Original Research Article

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GREENHOUSE GASES — SCIENCE AND TECHNOLOGY

The enhanced enzymatic performance of carbonic anhydrase on the reaction rate between CO_2 and aqueous solutions of sterically hindered amines

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Abstract: The kinetics of the reactions of carbon dioxide (CO_2) with aqueous solutions of two different sterically hindered amines (SHAs), 2-amino-2-ethyl-1,3-propanediol (AEPD) and 2-amino-2-methyl-1,3-propanediol (AMPD), in the presence and absence of carbonic anhydrase (CA) was investigated experimentally using stopped-flow conductimetry. The amine concentration, CA concentration, and temperature were varied within the ranges of 0.1–0.5 $kmol \cdot m^{-3}$, 0–125 $g \cdot m^{-3}$, and 298–353 K, respectively. Based on pseudo first-order reaction conditions, the intrinsic reaction rate (k_o) was obtained according to a modified termolecular reaction mechanism. The obtained results showed that the reaction rate between the SHA solutions (either aqueous AEPD or aqueous AMPD) and CO_2 was enhanced significantly upon adding small amounts of CA as a promoter. Such a result supports the use of the aforementioned solvent system as a candidate for CO_2 capture. © 2020 Society of Chemical Industry and John Wiley & Sons, Ltd.

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Keywords: 2-amino-2-ethyl-1,3-propanediol (AEPD); 2-amino-2-methyl-1,3-propanediol (AMPD); carbon dioxide capture; carbonic anhydrase; sterically hindered amines; stopped-flow

Introduction

Carbon dioxide (CO_2) is one of the major greenhouse gases, and CO_2 emission into the atmosphere is a global concern due to its direct relation to global warming.[1] According to the International Energy Agency (IEA), to limit the rise in temperature to within 2°C by 2050, efforts are needed to minimize emissions and prevent climate change.[2–4] Therefore, research into CO_2 capture, utilization, and storage (CCUS) has recently gained increasing importance as CO_2 emissions continue to increase.[5–8] To address such a problem, several solvent-based approaches are currently being developed. Particularly,
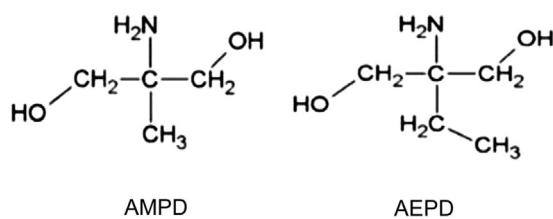
Figure 1. Structure of AMPD and AEPD.

Figure 2. Catalytic hydration reaction mechanism of CO_2 by CA.[33]

chemical solvents that can effectively increase both the CO_2 loading and the reaction rate are being developed as alternatives to 30 wt% aqueous monoethanolamine (MEA) solution, which continues to be the accepted benchmark for CO_2 capture agent.[9–11] However, an aqueous MEA solution has several drawbacks such as corrosion, degradation, and, in particular, a high energy demand during conventional solvent regeneration. Moreover, such a solution has low CO_2 loadings (the theoretical maximum amount is 0.5 mol CO_2/mole amine) due to its stable carbamate ion.[12–15] In contrast, certain sterically hindered amines (SHAs) have higher loading capacities, as much as approximately 1, due to their unstable carbamate ions.[16,17] Reduced carbamate stability may allow the existence of a high free amine concentration in solution, which results in rapid amine-CO_2 reaction rates.[16] However, steric hindrance, though increasing the loading capacity, decreases the reaction rate with CO_2 due to the physical presence of surrounding ligands around the nitrogen atom.[18–21] The catalytic hydrogenolysis of glycerol, which is considered as one of the most well-known bio-based chemicals, to 1,3-propanediol is a promising approach for the production of value-added chemicals.[22,23] As such, the transformation of glycerol from biodiesel waste into highly value-added chemicals has gained global interest.[24,25] In particular, 1,3-propanediol is an important industrial commodity and a building block for 2-amino-2-ethyl-1,3-propanediol (AEPD) and 2-amino-2-methyl-1,3-propanediol (AMPD) (Fig. 1), which is abundant and inexpensive renewable resource. Previously, we found that sterically hindered primary amines (AEPD and AMPD) have a high capacity for CO_2 capture but relatively slow reaction kinetics.[26] It has been studied that the reduced chemical reaction rate could be enhanced by adding highly active amine promoters, such as cyclic polyamines.[27] In this study, we investigated an alternative promoter and proposed a novel approach for the enzymatic enhancement of CO_2 capture using carbonic anhydrase (CA), also called
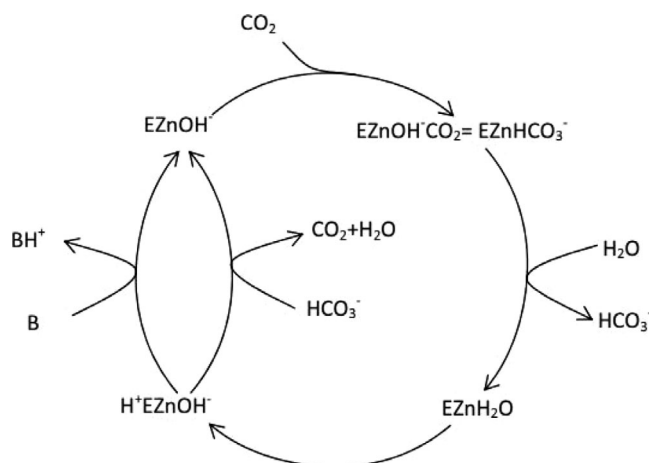
carbonate dehydratase, to improve the reaction rates of select SHAs for the first time.

CA is considerably efficient and one of the fastest biocatalysts. CA is found in various systems, including red blood cells, pancreatic cells, renal tubules of mammals, and gastric mucosa, and it facilitates the movement of CO_2 through biological membranes.[21,28–30] It plays a critical role in respiration by catalyzing the reversible reactions of CO_2 and water to bicarbonate (HCO_3^-) and by influencing CO_2 transportation in the blood.[31] CA also helps minimize the activation energy of biochemical reactions.[32]

Genetically modified CA is also capable of catalyzing the reaction between CO_2 and aqueous alkanolamine solutions (or buffer solutions) in industrial applications.[29,33–35] In a recently published paper, the authors also proposed the acceleration of carbon capture performance using proprietary enzymatic technology.[36] The authors claimed that a large quantity of steam in conventional stripping technologies was no longer needed due to the improved performance of the carbonate solvent enhanced by the proprietary enzyme. The mechanism of the catalytic hydration reaction of CO_2, as shown in Fig. 2, has been proposed in the previous literature.[31,37] Moreover, the catalytic hydration of CO_2 by CA is dominant above pH 7.[28–31,36–38]

The limiting step of the suggested CA-promoted SHA systems is the regeneration process of the solvent containing the enzyme (CA). As evidenced by experimental results, CA from bovine erythrocytes is not active above 65°C. Moreover, one of the most

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thermostable plant-type (β-Class) Cas in the archaea, *Cab*, is thermostable only up to 75°C.[39] As such, conventional regeneration methods using a desorber equipped with a reboiler are inappropriate for industrial applications. In contrast, a new method, which has been proposed recently, allows regeneration processes for molecules that do not form stable carbamate ions, such as tertiary amines or SHAs, even at ambient temperatures. Such a method involves bicarbonate precipitation followed by solvent treatment using calcium hydroxide.[40] During the aforementioned procedure, amine deprotonation occurs, and bicarbonate is transformed into carbonate ions to regenerate the solvent. This causes the precipitation of calcium carbonate ($CaCO_3$), and precipitated $CaCO_3$ can be separated via filtration to obtain the regenerated solvent. This revolutionary room temperature solvent-regeneration process allows a new means for CA to promote the CO_2 absorption of SHAs, such as AMPD and AEPD. Moreover, Osei et al. suggested an innovative strategy to reduce the energy consumption during CO_2 desorption through the application of solid acid catalysts.[41] Such an approach also increased the desorption efficiency at room temperature. The catalyst-assisted desorption process could possibly be an alternative means for low temperature regeneration, wherein CA does not lose its activity. Another alternative to the low temperature regeneration process is the ultrasound-assisted desorption of CO_2 from a loaded solution.[42] The main purpose of this study is to investigate the mechanism and kinetics of CO_2 absorption using CA as a promoter in aqueous AEPD or AMPD solutions. Insights gathered herein are vital for the optimal rate-based design of CO_2 absorbers.
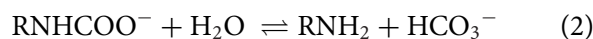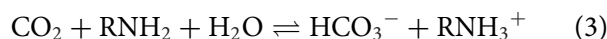
Experimental

Reaction mechanism

It is common to use zwitterion and termolecular reaction mechanisms to analyze experimental data.[43–45] The main principle of the termolecular reaction mechanism is the assumption that the amine (for instance, RNH_2) reacts simultaneously with a CO_2 molecule and a base molecule (B). The termolecular reaction mechanism proposed by Crooks and Donnellan is carried out in a single step, through the weakly-bonded intermediate product, as.[46]

$$CO_2 + RNH_2 \ldots\ldots B \rightleftharpoons RNHCOO^- \ldots\ldots BH^+ \tag{1}$$
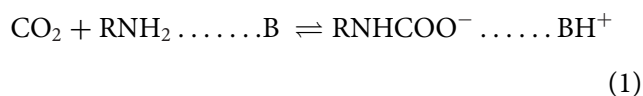
Here, B is H_2O. However, for sterically hindered amines; carbamate ion is unstable and hence has a preferential reaction with amine compared to water, so that 1 mole of amine can capture 1 mole of CO_2. The following reaction proceeds subsequently:

$$RNHCOO^- + H_2O \rightleftharpoons RNH_2 + HCO_3^- \tag{2}$$

Overall reaction

$$CO_2 + RNH_2 + H_2O \rightleftharpoons HCO_3^- + RNH_3^+ \tag{3}$$

The forward observed reaction rate (r_{obs}) of CO_2 in an aqueous sterically hindered amine solution is

$$r_{obs} = k_o\,[CO_2] \tag{4}$$

$$k_o = k_{H_2O}\,[H_2O]\,[A] + k_A[A][A] \tag{5}$$

where k_o is the pseudo-first-order rate constant, [A] is sterically hindered amine concentration (AEPD or AMPD) and [H_2O] is water concentration.

Taking the H_2O concentration to be constant considering the large volume of H_2O involved, a new rate constant, k, can be defined as

$$k = k_{H_2O}\,[H_2O] \tag{6}$$

$$k_o = k_A[A]^2 + k[A] \tag{7}$$

In addition, if the system exhibits first-order reaction kinetics, Eqn (7), in the presence of CA, simplifies to

$$k_o = k[A]. \tag{8}$$

Now considering a mixture of a sterically hindered amine and CA in water, Eqn (5) can be modified as

$$k_o = k_{H_2O}[H_2O][A] + k'_{H_2O}[H_2O][CA] + k_A[A][A]$$
$$+ k_{A-CA}[A][CA] \tag{9}$$

Eqn (9) is valid for the pseudo first-order rate constants of CA-promoted aqueous sterically hindered amine solutions according to the modified termolecular reaction mechanism.

The main difference between the termolecular reaction mechanism proposed by Crooks and Donnellan (1989) and Eqn (9) is that the former considers only an amine [A] as the third molecule, whereas the latter also considers water, as well as the SHA and CA.[47–49]

Now considering that water is in excess and nearly at a constant concentration, $k = k_{H_2O}[H_2O]$ and $k^* = k'_{H_2O}[H_2O]$ can be assumed to be constant thus

$$k_o = k[A] + k_A[A][A] + k^*[CA] + k_{A-CA}[A][CA] \tag{10}$$

For stopped-flow experiments, for a set of experiments, [CA] is kept constant that is nearly at its initial value of $[CA]_0$ and sterically hindered amine concentration [A] is varied to obtain the following equation:

$$k_o = k[A] + k_A[A][A] + k^*[CA]_0$$
$$+ k_{CA-A}[CA]_0[A] \quad (11)$$

or

$$k_o = k_1 + k_2[A] + k_A[A][A] \quad (12)$$

where, $k_1 = k*[CA]_0$ and $k_2 = k + k_{CA-A}[A]_0$ and both k_1 and k_2 are constant under experimental conditions.

For another set of experiments, [A] is kept constant at $[A]_0$ and [CA] is varied, the following equations are obtained:

$$k_o = k[A]_0 + k_A[A]_0[A]_0 + k^*[CA]$$
$$+ k_{A-CA}[A]_0[CA] \quad (13)$$

which reduces to

$$k_o = k_4 + k_3[CA] \quad (14)$$

where $k_3 = (k* + k_{A-CA}[A]_0)$ and $k_4 = (k + k_A[A]_0)[A]_0$ are constant under experimental conditions.

In this work, the forward reaction rate constants of promoted systems were obtained by using Eqn (12) or Eqn (14).

Reagents

Carbonic anhydrase (CAS no. 9001-03-0) from bovine erythrocytes and AMPD (CAS no. 115-69-5) with a purity of 99% were provided from Sigma-Aldrich (St. Louis, MO, USA). AEPD (CAS no. 115-70-8) with a purity 99% was also obtained by Acros Organics (Morris Plains, NJ, USA). CO_2 with a minimum 99.99% purity was purchased by Linde (Germany). No further purifications were applied to these chemicals.

Stopped-flow experiments

Experiments on the reaction kinetics, which are one of the important parameters for estimating CO_2 absorption efficiency, were performed. There are several techniques for the investigation of reaction kinetics, namely wetted-wall column, laminar jet, and stirred cell techniques. However, these techniques have drawbacks such as the limited ranges of the average contact time and liquid mass transfer coefficient. However, stopped-flow is a direct technique that enables the determination of the intrinsic reaction rate of homogeneous systems within a wide range of reaction rates while providing reproducible experimental data.

Kinetics experiments were performed using stopped-flow equipment (Hi-Tech Scientific, UK; Model SF-61SX2) to measure pseudo first-order reaction kinetics for different combinations of aqueous SHAs with CO_2 in the presence and absence of CA. The stopped-flow system is an improved method for measuring the reaction rates of considerably fast reactions and is designed to measure sudden signal changes.

First, CO_2 gas was passed through the water in a gas washing bottle for an appropriate duration (approximately 5–10 min depending on the reagent concentration). This ensured that CO_2 passed through the liquid medium. Then, the freshly saturated CO_2 dissolved in water was placed into one of the syringes, and a fresh amine solution (aqueous solutions of SHAs in the presence or absence CA) was placed into the other syringe. The stopped-flow equipment instantaneously mixed equal volumes of the two mixtures in the mixing chamber, and then the flow was stopped for the reaction to occur. The ion formation initiated a voltage change that was directly related to the conductivity change monitored continuously by the conductivity detection unit as a function of time. Then, Kinetic Studio was used to automatically calculate the observed pseudo first-order rate constant (k_o) based on least squares regression. To achieve the pseudo first-order reaction conditions, the molar concentration of the amine solution was kept 20 times higher than that of the dissolved CO_2 for every run.[48] All experimental pseudo first-order rate constants reported herein were repeated at least 10 times to achieve consistent k_o (s^{-1}) values at the specified conditions. Average k_o values were calculated for each experimental set using the aforementioned software. Fig. 3 shows a typical combined graph obtained from the standard stopped-flow equipment. Similar graphs were obtained for the other reaction systems studied. Additional details regarding the experimental procedure were based on the previous literature.[18,20,21,50]

Normally, the stopped-flow system can operate at a maximum temperature of 313 K. However, a TPod (Hi-Tech Scientific, UK), which was attached to the
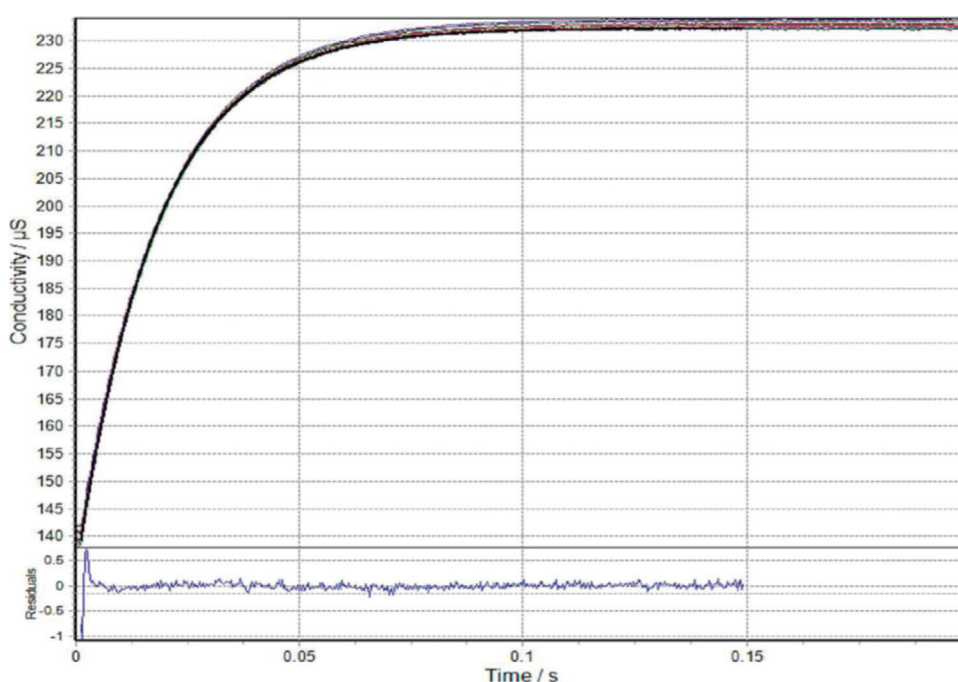
Figure 3. Sample data run for 0.5M aqueous AMPD–CO$_2$ reaction at 298 K.

stopped-flow device to expand the operating temperature range (253–373 K), was designed and used for the first time. Therefore, obtaining reaction kinetics without extrapolating from industrial absorber temperature ranges is one of the unique aspects of this work.

Results and discussion

The kinetics of the reaction between the aqueous solutions of SHAs and CO$_2$ in the presence and absence of CA was analyzed using stopped-flow. The experiments were carried out within a temperature range of 298–353 K. The concentrations of the aqueous AEPD and AMPD solutions were within 0.1–0.5 M. To analyze the effect of CA concentration, the concentration of the aqueous SHA solutions was kept constant (0.5 M), and the amount of CA was varied from 25 to 125 g·m^{-3}.

CO$_2$ absorption into aqueous sterically hindered amine solutions without enzyme

The experimentally obtained k_o values were correlated using the modified termolecular reaction mechanism (Eqn 5) to determine the forward reaction rate constants of two different aqueous SHA (AEPD, AMPD) systems at specified temperatures. The observed pseudo first-order reaction rate constants (k_o)

Table 1. Summary of the forward reaction rate constants of CO$_2$ absorption into aqueous AEPD and AMPD solutions at various temperatures.

T (K)	k_{AEPD} (m^3·kmol^{-1}·s^{-1})	k_{AMPD} (m^3·kmol^{-1}·s^{-1})
298	65.8	90.9
303	86.3	99.3
308	106.9	113.3
313	123.8	120.5
323	139.4	130.0
333	151.9	145.3
338	160.5	128.1
343	170.8	216.6
348	186.2	248.4
353	214.1	284.6

achieved at 298–353 K were presented as a function of AEPD and AMPD concentrations as shown in Fig. 4. As expected, increase in k_o values with increasing concentration and temperature confirms the direct dependency of the rate constant on these experimental parameters.

From the slopes of the fitted lines in Fig. 4, the forward reaction rate constants k (m^3·kmol^{-1}·s^{-1}) for AEPD-CO$_2$-H$_2$O and AMPD-CO$_2$-H$_2$O systems were determined and are presented in Table 1.
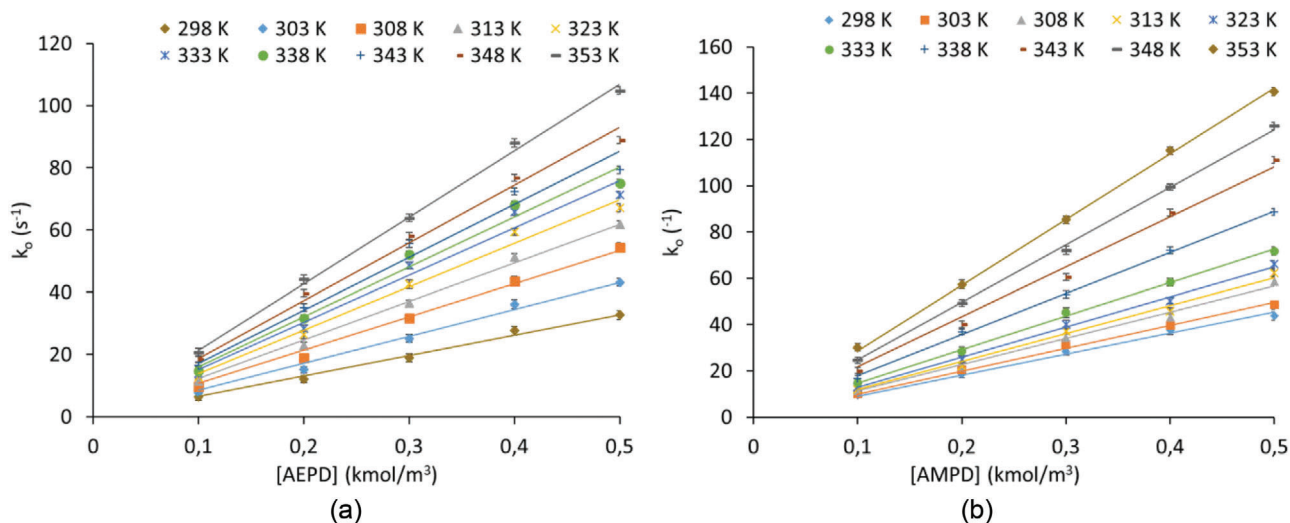
Figure 4. Effect of AEPD and AMPD concentrations on k_o values at various temperatures. All data are the average of ten replicate experiments, and error bars are the standard deviation of the mean.
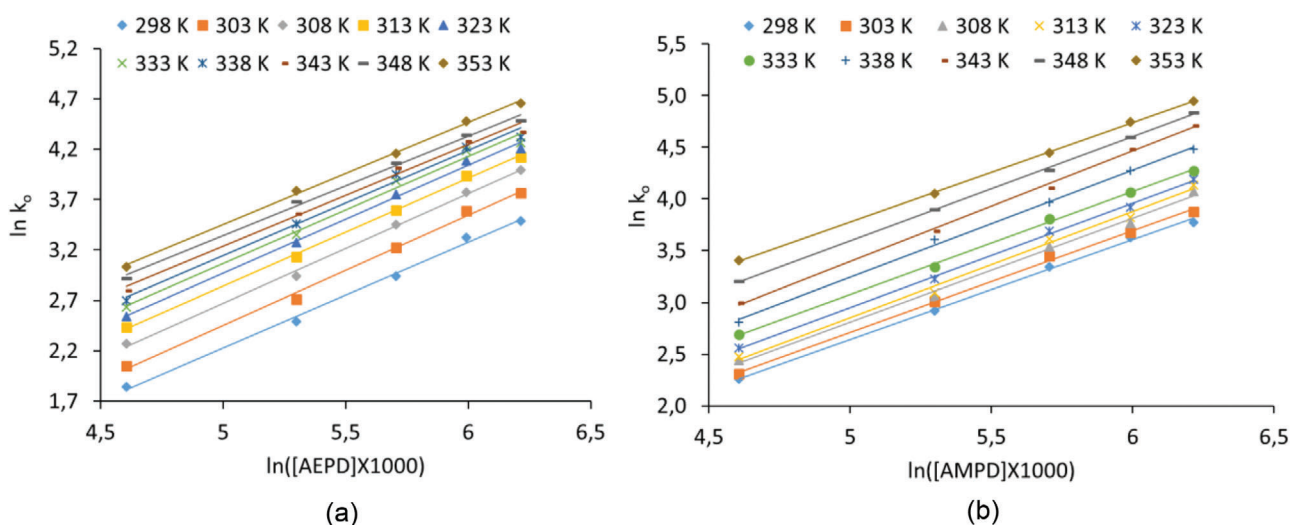

Figure 5. Reaction order plot of CO₂ absorption into aqueous AEPD and AMPD solutions at various temperatures.

The apparent reaction orders of the aqueous SHA systems were determined according to the power law kinetics; that is, by plotting the natural logarithm of reaction rate constants versus SHA concentration as illustrated in Fig. 5. Regarding the slope of the fitted lines, reaction orders for the aqueous SHA systems at various temperatures are approximately equal to one which indicates that the termolecular reaction mechanism is appropriate for these chemical reactions.

Furthermore, the Arrhenius diagram was plotted (Fig. 6) and the activation energies of aqueous SHA systems were determined at five concentrations and ten temperatures by evaluating the Arrhenius Equation

as follows:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (15)$$

where A is Arrhenius factor ($m^3 \cdot kmol^{-1} \cdot s^{-1}$), and E_a is the activation energy ($kJ \cdot mol^{-1}$).

The average activation energy value for both AEPD-CO₂-H₂O and AMPD-CO₂-H₂O systems was calculated to be approximately 16.3 $kJ \cdot mol^{-1}$.

In conclusion, the experimentally observed pseudo first-order reaction rate constants of the examined aqueous SHA systems were compared with the literature at specified concentrations and temperatures as shown in Table 2.
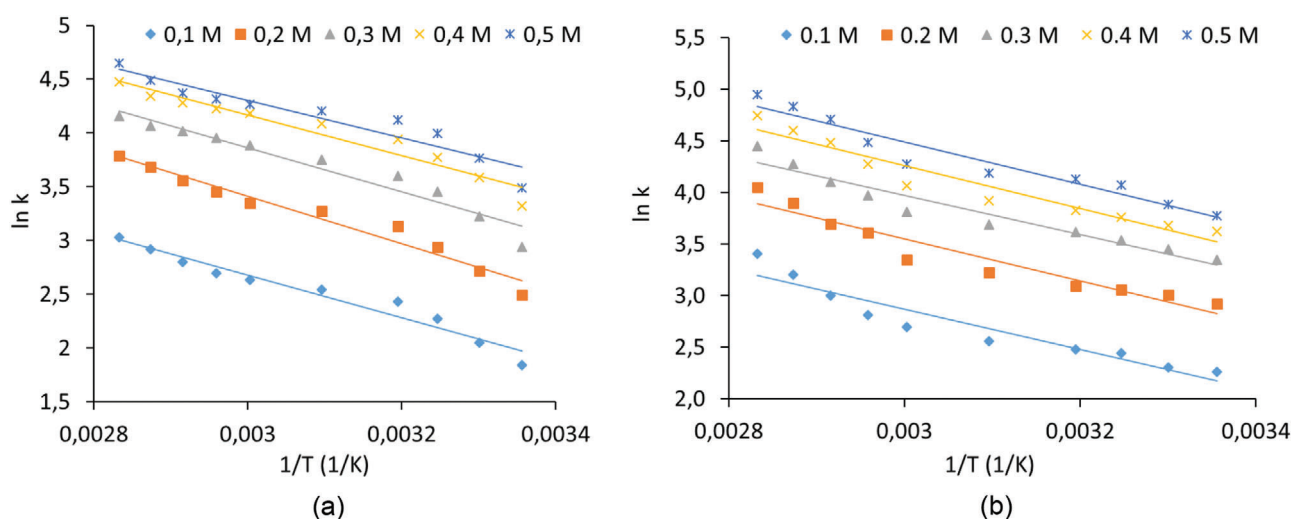
Figure 6. Arrhenius diagram for aqueous AEPD and AMPD solutions. (a) AEPD-CO_2-H_2O system. (b) AMPD-CO_2-H_2O system.

Table 2. Comparison of kinetic properties of AEPD-CO_2-H_2O and the AMPD-CO_2-H_2O systems at specified concentrations and temperatures.

| AMPD (kmol·m^{-3})	$k_{o,303K}$ (s^{-1})	$k_{o,313K}$ (s^{-1})	$k_{o,323K}$ (s^{-1})	Method	Source
0.24	28.8	43.3	62.8	Wetted-wall column	51
0.47	72.5	112	158	Wetted-wall column	51
0.95	189	310	439	Wetted-wall column	51
1.95	505	800	1109	Wetted-wall column	51
AMPD (kmol·m^{-3})	**$k_{o,278K}$ (s^{-1})**	**$k_{o,288K}$ (s^{-1})**	**$k_{o,298K}$ (s^{-1})**	**Method**	**Source**
0.1	3.2	5.5	8.2	Stopped-Flow	20
0.25	7.2	12.0	21.0	Stopped-Flow	20
0.5	18.7	29.1	55.9	Stopped-Flow	20
0.75	30.7	53.8	95.9	Stopped-Flow	20
1.0	50.4	95.8	141.5	Stopped-Flow	20
AEPD (kmol·m^{-3})	**$k_{o,278K}$ (s^{-1})**	**$k_{o,288K}$ (s^{-1})**	**$k_{o,298K}$ (s^{-1})**	**Method**	**Source**
0.03	1.2	2.0	4.3	Stopped-Flow	21
0.25	12.1	14.5	23.7	Stopped-Flow	21
0.50	20.1	42.1	59.7	Stopped-Flow	21
0.75	33.9	70.6	111.4	Stopped-Flow	21
1.00	59.3	111.8	179.7	Stopped-Flow	21
AEPD (kmol·m^{-3})	**$k_{o,303K}$ (s^{-1})**	**$k_{o,313K}$ (s^{-1})**	**$k_{o,318K}$ (s^{-1})**	**Method**	**Source**
0.42	52.26	99.37	142.84	Wetted-wall column	52
0.84	155.2	320.78	425.88	Wetted-wall column	52
1.27	283.16	567.36	790.44	Wetted-wall column	52
1.7	432.99	816.5	1157.9	Wetted-wall column	52
2.13	570.55	1169.51	1694.61	Wetted-wall column	52
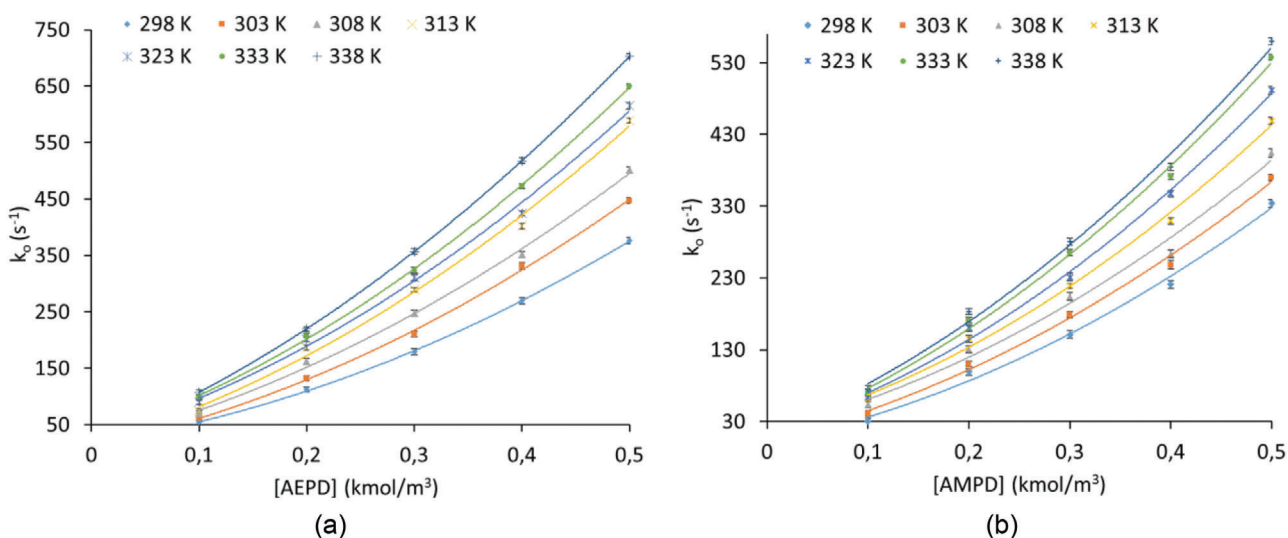
Figure 7. Effect of amine concentration on k_o values of CO_2 reacted with aqueous AEPD and AMPD solutions containing 100 $g \cdot m^{-3}$ of CA at various temperatures. All data are the average of ten replicate experiments, and error bars are the standard deviation of the mean.

CO_2 absorption into aqueous sterically hindered amine solutions with enzyme

The effect of amine concentration (0.1–0.5 $kmol \cdot m^{-3}$ aqueous AEPD solutions or aqueous AMPD solutions) on CA activity was investigated with constant CA concentration (at 100 $g \cdot m^{-3}$) over a temperature range of 298–353 K as seen in Fig. 7. The pseudo first-order reaction rates of CO_2 absorption into aqueous SHSs in the presence of 100 $g \cdot m^{-3}$ CA are presented in the Supporting Information (Table S2). The k_o (s^{-1}) values were decreased significantly after 338 K. It is clear that the activity of the enzyme begins to drop after this temperature.

The forward reaction rate constants are presented in Table 3. When the table is examined, a slight increase in the reaction rate constants was observed after 313 K. This can be explained by the decrease in enzyme activity due to increase in temperature.

A summary of reaction rate constant of CO_2 absorption into conventional aqueous solutions, namely, MEA, 4-diethylamino-2-butanol (DEAB), 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA), diethanolamine (DEA) and piperazine (PZ) is given in Table 4. According to Table 4, the forward reaction rate constants of aqueous AEPD and AMPD solutions containing 100 $g \cdot m^{-3}$ of CA are lower than those of aqueous amine solutions, except aqueous MDEA solution.

Table 3. Summary of forward reaction rate constants of CO_2 absorption into aqueous AEPD and AMPD solutions containing 100 $g \cdot m^{-3}$ of CA at various temperatures.

T (K)	k_{AEPD} ($m^6 \cdot kmol^{-2} \cdot s^{-1}$)	$k_{2, AEPD}$ ($m^3 \cdot kmol^{-1} \cdot s^{-1}$)	$k_{1, AEPD}$ (s^{-1})
298	851.0	290.1	17.6
303	947.0	402.7	11.4
308	961.0	474.1	18.5
313	1141.5	559.7	14.7
323	1166.8	573.5	27.9
333	1221.4	632.5	26.5
338	1215.7	759.6	19.5

T (K)	k_{AMPD} ($m^6 \cdot kmol^{-2} \cdot s^{-1}$)	$k_{2, AMPD}$ ($m^3 \cdot kmol^{-1} \cdot s^{-1}$)	$k_{1, AMPD}$ (s^{-1})
298	746.4	281.1	0.7
303	749.7	346.8	3.0
308	813.4	344.9	18.3
313	916.4	389.8	19.1
323	1001.9	441.5	16.1
333	1013.6	526.0	13.8
338	1021.7	557.2	17.1

The apparent reaction orders of aqueous AEPD and AMPD solutions containing 100 $g \cdot m^{-3}$ of CA were determined according to power law kinetics. Empirical power law kinetics was fitted to all experimental data

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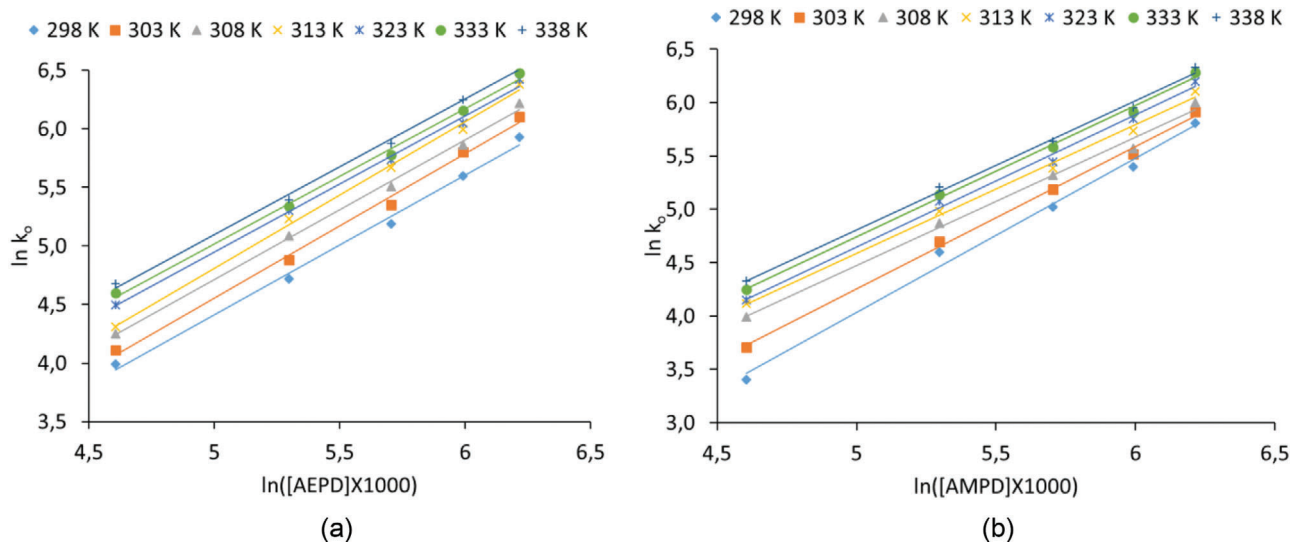
Figure 8. Reaction order plot of CO_2 absorption into aqueous AEPD and AMPD solutions catalyzed by 100 g·m⁻³ of CA at various temperatures.

Table 4. Reaction rate constant of CO_2 absorption into aqueous amine solutions at 298 K.

Amine	k ($m^3 \cdot kmol^{-1} \cdot s^{-1}$)	References
Methyldiethanolamine	6.71	53
Diethanolamine	412	54
4-diethylamino-2-butanol	429	55
2-amino-2-methyl-1-propanol	473	56
Monoethanolamine	5,939	57
Piperazine	65,460	58

using the least square method and fractional orders were obtained as illustrated in Fig. 8.

The reaction orders for the AEPD-CO_2-H_2O and the AMPD-CO_2-H_2O systems in the presence of 100 g·m⁻³ of CA were found to be between 1.2 and 1.3, respectively, depending on the concentration range.

Furthermore, to determine the activation energies of aqueous AEPD and AMPD solutions containing 100 g·m⁻³ of CA at five concentrations and seven temperatures, the Arrhenius diagrams were plotted as seen in Fig. 9. The average activation energy values of AEPD-CO_2-H_2O system in the presence of 100 g·m⁻³ of CA and the AMPD-CO_2-H_2O system in the presence of 100 g·m⁻³ of CA were 12.7 kJ·mol⁻¹ and 12.2 kJ·mol⁻¹, respectively.

Fig. 10 presents the effect of 100 g·m⁻³ CA on experimentally obtained pseudo first-order reaction rate constants. The change in k_o (s⁻¹) values of

aqueous SHA systems was presented under the same temperatures and concentrations in the absence and presence of 100 g·m⁻³ CA.

As seen from Fig. 10, k_o (s⁻¹) values of CO_2 absorption in the presence of 100 g·m⁻³ CA at various concentrations of AEPD-CO_2-H_2O and AMPD-CO_2-H_2O systems increase substantially in a temperature range of 298–313 K.

In order to evaluate the effect of CA amount on experimentally obtained pseudo first-order reaction rate constants, the SHA concentration was kept constant at 0.5 kmol m⁻³ and the CA concentration was varied between 25 and 125 g·m⁻³.

The k_o (s⁻¹) values of CO_2 reacting with 0.5 kmol·m⁻³ AEPD and 0.5 kmol m⁻³ AMPD containing various amounts of CA over a temperature range of 298–338 K are presented in Fig. 11. It can be observed that both temperature and CA concentration have significant influences on the k_o values, as expected.

Conclusions

The kinetics of the reaction between SHAs and CO_2 in the presence and absence of CA was investigated experimentally using a stopped-flow method and modeled according to the modified termolecular mechanism. The results showed that the absorption kinetics of CO_2 increased as the temperature and concentration of the SHA (AEPD or AMPD) or the promoter (CA) increased. The reaction orders between the SHAs and CO_2 were found to be 1.0. Based on the
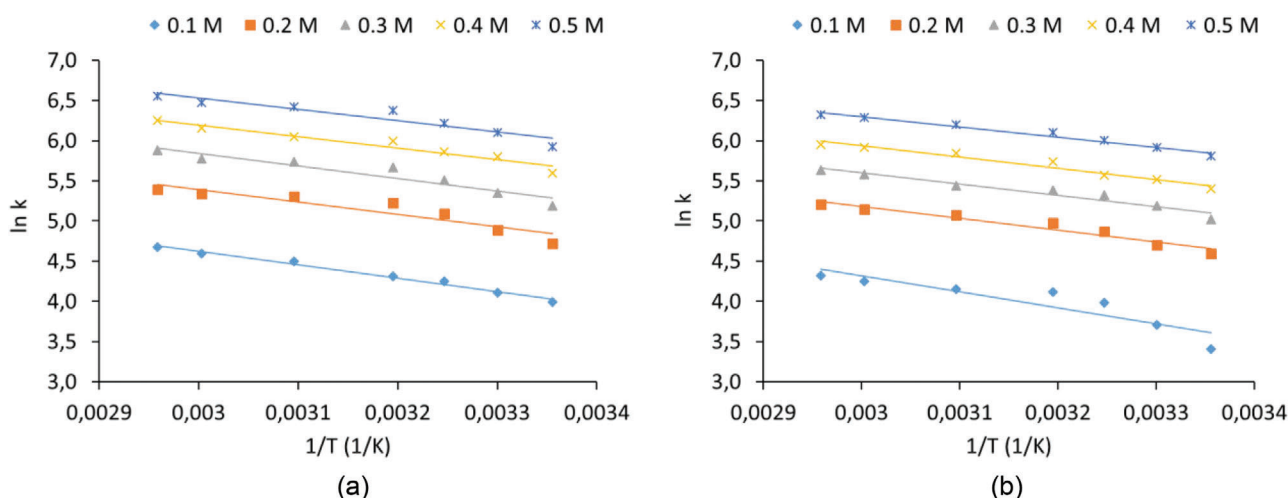
Figure 9. The Arrhenius diagram for aqueous AEPD and AMPD solutions containing 100 g·m^{-3} of CA. (a) AEPD-CO_2-H_2O system and 100 g·m^{-3} of CA. (b) AMPD-CO_2-H_2O system 100 g m^{-3} of CA].
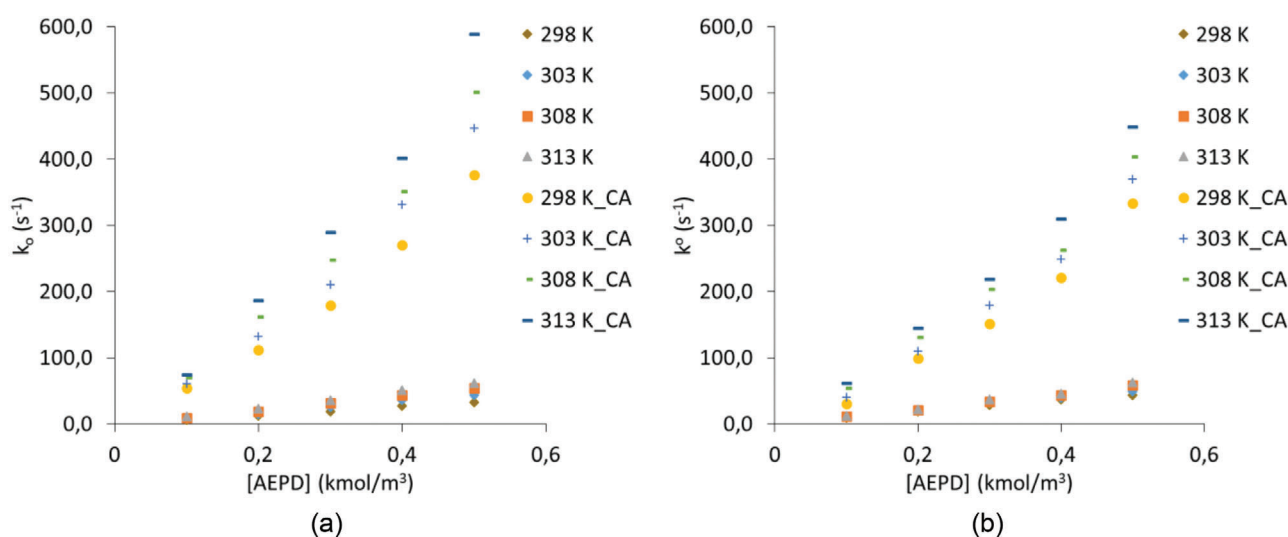

Figure 10. Comparison of experimentally obtained k_o values in the presence and absence of CA for AEPD-CO_2-H_2O system and AMPD-CO_2-H_2O system at various temperatures.

forward reaction rate constants, the reaction kinetics of the AEPD-CO_2-H_2O system was more enhanced than that of the AMPD-CO_2-H_2O system upon the addition of CA. Average activation energies of the AEPD-CO_2-H_2O and AMPD-CO_2-H_2O systems were determined to be 16.3 kJ·mol^{-1} for both systems, and the activation energies seemed consistent at different concentrations. The activation energies were further reduced to approximately 12 kJ·mol^{-1} for both systems upon the addition of CA. It was found that the slow reaction rate of the SHAs could be enhanced significantly by adding small amounts of CA. However, SHAs with CA still had lower reaction rates compared

with that of a 30% aqueous MEA solution. However, the reaction rates of the SHAs with CA were comparable to that of other benchmark alkanolamines, such as DEA and MDEA. One of the advantages of the AMPD-CO_2-H_2O and AEPD-CO_2-H_2O systems is the use of renewable resources that are abundant and inexpensive. Another advantage is the higher capacity for CO_2 capture compared with that of primary and secondary amines.

In conclusion, the enzyme-activated SHAs are promising alternative candidates for capturing CO_2 from various industrial gas streams. The challenge remains in the regeneration of the solvent since CA
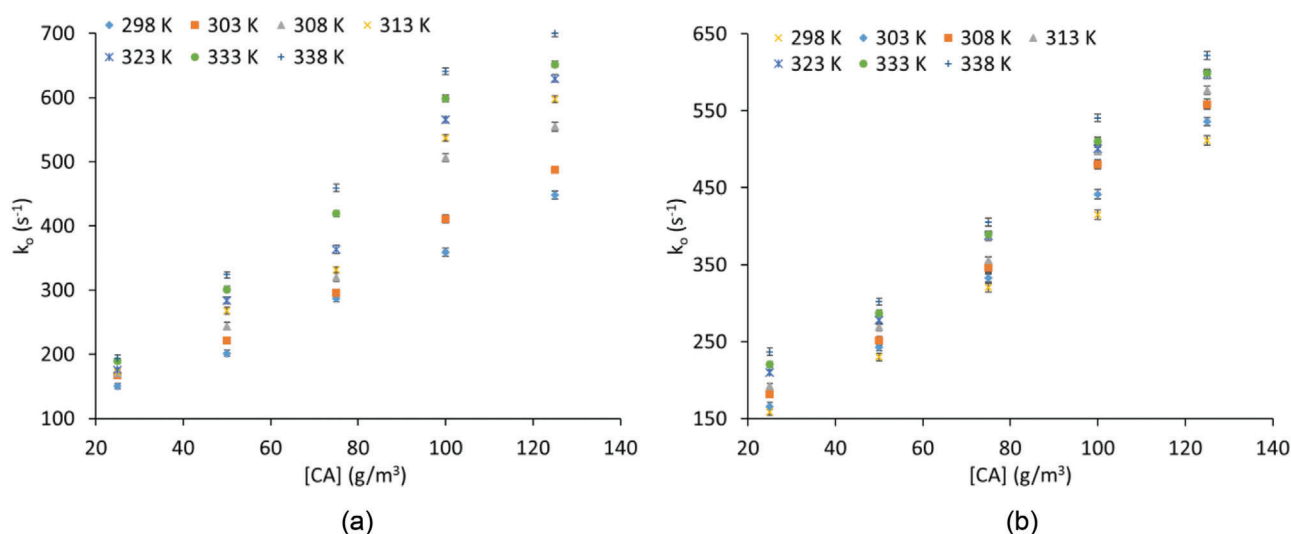
Figure 11. Effect of carbonic anhydrase (CA) concentration on k_o values of CO_2 reacted with 0.5 kmol·m^{-3} AEPD and 0.5 kmol·m^{-3} AMPD at various temperatures. All data are the average of ten replicate experiments, and error bars are the standard deviation of the mean. (a) AEPD-CO_2-H_2O with various amounts of CA. (b) AMPD-CO_2-H_2O with various amounts of CA.

loses its activity at temperatures above 65°C. However, there are novel techniques currently being developed which can enable solvent regeneration at ambient temperatures. As such, the use of bicarbonate separation via precipitation or ultrasound-assisted desorption can be envisaged as appropriate solvent-regeneration steps for CO_2 capture using aqueous SHAs.

Acknowledgements

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