



Regeneration of 2-amino-2-methyl-1-propanol used for carbon dioxide absorption

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Received 6 March 2007; revised 14 May 2007; accepted 20 June 2007

Abstract

To improve the efficiency of the carbon dioxide cycling process and to reduce the regeneration energy consumption, a sterically hindered amine of 2-amino-2-methyl-1-propanol (AMP) was investigated to determine its regeneration behavior as a CO₂ absorbent. The CO₂ absorption and amine regeneration characteristics were experimentally examined under various operating conditions. The regeneration efficiency increased from 86.2% to 98.3% during the temperature range of 358 to 403 K. The most suitable regeneration temperature for AMP was 383 K, in this experiment condition, and the regeneration efficiency of absorption/regeneration runs descended from 98.3% to 94.0%. A number of heat-stable salts (HSS) could cause a reduction in CO₂ absorption capacity and regeneration efficiency. The results indicated that aqueous AMP was easier to regenerate with less loss of absorption capacity than other amines, such as, monoethanolamine (MEA), diethanolamine (DEA), diethylenetriamine (DETA), and *N*-methyldiethanolamine (MDEA).

Key words: carbon dioxide; 2-amino-2-methyl-1-propanol; regeneration efficiency; energy consumption

Introduction

Since the beginning of the industrial age, atmospheric carbon dioxide concentration has increased from 280 to 380 ppmv, which is probably responsible for a large part of the 0.6 K rise in the average global surface temperature over the past century (Service, 2004). Carbon dioxide is widely recognized as a major greenhouse gas produced in large quantity worldwide by many important industries, including fossil-fuel electric power generation, synthetic ammonia industries, steel production, and so on (Gadalla *et al.*, 2005). It is known that an economic process to capture CO₂ from fossil fuels has some difficulties at this time. In this situation, a more efficient CO₂ recovery process is ready to develop. New absorbents have been investigated by many scholars.

It is essential to reduce CO₂ emission, especially from the industrial flue gases, to mitigate the global warming problem (Falkowski *et al.*, 2000). Various technologies, which include absorption by chemical solvents, physical absorption, cryogenic separation, membrane separation, CO₂ fixation by biological or chemical methods, O₂/CO₂ combustion and so on, have been developed for CO₂ removal thus far (Lin and Shyu, 1999). Among these methods, CO₂ absorption/desorption by chemical solvents appears to offer an interesting and practical alternative. In the existing industrial absorption process-

es, alkanolamines, such as, monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), and *N*-methyldiethanolamine (MDEA) are commonly used (Rangwala *et al.*, 1992; Rinker *et al.*, 2000; Frhacker *et al.*, 2003; Ko *et al.*, 2001; de Montigny *et al.*, 2005). In addition, certain sterically hindered amines and polyamines also present interesting properties as absorbents because of their high CO₂ loading capacities (Sartori and Savage, 1983). However, energy consumption is still too expensive for large-scale application, such as, the sequestration of CO₂ from power plants. To reduce the cost of capture of CO₂, finding a solvent that has lower regeneration temperature and the higher regeneration efficiency has been studied by many scholars.

In recent years, various absorption and regeneration methods of CO₂, using different aqueous solutions, have been reported. Chiu and Li (1999) and Zhang *et al.* (2002), measured the heat capacity of aqueous alkanolamine solutions from 293 to 353 K. These researches proved that the sterically hindered amines, such as, 2-amino-2-methyl-1-propanol (AMP), had lower heat capacity. Sakwattanapong (Sakwattanapong *et al.*, 2005) studied the reboiler heat duty for regeneration of aqueous single and blended alkanolamine used in the carbon dioxide. Blended MEA-AMP generally required lower heat energy consumption for solvent regeneration than that of blended MEA-MDEA, and DEA-MDEA, which was attested by Sakwattanapong *et al.* (2005). However, the performance of a single AMP solution was not mentioned in this article.

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Hook (1997) investigated some sterically hindered amines as CO₂ scrubbing compounds. He demonstrated that using sterically hindered amines could improve the efficiency of the carbon dioxide cycling process and reduce amine emissions. Behavior of CO₂ capture plants using regenerable aqueous solution was investigated by Lin and Shyu (1999), Yeh *et al.* (2005), and Huang and Chang (2002). All the researches proved that the sterically hindered amines, such as, AMP, which had not only high CO₂ loading, but also low amine emissions were the potential CO₂ scrubbing solutions. Although these researches have reported the superiority of AMP, but the behavior of regeneration for AMP, the influence of the regeneration temperature, and the regeneration efficiency of AMP, which were not detailed in the open literature thus far. Hence, preliminary regeneration of the saturated AMP solution was performed to compare its regeneration efficiency.

In this study, the absorption of carbon dioxide into the aqueous solution of AMP was experimentally studied using a characterized double stirred-cell contactor. A simulative reboiler was used to study the regeneration of AMP. On the basis of the value of the experiment, the regeneration behavior, such as, temperature, time and pH was investigated. The value of industrial applications and the regeneration efficiency of different single-alkanolamine solutions were compared.

1 Theory

1.1 Absorption reaction mechanism

The reaction mechanism between CO₂ and sterically hindered amines such as AMP has been studied in the previous literature (Sartori and Savage, 1983; Saha and Bandyopadhyay, 1995; Xu *et al.*, 1995; Yoon *et al.*, 2002). The overall reaction of CO₂ with AMP in aqueous solution can be represented as follows:



In addition, it has also been generally adopted that the reaction of CO₂ with primary and secondary alkanolamines can be described by the zwitterion mechanism:



On the basis of this reaction mechanism, the amine, water, and hydroxyl ion can contribute to deprotonation of the zwitterion in aqueous solutions:



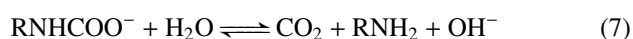
The zwitterion mechanism, originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979), is generally accepted as the reaction mechanism for the

carbamate formation between CO₂ with primary and secondary alkanolamines. The zwitterion mechanism is also found to be suitable for modeling the absorption of CO₂ into the aqueous solution of AMP (Saha and Bandyopadhyay, 1995; Xu *et al.*, 1995).

1.2 Regeneration reaction mechanism

In the regenerable carbamate, the absorption byproducts are thermally decomposed to release CO₂ from the solution of ammonium compounds.

Three potential reactions could be responsible for liberation of CO₂ during the thermal regeneration.



From Reaction (7), it can be seen that carbamate (RNHCOO⁻) transforms into amine and CO₂. The stability of the carbamate determines the enthalpy of dissociation for CO₂ release. AMP has a molecular structure of sterical hindering, and as a result carbamate dissociates easily and exhibits superior degradation resistance in comparison to other alkanolamines.

2 Experimental

2.1 Materials

Reagent grade AMP of 97.0% purity was obtained from Fluka (Switzerland), monoethanolamine (99.0%), and diethanolamine (98.8%) from WLRC (China), diethylenetriamine (99.0%) from SCRC (China), *N*-methyldiethanolamine (98.0%) from Zhejiang University Chemical Co. (China). Distilled water was used for making the amine solutions. The concentration of the aqueous solution was determined by titration with standard HCl, using the methyl orange indicator. A mixture of CO₂ in N₂ was obtained commercially and used as received.

2.2 CO₂ absorption and regeneration experiments

The double stirred-cell absorber with a gas-liquid interface used for the absorption measurements is similar to the literature (Shi *et al.*, 1997; Shi and Zhong, 2005). A schematic diagram of the experimental setup is shown in Fig.1a. The absorption chamber is a glass cylinder of 8.0 cm inner diameter with a length of 15.5 cm. The cylinder is sandwiched between two stainless steel flanges with ends sealed by rubber O-rings. Cooling or heating water is supplied to the jacket and recycled to a constant-temperature circulating bath. The temperature of absorption was controlled with a deviation of ± 0.2 K. The inlet concentration of CO₂ was about 15%.

Regeneration experiments (Fig.1b) measured the regeneration temperature and regeneration time when stirred in an oil bath. Interference from the evaporation of water was prevented by an efficient condenser system. The

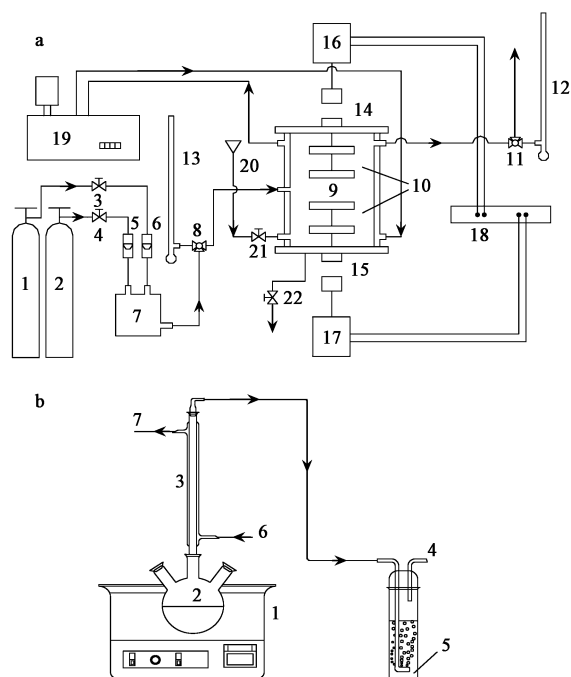


Fig. 1 Experimental apparatus for determining CO₂ absorption (a) and regeneration (b). In (a): (1, 2) gas feed; (3, 4, 21, 22) gas/liquid controller; (5, 6) rotameter; (7) buffer bottle; (8, 11) three throw tap; (9) stirred-cell absorber; (10) impellers; (12, 13) soap-film meter; (14, 15) magnetic gearing; (16, 17) variable-speed motor; (18) stirrer-speed controller; (19) constant-temperature circulating bath; (20) liquid feed, in (b): (1) magnetic stirring apparatus with oil bath; (2) flask; (3) condenser tube; (4) suction bottle; (5) Ca(OH)₂; (6, 7) condensation water.

lean of calefaction was 9–10 K/min. The temperature of regeneration was controlled with a deviation of ± 1.0 K. Deposits of calcium carbonate had been found in the suction bottle, which filled saturated calcium hydroxide when the carbon dioxide desorption reaction occurred. Carbon dioxide absorption/desorption cycling experiments were performed, incorporating at least three absorptions and two desorptions sequentially.

The volumetric flow rate of CO₂ was measured by a soap-film meter. The measured flow rate was always corrected for vapor pressure of water, as a function of temperature. The CO₂ concentrations of the inlet and outlet gas were measured with gas chromatography (GC-7890 II, Techcomp, Shanghai). The partial pressure of CO₂ in the gas streams was determined by subtracting the partial pressure of water from the total pressure and multiplying the percentage of CO₂. The absorption rate of CO₂ into the aqueous solution of AMP could be calculated as follows:

$$N = \frac{P_1 \times (V_{in} - V_{out})}{A \times R \times T} \quad (10)$$

The regeneration efficiency can be calculated as:

$$\eta = \frac{L'}{L} \times 100\% \quad (11)$$

where, N is the absorption rate of CO₂ per unit interfacial area (kmol/(m²·s)); P_1 is the partial pressure of CO₂ (kPa); V_{in} and V_{out} were the volumetric flow rate of inlet and exit CO₂ (m³/s); R is ideal gas law constant; A is gas-liquid

surface area (m²); T is absorption temperature (K); η is the regeneration efficiency; L is the saturated absorption capacity (mol); L' is saturated absorption capacity of regeneration barren solution (mol).

All the absorption experiments were conducted with a temperature of 303 K, gas mixture of 15% CO₂ and 85% N₂, and an aqueous AMP concentration range of 1.0 kmol/m³. The stirring speed for gas phase was 250 r/min. Regeneration experiments were run with regeneration temperatures of 358 K, 368 K, 378 K, 383 K, 393 K, and 403 K, respectively. Each regeneration run lasted 2–3 h. After regeneration, the amine solution was adjusted at the same concentration as the first absorption, which was 1.0 kmol/m³ and a new CO₂ absorption run was repeated. The absorption/regeneration cycle was repeated six times at least.

The concentration of different single-alkanolamine solutions was 1.0 kmol/m³. All experiments that were investigated to determine regeneration behavior of different single-alkanolamine solutions, were run at a regeneration temperature of 383 K. Each regeneration run lasted 1.5 h. The absorption/regeneration cycle was repeated thrice. The efficiency of different amine solutions were compared using the same experiment conditions.

3 Results and discussion

3.1 Regeneration of CO₂ saturated AMP solutions

The results presented in Fig.2 clearly demonstrate that the regeneration efficiency is exceedingly sensitive to changes in regeneration temperature. The regeneration efficiency increases as the regeneration temperature increases. It is observed that the regeneration efficiency increases from 86.2%–98.3% when the regeneration temperature is aggrandized from 358 to 383 K. However, the increase in the regeneration rises very slightly above the regeneration temperature value of 383 K. Nevertheless, there is a decrease in the CO₂ generating period with an increase in the regeneration temperature. As the temperature changes from 358 to 383 K, the CO₂ generating period decreases from 166 to 44 min. The profile becomes slightly curved when the regeneration temperature reaches 383 K. Energy consumption for solvent regeneration is an important parameter. The temperature of 383 K is the most appropriate for regeneration because of higher regeneration efficiency and the less regeneration time.

The increase in the amount of OH⁻ in the solution, as regeneration temperature rises, can be illustrated in terms of the pH change in Fig.3. When the amount of OH⁻ increases, because of the escalating capability of its reaction with CO₂, the regeneration efficiency increases. This phenomenon demonstrates the effect of regeneration temperature on regeneration efficiency.

3.2 Carbon dioxide desorption and cycling ability of AMP solutions

Both the absorption rate and absorption capacity have similar curves for all six cycles. This is shown in Fig.4. The regeneration efficiency throughout the whole absorp-

tion/regeneration process descends from 98.3%–94.0% (Fig.5a). It is of interest to note that there is only 4.4% decrease in the total CO₂ absorption capacity between the first and the sixth cycles. A number of heat-stable salts (HSS) that are essentially the reaction products of alkanolamines and acid gas are nonregenerable under solvent regeneration conditions (Winyu *et al.*, 2006). The accumulation of heat-stable salts not only causes a reduction in CO₂ absorption capacity and regeneration efficiency, but

also claims to cause a significant increase in the system corrosiveness.

From the first to the sixth cycle, the change in the pH is shown in Fig.5b. The pH after regenerating in the whole process has a tiny 1.8% decrease. The pH ranges from 11.1 to 10.1 in the whole cycle. This phenomenon reflects the process of the absorption/regeneration cycle. The pH also affects the formation of the carbamate and dicarbamate. The regeneration efficiency is determined by

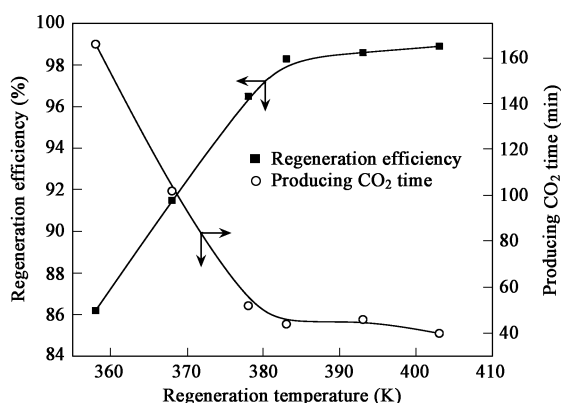


Fig. 2 Effect of regeneration temperature on regeneration efficiency and producing CO₂ time.

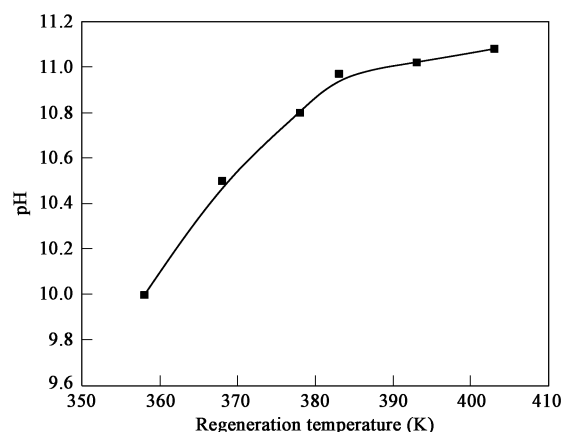


Fig. 3 Relationship between regeneration temperature and pH.

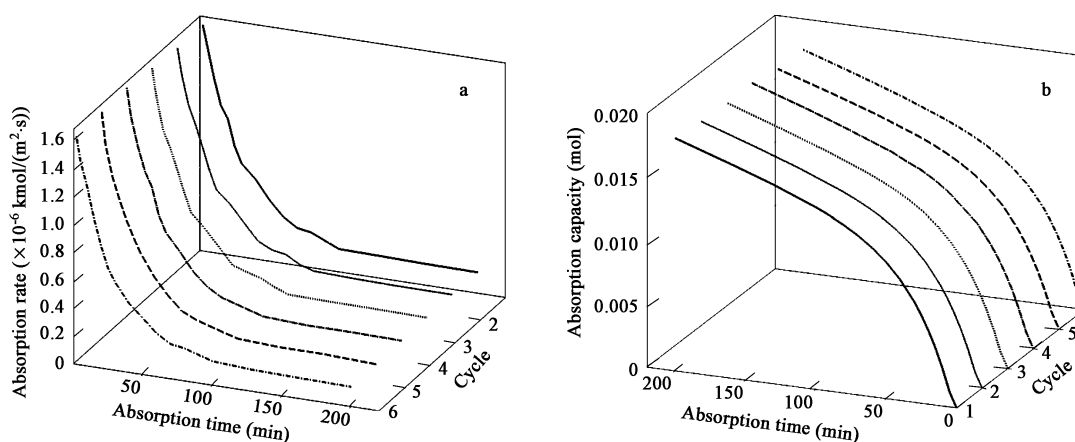


Fig. 4 Absorption rate of CO₂ into aqueous AMP (a); absorption capacity of CO₂ into aqueous AMP (b).

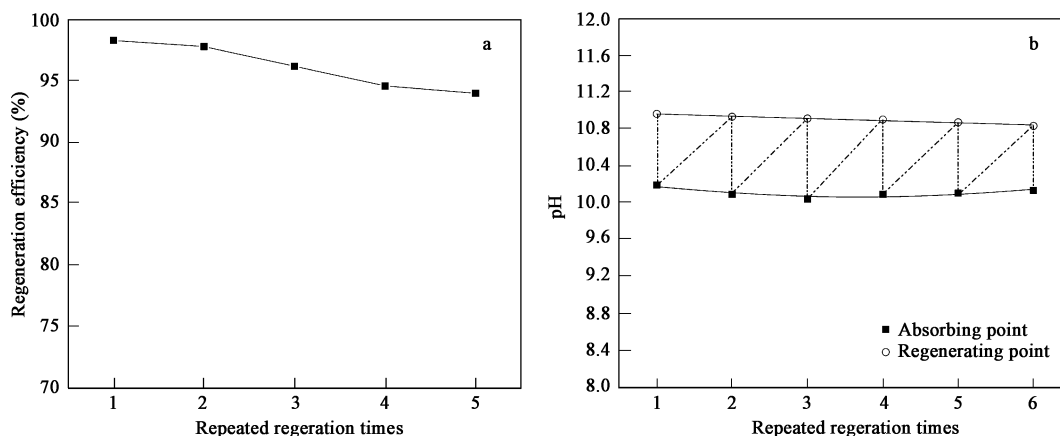


Fig. 5 Absorption efficiency change (a) and pH change (b) defines absorption/regeneration cycle.

parameters, such as, amine character, solution pH, and chemical stability of the carbamate. The change in pH proves the decrease in regeneration efficiency in another way.

3.3 Regeneration efficiency of different single-alkanolamine solutions

The corresponding regeneration efficiency for each amine is presented in Fig.6. It is apparent that MEA gave the lowest regeneration efficiency of 88.3% in the first cycle, whereas, AMP offered the highest performance of 98.3%. With this figure, the regeneration performance can be ranked in the following order: AMP > MDEA > DETA > DEA > MEA. This performance order is similar to that of the regeneration performance in the second cycle. The regeneration efficiency of MEA has the most degressive proportion of 12.1% in the second cycle. However, AMP maintains the highest regeneration efficiency of 97.8%. This is because AMP has a molecular structure of sterical hindering, which results in the sterically hindered amines being easily regenerated and exhibits superior degradation resistance, in comparison to other alkanolamines. The order of reboiler heat duty of the amines reported by Sakwattanapong *et al.* (2005) is AMP > MDEA > DEA > MEA, which is the same as the order of regeneration

efficiency. Therefore, AMP will become a potential competitor against conventional absorption solvents because of the better behavior of energy consumption.

3.4 Absorption of carbon dioxide by different single-alkanolamine solutions

Figure 7 illustrates the results of absorption rate and absorption capacity of CO₂ into aqueous amines, respectively. It shows that the absorption rates of MEA, DEA, DETA, and AMP are obviously higher than MDEA. The order of absorption rate of different amines is DETA > MEA > DEA > AMP > MDEA at the beginning of the reaction, which confirms the results of Sheng and Ching (1999), Robert (1997), and Adisorn and Amornvadee (2003). However, the order of absorption capacity of the different amines is DETA > AMP > MEA > DEA > MDEA. The absorption capacity of AMP is about twice as much as that of MEA. It is suggested that because of low stability constants, the hindered amine carbamates readily undergo hydrolysis, forming bicarbonate and releasing free amine. The free amine molecule again reacts with CO₂, thus leading to an overall stoichiometric loading capacity of 1 mol of CO₂ per mol of amine, with an appreciable rate of absorption (Sartori and Savage, 1983). Thus, the equilibrium capacity of AMP for CO₂ is much higher than that of MEA.

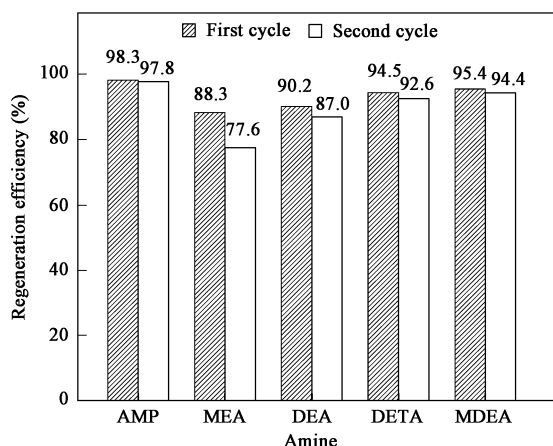


Fig. 6 Single-alkanolamine solution regeneration efficiency. Alkanolamine concentration 1.0 kmol/m³; regeneration temperature 383 K.

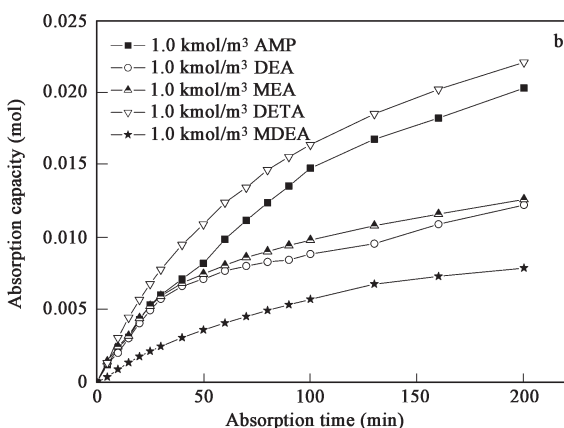
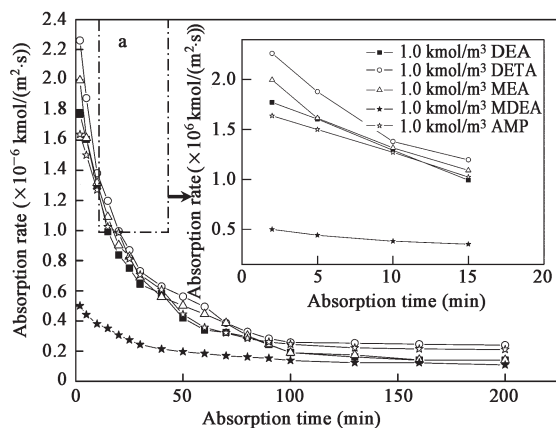


Fig. 7 Absorption rate (a) and capacity (b) of CO₂ for different single-alkanolamine solutions.

4 Conclusions

Under the experimental condition, solutions of the sterically hindered AMP show enhanced CO₂ absorption capacities and regeneration efficiencies in comparison to other amines. The regeneration efficiency increases from 86.2%–98.3% when the regeneration temperature is aggrandized from 358 to 383 K. The most appropriate regeneration temperature is 383 K. After six absorption/regeneration cycles, the regeneration efficiency still has a high value of 94.0%.

Although all the amines investigated are found to successfully cycle CO₂, the regeneration performance can be ranked in the following order: AMP > MDEA > DETA > DEA > MEA. The effect of sterical hindering, for example,

AMP makes the carbamates less stable, compared to other primary alkanolamines such as MEA, facilitating formation of bicarbonates through reversion of carbamate. The order of absorption capacity of different amines is DETA > AMP > MEA > DEA > MDEA. The absorption rate of CO₂ into aqueous AMP is not much more ascendant than others, whereas, the higher absorption capacity makes it more suitable for CO₂ absorbents. AMP may be more suited for application in industrial processes, where CO₂ partial pressures are higher, because it has less reboiler heat energy for regeneration, higher regeneration efficiency, and higher absorption capacity.

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