DIPA-H₂O at various temperatures

Temperature (K)	K _{eq} (m ³ /mol)
273	16.1
293	6.1
298	1.60
318	0.31
333	0.093
373	0.0097

(1977, 1978) published data on the solubility and diffusivity and these data have been used by many authors (Blanc and Demarais, 1981; Laddha and Danckwerts, 1981; Blauwhoff *et al.*, 1984). The agreement between these authors is good. However, if other

experimental techniques were used, in which the solubility and diffusivity were not required to interpret the experiments, the agreement is less satisfactory (Hikita *et al.*, 1977a; Barth *et al.*, 1984).

Recently, Versteeg *et al.* (1988a) published new, additional data on the combined solubility-diffusivity parameter $m_{N_2O} \sqrt{D_{N_2O}}$ for several aqueous amine solutions (DEA, DIPA, MDEA) at 298 K and the results are in good agreement with Sada *et al.* (1977, 1978) and Haimour and Sandall (1984) except for DEA solutions. The experimental results for DEA at 298 K of Blauwhoff *et al.* (1984) have therefore been re-evaluated with the new data for the solubility and diffusivity of CO₂. In Table 9 the results of the re-evaluation and the original results of the fitted values of the kinetic constants are presented.

In Fig. 10 the results of Hikita *et al.* (1977a,b) and Barth *et al.* (1984) are compared with the recalculated results of Blauwhoff *et al.* (1984) for solutions with a 1 mol·m⁻³ CO₂ liquid load.

The results of Blauwhoff *et al.* (1984) and Hikita *et al.* (1977a) are in good agreement. However, it should be noted that a completely correct comparison is not possible, because the CO₂ liquid load of Hikita *et al.* (1977a) is not exactly known. The discrepancy between the results of Barth *et al.* (1984) and the other authors found previously still remains although the gap is reduced considerably. For very low amine concentrations the recalculated kinetic values of Blauwhoff *et al.* (1984) give k_2 ($\approx [H_2O]^* k_{-1}/k_2 k_{H_2O}$) = 0.202 m³·mol⁻¹·s⁻¹ and Barth *et al.* (1984) k_2 = 0.110 m³·mol⁻¹·s⁻¹. However, the experimental concentrations used were very different for the two studies and it is throughout possible that the value of $k_{-1}/k_2 k_{H_2O}$ can be determined more accurately in case absorption experiments are conducted at very low amine concentrations and therefore the discrepancy may still further decrease.

4.5. Discussion

In reaction (3) the formation of the zwitterion is an acid-base reaction and therefore it is possible that a

Table 9. Fitted values of kinetic constants for the system CO₂-DEA-water at 298 K

Reference	k_2 (m ³ ·mol ⁻¹ ·s ⁻¹)	$k_2 \cdot k_{H_2O}/k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹)	$k_2 \cdot k_{OH^-}/k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹)	$k_2 \cdot k_{Am}/k_{-1}$ (m ⁶ ·mol ⁻² ·s ⁻¹)
Our original results	> 5.80	5.3 × 10 ⁻⁶	70.5 × 10 ⁻³	0.228 × 10 ⁻³
Our re-evaluated results	> 7.30	3.7 × 10 ⁻⁶	85.2 × 10 ⁻³	0.479 × 10 ⁻³

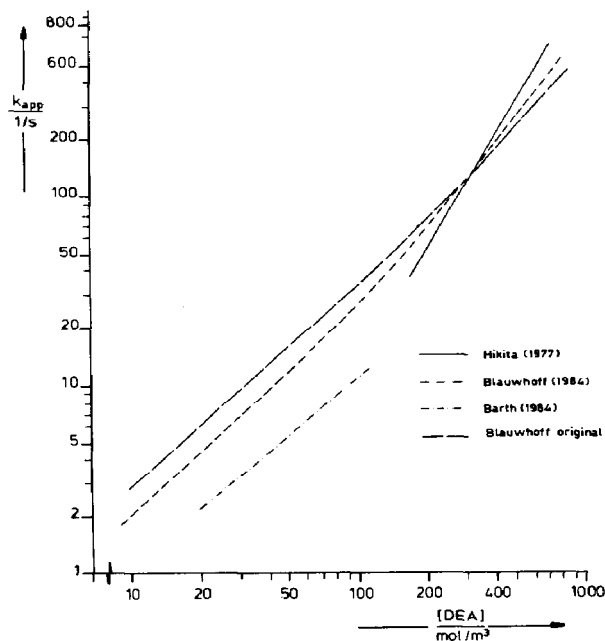


Fig. 10. Comparison between results of Hikita, Barth and Blauwhoff for DEA-H₂O at 298 K.

Brønsted relation exists between the rate constant for this step of the reaction, k_2 , and the base strength of the amine. Blauwhoff *et al.* (1984) have already demonstrated that a Brønsted relation exists for the 'partial rate constants' of reaction (4) and that the rate constants of DEA are larger than for DIPA, which is most likely caused by the larger steric hindrance for DIPA in the proton removal step.

In order to obtain a Brønsted relation for k_2 , our results, the results of Laddha and Danckwerts (1981) and the results of Sada *et al.* (1985) for DEA-H₂O were re-evaluated according to the zwitterion mechanism without taking into account the contribution of the OH⁻ ion to the deprotonation step. This contribution was neglected because no information on the CO₂ liquid-load was available (Laddha and Danckwerts, 1981; Sada *et al.*, 1985). In Table 10 all the rate constants used are presented. In Fig. 11 a Brønsted plot for the rate constant k_2 for alkanolamines is presented.

From Fig. 11 it can be concluded that there is a linear correlation between the logarithm of k_2 and the pK_a for all three temperatures studied. The value of k_2 can be calculated with the correlation:

$$\ln k_2 = pK_a + 16.26 - (T_a/T) \quad (20)$$

in which $T_a = 7188$ K.

It should be noted that both values of k_2 for DEA at 298 K do not fit at all in the Brønsted plot and that therefore the evaluation of the kinetic constants from the experiments, presented in Table 9, may be wrong. For a better evaluation of k_2 and also the other 'partial reaction rate constants' experiments need to be carried out at high DEA concentrations because at these conditions the influence of k_2 on the reaction rate may be large enough to determine the value of this constant more accurately.

5. CONCLUSIONS

The determination of reaction mechanism and reaction rate constants from mass transfer experiments can be substantially affected by effects of reversibility of

Table 10. Experimental values of k_2 for alkanolamines

Amine	Reference	Temperature (K)	k_2 (m ³ ·mol ⁻¹ ·s ⁻¹)	pK_a †	Symbol
MEA	Penny and Ritter (1983)	293	3.70	9.55	●
MEA	Hikita <i>et al.</i> (1977a)	293	4.42	9.66	●
MEA	Alvarez-Fuster <i>et al.</i> (1980)	293	4.30	9.66	◇
MPA‡	Penny and Ritter (1983)	293	6.38	10.08	■
MIPA	Hikita <i>et al.</i> (1977b)	293	3.16	9.52	□
DIPA	present work	293	2.09	9.02	■
MMEA	present work	293			
MEA	Penny and Ritter (1983)	298	4.89	9.51	●
MEA	Hikita <i>et al.</i> (1977a)	298	5.87	9.51	●
MEA	Laddha and Danckwerts (1981)	298	5.72	9.51	◇
MPA‡	Penny and Ritter (1983)	298	8.46	9.96	■
MIPA	Hikita <i>et al.</i> (1977b)	298	4.22	9.40	□
DIPA	present work	298	2.70	8.89	■
DEA	present work	298	5.79	8.95	×
DEA	Laddha and Danckwerts (1981)	298	8.59	8.95	+
MEA	Penny and Ritter (1983)	303	6.48	9.36	●
MEA	Hikita <i>et al.</i> (1977a)	303	7.72	9.36	●
MEA	Sada <i>et al.</i> (1985)	303	7.74	9.36	⊕
MPA‡	Penny and Ritter (1983)	303	11.5	9.80	■
MIPA	Hikita <i>et al.</i> (1977b)	303	5.57	9.28	□
DIPA	present work	303	3.45§	8.76	■
DEA	Sada <i>et al.</i> (1985)	303	4.19	8.86	●

† Perrin (1965).

‡ 3-Aminopropan-1-ol.

§ Extrapolated from 293 K and 298 K.

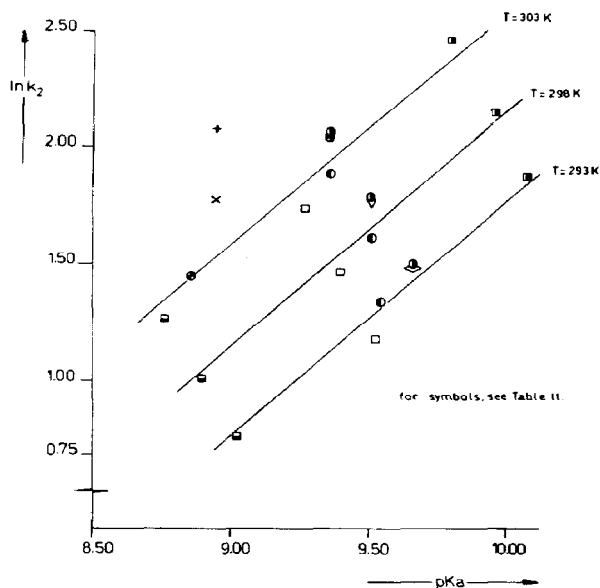


Fig. 11. Brønsted plot for primary and secondary alkanolamines.

the absorption reactions or by amine contaminants. The condition of pseudo first order irreversible reaction cannot always be met, e.g. in those cases where the conversion is relatively high or the equilibrium constant is low as is found for the system DEA-*n*-butanol. If this assumption is not verified the interpretation of the mass transfer experiments can lead to erroneous conclusions.

The reaction between CO₂ and amines can be described with the zwitterion-mechanism as proposed by Danckwerts (1979) over a wide range of conditions and amine concentrations. All published results can be satisfactorily explained with this mechanism.

For aqueous solutions the contribution of H₂O and OH⁻ ions in the deprotonation step of the zwitterion should be taken into account. However, due to experimental inaccuracies it is very difficult to determine this contribution accurately. In industrial processes the amine conversion is nearly always larger than 1% and for these conditions the contribution of the deprotonation of the zwitterion through the OH⁻ ions can be neglected (Blauwhoff *et al.*, 1984). Therefore, only the deprotonation by means of H₂O and the amine are taken into account for the determination of the reaction rate expression.

Due to the reversibility of the absorption reaction it is not possible to measure purely kinetic data from absorption experiments for aqueous DIPA solutions at temperatures higher than 298 K. In order to determine the influence of the temperature on the reaction rate absorption experiments should be carried out at low temperatures ($T < 293$ K) for the forward reaction and at high temperatures for the reverse reaction. However, it may also be possible to obtain kinetic data for these systems if the experiments will be carried out in a model reactor with substantially

shorter contact times like the laminar jet absorber as was used by Schrauwen (1985).

A linear relationship exists between the second order reaction rate constant, k_2 , of the formation of the zwitterion and the acid dissociation constant of the alkanolamine.

The solvent used has a pronounced effect on both reaction order and reaction rate.

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NOTATION

A	interfacial area, m ²
A_m	amine
B	base
$E_{CO_2, i}$	infinite enhancement factor for mass transfer for CO ₂ , 1
D_{Am}	amine diffusion coefficient, m ² .s ⁻¹
D_{CO_2}	CO ₂ diffusion coefficient, m ² .s ⁻¹
Ha	Hatta number, 1
J_{CO_2}	CO ₂ molar flux, mol.m ⁻² .s ⁻¹
k_1	forward first order reaction rate constant, s ⁻¹
k_{-1}	backward first order reaction rate constant, s ⁻¹
k_2	forward second order reaction rate constant, m ³ .mol ⁻¹ .s ⁻¹
k_3	forward third order reaction rate constant, m ⁶ .mol ⁻² .s ⁻¹
k_b	forward second order reaction rate constant for base B, m ³ .mol ⁻¹ .s ⁻¹
k_{-b}	reverse second order reaction rate constant for base B, m ³ .mol ⁻¹ .s ⁻¹
k_{OH^-}	forward second order reaction rate constant for OH ⁻ , m ³ .mol ⁻¹ .s ⁻¹
k_{H_2O}	forward second order reaction rate constant for H ₂ O, m ³ .mol ⁻¹ .s ⁻¹
$(k_{OH^-})'$	reaction rate constant for bicarbonate formation, m ³ .mol ⁻¹ .s ⁻¹
$(k_{H_2O})'$	reaction rate constant for carbonate formation, s ⁻¹
k_{app}	apparent rate constant, s ⁻¹
k_{ov}	overall pseudo first order reaction rate constant, s ⁻¹
k_l	liquid phase mass transfer coefficient, m.s ⁻¹
K	chemical equilibrium constant
m	dimensionless solubility, 1
P	pressure, Pa
R	gas constant (= 8.3143 J.mol ⁻¹ .K ⁻¹), J.mol ⁻¹ .K ⁻¹
T_a	activation temperature, K.
r	rate of reaction, mol.m ⁻³ .s ⁻¹
γ	stoichiometric coefficient, 1
η	viscosity, Pa.s
[]	concentration, mol.m ⁻³

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