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Research Article

CO₂-Alkanolamine Reaction Kinetics: A Review of Recent Studies

Alkanolamines are the most popular absorbents used to remove CO_2 from process gas streams. Therefore, the CO_2 reaction with alkanolamines is of considerable importance. The aim of this article is to provide an overview on the kinetics of the reaction of CO_2 with aqueous solutions of alkanolamines. The various reaction mechanisms that are used to interpret experimental kinetic data – zwitterion, termolecular and base-catalyzed hydration – are discussed in detail. Recently published data on reaction kinetics of individual amine systems and their mixtures are considered. In addition, the kinetic behavior of several novel aminebased solvents that have been proposed in the literature is analyzed. Generally, the reaction of CO_2 with primary, secondary and sterically hindered amines is governed by the zwitterion mechanism, whereas the reaction with tertiary amines is described by the base-catalyzed hydration of CO_2 .

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1 Introduction

The reaction of CO_2 with alkanolamines is of considerable industrial importance, e.g., in ammonia plants to make the gaseous streams free of CO_2 , in the manufacture of hydrogen via steam reforming of natural gas, in treating natural/associated gas streams and in thermal power stations to meet the discharge limits for CO_2 in flue gas. Industrially important alkanolamines for CO_2 removal are the primary amines monoethanolamine (MEA) and diglycolamine (DGA), the secondary amines diethanolamine (DEA) and diisopropanolamine (DIPA) and the tertiary amines methyldiethanolamine (MDEA) and triethanolamine (TEA) [1].

Primary and secondary alkanolamines react rapidly with CO_2 to form carbamates. However, the heat of absorption associated with the carbamate formation is high, which results in high solvent regeneration costs. Further, the CO_2 loading capacity of such alkanolamines is limited to 0.5 mol of CO_2 per mol of amine. Tertiary alkanolamines possess no hydrogen atom attached to the nitrogen atom, as in the case of primary and secondary alkanolamines. Thus, the carbamation reaction cannot take place, resulting in a low reactivity with respect to CO_2 . Instead, tertiary amines facilitate the CO_2 hydrolysis reaction forming bicarbonates. The reaction heat released in

bicarbonate formation is lower than that of carbamate formation, thus reducing solvent regeneration costs. Moreover, tertiary amines have a high CO_2 loading capacity of 1 mol of CO_2 per mol of amine. The CO_2 absorption rates of tertiary amines can be enhanced by the addition of small amounts of primary or secondary amines [2]. In addition, other absorption activators such as piperazine (PZ) can also be used [3].

A new class of amines with regeneration costs lower than those of conventional primary and secondary amines – sterically hindered amines – has recently received considerable attention. A sterically hindered amine is a primary amine in which the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino group is attached to a secondary or tertiary carbon atom [4]. 2-Amino-2-methyl-1propanol (AMP) and 2-piperidineethanol (PE) are examples of sterically hindered primary and secondary amines, respectively. Due to a large group attached to the nitrogen atom, these amines form carbamates of low stability, thereby resulting in a CO_2 capacity of 1 mol of CO_2 per mol of amine.

There are two comprehensive reviews on the reactions between CO_2 and alkanolamines available [5, 6]. However, both were published more than ten years ago, and thus, an evaluation of recent developments appears desirable. The present article provides an overview on the kinetic behavior of various amine-containing aqueous systems. Three reaction mechanisms used to interpret kinetics – zwitterion, termolecular and base-catalyzed hydration – are described in detail. Recent kinetic studies on novel absorbents are discussed. Furthermore, experimental kinetic data on mixed amine systems that have been proposed in the literature are presented.

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2 Theory

The reaction of CO_2 with primary, secondary and sterically hindered amines is usually described by the zwitterion mechanism, whereas the reaction with tertiary amines is described by the base-catalyzed hydration of CO_2 .

2.1 Zwitterion Mechanism

This two-step mechanism, originally proposed by Caplow [7] and later reintroduced by Danckwerts [8], suggests that the reaction between CO_2 and the amine (denoted here as AmH) proceeds through the formation of a zwitterion as an intermediate:

$$CO_2 + AmH \xrightarrow{k_1} AmH^+COO^-$$
 (1)

This zwitterion undergoes deprotonation by a base (or bases) *B*, thereby resulting in carbamate formation:

$$\operatorname{AmH^+COO^-} + B \xrightarrow{k_{\rm B}} \operatorname{AmCOO^-} + B\mathrm{H^+}$$
 (2)

Applying the steady-state principle to the intermediate zwitterion, the rate of reaction of CO_2 in aqueous solutions can be expressed as:

$$r = \frac{k_1 (\text{CO}_2) (\text{AmH})}{1 + \frac{k_{-1}}{k_{\text{B}}(B)}}$$
(3)

where $k_{\rm B}(B)$ represents deprotonation of the zwitterion by any base, such as H₂O, OH⁻ or AmH, as well as by a combination of bases. The reaction rate given by Eq. (3) exhibits a fractional order between one and two with respect to the amine concentration.

When deprotonation is almost instantaneous as compared to the reverse reaction in Eq. (1) ($k_{-1} \ll k_B(B)$) and zwitterion formation is rate-determining, Eq. (3) becomes:

$$r = k_1 (\text{CO}_2) (\text{AmH}) \tag{4}$$

thereby suggesting that the reaction is of the first order with respect to both CO_2 and amine. When zwitterion deprotonation is rate-determining ($k_{-1} >> k_B(B)$), Eq. (3) takes the form:

$$r = \frac{k_1 k_{\rm B}(B)}{k_{-1}} \,({\rm CO}_2) \,({\rm AmH})$$
(5)

Similar to Eq. (3), the latter expression suggests a fractional reaction order between one and two with respect to the amine concentration. In the limiting case when the contribution of amine to zwitterion deprotonation is much more significant than that of other bases, such as H_2O and OH^- , the overall reaction is of the second order with respect to amine.

If the base B in the reaction described by Eq. (2) is the amine itself, the carbamate formation can be represented as follows:

$$AmH^{+}COO^{-} + AmH \rightarrow AmCOO^{-} + AmH_{2}^{+}$$
(6)

In this case, the overall reaction, which accounts for carbamate formation in a solution, is given by the sum of reactions represented by Eqs. (1) and (6):

$$CO_2 + 2 AmH \rightleftharpoons AmCOO^- + AmH_2^+$$
 (7)

If the amine is sterically hindered, the zwitterion reacts more easily with water than with AmH and bicarbonate formation takes place:

$$AmH^{+}COO^{-} + H_2O \rightarrow HCO_3^{-} + AmH_2^{+}$$
(8)

In this case, the reaction, which accounts for bicarbonate formation, is given by the sum of reactions represented by Eqs. (1) and (8):

$$CO_2 + AmH + H_2O \rightleftharpoons HCO_3^- + AmH_2^+$$
 (9)

Sharma [9, 10] reported that steric effects reduce the stability of the carbamates formed by the amine with CO_2 . Danckwerts [8] suggested that the zwitterion is as stable as the carbamate. Due to the low stability, the carbamates of sterically hindered amines may also readily undergo hydrolysis, forming bicarbonates and releasing free amine molecules. This can be represented as:

$$AmCOO^{-} + H_2O \rightarrow HCO_3^{-} + AmH$$
(10)

These free amine molecules will again react with CO_2 . Thus, bicarbonate ions will be present in larger amounts than carbamate ions. The following reactions may also take place simultaneously in an aqueous amine solution:

$$AmH + H_2O \rightleftharpoons AmH_2^+ + OH^-$$
(11)

$$H_2 O \rightleftharpoons H^+ + O H^-$$
(12)

$$CO_2 + OH^- \stackrel{k_{OH^-}}{\rightleftharpoons} HCO_3^-$$
 (13)

$$\operatorname{CO}_2 + \operatorname{H}_2 \operatorname{O} \stackrel{\operatorname{K}_{\operatorname{H}_2 \circ}}{\rightleftharpoons} \operatorname{HCO}_3^- + \operatorname{H}^+$$
 (14)

The amine dissociation reaction (see Eq. (11)) is almost instantaneous. The reaction between CO_2 and OH^- (see Eq. (13)) is also fast. The total rate of all CO_2 reactions in an aqueous solution is given by the sum of the reaction rates given by Eqs. (13) and (14) and by Eq. (3):

$$r_{\text{overall}} = \left[\frac{k_1 (\text{CO}_2) (\text{AmH})}{1 + \frac{k_{-1}}{k_{\text{B}} (B)}} \right] \\ + \left\{ \left[k_{\text{H}_2\text{O}} (\text{H}_2\text{O}) + k_{\text{OH}^-} (\text{OH}^-) \right] (\text{CO}_2) \right\}$$
(15)

Chem. Eng. Technol. 2007, 30, No. 11, 1467-1474

$$=k_{\rm obs}\,(\rm CO_2)\tag{16}$$

 $k_{\rm obs}$ denotes the observed reaction rate constant which can be measured and is given by:

$$k_{\rm obs} = \left[\frac{k_1 \,({\rm AmH})}{1 + \frac{k_{-1}}{k_{\rm B} (B)}}\right] + \left[k_{\rm H_2O} \,({\rm H_2O}) + k_{\rm OH^-} \,({\rm OH^-})\right] \quad (17)$$

The apparent reaction rate constant (k_{ap}) , which is used for the analysis of experimental data, is given by:

$$k_{\rm ap} = \left[\frac{k_1 \left({\rm AmH} \right)}{1 + \frac{k_{-1}}{k_{\rm B} \left(B \right)}} \right] \tag{18}$$

 $k_{\rm ap}$ can be obtained from $k_{\rm obs}$ as follows:

$$k_{\rm ap} = k_{\rm obs} - \left[k_{\rm H_2O} \left({\rm H_2O} \right) + k_{\rm OH^-} \left({\rm OH^-} \right) \right]$$
(19)

The contribution of Eq. (13) to the overall rate depends on (OH^{-}) , the concentration of hydroxyl ions in aqueous solutions. (OH^{-}) increases with the pK_a value of the amine. The pK_a values of various alkanolamines are given in Tab. 1 [11].

Table 1. pK_a values of alkanolamines at 298 K [11].

Alkanolamine	pK _a
MEA	9.50
DEA	8.88
DIPA	8.80
TEA	7.76
MDEA	8.57
AMP	9.70
DEMEA	9.82

2.2 Termolecular Mechanism

This mechanism, originally proposed by Crooks and Donnellan [12] and recently revisited by da Silva and Svendsen [13], assumes that an amine reacts simultaneously with one molecule of CO_2 and one molecule of a base. The reaction proceeds in a single step via a loosely-bound encounter complex as the intermediate. This can be represented as:

$$CO_2 + AmH \cdots B \rightleftharpoons AmCOO^{-} \cdots BH^{+}$$
 (20)

This complex breaks up to form reactant molecules (CO_2 and amine), while its small fraction reacts with a second molecule of the amine or a water molecule to give ionic products. The forward reaction rate for this mechanism is given by:

$$r = k_{\rm obs} \,({\rm CO}_2) \tag{21}$$

where k_{obs} is given by:

$$k_{\rm obs} = [k_{\rm H_2O} ({\rm H_2O}) + k_{\rm OH^-} ({\rm OH^-}) + k_{\rm AmH} ({\rm AmH})] ({\rm AmH})$$

(22)

Eq. (21), whose form is similar to that of the limiting case of the zwitterion mechanism represented by Eq. (5), can describe fractional and higher-order kinetics [13].

2.3 Base-Catalyzed Hydration Mechanism

Donaldson and Nguyen [14] suggested that tertiary alkanolamines (denoted here as R_3N) cannot react directly with CO₂. Such amines have a base-catalytic effect on the hydration of CO₂. This can be represented as:

$$R_3N + H_2O + CO_2 \xrightarrow{k'} R_3N^+H + HCO_3^-$$
(23)

In aqueous solutions, an amine dissociation reaction may also occur:

$$R_3N + H_2O \rightleftharpoons R_3N^+H + OH^-$$
(24)

In principle, as reported in [15], a direct reaction between CO_2 and tertiary amines still may occur at extremely high pH, thereby resulting in monoalkylcarbonate formation. However, at pH values lower than 12, the rate of this reaction can be neglected [16]. The total rate of all CO_2 reactions in an aqueous solution is thus represented by the sum of the reaction rates given by Eqs. (13), (14) and (23):

$$r_{\text{overall}} = \left[k_{\text{H}_{2}\text{O}} \left(\text{H}_{2}\text{O} \right) + k_{\text{OH}^{-}} \left(\text{OH}^{-} \right) + k' \left(\text{R}_{3}\text{N} \right) \right] \left(\text{CO}_{2} \right)$$
(25)

 $k_{\rm obs}$ is given by:

$$k_{\rm obs} = \left[k_{\rm H_2O} \left({\rm H_2O} \right) + k_{\rm OH^-} \left({\rm OH^-} \right) + k' \left({\rm R_3N} \right) \right] \tag{26}$$

and k_{ap} by:

$$k_{\rm ap} = [k'(R_3N)] \tag{27}$$

The base-catalysis reaction could also be explained by a zwitterion-type mechanism earlier proposed by Yu and Astarita [17]:

$$R_3N + CO_2 \rightleftharpoons R_3NCOO^-$$
 (28)

$$R_3 NCOO^- + H_2 O \rightarrow R_3 N^+ H + HCO_3^-$$
(29)

Eq. (28) represents a reaction of the amine with CO_2 to form an unstable complex. Eq. (29) describes the homogeneous hydrolysis reaction in which water reacts with the zwitterion-type complex to yield a bicarbonate.

3 Discussion of Reaction Kinetics

In this section, recently published data on reaction kinetics of individual amine systems and their mixtures is discussed. The experimental kinetic parameters are analyzed in terms of the mechanisms described in the previous section.

3.1 Individual Amine Systems

MEA remains the most popular absorbent due to its high reactivity with CO₂. The kinetics of the CO₂-MEA reaction has been widely studied, and previously published literature is summarized by Mahajani and Joshi [5], Versteeg et al. [6] and Aboudheir et al. [18]. The zwitterion mechanism adequately describes the reaction kinetics. The reaction is of the first order with respect to both CO₂ and MEA in aqueous systems (see Eq. (4)), thereby suggesting that zwitterion deprotonation is instantaneous. The reaction of CO₂ with MEA has been recently revisited in [18–21] and these studies are presented in Tab. 2. Aboudheir et al. [18] analyzed the reaction in high CO₂-loaded, concentrated aqueous MEA solutions and described the kinetics using the termolecular mechanism. A new termolecular-kinetic model was developed, in which k_{obs} was given by:

$$k_{\text{obs}} = \left[k_{\text{H},\text{O}} \left(\text{H}_2\text{O}\right) + k_{\text{AmH}} \left(\text{AmH}\right)\right] \left(\text{AmH}\right)$$
(30)

Another primary amine – DGA – was recently studied by Al-Juaied and Rochelle [22]. Previous studies on the absorption of CO₂ by an aqueous DGA solution, which are outlined by Versteeg et al. [6], suggest that the overall reaction order has a value of two. The reaction rate constant (6660 m³/ (kmol s)), reported by Al-Juaied and Rochelle [22] at low concentration (25 wt % DGA) and at 298 K, is in agreement with the values available in literature. However, at high concentration (65 wt % DGA), the rate constant was four times larger than the previously published values, thereby suggesting its dependence on the DGA concentration.

DEA is the most popular secondary alkanolamine used for CO_2 removal. The literature on the absorption of CO_2 by an aqueous DEA solution, which exhibits complex kinetic behavior, was reviewed earlier [23]. Depending on the rate-limiting step (zwitterion formation or deprotonation) and the amine concentration, the reaction order with respect to DEA lies between one and two. Rinker et al. [23] estimated the rate constant of the zwitterion formation reaction and expressed it as a

function of temperature (293 < T < 343 K) in the DEA concentration range of 0.25 to 2.8 kmol/m³. This expression is as follows:

$$k_{\rm DEA} = 1.24 \cdot 10^6 \exp\left(-\frac{1701}{T}\right)$$
 (31)

Cadours et al. [24] determined the kinetic parameters of this system, with the assumption that zwitterion formation is ratelimiting. The reaction rates of the zwitterion formation reaction were consistent with the results of Rinker et al. [23].

The kinetics of the reaction of CO_2 with another secondary amine –DIPA– in aqueous solutions was studied by Camacho et al. [25]. The reaction was found to be of the second order with respect to DIPA, and hence, of the third order totally. The dependence of the rate constant on temperature (288 < T < 313 K) was given by:

$$\ln k_{\rm DIPA} = 26.0 - \frac{7360.5}{T}$$
(32)

Secondary alkanolamines linked to an alkyl group, e.g., methyl, ethyl, *n*-butyl and *t*-butyl groups, have recently been investigated [26–28], and these studies are presented in Tab. 3. Methylmonoethanolamine (MMEA) reacts faster than MEA, thereby suggesting that the methyl group increases the basicity of the amine without appreciably increasing the hindrance around the nitrogen atom. Due to the large *n*-butyl group attached to the nitrogen atom, the reaction with *n*-butylmonoethanolamine (NBMEA) is slower than that with MEA. The reactions of MMEA and NBMEA have been described by the zwitterion mechanism. The reaction of *t*-butylmonoethanolamine (TBMEA) – a severely hindered amine – is described by the termolecular mechanism [26]. The rate in aqueous ethylmonoethanolamine (EMEA) was found to be faster than that in DEA [27].

The CO₂ reaction with other sterically hindered amines such as AMP, 2-amino-2-methyl-1,3-propanediol (AMPD) and 2amino-2-ethyl-1,3-propanediol (AEPD) was studied in [29– 31]. The relevant kinetic data are presented in Tab. 4. The overall reaction is represented by Eq. (9), and the contribution of Eq. (13) to the overall rate is negligible. In aqueous AMP solutions, the zwitterion is instantaneously deprotonated. Furthermore, the carbamate undergoes rapid hydrolysis according to Eq. (10) [29].

MDEA and diethylmonoethanolamine (DEMEA) are the tertiary alkanolamines that were recently investigated. Ko and

Table 2. Recent kinetic studies of CO₂/aqueous MEA reaction system.

T [K]	MEA concentration	Order with respect to MEA	Reaction rate constant	Reference
293–333	3–9 kmol/m ³	2	$k_{\rm MEA} = 4.61 \cdot 10^9 \exp\left(-\frac{4412}{T}\right)$	18
303	0.22-2.02 kmol/m ³	1	6674 m ³ /(kmols)	19
293–324	20 wt %	1	$k_1 = 4.4947 \cdot 10^{11} \exp\left(-\frac{44940}{R'T}\right)$	20
303	2.5 kmol/m ³	1	7311 m ³ /(kmol s)	21

Table 3. Recent kinetic studies of CO₂ reaction with secondary amines linked to alkyl group.

Amine	Amine concentration [kmol/m ³]	Order with respect to amine	Reaction rate constant at 298 K [m ³ /(kmols)]	Reference
MEA	not available	1	4090	26
MMEA	0-0.04	1	5010	26
NBMEA	not available	1	2000	26
TBMEA	not available	1	190	26
EMEA	0.028-0.082	2	8000	27
MEA	0.9–2.5	1	3630	28
MMEA	0.9-2.5	1	7940	28
EMEA	0.9-2.5	1	4170	28
NBMEA	0.9-2.5	1	4760	28
MDEA	0.9–2.5	1	18.2	28

Table 4. Recent kinetic studies of CO₂ reaction with sterically hindered amines.

Amine	Temperature [K]	Amine concentration [kmol/m ³]	Reaction rate constant at 298 K [m ³ /kmol s]	Reference
AMP	288-318	0.25-3.5	810.4	29
DEA	288-318	0.25-3.5	2375	29
DIPA	288-318	0.25–3.5	2585	29
AMPD	303–318	5–25 wt %	382 (at 303 K)	30
AEPD	303–318	5–25 wt %	378 (at 303 K)	31

Li [32] determined the second-order rate constant for the CO_2 reaction with MDEA in aqueous solutions as a function of temperature in the range of 303 to 313 K:

$$k_{\rm MDEA} = 4.01 \cdot 10^8 \exp\left(-\frac{5400}{T}\right)$$
 (33)

DEMEA comprises two ethyl groups replacing the hydrogen atoms of the amino group in MEA. Vaidya and Kenig [33] studied the kinetics of the CO₂-DEMEA system. The reaction rate in DEMEA was found to be much faster than that in MDEA. At 303 K, the second order reaction rate constant attained a value of 173 m³/(kmol s). Li et al. [27] expressed the dependence of the rate constant on temperature (298 < T < 313 K) as follows:

$$k_{\text{DEMEA}} = 9.95 \cdot 10^7 \exp\left(-\frac{6238.4}{T}\right)$$
 (34)

Bishnoi and Rochelle [34] studied kinetics of the CO_2 reaction with PZ, a cyclic diamine. The reaction is of the first order with respect to both CO_2 and PZ. At 298 K, the second-order rate constant attained a value of 53700 m³/(kmol s), which is considerably higher than that for primary amines such as MEA and DGA. PZ reacts with CO_2 rapidly, which results in carbamate formation. In addition, the dissociation reaction for PZ may occur [35, 36]. The reactions that may take place in the presence of PZ (here denoted by $R''(NH)_2$) can be represented as:

$$R''(NH_2) + 2 CO_2 \rightleftharpoons R''(NHCOO)_2$$
(35)

$$R'' (NHCOO)_2 + 2 H_2O \to R'' (NH_2)_2^+ + 2 HCO_3^-$$
(36)

Another diamine, 2-((2-aminoethyl) amino)ethanol (AEEA), was recently investigated by Ma'mun et al. [37]. The termolecular mechanism (see Eq. (22)) was used to interpret the kinetic behavior of this new solvent, which comprises a primary and a secondary amine group. The reaction order with respect to AEEA was found to be between one and two in the AEEA concentration range of 1.19 to 3.46 kmol/m³. The dependence of the reaction rate constants on temperature (305 < T < 322 K) was given by:

$$k_{\text{AEEA}} = 6.07 \cdot 10^7 \exp\left(-\frac{3030}{T}\right)$$
 (37)

$$k_{\rm H_2O} = 3.19 \cdot 10^8 \exp\left(-\frac{4320}{T}\right)$$
 (38)

Bouhamra and Alper [38] reported that the reaction is of the first order with respect to AEEA at low concentration $(0.015-0.05 \text{ kmol/m}^3)$, thereby suggesting

a shift in the reaction order when passing from low to high AEEA concentrations.

It can be concluded that the reaction of CO_2 with several new amine-based solvents has been investigated in the past few years. MMEA, EMEA, DEMEA and AEEA are candidate alkanolamines having good potential for the bulk removal of CO_2 from gaseous streams. EMEA and DEMEA have an additional advantage for an extensive use for CO_2 capture, as they can be prepared from renewable resources [39]. AEEA, which is characterized by high reactivity with CO_2 and high loading capacity, may provide a promising alternative to existing absorbents, such as MEA [40]. However, more experimental work needs to be conducted to provide a comprehensive insight into the performance of these absorbents for CO_2 capture.

3.2 Mixed Amine Systems

MDEA, which has low reactivity with respect to CO_2 due to its tertiary amine characteristics, can be promoted with amines with stronger reactivity, such as MEA, DEA or PZ. Liao and Li [41] investigated kinetics of the reaction of CO_2 with aqueous blends of MDEA and MEA. They found that the presence of MEA accelerates the CO_2 reaction with MDEA. Therefore, the absorbent blend consisting of MDEA, MEA and H₂O can be considered as promising for bulk CO_2 removal. A reaction model comprising a zwitterion mechanism for MEA and a first-order reaction mechanism for MDEA was used to represent the kinetic data. The overall reaction rate could be represented as: Г

$$r_{\text{overall}} = \left[\frac{k_1 (\text{CO}_2) (\text{MEA})}{1 + \left[\frac{k_{-1}}{\{ \left[k_{\text{H}_2\text{O}} (\text{H}_2\text{O}) \right] + \left[k_{\text{OH}^-} (\text{OH}^-) \right] + \left[k_{\text{MEA}} (\text{MEA}) \right] + \left[k_{\text{MDEA}} (\text{MDEA}) \right] \}} \right]} \right]$$

Contrary to the model proposed in [41], Ramachandran et al. [42] reported that reaction kinetics of the CO_2 -MDEA-MEA system cannot be interpreted by the zwitterion and the termolecular mechanism in their original forms. They proposed a modified termolecular mechanism, which included the contribution of OH⁻ ions, to predict reaction kinetics in CO_2 -loaded aqueous solutions. The reaction rate was expressed as follows:

$$r_{\text{overall}} = \{ [k_{\text{OH}^{-}} (\text{OH}^{-}) + k_{\text{MEA}} (\text{MEA})] (\text{MEA})(CO_2) \} + \{ k_{\text{MDEA}} (\text{MDEA}) (\text{CO}_2) \}$$

$$(40)$$

The reaction rate constants in Eq. (40) were given by:

$$k_{\rm MEA} = 9.56 \cdot 10^8 \exp\left(-\frac{3802.4}{T}\right)$$
 (41)

$$k_{\rm OH^-} = 5.04 \cdot 10^{12} \exp\left(-\frac{5411}{T}\right)$$
 (42)

$$k_{\rm MDEA} = 2.58 \cdot 10^8 \exp\left(-\frac{3736.5}{T}\right)$$
 (43)

The acceleration of the CO₂ reaction with MDEA by DEA was recently investigated [43]. MDEA did not contribute to zwitterion deprotonation, whereas the contribution of DEA was significant. Zhang et al. [44] investigated the CO₂-MDEA-DEA system and suggested that the overall reaction can be regarded as a reaction of CO₂ and MDEA in parallel with the reaction of CO₂ with free DEA, due to the fact that the free DEA transfers CO₂ to MDEA, thereby regenerating itself. The second-order rate constant of the reaction between CO₂ and DEA was represented as:

$$\ln k_{\rm DEA} = 24.515 - \left(\frac{5411.3}{T}\right) \tag{44}$$

In the context of the activated MDEA technology used by BASF, PZ is applied as an efficient activator. It is more effective than other absorption activators, such as MEA and DEA [3]. In the CO₂-MDEA-PZ system, the reaction described by Eq. (35) occurs simultaneously with that described by Eq. (28), and CO₂ could be transferred by $R''(NHCOO)_2$ to MDEA (here denoted by R_3N). This is reflected by the following reaction [45]:

$$R'' (NHCOO)_2 + 2 R_3 N \rightleftharpoons R'' (NH)_2 + 2 R_3 NCOO^-$$
 (45)

Thus, PZ contributes to absorption of CO_2 and enhances the overall rate of absorption. The second-order rate constant of the CO_2 -PZ reaction was given by:

+ { [
$$k_{\text{OH}^-}$$
 (CO₂)(OH⁻)] + [k_{MDEA} (CO₂)(MDEA)] } (39)

$$k_{\rm PZ} = 4 \cdot 10^{10} \exp\left(-\frac{4059.4}{T}\right) \tag{46}$$

Xiao et al. [46] studied the kinetics of the CO_2 reaction with an absorbent blend consisting of AMP, MEA and H₂O. In order to represent the kinetic data, they suggested a reaction model consisting of a first-order reaction mechanism for MEA and a zwitterion mechanism for AMP. The overall rate of reaction could be represented as:

$$r_{\text{overall}} = \left[\frac{k_1 (\text{CO}_2) (\text{AMP})}{1 + \left[\frac{k_{-1}}{\{ [k_{\text{H}_2\text{O}} (\text{H}_2\text{O})] + [k_{\text{OH}^-} (\text{OH}^-)] + [k_{\text{MEA}} (\text{MEA})] + [k_{\text{AMP}} (\text{AMP})] \} \right]} + \{ [k_{\text{OH}^-} (\text{CO}_2) (\text{OH}^-)] + [k_{\text{MEA}} (\text{CO}_2) (\text{MEA})] \}$$

$$(47)$$

The effect of PZ on reaction kinetics of the CO₂-AMP system was recently investigated in [47, 48]. PZ, which facilitates zwitterion deprotonation, promotes the overall CO₂-AMP reaction. PZ also accelerates the CO₂ reaction with another tertiary amine, DEMEA [49]. The CO₂ absorption rate increases even when a small amount of PZ is added into an aqueous DEMEA solution. Further, a substantial increase in the rate can be observed at higher PZ concentrations.

EMEA is another amine, which promotes the CO_2 -DEMEA reaction [39]. The absorbent blend comprising DEMEA, EMEA and H₂O combines the high CO_2 loading capacity of DEMEA with the high reactivity of EMEA.

These investigations show that the promotion of the CO_2 reaction with tertiary or sterically hindered amines by activators such as MEA, DEA and PZ is attractive for the enhancement of CO_2 capture. Therefore, further experimental work should be focused on studying the performance of such amine blends in gas treating applications.

4 Conclusions

In this work, recent kinetic studies of the CO_2 reaction with aqueous alkanolamines are considered. Different mechanisms, such as zwitterion, termolecular and base-catalyzed CO_2 hydration, which describe the reaction pathways, are discussed in detail. The reaction of CO_2 with primary, secondary and sterically hindered amines is usually described by the zwitterion mechanism, whereas the reaction with tertiary amines is governed by the base-catalyzed hydration of CO_2 . New kinetic data on conventional amines, such as MEA, DEA, DGA and MDEA, are outlined. In addition, investigations of novel amine-based solvents are discussed. MMEA, EMEA, DEMEA and AEEA are candidate alkanolamines having good potential for the bulk removal of CO₂ from gaseous streams. The acceleration of the CO₂ reaction with MDEA, AMP and DEMEA by promoters such as MEA, DEA and PZ is highlighted. Amine blends are found to be attractive for the enhancement of CO₂ capture. Further experimental work should be conducted to provide a comprehensive insight into performance of novel individual amine systems and their mixtures.

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Symbols used

AmH	[-]	alkanolamine
(AmH)	[kmol/m ³]	concentration of alkanolamine
(AMP)	[kmol/m ³]	concentration of AMP
В	[-]	base
(<i>B</i>)	[kmol/m ³]	concentration of base B
(CO_2)	[kmol/m ³]	concentration of CO ₂
(H_2O)	[kmol/m ³]	concentration of H ₂ O
k_1	$[m^3/(kmol s)]$	forward reaction rate constant in
		Eq. (1)
k_{-1}	[1/s]	backward reaction rate constant
		in Eq. (1)
k'	[-]	reaction rate constant in
		Eq. (23)
Ka	[-]	amine protonation constant
$k_{\rm AmH}$	$[m^6/(kmol^2 s)]$	rate constant in Eq. (22)
k_{ap}	[1/s]	apparent reaction rate constant
k _B	$[m^3/(kmol s)]$	rate constant in Eq. (2)
$k_{\rm H_2O}$	[-]	forward reaction rate constant in
2 -		Eq. (14)
$k_{\rm obs}$	[1/s]	observed reaction rate constant
$k_{\rm OH^-}$	$[m^3/(kmol s)]$	forward reaction rate constant in
		Eq. (13)
(MDEA)	[kmol/m ³]	concentration of MDEA
(MEA)	[kmol/m ³]	concentration of MEA
(OH ⁻)	[kmol/m ³]	concentration of hydroxyl ions
pK_a	[-]	-log K _a
r	$[\text{kmol}/(\text{m}^3 \text{s})]$	rate of reaction
r _{overall}	$[\text{kmol}/(\text{m}^3 \text{s})]$	overall rate of reaction defined
		by Eq. (15)
R′	[kJ/(kmol K)]	gas constant (8.3144)
R ₃ N	[-]	tertiary alkanolamine
(R_3N)	[kmol/m ³]	concentration of tertiary
		alkanolamine
$R''(NH)_2$	[-]	piperazine
Т	[K]	temperature

Abbreviations

AEEA	2-((2-aminoethyl)amino)ethanol
AEPD	2-amino-2-ethyl-1,3-propanediol
AMP	2-amino-2-methyl-1-propanol
AMPD	2-amino-2-methyl-1,3-propanediol

DEA	diethanolamine
DEMEA	diethylmonoethanolamine
DGA	diglycolamine
DIPA	diisopropanolamine
EMEA	ethylmonoethanolamine
MDEA	methyldiethanolamine
MEA	monoethanolamine
MMEA	methylmonoethanolamine
NBMEA	n-butylmonoethanolamine
PE	2-piperidineethanol
PZ	piperazine
TBMEA	t-butylmonoethanolamine
TEA	triethanolamine

References

- A. Kohl, R. Nielsen, *Gas Purification*, 5th ed., Gulf Publishing Company, Houston 1997.
- [2] T. Chakravarty, U. K. Phukan, R. H. Weiland, *Chem. Eng. Prog.* **1985**, *81* (4), 32.
- [3] M. Appl, U. Wagner, H. J. Henrici, K. Kuessner, K. Voldamer, E. Fuerest, US Patent 4,336, 233, 1982.
- [4] G. Sartori, D. W. Savage, *Ind. Eng. Chem. Fundam.* **1983**, *22*, 239.
- [5] V. V. Mahajani, J. B. Joshi, Gas Sep. Purif. 1988, 2, 50.
- [6] G. F. Versteeg, L. A. J. van Dijck, W. P. M. van Swaaij, *Chem. Eng. Comm.* **1996**, 144, 113.
- [7] M. Caplow, J. Am. Chem. Soc. 1968, 90, 6795.
- [8] P. V. Danckwerts, Chem. Eng. Sci. 1979, 34, 443.
- [9] M. M. Sharma, Ph.D. Thesis, Cambridge University 1964.
- [10] M. M. Sharma, Trans. Faradey Soc. 1965, 61, 681.
- [11] D. D. Perrin, Dissociation Constants of organic bases in aqueous solutions, Butterworths, London 1965.
- [12] J. E. Crooks, J. P. Donnellan, J. Chem. Soc., Perkin Trans. 1989, 2, 331.
- [13] E. F. da Silva, H. F. Svendsen, *Ind. Eng. Chem. Res.* **2004**, *43*, 3413.
- [14] T. L. Donaldson, Y. N. Nguyen, Ind. Eng. Chem. Fundam. 1980, 19, 260.
- [15] E. Jorgensen, C. Faurholt, Acta Chem. Scand. 1954, 8, 1141.
- [16] J. Benitez-Garcia, G. Ruiz-Ibanez, H. A. Al-Ghawas, O. C. Sandall, *Chem. Eng. Sci.* **1991**, *46*, 2927.
- [17] W.-C. Yu, G. Astarita, D. W. Savage, Chem. Eng. Sci. 1985, 40, 1585.
- [18] A. Aboudheir, P. Tontiwachwuthikul, A. Chakma, R. Idem, *Chem. Eng. Sci.* 2003, 58, 5195.
- [19] A. Aboudheir, P. Tontiwachwuthikul, A. Chakma, R. Idem, Ind. Eng. Chem. Res. 2004, 43, 2568.
- [20] L. Kucka, J. Richter, E. Y. Kenig, A. Gorak, Sep. Purif. Technol. 2003, 31, 163.
- [21] P. D. Vaidya, V. V. Mahajani, Ind. Eng. Chem. Res. 2005, 44, 1868.
- [22] M. Al-Juaied, G. T. Rochelle, *Ind. Eng. Chem. Res.* 2006, 45, 2473.
- [23] E. B. Rinker, S. S. Ashour, O. C. Sandall, *Ind. Eng. Chem. Res.* 1996, 35, 1107.
- [24] R. Cadours, D. Roquet, G. Perdu, Ind. Eng. Chem. Res. 2007, 46, 233.

- 1474 P. D. Vaidya et al.
- [25] F. Camacho et al., Ind. Eng. Chem. Res. 2005, 44, 7451.
- [26] S. H. Ali, S. Q. Merchant, M. A. Fahim, Sep. Purif. Technol. 2002, 27, 121.
- [27] J. Li, A. Henni, P. Tontiwachwuthikul, Ind. Eng. Chem. Res. 2007, 46, 4426.
- [28] T. Mimura, T. Suda, I. Iwaki, A. Honda, H. Kumazawa, *Chem. Eng. Comm.* **1998**, 170, 245.
- [29] S. Xu, Y-W. Wang, F. D. Otto, A. E. Mather, *Chem. Eng. Sci.* 1996, 51, 841.
- [30] J.-H. Yoon et al., Chem. Eng. Sci. 2003, 58, 5229.
- [31] S. J. Yoon et al., Ind. Eng. Chem. Res. 2002, 41, 3651.
- [32] J.-J. Ko, M.-H. Li, Chem. Eng. Sci. 2000, 55, 4139.
- [33] P. D. Vaidya, E. Y. Kenig, in Proc. of 10th Conf. on Process Integration, Modelling and Optimization for Energy Saving and Pollution Reduction (Ed: J. Klemes), AIDIC Servizi S.r.l., Ischia 2007.
- [34] S. Bishnoi, G. T. Rochelle, Chem. Eng. Sci. 2000, 55, 5531.
- [35] H.-B. Liu, C.-F. Zhang, G.-W. Xu, Ind. Eng. Chem. Res. 1999, 38, 4032.
- [36] X. Zhang, C.-F. Zhang, S.-J. Qin, Z.-S. Zheng, Ind. Eng. Chem. Res. 2001, 40, 3785.

- [37] S. Ma'mun, V. Y. Dindore, H. F. Svendsen, Ind. Eng. Chem. Res. 2007, 46, 385.
- [38] W. Bouhamra, E. Alper, Chem. Eng. Technol. 2000, 23 (5), 421.
- [39] P. D. Vaidya, E. Y. Kenig, 2007, 62, in print.
- [40] S. Ma'mun, H. F. Svendsen, K. A. Hoff, O. Juliussen, Energy Convers. Manage. 2007, 48, 251.
- [41] C.-H. Liao, M.-H. Li, Chem. Eng. Sci. 2002, 57, 4569.
- [42] N. Ramachandran, A. Aboudheir, R. Idem, P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.* 2006, 45, 2608.
- [43] E. B. Rinker, S. S. Ashour, O. C. Sandall, *Ind. Eng. Chem. Res.* 2000, 39, 4346.
- [44] X. Zhang, C.-F. Zhang, Y. Liu, Ind. Eng. Chem. Res. 2002, 41, 1135.
- [45] X. Zhang, C.-F. Zhang, S.-J. Qin, Z.-S. Zheng, Ind. Eng. Chem. Res. 2001, 40, 3785.
- [46] J. Xiao, C.-W. Li, M.-H. Li, Chem. Eng. Sci. 2000, 55, 161.
- [47] D. J. Seo, W. H. Hong, Ind. Eng. Chem. Res. 2000, 39, 2062.
- [48] W.-C. Sun, C.-B. Yong, M.-H. Li, Chem. Eng. Sci. 2005, 60, 503.
- [49] P. D. Vaidya, E. Y. Kenig, Ind. Eng. Chem. Res. 2007, 46, in print.