

Studies of the coordination effect of DEA-MEA blended amines (within 1 + 4 to 2 + 3 M) under heterogeneous catalysis by means of absorption and desorption parameters

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ARTICLE INFO

Keywords:

Energy reduction
Co-ordination effect
Solvent regeneration
Catalyst-aided CO₂ desorption
Catalyst-aided CO₂ absorption
Catalytic reaction mechanism

ABSTRACT

One of the energy-efficient approach was to adopt amine blends with the combination of heterogeneous catalysts as a new solution for an amine scrubbing process of a coal-fired pilot plant. The major challenge was the contradiction that the energy-efficient amine solvents in the desorber usually behave poorly in the absorber. This study re-investigated the “coordination effect” of “MEA + DEA amine blends” and “heterogeneous catalytic CO₂ absorption and CO₂ desorption” in theory first, and then conducted the heterogeneous catalytic CO₂ absorption with solid alkaline catalyst and CO₂ desorption with solid acid catalysts onto 1 + 4 ~ 2 + 3 mol/L MEA + DEA blends. After the comprehensive analyses of the “absorption parameter” and “desorption parameter” into 1.25 + 3.75 to 2 + 3 mol/L blended amines with CaCO₃ and blended γ-Al₂O₃ + H-ZSM-5(2:1), it’s found that the most suitable combination was 1.50 + 3.50 mol/L MEA + DEA with heterogeneous catalysis. This combination was more suitable and applicable to both absorber and desorber with catalytic packing than 2 + 3 mol/L MEA + DEA in an amine scrubbing process of capture pilot plant.

1. Introduction

To mitigate the environmental issue of global warming and climate changes, the CO₂ emission control and Carbon Capture Utilization and Storage (CCUS) are potentially viable approaches and promising options to alleviate increasing carbon dioxide (CO₂) emissions in human society [1,2]. One of the most developed technology for post-combustion CO₂ capture (PCCC) in a large-scale plant is the amine scrubbing, owing to the excellent CO₂ removal efficiency [1]. For the purpose of reducing the regeneration energy and capital expenses, the development of highly efficient absorbents with outstanding CO₂ capture performance is a quite urgent research [3]. To date various methods have been developed and introduced to address the problem, such as solvent improvement, process intensification [3], along with heterogeneous catalysis [2].

One of the energy-efficient solutions to reduce heat duty is solvent

improvement by synthesis and preparation of various blended amine solutions [3]. In preparation of blended amines [4], the tri-solvent is a promising research area with too many combinations [5–8], but the intrinsic mechanism is quite complicated [9]. For the past decade, intensive researches have focused on the blending of amine solvents (binary solvent). There are three major categories of binary amine blends: (1) MEA and MEA + R₃N (MDEA, DEAB, DEEA, etc.) with acidic catalysts had been investigated since 2012 [10–17]. This combination had been widely accepted in the field, for MEA possesses a high absorption rate, and the tertiary amine (R₃N) possesses high cyclic capacity [13]. (2) BEA-AMP (2 + 2 M) blended amine solvents since 2017 [18–21]. Idem et al. discovered the amine blends with very good absorption – desorption parameters among different amine blends [18]. (4) DEA-MEA blended amine with/without catalysts since 2017 [22–28].

After study, blended amine of DEA-MEA blended solutions have

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drawn strong research interests with multiple publications since 2017 [22–28]. Nwaoha et al. conducted the process simulation of 115 MW CO₂ capture coal-fired plant with 3 + 2 M MEA + DEA blended [23]. Their choice for this blending molar ratio is intended to maximize the reaction rate of MEA and lower the regeneration energy of DEA [23]. However, whether this molar ratio is exactly the optimized one has not been studied or verified by comprehensive experiments. Later on, Xiao et al. conducted the kinetics of MEA + DEA(dominant) blended solvents and reported “synergy effect” of the blended solution, for the absorption rate constant of 0.01 + 0.16 M MEA + DEA was increased by 131% compared with that of 0.16 M DEA solvent [24]. Liu et al. also reported the “coordination effect” of MEA + DEA solvents with ion speciation plots [25]. The “synergy effect” and “coordination effect” has drawn the research attention since 2018, and the CO₂ desorption has been studied with MEA + DEA blended amine without [26] and with solid catalysts [27]. From those publications, the specific molar ratio with minimized heat duty was discovered [26,27]. Finally, a recent publication on 2019 studied the “coordination effect” by catalytic CO₂ absorption with MEA + DEA at different blended concentrations (4 + 1, 3 + 2, 2 + 3, and 1 + 4 M) with CaCO₃ and MgCO₃ [28]. It's discovered that the blended DEA + MEA could hardly be satisfactory for both absorber and desorber without catalysis [28], but there might be an optimized combination of blended solvents + heterogeneous catalysts at a specific molar ratio, which is mostly likely to be within the range of 1 + 4 and 2 + 3 M [28]. However, the more detailed investigations are not developed within that range with/without heterogeneous catalysts [28]. Therefore, the optimized blended amine solution with heterogeneous catalysts filled with both absorption and desorption columns has drawn strong research interests, and it is very close to discover the most suitable combination of blended MEA + DEA amine solution + heterogeneous catalysts installed in the absorber and desorber, which can be adopted onto the amine scrubbing process of a CO₂ capture pilot plant [23]. In order to fill the catalyst into the absorber and desorber, two methods were applicable: either random packing [14,15] with catalysts blended with inert beads or structured packing with pelletized catalysts paved in the layer between two pieces [28]. Based on the mass transfer performance, the structured packing was preferred to random packing [1].

Therefore, this study narrowed the range down to 1 + 4 mol/L to 2 + 3 mol/L MEA-DEA with heterogeneous catalysis of Lewis base CaCO₃ + blended acid (γ -Al₂O₃ + H-ZSM-5 = 2:1). It focused on the re-investigation of the theory of “coordination effects” of DEA-MEA amine blends and mechanism of “heterogeneous catalytic CO₂ absorption” and “desorption” first. Then, 3 amine blends of MEA-DEA 1.25 + 3.75, 1.50 + 3.50 and 1.75 + 3.25 mol/L were studied with experiments with aid of both catalytic absorption and catalytic desorption. The boundary conditions of 1 + 4 and 2 + 3 mol/L were already studied [27,28] and compared as a benchmark.

This study (1) summarized the recent mechanism studies of coordination effects of DEA-MEA solvents, in combination with heterogeneous catalysis of absorption and desorption, (2) conducted the experimental investigations to find out the most suitable/applicable blended molar ratios under heterogeneous catalysis in the absorber and desorber. The heterogeneous catalytic CO₂ absorption were investigated via a batch process [29,30] and a semi-batch process [28,30]. The heterogeneous catalytic CO₂ desorption were investigated with a recirculation process [27]. The solid base catalyst was CaCO₃ for CO₂ absorption (MgCO₃ was not selected because of agglomeration [19]). The γ -Al₂O₃, H-ZSM-5 and blended (γ -Al₂O₃ + H-ZSM-5 = 2:1) were selected as the solid acid catalysts for desorption, which had been successfully adopted onto MEA, DEA, MEA-R₃N blends, and MEA-DEA blends [10,13–15,26]. Finally, the blended solvents with catalysis were evaluated by means of the absorption parameter and desorption parameters [18] to find out the most suitable and practical energy efficient approach of combination of amine blends with heterogeneous catalytic packing columns. Afterward, a mass transfer performance was required

to discover the height (H) of absorber, and a bench scale “Steady-state Process” was required to develop the operation parameter and verify whether this combination can be safely operated in a pilot plant, which is the final step before the industrial implication into a CO₂ absorption-desorption process.

2. Theory and mechanisms of the co-ordination effects of DEA-MEA amine blends

2.1. The mechanisms of co-ordination effect of DEA-MEA amine blends, along with heterogeneous catalysis

The coordination effect is the theoretical foundation of this work, which contained two sub-sections: (1) the mechanism of the coordination effects without catalysis (2) heterogeneous catalysis of CO₂ absorption and desorption. For the first part, the Zwitterion mechanism for primary/secondary amines has been developed for decades [31]. MEA and DEA were typical primary and secondary amines and the kinetic studies with mechanisms of which have been studied intensively [31]. Recently, two studies revealed part of the mechanism: the “coordination effect” and “synergy effect” of CO₂ absorption with MEA-DEA by VLE and kinetic models [24,25]. Other experimental results repeatedly indicated that blending MEA with DEA at a specific molar ratio of 10–20% (RNH₂/RR'NH) could not only promote the absorption but also reduce the heat duty of desorption [26].

For the second sub-section, our recent study [26] investigated the heterogeneous catalysis of CO₂ desorption of DEA + MEA solvents with Lewis acid and Brønsted acid catalysts. The mechanism and role of solid acid catalysts of CO₂ desorption have been developed and repeatedly published since 2016 [10,17]. On the absorption side, two most recent publications developed the mechanism and kinetics of heterogeneous catalytic CO₂ absorption [32,33]. Idem et al proposed the mechanism of heterogeneous catalysis of CO₂-MEA with K/MgO [32]. Shi et al. also proposed the Ealey-Rideal mechanism of CO₂-MEA absorption with CaCO₃, MgCO₃ and BaCO₃ [33]. There was no unanimous conclusion for the heterogeneous catalysis yet because of two reasons: (1) the different catalysts might contain their specific catalytic mechanism based on different material structures, surface areas and pore volume, and (2) there was limited publication and experimental results reported so far since it was a new topic of heterogeneous catalytic CO₂ absorption of MEA [30], DEA [29] and blended MEA + DEA [28] initiated since 2017. The mechanism need to be developed in detail with further molecular simulation and quantitative reaction kinetics with mechanistic models or comprehensive mathematical models. Without adequate and intensive studies, it is still premature to make conclusions onto the mechanism currently.

Among these mechanisms, all of them partly revealed the theory of the catalytic CO₂ absorption and desorption of DEA-MEA solvents. The details of “co-ordination effects”, the heterogeneous catalysis of CO₂ absorption were re-investigated to discover the potential of MEA + DEA amine blended with a combination of heterogeneous catalysts.

2.1.1. The coordination effects main reactions in DEA (dominant)-MEA blended amines

The coordination effect was recently discovered in CO₂ reaction with DEA + MEA solvents via Zwitterion mechanism [25]. It was proposed in Fig. 1a [34]. As discovered, carbamate formation can be divided into two steps: (1) Zwitterion formation, (2) deprotonation of an amine molecule to combine with zwitterion by H⁺ transfer to generate a “carbamate-ammonium salt” [25]. For the MEA-DEA blended solutions, DEA was a proton acceptor/Brønsted base that combined with Zwitterion to generate the “carbamate-ammonium salt” to decrease MEA consumption. Furthermore, DEA could exchange and release MEA from “carbamate-ammonium salt” [25]. As a result, more free MEA was released in the blended amine solvent and then activated the CO₂

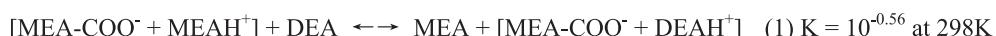
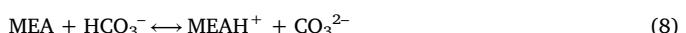
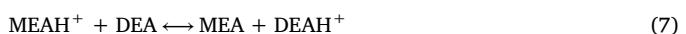
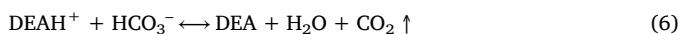
absorption reaction to improve the reaction rate and absorption capacity [25].

We re-investigated the coordination effect of Fig. 1.a by means of pKa of both amines. Since the pKa was 8.95 for DEA, 9.51 for MEA at 298 K, the proton transfer is more favored to MEA than DEA [26]. If the solvent contains much more free DEA molecules than MEA, the Zwitterion would have a better chance to release to DEA nearby. Furthermore, the equilibrium constant K° of proton exchange from MEAH^+ to DEAH^+ is $10^{8.95 - 9.51} = 10^{-0.56}$ (0.2754) at 298 K, the H^+ transfer conversion of DEA with "Carbamate – Ammonium Salt" reached an average conversion of 34.4% at 1:1. Afterward, if the concentration of [DEA] carbamate-ammonium salt $[\text{MEA-COO}^- + \text{MEA}\text{H}^+]$ is increased, the reaction would be pushed forward to release more free MEA molecules. From Eq. (1) below, the maximum conversion of carbamate-ammonium salt is only 50%, where $[\text{MEA}\text{H}^+]$ was totally converted to $[\text{DEAH}^+]$. The rest component of the salt is carbamate $[\text{MEA-COO}^-]$. Therefore, we set the molar ratio of DEA to MEA as " a " to 1, then estimated the extreme condition of $x = 0.50$. After calculation, the molar ratio a is preferred > 2.315 (DEA:MEA).

Specific reactions within MEA-DEA at regeneration conditions ($> 90^\circ\text{C}$) [26]:

These reactions of DEA (dominant)-MEA were studied as Eqs. (4), (6)–(10) under desorption conditions [26]. It could help to reduce the overall heat duty if 10–20% MEA was blended with DEA. From previous study, the heat duties of 0.5 + 4.5 and 1 + 4 M MEA + DEA amine blend are lower than that of 5.0 M DEA solvents without catalysts [26]. The reason was that these specific endothermic reactions (4), (6)–(10) occurred under regeneration conditions $> 90^\circ\text{C}$. From reaction (10), 10–20% of MEA blended with DEA solvents effectively facilitated the deprotonation of $[\text{DEAH}^+]$, and then boosted the carbamate breakdown of $[\text{DEA-COO}^-]$. The CO_2 production rate was significantly enhanced [26].

(a) The rich loading solvent with abundant $[\text{HCO}_3^-]$:



Initial	1	1	0		0
Equilibrium	1-x	1-x	x	x	$K^\circ = \frac{x \times x}{(1-x)(1-x)} = 0.2754$

Therefore, $x = 0.3442 = 34.4\%$

Initial	1	a	0	0
Equilibrium	1-x	a-x	x	x

Optimized condition, $x = 0.50$, where all the $[\text{MEA}\text{H}^+]$ was converted to $[\text{DEAH}^+]$:

Therefore, $a = 2.315$

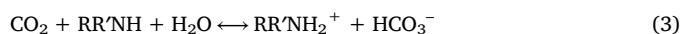
Thus, two clues were reported here: (1) the coordination effect was more favored in DEA (dominant)-MEA blended amine (2) the molar ratio of DEA + MEA blended amine should be higher than 2.315 to 1 (69.8% to 30.2%) to facilitate the H^+ transfer and liberate free MEA at 298 K in theory.

Furthermore, the main reactions within CO_2 -MEA-DEA solvents were introduced under both absorption and desorption conditions as below, while the detailed energy diagram, ion speciation plots and reaction free energy were published elsewhere [26].

Carbamate formation: $\text{CO}_2 + \text{MEA}$ and $\text{CO}_2 + \text{DEA}$ (where $\text{R}' = \text{H}$ for MEA, $\text{R}' = \text{for DEA}$)



Bicarbonate formation:



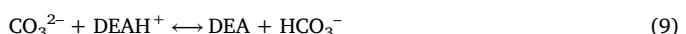
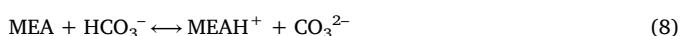
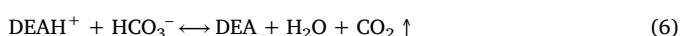
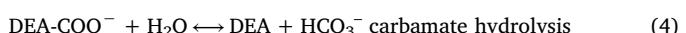
Carbamate hydrolysis:



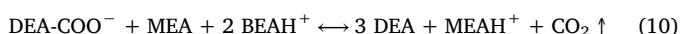
Minor reactions of CO_2 with trace amount of OH^- :



(b) The lean loading solvent with negligible $[\text{HCO}_3^-]$:



The overall reaction with small amount of free MEA: sum of (4) + (6) + (8) + (9):



2.1.2. The molecular simulations for Zwitterion mechanism with the coordination effects and with heterogeneous catalysis

The Zwitterion mechanisms were simulated for MEA + CO_2 with the existence of DEA and MEA + CO_2 under heterogeneous catalysis with Gaussian 09 to estimate the coordination effect quantitatively on a molecular level. Xie et al. [34] simulated the zwitterion mechanism of MEA + CO_2 with MEA and developed the PES energy diagram of the process for carbamate formation [34]. The activation energies E_a were calculated based on the relative energy difference of transition state toward the INT reactant [34].

From the Energy diagram, it can be divided into two sections corresponding to the two-step Zwitterion mechanism: the left part is Zwitterion generation (Step 1), and the right part is proton transfer (Step 2). The heterogeneous catalysis of CO₂-MEA affects the TS state and activation energy Ea (Step 1), while it hardly changes Step 2. The co-ordination effect of MEA + DEA affects proton transfer (Step 2), while it hardly changes Step 1. Both effects make contributions to the PES diagram of Zwitterion mechanism, therefore, they need to be simulated and discussed together. Hence, the simulation was conducted promptly of the Zwitterion mechanism of CO₂-MEA with heterogeneous catalyst: CaCO₃. The energy diagram was helpful to understand the heterogeneous catalysis via Eley-Rideal model with CaCO₃ [33]. Meanwhile, the “coordination effects” of CO₂-MEA-DEA solvents were simulated and plotted the energy diagram and compared it with the Energy diagram of CO₂ + MEA [34].

2.1.3. The mechanism and role of solid alkaline catalysts such as CaCO₃

Heterogeneous catalytic CO₂ absorption with amines was a new area of strong research interest. A recent study developed the mechanistic kinetic models of CO₂ + MEA with heterogeneous catalysts CaCO₃, MgCO₃ and BaCO₃ [33]. It was reported that the heterogeneous is likely to undergo an Eley-Rideal model (Fig. 1.b) [33]. There are 4 elementary steps, and the “rate determine step” is the first step of “Amine adsorption”.

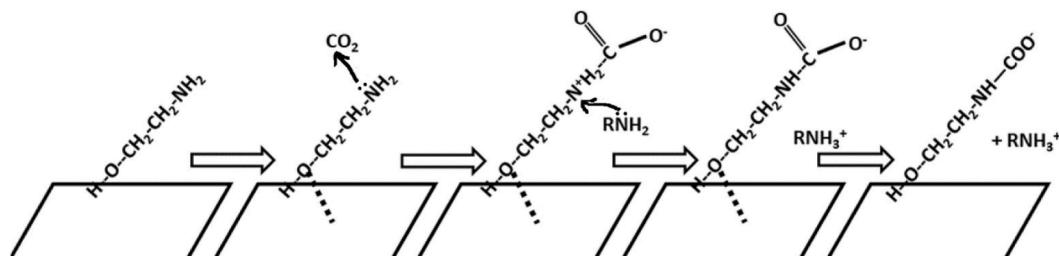
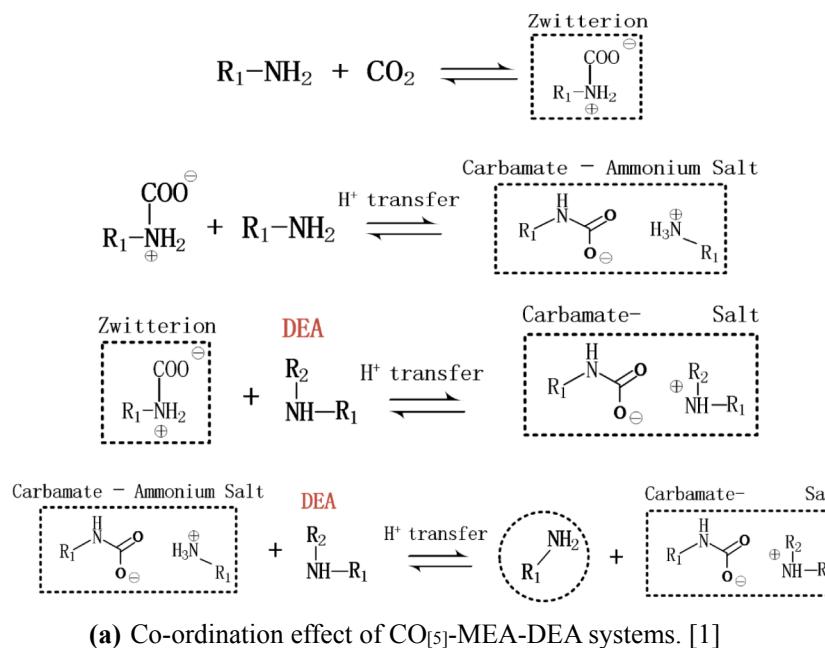
Another study also developed a different mechanism of CO₂-MEA-DEA with K/MgO [32]. The mechanism was demonstrated in Fig. 1c,

with the catalytic CO₂ absorption divided into 3 steps with the existence of K/MgO: (1) An MgO donates a lone pair of electrons to CO₂. (2) C = O bond breaking and an electron is transferred onto O atom. (3) The N atom on the amine donates the electrons to Carbon, which breaks and forms the N-C bond of the Zwitterion [32].

Both mechanisms are reasonable, for both heterogeneous catalyses undergoes Zwitterion mechanism. The first step is “adsorption” for both mechanisms, but the reactant of adsorption is different due to different catalysts [33]. The Eley-Rideal model [33] indicates that the amine (RNH₂) adsorbs onto the catalyst surface first, and then reacts with CO₂ via Zwitterion mechanism (Fig. 1b). The mechanism of K/MgO indicates that CO₂ adsorbs onto the solid surface first, and then reacted with amines (RNH₂) via Zwitterion mechanism [32]. Because of different catalysts and characteristics, the mechanisms are different. There has been no unanimous decision of the mechanism so far, and intensive researches are required.

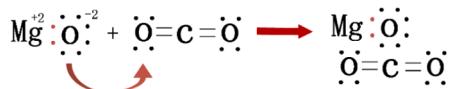
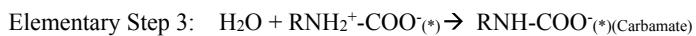
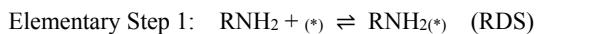
2.1.4. The role of solid acid catalysts such as Lewis acid and Brønsted acid

The role of Lewis acid and Brønsted acid as catalysts have been intensively studied for CO₂ desorption since 2014 [10,13,17,27]. Briefly, the γ-Al₂O₃ act as the Lewis acid to replace part of HCO₃⁻ at lean CO₂ loading where most bicarbonate (HCO₃⁻) exhausted [13]. At lean CO₂ loadings, the Al₂O₃ was converted to [AlO₂⁻] in basic conditions [35]. A recent study developed the role of [AlO₂⁻] for proton transfer from AmineH⁺ to free amines [35], with reactions below:



(b) Mechanism of catalytic carbamate formation via Eley-Rideal model.[2]

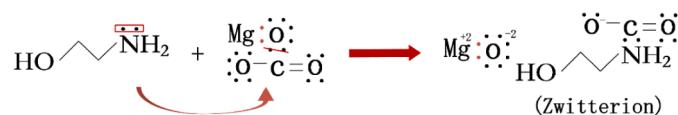
Fig. 1. The proposed mechanisms of (a) Co-ordination effect [25], (b) catalytic CO₂ absorption with CaCO₃ via Eley-Rideal model [48], (c) Catalytic CO₂ absorption via K/MgO [19], and (d) Catalytic CO₂ desorption with solid acid [49,50].



Step 1. An oxygen-containing catalyst donates a lone pair of electrons to CO_2 .

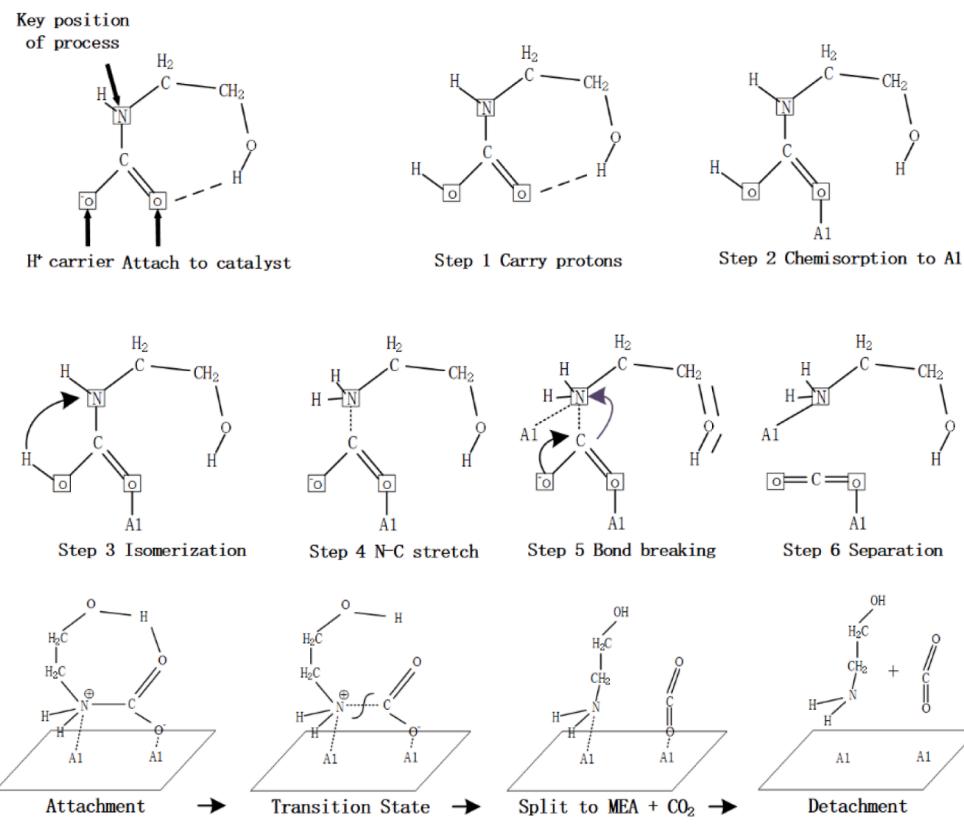


Step 2. C=O bond breaking and electron transfer onto O.



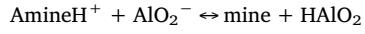
Step 3. N atom donates its electrons to carbon, which breaks and forms the N-C bond of the zwitterion.

(c) Mechanism of catalytic CO_2 absorption with MEA with K/MgO. [3]

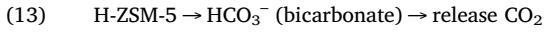


(d) Catalytic CO_2 desorption with solid acid. [4, 5]

Fig. 1. (continued)



The H-ZSM-5 act like Brønsted acid/proton donor. It performs two roles to facilitate CO_2 release [17,27].



Recently, several publications reported heterogeneous catalysis of CO_2 desorption with synthesized catalysts [8,11,12,36]. Besides, a large

number of experimental results verified the heterogeneous catalysis of CO₂ desorption in the reduction of heat duty. The mechanistic investigation of the carbamate breakdown had begun since 2011 [37]. It was published onto the patent disclosed in 2013 [37]. Later on, several recent publications re-investigated the mechanism via different solid acid catalysts during 2017–2018 [8,11,12]. These mechanisms were quite similar to each other, the overall desorption process with solid acid catalysts would probably undergo 5–6 steps [11,37]: (1) MEA-COO⁻ Carry protons at O atom and converted to carbamate acid. (2) MEA-COOH Chemisorption onto a solid surface (Lewis acid as Al/Ti etc.). (3) Isomerization to Zwitterion. (4) N-C bond stretching. (5) Bond breaking of carbamate breakdown. (6) Separation of CO₂.

2.2. The evaluation of the coordination effects by means of the heat of CO₂ absorption, the CO₂ absorption parameter and desorption parameters

2.2.1. The heat of CO₂ absorption (H_{abs}) of different amine blends

The heat of absorption (H_{abs} kJ/mol CO₂ absorbed) was an important parameter for evaluation of amine blends [4], and it was determined with the exothermic reaction heat [38]. The H_{abs} of single amine MEA and DEA was published as 88.91 kJ/mol [38] and 70.44 kJ/mol [38]. Therefore, H_{abs} of blended solvents are could be approximately estimated as the weighted average of single amines with various ratios, which are 77.83 kJ/mol for 2 + 3 M, 76.90 kJ/mol for 1.75 + 3.25 M, 75.98 kJ/mol for 1.5 + 3.5 M, 75.06 kJ/mol for 1.25 + 3.75 M and 74.13 kJ/mol for 1 + 4 M. The accurate Habs values of blended amine solutions require experimental performance CO₂ solubility tests [5].

2.2.2. The absorption parameter and desorption parameter for amine blends.

Narku-Tetteh et al. [18] established the absorption parameters and desorption parameter on 2017 as useful criteria to compare and select good amine blends of different categories and concentrations. Therefore, the criteria were adopted to find out the energy-efficient approach: the combination of amine blends + heterogeneous catalysis. The slight difference of this study narrowed the amines solutions into MEA + DEA amine blends with small ranges of concentrations (1.25 + 3.75 ~ 1.75 + 3.25 mol/L) while expanding the performance with heterogeneous catalysis on both sides.

Based on Narku-Tetteh et al. [18] the absorption parameter was presented in Eq. (15), with initial absorption rates in Eq. (16) to compare different amine blends. From Eq. (15), both MEA and DEA had comparable equilibrium CO₂ loading of 0.50 mol/mol. The initial absorption rates turned out to be the research focus.

The initial absorption rates were developed in Eq. (16) based on the slope of absorption profiles (α vs. t). Eq. (16) describes the CO₂ absorption for 1L of amine solvents for normalization.

Absorption parameter

$$= \text{Initial absorption rate} \times \text{equilibrium loading} \quad [18] \quad (15)$$

$$I_{abs_rate} = \frac{C}{V} \frac{d\alpha}{dt} (\text{mol CO}_2/\text{Lamine. soln. min}) \quad [18] \quad (16)$$

Similarly, the desorption parameter was proposed [18] for the evaluation of desorption efficiency of various amine blends. The desorption parameter was in Eq. (17), cyclic capacity was listed in Eq. (18), and the initial desorption rate was listed in Eq. (19), which was generated from the plot of CO₂ desorption profile of α vs t [18]. The cyclic capacity for 5.0 MEA + DEA solvents was 1.5 mol CO₂/L (amine solution), based on the rich CO₂ loading of 0.50 mol/mol and lean loading of 0.20 mol/mol under operation conditions.

$$\text{Desorption parameter} = \frac{\text{Initial desorption rate} \times \text{cyclic capacity}}{\text{heat duty}} \quad (17)$$

$$\text{Cyclic capacity} = (\alpha_{rich} - \alpha_{lean})C \times V \quad (\text{mol CO}_2/\text{L}) \quad (18)$$

$$I_{des_rate} = \frac{nCO_2}{dt} = \frac{C}{dt} (\text{mol CO}_2/\text{L min}) \quad (19)$$

As we repeatedly studied, the heat duty (H) of the CO₂ desorption tests was calculated with Eqs. (20) and (21) [13,27]. The heat input was tested with an electrometer and the CO₂ production (nCO₂) was calculated with CO₂ loading. The amine blends with lower heat duty (H) are considered as energy-efficient candidates.

$$H = \frac{Q_{input} \text{ kJ/h}}{nCO_2 \text{ mol/h}} \quad (20)$$

$$nCO_2 = C \times V \times (\alpha_{rich} - \alpha_{lean}) \quad (21)$$

3. Materials, experimental apparatus and procedures

3.1. Materials

The CaCO₃ were purchased from HuiShan Chemical Ltd. The solid acid catalysts were purchased from Yinghe Catalyst Ltd. The CO₂ (99%) and CO₂/N₂ (15%/85%) gas were purchased from Tansool Chemical Ltd. MEA, DEA and HCl were commercially available from Guoyao Chemical Ltd.

3.2. The molecular simulation of blended DEA-MEA solvents with the coordination effect

The Zwitterion mechanism of MEA + CO₂ with DEA or with CaCO₃ was simulated with Gaussian 09, the same as Xie et al. [34]. The same as other studies, the solvent effect is considered along with the Conductive Polarization Continuous Medium Model (CPCM) [34]. Since the atomic radius was one of the most important conditions for the accuracy of the solvation model, we used the Pauling atom. The radius calculated the reaction capacity and other properties. The relationship between the transition state and the specified local minimum was determined by the intrinsic reaction coordinate (IRC) calculation at the B3lyp/6-311 + + g(d,p) level. At this level of theory B3lyp/6-311 + + g(d,p), the conformational optimization and vibration frequency calculations of reactants, products, intermediates and transition states were carried out with a class-conductor-polarized continuum model(CPCM) [34].

3.3. The catalytic CO₂ – Amine absorption process in a batch apparatus:

Same as previous work, the batch process was built as a stirred cell reactor (Fig. S2 with photos of the process) with the same parameters of (i.d. = 11 cm, and interfacial area = 95.0 cm²) [28,30]. The reactor contained 300 ml MEA-DEA blended solvents at 20 ± 0.2 °C with a cooling water bath to keep a constant temperature. The magnetic stir was placed inside the reactor and kept at 250 rpm (round per minute) to enhance the mass transfer. The solid chemicals CaCO₃ were wrapped into several balls with fabricated nets with sizes close to 2 mm, (diameter = 2.4–2.5 cm, surface area = 9.05–9.8 cm²). The balls wrapping solid chemicals were suspended onto the gas-liquid interface, and the amine solution passed through the nets easily to reach the solid surface. The absorption was conducted with bubbling, reflecting the realistic absorption. The side reaction of CO₂ + H₂O + CaCO₃ → Ca(HCO₃)₂ was extremely slow and negligible under strong basic conditions [30].

3.3.1. Experimental procedures and absorption profiles CO₂ loading vs time with initial absorption rates

300 ml of 5.0 mol/L blended MEA-DEA solvents were prepared at 1.25 + 3.75, 1.5 + 3.5, 1.75 + 3.25 mol/L. The experimental studies were completed for 1 + 4 and 2 + 3 mol/L with CaCO₃ [28] at 293 K as boundary conditions. Even though CO₂ absorption commonly occurred

at 40–60 °C (313–333 K) in industry, we also selected the 20 °C (293 K) as absorption temperature to compare the absorption parameters at the same level. Then CO₂ (99%) was introduced with a fixed flow rate at 1.50 L/min.

After CO₂ absorption, a timer was used to record the process; and 1–1.5 ml solutions was pipetted every 2–3 min during the process and sampled into small bottles [30]. This pipette process was independent from the CO₂ absorption process, where the introduction of CO₂ gas was stopped temporarily. Based on Fig. S2, There is a sideway in the gas path. During the CO₂ absorption tests at a fixed gas flowrate, the valve was closed. The gas underwent into the reactor. During pipette, the valve was open, and the CO₂ gas went through the exit instead. There is no CO₂ gas in the reactor temporarily, and then we pipette 1–2 ml amine solutions from the top of the reactor with tubes and stored them. Afterward, the valve was closed again, and CO₂ was introduced back to the reactor again to continue the absorption process.

There were around 20 samples pipetted for each run of CO₂ absorption curves, and the solvent loss was about 30–40 ml based on 300 ml solutions. The solvent loss was around 10–14%. The decrease of the liquid volume had little effect on the absorption rates, for the reaction rate is determined by the “Concentration” of amine solution, $r = k[\text{CO}_2][\text{Amine}]^n$. The reaction order is 1 for CO₂ and MEA, but within 1–2 for DEA [31]. As discussed, 10–15% solvent losses did not affect the reaction rate remarkably, with decreased volume instead of amine concentration change [Amine] [28].

Similar to another study [2], the absorption profiles of CO₂ loadings (mol/mol) vs time (minute) were plotted from fresh to equilibrium (0.5 mol/mol) of blended MEA-DEA solvents. These CO₂ loadings were repeatedly tested by different persons at least twice to ensure the accuracy of AAD = 5% [39].

Besides the absorption profiles, the initial absorption rates were calculated with Section 2.2.2 from Eq. (16) [12]. This rate was calculated at CO₂ loading = 0 mol/mol, with t = 0 min, based on the slopes of the CO₂ absorption curves at CO₂ loading ranges of 0–0.2 mol/mol. The change of volume with sampling was less than 15 ml (5%) at the range of 0.0–0.2 mol/mol. The “initial absorption rate” was still highly accurate at t = 0 min.

$$I_{\text{abs_rate}} = \frac{C}{V} \frac{d\alpha}{dt} \left(\text{mol} \frac{\text{CO}_2}{\text{L}} \cdot \text{min} \right) [18] \quad (16)$$

3.4. The catalytic CO₂ – Amine absorption process in a semi-batch apparatus

The semi-batch process was built in Fig. S3, similar to other work [28,30]. The length of glass absorption column was 66 cm. The outside diameter (o.d.) was 33 mm and internal diameter (i.d.) was 28 mm for the column. The absorption column was filled with 24 pieces of pall rings (25 mm in length with i.d. = 25 mm), made of stainless steel. There were 24 pieces of pall rings installed into the absorber and covered 600 mm of 660 mm of the column, which was 91% (Photos in Fig. S3). A gas cylinder and a centrifuge pump with liquid storage tank were prepared for the process.

For the CO₂ absorption tests, the mixed gas was firstly introduced into the column, with most part of the column sealed. There was only one gas exit, and the CO₂ % was tested with a CO₂ analyzer (0–20%) located at the gas exit. The mixed gas was saturated inside the whole column first, and the CO₂% reached a steady value of 13.5–13.8%. The CO₂ % decreased from 13.5% to 1–2% within the absorber column, from the beginning to full absorption. The CO₂ absorption reactions took place in the area of pall rings all along the columns. Right after the first drop of liquid amines flowed down the column, the CO₂% of the exit gas was detected and recorded. Usually, it took 12–15 s delay for a

fall of CO₂%, for the reactions took place in the column while the CO₂% was detected from the exit.

For semi-batch tests, we used 0, 1, 2, 3, 4 g CaCO₃ to test several blended amine solvents: 1.25 + 3.75, 1.5 + 3.5, and 1.75 + 3.25 mol/L. Each solvent had two initial CO₂ loadings: 0.0 mol/mol as fresh and 0.2 mol/mol as operating conditions [40]. The gas flow rate was 1.35 ± 0.02 L/min, and the liquid flow rate was 28 rpm (66.67 ml/min) at a consistent level. The absorption curves (CO₂% vs time(s)) were plotted and the average absorption efficiency (%) was calculated in Eq. (22) with non-catalytic and catalytic absorption below [28,41]. The average absorption efficiency should be > 90%.

$$\text{Absorption Efficiency}(\%) = \frac{G_{\text{in}}X_{\text{CO}_2,\text{in}} - G_{\text{out}}X_{\text{CO}_2,\text{out}}}{G_{\text{in}}X_{\text{CO}_2,\text{in}}} \times 100\% [28, 41] \quad (22)$$

3.5. The catalytic CO₂ – Amine desorption process in the recirculation process

This process was the same as that of other studies [17,26]. The operation temperature was fixed at 90 °C, and the volume of amine solvents was 500 ml. Each sample was pipetted at 2 ml every 2–15 min for CO₂ loading tests. The CO₂ loading tests were also conducted with a Chittick apparatus at 25 °C, after the cooling of solvent sample [39]. The CO₂ loading(α) vs time(t) was plotted to generate CO₂ desorption profiles, similar to other studies [18]. CO₂ loadings (mol/mol) vs time (minute) were plotted from equilibrium (0.5 mol/mol) to 0.20/0.15 mol/mol of blended MEA-DEA solvents. The operation CO₂ loading of desorption is 0.50–0.20 mol/mol as a pilot plant [42]. The initial CO₂ loading was regarded as 0.50 mol/mol, and extra loading was the CO₂ weakly bonded with water. These CO₂ loadings were repeatedly conducted by different persons at least twice to ensure the accuracy of AAD = 5%.

Besides the desorption profiles, the initial desorption rates were calculated with Eq. (19) [18]. This rate was calculated at the start point where CO₂ loading = 0.50 mol/mol, with t = 0 min. The rate was based on the slopes of the CO₂ absorption curves at CO₂ loading ranges of 0.50–0.30 mol/mol as rich region for MEA + DEA amine blends [26]. The change of volume with sampling was less than 15 ml (5%) at the range of 0.5–0.30 mol/mol. The “initial desorption rate” was accurate at t = 0 min.

Finally, the heat duty was calculated for the first 60 min based on Section 2.2.2 with Eqs. (20) and (21). The overall desorption processes took 180–240 min for most cases, with the main desorption process completed during the first hour. For some energy sufficient solvents, the process completed within 120 min. Therefore, the heat duties for the 60 min were more indicative. The heat duties of the amines along with the desorption parameter were very important to evaluate the “energy-efficient” solvents + heterogeneous catalysis. The amine blends that with reduced heat duties and better desorption parameters were preferred as “good-performance desorption solvents” under the same operating conditions [41].

4. Results and discussion

This part consisted of 6 sub-sections: (1) The molecular simulation of the “co-ordinate effect” and “Heterogeneous catalysis”, (2) CO₂ absorption profiles of 1.25 + 3.75 to 1.75 + 3.25 mol/L MEA + DEA blended amines with CaCO₃ in a batch process, (3) Initial absorption rates (4) CO₂ absorption of amine blends in a semi-batch process, and time to reach 90% absorption efficiency, (5) the CO₂ desorption tests of 1.25 + 3.75 to 1.75 + 3.25 mol/L MEA + DEA with solid acid catalysts γ-Al₂O₃ and H-ZSM-5. (6) The absorption parameter and desorption parameters were evaluated of the combination of blended amine

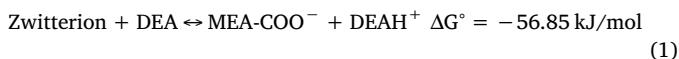
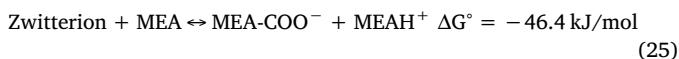
($1.25 + 3.75$ to $2 + 3$ mol/L) with heterogeneous catalysts on both absorber and desorber.

4.1. The molecular simulation of the “Coordination Effect” of CO_2 -DEA-MEA in aqueous solution and the heterogeneous catalytic absorption of CO_2 -MEA with CaCO_3

The reactants, intermediates, transition state and products were simulated and their relative energies were calculated with high accuracy. Compared with the potential energy diagram (PES) CO_2 -MEA of Fig. 2.a [34], Fig. 2.b exhibited PES of CO_2 -DEA-MEA in aqueous solutions with CPCM model, Pauling radius and B3LP/6-311G(d,p) level. The intermediates (complex) and transition state configurations of $\text{CO}_2 + \text{MEA}$ with CaCO_3 (Fig. 2.c) were simulated as well.

After comparison of $\text{CO}_2 + \text{MEA}$ (Fig. 2.a) and $\text{CO}_2 + \text{MEA} + \text{DEA}$ (Fig. 2.b), the first step of Zwitterion formation was the same as $\text{CO}_2 + \text{MEA}$ in both cases, and the left half of the energy diagram of Fig. 2.a and Fig. 2.b were the same. The energy of Complex1 and the transition state TS1 were the same, the activation energy was also 12.0 kcal/mol (50.16 kJ/mol) [34]. The relative energy of Zwitterion was 7.4 kcal/mol [34]. However, the second step of “proton transfer” was slightly different. The Zwitterion + MEA to reach carbamate-ammonium salt of $[\text{MEA}-\text{COO}^- + \text{MEA}\text{H}^+]$ was -11.1 kcal/mol (-46.4 kJ/mol). The Zwitterion + DEA to reach salt of $[\text{MEA}-\text{COO}^- + \text{DEAH}^+]$ was -13.6 kcal/mol (-56.85 kJ/mol), about 10 kJ/mol lower. The reaction enthalpy of proton transfer from Zwitterion is preferred to DEA instead of MEA. This energy diagram of Fig. 2.b and a could partly reflect the “coordination effect” of MEA-DEA blended solvents.

However, based on the pKa value of MEA (9.51) and DEA (8.95), it's indicated that MEA was a stronger base than DEA. From Eqs. (23) and (24), the energy of proton transfer was -68.37 kJ/mol for MEA and -60.80 kJ/mol for DEA, thus the “free” proton transfer to MEA was preferred [27]. These reactions (23)–(25), (1) below were illustrated for the proton transfer under different cases. If the protons transferred from Zwitterion to MEA and DEA, the relative energies from molecular simulation were slightly different, which is 10 kJ/mol preferred to DEA (with simulation), contrary to free proton transfer 8 kJ/mol preferred to MEA. The intrinsic reason awaited further investigation, and such an abnormal result could partly explain the “coordination effect” of $\text{CO}_2 + \text{MEA} + \text{DEA}$ complex.



For heterogeneous catalytic CO_2 -MEA with CaCO_3 , the plot was demonstrated in Fig. 2.c. The right part of Fig. 2.c is the same as Fig. 2.a, and the only difference is the left part (Zwitterion formation). The relative energy of Complex1 and transition state TS1 was reduced to 1.4 and 10.9 kcal/mol from 2.9 and 12.0 kcal/mol. Then activation energy (E_a) was reduced from 12 to 10.9 kcal/mol (45.6 kJ/mol) about 9%. The decrease of the energy barrier accelerate CO_2 -MEA absorption. The catalysis of $\text{CO}_2 + \text{MEA}$ with CaCO_3 was experimentally verified [28,30], which fitted the energy diagram of Fig. 2.c. Comparing Fig. 2.a to 2c. The energy difference of initial reactant (INT) to product carbamate was -11.1 kcal/mol without catalysis [34] and -11.0 kcal/mol with CaCO_3 . It verified the role of CaCO_3 as a catalyst: it reduces the activation energy, but could not change the free energy of the reactant and products. Finally, the simulation results partly verify the “heterogeneous catalysis”.

4.2. Catalytic CO_2 absorption in batch reactor with CaCO_3

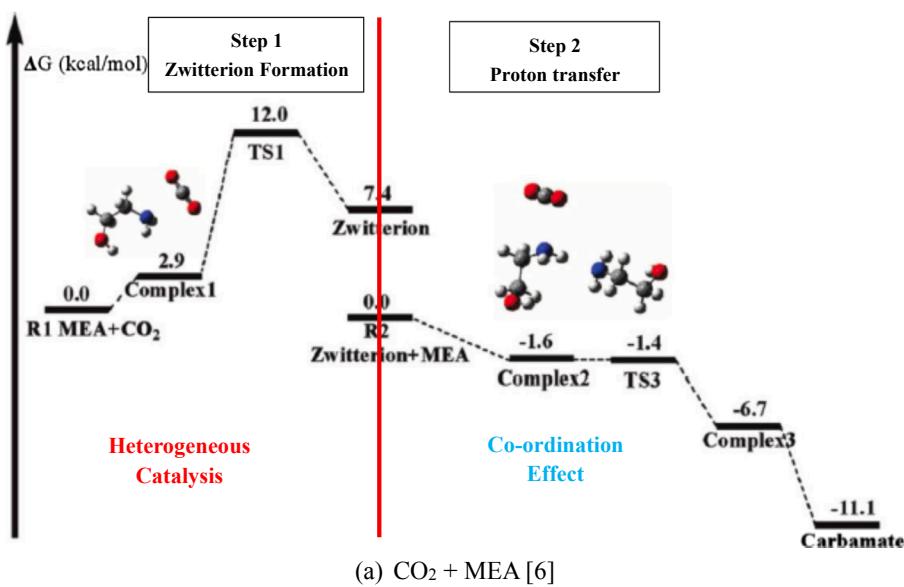
Fig. 3.a-c represented 3 non-catalytic CO_2 absorption curves from $1.25 + 3.75$ to $1.75 + 3.25$ mol/L MEA + DEA. The absorption curves of $1.0 + 4.0$ and $2.0 + 3.0$ mol/L were published elsewhere [28]. Each curve represented 0.5 L of 5.0 M blended amine solutions, with 2.5 mol of free amine molecules contained. At the same concentration of $1.25 + 3.75$ mol/L, the amount of MEA and DEA were exact the same except different amount of CaCO_3 added. The equilibrium loading of MEA and DEA were both 0.50 mol/mol, because the stoichiometric ratio of $\text{RR}'\text{NH} + \text{CO}_2$ is 2:1. At the equilibrium loading of 0.50 mol/mol, the conversion of amine was almost 100% with negligible free amine molecules existed. Then, the amine solution + catalyst with better CO_2 absorption capability should take less time to reach equilibrium loading of 0.50 mol/mol. Less time to reach 100% conversion indicated higher absorption rates of solution + catalysis at different stages from lean to rich loading.

Under non-catalytic conditions, it took about 70 min for $1.25 + 3.75$ mol/L MEA + DEA to reach equilibrium, which was close to $1 + 4$ mol/L of 70 min [28]. It took about 60 min for $1.75 + 3.25$ mol/L MEA + DEA to reach equilibrium, which was close to $2 + 3$ mol/L of 60 min [28]. With increased ratios of MEA, the overall time to reach equilibrium was shortened. The order was $2 + 3$ mol/L MEA + DEA > $1.75 + 3.75 > 1.50 + 3.50 > 1.25 + 3.75 > 1 + 4$ mol/L MEA + DEA without catalysis.

Fig. 3.a-c also represented the catalytic CO_2 absorption of $1.25 + 3.75$ to $1.75 + 3.25$ mol/L with (a) 0–10 g CaCO_3 . Fig. 3.a indicated $1.25 + 3.75$ mol/L MEA + DEA took 70–75 min without catalysis, while the optimized catalytic absorption for 5–7.5 g CaCO_3 took 60 min. Fig. 3.b represented $1.5 + 3.5$ mol/L MEA + DEA took 65 min without catalysis, while the optimized catalytic absorption took 35–37 min for 10 g CaCO_3 . Fig. 3.c represented that $1.75 + 3.25$ mol/L MEA + DEA took about 60 min without catalysis, while the optimized catalytic CO_2 absorption took 50 min for 10 g CaCO_3 . Therefore, the $1.5 + 3.5$ mol/L with optimized catalysis of CaCO_3 , turned out to be the best among $1.25 + 3.75$, $1.5 + 3.5$ and $1.75 + 3.25$ mol/L. Furthermore, with optimized amount of CaCO_3 , the time for $2 + 3$ M was published to be around 30 min, and it was 25–30 min for $1 + 4$ M [28]. Combining the results with previous publications [28], the order of catalytic CO_2 absorption was $2 + 3$ mol/L $\text{CaCO}_3 \approx 1 + 4$ mol/L CaCO_3 [34] > $1.50 + 3.50$ mol/L CaCO_3 > $1.75 + 1.25$ mol/L CaCO_3 > $1.25 + 3.75$ mol/L CaCO_3 . The $1.50 + 3.50$ mol/L CaCO_3 ranked the 3rd among 5 amine blends between $1 + 4 \sim 2 + 3$ mol/L.

The CO_2 absorption curves for $1 + 4$ and $2 + 3$ mol/L MEA + DEA were quite different from MEA (dominant)-DEA- H_2O solvents [28]. The non-catalytic absorption process was relatively slow, but the catalytic process was much faster, especially under optimized catalysis [28]. This study of $1.25 + 3.75$ to $1.75 + 3.75$ mol/L MEA + DEA with CaCO_3 repeatedly the phenomena and verified the “coordination effect” since they were within the range of $1 + 4$ to $2 + 3$ mol/L. The “coordination effect” of MEA-DEA- CO_2 - H_2O system was reported [25]. With the mechanism already demonstrated in Eq. (1) and Fig. 1a, indicating that excessive DEA helped to release free MEA out of “Carbamate-Ammonium Salt” via “ H^+ transfer”. Furthermore, 3 mol/L DEA had optimized catalytic absorption effects with CaCO_3 among 1, 3, and 5 mol/L MEA + DEA, and the catalysis was 28% at 3 mol/L compared with 11–20% at 1 and 5 M [29].

Another interesting thing was that the $1.5 + 3.5$ mol/L + CaCO_3 was the best among $1.25 + 3.75$ to $1.75 + 3.25$ mol/L, with all of them contained coordination effects. It verified the concept in Section 2.1.1: the ratio of DEA + MEA blended molar ratio should be higher than 2.315 to 1 (69.8% to 30.2%) to facilitate the H^+ transfer and liberate free MEA at 298 K in theory. The $1.50 + 3.50$ mol/L (30% to 70% MEA/DEA) was very close to the theoretical ratio, which made it better than $1.75 + 3.25$ mol/L (35% to 65%). On the other hand, even the $1.25 + 3.75$ mol/L (25% to 75% MEA to DEA) met the criteria, the concentration of free MEA is relatively smaller. Less free MEA in the



The structures of the Intermediates and Transition states were published there [6].

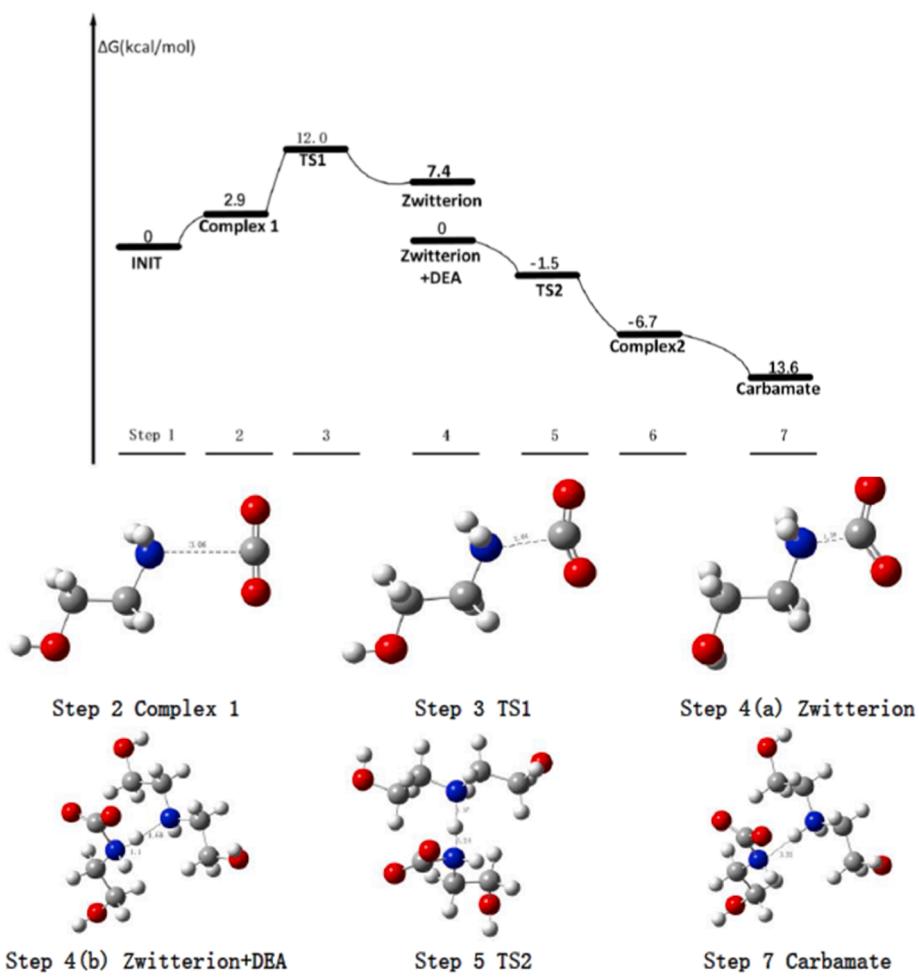


Fig. 2. The simulation results of the Zwitterion Mechanisms of (a) $\text{CO}_2 + \text{MEA}$ [51], (b) $\text{CO}_2 + \text{MEA}$ with DEA for coordination effect, (c) $\text{CO}_2 + \text{MEA}$ with CaCO_3 for heterogeneous catalysis.

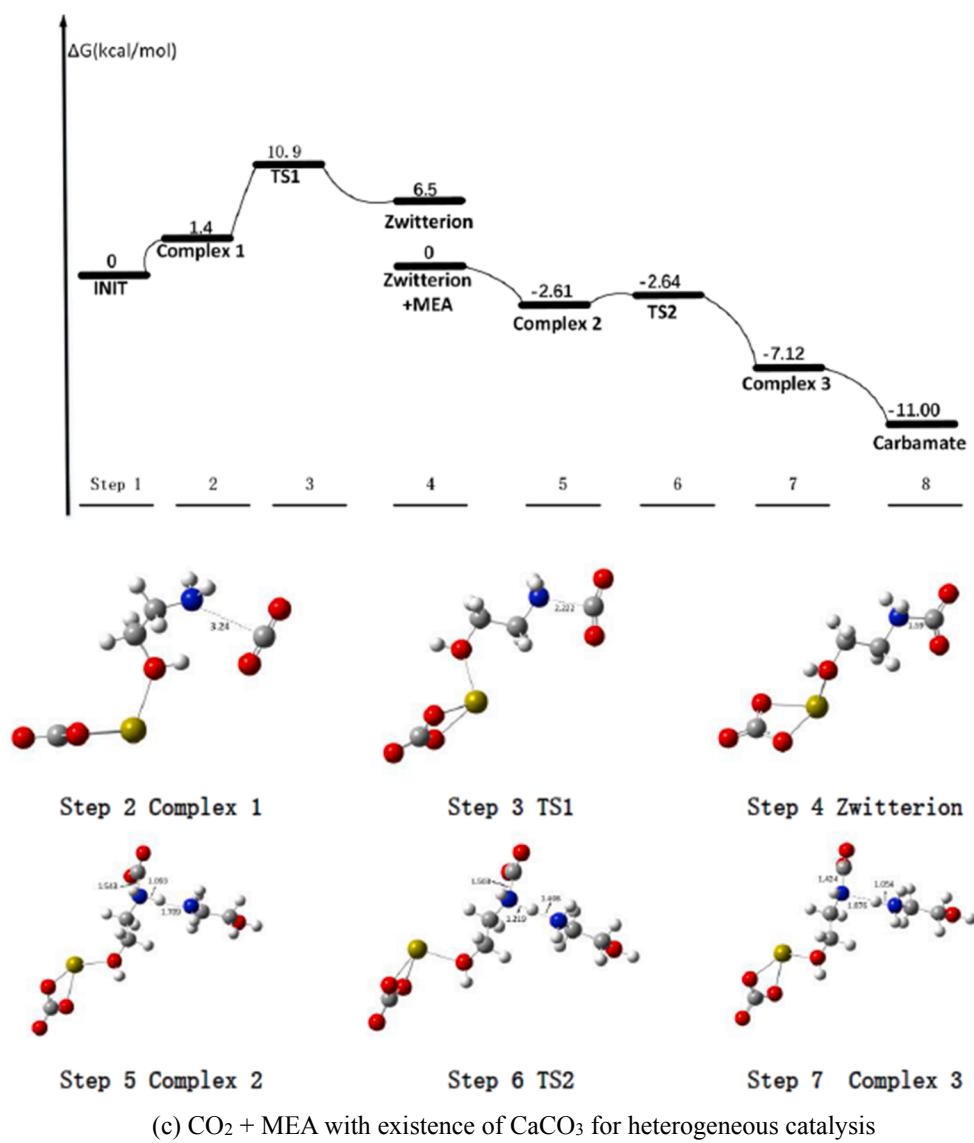


Fig. 2. (continued)

blended solvents result in slower the absorption rates.

4.3. Initial absorption rates and absorption parameter of MEA-DEA blend under catalytic and non-catalytic conditions

The initial absorption rates were plotted in Fig. 4 based on the slopes of CO₂ absorption profiles of Fig. 3a-c in 0–0.20 mol/mol. The rates of 1 + 4 and 2 + 3 mol/L were from other publication [28] placed in the edge of Fig. 4. From Fig. 4, the initial rates under non-catalytic conditions were comparable to each other for these 5 amine blends, which is 0.31–0.36 mol/CO₂.L.min. It was significantly increased under optimized catalytic conditions. From Fig. 4, the order of initial absorption rate with catalyst CaCO₃ was: 1 + 4 M > 2 + 3 M > 1.75 + 3.25 M ≈ 1.50 + 3.50 M > 1.25 + 3.75 M.

All these five amine blends within 2 + 3 and 1 + 4 M solvents exhibited the “synergy effect” [19] of blended amine + solid chemicals. Since the initial absorption rate was at a loading of 0.0 mol/mol, it was the “first stage” of MEA-DEA-CO₂-H₂O system, where MEA-COO⁻ was the only anions of CO₂ at loading range of 0–0.18 mol/mol [25] from ion speciation plot via NMR study [43,44]. The CO₂ mostly reacted with MEA in blended solvents at a stoichiometric ratio of 1:1. Therefore, the initial absorption rates of 5 amine blends didn’t include CO₂ + DEA reactions, which makes the initial absorption rates close to each other.

From Fig. 4, with the catalyst, the 1 + 4 mol/L was a special case with high initial absorption rates but lower absorption efficiency at loading of 0.20 mol/mol [28]. The amine blends 1 + 4 mol/L can be considered as 1 + 1 mol/L with 3 mol/L DEA, which contains the coordination effect, and optimized catalysis of 3 mol/L DEA [29]. The absorption rates of the rest 4 amine blends followed the order of 2 + 3 M > 1.75 + 3.25 M ≈ 1.50 + 3.50 M > 1.25 + 3.75 M, indicating the more-MEA the better. This trend was reasonable. Since the rate determine step of catalytic CO₂ absorption was “Amine adsorption” onto solid surface of CaCO₃ via Eley-Rideal model [33], there was only a portion of free MEA (along with DEA) adsorbed onto solid surface according, and it desorbed the solid surface with the product format of MEA-COO⁻ with heat release [33]. Then, the other free MEA/DEA molecules attached the active site of solid surface again. In that case, the solvent contained more free MEA was preferred because the absorption of CO₂ + MEA is much faster than CO₂ + DEA, follow the order of 1.25 + 3.75 (0.25:0.75) < 1.5 + 3.5 (0.3:0.7) < 1.75 + 3.25 (0.35:0.65).

Finally, the absorption parameter was calculated in Eq. (16), and categorized into Table 1a.b. The catalytic absorption with 3 amines with 5–10 g of CaCO₃ was listed in Table 1a. Moreover, the absorption parameters for 5 blended amines were listed in Table 1b. The 2 + 3 mol/L MEA + DEA was as benchmarks (100%), for it was

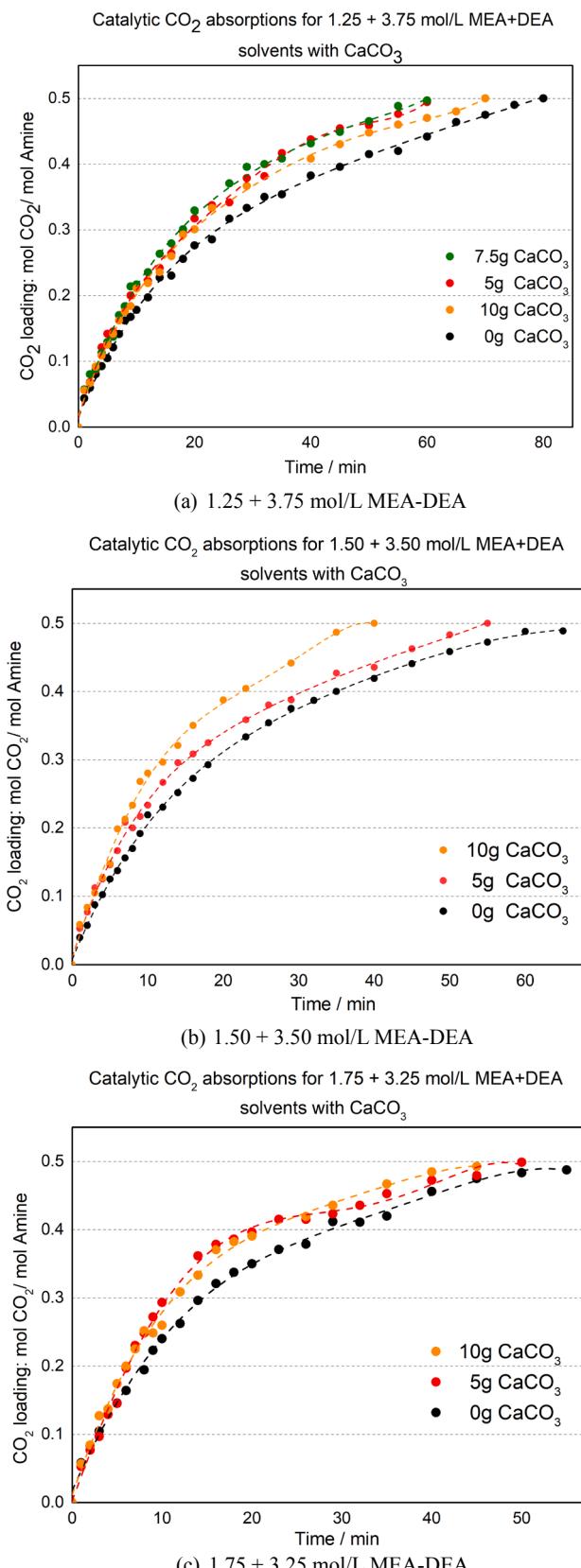


Fig. 3. Catalytic CO_2 absorption with CaCO_3 for 3 blended amine solvents in a batch process.

reported as "good performance" blended amines among 4 + 1, 3 + 2, 2 + 3 and 1 + 4 mol/L [28]. The 1.75 + 3.25 mol/L covered 89% under non-catalytic and 91% under optimized catalysis; while 1.50 + 3.50 mol/L covered 94% under non-catalytic and 85% under optimized catalysis. All these three amines (1.5 + 3.5, 1.75 + 3.25 and 2 + 3 mol/L) were good performance candidates for CO_2 absorption.

4.4. Catalytic CO_2 absorption in a semi-batch process with CaCO_3

For practice, the catalytic CO_2 absorption were also conducted in a semi-batch process to simulate the performance in an absorption column. **Table 1b** indicated that the 1 + 4 mol/L MEA + DEA had the superior performance among these five amine blends, even better than 2 + 3 mol/L [28]. However, the semi-batch tests already reported that the absorption efficiency of 1 + 4 M was 93% (0.0 mol/mol) at very large liquid flow rate of 83.3 ml/min, but it was only 83% at CO_2 loading of 0.20 mol/mol under operation conditions [28]. This absorption efficiency was < 90% CO_2 removal, which made 1 + 4 mol/L amine solution unqualified for industrial application. The reason for this contradiction was that the "initial absorption rate" was tested at 0.0 mol/mol, but the operation conditions in a CO_2 capture plant was usually 0.20–0.50 mol/mol for MEA and DEA [42]. Hence, such contradiction made the semi-batch tests necessary to verify the adoptability of the solvents in industry.

Therefore, the catalytic CO_2 absorption curves were plotted in **Fig. 5.a-f**, for 1.25 + 3.75, 1.50 + 3.50 and 1.75 + 3.25 mol/L amine solvents with CaCO_3 under a consistent level. The liquid flowrate was 66.67 ml/min, which was the same as that of 2 + 3 and 3 + 2 mol/L [28]. Each amine blend was tested with CaCO_3 at initial loading of 0.0 mol/mol and 0.2 mol/mol under operation conditions. From **Fig. 5**, the CaCO_3 helped to reduce the time to reach equilibrium, in some cases, 2 g CaCO_3 was the optimized condition, while 4 g was optimized in other cases.

Meanwhile, the catalyst CaCO_3 can accelerate the time to reach Vapor-Liquid equilibrium, but it could hardly shift the equilibrium efficiency under a constant temperature [30]. In summary, the average absorption efficiencies (non-catalytic and catalytic absorption) were calculated in Eq. (22) for each concentration and categorized into **Table 2** according to **Fig. 5.a-c**.

Fig. 6 indicated the absorption performance of three amine solvents. Under fresh loadings, these three amines were comparable at 57–63 s with and without catalysts. At 0.20 mol/mol, the order was 1.50 + 3.50 mol/L (71 s, 60 s) > 1.75 + 3.25 mol/L (81 s, 66 s) > 1.25 + 3.75 mol/L (84 s, 78 s) under non-catalytic and optimized catalysis. This order was the same as that of batch process, the 1.50 was the best among these 3 amines (optimized ratio of 30% to 70%), and 1.75 + 3.25 mol/L was better than 1.25 + 3.75 mol/L due to higher MEA concentrations. If compared with 2 + 3 M, the time to reach 90% was 35–41 s at 0.0 mol/mol, and 39–46 s at 0.20 mol/mol [28]. All these three amines were not better than 2 + 3 M with CaCO_3 . The semi-batch process indicated the order of 2 + 3 > 1.5 + 3.5 > 1.75 + 3.25 > 1.25 + 3.75 mol/L.

The average absorption efficiencies were listed in **Table 2**. This absorption efficiency was affected by gas flowrate, liquid flowrate, amine concentration, blended ratios and the initial CO_2 loadings [28]. The efficiency from 1.25 + 3.75 to 2 + 3 mol/L were higher than 90% under fresh and operational conditions, making them qualified for an absorber. The 1 + 4 mol/L + CaCO_3 had poor absorption performance with the absorption efficiency < 90% under the operational condition of 0.20 mol/mol, which was unqualified for industrial operation [28]. The amine concentration was fixed at 5 M and the gas flowrate was 1.35 L/min for this study, and liquid flowrate was fixed at 66.67 ml/min.

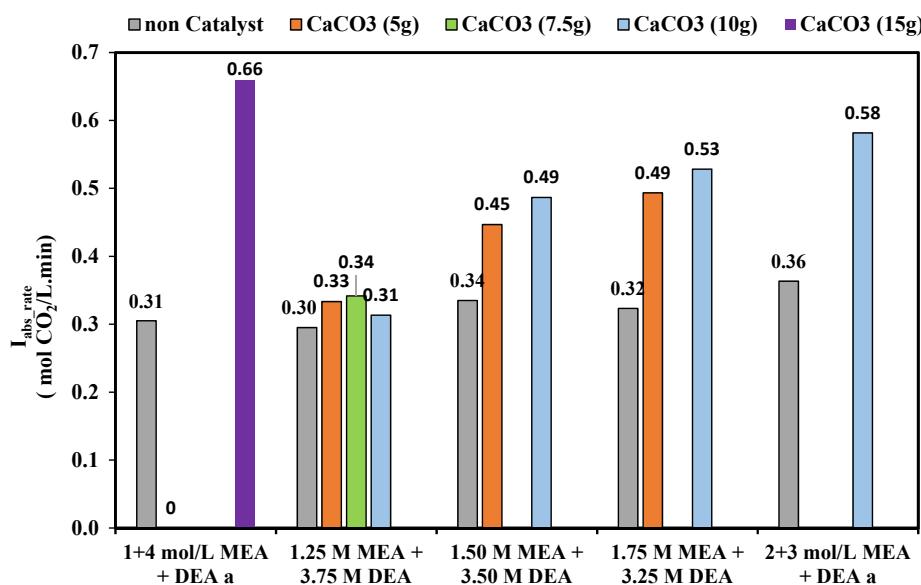


Fig. 4. The initial absorption rates (mol CO₂/L min) of blended amine solvents.

In summary, Sections 4.2–4.4 studied the absorption performance of 1.25 + 3.75 to 1.75 + 3.25 mol/L MEA + DEA solvents with and without CaCO₃, and compared with 1 + 4 and 2 + 3 mol/L (with and without CaCO₃) as boundary condition [28]. The absorption parameters were summarized in Table 1b, with absorption efficiency in Table 2. Even the 1 + 4 mol/L MEA + DEA with CaCO₃ had the highest absorption parameter, it was not selected in the absorber for its relatively low absorption efficiency at 0.20 mol/mol. In an absorber with a steady state process, the CO₂ loading of the amine solution can hardly be 0 mol/mol, the initial super absorption rates of CaCO₃ + 1 + 4 mol/L may not be helpful or applicable in an absorber, despite its enhanced CO₂ desorption performance.

Therefore, four amine blends + CaCO₃ was applicable in an industrial absorber. The absorption parameters in Table 1.b indicated the order of amine blends without catalysts: 2 + 3 M (100%) > 1.5 + 3.5 M (94%) > 1.75 + 3.25 M (89%) > 1.25 + 3.75 M (83%). The order with optimized catalysts was: 2 + 3 M (100%) > 1.75 + 3.25 M (91%) > 1.5 + 3.5 M (85%) > 1.25 + 3.75 M (55%). The first 3 amines (2 + 3, 1.50 + 3.50 and 1.75 + 3.25 mol/L) were good candidates for absorption based on experiments on batch and semi-batch process.

4.5. Catalytic CO₂ desorption with aid of γ-Al₂O₃ and H-ZSM-5

The CO₂ desorption of MEA + DEA blended amine with the aid of γ-Al₂O₃ and H-ZSM-5 was previously studied at these ranges, which were 4 + 1, 3 + 2, 2 + 3, 1 + 4, 0.5 + 4.5 mol/L MEA + DEA and 0 + 5 M DEA [26,27]. This study filled the gaps between 1 + 4 and 2 + 3 mol/L, which were 1.25 + 3.75, 1.50 + 3.50, and 1.75 + 3.25 mol/L. As discussed in Section 2.1.1, the “co-ordination effect” of CO₂ desorption in MEA + DEA solution was significant at the range of 0.5 + 4.5 and 1 + 4 mol/L based on specific reactions (10), where the concentration of MEA to overall amine is within 10–20%. The coordination effect is not as strong in the range of 1.25 + 3.75 ~ 2 + 3 mol/L as that of 0.5 + 4.5 ~ 1 + 4 mol/L.

The reason to use these solid acids and the ratio of blended catalysts had already been discussed in Section 2.1.4 [10,25]. These solid catalysts were repeatedly verified to be highly energy effective [14]. Recently, some other solid catalysts were catalytic effective such as Fe Promoted SO₄²⁻/ZrO₂/MCM-41 Catalyst [45]. Furthermore, the main difference between this study and the previous study [27] was the operation temperature. The operation temperature is 90 °C at the rich

Table 1

Absorption parameters of DEA-MEA blend amines at 1 + 4 to 2 + 3 M.

a. The absorption parameter for 1.25 + 3.75 to 1.75 + 3.25 M with CaCO₃ at 0–10 g

Absorption parameter (mol CO ₂ /L min * mol/mol)			
	Non Catalyst	CaCO ₃ (5 g)	CaCO ₃ (10 g)
1.25 + 3.75 mol/L MEA + DEA	0.131	0.167	0.157
1.50 + 3.50 mol/L MEA + DEA	0.168	0.223	0.243
1.75 + 3.25 mol/L MEA + DEA	0.147	0.247	0.264

b. The absorption parameters of DEA-MEA solvent at 1+4 to 2+3 M at non-catalytic and optimized catalysis.

MEA + DEA solvents (mol/L)	Catalyst (g) non/optimized	Initial absorption rate (mol CO ₂ /L min)	CO ₂ loading (mol/mol)	Absorption Parameter (mol CO ₂) ² /L min mol amine
1.0 + 4.0 [28]	0	0.31	0.5	0.155 (86.1)
	15	0.66	0.5	0.330 (113.8%)
1.25 + 3.75	0	0.30	0.5	0.150 (83.3)
	7.5	0.34	0.5	0.170 (54.8%)
1.50 + 3.50	0	0.34	0.5	0.170 (94.4)
	10	0.49	0.5	0.245 (84.6%)
1.75 + 3.25	0	0.32	0.5	0.160 (88.9%)
	10	0.53	0.5	0.265 (91.4%)
2.0 + 3.0 [28]	0	0.36	0.5	0.180 (100%)
	10	0.58	0.5	0.290 (100%)

loading of 0.50–0.30 mol/mol and increased to 105 °C at 0.30–0.10 mol/mol [27] to speed up the desorption process. In this study, the temperature maintained at a constant temperature of 90 °C.

Fig. 7.a-c demonstrated the CO₂ desorption profiles of 1.25 + 3.75 to 1.75 + 3.25 mol/L under 6 conditions: blank, 8 g γ-Al₂O₃, 15 g γ-Al₂O₃, 8 g H-ZSM-5, 15 g H-ZSM-5, 15 g blended γ-Al₂O₃ + H-ZSM-5(2:1). The overall process of 18 runs took 120–180 min from 0.50 to 0.20 mol/mol. For each amine solvent, the time period was only about 30 min at rich loading from 0.50 to 0.30 mol/mol. The rest part of desorption was below 0.30 mol/mol. From Fig. 7a, the order of catalyst of 1.25 + 3.75 mol/L is blended catalyst > H-ZSM-5 > γ-Al₂O₃, similar to 1 + 4 and 5 mol/L DEA [27]. At 1.5 + 3.5 mol/L the trend is blended catalyst > γ-Al₂O₃ > H-ZSM-5, the same as that of the other study [27]. At 1.75 + 3.25 M, the trend is blended > γ-Al₂O₃ ≈ H-

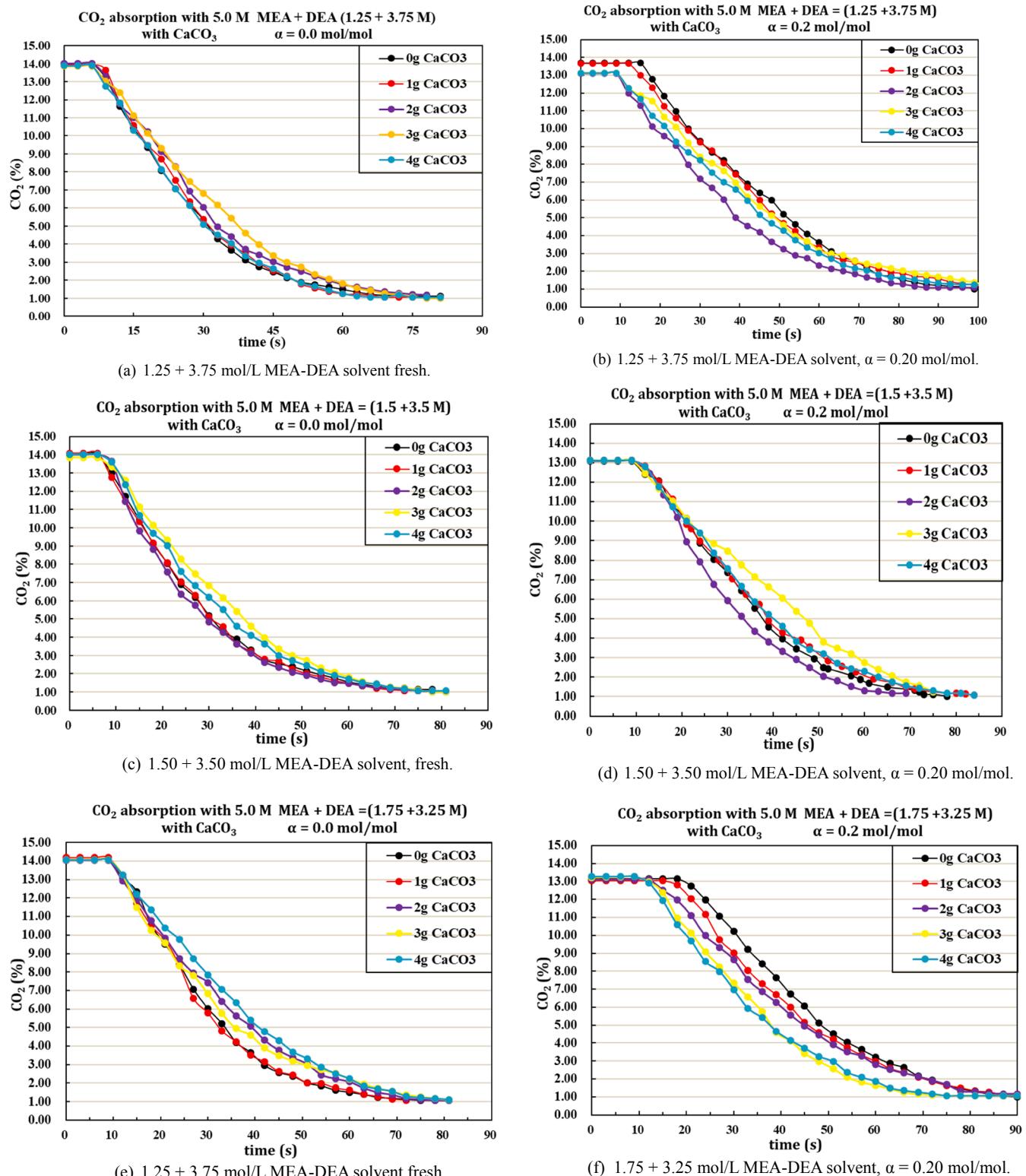


Fig. 5. Catalytic CO_2 absorption with CaCO_3 for 3 blended amine solvents in a semi-batch process.

Table 2

The average absorption efficiency (%) of blended solvents at semi-batch process. (a) $\alpha = 0$ mol/mol (b) $\alpha = 0.20$ mol/mol (independent of CaCO_3).

Amine solvents	Liquid flowrate (ml/min)	Gas flowrate (L/min)	$\alpha = 0$ (mol/mol)	$\alpha = 0.2$ (mol/mol)	Reference
5 M MEA	52.17	1.35	98%	97%	[30]
2.0 + 3.0 M MEA + DEA	66.67	1.35	93%	93%	[28]
1.75 + 3.25 M MEA + DEA	66.67	1.35	92%	92%	This work
1.50 + 3.50 M MEA + DEA	66.67	1.35	93%	92%	This work
1.25 + 3.75 M MEA + DEA	66.67	1.35	92%	92%	This work
1.0 + 4.0 M MEA + DEA	83.33	1.35	93%	83%	[28]

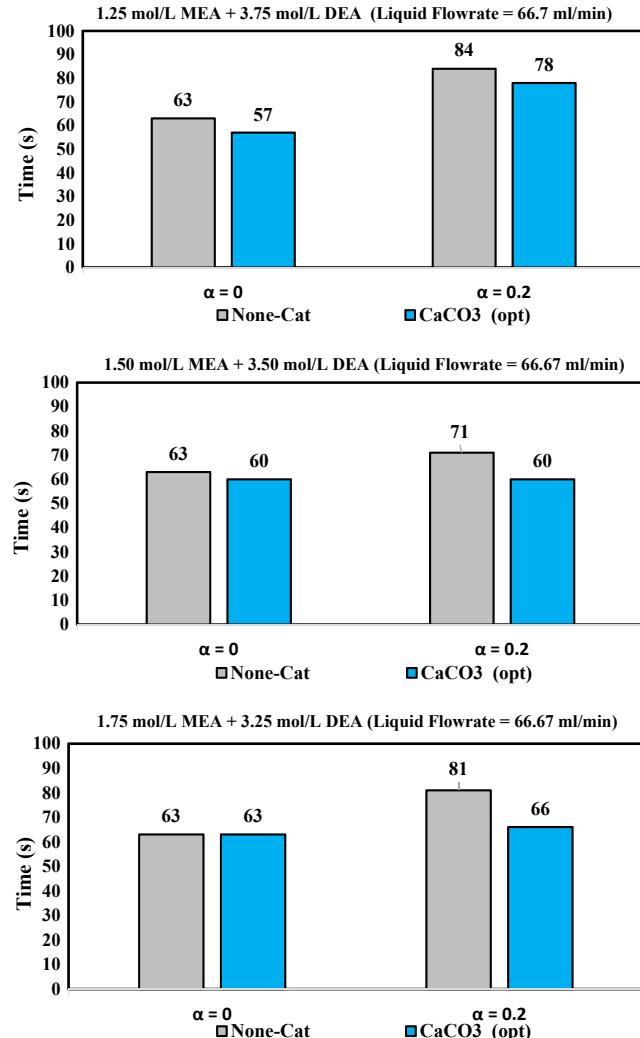


Fig. 6. The time to reach 90% absorption efficiency of different amine blends under non-catalytic and optimized catalysts.

ZSM-5, slightly different from 2 + 3 M of blended catalyst > $\gamma\text{-Al}_2\text{O}_3$ > H-ZSM-5 [27].

From Fig. 7.a-c, the time of 1.25 + 3.75 mol/L took 180 min to reach 0.20 mol/mol, and under optimized catalysis of blended solid, the time was reduced to 105 min. From Fig. 7.b, the time of 1.5 + 3.5 M was reduced from 210 min without catalysis to 105 min with blended solid catalysts. From Fig. 7.c, the time of 1.75 + 3.25 M was reduced from 210 min without catalysis to 180 min under optimized catalysis.

After comparison, the order was $1.50 + 3.50 \approx 1.25 + 3.75 > 1.75 + 3.25 \text{ mol/L}$.

Later on, the initial desorption rates were calculated with Eq. (19) and plotted in Fig. 8.a-c below. The range of desorption curve was 0.50–0.30 mol/mol, preferred at rich loading. The initial CO_2 loading was set as 0.50 mol/mol. After comparison, the 1.75 + 3.25 mol/L was poor and the initial desorption rates were relatively low. However, both the 1.25 + 3.75 mol/L and 1.5 + 3.5 mol/L with blended solid catalysts and H-ZSM-5 had good initial desorption rates. After analysis, these 4 combinations (2×2) were preferred among these 18 runs.

Furthermore, the heat duty (H) of the first 60 min of these 18 runs were plotted in Fig. 9.a-c. It was calculated with Eq. (20). Since it took 105 to 180 min to finish most of the desorption process, the heat duty of 60 min could properly reflect the desorption performance. The heat duty contains the heat of reaction and sensible heat, along with heat loss, but the latent heat is negligible at 90 °C [46]. For 1.25 + 3.75 mol/L, the heat duty was 357 kJ/mol CO_2 under non-catalytic condition, and 323 kJ/mol CO_2 with blended catalysts. For 1.5 + 3.5 mol/L, the heat duty was 366 kJ/mol and 320 kJ/mol respectively. For 1.75 + 3.25 mol/L, the heat duty was 398 kJ/mol and 336 kJ/mol. Among these three amine blends, the heat duty of 1.75 + 3.25 mol/L was the highest (worst), since it contained the most MEA and the least DEA. The 1.5 + 3.5 mol/L was comparable to 1.25 + 3.75 mol/L under non-catalytic and catalytic conditions. Since the ratio of minimum heat duty is 0.5 + 4.5 and 1 + 4 M MEA + DEA, then the blended amine solution containing more MEA molecules has bigger heat duty at a range of 1 + 4 to 2 + 3 M MEA + DEA [27,28].

4.6. The energy-efficient solutions with combination of blended amine with catalysts by means of absorption parameter and desorption parameter study

From previous study [27], the optimized desorption combination for MEA + DEA amine blends with catalysts was 5.0 mol/L DEA + blended catalysts, and 0.5 + 4.5 mol/L MEA + DEA + blended catalysts. They had the optimized desorption parameters in DEA (dominant)-MEA-H₂O [27]. However, these two blended amines had poor performance in CO_2 absorption column, due to the slow absorption rates [27].

After the intensive studies of these 3 blended amines under 6 catalytic conditions Table 3 evaluated the desorption performance of the amine blends + catalysis at the range of 1.25 + 3.75 to 2 + 3 mol/L, by means of the desorption parameter Eq. (18). From Table 3, the desorption parameter of the 4 well-performed combinations followed the order: 1.25 + 3.75 M + blended solid (1.110) > 1.50 + 3.50 M + blended solid (0.984) > 1.25 + 3.75 M + H-ZSM-5 (0.965) \approx 1.50 + 3.50 M + H-ZSM-5 (0.945) with unit of $\times 10^{-3} (\text{mol CO}_2)^3/\text{L}^2 \cdot \text{kJ}$. min. The 2 + 3 M had poor CO_2 desorption performance with smaller desorption parameter due to high MEA concentration, the carbamate of MEA is much more stable than DEA [28].

Finally, the absorption-desorption parameter of amine blends from

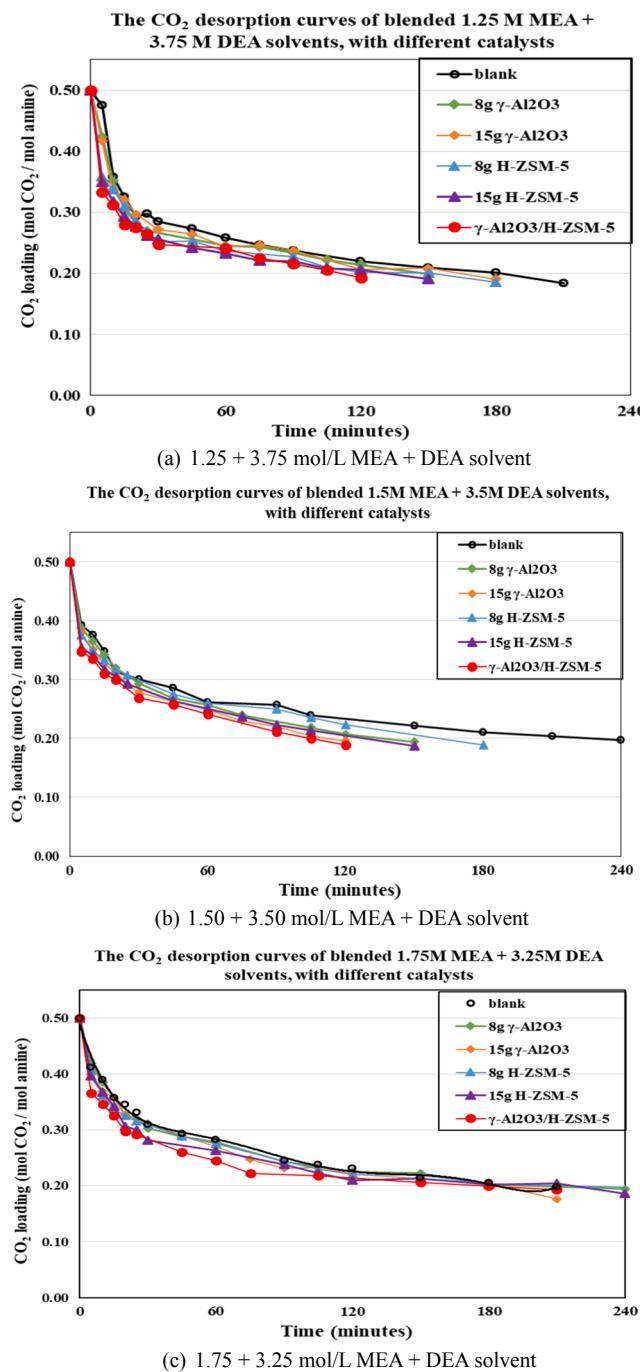


Fig. 7. The CO₂ desorption tests of DEA-MEA blended amine solvents at 90 °C.

1.25 + 3.75 to 2 + 3 mol/L was categorized in Table 4 and plotted in Fig. 10. These 4 blended solvents with heterogeneous absorption and desorption needed to be studied and compared comprehensively with absorption parameter and desorption parameters [28]. Any preference on absorption performance could result in the negative effect on desorption, and vice versa [18]. Therefore, Table 4 clearly demonstrated the values of absorption and desorption parameter as a database. Fig. 10 demonstrated the performance of these 8 combinations. Finally,

after comprehensive analysis, the 1.5 + 3.5 mol/L with CaCO₃ and blended γ-Al₂O₃ + H-ZSM-5 (2:1) turned out to be the most suitable approaches of “blended amine of MEA + DEA + heterogeneous catalysis” for both absorber and desorber among 1.25 + 3.75 to 2 + 3 mol/L. The absorption parameter of 1.5 + 3.5 mol/L solution is 85% comparing to 2 + 3 M MEA + DEA with CaCO₃, which is also about 63.5% comparing to 5.0 M MEA without catalysts [28] as benchmark. The heat duty of desorption at 120 min was reported as 518.2 kJ/mol CO₂, for 1.5 + 3.5 mol/L, < 530.7 kJ/mol of 2 + 3 mol/L and it covers only 44.5% of 5.0 M MEA without catalysts as benchmark (1164.7 kJ/mol) [27]. The desorption parameter of 1.5 + 3.5 mol/L + blended catalysts is 163% comparing to 2 + 3 M + blended catalysts. These results could answer the discussions in the previous study: “The optimized of blended amine solvents might range from 1 + 4 to 2 + 3 M MEA + DEA with optimized catalysis, which awaits further investigations in batch, semi-batch and desorption performances.” [28]. Afterward, the next step is the mass transfer performance [47], and bench scale steady-state process of the combination to settle down the operation parameters.

5. Conclusion

This study conducted catalytic absorptions of CO₂-MEA-DEA solvents (1.25 + 3.75 to 1.75 + 3.25) with solid alkalis CaCO₃, and catalytic CO₂ desorption with H-ZSM-5 and γ-Al₂O₃. The theory and mechanism of the “coordination effect” and “heterogeneous catalysis” were re-investigated with molecular simulation. Experimentally, the absorption performance and desorption performance were carefully compared with 1 + 4 and 2 + 3 mol/L MEA + DEA blended amine solution [27,28] as boundary conditions. The absorption and desorption parameter were calculated to discover the energy-efficient approach of blended amine solvents and heterogeneous catalysis.

- (1) The simulation of the “coordination effect” was investigated. The replacement of DEA + [MEA-COO⁻ + MEAH⁺] (salt) was favored to at room temperature about 10 kJ/mol lower free energy. The molar ratio of DEA to MEA was preferred to be higher than > 2.31 to 1 (higher than 69.8% to 30.2%). Thus the 1.5 + 3.5 M perfectly met the criterion at 70.0% to 30%.
- (2) The simulation of catalytic CO₂-MEA with solid CaCO₃ indicated the reduction of activation energy by 9%. The heterogeneous catalysis were proposed to be mechanism of Eley-Rideal, and verified with experiments [33].
- (3) The CO₂ absorption of MEA + DEA solvents with CaCO₃ was performed. Without catalyst, the initial absorption rate was very close to each other because the reactions were CO₂ + MEA. The absorption parameters indicated the 1.5 + 3.5, 1.75 + 3.25 and 2 + 3 mol/L + CaCO₃ were good candidates. If the absorption parameter of 2 + 3 mol/L with and without optimized catalysis were regarded as 100%. The parameter of 1.75 + 3.25 mol/L was 89% non-catalyst and 91% with optimized catalysis, and the parameter of 1.5 + 3.5 mol/L would be 94.4% non-catalyst and 84.6% with optimized catalysis.
- (4) The absorption parameter had its limitations, for it was determined by “initial absorption rates” in fresh solvent. The semi-batch absorption tests discovered that the 1 + 4 mol/L cannot reach 90% absorption efficiency at operational conditions of 0.20 mol/mol, which made itself unqualified for industrial absorber despite its superior absorption parameter. The semi-batch tests were necessary aids for solvent selection with its analyses of absorption under loadings > 0.0 mol/mol.

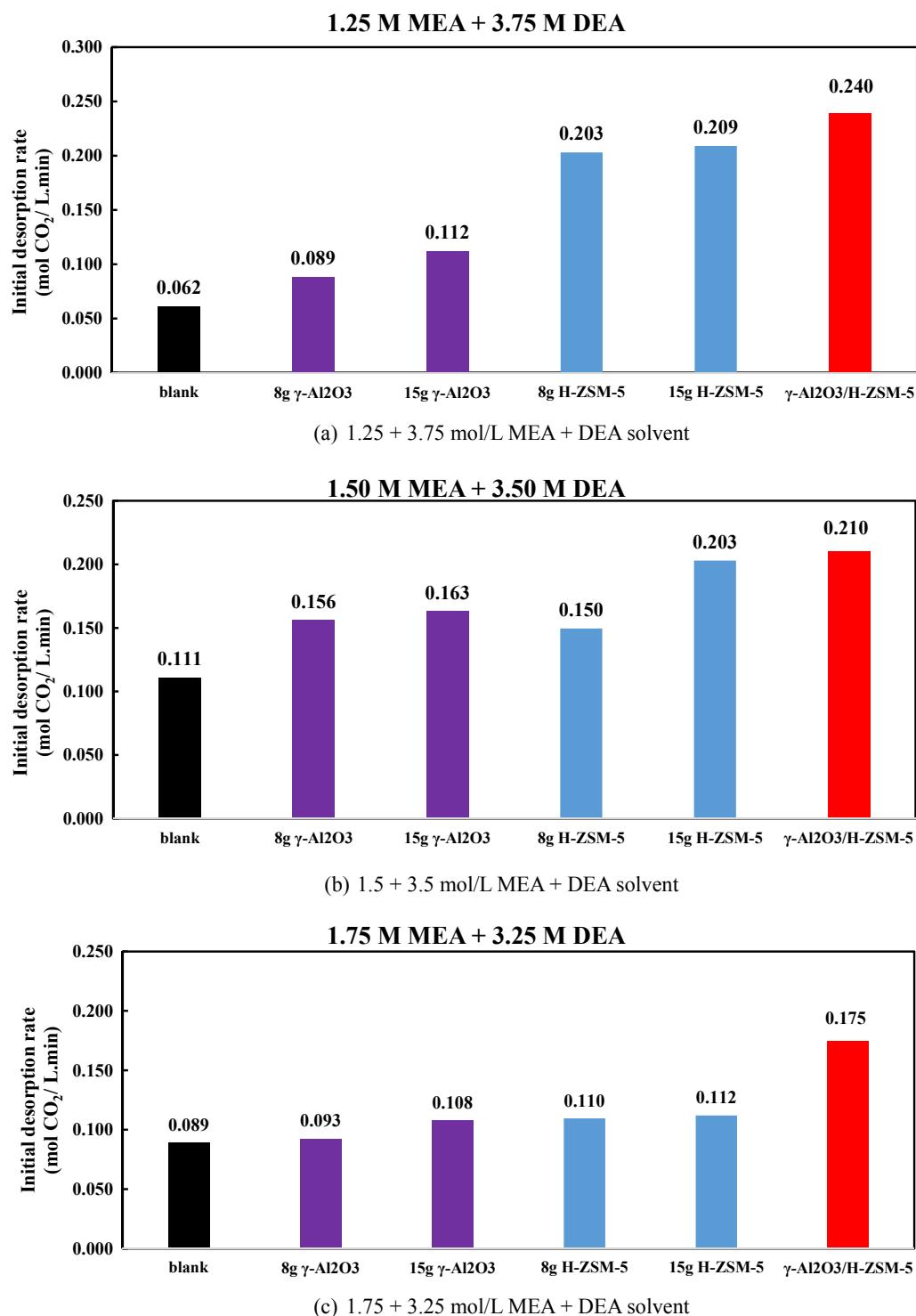


Fig. 8. The initial CO₂ desorption rates (molCO₂/L min) of DEA-MEA blended amine solvents.

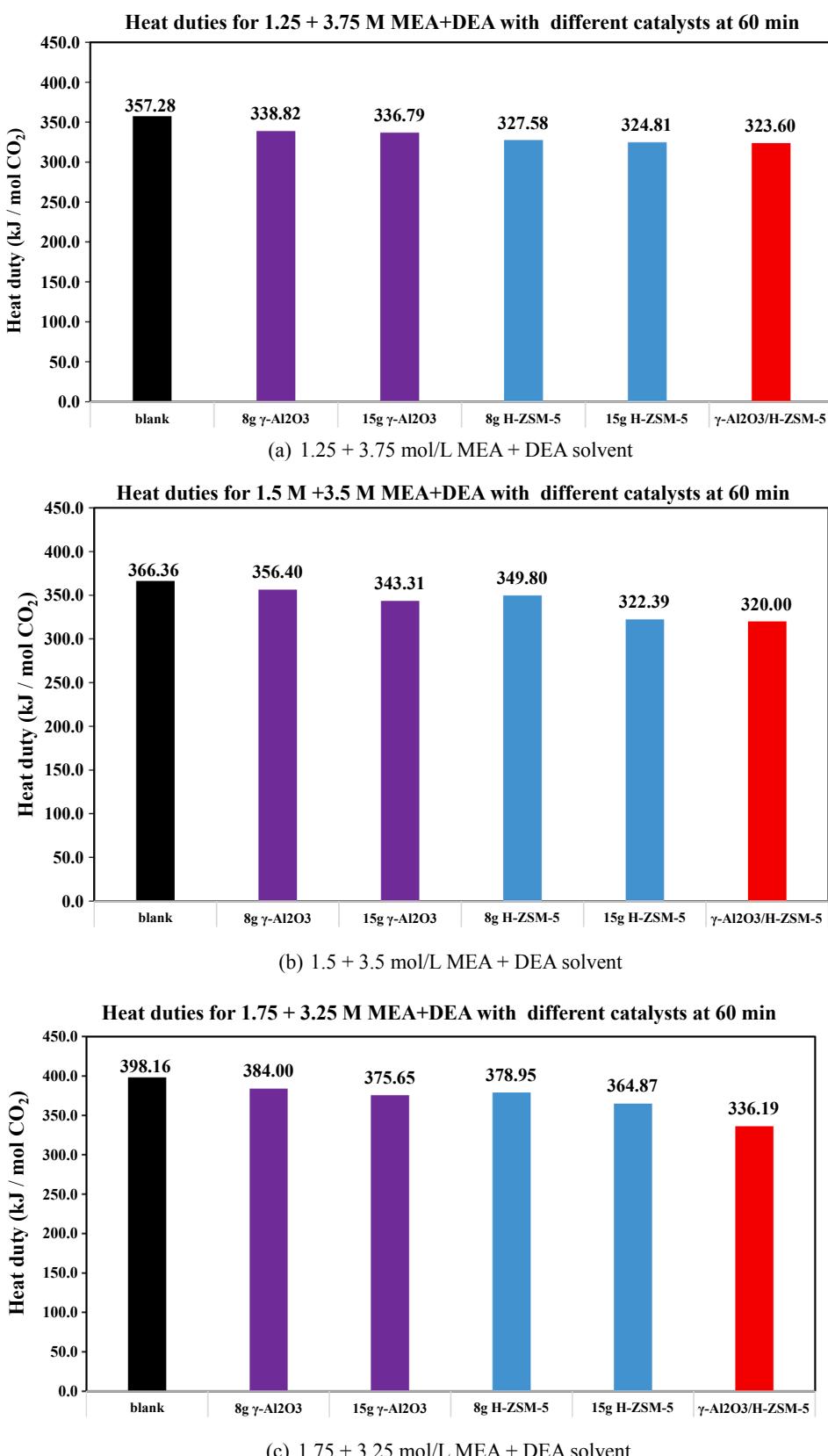


Fig. 9. The heat duties of blended amines with different catalysts at $1.25 + 3.75$ to $1.75 + 3.25$ mol/L.

Table 3

The desorption parameters of blended amine solvents with different catalysts:

Desorption parameter * 10^{-3} (mol CO ₂) ³ /L ² kJ min						
Amine solvents + Catalysts	blank	8 g γ -Al ₂ O ₃	15 g γ -Al ₂ O ₃	8 g H-ZSM-5	15 g H-ZSM-5	γ -Al ₂ O ₃ /H-ZSM-5
1.25 M MEA + 3.75 M DEA	0.258	0.392	0.499	0.930	0.965	1.110
1.50 M MEA + 3.50 M DEA	0.454	0.657	0.712	0.641	0.945	0.984
1.75 M MEA + 3.25 M DEA	0.335	0.361	0.431	0.433	0.460	0.781
2.0 M MEA + 3.0 M DEA [27]					0.508	0.604

a. From the literature, the initial desorption rates are 0.124 and 0.138 mol CO₂/L amin for 2 + 3 M MEA + DEA with 15 g H-ZSM-5 and 15 g blended catalysts. Their heat duties are 366.10 and 342.86 kJ/mol CO₂ for 15 g H-ZSM-5 and 15 g blended catalysts [27].

Table 4

The Absorption - Desorption parameters of blended amine solvents.

Amine solvents + Catalysts	CaCO ₃ (opt)	Absorption parameter (mol CO ₂) ² /L min mol amine		Desorption parameter *10 ⁻³ (mol CO ₂) ³ /L ² kJ min	
		15 g H- ZSM-5	γ -Al ₂ O ₃ /H- ZSM-5	15 g H- ZSM-5	γ -Al ₂ O ₃ /H- ZSM-5
1.25 M MEA + 3.75 M DEA	0.170	0.965	1.110		
1.50 M MEA + 3.50 M DEA	0.245	0.945	0.984		
1.75 M MEA + 3.25 M DEA	0.265	0.460	0.781		
2.0 M MEA + 3.0 M DEA [27,28]	0.290	0.508	0.604		

a. The cyclic capacities for all these blended amine are 1.5 mol CO₂/L, based on 5.0 M amine blends at CO₂ loading range from 0.50 to 0.20 mol/mol.

(5) The CO₂ desorption of blended DEA + MEA solvents (1.25 + 3.75 to 2 + 3 mol/L) with γ -Al₂O₃ and H-ZSM-5 was performed. The desorption parameters indicated 4 top combinations and indicated

the order of: 1.25 + 3.75 M + blended solid (1.110×10^{-3} (mol CO₂)³/L² kJ min) > 1.50 + 3.50 M + blended solid (0.984×10^{-3} (mol CO₂)³/L² kJ min) > 1.25 + 3.75 M + H-ZSM-5 (0.965×10^{-3} (mol CO₂)³/L² kJ min) ≈ 1.50 + 3.50 M + H-ZSM-5 (0.945×10^{-3} (mol CO₂)³/L² kJ min).

(6) If these four amine blends (1.25 + 3.75 to 2 + 3 mol/L) with optimized catalysis were evaluated with the absorption parameters and desorption parameters. The results indicated 1.5 + 3.5 mol/L MEA + DEA with CaCO₃ and blended γ -Al₂O₃ + H-ZSM-5 (2:1) as energy efficient and good-performance candidates, even though its parameters were not the best among the others. In practice, the 1.5 + 3.5 M MEA + DEA could be prepared, with CaCO₃ packed in the absorber and blended acid catalysts packed in the desorber in an amine scrubbing process of a pilot plant.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

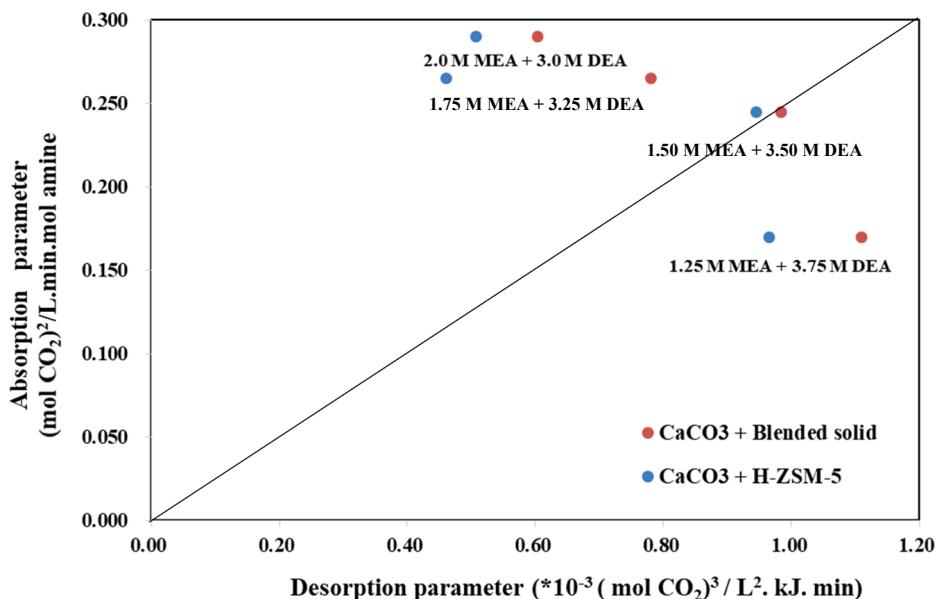


Fig. 10. Absorption parameter vs Desorption parameters of blended amines + catalysis.

Acknowledgment

We would like to thank the National Natural Science Foundation of China (NSFC Nos. 21606150, 61775139). Natural Sciences and Engineering Research Council of Canada (NSERC) are acknowledged.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.116179>.

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