2011-07-21

Desorption Kinetics of an Alternative Monoethanolamine Based CO2 Capture Process

Morris D. Argyle
mdargyle@byu.edu

Zhuoyan Sun

See next page for additional authors

Follow this and additional works at: https://scholarsarchive.byu.edu/facpub

Part of the Chemical Engineering Commons

Original Publication Citation

BYU ScholarsArchive Citation
Argyle, Morris D.; Sun, Zhuoyan; and Fan, Maohong, "Desorption Kinetics of an Alternative Monoethanolamine Based CO2 Capture Process" (2011). All Faculty Publications. 83.
https://scholarsarchive.byu.edu/facpub/83

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in All Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact scholarsarchive@byu.edu, ellen_amatangelo@byu.edu.
Desorption kinetics of an alternative monoethenalamine based CO₂ capture process

Zhuoyan Sun,§ Maohong Fan,§,* and Morris Argyle§,ζ

§ Department of Chemical & Petroleum Engineering, University of Wyoming, Laramie, WY 82071
ζ Department of Chemical Engineering, Brigham Young University, Provo, UT 84602

ABSTRACT

Supported monoethenalamine (MEA) sorbents are promising materials for CO₂ separation due to their low energy demands. Like any other CO₂ separation technologies, CO₂ desorption from supported MEA sorbents is the most energy-expensive step in the overall CO₂ separation process. The presence of water during CO₂ desorption process leads to a significant increase in energy consumption. Therefore, CO₂ desorption in the absence of water is an important method to reduce energy consumption of CO₂ separation using supported MEA, which is determined by several major factors, including desorption kinetics. However, study on CO₂ desorption kinetics of supported MEA is lacking. This research was designed to make progress in this area. The CO₂ desorption kinetic model of TiO₂-supported MEA is experimentally derived with the data collected within water-free desorption environment and theoretically proved by pseudo-steady state theory. The Avrami–Erofeyev mechanism controls the CO₂ desorption process, which is first order with respect to \([RNH_3^+RNHCOO^-]\) or RNH₃⁺ or RNHCOO⁻. The activation

---

*Corresponding author. E-mail: mfan@uwyo.edu.
energy of the CO\textsubscript{2} desorption process is 80.79 kJ/mol. The kinetic characteristics of the CO\textsubscript{2} desorption are much superior to those associated with aqueous MEA based CO\textsubscript{2} separation. The energy saving due to the use of supported MEA for CO\textsubscript{2} separation not only results from avoiding the use of water, with its high specific-heat capacity and high vaporization enthalpy, but also from the favorable desorption kinetics of the supported MEA based CO\textsubscript{2} separation.

INTRODUCTION

People are increasingly concerned about the continuous elevation of atmospheric CO\textsubscript{2} concentration. Fossil fuel based power generation plants have been and will continue to be among the major CO\textsubscript{2} emission sources due to their availability and prices.\textsuperscript{1-4} Therefore, cost-effective technologies should be developed and adopted for capture of CO\textsubscript{2} from fossil fuel power plants while renewable or low-carbon-emission fuels are sought.\textsuperscript{5, 6}

Amine compounds have been considered to be good candidates for CO\textsubscript{2} separation due to their good reactivity with CO\textsubscript{2}.\textsuperscript{7, 8} Monoethanolamine (MEA) has high potential as a CO\textsubscript{2} capture agent, since it has a high mass-based CO\textsubscript{2} sorption capacity and fast reaction rate with CO\textsubscript{2}. CO\textsubscript{2} absorption with aqueous solutions can be expressed as

\[2\text{RNH}_2 + \text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons[k_1][k_2] \text{[RNH}_3^+\text{HCO}_3^-].\] (R1)

MEA has been commercially used for separation of CO\textsubscript{2} in the natural gas, synthesis gas, and refinery industries. However, to date, conventional coal-fired power plants still cannot use aqueous MEA for CO\textsubscript{2} separation due to the high operating cost of the technology.
resulting from its energy-intensive desorption process. In addition, thermal and oxidative
degradations are issues of CO$_2$ separation with aqueous MEA, since CO$_2$ desorption
needs to be operated within a relatively high temperature range, which leads to the loss of
MEA during multiple sorption-desorption cycles.

To overcome the shortcomings of aqueous MEA based CO$_2$ separation processes,
two major methods have been investigated. The first is to mix MEA with other amines to
use their advantages to overcome the shortcomings of MEA. For example, the CO$_2$
absorption rate can be enhanced significantly when MEA is blended with N-
methyldiethanolamine (MDEA), while the associated CO$_2$ desorption is improved.$^9,^{10}$
However, these CO$_2$ sorption systems are still aqueous-phase. People have been
interested in this type of method for a long time; thus, the thermodynamic and kinetic
characteristics of CO$_2$ separation with blended aqueous amines have been well studied.$^{11-}
16$ The second method is to replace water with organic solvents. Jou et al. found that
diethylene glycol (DEG) can dissolve much more CO$_2$ than water.$^{17}$ Glycol compounds,
including ethylene glycol (EG), DEG, and triethylene glycol (TEG), have shown high
CO$_2$ solubility and low vapor pressure, which is desired for reducing the total energy
consumption needed for overall CO$_2$ separation process.$^{18}$ Essentially, replacing water
with organic solvents is used to eliminate the dissociation of protonated MEA or
formation of carbonate or carbamate within the aqueous environment or recombination of
water and MEA, and thus reduce energy consumption.$^{19}$

Recently, researchers have been very interested in developing solid CO$_2$ sorbents
with various amines, making significant progress in increasing CO$_2$ sorption capacities
and lowering CO$_2$ desorption temperatures.$^{20-28}$ When used for separation of CO$_2$ from
flue gases in power plants, they could save much energy by avoiding circulation of large amounts of water. One of the methods used for preparing those solid sorbents is to physically impregnate amines, including MEA, onto the surfaces of porous supporting materials.

Recently, this research team has developed an alternative, semi-immobilization method for preparing supported MEA sorbent. Specifically, pure MEA is immobilized during the CO₂ sorption process, but is mobilized during the CO₂ desorption phase. In other words, immobilized pure MEA reacts with CO₂ in one sorption reactor, and then is transferred to another reactor during the CO₂ desorption process through vaporization. In the absence of water, the MEA based CO₂ separation process can be written as

\[ 2\text{RNH}_2 + \text{CO}_2 \xrightleftharpoons[k_{\text{des}}][k_{\text{ads}}] \text{RNH}_3^+\text{RNHCOO}^- \] (R2)

The alternative MEA application method is designed to use the advantages of solid sorbents while avoiding their hydrothermal/steam stability issues. It could be used to further reduce the energy needed for MEA-based CO₂ separation technologies. As mentioned earlier, desorption step is the key process for any CO₂ separation technology. Therefore, understanding the kinetics of CO₂ desorption in R2 is important to the development of the technology. However, the study on the kinetics of CO₂ desorption of R2, in the absence of water, is lacking. Thus, this research was focused on building a kinetic model for CO₂ desorption in R2 (the reverse reaction of R2, designated as -R2).

**EXPERIMENTAL SECTION**

*TiO₂ preparation and characterization and sorbent preparation*
The TiO\textsubscript{2} used as a support for MEA in this research was prepared with Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} (99 wt%, Acros) through several steps. The first was to add the needed quantity of Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} to water with the H\textsubscript{2}O:Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} molar ratio being 26.3. Next, the mixture was stirred for 1 hr. Then, the obtained precipitate, [TiO(OH)\textsubscript{2}], was filtered, washed with deionized water, and dried at 393K for ~1.5 hrs. TiO\textsubscript{2} was made after calcining the TiO(OH)\textsubscript{2} at 1023K in flowing air for 3 hours.

The prepared TiO\textsubscript{2} was characterized using a Micromeritics TriStar 3000 V6.04 A nitrogen physisorption analyzer to determine its surface area by the BET (Brunauer, Emmett, and Teller) method. The morphological characteristics of this MEA supporting material (TiO\textsubscript{2}) were analyzed using a Hitachi TM-1000 tabletop scanning electron microscope (SEM).

MEA-TiO\textsubscript{2} (MT) sorbent was made by mixing a defined amount of as-received MEA (99 wt%, Acros) with the prepared TiO\textsubscript{2}. The mass ratio of MEA:TiO\textsubscript{2} used for the sorption tests in this research was 40:60.

\textit{Apparatus and CO\textsubscript{2} sorption/desorption}

The experimental apparatus constructed for this research is shown in Figure 1. It consists of three parts, including a gas simulation unit, a CO\textsubscript{2} sorption/desorption system, and CO\textsubscript{2} on-line measurement equipment. Dilute CO\textsubscript{2} from cylinder 1 (1 vol\%, CO\textsubscript{2} and 99 vol\% N\textsubscript{2}) was used for the sorption tests while N\textsubscript{2} from cylinder 2 (100 vol\%) was used during CO\textsubscript{2} desorption and the apparatus cleaning process. The flow rates of the two inlet gases were controlled by their corresponding flow meters (Matheson Tri-gas FM-
1050, numbed as 3’ and 3’’). Another flow meter (3’’) was placed to measure the flow of the whole system.

This research focused on studying the kinetics of CO₂ desorption in a water-free environment. The sorption performance of the MT will be reported separately. For the present work, the purpose of doing sorption tests was to generate the spent sorbents used for the CO₂ desorption kinetic study. Sorption tests were performed in the reactor (#8 in Figure 1, 9 mm x 610 mm). The sorbent bed (#6) was made by loading MT sorbent between two bed holders (#5) made from quartz wool. The reactor (#8) was held in a tube furnace (#7, Thermo Corporation, TF55030A-1) whose temperature was adjusted by a temperature controller (#4, Yokogawa M&C Corporation, UT150). The effluent gas from the reactor (#8) entered a water removal unit (#10) and then an infrared gas analyzer (#11, ZRE, Fuji Electric System Co. Ltd.). The sorption profiles were collected by a data collection computer (#12). All the sorption tests were done under the following conditions: 1.0 vol% CO₂; 99.0 vol% N₂; 0.3 L/min gas flow rate, and 40°C sorption temperature. Each sorption test was stopped when the CO₂ concentration in outlet gas was the same as the initial CO₂ concentration (1.0 vol%).

Desorption tests were performed to study the kinetics of CO₂ desorption in R2 (-R2). The first step of the CO₂ desorption operation was to load the spent MT generated during sorption step into the reactor (#8). All the desorption tests were performed with pure N₂ from cylinder 2 as a carrier gas with a flow rate of 0.3 L/min. The initial amount of [RNH₃⁺RNHCOO⁻] in the spent sorbent used for each CO₂ desorption was obtained by integrating the corresponding CO₂ sorption or desorption profiles. During the desorption process, the MEA and CO₂ decomposed from [RNH₃⁺RNHCOO⁻] passed through a MEA
removal bottle (#10) loaded with 1.0 M H₂SO₄ solution. The MEA-stripped gas from the bottle passed through the gas analyzer (#11) for CO₂ concentration measurement. CO₂ desorption tests were done at five temperatures to obtain the Arrhenius form of -R2.

3. Results and Discussion

3.1 Characteristics of TiO₂

The BET surface area, average pore size, and volume of the TiO₂ as the supporting material of the MT sorbent are 5.68 m²/g, 66.4 nm, and 0.11 cm³/g, respectively. A typical SEM image of the TiO₂ is shown in Figure 2, indicating that the TiO₂ is porous and has a well developed network structure.

3.2 CO₂ desorption kinetic model obtained by experiment

Theory

Essentially, CO₂ desorption, or spent sorbent \([RNH₃⁺RNHCOO⁻]\) decomposition (-R2), is the reverse reaction of R2. Under isothermal conditions, the experimental set-up shown in Figure 1 was used to study the kinetics of CO₂ desorption from or thermal decomposition of the spent sorbent \([RNH₃⁺RNHCOO⁻]\) obtained through the sorption of CO₂ with pure MEA. Like the thermal decomposition processes of many other compounds, 31-36 the general thermal decomposition model of \([RNH₃⁺RNHCOO⁻]\), or CO₂ desorption, can be represented with the following equation

\[
F(\alpha) = kt
\]  
(E1)
where $k$ is the rate coefficient of -R2, or CO$_2$ desorption, and $t$ is the reaction time of -R2. $F(\alpha)$ is the function of $\alpha$, the mass fraction of decomposed [(RNH$_3$)$^+$(RNHCOO)$^-$] at any reaction time ($t$).

The specific definition of $\alpha$ in E1 of -R2 is expressed as

$$
\alpha = \frac{W_{[\text{RNH}_3^+\text{RNHCOO}^-]} - W_{[\text{RNH}_3^+\text{RNHCOO}^-]}_0}{W_{[\text{RNH}_3^+\text{RNHCOO}^-]}_0}
$$

(E2)

where $W_{[\text{RNH}_3^+\text{RNHCOO}^-]}_0$ is the initial mass (g) of [RNH$_3^+$RNHCOO$^-$], $W_{[\text{RNH}_3^+\text{RNHCOO}^-]}$ is the mass (g) of [RNH$_3^+$RNHCOO$^-$] at any CO$_2$ desorption or [RNH$_3^+$RNHCOO$^-$] decomposition time, $t$, $\Delta W_{[\text{RNH}_3^+\text{RNHCOO}^-]}$ is the decomposed [RNH$_3^+$RNHCOO$^-$] at $t$. Both $W_{[\text{RNH}_3^+\text{RNHCOO}^-]}_0$ and $W_{[\text{RNH}_3^+\text{RNHCOO}^-]}$ can be calculated by integration since 1 mole of desorbed CO$_2$ results from the decomposition of 1 mole of [RNH$_3^+$RNHCOO$^-$], according to R2. $W_{(\text{RNH}_3^+\text{RNHCOO}^-)}$ can be obtained by using both CO$_2$ sorption and the corresponding desorption profiles of [RNH$_3^+$RNHCOO$^-$] formed during sorption step. Typical profiles of CO$_2$ sorption with MEA and CO$_2$ desorption from [RNH$_3^+$RNHCOO$^-$] are presented in Figures 3 and 4, respectively. [RNH$_3^+$RNHCOO$^-$] was completely decomposed into RNH$_2$ and CO$_2$ at 80°C. In other words, the spent sorbent is totally regenerable at 80°C. The values of $\alpha$ should change from 0 to 1 from the beginning to the end of [RNH$_3^+$RNHCOO$^-$] decomposition. Based on the CO$_2$ desorption profiles collected with the gas analyzer at different temperatures, the corresponding $\alpha$ vs $t$ relationships were calculated.
F(α) can be represented by different kinetic expressions, although only one of them should fit a specific reaction best. The seven major functional representations of 
\( F(\alpha) \) include 
\[ \alpha^2, \; \alpha + (1-\alpha)\ln(1-\alpha), \; [1-(1-\alpha)^{1/3}]^2, \; 1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3}, \]
\[ \ln[\alpha/(1-\alpha)], \; 1 - (1-\alpha)^{1/n}, \; \text{and} \; -\ln(1-\alpha)^{1/m}. \]

However, the most frequently used forms of F(α) are
\[
F(\alpha) = 1 - (1-\alpha)^{1/n} \quad (n = 1, 2, \text{and} \; 3) \quad \text{(E3)}
\]
\[
F(\alpha) = -\ln(1-\alpha)^{1/m} \quad (m = 1, 1.5, 2, 3, \text{and} \; 4). \quad \text{(E4)}
\]
They have been successfully used by researchers to study the kinetics of many chemical processes, especially those associated with decomposition of chemical compounds.31-37 For example, Marinoni et al.31 found that E4 (also called Avrami–Erofeyev equation) can well represent the kinetics of mullitization in a porcelain-like precursor system. Tang et al. found that E3 applied to the kinetics of thermal dehydration of \( \text{CaCO}_3 \cdot \text{H}_2\text{O}. \)32 Koga confirmed that E3 and E4 apply separately for the thermal dehydration of \( \alpha \)-nickel sulfate hexahydrate under different conditions.33 Furthermore, the Avrami–Erofeyev equation can be used for modeling the kinetic data Konieczny et al. collected when they studied methane decomposition reactions catalyzed by iron based catalysts for hydrogen production.34

**Experimentally derived rate equation and Arrhenius form of CO\textsubscript{2} desorption**

The CO\textsubscript{2} desorption (-R2) studied in this research is a typical decomposition reaction. Therefore, all of the aforementioned seven F(α) forms were tested against preliminary experimental results for their relationships with \( t \), as shown in E1. The
derived regression coefficients indicated that E3 and E4 deserved more evaluation since they resulted in higher regression coefficients. Thus, E3 and E4 were chosen for further comparative studies. The values of the CO₂ desorption reaction order (n and m), CO₂ desorption rate coefficient (k), and corresponding correlation coefficient (r²) obtained at different temperatures of the two models are listed in Table 1.

Table 1 shows that the regression coefficients of both models at all the sorption temperatures are high; however, the obtained reaction orders (n) in \( F(\alpha) = 1 - (1 - \alpha)^{1/n} \) vary considerably within the temperature range. Therefore, Avrami–Erofejev equation (E4) represents the CO₂ desorption mechanism of -R2 better than E3 does. All five of the \(-\ln(1 - \alpha)^{1/m}\) versus t plots obtained at 45°C, 52°C, 66°C, 70°C and 73°C are shown in Figure 5. The average reaction order at the five desorption temperatures is 1.21. Therefore, the reaction order of CO₂ desorption with respect to \([RNH_3^+RNHCOO^-] \) can be considered to be approximately 1. Thus, the rate equation of CO₂ desorption without presence of water (-R2) is

\[
\frac{d\alpha}{dt} = k(1 - \alpha). \quad (E5)
\]

Figure 6 compares this first order model with the experimental data for \( F(\alpha) \) vs t. The model produces an excellent fit for the data when \( m = 1.09 \), which further reinforces how closely the reaction order can be approximated as unity.

The relationship between rate constants (k) of -R2 listed in Table 1 and the corresponding CO₂ desorption temperature (T) can be correlated by the Arrhenius equation\(^{38}\)

\[
k = Ae^{\frac{E}{RT}} \quad (E6)
\]
where $A$ is the pre-exponential factor (min$^{-1}$), which is treated as a constant in the studied temperature range; $E$ is the activation energy (J/mol) of CO$_2$ desorption in the absence of water; and $R$ is the ideal gas constant (J/mol·K).

The $\ln k \sim \frac{1}{T}$ plot for CO$_2$ desorption, based on the values of $k$ at 45°C, 52°C, 59°C, 66°C, and 73°C, is shown in Figure 7. An $E$ value of 80.79 kJ/mol and an $A$ value of 4.2999×10$^{11}$ (min$^{-1}$), respectively, were regressed. Therefore, the Arrhenius form of CO$_2$ desorption from [RNH$_3^+$RNHCOO$^-$] is

$$k = 4.2999 \times 10^{11} e^{-\frac{8.079 \times 10^4}{RT}} \quad (E7)$$

### 3.3 CO$_2$ desorption kinetic model derived from pseudo-steady state theory

*Integrating pseudo-steady state theory with the studied CO$_2$ desorption*

CO$_2$ sorption and desorption without the presence of water proceeds through the following steps, based on the theory of CO$_2$ sorption with MEA$^{39, 40}$

$$\text{CO}_2 + \text{RNH}_2 \xleftarrow{k_{R1}, k_{R2}, k_{R3}} \text{RNH}_3^+ \text{RNHCOO}^- \quad (R3)$$

$$\text{RNH}_3^+ \text{COO}^- + \text{RNH}_2 \xleftarrow{k_{R2}, k_{R3}, k_{R4}} \text{RNH}_3^+ \text{RNHCOO}^- \quad (R4)$$

RNH$_3^+$COO$^-$ is the intermediate species. Then, according to pseudo-steady state theory, the generation and consumption rates of RNH$_3^+$COO$^-$ in R3 and R4 should be equal, or

$$\frac{d[\text{RNH}_3^+ \text{COO}^-]}{dt} = k_{R3}[\text{CO}_2][\text{RNH}_2] - k_{R3}[\text{RNH}_3^+ \text{COO}^-] - k_{R4}[\text{RNH}_3^+ \text{COO}^-][\text{RNH}_2] + k_{R4}[\text{RNH}_3^+ \text{RNHCOO}^-]$$

$$= 0 \quad (E8)$$

or
\[
[R\text{NH}_2\text{COO}^-] = \frac{k_{R3}[\text{CO}_2][R\text{NH}_2] + k_{R4}[R\text{NH}_3\text{RNCHCOO}^-]}{k_{-R3} + k_{R4}[R\text{NH}_2]}.
\] (E9)

Based on the rate law, the change of \([R\text{NH}_3\text{RNCHCOO}^-]\) with time \((t)\) can be expressed in terms of conversion fraction \((\alpha)\) as

\[
M_0 \frac{d\alpha}{dt} = -\frac{d[R\text{NH}_3\text{RNCHCOO}^-]}{dt} = k_{-R4}[R\text{NH}_3\text{RNCHCOO}^-] - k_{R4}[R\text{NH}_2][R\text{NH}_2\text{COO}^-]
\] (E10)

where \(M_0\) is the initial concentration of \([R\text{NH}_3\text{RNCHCOO}^-]\). Combining E9 and E10 leads to

\[
M_0 \frac{d\alpha}{dt} = k_{-R4}[R\text{NH}_3\text{RNCHCOO}^-] - k_{R4}[R\text{NH}_2][R\text{NH}_2\text{COO}^-]
\] (E11)

Based on the stoichiometry of R2, when \(\alpha M_0\) of \([R\text{NH}_3\text{RNCHCOO}^-]\) is consumed at time, \(t\), the concentrations of \([R\text{NH}_3\text{RNCHCOO}^-]\), \([R\text{NH}_2]\), and \([\text{CO}_2]\) at that moment should be

\[
[R\text{NH}_3\text{RNCHCOO}^-] = (1-\alpha)M_0
\] (E12)

\[
[R\text{NH}_2] = 2\alpha M_0
\] (E13)

\[
[\text{CO}_2] = \alpha M_0
\] (E14)

respectively. Integrating E11, E12, E13, and E14 results in

\[
M_0 \frac{d\alpha}{dt} = \frac{k_{R3}k_{-R4}[1 - \alpha]M_0 - 4k_{R3}k_{R4}\alpha^3 M_0^3}{k_{-R3} + 2k_{R4}\alpha M_0}
\] (E15)
or

\[
\frac{d\alpha}{dt} = \frac{k_{R3} k_{-R4}[1 - \alpha] - 4k_{R3}k_{R4}\alpha^3M_0^2}{k_{-R3} + 2k_{R4}\alpha M_0}. 
\]  

(E16)

During the \([RNH_3^+RNHCOO^-]\) decomposition or \(CO_2\) desorption period, \(k_{R4}\) and \(k_{R5}\) are much larger than \(k_{R4}\) and \(k_{R5}\), respectively; therefore, E16 can be simplified as

\[
\frac{d\alpha}{dt} = k_{-R4}[1 - \alpha] = k[1 - \alpha]  
\]

(E17)

or

\[
-\frac{d(1 - \alpha)M_0}{dt} = -\frac{d[RNH_3^+RNHCOO^-]}{dt} = k[1 - \alpha]M_0  
\]

(E18)

or

\[
r_{\text{CO}_2\text{-desorption}} = \frac{d[RNH_3^+RNHCOO^-]}{dt} = k[RNH_3^+RNHCOO^-].  
\]

(E19)

In other words, the \(CO_2\) desorption or \([RNH_3^+RNHCOO^-]\) decomposition rate is 1st order with respect \([RNH_3^+RNHCOO^-]\), which is consistent with that derived with Avrami-Erofeev mechanism and the experimental data, as discussed earlier.

**Activity based rate equation**

According to the thermodynamic definition of activity \((a)\), \(a_{[RNH_3^+RNHCOO^-]}\) is related to \(a_{[RNH_3^+]}\) and \(a_{[RNHCOO^-]}\) as follows

\[
a_{[RNH_3^+RNHCOO^-]} = a_{[RNH_3^+]}a_{[RNHCOO^-]}  
\]

(E20)

or
\[ \gamma_{[RNH_3^+RNHCOO^-]} [RNH_3^+] [RNHCOO^-] = \gamma_{[RNHCOO^-]} [RNHCOO^-] \]  
(E21)

where \( \gamma_i \) \( i = [RNH_3^+RNHCOO^-], RNH_3^+, RNHCOO^- \) is the activity coefficient of species, \( i \). Assuming

\[ \gamma_{[RNH_3^+RNHCOO^-]} = \gamma_{[RNHCOO^-]} = 1, \]  
(E22)

then, combining E19 through E22 leads to

\[ r_{\text{CO}_2\text{-desorption}} = k a_{RNH_3^+} a_{RNHCOO^-} \]

\[ = 4.2999 \times 10^{11} e^{8.075 \times 10^4 \frac{RT}{a_{RNH_3^+} a_{RNHCOO^-}}}. \]  
(E23)

The reaction orders with respect to the two species, \( RNH_3^+ \) and \( RNHCOO^- \), in \( [RNH_3^+RNHCOO^-] \) are both 1. E23 shows that the \( CO_2 \) desorption rate is proportional to the product of the activities of \( RNH_3^+ \) and \( RNHCOO^- \).

### 3.4 Effect of water on \( CO_2 \) desorption kinetics

The sorption kinetics of \( CO_2 \) separations with aqueous MEA solutions have been extensively studied, although more work needs to be done to study their desorption kinetics. However, to the knowledge of this research team, little research has been performed on the kinetics of \( CO_2 \) separation with MEA in absence of water. Plaza et al. studied the kinetics of \( CO_2 \) desorption under conditions of aqueous and highly concentrated MEA solutions. All major kinetic parameters of their models are listed in Table 2. The \( CO_2 \) desorption reaction orders with respect to \( RNH_3^+ \) and \( RNHCOO^- \) within highly concentrated MEA solutions shown in Table 2 are exactly the same as those this research team obtained as given in E23. Comparison of Table 2 with E7/E23 also indicates that the activation energy values of \( CO_2 \) desorption are different under the
three sorption and desorption conditions: aqueous, highly concentrated MEA, and a water-free environment.

*Desorption reaction order*

Table 2 shows that water plays a negative role in CO2 desorption within an aqueous environment. The rate of the reverse reaction of R1, or CO2 desorption, is inversely proportional to the activity of water. In other words, lower water activity within MEA-based CO2 separation systems is beneficial to CO2 desorption.

Understanding the effect of water on CO2 desorption kinetics can start with that on CO2 sorption kinetics. Water affects the overall CO2 sorption kinetics of aqueous MEA based CO2 separation, although the degree of influence needs further investigation because scientists have some disagreement on this subject. Water affects CO2 sorption in aqueous or even highly concentrated MEA solutions in different ways. The first one is its own dissociation:

\[
2\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+. \quad \text{(R5)}
\]

The active hydroxyl ion, OH\(^-\), resulting from R5 can directly react with CO2 to form bicarbonate

\[
\text{OH}^- + \text{CO}_2 \leftrightarrow \text{HCO}_3^- \quad \text{(R6)}
\]

The rate equation of R6 has been found to be

\[
-\frac{d[\text{OH}^-]}{dt} = k_{R6}[\text{CO}_2][\text{OH}^-] \quad \text{(E24)}
\]

where \(k_{R6} \text{ [m}^3/(\text{kmol}\cdot\text{s})\] is the specific reaction rate with respect to [OH\(^-\)]. The Arrhenius form of R6\(^{51-53}\) is
\[ k_{R6} = 4.48 \times 10^{13} e^{-\frac{5.5429 \times 10^4}{RT}}. \quad (E25) \]

The low activation energy and high pre-exponential factor in E25 indicate R6 is a fast reaction. Next, H\textsubscript{2}O molecules can also directly interact with CO\textsubscript{3}\textsuperscript{2-} to form hydroxyl ions (OH\textsuperscript{-}) through the following reaction

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^- \quad (R7) \]

R6 and R7 indicate that H\textsubscript{2}O positively affects CO\textsubscript{2} sorption. Moreover, H\textsubscript{2}O can react with RN\textsubscript{H}_3\textsuperscript{+}COO\textsuperscript{-}, RNHC\textsubscript{O}O\textsuperscript{-}, and RN\textsubscript{H}\textsubscript{3}\textsuperscript{+} resulting from the overall MEA sorption process. It also plays a positive role in CO\textsubscript{2} sorption through these reactions\textsuperscript{45, 48, 52}

Therefore, the overall CO\textsubscript{2} sorption rate should be affected positively to some degree by the activity of H\textsubscript{2}O (\(a_{H_2O}\))\textsuperscript{45} which leads to conclusion that water negatively affects CO\textsubscript{2} desorption, since all the reaction steps involved with H\textsubscript{2}O are reversible and H\textsubscript{2}O is present as a reactant there. This is confirmed by the negative reaction order (-1) of CO\textsubscript{2} desorption with respect to H\textsubscript{2}O in the aqueous H\textsubscript{2}O-CO\textsubscript{2} system, as shown in Table 2.

Furthermore, \(a_{H_2O}\) is not only affected by the concentration of water, but also by that of RN\textsubscript{H}_3\textsuperscript{+}HCO\textsubscript{3}\textsuperscript{-} formed within the aqueous H\textsubscript{2}O-CO\textsubscript{2} environment according to Blandamer et al.\textsuperscript{54} The value of \(a_{H_2O}\) is related to the molality of RN\textsubscript{H}_3\textsuperscript{+}HCO\textsubscript{3}\textsuperscript{-} and other parameters as follows\textsuperscript{54, 55}

\[
\ln a_{H_2O} = -2M_{H_2O}m_{RNH_3^+HCO_3^-} + 2(S_f / 3)M_{H_2O}(m^o)^{\frac{1}{2}}(m_{RNH_3^+HCO_3^-})^{\frac{3}{2}} \quad (E27)
\]

where \(M = 0.018 \text{ kg mol}^{-1}\), \(m_{RNH_3^+HCO_3^-}\) is the molality of RN\textsubscript{H}_3\textsuperscript{+}HCO\textsubscript{3}\textsuperscript{-}, \(m^o = 1 \text{ mol kg}^{-1}\), and \(S_f\) is defined as
\[
S_y = \frac{e^3 [2N_A \rho_{H_2O} m^o]^1}{8\pi \varepsilon_0 \varepsilon_r kT^2}
\]

(E28)

where \(e = 2.718\), \(N_A\) = Avogadro’s number, \(\rho_{H_2O}\) is the density of water, \(\varepsilon_0\) is the permittivity of vacuum, \(\varepsilon_r\) is the relative permittivity of \(H_2O\), and \(k\) is Boltzmann’s constant. E27 and E28 indicate that \(a_{H_2O}\) is increased or \(CO_2\) desorption rate decreases according to Plaza et al.\(^{46}\) in an aqueous MEA-based \(CO_2\) sorption system.

Desorption activation energy

The activation energy values of \(CO_2\) desorption decrease from \(\sim 114\) kJ/mol to \(\sim 103\) kJ/mol when the \(CO_2\) sorption environment changes from an aqueous to a highly concentrated MEA solution. Furthermore, the activation energy obtained with this research within a completely nonaqueous \(CO_2\) sorption-desorption system is \(\sim 81\) kJ/mol. The \(\sim 20\%\) activation energy difference between our and Plaza’s reported activation energies can be attributed to the difference in the experimental conditions under which \(CO_2\) desorption data were collected and upon which the corresponding kinetic models were built. Plaza’s \(CO_2\) desorption model\(^{46}\) for R2 was based on data from \(CO_2\) sorption and desorption experiments performed with concentrated MEA which still contained water, unlike the pure MEA used in this research. The information provided from comparison of the three activation energy values obtained from the different conditions (aqueous MEA, highly concentrated MEA, and water-free MEA) is that the presence of water leads to the increase of activation energy of the \(CO_2\) desorption reaction.
Conclusion

The CO₂ desorption kinetic model for CO₂ separation using TiO₂-supported MEA is different from those using aqueous MEA and highly concentrated MEA solutions. Separation of CO₂ with supported but semi-immobilized pure MEA could significantly reduce energy consumption compared to conventional aqueous MEA, not only due to the elimination of the use of a large amount of water with its high specific-heat-capacity and latent heat of vaporization, but also the improvement of CO₂ desorption kinetics resulting from avoiding dissociation of the protonated MEA.

The findings in this CO₂ desorption kinetic research are not only of importance to the economics of MEA-based CO₂ separation technologies, but also to its environmental considerations. Improvement in CO₂ desorption kinetics through use of supported but semi-immobilized pure MEA implies that lower temperatures can be used for CO₂ desorption, which can alleviate the thermal and oxidative degradation problems observed in aqueous MEA-CO₂ separation system. In addition, lower CO₂ sorption temperatures can help coal-fired power plants mitigate the corrosion issues associated with aqueous MEA-CO₂ separation systems. Decreased corrosion can result in a decrease in the amount of iron carbonate particles in the MEA-CO₂ reaction system, avoiding operational difficulties that include foaming, emulsions, and fouling of aqueous systems, and thus improve the stability and reliability of CO₂ separation facilities in terms of operation, CO₂ sorption capacity, and MEA regeneration ability.
Reference


List of Figures


Figure 2. SEM image of TiO₂ at a magnification of 4,000.

Figure 3. Typical adsorption profile of MT sorbent (CO₂: 1.0 vol%; N₂: 99.0 vol%; gas flow rate: 0.3 L/min; sorption temperature: 40°C).

Figure 4. Typical desorption profile of MT sorbent (CO₂: 0 vol%; N₂: 100 vol%; gas flow rate: 0.3 L/min; sorption temperature: 80°C).

Figure 5. The relationship between α and t. Desorption temperature: A, 45°C; B, 52°C; C, 66°C; D, 70°C; E, 73°C.

Figure 6. Experimental data and model fit of F(α) versus t.

Figure 7. Arrhenius plots for the isothermal decomposition of [RNH₃⁺RNHCOO⁻].
Figure 3
Figure 4
Figure 5
\[ F(\alpha) = \left[ - \ln (1 - \alpha) \right]^{1/1.09} = k t \]

\[ R^2 = 0.9963 \]

Figure 6
$y = -9.7174x + 26.7898$

$R^2 = 0.9973$

Figure 7
List of Tables

Table 1. The order parameters $m$ and $n$ with the corresponding $k$ and $r$ values

Table 2. Comparison of kinetic models of CO$_2$ separation with and without presence of water$^{46}$
Table 1

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>F(α) = [− ln(1 − α)]^{1/m}</th>
<th>F(α) = 1 − (1 − α)^{1/n}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m</td>
<td>k (min^{-1})</td>
</tr>
<tr>
<td>45.0</td>
<td>1.32</td>
<td>0.02319</td>
</tr>
<tr>
<td>52.0</td>
<td>1.16</td>
<td>0.04800</td>
</tr>
<tr>
<td>66.0</td>
<td>1.29</td>
<td>0.1564</td>
</tr>
<tr>
<td>70.0</td>
<td>1.09</td>
<td>0.2014</td>
</tr>
<tr>
<td>73.0</td>
<td>1.22</td>
<td>0.2897</td>
</tr>
</tbody>
</table>
Table 2. Kinetic models of CO$_2$ desorption with and without presence of water$^{46}$

<table>
<thead>
<tr>
<th></th>
<th>With water</th>
<th>Without water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2RNH_2 + CO_2 + H_2O$</td>
<td>$\xrightarrow{k_{R1}^{-1},k_{R1}} <a href="R1">RNH_3^+HCO_3^-</a>$</td>
<td>$\xrightarrow{k_{R2}^{-1},k_{R2}} <a href="R2">RNH_3^+RNHCOO^-</a>$</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>$n_i$ (reaction order)</td>
<td>$E_a$ (kJ/mol)</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>114.25</td>
<td>$n_{RNH_3^+} = 1$</td>
<td>102.74</td>
</tr>
<tr>
<td></td>
<td>$n_{HCO_3^-} = 1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$n_{H_2O} = -1$</td>
<td></td>
</tr>
</tbody>
</table>