Kinetics of the Absorption of CO₂ into Mixed Aqueous Loaded Solutions of Monoethanolamine and Methyldiethanolamine

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The kinetics of absorption of CO_2 in loaded mixed methyldiethanolamine (MDEA) and monoethanolamine (MEA) solutions was investigated in a laboratory laminar jet apparatus. The experiments were conducted over the temperature range of 298−333 K, MDEA/MEA wt ratio of 27/03, 25/05 and 23/07, total amine concentration of 30 wt %, and CO_2 loading from 0.005 to 0.15 (mol of CO_2)/(mol of total amine). Physical properties such as density, viscosity, diffusivity, and solubility of the system were calculated from published data and/or models. Reaction mechanisms, namely, zwitterion and termolecular, were used to interpret the kinetic data. It was observed that the zwitterion mechanism in its original form could not predict the individual kinetic rate constants. Equally, the termolecular mechanism with water in the apparent reaction rate term also did not yield any reasonable results. A modified termolecular mechanism, which included the contribution of hydroxide ions, was able to predict the kinetics of a CO_2 loaded mixed alkanolamine solution satisfactorily with MDEA not participating with MEA in the kinetics. Individual reaction rate constants were predicted based on the modified termolecular mechanism.

1. Introduction

The absorption of acid gases into alkanolamines is of significant industrial importance. This technique is applied during natural gas sweetening to meet pipeline standards as well as in the removal of carbon dioxide (CO_2) from power plant and other industrial plant flue gases for environmental reasons. Alkanolamines, such as primary, secondary, and tertiary amines as exemplified, respectively, by monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), have been used in the industry for a number of years for industrial absorption.[1] Aqueous primary and secondary amines when reacted with carbon dioxide form carbamates. Since high heat of absorption is associated with carbamate formation reaction, solvent regeneration costs are high when primary or secondary amines are used exclusively. Another disadvantage is the capacity for absorption of CO_2, whereby two moles of primary amines or secondary amines can only absorb up to one mole of CO_2. As such, their loadings are limited to 0.5 (mol of CO_2)/(mol of amine). The advantage of MDEA, on the other hand, is that it not only has a low heat of regeneration, and hence, a low heat duty is required during regeneration, but also it has a maximum loading capacity of 1.0 (mol of CO_2)/(mol of amine). In addition, it is less corrosive than MEA. However, pure aqueous MDEA (a tertiary amine) does not react with CO_2 directly because it lacks the N−H bond required to form the carbamate ion with CO_2. Instead, an aqueous solution of MDEA will promote the hydrolysis of CO_2 to form a bicarbonate and a protonated amine. Chakravarty and Phuken[2] have demonstrated that the addition of a primary or secondary amine to the tertiary amine can enhance absorption of CO_2 without changing the stripping characteristics. Modeling and simulation of an absorption column for the absorption of CO_2 into an amine blend requires information on the kinetics of the process. Critchfield and Rochelle[3] have studied the absorption of CO_2 into aqueous solutions of MDEA−MEA in a stirred-cell absorber. The

kinetics of the reactive absorption of CO_2 into a mixed amine solution at low and moderate CO_2 loadings have not been reported except for the work of Glasscock et al.,[4] Versteeg and Van Swaaij,[5] Rangwala et al.,[6] and Hagewiesche et al.[7] Versteeg and Van Swaaij,[5] in their work, carried out a study of CO_2 absorption into various mixed alkanolamines including MEA−MDEA, MEA−MDEA, DIPA−MDEA, and MEA−DEA−MDEA. The experiments were carried out in a stirred vessel. On the other hand, Glasscock and Rochelle[4] investigated the absorption/desorption of aqueous MDEA/MEA and MDEA/DEA solutions with a gas-stirred cell reactor, whereas Rangwala et al.[6] measured the absorption of CO_2 into aqueous blends of MDEA and MEA solutions in a stirred cell absorber. In contrast, Hagewiesche et al.[7] have reported the absorption of CO_2 into aqueous blends of MDEA and MEA solutions in a laminar jet apparatus at low contact times. However, the experiments were performed only at 313 K. Rinker et al.[8] measured the rate of absorption of CO_2 into an aqueous solution of MDEA and DEA in a laminar jet absorber and a stirred cell absorber, whereas Xiao et al.[9] studied the kinetics of absorption of CO_2 into aqueous blends of MDEA and 2-amino-2-methyl-1-propanol (AMP) solutions in a laboratory wetted-wall column. Horng and Li[10] explored the kinetics of absorption of CO_2 into aqueous blends of triethanolamine (TEA) and MEA solutions in a laboratory wetted-wall column, while Zhang et al.[11] measured the absorption rates (and, thus, the kinetics) of CO_2 into aqueous blends of MDEA and DEA solutions in a laboratory disk column. Also, Liao and Li[12] measured the absorption rates of CO_2 into aqueous blends of MDEA and MEA solutions in a laboratory disk column. A summary of work done by various researchers on the kinetics of CO_2 in mixed amines is given in Table 1.

Table 1 shows that all the experimental data were obtained either at a single temperature[7,11] or at two or three temperatures.[4,9,12] This does not enable the evaluation of the kinetic rate constant over a wide temperature range (e.g., 298−343 K, in which a typical industrial absorber is operated) outside the range in which data was obtained. Also, the experiments were not performed for more than three concentrations of the mixed

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Table 1. Compilation of Kinetics of CO_2 in Mixed Amine System

mixed amine solution	composition (mol/L)	temp. (°C)	experimental technique	calculation method	reference
MDEA + MEA	1.34 + 0.65	25	stirred cell	numerical model	Glasscock et al.[4]
MDEA + DEA	0.59−1.85 + 0.10−0.57	25, 40	stirred cell	numerical model	Glasscock et al.[4]
MDEA + MEA	2.43 + 0.25	40	laminar jet absorber	numerical model	Hagewiesche et al.[7]
	2.30 − 0.50				
	2.17 + 0.75				
AMP + MEA	1.5 + 0.1, 0.2, 0.3, and 0.4	30, 35, 40	wetted-wall column	simplified model	Xiao et al.[9]
	1.7 + 0.1, 0.2, 0.3, and 0.4				
TEA + MEA	0.5 + 0.1, 0.2, 0.3, 0.4, and 0.5	30, 35, 40	wetted-wall column	simplified model	Horng and Li[10]
	1.0 + 0.1, 0.2, 0.3, 0.4, and 0.5				
MDEA + MEA	1.0 + 0.1, 0.2, 0.3, 0.4, and 0.5	30, 35, 40	wetted-wall column	simplified model	Liao and Li[12]
	1.5 + 0.1, 0.2, 0.3, 0.4, and 0.5				
MDEA + DEA	2.8 + 0.2	60	disk column	simplified model	Zhang et al.[11]
	2.4 + 0.6				
	2.7 + 0.3	40, 50, 60, 70			

amine solution systems except in two cases.[10,12] Finally, with the exception of the work of Glasscock and Rochelle,[4] the above-cited studies did not take into consideration the effect of CO_2 loading. This last issue was the reason that, even for a single amine system (CO_2−MEA), Littel et al.[16] questioned the data reported by Savage and Kim,[17] because they did not consider CO_2 loading effects on the physical properties and kinetics of the system. It is well-known that a laminar jet absorber is one of the most accurate pieces of equipment that can be used to study gas absorption rates.[13,14] Aboudheir et al.[14] designed and used a laminar jet absorber to obtain accurate kinetic data for the absorption of CO_2 into CO_2 loaded, concentrated MEA solutions. On the basis of the limitation highlighted in the studies summarized in Table 1, we decided to evaluate the kinetics of the absorption of CO_2 into a CO_2 loaded MEA−MDEA blend using a laminar jet absorber within the temperature range of 298−333 K. This evaluation was done under conditions where interfacial turbulence was absent.

2. Theory

The mechanisms for the reaction between CO_2 and primary and tertiary amines are presented, and a vapor−liquid equilibrium (VLE) model to predict the bulk concentrations of all chemical species is developed. The zwitterion mechanism and the termolecular mechanism by Crooks and Donnellan[15] are adopted to predict the kinetics.

2.1. Chemical Reactions. A generic chemical reaction between CO_2 and primary amines such as aqueous MEA or a tertiary amine such as MDEA has been illustrated by Blauwhoff et al.,[18] Versteeg and van Swaaij,[19] Littel et al.,[16] and Liao and Li.[12] Briefly, this mechanism involves the reaction of MEA (RNH_2) with CO_2 to produce a carbamate (RNH_2COO) by the deprotonation of the zwitterion by the base. Any base present in the solution may contribute to the deprotonation reaction. The contribution of each base to the overall reaction rate depends on both its concentration and its strength. Here, R refers to CH_2-CH_2OH. Although the contributions to the deprotonation of zwitterion in aqueous solutions of mixed alkanolamine can come from MDEA, MEA, OH^-, or H_2O,[12] the contributions are mainly from MDEA and MEA. It is only to a lesser extent that they do come from OH^- and H_2O.[7]

According to Rinker et al.,[8] Hagewiesche et al.,[7] and Versteeg et al.,[20] eqs 1−9 show the reaction scheme for the reaction of CO_2 with primary and tertiary amines when CO_2 is absorbed into and reacts with an aqueous MDEA−MEA solution. Specifically, the mechanism for the reaction between CO_2 and a tertiary amine as represented by reactions 5 and 6 indicates

that MDEA does not react directly with CO_2. Instead, tertiary amines act as bases, which catalyze the hydration of CO_2.[7,9,21,22]
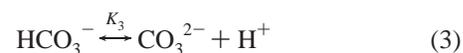
Ionization of water

$$H_2O \xrightleftharpoons{K_1} OH^- + H^+ \tag{1}$$

Dissociation of dissolved carbon dioxide through carbonic acid

$$CO_2 + H_2O \xrightleftharpoons{K_2, k_2, k_{-2}} HCO_3^- + H^+ \tag{2}$$

Dissociation of bicarbonate

$$HCO_3^- \xrightleftharpoons{K_3} CO_3^{2-} + H^+ \tag{3}$$

Formation of bicarbonate

$$CO_2 + OH^- \xrightleftharpoons{K_4, k_4} HCO_3^- \tag{4}$$

Reaction of CO_2 with tertiary amine

$$CO_2 + RRCH_3N + H_2O \xrightleftharpoons{K_5, k_5} RRCH_3NH^+ + HCO_3^- \tag{5}$$

$$RRCH_3N + H^+ \xrightleftharpoons{K_6} RRCH_3NH^+ \tag{6}$$

Reaction of CO_2 with primary amine

$$RNH_2 + CO_2 \xrightleftharpoons{K_7, k_7, k_{-7}} H^+ + RNHCOO^- \tag{7}$$

$$RNH_2 + H^+ \xrightleftharpoons{K_8, k_8, k_{-8}} RNH_3^+ \tag{8}$$

$$RNHCOO^- + H_2O \xrightleftharpoons{K_9, k_9, k_{-9}} RNH_2 + HCO_3^- \tag{9}$$
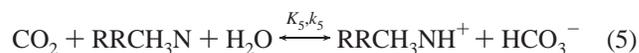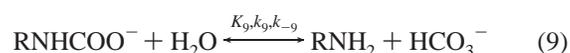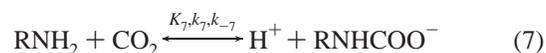
where K_i is the equilibrium constant, k_i is the forward rate coefficient, and k_{-i} is the backward rate coefficient for the reaction i. The carbamate-to-bicarbonate reversion (reaction 9) is neglected while calculating the bulk concentrations of the species because of the low reaction rates and short contact times, typical of the laminar jet absorber. Also, it has been found that this reaction (eq 9) does not have a noticeable effect on the vapor−liquid-equilibrium (VLE) model and the overall reaction of CO_2 in mixed alkanolamine systems.[7]

2.2. Vapor−Liquid-Equilibrium (VLE) Model. A computer thermodynamic model was developed based on reactions 1−9 to estimate the liquid bulk concentration of all chemical species. The input data of the model included the initial concentration

of the mixed MEA and MDEA solution ($[MEA]_0$ and $[MDEA]_0$, respectively), initial CO_2 loading of the mixed amine solution (α), the equilibrium constants of the reactions, and the solubility of CO_2 into the mixed MEA and MDEA solution as a function of both amine concentration and temperature. All the chemical reactions were assumed to be at equilibrium, while the concentration of water was assumed to remain constant because its concentration was much larger than the concentrations of all other chemical species. The concentrations for the remaining eleven chemical species shown in the above chemical reactions were calculated by solving the mass balance equations shown in eqs 10−19 and the Henry's law correlation given in eq 20:

MEA balance:

$$[RNH_2] + [RNH_3^+] + [RNHCOO^-] = [MEA]_0 \quad (10)$$

MDEA balance:

$$[RRCH_3N] + [RRCH_3NH^+] = [MDEA]_0 \quad (11)$$

Carbon balance:

$$[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] = \\ ([MDEA]_0 + [MEA]_0)\alpha \quad (12)$$

Charge balance:

$$[RNH_3^+] + [RRCH_3NH^+] + [H^+] = [RNHCOO^-] + \\ [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (13)$$

Independent equilibrium constants:

$$K_1 = [OH^-][H^+] \quad (14)$$

$$K_3 = [CO_3^{2-}][H^+]/[HCO_3^-] \quad (15)$$

$$K_5 = [RRCH_3NH^+][HCO_3^-]/[CO_2][RRCH_3N] \quad (16)$$

$$K_6 = [RRCH_3NH^+]/[RRCH_3N][H^+] \quad (17)$$

$$K_7 = [H^+][RNHCOO^-]/[RNH_2][CO_2] \quad (18)$$

$$K_8 = [RNH_3^+]/[RNH_2][H^+] \quad (19)$$
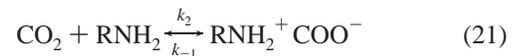
Henry's law relationship:

$$P_{CO_2} = He[CO_2] \quad (20)$$

As mentioned earlier, although K_9 is an independent equilibrium constant, it is not included while solving the system of equations because of the negligible rate of the carbamate reversion to bicarbonate reaction at lower CO_2 loadings. The values of the solubility (in terms of Henry's law constant, He) and the equilibrium constants are required in order to solve these nonlinear algebraic equations for the bulk concentrations of the species. The solubility of CO_2 into the mixed amine solution was calculated using the N_2O analogy. Details of the calculation are based on the work of Wang et al.[23] The equilibrium constants K_1, K_3, K_5, K_7, and K_8 developed by various researchers[24−26] and expressed as a function of temperature were used in this work for the calculations. The 11 nonlinear algebraic equations, eqs 10−20, were solved for the 11 unknowns of the bulk concentrations and equilibrium partial pressures.

2.3. Kinetics. The reactions between CO_2 and MEA solution have been described in the literature by two mechanisms, namely, zwitterion and termolecular mechanisms, and the reaction of CO_2 and MDEA solution has been explained based on the base-catalyzed hydration of CO_2.

2.3.1. Zwitterion Mechanism. The zwitterion mechanism consists of the reaction of CO_2 with primary amines such as MEA to form a zwitterion intermediate ($RNH_2^+COO^-$) followed by the deprotonation of the zwitterion by a base to form a carbamate ($RNHCOO^-$), where R is CH_2CH_2OH.[12,18,19,30] Any base in the reaction will contribute to the deprotonation of the zwitterion. The contribution of each base to the reaction rate depends on both its concentration and its strength as a base. The main contributions for the deprotonation of zwitterion in an aqueous solution of primary and tertiary amine are from the amines (MEA and MDEA), hydroxide (OH^-), and water.[8,12,18,19]

The zwitterion mechanism, which consists of the formation of a *zwitterion complex* followed by the deprotonation of the zwitterion by a base,[18,30] can be represented as eqs 21 and 22, whereas the overall carbamate formation reaction is as represented earlier in eq 7.

$$CO_2 + RNH_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} RNH_2^+COO^- \quad (21)$$

$$RNH_2^+COO^- + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} RNHCOO^- + BH^+ \quad (22)$$

where B corresponds to any species in the solution that can act as a base to abstract the proton from the zwitterion and, in the case of a loaded mixed amine solution, such species are $[RNH_2]$, $[H_2O]$, $[OH^-]$, $[R_3N]$, $[HCO_3^-]$, and $[CO_3^{2-}]$. On the other hand, Donaldson and Nguyen,[21] Versteeg and vanSwaaij,[19] Littel et al.,[16,32] and Hagewiesche et al.[7] have shown that, for MDEA and CO_2, the base-catalyzed hydration of CO_2 by the tertiary amines is the most widely accepted rate mechanism. As mentioned earlier, these authors also observed that a tertiary amine does not directly react with CO_2. Instead, it acts as a base to catalyze the hydration of CO_2. On the basis of this observation, the overall reaction rate of CO_2 into a mixed amine system can be expressed according to Liao and Li[12] as

$$r_{ov} = r_{CO_2-MEA} + r_{CO_2-MDEA} + r_{CO_2-OH^-} + r_{CO_2-H_2O} \quad (23)$$

where the terms on the right-hand side are the reaction rates of CO_2 with MDEA, MEA, hydroxyl ion, and water. Owing to the insignificant contribution of the reaction of CO_2 with water, i.e., $r_{CO_2-H_2O}$ in eq 23, this term can be neglected, as suggested by Blauwhoff et al.[18]

The reaction of CO_2 with hydroxyl ion is taken to result in the formation of a bicarbonate:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (24)$$
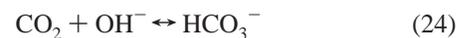
This reaction is fast and can enhance mass transfer even when the concentration of the hydroxyl ion is low. The forward reaction has been described by Pinset et al.[33] as

$$r_{CO_2-OH^-} = k^*_{OH^-}[CO_2][OH^-] \quad (25)$$

$$\log_{10}(k^*_{OH^-}/m^3\,kmol^{-1}\,s^{-1}) = 13.635 - 2895/T(K) \quad (26)$$

2.3.2. Reaction Rate Dependence on MEA. Carbamate formation occurs when CO_2 reacts with primary and secondary

amines as in eq 7. The zwitterion mechanism is generally accepted as the reaction mechanism for carbamate formation in aqueous alkanolamine solutions[18,25] as well as in some organic and viscous solution.[34,35] As described by reactions 21 and 22, the steps involve the formation of zwitterion and subsequent removal of proton by a base B (i.e., base catalysis). Danckwerts[30] reintroduced the mechanism originally proposed by Caplow[35] to derive the reaction rate equation for CO_2 absorption into amines. The general rate of reaction of CO_2 with a primary amine solution such as MEA by the zwitterion mechanism can be given by[4,18,20]

$$r_{CO_2} = \frac{[CO_2][RNH_2] - \dfrac{k_{-1}}{k_{2,MEA}}[RNHCOO^-]\dfrac{\sum k_{-b}[BH^+]}{\sum k_b[B]}}{\dfrac{1}{k_{2,MEA}} + \dfrac{k_{-1}}{k_{2,MEA}\sum k_b[B]}} \quad (27)$$

For the system under consideration (i.e., MEA with CO_2), the second term in the numerator is usually considered to be negligible under low loading absorption conditions, and hence, the rate of reaction can be given by

$$r_{CO_2-amine} = \frac{[CO_2][MEA]}{\left(\dfrac{1}{k_{2,MEA}} + \dfrac{k_{-1}}{k_{2,MEA}\sum k_b[B]}\right)} \quad (28)$$

The zwitterion mechanism can cover shifting reaction orders in which the overall reaction order changes between 2 and 3, for the reaction of CO_2 with primary and secondary amines. The zwitterion mechanism is applied in this study to the reaction between CO_2 and MEA for CO_2 absorption into MEA + MDEA + H_2O. Since the bases in eq 22 could be MEA, MDEA, OH^-, or H_2O, the forward reaction rate for CO_2-MEA, i.e., eq 28, can be expanded to eq 29.

$$r_{CO_2-MEA} = \{[CO_2][MEA]\}/\{(1/k_{2,MEA} +$$
$$k_{-1}/(k_{2,MEA}k_{H_2O}[H_2O] + k_{2,MEA}k_{OH^-}[OH^-] +$$
$$k_{2,MEA}k_{MEA}[MEA] + k_{2,MEA}k_{MDEA}[MDEA]))\} \quad (29)$$

2.3.3. Reaction Rate Dependence on MDEA. For the reaction of CO_2 with tertiary alkanolamines (R_3N), Donaldson and Nguyen[21] proposed the mechanism as given by eq 30. This mechanism implies that tertiary amines cannot react directly with CO_2. In most of the literature on CO_2 kinetics with aqueous tertiary amine solutions, it is assumed that the reaction of CO_2 with MDEA is a pseudo-first-order reaction with respect to CO_2 as follows:[18,35,36]

$$r_{CO_2-MDEA} = k_{2,MDEA}[CO_2][MDEA] \quad (30)$$

The kinetics study based on the pseudo-first-order reaction assumption means that, since MDEA is in a large excess, there is no concentration gradient of MDEA in the liquid reactant, and therefore, the interface conditions can be represented by bulk conditions. The reaction rate equation, i.e., eq 30, is used in this study to represent the reaction kinetics of CO_2 with MDEA in the MEA + MDEA + H_2O system.
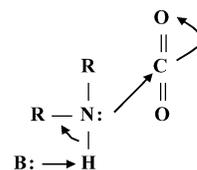

Figure 1. Single-step, termolecular reaction mechanism for the formation of carbamate.[15]

2.3.4. Overall Reaction Rate for CO_2 with MEA + MDEA + H_2O. Substituting the zwitterion mechanism for CO_2-MEA, i.e., eq 29, and CO_2-MDEA, i.e., eq 30, in eq 23,

$$r_{ov} = k_{ov}[CO_2]$$
$$= k_{2,MEA}[CO_2][MEA]/$$
$$\left(1 + \frac{k_{-1}}{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{MEA}[MEA] + k_{MDEA}[MDEA]}\right) +$$
$$k_{2,MDEA}[CO_2][MDEA] + k^*_{OH^-} - [CO_2][OH^-] \quad (31)$$

and the apparent reaction rate constant, k_{app}, is defined as

$$k_{app} = k_{ov} - k^*_{OH^-}[OH^-] \quad (32)$$

$$k_{app} = k_{2,MEA}[MEA]/$$
$$\left(1 + \frac{k_{-1}}{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{MEA}[MEA] + k_{MDEA}[MDEA]}\right) +$$
$$k_{2,MDEA}[MDEA] \quad (33)$$

Though HCO_3^{2-} and CO_3^{2-} are among the bases contributing to the zwitterion mechanism, the contributions of these species to the zwitterion deprotonation is considered negligible,[8] as was mentioned earlier, because of the short contact time in the laminar jet. Hence, the terms involving these species are not included in the rate expression given in eq 33.

It is interesting to examine two asymptotic situations of the zwitterion mechanism, which results in the following: (1) The second term in the denominator of eq 33 is $\ll 1$. This results in a simple second-order kinetics, and the zwitterion formation reaction is rate limiting. (2) The second term in the denominator of eq 33 is $\gg 1$. This results in the expression in eq 34. Here, the zwitterion deprotonation is the rate-determining step, and the overall reaction order is 3.

$$k_{app} = (k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{MEA}[MEA] +$$
$$k_{MDEA}[MDEA])[MEA] + k_{2,MDEA}[MDEA] \quad (34)$$

In the transition region between the two asymptotic cases, the overall reaction order changes between 2 and 3. The zwitterion mechanism covers these shifting reaction orders between 2 and 3.

2.3.5. Termolecular Mechanism. The termolecular mechanism assumes that the reaction takes place in a single step, where the initial product is not a zwitterion but a loosely bound encounter complex, as shown in Figure 1. The complex breaks up to form reactant molecules, while a small fraction reacts with a second molecule of amine, or a water molecule, to give ionic products. Crooks and Donnellan[15] and Versteeg et al.[20] presented the forward reaction rate for this mechanism by eq 35:

$$r_{CO_2} = (k_{H_2O}[H_2O] + k_{MEA}[MEA])[MEA][CO_2] \quad (35)$$

The rate of reaction expression using the termolecular mechanism for the reaction of MEA/MDEA with CO_2 is

presented by eq 36 based on an analogy of the reported termolecular mechanism of single amine by Crooks and Donnellan:[15]

$$r_{CO_2} = (k_{H_2O}[H_2O] + k_{MEA}[MEA] + k_{MDEA}[MDEA])[MEA][CO_2] \quad (36)$$

On the basis of this, the termolecular apparent rate constant for the mixed alkanolamine will result in an expression similar to the one in eq 34.

2.3.6. Methodology to Determine Kinetics. The experimental rate of absorption of CO_2 into a mixed amine system can be obtained by using the laminar jet apparatus. Given the data for physical absorption at a short contact time as well as an initial gas-free liquid, the specific absorption rate and liquid mass transfer for physical absorption, based on Higbie's penetration theory, is given by

$$N_A = 2(D_1/\pi\tau)^{1/2}(p_A/H) \quad (37)$$

$$k_l^0 = 2\sqrt{D_1/\pi\tau} \quad (38)$$

where τ is the contact time (as given by $\tau = \pi d^2 l/4Q$, where d and l are the diameter and length of the laminar jet, respectively, and Q is the volumetric flow rate), k_l^0 is the physical mass transfer coefficient, p_A is the partial pressure of CO_2, H is the Henry's law constant, D_1 is the diffusivity, and the enhancement factor, E, of CO_2 is determined by

$$E = N_A/(k_l^0[CO_2^*] - [CO_2]_b) \quad (39)$$

$[CO_2^*]$ and $[CO_2]_b$ are concentrations of CO_2 at the interface and in the liquid bulk, and N_A is the average rate of absorption per unit area. The conditions for the absorption of CO_2 was selected in such a way as to ensure that absorption occurs in the fast pseudo-first-order regime which is given by

$$3 < Ha < E \quad (40)$$

where the Hatta number Ha is

$$Ha = \frac{\sqrt{k_{ov}D_{CO_2}}}{k_L} \quad (41)$$

The specific rate of mass transfer of CO_2 is given by

$$N_A = \frac{[CO_2]_i\sqrt{k_{ov}D_{CO_2}}}{\tanh(\sqrt{k_{ov}D_{CO_2}/k_l})} \quad (42)$$

For $Ha > 3$, tanh Ha approaches 1; thus, the specific rate of mass transfer of CO_2 becomes

$$N_A = [CO_2]_i\sqrt{k_{ov}D_{CO_2}} = \frac{p_{CO_2}}{H_{CO_2}}[(\sqrt{k_{ov}D_{CO_2}})] \quad (43)$$

$$k_{ov} = N_A^2 \frac{H_{CO_2}^2}{p_{CO_2}^2}\frac{1}{D_{CO_2}} \quad (44)$$

The specific absorption of CO_2 (N_A) into MEA + MDEA + H_2O can be measured for various systems at different temperatures and CO_2 loadings. The k_{ov} is calculated by eq 44, knowing the diffusivity of CO_2 in the solution, D_{CO_2}, the partial pressure
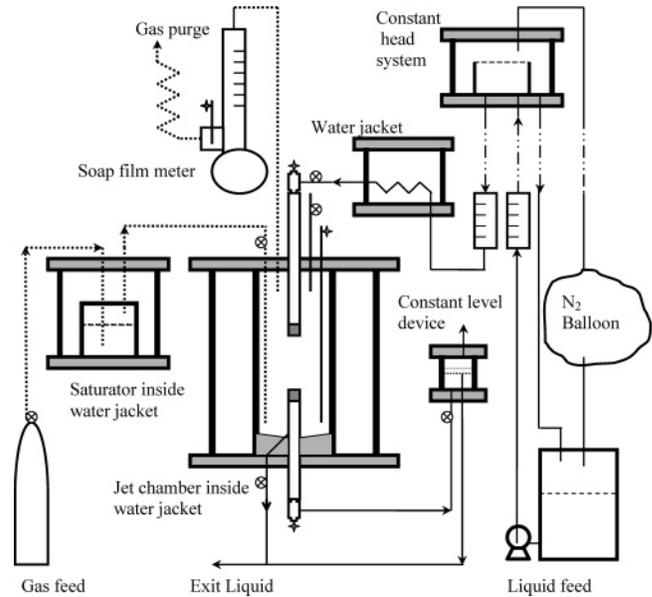

Figure 2. Schematic drawing of laminar jet apparatus.

of CO_2, P_{CO_2}, and the Henry's law constant, H_{CO_2}, in the solution. The Henry's law constant is obtained from the Wang et al.[23] model, while k_{app} is calculated from k_{ov} by eq 32. The values of the experimental k_{app} values are fitted to the zwitterion mechanism rate expression or the termolecular mechanism rate expression to obtain the individual rate constants, $k_{2,MEA}$, $(k_{2,MEA}k_{H_2O})/k_{-1}$, $(k_{2,MEA}k_{OH^-})/k_{-1}$, $(k_{2,MEA}k_{MEA})/k_{-1}$, $(k_{2,MEA}k_{MDEA})/k_{-1}$, and $k_{2,MDEA}$ in the expression of k_{app} given by eq 33.

3. Experimental Apparatus and Procedure

The schematic of the laminar jet apparatus used for the measurements of the experimental absorption rates is presented in Figure 2. A detailed description of the laminar jet absorber and its operation can be seen in Aboudheir et al.[28] In brief, for each test run, the absorbing liquid was prepared and degassed by spraying it into a vacuum. A jet of the liquid issuing from a circular nozzle flowed intact downward through an atmosphere of the gas to be absorbed and was collected in a capillary receiver. The nozzle, a circular hole in a 0.07 ± 0.005 mm thick stainless steel sheet, was 0.63 mm in inside diameter. The receiver was a capillary hole drilled in an acrylic rod. The length and the diameter of the hole were 2.0 and 0.1 cm, respectively. A two-dimensional traveling microscope was used to measure the jet length and the jet diameter to within one-thousandth of a millimeter. The actual flow rate of liquid was determined by weighing the liquid discharged in a timed interval during each experiment. A volumetric technique was used to measure the absorption rates of gas into liquid. The flow meter (digital soap-film meter) used to measure the absorption rate was designed to measure flows from 0.1 to 50 cm^3/min with an accuracy of $\pm3\%$ of the readings. The temperatures of the liquid entering and leaving the jet chamber, of the gas entering the jet chamber, and of the gas entering the gas-flow meter were measured. The temperatures of the liquid and the gas entering the jet chamber were controlled to within ±0.3 °C. This was achieved by having two separate heating/cooling circulator units, one for controlling the gas-stream temperature and the other for controlling the liquid-stream temperature. The absorption experiments at predetermined operating conditions were repeated several times, and an average was taken for the absorption data.

Table 2. Diffusivity of CO₂ in Water at 298 K and Atmospheric Pressure

D, cm²/s	reference
1.95×10^{-5}	Al-Ghawas et al.[29]
1.96×10^{-5}	Perry and Green[40]
1.94×10^{-5}	Tamimi et al.[31]
1.96×10^{-5}	Aboudheir et al.[28]
1.93×10^{-5}	**this work**

4. Results and Discussion

Kohl and Neilsen[1] have reported that the latest trends on gas treating are based on mixed amine systems where the properties of one of the amines help to compensate for the undesirable effects of the second amine. For example, the addition of a small amount of a primary amine, i.e., MEA, to a tertiary amine, i.e., MDEA, enhances the rate of absorption of CO_2 largely without changing the stripping characteristics. Also, one of the main objectives of this work is to minimize the heat duties of the stripping section. These are the reasons that the composition range of the mixture was selected from an MDEA/MEA weight ratio of 27/03 to 23/07, over a concentration range for MDEA of 2.316−1.996 kmol/m³ and for MEA of 0.490−1.147 kmol/m³, to study the kinetics of the absorption of CO_2 into MDEA−MEA solutions at temperatures ranging from 298 to 333 K. To check the validity of the laminar jet absorber, the diffusion coefficient of the absorption of CO_2 into water at 298 K using this apparatus was determined. The total absorption into the jet for a case where there is diffusion without chemical reaction can be calculated theoretically as in eq 45,[13,27]

$$R_A = 4C_e^*\sqrt{DLh} \tag{45}$$

where R_A is the total rate of absorption of gas, C_e^* is the equilibrium concentration of gas at the interface, D is the diffusivity of gas in the liquid, L is the liquid flow rate, and h is the jet length. A plot of R_A against $(Lh)^{1/2}$ at various flow rates and jet lengths gives a straight line through the origin with a slope equal to $4C_e D^{1/2}$. The average experimental value found for the diffusion coefficient of CO_2 in water at 298 K and atmospheric pressure was 1.93×10^{-5} cm²/s. This value is calculated from the slope of the experimental data which is 5.79×10^{-7} and the solubility of water at 298 K and by substituting into eq 45. The experimental diffusivity values obtained by this work shows good agreement with those available in the literature, as shown in Table 2.

The experiments to determine kinetics were performed for the MDEA/MEA concentrations of 27/03, 25/05, and 23/07 (all in weight %). Various absorption rates were obtained at different contact times by changing the jet length and/or the liquid flow rates. Since the CO_2 loading of the solution is also considered, a vapor−liquid-equilibrium model was used for species concentration prediction instead of directly using the molarities of the mixed amines, as was done by Liao and Li.[12] The specific rate of absorption of CO_2 (N_A) in a mixed amine solution was measured by the laminar jet apparatus. From eq 44, the overall rate constant, k_{ov}, for the reaction was calculated by knowing the partial pressure of CO_2, the Henry's law constant, and the diffusivity of CO_2 in MEA + MDEA + H₂O. The partial pressure of CO_2 was calculated by subtracting the vapor pressure from the total pressure, which is recorded for each run. Solubility and diffusivity were determined by the empirical correlations of Wang et al.[23] and Li and Lai,[41] respectively. The formation of the bicarbonate by the reaction of CO_2 with the hydroxyl ion, OH^- (see eq 4), is considered in the overall rate expression given by eq 23, since even at low concentrations of the
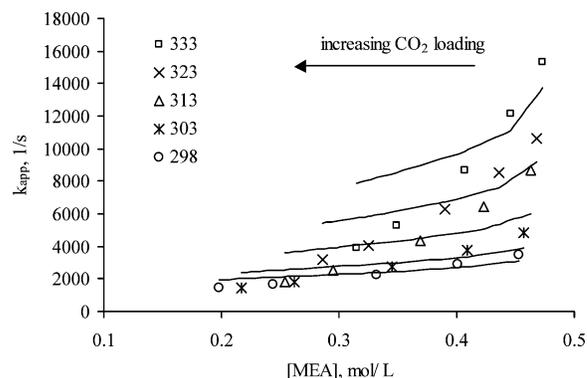

Figure 3. Apparent rate constant for the reaction of CO_2 with 27 wt % MDEA−3 wt % MEA solution as a function of free MEA concentration. Solid lines are predicted by eq 46.
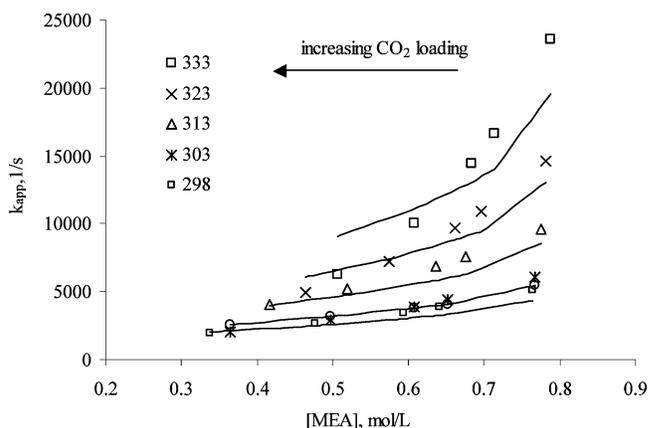

Figure 4. Apparent rate constant for the reaction of CO_2 with 25 wt % MDEA−5 wt % MEA solution as a function of free MEA concentration. Solid lines are predicted by eq 46.
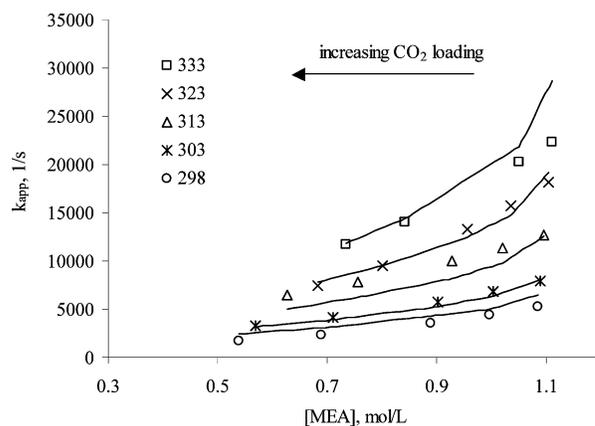

Figure 5. Apparent rate constant for the reaction of CO_2 with 23 wt % MDEA−7 wt % MEA solution as a function of free MEA concentration. Solid lines are predicted by eq 46.

alkanolamines, the bicarbonate formation reaction contributes significantly to the absorption rates and the overall reaction rate constant.[18] Hence, to obtain the apparent rate constant, k_{app}, the contribution of bicarbonate formation reaction is deducted from the overall rate of reaction. Figures 3−5 illustrate temperature dependence of the apparent reaction rate for all the five temperatures studied. The k_{app} vs concentration curves for CO_2 absorption in MEA is not linear but follows an exponential trend, which is typical of temperature dependence following the Arrhenius law. Similar trends were observed by Liao and Li[12] for unloaded mixtures of MDEA and MEA at various concentrations at three different temperatures. Also, it was observed

that k_{app} decreased with increasing CO_2 loading in the liquid (Figures 3−5). This can be explained by the decrease in free MEA with an increase in the CO_2 loading in the solution. This free MEA concentration is obtained by loading the MEA with CO_2. Reactions 21 and 22 describe the formation and deprotonation of the zwitterion.[30,35]

The experimental k_{app} at each temperature were fitted to the Zwitterion mechanism rate expression given in eq 33 using a nonlinear regression procedure to obtain individual reaction rate constants $k_{2,MEA}$, k_{H_2O}, k_{OH^-}, k_{MEA}, and k_{MDEA}. The nonlinear regression procedure was based on the modified Levenburg−Marquardt algorithm. The subroutine DBCLSF documented in the IMSL MATH/library (Visual Numerics, Inc.[38]) was used to obtain the fitting parameters (individual rate constants). This algorithm has proven to be efficient and has been adopted by Aboudheir et al.[14] in a previous study. No meaningful values were obtained for any of the five parameters $k_{2,MEA}$, k_{H_2O}, k_{OH^-}, k_{MEA}, and k_{MDEA}. It was, thus, concluded that the Zwitterion mechanism was not applicable for the loaded mixed amine system under investigation. Although Liao and Li[12] could predict the kinetics of absorption of CO_2 in aqueous MDEA−MEA by the Zwitterion mechanism, the mixed amine solutions used in their study were not loaded. In addition, the equipment for their experiment was the wetted-wall column, which could provide a sufficiently long contact time for a slow-reacting system such as the MDEA−MEA blend.

The termolecular mechanism was used to fit the experimental apparent rate constants, k_{app}. A multiple linear regression was used to fit eq 34 and to determine individual rate constants k_{H_2O}, k_{MEA}, k_{OH^-}, and k_{MDEA} at each temperature. The subroutine called RLSE documented in the IMSL STAT/library (Visual Numerics, Inc.[39]) was used to obtain the optimum fitting parameters. This routine was also successfully utilized by Aboudheir et al.[14] for a single aqueous primary amine, MEA. In eq 34, water is an integral part of the reaction rate. However, no meaningful results were obtained when all the contributing bases (which included water) were included. Hence, it was concluded that the termolecular mechanism as proposed by Crooks and Donnellan[15] could not adequately predict the kinetics of the CO_2 loaded mixed aqueous MDEA−MEA solution. Littel et al.[16] have observed that the kinetics of CO_2 in blends of secondary and tertiary amine cannot be understood in terms of the termolecular mechanism. This scenario is contrary to what was observed by Crooks and Donnellan[15] and Aboudheir et al.[14] for a single alkanolamine system. When all the experimental apparent reaction-rate constants ($k_{app,average}$) were fitted to the termolecular expression, eq 34, by a multiple linear regression procedure, only two parameters, k_{OH^-} and k_{MEA}, were found to fit the experimental data for k_{app}. For the MDEA−MEA system under investigation, if H_2O was left out in eq 34, eq 46 was obtained.

$$k_{app} = (k_{OH^-}[OH^-] + k_{MEA}[MEA])[MEA] + k_{2,MDEA}[MDEA] \quad (46)$$

This is the modified termolecular mechanism, which is subsequently used for all discussions and for predicting k_{app}.

The multiple linear regression routine RLSE was used to fit eq 46. Equation 46 is identical to the second case of the zwitterion mechanism, when deprotonation of the zwitterion is rate determining. Previous researchers[18,19,32] observed that H_2O contributed to the deprotonation of the zwitterion, while Crooks and Donnellan,[15] and Aboudheir et al.[14] also observed that H_2O contributed to the termolecular mechanism as well. However,

we observed that the inclusion of H_2O for regression yielded meaningless results. A possible reason is that the deprotonation reaction of the zwitterion by water is a very slow reaction. Thus, given the short contact time of the absorption experiments in a laminar jet absorber, a slow reaction is not expected to have an effect in the overall reaction rate.[37] Aboudheir et al.[14] observed that H_2O contributed to the overall reaction rate using a laminar jet apparatus because the system investigated was aqueous monoethanolamine, which reacts extremely quickly with CO_2 as compared to the slow-reacting mixed amine system, MEA−MDEA. Instead of H_2O, OH^- ions were observed to contribute to the apparent reaction rate for CO_2 loaded mixed aqueous MEA and MDEA blends, because the mixed alkanolamine solution used were loaded. For loaded solutions, the free amine available is very small. Also, when the partial pressure of CO_2 is low (at low loading), the hydroxide (OH^-) concentration at the interface increases, hence yielding the observation that OH^- influences the apparent reaction rate and is, thus, present in the apparent rate constant equation in eq 46. The studies conducted by Liao and Li[12] were on unloaded solutions. Possibly, that could explain why they did not consider it necessary to include OH^- ions in obtaining the predicted k_{app}. This is in contrast with the work of Blauwhoff et al.,[18] who have reported that the data on the CO_2 absorption in single alkanolamines have a significant dependence on OH^-; hence, the latter authors incorporated hydroxide ions in the reaction mechanism.

In this study, when MDEA was included in the termolecular mechanism term (refer to eq 34) for the multiple linear regressions, the results were meaningless. Hence, MDEA was excluded from the mechanism term in this work. The exclusion of MDEA is supported by the fact that the contribution of MDEA to the termolecular mechanism in mixed alkanolamine system is still highly debatable. Littel et al.[16] reported that MDEA has a measurable contribution to the deprotonation of zwitterion (since the deprotonation of zwitterion is similar to the termolecular mechanism) for CO_2 absorption into aqueous blends of DEA and MDEA. On the contrary, Rinker et al.[8] observed that, when the rates of absorption were predicted by excluding the contribution of MDEA to the zwitterion ion deprotonation, there was good agreement between the predicted and experimental absorption rates. This suggests that MDEA does not significantly contribute to the deprotonation of zwitterion. Littel et al.[16] have used a reactor, which operates under transient conditions and over much longer contact times that may facilitate the deprotonation reaction by MDEA, whereas the laminar jet operates at very short contact times. Since the experimental conditions used in this work were identical (i.e., the laminar jet) to those for the work by Rinker et al.,[8] the exclusion of MDEA in the deprotonation reaction in our work was considered justifiable. This is also supported by Glasscock et al.,[4] who have demonstrated that MDEA does not participate in the MEA reaction rate in an aqueous blend of the MDEA−MEA system. The multiple linear regression based on the modified termolecular mechanism was performed at each temperature (298−333 K) for all concentrations of the amine under consideration (27 wt % MDEA/03 wt % MEA, 25 wt % MDEA/05 wt % MEA, and 23 wt % MDEA/07 wt % MEA). The results obtained are given in Table 3. The average absolute deviation (AAD) between the experiments and fitted model for each temperature are shown, which indicates that all experimental kinetics data of this work are fitted with an AAD% of 19% by the rate constants reported in Table 3. The AAD% for the current study is comparable with the <16% reported for the loaded MEA system by Aboudheir et al.[14]

Table 3. Fitted Values of Kinetics Constants of CO_2 Absorption into Aqueous MDEA−MEA Solution Based on the Deprotonation of Zwitterion Mechanism

temperature, K	298	303	313	323	333
k_{MEA}, $L^2/(mol^2 s)$	2056	3884	6790	7868	8586
k_{OH^-}, $L^2/(mol^2 s)$	72420	94087	112497	299192	469037
k_{MDEA}, $L/(mol s)$	963	1068	1799	2325	3540
AAD% in k_{app}	18	16	22.8	15.5	23

The estimates of the rate constants from this work were fitted as a function of temperature by the following Arrhenius equations,

$$k_{MEA} = 9.56 \times 10^8 \exp\left(\frac{-3802.4}{T}\right) \qquad (47)$$

$$k_{OH^-} = 5.04 \times 10^{12} \exp\left(\frac{-5411.0}{T}\right) \qquad (48)$$

$$k_{MDEA} = 2.58 \times 10^8 \exp\left(\frac{-3736.5}{T}\right) \qquad (49)$$

where the reaction rate constants for k_{MEA} and k_{OH^-} are in $L^2/$(mol s), the constant for k_{MDEA} is in $L/$(mol s), and the temperature is in K. The individual reaction rate constants were substituted in eq 46, and the predicted k_{app} was determined for each temperature and free amine concentration.

The predicted and experimental k_{app} values were plotted as a function of MEA concentration at each temperature for all three mixed amine concentrations, as shown in Figures 3−5. From these figures, a satisfactory agreement between the experimental and predicted k_{app} is observed.

5. Conclusion

Two reaction mechanisms, namely, zwitterion and termolecular, were used to interpret the kinetic data. It has been observed that both mechanisms in their original forms could not predict the individual kinetic rate constants. A new kinetic model of the absorption of CO_2 in CO_2 loaded aqueous MDEA−MEA solution was developed. The kinetic model is based on the modification of the termolecular mechanism. The reaction-rate model is given by

$$r_{CO_2} = (k_{OH^-}[OH^-] + k_{MEA}[MEA])MEA +$$
$$(k_{2,MDEA}[MDEA])CO_2$$

with the following three reaction-rate constants,

$$k_{MEA} = 9.56 \times 10^8 \exp\left(\frac{-3802.4}{T}\right)$$

$$k_{OH^-} = 5.04 \times 10^{12} \exp\left(\frac{-5411.0}{T}\right)$$

$$k_{MDEA} = 2.58 \times 10^8 \exp\left(\frac{-3736.5}{T}\right)$$

where the reaction rate constants for k_{MEA} and k_{OH^-} are in $L^2/$(mol s), the constant for k_{MDEA} is in $L/$(mol s), and the temperature is in K.

It was observed that water did not contribute to the zwitterion deprotonation reaction. OH^- was found to contribute to the

apparent rate constant. The reaction-rate model developed could predict the kinetics of the CO_2 loaded MDEA−MEA system.

Literature Cited

(1) Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, TX, 1997.

(2) Charkravarty, T.; Phuken, U.K. Reaction of Acid gases with mixtures of amines. *Chem. Eng. Prog.* **1985**, *40*, 32−36.

(3) Critchfield, J.; Rochelle, G. T. Absorption of Carbon Dioxide in Aqueous MDEA and MDEA/MEA Solutions. Presented at the AIChE National Meeting, Houston, TX, March 30, 1987.

(4) Glasscock, D. A.; Critchfield, J. E.; Rochelle, G. T. Absorption of carbon dioxide in mixtures of MDEA with MEA or DEA. *Chem. Eng. Sci.* **1991**, *46* (11), 2829−2845.

(5) Versteeg, G. F.; Van Swaaij, W. P. M. On the kinetics between CO_2 and alkanolamines both in aqueous and nonaqueous solutions. I. Primary and secondary amines. *Chem. Eng. Sci.* **1988**, *43* (3), 573−585.

(6) Rangwala, H. A.; Morrell, B. R.; Mather, A. E. Absorption of CO_2 into aqueous tertiary amine/MEA solutions. *Can. J. Chem. Eng.* **1992**, *70*, 482−490.

(7) Hagewiesche, D. P.; Ashour, S. S.; Al-Ghawas, H. A.; Sandall, O. C. Absorption of carbon dioxide into aqueous blends of monoethanolamine and *N*-methyldiethanolamine. *Chem. Eng. Sci.* **1995**, *50* (7), 1071−1079.

(8) Rinker, E. B.; Ashour, S. S.; Al-Ghawas, H. A.; Sandall, O. C. Absorption of carbon dioxide into aqueous blends of diethanolamine and methyldiethanolamine. *Ind. Eng. Chem. Res.* **2000**, *39*, 4346−4356.

(9) Xiao, J.; Li, C.-W.; Li, M.-H. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + 2-amino-2-methyl-1-propanol. *Chem. Eng. Sci.* **2000**, *55* (1), 161−175.

(10) Horng, S.-Y.; Li, M.-H. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + triethanolamine. *Ind. Eng. Chem. Res.* **2002**, *41*, 257−266.

(11) Zhang, X.; Zhang, C.-F.; Liu. Y. Kinetics of absorption of carbon dioxide into aqueous solution of methyldiethanolamine blended with diethanolamine *Ind. Eng. Chem. Res.* **2002**, *41*, 1135−1141.

(12) Liao, C.-H.; Li, M.-H. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + *N*-methyldiethanolamine. *Chem. Eng. Sci.* **2002**, *57* (21), 4569−4582.

(13) Astarita, G.; Savage, D.; Bisio, A. *Gas Treating with Chemical Solvents*; John Wiley & Sons: New York, 1983.

(14) Aboudheir, A.; Tontiwachwuthikul, P.; Chakma, A.; Idem, R. Kinetics of reactive absorption of carbon dioxide in high CO_2-loaded, concentrated aqueous monoethanolamine solutions. *Chem. Eng. Sci.* **2003**, *58* (23), 5195−5210.

(15) Crooks, J. E.; Donnellan, J. P. Kinetics and Mechanism of the Reaction between Carbon Dioxide and Amines in Aqueous Solution. *J. Chem. Soc., Perkin Trans. 2* **1989**, 331−333.

(16) Littel, R. J.; Versteeg, G. F.; Van Swaaij, W. P. M. Kinetics of CO_2 with primary and secondary amines in aqueous solutions. I. Zwitterion deprotonation kinetics for DEA and DIPA in aqueous blends of alkanolamines. *Chem. Eng. Sci.* **1992**, *47* (8), 2027−2035.

(17) Savage, D. W.; Kim, C. J. Chemical Kinetics of Carbon Dioxide Reactions with Diethanolamine and Diisopropanolamine in Aqueous Solvents. *AIChE J.* **1985**, *31* (2), 296−301.

(18) Blauwhoff, P. M.; Versteeg, G. F.; van Swaaij, W. M. A study on the reaction between carbon dioxide and alkanolamines in aqueous solutions. *Chem. Eng. Sci.* **1984**, *39* (2), 207−225.

(19) Versteeg, G. F.; Van Swaaij, W. P. M. On the kinetics between CO_2 and alkanolamines both in aqueous and nonaqueous solutions. II. Tertiary amines. *Chem. Eng. Sci.* **1988**, *43* (3), 587−591.

(20) Versteeg, G. F.; Van Dijck, A. J.; van Swaaij, W. P. M. On the kinetics between CO_2 and alkanolamines both in aqueous and nonaqueous solutions. An Overview. *Chem. Eng. Commun.* **1996**, *144*, 113−158.

(21) Donaldson, T. L.; Nguyen, Y. N. Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes. *Ind. Eng. Chem Fundam.* **1980**, *19*, 260−266.

(22) Littel, R. J.; Van Swaaij, W. P. M.; Versteeg, G. F. Kinetics of CO_2 with tertiary amines in aqueous solutions. *AIChE J.* **1990**, *36* (11), 1633−1640.

(23) Wang, Y. W.; Otto, D.; Mather, A. E. Solubility of N_2O in aqueous mixtures of alkanolamines and in mixed solvents. *Chem. Eng. J.* **1992**, *48*, 31−40.

(24) Danckwerts, P. V.; Sharma, M. M. Absorption of Carbon Dioxide into Solutions of Alkalis and Amines (with Some Notes on Hydrogen Sulphide and Carbonyl Sulphide). *Chem. Eng.* **1966**, *October*, CE244−CE280.

(25) Barth, D.; Tondre, C.; Delpuech, J. J. Kinetics and mechanisms of the reactions of carbon dioxide with alkanolamines: A discussion concerning the cases of MDEA and DEA. *Chem. Eng. Sci.* **1984**, *39* (12), 1753−1757.

(26) Austgen, D. M.; Rochelle, G. T. Model of Vapor−Liquid Equilibria for Aqueous Acid Gas−Alkanolamine Systems. A Representation of H_2S and CO_2 Solubility in Aqueous MDEA and CO_2 Solubility in Aqueous Mixtures of MDEA with MEA or DEA. *Ind. Eng. Chem. Res.* **1991**, *30*, 543−555.

(27) Danckwerts, P. V. *Gas liquid reactions*; McGraw-Hill: New York, 1970.

(28) Aboudheir, Ahmed; Tontiwachwuthikul, P.; Chakma, A.; Idem, R. A Novel Design for the Nozzle of the Laminar Jet Absorber. *Ind. Eng. Chem. Res.* **2004**, *43*, 2568−2574.

(29) Al-Ghawas, H.; Hagewiesche, D.; Ruiz-Ibanez, G.; Sandall, O. C. Physicochemical properties important for carbon dioxide absorption in aqueous methyldiethanolamine. *J. Chem. Eng. Data* **1989**, *34*, 385−391.

(30) Danckwerts, P. V. The reaction of carbon dioxide with ethanolamines. *Chem. Eng. Sci.* **1979**, *34* (4), 443−446.

(31) Tamimi, A.; Rinker, E. B.; Sandall, O. C. Diffusion Coefficients for Hydrogen Sulfide, Carbon Dioxide, and Nitrous Oxide in Water over the Temperature Range 293−368 K. *J. Chem. Eng. Data*. **1994**, *39* (2), 330−332.

(32) Littel, R. J.; Versteeg, G. F.; Van Swaaij, W. P. M. Kinetics of CO_2 with primary and secondary amines in aqueous solutions. II. Influence of temperature on zwitterion formation and deprotonation rates. *Chem. Eng. Sci.* **1992**, *47* (8), 2037−2045.

(33) Pinset, B. R. W.; Pearson, L.; Roughton, F. J. W. The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions. *Trans. Faraday Soc.* **1956**, *79*, 1512−1520.

(34) Sada, E.; Hidehiro, K.; Han, Z. Q.; Matsuyama, H. Chemical kinetics of the reaction of carbon dioxide with ethanolamine in nonaqueous solvents. *AIChE J.* **1985**, *31* (8), 1297−1303.

(35) Caplow, M. Kinetics of carbamabte formation and breakdown. *J. Am. Chem. Soc.* **1968**, *90*, 6795−6803.

(36) Tomcej, R.; Otto, F. Absorption of CO_2 and N_2O into aqueous methyldiethanolamine. *AIChE J.* **1989**, *35* (5), 861−864.

(37) Rinker, E. B.; Ashour, S. S.; Sandall, O. C. Kinetics and Modeling of Carbon Dioxide into Aqueous Solutions of Diethanolamine. *Ind. Eng. Chem. Res.* **1996**, *35* (4), 1107−1114.

(38) Visual Numerics, Inc. *IMSL MATH/Library: Fortran Subroutines for Mathematical Applications*; Visual Numerics, Inc.: Houston, TX, 1994.

(39) Visual Numerics, Inc. *IMSL STAT/Library: Fortran Subroutines for Statistical Applications*; Visual Numerics, Inc.: Houston, TX, 1994.

(40) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1997.

(41) Li, M.-H.; Lai, M.-D. Solubility and diffusivity of nitrous oxide and CO_2 in (MEA + MDEA + water) and (MEA + AMP + Water). *J. Chem. Eng. Data* **1995**, *40*, 486−492.