

## An experimental investigation on the rate of CO<sub>2</sub> absorption into aqueous methyldiethanolamine solutions

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**Abstract**—In this paper, the CO<sub>2</sub> absorption rates into aqueous solutions of Methyldiethanolamine (MDEA) at various concentrations of 1, 2, 3 and 4 M and temperatures varying from 293 to 323 K were measured by using a laboratory stirred reactor. The kinetics experiments were conducted under a pseudo first order regime. The data were analyzed by means of chemical absorption theory and the kinetic parameters associated with the reaction, such as the reaction order and the reaction rate constants, were evaluated. The effect of temperature on the reaction rate constant was assessed and the activation energy was evaluated at about 44.12 kJoule/mol.

Key words: Reaction, Methyldiethanolamine, Carbon Dioxide, Kinetics, Absorption

### INTRODUCTION

The removal of acid gases such as CO<sub>2</sub> and H<sub>2</sub>S from natural and refinery gases is an important industrial process. The use of alkanolamine-based solvents such as MEA, DEA, and MDEA is still the choice in gas treating technology. The design and analysis of separation processes involving aqueous solutions of such species require accurate knowledge of the kinetics of the reactions involved.

The use of aqueous solutions of methyldiethanolamine (MDEA) for the removal of acid gases is a well-known process in gas treating technology. Due to its instantaneous reaction with H<sub>2</sub>S as compared to the slower one with CO<sub>2</sub>, aqueous solutions of MDEA are usually used for the selective removal of H<sub>2</sub>S from sour gases containing both CO<sub>2</sub> and H<sub>2</sub>S [Kohl and Riesenfeld, 1985]. Owing to its higher loading capacity and lower heat of reaction compared to DEA, which implies less energy of regeneration, MDEA is still the choice for the removal of CO<sub>2</sub> from gas streams. The reaction between carbon dioxide and aqueous and non-aqueous solutions of methyldiethanolamine (MDEA) has been frequently studied in the last two decades. There appear to be no discrepancies among investigators with regard to the overall reaction order of two. However, there are still variations in the observed reaction rate constant. Versteeg et al. [1996] correlated most of the available data for the second order reaction rate constant in the following form:

$$k_2 = 3.1 \times 10^5 \exp\left(-\frac{5080}{T}\right) \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad (1)$$

However, this equation does not agree well with many other published works. For example, the reaction rate at 20°C varies from 1.35 [Haimour et al., 1987] to 4.7 m<sup>3</sup>·kmol<sup>-1</sup>·s<sup>-1</sup> [Rinker et al., 1995]. The work of Yu et al. [1985] deviates by about a factor of two from the above equation, even though the activation energy is well in line with the values reported by others.

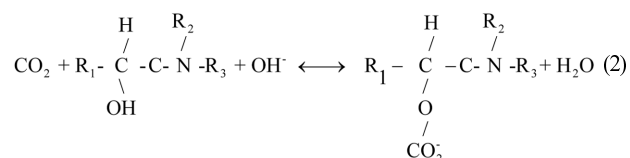
The observed discrepancies may be attributed to the different experimental techniques used in collecting the data and/or the inconsistency of the physical data such as solubility and diffusivity used in the analysis. Versteeg and Van Swaaij [1988a] attributed the major part of these discrepancies to the influence of primary and secondary amine contaminants on the absorption rate.

In this work, additional data on the kinetics of the reaction between CO<sub>2</sub> and aqueous solutions of methyldiethanolamine (MDEA) are reported at 293, 303, 313, and 323 K. Carbon dioxide partial pressure was varied over a wide range and the order of each reaction with respect to the reacting gas was assessed. The amine concentrations were varied from 1 M to 4 M leading to the evaluation of the order of the reaction with respect to the amine concentration.

### REACTION SCHEME

#### 1. Reaction Mechanism

A general agreement exists among investigators concerning the reaction mechanism between CO<sub>2</sub> and tertiary amines. Except for a few, most investigators have indicated that tertiary amines such as MDEA could not react directly with CO<sub>2</sub>. Jensen et al. [1954] studied the reaction of CO<sub>2</sub> with triethanolamine (TEA) at high pH values (pH≅13) and concluded the formation of monoalkylcarbonate according to the following reaction:



However, the contribution of this reaction at low pH values can be neglected. Generally, the accepted mechanism for the reaction between CO<sub>2</sub> and tertiary amine such as MDEA is the one proposed by Donaldson and Nguyen [1980]. In this case, the reaction can be described as a base catalyzed hydration of CO<sub>2</sub> according to the reaction

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Based on this mechanism, the amine is assumed to be initially associated with H<sub>2</sub>O molecules and weakens the H-O bond. As a result, an increase in the nucleophilic reactivity of the water toward CO<sub>2</sub> is observed. Versteeg and Van Swaaij [1988a] and Benitez Garcia et al. [1990] studied the absorption of CO<sub>2</sub> into aqueous solution of triethylamine and demonstrated that it was identical to that of alkanolamines. They concluded that the reaction of CO<sub>2</sub> at low pH values could not be attributed to the formation of monoalkylcarbonate. Furthermore, experimental studies for the absorption of CO<sub>2</sub> in non-aqueous solutions of MDEA conducted among others by Versteeg and Van Swaaij [1988a] showed that this type of reaction could be satisfactorily described as physical absorption. These results uphold the validity of the mechanism given by reaction (3).

## 2. Reaction Rate

The reaction of CO<sub>2</sub> with MDEA as given by Eq. (3) is mostly assumed to be a pseudo first-order reaction. By neglecting the effect of the reverse reaction, its reaction rate is given by

$$R_{\text{CO}_2\text{-MDEA}} = k_{2,\text{MDEA}}[\text{CO}_2][\text{MDEA}] \quad (4)$$

Besides reaction (3), the bicarbonate formation reaction must also be considered, since its contribution to the overall reaction rate is very important.



This reaction can enhance mass transfer even at lower concentrations of hydroxyl ion as was shown by Blauwhoff et al. [1984]. The forward rate of reaction first given by Pinsent et al. [1956] can be described as follows:

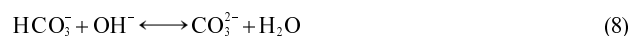
$$R_{\text{CO}_2\text{-OH}^-} = -k_{\text{OH}^-}^*[\text{CO}_2][\text{OH}^-] \quad (6)$$

Where,

$$\text{Log}_{10}k_{\text{OH}^-}^* = 13.635 - 2895/T \quad \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1} \quad (7)$$

Thus, the effect of this reaction on the overall reaction rate should be carefully assessed. Accurate estimation of the hydroxyl ion concentration in the solution is very important in order to generate a reliable value for the reaction rate constant. Versteeg et al. [1996]

concluded that, in a large number of studies, especially those for tertiary amines performed by using absorption techniques, the influence of OH<sup>-</sup> on the reaction with CO<sub>2</sub> was overestimated due to the presence of other negative charged ions such as HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The latter species are produced by the reaction between bicarbonate ion and hydroxyl ion as follows:



Another parallel reaction taking place in the aqueous medium is the CO<sub>2</sub> hydration reaction according to the following scheme:



The contribution of reaction (9) to the overall reaction rate is insignificant in the case of MDEA solutions and is usually neglected. Thus, from Eqs. (4) and (6), the overall reaction rate can be expressed as

$$R_{ov} = R_{\text{CO}_2\text{-MDEA}} + R_{\text{CO}_2\text{-OH}^-} = k_{ov}[\text{CO}_2] \quad (9)$$

Hence, the overall reaction rate  $R_{ov}$  can be written as

$$R_{ov} = k_{ov}[\text{CO}_2] = k_{2,\text{MDEA}}[\text{CO}_2][\text{MDEA}] + k_{\text{OH}^-}^*[\text{CO}_2][\text{OH}^-] \quad (10)$$

Where the overall reaction rate constant  $k_{ov}$  becomes

$$k_{ov} = k_{2,\text{MDEA}}[\text{MDEA}] + k_{\text{OH}^-}^*[\text{OH}^-] \quad (11)$$

The apparent reaction rate constant is defined as follows:

$$k_{app} = k_{ov} - k_{\text{OH}^-}^*[\text{OH}^-] = k_{2,\text{MDEA}}[\text{MDEA}] \quad (12)$$

## THEORY

The theory of gas-liquid absorption with chemical reaction is well established [Danckwerts, 1970] and will not be discussed in this paper. Only the relevant points that are necessary to analyze the experimental results will be highlighted. For a chemical reaction between a gaseous constituent A and a liquid reactant B in an aqueous solution to yield a product P,



The rate of the reaction,  $r$ , obeys the relationship

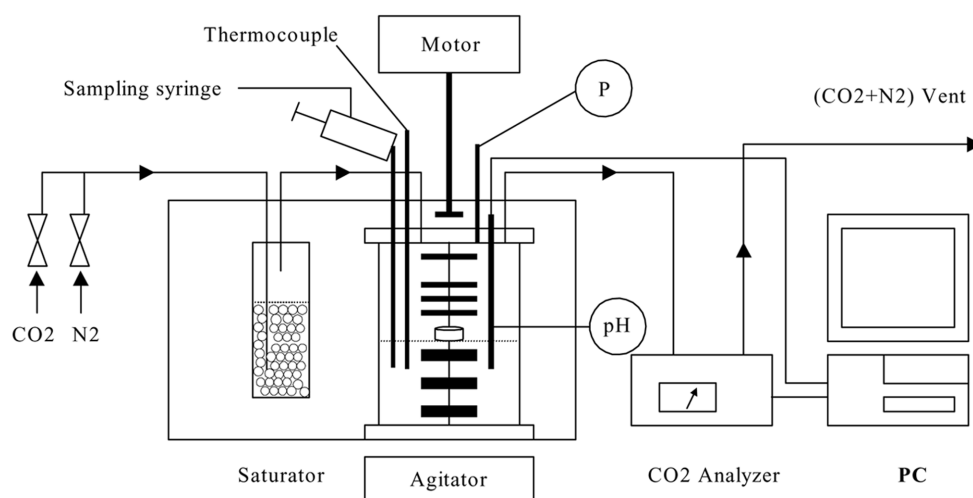


Fig. 1. Schematic diagram of the experimental set up.

$$r = -\frac{dC_A}{dt} = \frac{dP}{dt} = k_i C_A C_B \quad (14)$$

Where  $C_A$ ,  $C_B$  are the concentrations of components of A and B, respectively, and  $k_i$  is the overall reaction rate constant.

The molar flux of constituent A being transferred per unit time in a volume of liquid,  $dv$ , through an interfacial area,  $a$ , is given by:

$$R_A = \frac{dP_A}{adv} = k_i C_i E \quad (15)$$

Where  $k_i$  is mass transfer coefficient in the liquid phase,  $C_i$  is the concentration and  $E$  is the enhancement factor that takes into account the contribution of chemical reaction to the total flux. The relationship given by Eq. (15) is only valid with the assumptions that there is no resistance to mass transfer in the gas phase and the bulk liquid is initially free from A. According to Whitman [1923], the mass transfer coefficient,  $k_i$ , in the film model is given by the following expression:

$$k_i = R_A / (C_A^i - C_A^b), \quad (16)$$

In this case,  $C_A^i$ ,  $C_A^b$  are the concentrations of A at the interface and in the liquid bulk, respectively.

Dankwerts [1970] analyzed the relationship between the enhancement factor,  $E$ , and the Hatta number [1928],  $Ha$ , which is defined as

$$Ha = \left( \frac{2}{m+1} D_A k_{mn} (C_A^*)^{m-1} C_B^n \right)^{1/2} / k_i \quad (17)$$

Where  $C_A^*$  is the concentration of the gas at interface and is given by

$$C_A^* = \frac{P_A}{H_A} \quad (18)$$

And  $C_B$  is the concentration of the liquid reactant able to participate in the chemical reaction. He concluded that three different reaction zones could be identified:

- First zone is where  $E$  has a value close to 1 and corresponds to the slow reaction regime.
- Second zone in which  $E$  is approximately equal to  $Ha$  and the reaction is considered to be moderately fast. The regime of this zone is also defined as the pseudo  $m$ - $n^{\text{th}}$  order regime. The kinetics of a chemical reaction in this regime can be determined by measuring the flux of the absorbed gas.
- Third zone corresponds to the instantaneous reaction regime. In this case the instantaneous enhancement factor is given by

$$E_i = \left( \frac{D_A}{D_B} \right)^{1/2} + \left( \frac{D_B}{D_A} \right)^{1/2} \frac{C_B}{z C_A^*} \quad (19)$$

The region of pseudo  $m$ - $n^{\text{th}}$  order is characterized as satisfying the condition [Alvarez-Fuster et al., 1980]:

$$3 < E = H_a < E_i \quad (20)$$

In this region, the specific absorption rate can be expressed as

$$R_A = \left( \frac{P_A}{H_A} \right)^{\frac{m+1}{2}} \left( \frac{2}{m+1} D_A k_{mn} C_B^n \right)^{1/2} \quad (21)$$

If the resistance in the gas phase is not negligible, the specific absorption rate is given as follows:

$$\frac{P_A}{R_A} = \frac{1}{k} + \frac{H_A}{\sqrt{\frac{2}{m+1} k_{mn} C_i^{m+1} C_B^n}} \quad (22)$$

Using Eq. (21) the overall reaction rate can be calculated as follows:

$$k_{ov} = k_{mn} = \left( R_A H_A^2 / P_A^2 D_A^{0.5} \right)^2 \quad (23)$$

## PHYSICO-CHEMICAL PROPERTIES

The use of Eq. (21) to determine the different kinetic constants associated with  $\text{CO}_2$ -alkanolamine reactions requires knowledge of the values of several parameters. Among the important parameters are the solubility and the diffusivity of  $\text{CO}_2$  as well as the diffusivity of the alkanolamine in the aqueous solutions. Carbon dioxide reacts with alkanolamine and therefore it is not possible to determine directly its solubility and diffusivity. Based on the similarity in molecular configuration, molecular volume and electronic structure, the  $\text{CO}_2/\text{N}_2\text{O}$  analogy has been used to estimate the required physical properties [Laddha et al., 1979]. Thus the solubility of  $\text{CO}_2$  is given by:

$$H_{\text{CO}_2\text{-a min e}} = \frac{H_{\text{CO}_2\text{-water}}}{H_{\text{N}_2\text{O-water}}} \cdot H_{\text{N}_2\text{O-a min e}} \quad (24)$$

To calculate the diffusion coefficient of  $\text{CO}_2$  in the solution the following expression is used:

$$D_{\text{CO}_2\text{-a min e}} = \frac{D_{\text{CO}_2\text{-water}}}{D_{\text{N}_2\text{O-water}}} \cdot D_{\text{N}_2\text{O-a min e}} \quad (25)$$

For the determination of  $D_{\text{CO}_2}$ ,  $D_{\text{N}_2\text{O}}$ ,  $H_{\text{CO}_2}$ ,  $H_{\text{N}_2\text{O}}$  in water, the correlations of Versteeg and van Swaaij [1988b] were used according to the following relationships:

$$D_{\text{CO}_2\text{-water}} = 2.35 \times 10^{-6} \exp(-2119/T) \quad (27)$$

$$D_{\text{N}_2\text{O-water}} = 5.07 \times 10^{-6} \exp(-2371/T) \quad (28)$$

$$H_{\text{CO}_2\text{-water}} = 2.82 \times 10^6 \exp(-2044/T) \quad (29)$$

$$H_{\text{N}_2\text{O-water}} = 8.55 \times 10^6 \exp(-2284/T) \quad (30)$$

**Table 1. Published data on the solubility of  $\text{N}_2\text{O}$  in MDEA aqueous solutions**

Temperature K	Concentration mol/liter	Reference
283-333	4.27	Davis and Pogainis [1995]
293-353	0-4.27	Rinker and Sandall [1996]
288-323	0-8.806	Al-Ghawas et al. [1989]
293-333	0-2.75	Versteeg and Van Swaaij [1988a]
298	1.69-4.27	Browning and Weiland [1994]
288-308	0-3.2	Haimour and Sandall [1984]
298	0-2.517	Versteeg et al. [1987]
303-313	2.55	Li and Lai [1995]

**Table 2. Published data on the diffusion coefficient of N<sub>2</sub>O aqueous MDEA solutions**

Amine	Temperature K	Concentration mol/liter	Reference
MDEA	293-333	0-2.865	Versteeg and Van Swaaij [1988b]
	288-323	0-8.806	Al-Ghawas et al. [1989]
	298-347.7	0-3.350	Tomcej and Otto [1989]
	288-308	0-3.200	Haimour and Sandall [1984]
	293.15-368.15	0.84-4.27	Tamimi et al. [1994]
	303-313	2.55	Li and Lai [1995]

Similarly to the work of Snijder et al. [1993], the available solubility data of N<sub>2</sub>O in aqueous MDEA solutions summarized in Table 1 were compiled in a single relationship that takes into account the effects of both temperature and amine concentration,  $C_{MDEA}$ , as follows:

$$H_{N_2O-MDEA} = \exp\left(14.964814 - \frac{1977.4}{T} + 0.03989C_{MDEA}\right) \quad (31)$$

The range of validity of this equation is  $288 < T < 333$  K and  $0.348 < C_{MDEA} < 4.35$  mol/l with an overall average absolute deviation of 0.2% and a maximum deviation of 13.6%.

The available data in the open literature on the diffusivity of N<sub>2</sub>O in aqueous MDEA summarized in Table 2 were correlated as follows:

$$D_{N_2O-MDEA} = 10^{-9} \cdot \exp\left(8.161613 - \frac{2252.944}{T} - 0.300062 \cdot C_{MDEA}\right) \quad (32)$$

with an overall average absolute deviation of 3.54% and a maximum deviation of 22.6%. The range of validity of this relationship is specified as follows:

$$288 < T < 342.1 \text{ K and } 0 < C_{MDEA} < 4.35 \text{ mol/l}$$

For the diffusivity of MDEA in MDEA solutions, the correlation of Snijder et al. [1993] was used as follows:

$$\ln(D) = -13.088 - \frac{2360.7}{T} - 24.727 \times 10^{-5} C_{MDEA} \quad (33)$$

The range of validity of this relationship with respect to amine concentration and temperature is  $0.9 < C < 4.01$  mol/l and  $298 < T < 348$  K, respectively.

To estimate the viscosity of the amine solution, the correlation developed by Glasscock et al. [1991], which originally proposed mixtures of DEA, MDEA, and MEA with water, was found to be valid even for single solutions of MDEA with water and is used in this work as follows:

$$\ln \mu = B_1 + B_2/T + B_3 T \quad (34)$$

The viscosity of water at different temperatures was taken from Handbook of Chemistry and Physics [2002].

For the density of the MDEA solution, the following relationship was used:

$$d = \frac{1055.3 + 0.7663 \cdot (T - 273.15)}{1000} \quad (35)$$

## EXPERIMENTAL

### 1. Material

The chemicals used in the investigation were 98.5% assay Methyldiethanolamine obtained from Riedel deHaën, commercially available carbon dioxide and nitrogen with purity of 99.99% and 99.999%, respectively, and Reagecon standard 1.0 M aqueous NaOH and 0.1 M HCl solutions. All of these chemicals were used as received. Distilled water was used as the solvent throughout the experiment.

### 2. Experimental Set Up and Procedure

The experimental setup used in this work is somewhat similar to that described by Laddha and Danckwerts [1981]. The experiments were carried out in a 10 cm internal diameter double jacketed stirred cell reactor with a total volume of the about 1,800 cm<sup>3</sup>. The gas and liquid were stirred separately with individual stirrers

**Table 3. Experimental data for the reaction CO<sub>2</sub>-MDEA 1.0 M at different temperatures**

Temp K	Loading × 10 <sup>2</sup> mol/mol	P <sub>CO<sub>2</sub></sub> kPa	R <sub>CO<sub>2</sub></sub> × 10 <sup>6</sup> kmol/m <sup>2</sup> ·s	K <sub>ov</sub> s <sup>-1</sup>	k <sub>ov-avr</sub> s <sup>-1</sup>	k <sub>am</sub> l/mol·s <sup>-1</sup>
293	-	29.01	0.82	5.05		
293	2.37	38.86	1.1	5.33		
293	4.38	44.92	1.2	4.91	4.57	4.57
293	6.25	49.04	1.3	4.35		
293	1.03	19.42	0.44	3.22		
293	7.11	59.15	1.6	4.58		
303	0.42	9.49	0.3	7.57		
303	1.93	19.12	0.6	7.37		
303	3.12	28.94	0.86	6.60	7.16	7.16
303	4.55	38.81	1.2	6.74		
303	6.63	48.77	1.5	7.20		
303	8.63	58.89	1.9	7.47		
313	13.96	51.95	2.4	18.67		
313	16.96	57.96	2.8	20.33		
313	0.60	9.31	0.39	15.48		
313	1.46	18.85	0.74	13.76	15.99	15.99
313	3.07	28.43	1.2	14.82		
313	5.18	38.30	1.5	13.82		
313	8.35	48.09	2.1	16.21		
313	11.85	58.35	2.4	14.85		
323	7.90	43.63	2.2	26.74		
323	10.76	47.58	2.5	27.65		
323	13.28	51.56	2.7	28.53		
323	16.75	57.73	3	27.69	27.33	27.33
323	0.53	9.10	0.49	29.50		
323	1.86	18.45	0.96	27.52		
323	4.75	27.96	1.4	27.26		
323	7.28	37.85	1.8	23.74		

with separate variable gearboxes. The liquid stirrer speed was maintained during all experiment at 35 rpm, while that of the gas was set at about 1,200 rpm. Temperature in the reactor was measured with a J type thermocouple and was controlled by an RC20 LAUDA water circulator. A pressure transducer was used to record the total pressure in the reactor. Another accessory fitted to the reactor was a pH probe that was linked to a data acquisition system. In a typical experiment, 600 ml of freshly prepared solution was initially charged into the reactor and stirred at a constant speed. The system was then purged with nitrogen for a few minutes to remove any possible gas contaminants that might have been present before switching to the reaction gas containing CO<sub>2</sub> and N<sub>2</sub> mixed in the desired proportion. The total flowrate of the reaction gas was controlled by using Brooks Mass Flow Controllers. The exhaust leaving the reactor was sent to an infrared Rosemount® model 880A CO<sub>2</sub> analyzer. The outlet CO<sub>2</sub> concentration was monitored through a computerized data acquisition system. At the end of each experiment, the total CO<sub>2</sub> in the liquid was determined by precipitation method. There was no significant difference between the results obtained by using the physical technique and that from the wet chemistry analytical method. However, the results discussed in this work are those obtained by using the physical method.

## RESULTS AND DISCUSSION

The CO<sub>2</sub> absorption data into aqueous solutions of methyldiethanolamine were analyzed by means of chemical absorption theory,

**Table 4. Experimental data for the reaction CO<sub>2</sub>-MDEA 2.0 M at different temperatures**

Temp K	Loading×10 <sup>2</sup> mol/mol	P <sub>CO2</sub> kPa	R <sub>CO2</sub> ×10 <sup>6</sup> kmol/m <sup>2</sup> ·s	K <sub>ov</sub> s <sup>-1</sup>	k <sub>ov-avr</sub> s <sup>-1</sup>	k <sub>am</sub> l/mol·s <sup>-1</sup>
293	0.439	19.22	0.54	7.48		
293	1.164	28.94	0.86	8.18		
293	2.29	38.73	1.2	9.28	9.24	4.62
293	3.286	48.63	1.6	10.34		
293	4.606	53.21	1.7	9.72		
293	6.343	58.78	2	10.43		
303	0.485	19.02	0.65	12.92		
303	1.304	28.73	0.98	12.92		
303	2.522	38.53	1.4	13.62	14.74	7.37
303	3.159	48.41	1.8	15.31		
303	4.471	52.85	2	16.50		
303	5.802	58.44	2.3	17.19		
313	0.793	18.75	0.8	23.36		
313	1.737	28.31	1.2	24.56		
313	2.927	37.98	1.7	26.99	27.42	13.71
313	4.331	47.86	2.2	28.38		
313	6.042	52.31	2.5	30.19		
313	8.089	57.90	2.8	31.03		
323	0.836	18.47	0.95	39.01		
323	1.857	27.92	1.5	41.54		
323	3.089	37.59	2	42.30	44.48	22.24
323	5.052	47.31	2.7	48.04		
323	7.725	51.89	2.9	46.41		
323	10.654	57.41	3.3	49.56		

**Table 5. Experimental data for the reaction CO<sub>2</sub>-MDEA 3.0 M at different temperatures**

Temp K	Loading×10 <sup>2</sup> mol/mol	P <sub>CO2</sub> kPa	R <sub>CO2</sub> ×10 <sup>6</sup> kmol/m <sup>2</sup> ·s	K <sub>ov</sub> s <sup>-1</sup>	k <sub>ov-avr</sub> s <sup>-1</sup>	k <sub>am</sub> l/mol·s <sup>-1</sup>
293	0.36	18.95	0.63	15.03		
293	1.03	28.66	0.93	14.45		
293	0.74	38.41	1.30	15.94	16.20	5.40
293	1.56	48.32	1.70	17.05		
293	2.65	58.38	2.10	18.52		
303	0.35	18.75	0.80	29.25		
303	0.96	28.38	1.20	28.55		
303	1.67	38.15	1.60	29.10	30.99	10.33
303	3.13	48.02	2.10	31.36		
303	4.97	52.47	2.40	33.47		
303	6.27	58.07	2.70	34.20		
313	0.42	18.52	0.92	46.32		
313	1.10	28.06	1.40	46.24		
313	2.11	37.77	1.90	46.64	48.74	16.25
313	3.29	47.66	2.40	48.24		
313	4.48	52.08	2.70	51.94		
313	5.82	57.67	3.10	53.07		
323	0.41	18.15	1.10	120.91		
323	1.34	27.37	1.80	137.65		
323	2.33	37.09	2.30	126.57	133.14	33.28
323	3.42	46.95	3.00	127.47		
323	4.59	51.30	3.40	139.68		
323	6.08	56.84	3.90	146.54		

**Table 6. Experimental data for the reaction CO<sub>2</sub>-MDEA 4.0 M at different temperatures**

Temp K	Loading×10 <sup>2</sup> mol/mol	P <sub>CO2</sub> kPa	R <sub>CO2</sub> ×10 <sup>6</sup> kmol/m <sup>2</sup> ·s	K <sub>ov</sub> s <sup>-1</sup>	k <sub>ov-avr</sub> s <sup>-1</sup>	k <sub>am</sub> l/mol·s <sup>-1</sup>
293	0.30	18.72	0.69	27.20		
293	0.92	28.38	1.00	25.61		
293	1.61	38.13	1.40	26.61	28.08	7.02
293	2.38	48.02	1.80	28.14		
293	3.23	52.40	2.00	30.43		
293	4.28	58.02	2.30	30.52		
303	0.30	18.72	0.81	44.32		
303	0.92	28.38	1.20	41.74		
303	1.61	38.13	1.60	43.37	46.44	11.61
303	2.38	48.02	2.10	45.86		
303	3.23	52.40	2.50	51.60		
303	4.28	58.02	2.70	51.74		
313	0.34	18.52	0.92	67.72		
313	1.07	28.03	1.40	69.09		
313	1.87	37.74	1.90	69.80	73.54	18.39
313	2.80	47.50	2.50	78.76		
313	3.75	52.05	2.80	77.13		
313	4.94	57.65	3.10	78.76		
323	0.41	18.15	1.10	120.91		
323	1.34	27.37	1.80	137.65		
323	2.33	37.09	2.30	126.57	133.14	33.28
323	3.42	46.95	3.00	127.47		
323	4.59	51.30	3.40	139.68		
323	6.08	56.84	3.90	146.54		

and are summarized in Tables 3-6. An evaluation of the data reproducibility revealed that the estimated error in the overall analysis was less than 5% except for less than 2 kPa where the error could be as high as 7%.

The concentration of amine in the solution,  $C_{MDEA}$ , was checked at the beginning and the end of each experiment by titrating an aliquot sample with a standard solution of 1 N HCl. In all cases, the discrepancy between the initial and the final amine concentration was found to be less than 3%. Thus the assumption of constant total amine concentration throughout the experiment was justified.

### 1. Mass Transfer Coefficient

Absorption data of pure CO<sub>2</sub> in water at 293 K were used to calculate  $k_L$ . The mixing speed of the liquid was varied substantially from low values to moderate values without affecting the smoothness of the gas-liquid interface. The values of  $k_L$  were calculated by using Eq. (15). The results are presented in Fig. 2 as a plot of  $\ln(\text{Sh}/\sqrt{\text{Sc}})$  versus  $\ln R_e$  where an equation relating Sherwood number to Schmidt and Reynolds numbers in the form of  $\text{Sh}=0.1217R_e^{0.6949}\text{Sc}^{0.5}$  is obtained. Since the Sc range for the experiment was not large, the exponent on Sc was assumed to be 0.5 in accordance with the penetra-

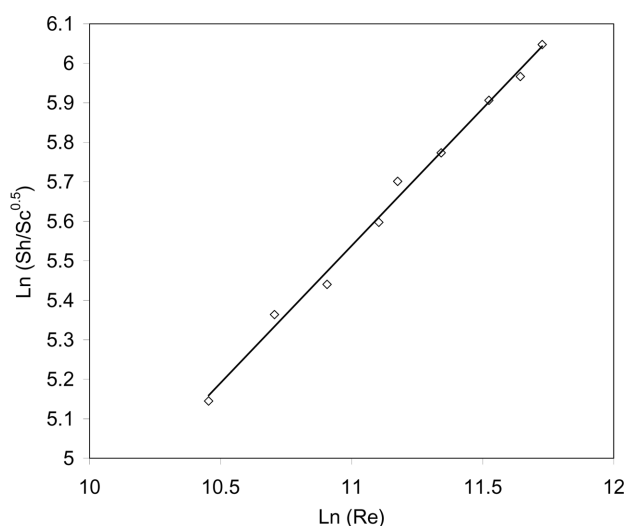


Fig. 2. Correlation of the liquid-phase mass-transfer coefficient.

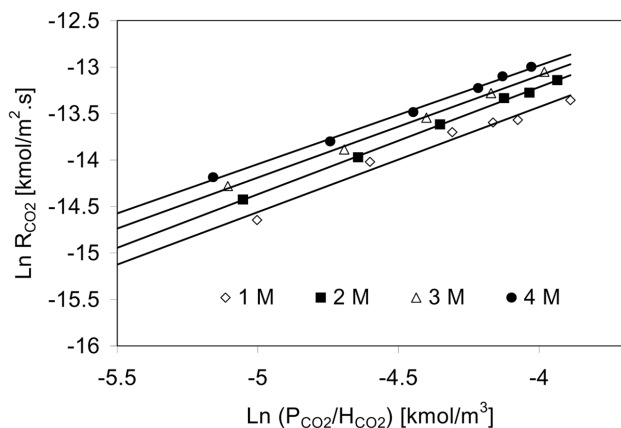


Fig. 3. Reaction order with respect to CO<sub>2</sub> partial at 293 K and different concentrations.

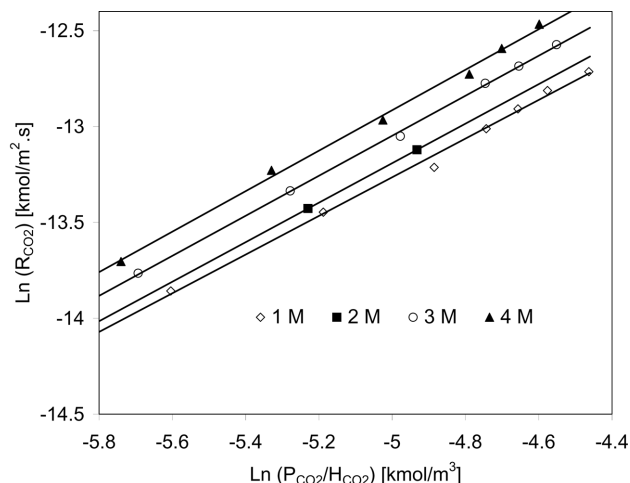


Fig. 4. Reaction order with respect to CO<sub>2</sub> at 323 K and different concentrations.

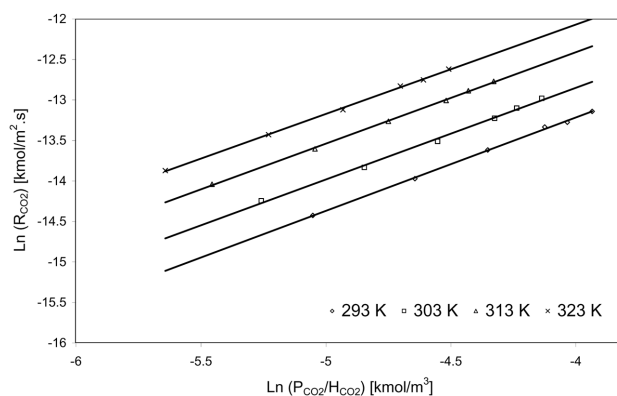


Fig. 5. Reaction order for MDEA 2.0 M with respect to CO<sub>2</sub> at different temperatures.

tion theory. The exponent on  $R_e$  (0.69) is in accordance with the range of values obtained by other investigators such as Rangwala et al. [1992] and Little et al. [1992] for the same type of experimental apparatus.

The experimental data for CO<sub>2</sub> absorption into aqueous solutions of MDEA were analyzed to determine the kinetics constants associated with this reaction. Plots of  $\ln R_{CO_2}$  versus  $\ln(P_{CO_2}/H_{CO_2})$  at different temperatures and MDEA concentrations are shown, respectively, in Figs. 3-6. It is evident that the relationship given by Eq. (21) is obeyed in all cases as indicated by the linear variations of  $R_{CO_2}$  with  $P_{CO_2}/H_{CO_2}$  (on log-log plot). From the slope of the lines it can be shown that the order of the reaction with respect to CO<sub>2</sub> is equal to unity. This finding is in agreement with the conclusion reported in the literature regarding the order of the reaction with respect to CO<sub>2</sub>.

Another factor that needs to be considered in the kinetics of CO<sub>2</sub> absorption into aqueous solutions of alkanolamine is the order with respect to the amine itself, if there is any. By substituting  $m=1$  into Eq. (21), a plot of  $\ln[(R_{CO_2}/H_{CO_2})^2/D_{CO_2}P_{CO_2}^2]$  versus  $\ln C_{MDEA}$  would generate a straight line with the slope equals to  $n$ . Such a plot for different temperatures is shown in Fig. 7. Evaluation of the different slopes revealed that the value of  $n/2$  is approaching a value of

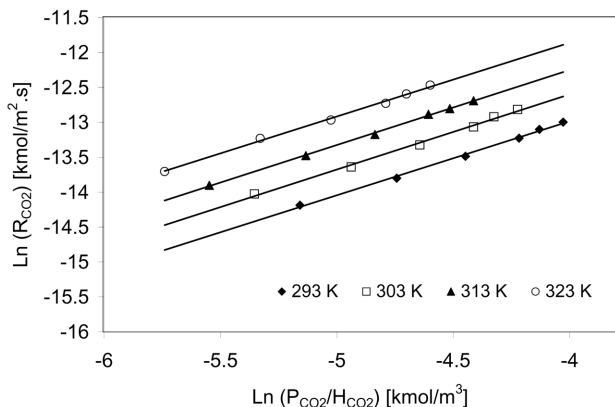


Fig. 6. Reaction order with respect to CO<sub>2</sub> partial pressure for MDEA 4.0 M at different temperatures.

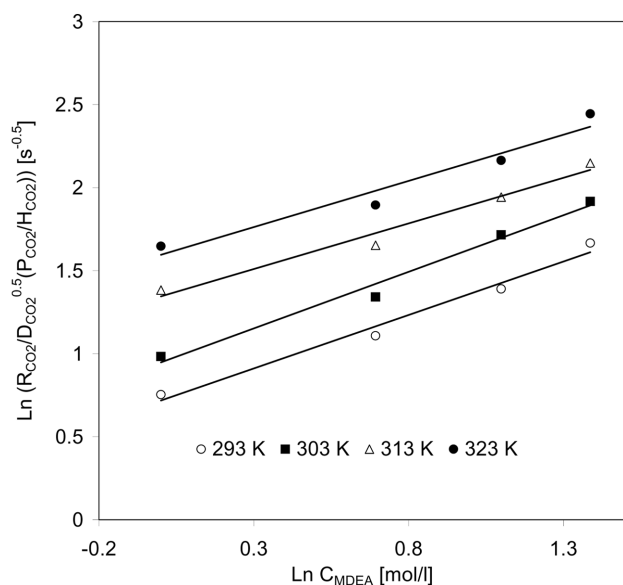


Fig. 7. Reaction order with respect to MDEA concentration at different temperatures.

0.5. Thus, the order of the reaction with respect to amine concentration is equal to unity, which is in agreement with the value reported in the literature.

## 2. Reaction Rate Constant

The overall rate of the reaction between CO<sub>2</sub> and the amine solution with the contribution of the reaction of CO<sub>2</sub> with the hydroxyl ion was calculated according to Eq. (23). The second order reaction rate,  $k_{app}$ , was obtained from the overall reaction rate and the amine concentration according to Eq. (12) by neglecting the contribution of the hydroxyl ion to the reaction. Solubility of CO<sub>2</sub> in aqueous solutions of MDEA required for the evaluation of  $k_v$  was estimated by using Eq. (23). The solubility of CO<sub>2</sub> and N<sub>2</sub>O in water is given by Eqs. (29) and (30), respectively; the solubility of N<sub>2</sub>O in amine solution is given by Eq. (31). The diffusivity of CO<sub>2</sub> in MDEA solutions was calculated in the same way as for the solubility by using Eqs. (25), (27), (28) and (32); the effect of the temperature on the viscosity and density of the solution is considered in Eqs. (34) and (35), respectively. Final results are summarized in Table 7. It is

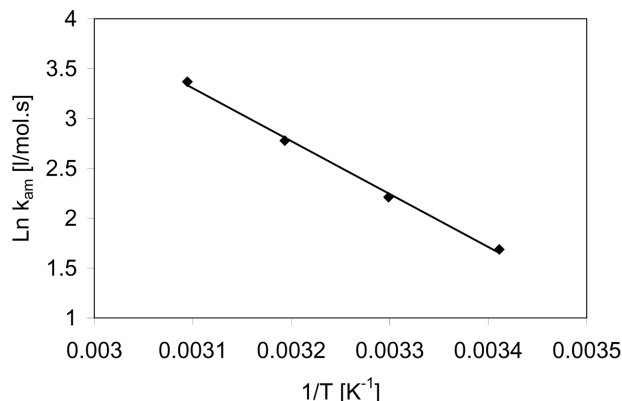


Fig. 8. Arrhenius plot for the reaction CO<sub>2</sub>-MDEA.

Table 7. Second order reaction rate constant at different temperatures

Temp (K)	$k_{am}$ (l/mol·s <sup>-1</sup> )				$k_{am\ average}$ l/mol·s <sup>-1</sup>
	1 M	2 M	3 M	4 M	
293	4.57	4.62	5.40	7.02	5.40
303	7.16	7.37	10.33	11.61	9.12
313	15.99	13.71	16.25	18.39	16.08
323	27.33	22.24	33.28	33.28	29.03

worth noticing here that the results summarized in the previous table verify the condition stated in Eq. (20).

Good agreement between the generated  $k_2$  values presented in Table 7 and those published by Versteeg et al. [1996] has been observed where the effects of temperature have been extensively studied. Fig. 4 shows the Arrhenius plot for  $k_2$  at 20, 30 and 40 °C. From this plot the activation energy has been found to be 44.12 kJ/mol, which is in line with the literature data. The temperature dependence of the rate constant was correlated as follows:

$$k_{am} = 3.82 \times 10^8 \cdot \exp(-5308.6/T)$$

Which is in excellent agreement with the correlation given in Eq. (1).

## CONCLUSION

The reaction between CO<sub>2</sub> and tertiary amine MDEA in aqueous solutions was analyzed by using the base catalysis of the CO<sub>2</sub> hydration proposed by Donaldson and Nguyen [1980]. The reaction is overall second order, first order with respect to free amine concentration. The contribution of the reaction between CO<sub>2</sub> and hydroxyl ion is insignificant and could be neglected in the analysis. The activation energy for the second order reaction rate constant,  $k_2$ , is evaluated at about 44.12 kJ/mol, while the temperature dependency of the rate constant,  $k_2$ , can be estimated from the following relationship:  $k_{am} = 3.82 \times 10^8 \exp(-5308.6/T)$

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### NOMENCLATURE

$C_i$	: concentration of components i [mol/l]
$C_A^*$	: concentration of the gas at the interface [mol/l]
$D_i$	: diffusion coefficient of component i [m <sup>2</sup> /s]
$E_i$	: instantaneous enhancement factor [-]
Ha	: Hatta number [-]
$H_i$	: solubility of component i [Pa·m <sup>3</sup> /mol]
$J_{CO_2}$	: instantaneous absorption flux per unit of time [mol/s]
$M_i$	: molecular weight of component i [g/mol]
$P_i$	: partial pressure of component i [kPa]
$R_{CO_2}$	: absorption flux per unit of time and surface [mol/m <sup>2</sup> ·s]
a	: gas-liquid contact area [m <sup>2</sup> ]
d	: density [kg/l]
$k_{H_2O}$	: CO <sub>2</sub> hydration rate constant [s <sup>-1</sup> ]
$k_{OH^-}^*$	: bicarbonate formation rate constant [s <sup>-1</sup> ]
$k_{ov}$	: overall reaction rate constant [s <sup>-1</sup> ]
$k_{app}$	: apparent reaction rate constant [s <sup>-1</sup> ]
$k_i$	: liquid mass transfer coefficient [m/s]
m	: reaction order with respect to CO <sub>2</sub> [-]
n	: reaction order with respect to amine [-]
$\mu$	: viscosity [cp]

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