Chemical Engineering Science, Vol. 43, No. 3, pp. 587–591, 1988.
Printed in Great Britain.

0009–2509/88 $3.00 + 0.00

ON THE KINETICS BETWEEN CO_2 AND ALKANOLAMINES BOTH IN AQUEOUS AND NON-AQUEOUS SOLUTIONS—II. TERTIARY AMINES

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(*Received* 9 *July* 1986; *accepted for publication* 27 *April* 1987)

Abstract—The reaction between CO_2 and tertiary alkanolamines (MDEA, DMMEA, TREA) has been studied in aqueous solutions at various temperatures. Also the absorption of CO_2 in a solution of MDEA in ethanol has been studied. Reaction kinetics have been established by chemically enhanced mass transfer of CO_2 into the various solutions. The experiments were performed in a stirred vessel with a horizontal interface which appeared to the eye to be completely smooth. The reaction of CO_2 with tertiary amines can be described satisfactorily with the base-catalysis mechanism proposed by Donaldson and Nguyen (1980). Also attention has been paid to the influence of reversibility and small amounts of impurities (primary and secondary amines) on the measured mass transfer rate. For the reaction rate constant, k_2, of the reaction between carbon dioxide and tertiary amines exists a Brønsted relation. There is a linear relation between the logarithm of k_2 and pK_a at 293 K.

1. INTRODUCTION

Selective absorption of H_2S from sour gas streams may lower the capital and operating costs of the treating process drastically (Blauwhoff *et al.*, 1985). Aqueous tertiary alkanolamine solutions have been found to be very effective solvents for the selective removal of H_2S, especially methyldiethanolamine (MDEA) and triethanolamine (TEA) are frequently used (Kohl and Riesenfeld, 1979).

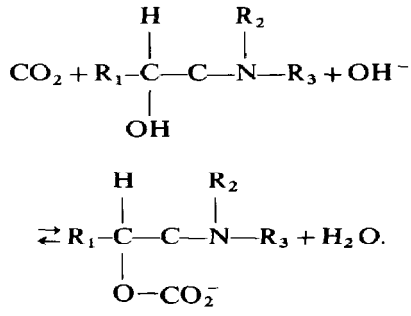
The absorption rate of H_2S into aqueous tertiary amine solutions can be calculated accurately because the reaction rate between H_2S and alkanolamines can be regarded as instantaneous with respect to mass transfer for all amines. In order to estimate the amount of coabsorption of CO_2 the kinetics of the reaction between carbon dioxide and tertiary amines are needed.

For aqueous tertiary amine solutions a good agreement among various investigations is reported for triethanolamine (TEA) at 298 K (Donaldson and Nguyen, 1980; Barth *et al.*, 1981; Blauwhoff *et al.*, 1984). Discrepancies remain with the high values for the reaction rate constant measured by Sada *et al.* (1976) and Hikita *et al.* (1977). The study of Jørgensen and Faurholt (1954) introduced another important aspect, the formation of monoalkylcarbonate at pH $\geqslant$ 13. For the reaction between MDEA and CO_2 in aqueous solutions at 298 K good agreement exists on the reaction rate constant and reaction order between the results of Blauwhoff *et al.* (1984) and Barth *et al.* (1984).

In order to check the reaction mechanism proposed for tertiary amines [base catalysis of the CO_2 hydration (Donaldson and Nguyen, 1980)], additional experimental work has been carried out.

2. THE REACTION MECHANISM

Tertiary amines can not react with CO_2 directly, although a limited number of authors reported that a reaction occurred at extremely high pH. Jørgensen and Faurholt (1954) studied the reaction for TEA at high pH-values (pH $\approx$ 13) and concluded that the formation of monoalkylcarbonate occurred (see eq. 1):



$$\rightleftarrows R_1\text{–}\underset{\displaystyle O\text{–}CO_2^-}{\overset{\displaystyle H}{\underset{|}{C}}}\text{–}\overset{\displaystyle R_2}{\underset{|}{C}}\text{–}N\text{–}R_3 + H_2O. \qquad (1)$$

At low pH-values (pH < 11) the rate of this reaction can be neglected. However, another reaction between CO_2 and tertiary amines in aqueous solutions is also observed. Donaldson and Nguyen (1980) proposed that the reaction may be described with a kind of base catalysis of the CO_2 hydratation according to:

$$CO_2 + R_1R_2R_3N + H_2O \xrightarrow{k_2} R_1R_2R_3NH^+ + HCO_3^-. \qquad (2)$$

In aqueous solutions the following reactions also occur:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (3)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^-. \qquad (4)$$

For aqueous TEA solutions at 298 K there is a good

agreement between the results of the various authors (Donaldson and Nguyen, 1980; Barth *et al.*, 1981; Blauwhoff *et al.*, 1984). Compared to Sada *et al.* (1976) and Hikita *et al.* (1977), however, the observed reaction rates are substantially lower. This discrepancy is likely due to small amounts of primary and secondary amine impurities. As is shown by Versteeg *et al.* (1988b) these impurities can have an overruling effect even in very low concentrations on the reaction rate measured experimentally. Also at 298 K good agreement is found for MDEA by Barth *et al.* (1984) and Blauwhoff *et al.* (1984).

In order to check the proposed reaction mechanism, additional experiments have been carried out in the present investigations. Therefore the reaction between CO_2 and an aqueous solution of triethylamine (TREA) at 292 K has been studied in order to investigate the reaction of CO_2 with tertiary amines in the absence of the formation of monoalkylcarbonate (see reaction 1). To investigate the influence of alkalinity of the various tertiary amines on the reaction rate constant CO_2 has been absorbed in an aqueous solution of dimethylethanolamine (DMMEA) at 293 K. Furthermore, CO_2 has been absorbed into a MDEA–ethanol mixture where no reaction should occur according to the proposed mechanism. Additional data are presented on the influence of temperature on the reaction between CO_2 and aqueous solutions of the industrially important amine MDEA.

3. EXPERIMENTAL

The experimental set-up and experimental procedure has been described in detail elsewhere (Blauwhoff *et al.*, 1984; Versteeg, 1986; Versteeg and van Swaaij, 1988).

The purity of all amines was $\geqslant 98\%$ wt and were used as supplied. However, in case of MDEA an attempt was made to purify the amine by means of a vacuum distillation. The results of the distillation are presented in Table 1. As can be concluded from Table 1 no real improvement of the purity of MDEA was reached and therefore all experiments were carried out with the amines as supplied. In order to check the influence of primary and secondary amines on the reaction rate of tertiary amines, the measured molfluxes were compared with calculated molfluxes according to the numerical multi-component model (Versteeg *et al.*, 1988b).

Table 1. Primary and secondary amine contaminants in MDEA before and after vacuum distillation

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

4. RESULTS

4.1. *TREA–H_2O*

When CO_2 is absorbed in aqueous tertiary alkanolamine solutions at high pH-values at least a part of the reaction may be accounted to the formation of monoalkylcarbonate. However, in the case of triethylamine the formation of this species is not possible. The only reaction that can occur is the base catalysis of the CO_2 hydratation as proposed by (Donaldson and Nguyen, 1980). In the present investigation the absorption of CO_2 in aqueous triethylamine solutions has been studied at 292 K in order to verify the proposed reaction mechanism (see eq. 2) for the reaction between CO_2 and tertiary amines.

For the interpretation of the results the solubility of N_2O is given in Table 2 and the diffusivity was calculated by means of the Stokes–Einstein relation (Versteeg and van Swaaij, 1987). From Fig. 1 it can be concluded that a reaction occurs with an order in amine equal to 1 and a second order reaction rate constant $k_2 = 0.029\ m^3 \cdot mol^{-1} \cdot s^{-1}$. The accuracy is not very high due to the fact that the contribution of reaction (4) (Versteeg and van Swaaij, 1988) to the overall reaction rate varies from 30 % up to 60 %. This result indicates that the observed reaction is in good agreement with the proposed reaction mechanism and that for tertiary alkanolamines another reaction besides the monoalkylcarbonate formation takes place.

Table 2. The solubility of N_2O in aqueous TREA solutions at 292 K

[TREA] (mol.m^{-3})	Solubility (mol.mol^{-1})
136	0.675
342	0.638
464	0.622
487	0.600
608	0.600
876	0.592

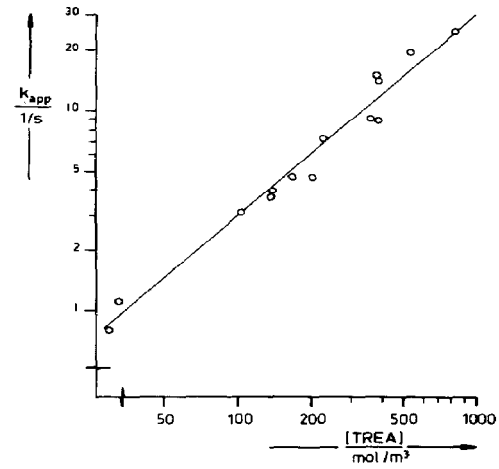


Fig. 1. Experimental results for TREA–H_2O at 292 K.

4.2. *MDEA–ethanol*

The absorption of CO_2 in a solution of MDEA and ethanol was studied in order to check the reactivity of this solution which should be equal to zero according to the proposed reaction mechanism. The absorption rate of CO_2 into this solution could be described completely with the non-stationary mass balance for physical absorption and was almost identical to the absorption rate of N_2O, corrected for the differences in physical constants, in the same solution. The total amount of CO_2 absorbed was nearly the same as the amount which can be physically solved in this solution and the difference can be completely accounted to the presence of primary and secondary amine impurities (see Table 1). From this result it is easy to conclude that in non-aqueous solutions no reaction, even no alkylcarbonate formation, occurs between CO_2 and tertiary (alkanol)amines. This is in good agreement with the proposed reaction mechanism. Moreover, in view of the selective removal of H_2S this result makes it possible to suppress the coabsorption of CO_2 to the lowest level possible, i.e. to that of the physical absorption.

4.3. *MDEA–H_2O*

The kinetics of the reaction between CO_2 and aqueous MDEA solutions has been studied at 293, 298, 308, 318 and 333 K. Hardly any data are yet available on the temperature influence on the reaction rate for this industrially important amine. In Fig. 2 the results of the kinetic experiments are presented. From Fig. 2 it can be concluded that the reaction order for all temperatures investigated is about equal to 1 and therefore is in good agreement with the proposed reaction mechanism. In Table 3 the reaction rate constants obtained by means of linear regression are presented. The reaction rate constant can be calculated with the following equation:

$$k_2 = 1.19 \times 10^5 . \exp(T_a/T) \qquad m^3.mol^{-1}.s^{-1} \quad (4)$$

in which $T_a = 5103$ K. Yu *et al.* (1985) reported an activation temperature of 4632 K which is well in line with the present results.

The assumption of pseudo first order irreversible reaction was valid for all experimental conditions studied as was verified with the absorption model (Versteeg *et al.*, 1988a).

However, the influence of primary and secondary amine contaminants on the absorption rate measured may have an overruling effect, in particular for tertiary amines. This effect has been evaluated with the absorption model for MDEA with the composition before the vacuum distillation (see Table 1). From Fig. 3 it can be

Table 3. Fitted values of kinetic constants for the system MDEA–water

T (K)	k_2 ($m^3.mol^{-1}.s^{-1}$)
293	0.0033
298	0.0043
308	0.0077
318	0.0124
333	0.0268

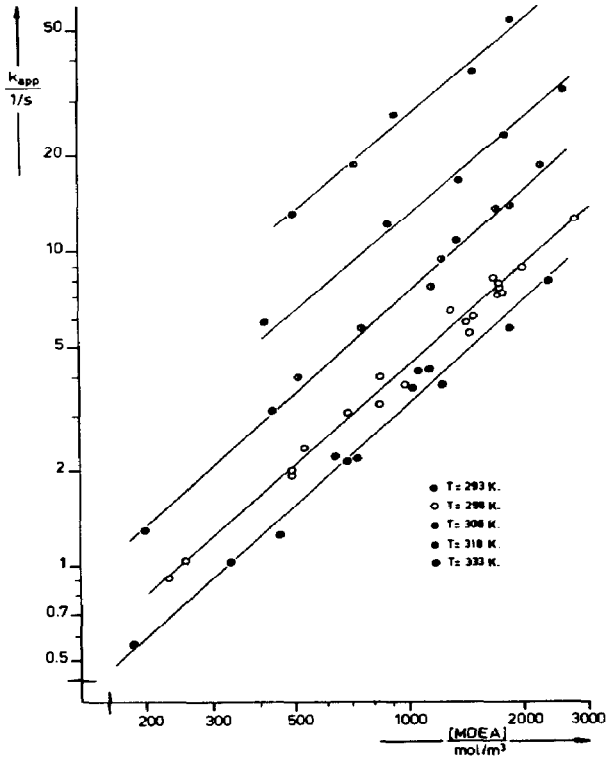


Fig. 2. Experimental results for MDEA–H_2O at various temperatures.

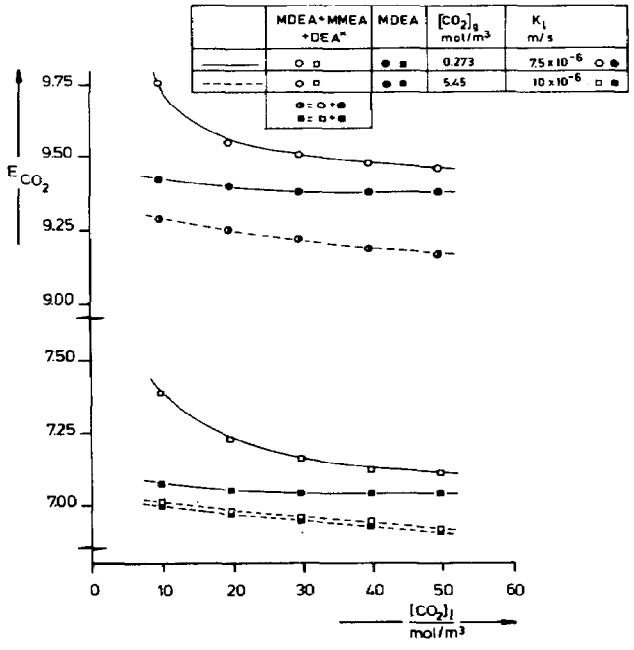


Fig. 3. Influence of contaminants on the enhancement factor for CO_2–2500 mol.m^{-3} amine–H_2O at 293 K.

concluded that for the experimental conditions studied the contribution of the contaminants to the absorption rate was always less than 5% and can be neglected. Therefore the true reaction rate of the reaction between CO_2 and MDEA has been determined. In Fig. 4 the influence of contaminants is shown for the situation that MDEA is contaminated with 0.5% DEA and 0.5% MMEA. From this figure it can be concluded that these amounts of contaminants can have an overruling effect on the reaction rate measured. This simulation also gives a possible explanation for the high reaction rate constants measured by Sada *et al.* (1976) and Hikita *et al.* (1977).

4.4. *DMMEA–H_2O*

For the reaction mechanism proposed it should be possible to make a Brønsted plot for the reaction rate constant of tertiary amines as a function of the acid dissociation constant (K_a) (Penny and Ritter, 1983). In order to obtain more kinetic data of tertiary amines the reaction between CO_2 and DMMEA has been investigated at 293 K.

The solubility of N_2O is presented in Table 4. The results of the kinetic experiments are given in Fig. 5. From Fig. 5 it appears that the reaction order in DMMEA is equal to 1 and that the reaction rate constant is $k_2 = 0.0066\ m^3.mol^{-1}.s^{-1}$. The experiments are in good agreement with the reaction mechanism proposed. Similar to the previous cases the influence of primary and secondary amine contaminants and reversibility was also taken into account. However, no influence was found on the reaction rate measured.

Table 4. The solubility of N_2O in aqueous DMMEA solutions at 293 K

[DMMEA] (mol.m^{-3})	Solubility (mol.mol^{-1})
324	0.677
611	0.680
830	0.667
1218	0.651
1591	0.630
1968	0.604
2049	0.586
2388	0.585

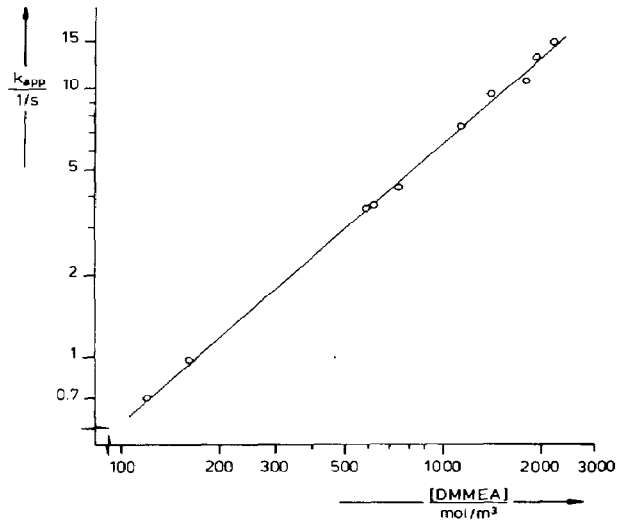


Fig. 5. Experimental results for DMMEA–H_2O at 293 K.

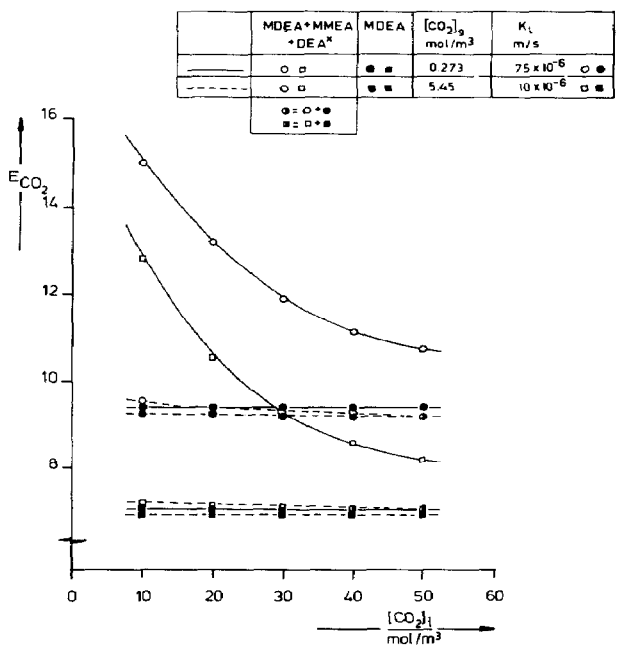


Fig. 4. Influence of contaminants on the enhancement factor for CO_2–2500 mol.m^{-3} amine–H_2O at 293 K.

In order to obtain a Brønsted plot at 293 K for the tertiary amines studied, the reaction rate constants for TREA and TEA (Blauwhoff *et al.*, 1984) were extrapolated with the aid of the activation temperature of MDEA, 5103 K. In Fig. 6 the Brønsted plot for DMMEA, TREA, TEA and MDEA at 293 K is given. This good correlation is an extra support for the proposed base catalysed CO_2-hydratation, and that the reactivity of tertiary amines is determined by the acid dissociation constant. There is a linear relation between the logarithm of k_2 and the pK_a for aqueous tertiary amine solutions. The value of k_2 at 293 K can be calculated with the following relation:

$$\ln k_2 = pK_a - 14.24. \quad (5)$$

5. CONCLUSIONS

The reaction between CO_2 and tertiary amines can be described with the base catalysis of the CO_2 hydration as proposed by (Donaldson and Nguyen, 1980). The formation of monoalkylcarbonate is not responsible for the reactivity measured in aqueous tertiary amine solutions at low pH as can be concluded from the experiments with TREA. In non-aqueous solvents no reaction occurs. This conclusion is relevant

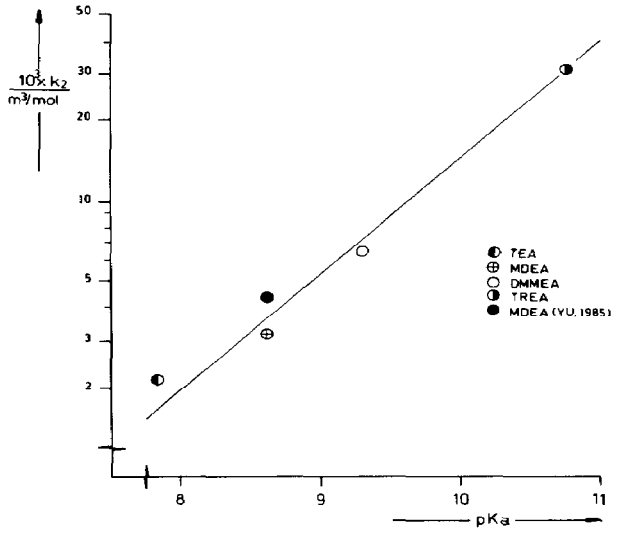


Fig. 6. Brønsted plot for tertiary amines at 293 K

to the development of gas treating processes for the selective removal of H_2S.

The determination of reaction mechanism and reaction rate constants from mass transfer expriments can be substantially affected by effects of reversibility or contaminants.

A Brønsted relation exists between the reaction rate constant, k_2, and the alkalinity of the tertiary amines.

Due to the small variation in H_2O concentration during the experiments it was not possible to investigate the influence of H_2O on the reaction rate. In order to obtain a complete description of the mechanism of the reaction between CO_2 and tertiary amines it is necessary to study this influence. In the near future results of absorption experiments for the system CO_2–H_2O–ethanol will be published.

NOTATION

k_2 second order reaction rate constant, $m^3.mol^{-3}.s^{-1}$

K_a acid dissociation constant.

T_a activation temperature, K

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