

Comparison of Carbon Dioxide Absorption in Aqueous MEA, DEA, TEA, and AMP Solutions

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The separation and capture process of carbon dioxide from power plants is garnering interest as a method to reduce greenhouse gas emissions. In this study, aqueous alkanolamine solutions were studied as absorbents for CO₂ capture. The solubility of CO₂ in aqueous alkanolamine solutions was investigated with a continuous stirred reactor at 313, 333 and 353 K. Also, the heat of absorption ($-\Delta H_{\text{abs}}$) between the absorbent and CO₂ molecules was measured with a differential reaction calorimeter (DRC) at 298 K. The solubility and heat of absorption were determined at slightly higher than atmospheric pressure. The enthalpies of CO₂ absorption in monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and 2-amino-2-methyl-1-propanol (AMP) were 88.91, 70.44, 44.72, and 63.95, respectively. This investigation showed that the heat of absorption is directly related to the quantity of heat for absorbent regeneration, and is dependent on amine type and CO₂ loading.

Key Words : Carbon dioxide, Absorption, Alkanolamine, Heat of reaction

Introduction

As the phenomenon of global warming has been recognized as a significant environmental problem by the worldwide scientific community, great attention has been concentrated on the reduction of carbon dioxide (CO₂) emissions. These emissions are known to be a primary cause of global warming. The consumption of fossil fuels is directly correlated with the carbon dioxide emissions; and the development of technology to reduce carbon dioxide emissions from industrial and power plants is the most important step to take for reducing these emissions.

Various methods for CO₂ separation and capture are being developed; and the post-combustion capture process using absorption-desorption has been determined to be the appropriate approach among currently available methods.^{1,2} Chemical absorption using an aqueous alkanolamine solution is one of the most mature technologies for CO₂ capture. The absorption processes use the increased CO₂ mass transfer through chemical reactions (such as direct reaction between an aqueous solution and CO₂ or acid-base neutralization reactions that form ionic intermediates).³⁻⁵ Alkanolamines used in this process are classified into primary amines, secondary amines, and tertiary amines based on the number of substituents for the amine group. An aqueous solution of primary amine, monoethanolamine (MEA) has been extensively used because of the rapid reaction rate and low cost of the raw material. However, methods for the MEA solution have disadvantages including high capital costs and high energy requirement for regeneration of the solvent.^{6,7} Therefore, the development of a process to compensate for these disadvantages is a vital area of study; and the selection of a suitable absorbent for carbon dioxide capture is the most

important factor in these studies.

The process to capture carbon dioxide using a chemical absorbent consists of an absorber and a stripper, and the solubility of carbon dioxide in aqueous alkanolamine solutions; and the heat of absorption are one of the most important data for the design of the CO₂ removal process. It is possible to reduce the construction cost of the entire process when an absorbent that has a high CO₂ capacity, high absorption rate and low heat of absorption is used for CO₂ capture. The heat of absorption is related to the amount of steam required in the stage of regeneration. The energy consumed to desorb carbon dioxide from the absorbent is very important, as it accounts for at least half of the operating cost. The reaction between the absorbent and carbon dioxide occurring in the stripper is the reverse reaction occurring in the absorber. Therefore, the heat generated by the absorption of CO₂ molecules in the absorbent is the similar to the quantity of heat for desorption of CO₂ molecules. The heat of absorption provides useful data in designing the reboiler.

Many researchers shown below have studied the heat of absorption of CO₂ in aqueous alkanolamine solutions. Mathonat *et al.*⁸ measured the enthalpy of CO₂ in an aqueous methyldiethanolamine (MDEA) solution using a calorimeter at 313-393 K. Arcis *et al.*⁹ measured the enthalpy of CO₂ in an aqueous AMP solution at 322 K. Kim *et al.*¹⁰ calculated the enthalpy of CO₂ in MEA or MDEA from the equilibrium constants of each of the key reactions using the Gibbs-Helmholtz equation. McCann *et al.*¹¹ provided the prediction results of the enthalpy of CO₂ in MEA, diethanolamine (DEA), MDEA, and 2-amino-2-methyl-1-propanol (AMP). However, it is difficult to compare the value of enthalpy among these absorbents because the concentration of amines

and reaction temperature were different.

In this study, CO₂ absorption experiments using aqueous alkanolamine solutions with different structures were conducted to examine the absorption characteristics of these absorbents. Furthermore, the effect of reaction temperature on the absorption characteristics was examined.

Experimental

Measurement of Solubility. MEA (> 99%), DEA (> 98%), TEA (> 99%) and AMP (> 95%) were obtained from Sigma-Aldrich and tested in an absorption apparatus. 30 wt % aqueous amine solutions were prepared by mixing amine and deionized water. The apparatus for measuring the CO₂ solubility is shown in Figure 1. The reactor is made of stainless steel. The internal volume of the reactor was 2 L, and 1 L of a fresh absorbent was injected into the reactor. T-type thermocouples were used for measuring the temperatures of CO₂ and absorbent. A water circulating bath was used to maintain a constant temperature. In order to remove impurities in the reactor before conducting the experiments, saturated N₂ gas was injected for one hour. The gas inlet was a bubbler type and an agitator was used to increase the contact area between the liquid phase and CO₂ gas phase.

30 mol % CO₂ containing N₂ was injected at a rate of 1 L/min when the temperature in the reactor reached the experimental temperature. A mass flow controller (MFC) was used to maintain a certain flow rate during the injection of CO₂. Gas chromatography (GC) was used to analyze the concentration of CO₂ at the outlet of the reactor. A Porapak-Q column (0.32 m by 1.83 m, Supelco Inc.) and TCD detector were installed in the GC. All the experiments were conducted over a temperature range of 313 to 353 K and at atmospheric pressure (1 atm). CO₂ loading was calculated by integrating differences between the concentrations of injected CO₂ and the concentrations of emitted CO₂. All the

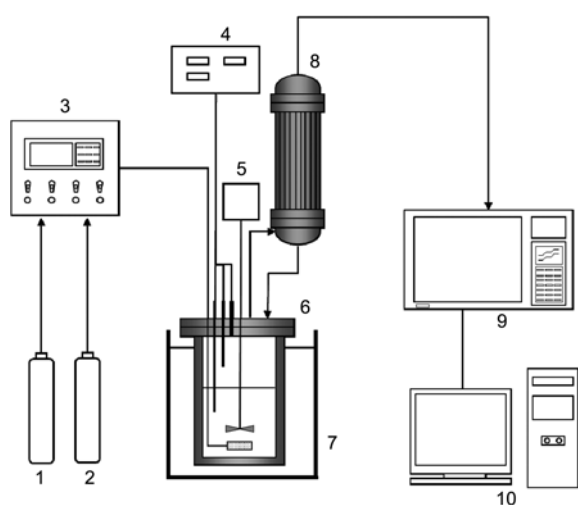


Figure 1. Experimental set-up for measuring the CO₂ solubility. 1. CO₂ gas; 2. N₂ gas; 3. Gas mixer; 4. Temperature and pressure indicator; 5. Motor; 6. Reactor; 7. Water bath; 8. Condenser; 9. Gas chromatography (GC); 10. Recorder.

absorbents used in the experiments reached equilibrium within five hours upon completion of the reactions between CO₂ and the absorbents. The amount of the CO₂ before being injected into the reactor and the amount of the CO₂ emitted after reactions were calculated by applying the ideal gas equation. The CO₂ dissolved in the absorbent was determined through Eq. (1).

$$n_{abs,CO_2} = \frac{(P_{CO_2,in} \cdot V_{CO_2,in}) - (P_{CO_2,out} \cdot V_{CO_2,out})}{R \cdot T} \quad (1)$$

The overall mole of CO₂ absorbed in the absorbent can be calculated by integration and the CO₂ loading can be calculated through Eq. (2). CO₂ loading is defined as mole of CO₂ absorbed per mole of amine.

$$CO_2 \text{ loading} = \frac{\text{absorbed moles of } CO_2}{\text{moles of absorbent}} \quad (2)$$

An increase in the CO₂ loading of an absorbent implies that the solubility of CO₂ is increased under the same absorption conditions.

Measurement of Heat of Absorption. The differential reaction calorimeter (DRC) was used to measure the heat of absorption ($-\Delta H_{abs}$). The amount of heat generated by reactions between the absorbent and CO₂ was measured in real time. Accordingly, the temperature difference (ΔT) occurring until equilibrium between the gas and liquid phases was drawn through integration as a function of time. However, this equipment has the disadvantage of being unable to measure the effect of reflux.¹² The absorbent may be evaporated at high temperatures and the evaporated solution is refluxed into the reactor by a condenser. Therefore, the experiments were conducted at room temperature and atmospheric pressure conditions.

A schematic diagram of DRC for measuring the heat of absorption is shown in Figure 2. The DRC apparatus (SETARAM Co.) consists of two glass vessels, a measurement reactor and a reference reactor. The reactors are in a dual jacket structure for isothermal analysis and temperature can be maintained with the circulated water. The DRC measurement

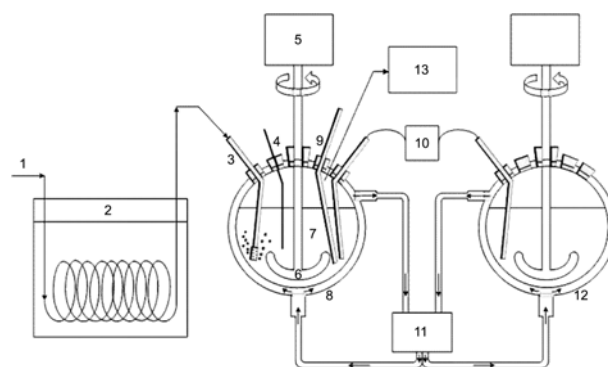


Figure 2. Schematic diagram of DRC apparatus. 1. CO₂/N₂ gases; 2. Water bath; 3. Inlet gas port; 4. Optional probe; 5. Motor; 6. Impeller; 7. Measurement reactor; 8. Thermostatic jacket; 9. Calibration probe; 10. Temperature and ΔT measurements; 11. Thermostat; 12. Reference reactor; 13. Gas chromatography (GC).

used isothermal methods and the temperature differences (ΔT) between the measurement reactor and the reference reactor. The absorbent injected into the reactor reacts with the CO_2 injected through the bubble type gas inlet to trigger exothermic reactions. The heat of absorption was measured by integrating the temperature difference (ΔT) curve of the quantities of generated heat. The apparatus was designed to record the temperatures of the reference reactor, which were maintained at the initial state before the reaction. Therefore, the measurement reactor into which CO_2 was injected during the experiment would not be affected by external temperature changes. The absorbents were considered to have reached equilibrium at the time when there was no temperature difference between the two reactors. This is expressed in Eq. (3) as follows:

$$\Delta T = (T_{\text{measurement}} - T_{\text{reference}}) = \text{constant} \quad (3)$$

However, the experiments were conducted at low temperatures (298 K) because the DRC apparatus was not designed to record the effect of reflux. The two reactors had the same volumes and the same values for parameters that impact our experiment (atmospheric pressure, reaction temperature, stirring speed, and the amounts of solutions injected). All the absorbents (30 wt % of aqueous amine solution) were injected in a quantity of 100 g and CO_2 (30 mol % containing N_2) was injected at 100 sccm using a MFC to ensure a constant flow rate.

In the absorption/regeneration process using an aqueous alkanolamine solution, the solution should be regenerated in order to achieve continuous process. The regeneration energy indicates the thermal energy necessary to remove binding between amine and carbon dioxide. The entire equation can be explained as the sum of three conditions as follows.¹

$$q_{\text{reg}} = q_{\text{sens}} + q_{\text{vap}, \text{H}_2\text{O}} + q_{\text{abs}, \text{CO}_2} \quad (4)$$

Where, q_{sens} means the sensible heat, defined as the quantity of heat necessary to increase the temperature of the absorbent input into the stripper to the regeneration temperature. In general, regeneration occurs at high temperatures of at least 373 K and the solution evaporates as a result. Therefore, evaporation heat ($q_{\text{vap}, \text{H}_2\text{O}}$) is generated in addition to regeneration of the absorbent. When the temperature of the solution reaches the regeneration temperature, the binding between the absorbent and CO_2 molecule is broken. This reaction occurs as a reverse reaction to the absorption reaction. Therefore, the regeneration energy and absorption energy of CO_2 are similar, and the quantity of heat necessary for regeneration can be predicted through the heat of absorption ($q_{\text{abs}, \text{CO}_2}$). In this study, it can be seen that the decreases in the right-hand side resulting from the heat of absorption, as shown in Eq. (4), indicate decreases in the requirement of overall reboiler heat duty.

Results and Discussion

Solubility of CO_2 . Experiments for measuring the solubility of CO_2 were performed at temperatures ranging from

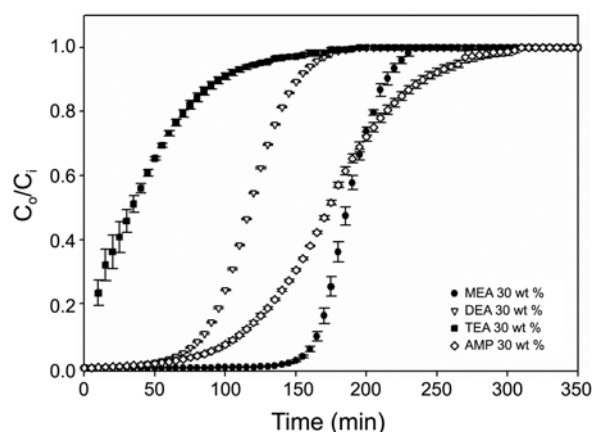


Figure 3. CO_2 absorption curves of the 30 wt % aqueous amine solutions at 313 K.

313 to 353 K. The range of this temperature is the temperature of the exhaust gases from actual combustion. Figures 3-5 show the curves of the CO_2 absorption. The plots and error bars represent the experimental data and standard errors in the Figures 3-5. The ranges of standard deviation and standard error for C_0/C_1 are 0.00-0.09 and 0.00-0.05 at the temperature ranges from 313 to 353 K.

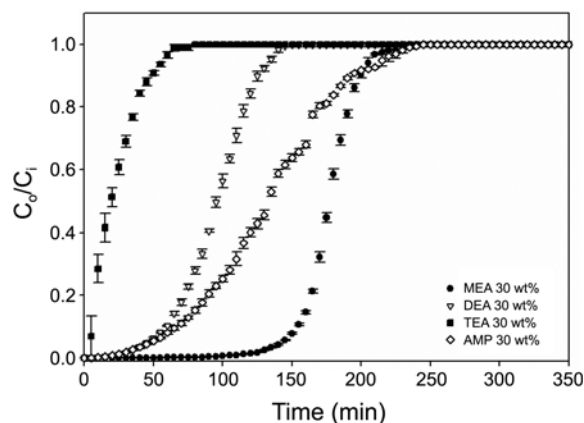


Figure 4. CO_2 absorption curves of the 30 wt % aqueous amine solutions at 333 K.

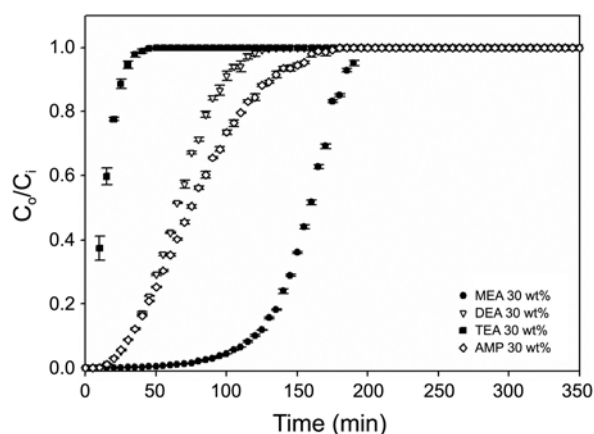


Figure 5. CO_2 absorption curves of the 30 wt % aqueous amine solutions at 353 K.

Table 1. Solubilities of CO₂ in the aqueous amine solutions at T = 313, 333, 353 K and P = 1.15 bar

Temperature (K)	CO ₂ loading (mol CO ₂ /mol amine) ^a			
	MEA 30	DEA 30	TEA 30	AMP 30
	wt %	wt %	wt %	wt %
313	0.469	0.502	0.266	0.626
333	0.426	0.404	0.141	0.466
353	0.384	0.279	0.090	0.285

^aThe ranges of standard deviation and standard error for CO₂ loading are 0.001-0.008 and 0.001-0.005 at the temperature ranges from 313 to 353 K.

The curves show the ratios of the initial CO₂ concentrations before reactions (C_i) to the emitted CO₂ concentrations after reactions (C_o) as a function of time. The slopes of the graphs of MEA and DEA rapidly increased at CO₂ loadings higher than a certain value, whereas TEA and AMP yielded curves with gentle slopes. These results show that the carbamate reactions, which major reactions of primary and secondary amines, occur quickly, while the unstable carbamate reactions and subsequent bicarbonate formation that appear in tertiary and sterically hindered amines occur slowly.

Table 1 presents the CO₂ loading of the aqueous amine solutions. The experiments for all absorbents were conducted more than 3 times to obtain reliable values of CO₂ loading. In general, CO₂ loading is defined as the mole of CO₂ absorbed per one mole of amine. All the absorbents had high CO₂ loadings at 313 K and AMP showed the largest value of CO₂ loading among the absorbents.

Table 2 shows the molecular structures of the species in the amine solutions. The reactions represented by Eqs. (5) and (6) occur in the case of primary and secondary alkanolamines.



The reaction between tertiary amines and CO₂ is represented by Eq. (7). TEA, a tertiary amine, cannot directly react with CO₂. TEA acts as a base catalyst to form hydroxyl ions.



It can be seen that, in the case of MEA, two moles of amines can absorb one mole of CO₂; therefore, the theoretical CO₂ loading of MEA is 0.5 (mol CO₂/mol amine). This result is also very close to the value measured in this study, 0.47 (mol CO₂/mol amine) at 313 K. On the other hand, AMP, which shows the highest loadings at 313 and 333 K, is restricted in spins due to the structure of alkyl groups, which are large in volume. For this reason, AMP formed unstable carbamate and hydrolysis easily occurred, leading to the formation of free amines and bicarbonate ions. Therefore, AMP had higher CO₂ loadings compared to those for unhindered primary and secondary amines.

From these results, it can be identified that along with temperature changes, carbamate which is the final product of

Table 2. Structures of the species in the CO₂ loaded amine solutions

Absorbent	Molecular structure of species	
	Free amine	Carbamate, bicarbonate/carbonate
MEA		
DEA		
TEA		
AMP		

Table 3. Heat of absorption (-ΔH_{abs}) and quantity of heat (-Q) of CO₂ in aqueous amine solutions at T = 298 K and P = 1 bar

Absorbent	CO ₂ loading	-ΔH _{abs}		-Q
	(mol CO ₂ /mol amine)	(kJ/mol CO ₂)	(kJ/g CO ₂)	(kJ)
MEA 30 wt %	0.565	88.91	2.02	24.63
DEA 30 wt %	0.658	70.44	1.60	13.24
TEA 30 wt %	0.486	44.72	1.02	4.38
AMP 30 wt %	0.862	63.95	1.45	18.55

CO₂ reaction is formed more stably compared to bicarbonate. If the characteristics of the regeneration of the absorbents assumed through these results, it is considered that as the reaction rate increases, the formation of bicarbonate will become unstable and the energy consumed in regeneration will become smaller. This leads to more favorable regeneration characteristics.

Heat of Absorption. Eq. (4) provided above refers to the entire quantity of heat generated from reactions between absorbent and CO₂. The CO₂ desorption energy and binding energy of each absorbent have the similar value. As for the heat of absorption, the enthalpy of the standard state (ΔH^o, heat of reaction) was obtained by calculating the heat of absorption generated per one mole of CO₂. The heat of absorption depends on the CO₂ loading and amine structure and is not greatly affected by pressure or temperature.^{2,12-14}

Table 3 shows the quantities of heat (-Q) and the heat of absorption (-ΔH_{abs}) generated in aqueous alkanolamine solutions measured at 298 K. Although MEA is considered the most advantageous absorbent in the absorption process, the heat of absorption of MEA was shown to be the highest at 88.91 kJ/mol CO₂. The MEA result is in agreement with the result of a previous study.¹⁵ On the other hand, TEA, a tertiary amine, that was shown to have the lowest absorption rate, presented the lowest heat of absorption, 44.71 kJ/mol

CO₂, while AMP showed 63.95 kJ/mol CO₂. The heat of absorption was shown to be in the order of precedence of TEA < AMP < DEA < MEA. However, it is difficult to compare these absorbents of heat of absorption because their CO₂ loadings are different.^{9,16} In the case of sterically hindered amines and tertiary amines, CO₂ molecules are more easily desorbed due to the unstable binding of carbamate. A notable point in the above results is that the results of the measurement of the heat of absorption do not show the same tendency as the absorption properties of the absorbents. Therefore, the heat of absorption and CO₂ solubility should be considered together to select an absorbent suitable for CO₂ capture.

Conclusion

In this study, the aqueous alkanolamine solutions with different structural characteristics were selected for the purpose of studying their absorption characteristics. Experiments were performed at a range of absorption temperatures (313 to 353 K) with the aim of finding the temperatures that have the greatest effect on CO₂ loading and provide optimum temperature conditions. All the experimental absorbents showed higher CO₂ loadings with lower reaction temperature. While a primary amine, MEA, and a secondary amine, DEA, showed CO₂ loading limited to 0.6 (mol CO₂/mol amine), a sterically hindered amine, AMP showed higher CO₂ loading. A tertiary amine, TEA, showed lower CO₂ loading compared to the other absorbents in all temperature ranges. MEA maintained C_o/C_i at a low value for a long time compared to the other absorbents. All absorbents except for TEA maintained C_o/C_i at low values when the reaction temperatures were lower. Therefore, it could be seen that the reaction temperatures were proportional to the reaction rate.

The regeneration energy of the absorbents was directly related with the heat of reaction and showed higher values

when the binding force between amines and CO₂ molecules was larger. Therefore, absorbents that formed carbamate required larger quantities of heat, and the absorption heats of the MEA and DEA were higher than those of TEA and AMP at high CO₂ loading.

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