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Analysis of the heat of reaction and regeneration in alkanolamine-CO_2 system

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Abstract−The estimation of regeneration heat of absorbent is important because it is a key factor that has an effect on the process efficiency. In this study, thermal stability and regeneration heat of aqueous amine solutions such as monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), N-methyldiethanolamine (MDEA), and 1,8-diamino-p-menthane (KIER-C3) were investigated by using TGA-DSC analysis. The thermal characteristics of the fresh and CO_2 rich amine solutions were estimated. The CO_2 rich amine solutions were obtained by VLE experiments at T=40 °C. The regeneration heat of aqueous MEA solution was 76.991-66.707 kJ/mol-CO_2, which is similar to heat of absorption. The reproducibility of the results was obtained. The regeneration heat of aqueous KIER-C3 20 wt% solution (1.68 M) was lower than that of aqueous MEA 30 wt% solution (4.91 M). Therefore, the KIER-C3 can be used as an effective absorbent for acid gas removal.

Key words: Absorption, Carbon Dioxide, Heat of Regeneration

INTRODUCTION

Capturing carbon dioxide (CO_2) from flue gas is important to control the global warming problem. Chemical absorption, physical adsorption, cryogenic methods, and membrane separation have been used to separate CO_2 from the flue gas of conventional fossil fuel-fired power plants and industrial process plants [1]. The absorption of acid gases by chemical solvents is the most mature method and suitable for large volume of gas treating. Alkanolamines have been extensively used for seven decades for the removal of acid gases (CO_2, H_2S, etc.). The major alkanolamine absorbents in industrial processes are monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP), *N*-methyldiethanolamine (MDEA) [2]. The factors that are considered in selection of the absorbents are absorption capacity, reactionkinetics, and regenerative potential and facility. Primary and secondary alkanolamines such as MEA and DEA have high reactivity due to the formation of stable carbamates. Especially, primary alkanolamine, MEA reacts rapidly with CO_2, whereas it has the limitation of low CO_2 absorption capacity (equilibrium absorption of 0.5 mole CO_2 per 1 mole of MEA). Furthermore, MEA has a high operation cost because of high heat of regeneration [3]. However, tertiary alkanolamine, MDEA can reach high CO_2 absorption capacity (equilibrium absorption of 1 mole CO_2 per 1 mole of MDEA). MDEA is cost-effective in comparison toMEA because the heat of regeneration of MDEA is lower than that of MEA. Absorbents for removal of CO_2 must be recycled because the large amount of absorbent is used in the CO_2 absorption process. Most regeneration processes using chemical solvent consume 50-80% of total energy in regeneration of solvent. Therefore, development of absorbents havinglow regeneration energy will be needed for reducing energy consumption.

There are two trends in the capture of CO_2 from flue gases by using absorbent. The first is to address the inefficiencies of the absorption process of the conventional amine and identify ways to improve it. The second is to develop alternative CO_2 capture technologies that have the potential for reducing the cost. Recently, the use of blended amines as a solution of two or more amines in varying concentration has been shown to produce absorbents with excellent absorption characteristics, a low energy requirement. Blending of primary and tertiary amines (such as mixtures of MEA and MDEA) or secondary and tertiary amines (such as mixtures of DEA and MDEA), which will improveits absorption capacity and reaction rate of each absorbent. Absorption rates of CO_2 into aqueous blends of MDEA and MEA were studied by Glasscock et al. [4], Rangwala et al. [5], Hagewiesche et al. [6], and Mandal et al. [7]. The researchers showed that the addition of a small amount of MEA to an aqueous MDEA solution significantly increased the CO_2 absorption rate.

The sterically hindered amine, AMP, does not form stable carbamate, bicarbonate and carbonate ions may be present in the solution in larger amounts than the carbamate ions. AMP has the same high absorption capacity for CO_2, but has a higher rate constant for reaction with CO_2, compared to MDEA. Therefore, aqueous blends of AMP and MEA may be an attractive new solvent for aqueous blends of MDEA and MEA for the gas-treating processes. In addition, the aqueous methyldiethanolamine (MDEA)/piperazine (PZ) has been investigated as an alternative to aqueous MEA and aqueous K^+/PZ [8].

The development of efficient absorbent is aimed at enhancement of absorption capacity, absorption rate, corrosion- and degradation-resistance to date. However, as anefficient approach method considering more cost efficiency, it is required to develop multi-functional high efficient absorbent and process design considering low power system, compact of facility and energy saving. The main factors considering the development of new multi-functional absorbent are reactivity for flue gas, absorption capacity, regeneration heat

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and so on. Among them, regeneration energy, reactivity and absorption capacity are main parameters for selection of absorbents in CO_2 capturing processes. In this study, a cyclic diamine, 1,8-diamino-p-menthane (KIER-C3) is used in CO_2 absorption as new absorbent. The regeneration energy was measured in alkanolamine-CO_2 system.

THEORETICAL BACKGROUND

1. Absorption Reaction Mechanism

The main reactions occurring in the CO_2-alkanolamine-water system can be found in a number of publications. The zwitterion mechanism originally proposed by Caplow [9] and reintroduced by Danckwerts [10] is generally accepted as the reaction mechanism for aqueous MEA and AMP solutions. The mechanism consists of two steps:

$$R_1NH_2+CO_2 \leftrightarrow R_1NH_2^+COO^- \tag{1}$$

$$R_1NH_2^+COO^-+R_1NH_2 \leftrightarrow R_1NHCOO^-+R_1NH_3^+ \tag{2}$$

Eqs. (1) and (2) mean that 1 mole of CO_2 is absorbed per 1 mole of amine. MEA reacts with CO_2 to form carbamate (R_1NHCOO^-). However, a certain amount of carbamate hydrolysis occurs with all amines so that even with MEA the CO_2 loading may exceed the stoichiometry (0.5 mol CO_2/1 mol MEA), particularly at high pressures. The reaction of carbamate hydrolysis is represented in Eq. (3). AMP carbamate is hydrolyzed to bicarbonate (HCO_3^-) more than MEA because of low stability of carbamate.

$$R_1NHCOO^-+H_2O \leftrightarrow R_1NH_2+HCO_3^- \tag{3}$$

A tertiary amine, MDEA cannot react with CO_2 directly. Donald-

Table 1. Physical property data of absorbent

	MEA	AMP	MDEA	1,8-Diamino-p-menthane
Mol. weight	61.09	89.14	119.17	170.30
Specific gravity (20/20 °C)	1.0179	0.934	1.0418	Not available
Boiling point (°C)				
101.3 kPa	170-172	165	247.2	Not available
1.333 kPa	69	-	128	107-126
Melting point (°C)	10.5	31	-21.0	−45
Vapor pressure (101.3 kPa at 20 °C)	0.36	1	0.01	10
Solubility in water (wt% at 20 °C)	100	Miscible in water	100	Miscible in water

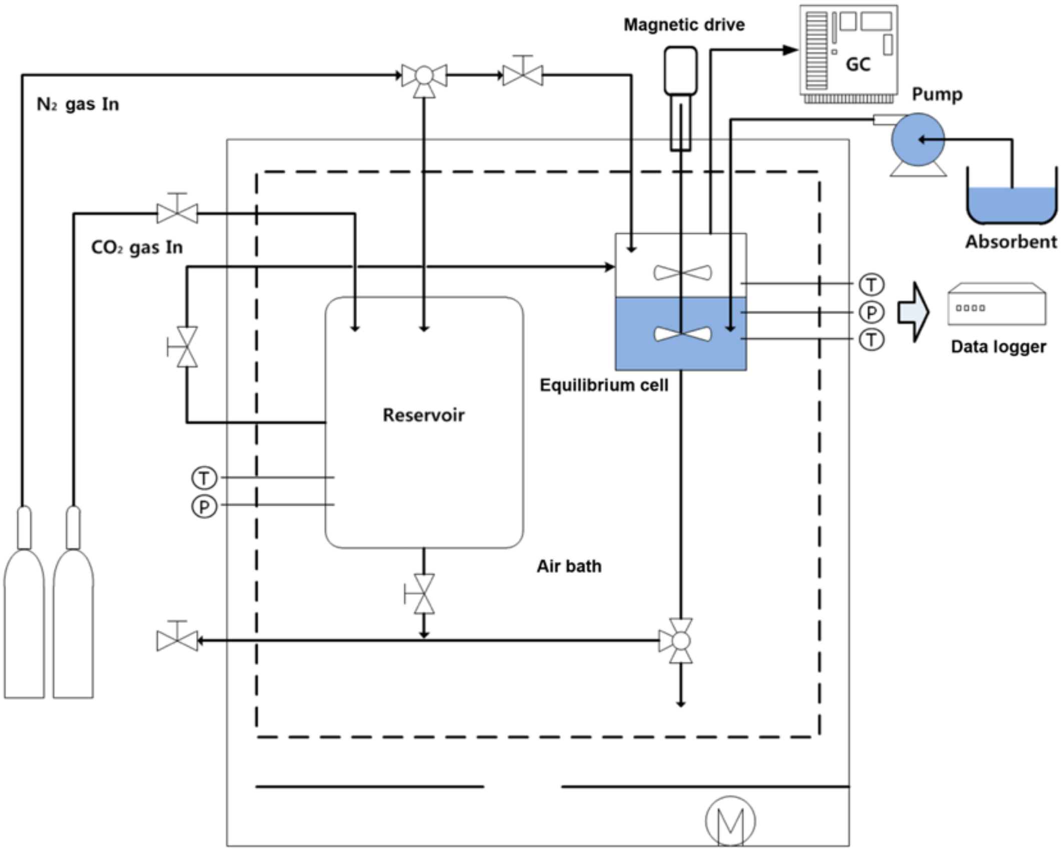


Fig. 1. Schematic diagram for VLE.

son and Nguyen [11] proposed the reaction that was described with base catalysis of the CO_2 hydration. The mechanism is represented as:

$$R_1R_2R_3N+N_2O \leftrightarrow R_1R_2R_3NH^+ + OH^- \tag{4}$$

$$OH^- + CO_2 \leftrightarrow HCO_3^- \tag{5}$$

The mechanism of the sterically hindered diamine, KIER-C3, is similar to AMP. However, KIER-C3 reacts with CO_2 to form carbamate and bicarbonate and bicarbamate ($R_1N(COO^-)_2$) because it has two nitrogen atoms.

EXPERIMENT

1. Materials

Analytical grade MEA, AMP, MDEA and KIER-C3 (1,8-diamino-p-menthane) solutions, with purities of 99, 95, 98 and 70% were supplied by Samchun Pure Chemicals (Korea), Sigma Aldrich (USA), Acros Organics (USA), and Sigma Aldrich (USA), respectively. Aqueous solutions were prepared with deionized water. The CO_2 and N_2 gases were of commercial grade, with purities of 99.99%. Physical property data of major amines are represented in Table 1.

2. Apparatus and Procedure

2-1. Vapor-liquid Equilibrium (VLE) Apparatus

The apparatus used for the measurement of CO_2 loading is given in Fig. 1. The partial pressure of CO_2 was measured with an equilibrium cell. The apparatus consisted of an equilibrium cell (605.7 mL), a reservoir (5921.1 mL), a mechanical agitator, a precision pressure gauge (±0.01 kg_f/cm^2), a pressure transducer-digital indicator, digital thermometer, and data acquisition system. The digital pressure gauge and thermometer were obtained from Data logger type GL800 (GRAPHTEC Co., USA).The air bath was controlled by a forced convection oven. The amount of aqueous solution of amine taken into the equilibrium cell was prepared by mass with a balance precision of $\pm 1\times 10^{-3}$ g. The degassed amine solution kept at the same temperature of the experiment was injected into the equilibrium cell. The CO_2 gas was fed from the reservoirto the cell by pressure difference, and two check valves were put in to prevent the reverse flow of N_2 from the cell to the reservoir. It required 4 h to attain equilibrium at each point. The partial pressure of CO_2 was approximately 0.1 to 600 kPa at T=40 °C. The experimental data were obtained using the device, which can be expressed as in Fig. 2. In this study, for checking the reliability of the measured experimental data, the experimental results are compared with results of previous researches [12,13].

2-2. TGA/DSC

Thermogravimetric analysis (TGA)/Differential Scanning Calorimeters (DSC) was used to measure the heat flow and weight change in a sample. The TGA serves the measurement of change of mass and temperature of a sample in function of the temperature. The DSC measures the difference of heat required to increase the temperature of a sample and reference as a function of temperature. The DSC was used to measure the heat of phase change. The TGA used for this study consisted of an SDT-Q600 and a thermal analysis controller from TA Instruments. The measurements were made at T=25-250 °C using nitrogen as a purge gas with a flow rate of 100 mL/min. The mass of absorbents were approximately 40 mg for TGA and DSC measurements. Heating rate was kept at 2 °C/min. Each data point reported was taken as an average of three readings.

RESULTS AND DISCUSSION

1. Equilibrium of CO_2

The CO_2 loading ratio is the most basic factor to evaluate performance of the absorbents. The CO_2 absorption capacity is represented by the CO_2 loading ratio, which means mole of CO_2 per mole of amine. Fig. 3 shows the CO_2 absorption capacity of the aqueous MEA 30 wt%, AMP 20 wt%, MDEA 20 wt%, KIER-C3 20 wt% solutions. Thus, MEA has low CO_2 absorption capacity (CO_2 loading=0.58 mol CO_2/mol MEA) at CO_2 partial pressure of 100 kPa. However, AMP and MDEA have a high CO_2 absorption capacity. These results are in excellent agreement with the theoretical mechanism. The CO_2 loading ratio of the KIER-C3 solution is approximately 2.5 and 4-times higher than that of AMP, MDEA and MEA respectively.

2. Heat of Absorption

Only one set of the experimental heats of absorption data, which are differential both in loading and temperature, has been reported

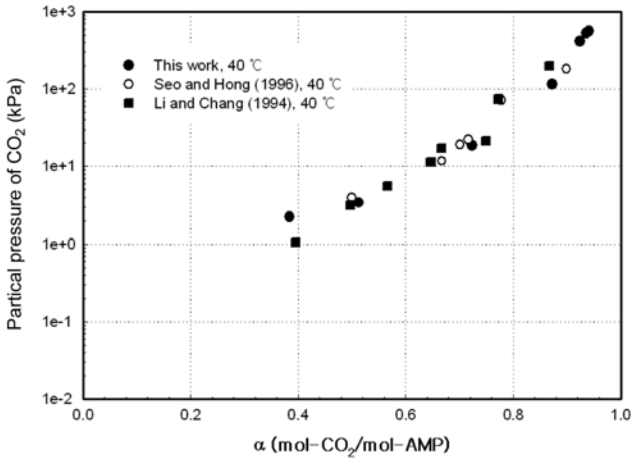


Fig. 2. Equilibrium of CO_2 in AMP 30 wt% solution at 40 °C.

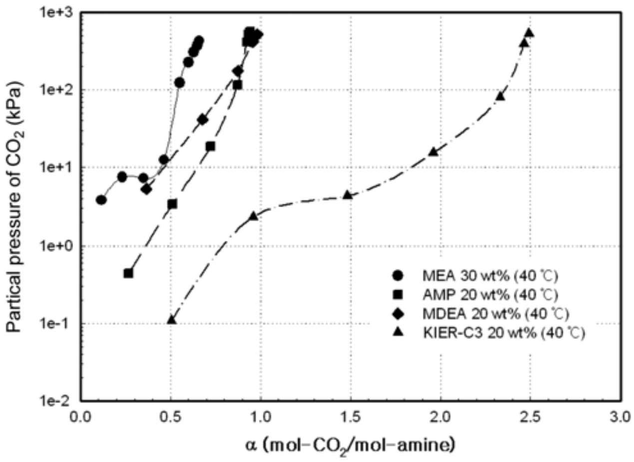


Fig. 3. Equilibrium of CO_2 in amines at 40 °C.

until now [14]. All other experimental data found in the literature are integral values, representing all heat released in bringing the solution acid gas content from zero loading to the final [2]. Integral heats of absorption in the literature are differential in temperature because experiments are conducted under isothermal conditions. However, those data cannot give accurate dependencies of the heats of absorption on CO_2 loading because high (or low) values of heats of absorption at lower loadings will be carried over to the values at higher loadings. As an example, integral enthalpies of CO_2 absorption with MEA 30 wt% solution were studied by Mathonat et al. [15].

From the other side, enthalpies of reaction differential in CO_2 loading, that can be found in the literature, are those calculated from P_{CO_2} data using the Gibbs-Helmholtz equation:

$$\frac{\Delta H_{obs}}{R}=\left[\frac{\partial \ln P_{CO_2}}{\partial (1/T)}\right]_{\alpha} \tag{6}$$

where P_{CO_2} is the equilibrium partial pressure of CO_2, T is the ab-

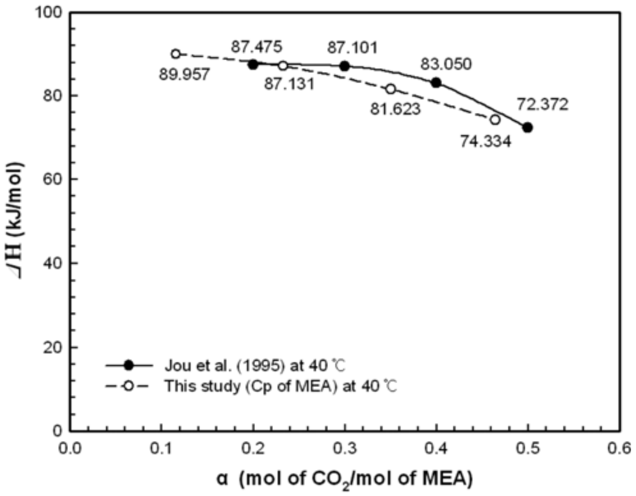


Fig. 4. Heat of absorption in MEA 30 wt%-CO_2 system at 40 °C.

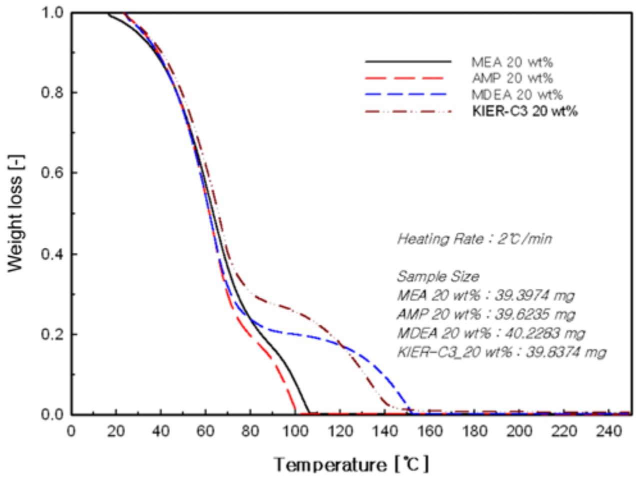


Fig. 5. TGA characteristic of various amines.

Table 2. Heat of regeneration

Absorbent	α	y_{CO_2}	$x_{amine-s}$	$\Delta H_{amine-s}{}^{a}$	$\Delta H_{amine-s}{}'^{b}$	$\Delta H_{amine+s}{}'^{a}$	ΔH_{reg}
	mole-CO_2/ mole-amine	-	-	kJ/kg	kJ/kg	kJ/kg	kJ/ mol-CO_2
MEA 30 wt% (40 °C)	0.0997	0.013	0.987	1603.754	1583.067	1605.638	76.991
	0.3336	0.037	0.963	1603.754	1543.774	1608.150	75.737
	0.5376	0.060	0.940	1603.754	1507.047	1601.870	69.190
	0.6130	0.069	0.931	1603.754	1493.574	1600.195	68.286
	0.6596	0.074	0.926	1603.754	1485.075	1597.264	66.707
AMP 20 wt% (40 °C)	0.2671	0.013	0.987	1703.609	1681.804	1701.934	69.202
	0.4380	0.021	0.979	1703.609	1668.172	1700.540	68.467
	0.7251	0.034	0.966	1703.609	1645.174	1696.772	66.188
	0.9327	0.044	0.956	1703.609	1628.992	1691.258	62.551
	0.9409	0.045	0.955	1703.609	1626.949	1686.443	58.174
MDEA 20 wt% (40 °C)	0.3350	0.012	0.988	1649.641	1629.515	1644.856	55.325
	0.6784	0.025	0.975	1649.641	1608.895	1639.383	54.312
	0.8624	0.031	0.969	1649.641	1597.842	1631.960	47.809
	0.8978	0.033	0.967	1649.641	1595.698	1630.298	46.557
	0.9815	0.036	0.964	1649.641	1590.750	1626.907	44.564
KIER-C3 20 wt% (40 °C)	0.5245	0.014	0.987	1495.324	1475.135	1497.703	57.259
	0.9721	0.025	0.975	1495.324	1457.940	1489.617	55.754
	1.3563	0.035	0.965	1495.324	1443.136	1483.132	50.426
	2.3037	0.059	0.941	1495.324	1406.648	1461.528	40.720
	2.4905	0.064	0.936	1495.324	1399.471	145.238	36.289

[a] Heat of phase change measured by DSC analysis

[b] Corrected value with mole fraction of CO_2 loaded absorbent

solute temperature of the system, α is the CO_2 loading, and R is the gas constant.

This method gives the heat of absorption which is differential in CO_2 loading but integral in temperature. Disadvantages of using Eq. (6) were discussed earlier by several authors. Differential enthalpies of CO_2 absorption for MEA 30 wt% solutions calculated by Jou et al. [16] from P_{CO_2} data using Eq. (6), were used here as an example for comparison. In the present investigations, the heat of absorption is compare an integral value representing all heat released in bringing the solution acid gas content from zero to the final CO_2 loading. The heat of absorption of CO_2 into aqueous amine solution can be calculated by Eq. (7).

$$Q=m\cdot Cp\cdot\Delta T \tag{7}$$

where Q is the heat of absorption of CO_2, m is mass of CO_2 absorbed in the absorbent, Cp is the heat capacity of absorbents after absorption of CO_2, and ΔT is temperature change after the injection of CO_2 in the equilibrium cell.

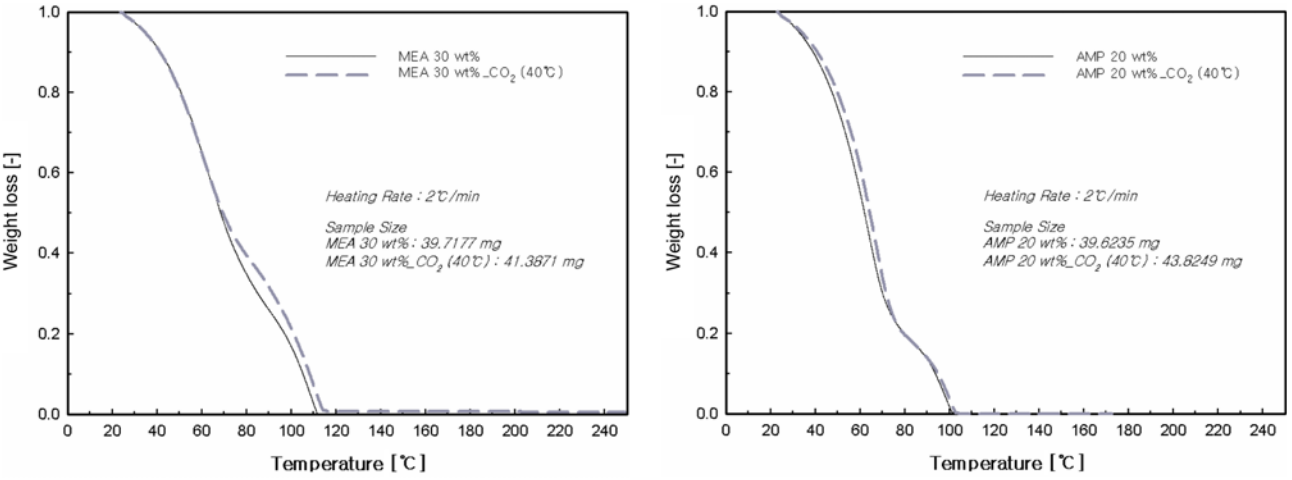
As a result of analysis, experimental measurements of aqueous MEA 30 wt% solution at 40 °C are in excellent agreement, as can be seen in Fig. 4.

3. Thermogravimetric Analysis (TGA)

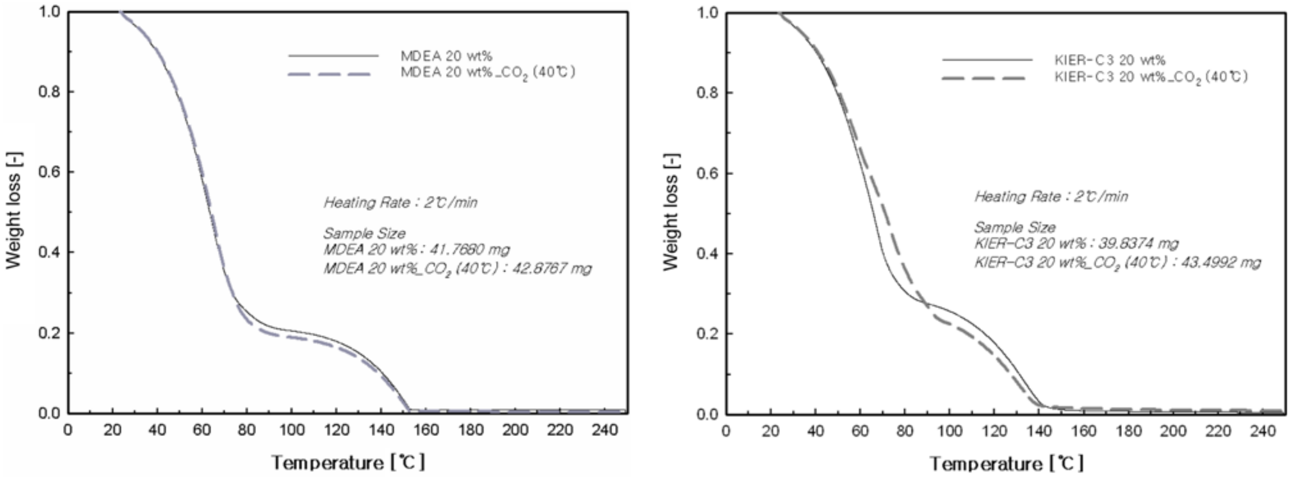
Thermal stability of KIER C-3 was investigated by a thermogravimetric analysis. The result was compared to MEA, AMP, MDEA in Fig. 5. This figure shows that the thermal stability of aqueous amine solutions is found as follows: AMP>MEA>KIER-C3 and MDEA.

One-step degradation of the TGA curves represents decomposition of water, whereas two-step degradation represents decomposition of amine. The two-step of the curves showsthat the thermal stability of amine after the stripping of CO_2. The MEA and AMP were decomposed rapidly increasing the temperature. The boiling points of amines arerepresented in Table 1. MEA and AMP have lower boiling points comparable to MDEA and KIER C-3. Therefore, MEA and AMP have risks of solvent loss and degradation of amine.

The TGA curves of the CO_2 loaded absorbents were compared with the fresh absorbents. The results of analysis are shown in Fig. 6. The difference of weight loss rate between fresh absorbents and CO_2 loaded absorbents is small. However, the curves have different characteristics depending on the type of the absorbent. The two-step degradation curve for CO_2 loaded MEA was located upper.



(a) MEA (b) AMP



(c) MDEA (d) KIER-C3

Fig. 6. TGA characteristic of (amine+water+CO_2) systems.

This means that weight loss of CO_2 loaded MEA is smaller than that of fresh MEA. It indicated that the thermal stability of CO_2 loaded MEA is high because MEA forms a stable carbamate. The two-step degradation curve for CO_2 loaded MDEA was different from that of CO_2 loaded MEA and AMP. The two-step degradation curve for CO_2 loaded MDEA was located lower than fresh MDEA. It shows that the amount of bicarbonate in the absorbent is increased. MDEA acts as a base catalyst for hydration of CO_2 and forms bicarbonate. The TGA curve of KIER-C3 is shown in Fig. 6(d). The curve has the characteristics of MEA, AMP and MEA because KIER-C3 reacts with CO_2 and forms the bicarbonate as well as the carbamate.

4. Differential Scanning Calorimetry (DSC)

The aqueous amine solutions contain a large amount of water. In Fig. 7(a), according to increase of the CO_2 loading, the left curves are decreased, whereas the right curves are increased. Therefore, the water is found to be predominant in the left curve, and the MEA was found to be predominant in the right curve.

Fig. 7(d) shows the DSC curves for according to increase of the CO_2 loading of KIER-C3. The curve of KIER-C3 is different from the curves of other amines. This result is caused by characteristic of structure. KIER-C3 is a diamine so that the regeneration takes place on the two nitrogen atoms, respectively. Therefore, the left curve of KIER-C3 appears as two peaks, whereas the left curves of other amines show as a single peak.

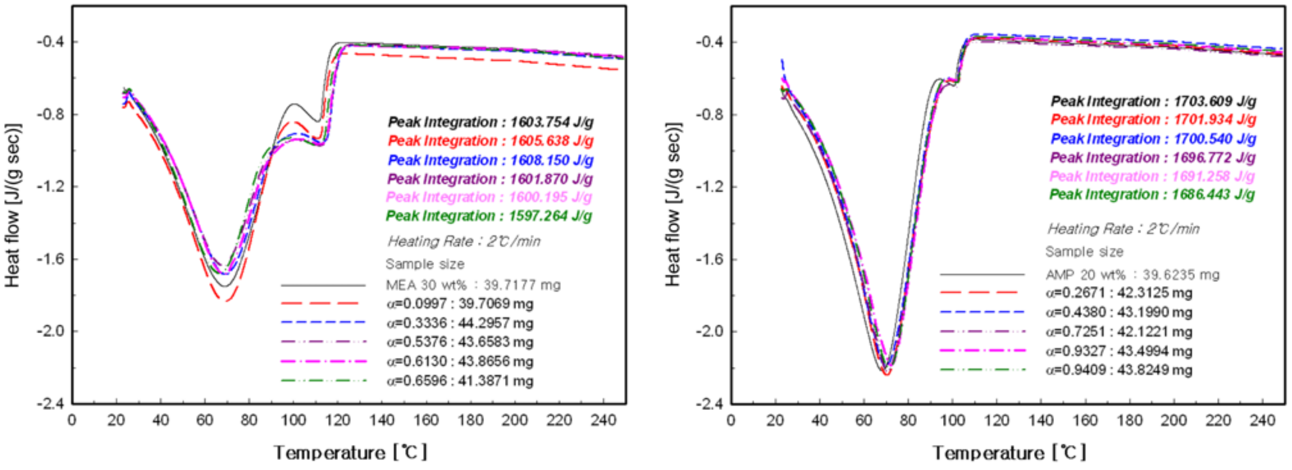
5. Heat of Regeneration

The most disadvantage of chemical absorption is the large requirement for regeneration. Therefore, the regeneration heat of absorbent is main factor with respect to the process design and economic feasibility. The heat of phase change of only absorbent and CO_2 loaded absorbent measured using the DSC. Then the regeneration heat of aqueous amine solution is calculated using the difference between two heat of phase change such as following Eqs. (8) and (9).

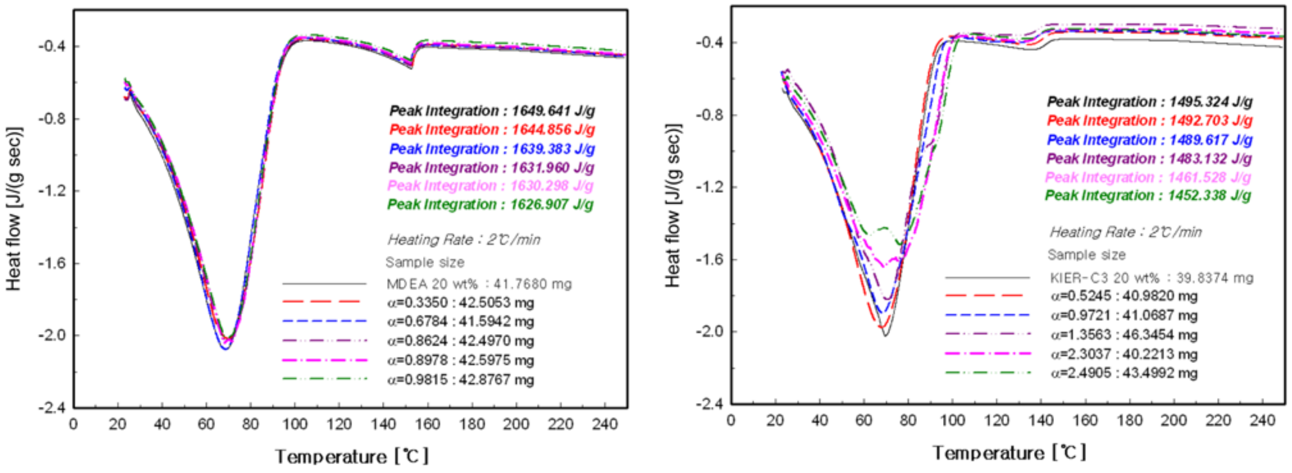
$$\Delta H_{a\,min\,e-s}' = \Delta H_{a\,min\,e-s} \times x_{a\,min\,e-s} \tag{8}$$

$$\Delta H_{reg} = (\Delta H_{a\,min\,e+H_2O+CO_2} - \Delta H_{a\,min\,e-s}') \div y_{CO_2} \tag{9}$$

where $\Delta H_{a\,min\,e-s}$ is the difference of heat of phase change for absorbent (kJ/kg), $\Delta H_{a\,min\,e-s}'$ is the corrected difference of heat of phase change (kJ/kg) for absorbent, $\Delta H_{a\,min\,e+H_2O+CO_2}$ is the difference of heat of phase change for absorbent+CO_2 (kJ/kg), ΔH_{reg} is the difference of heat of regeneration (kJ/mol-CO_2), $x_{a\,min\,e-s}$ is the mole fraction



(a) MEA (b) AMP



(c) MDEA (d) KIER-C3

Fig. 7. DSC curves with the CO_2 loading ratio.

of absorbent, and y_{CO_2} is the mole fraction of CO_2.

As a result of analysis, the regeneration heat of aqueous amine solutions was decreased in the order MEA>AMP>KIER-C3>MDEA. The regeneration heat of aqueous MEA solution is similar to the enthalpy of reaction however, this value is less than the enthalpy of reaction. The reliability of the experimental procedures and results was obtained considering the above results. The regeneration heat of aqueous KIER-C3 solution was 57.259-36.289 kJ/mol-CO_2, so it was about 19.733-30.418 kJ/mol-CO_2 lower than that of aqueous MEA solution, which means less energy is needed for desorbing same amount of CO_2. Hence, the enthalpy of reaction of aqueous KIER-C3 solution is expected to be lower than that of the conventional absorbents such as MEA.

CONCLUSIONS

This study investigated the reaction and regeneration heat of various amine-based absorbents. The CO_2 loading ratio is the most basic factor to evaluate performance of the absorbents. The CO_2 loading ratio of the KIER-C3 solution is approximately 2.5 and 4-times higher than that of AMP, MDEA and MEA, respectively. As a result of analysis of absorption heat, experimental measurements of aqueous MEA 30 wt% solution at 313.15 K are in excellent agreement. Thermal stability of aqueous KIER-C3 20 wt% solutions is similar that of aqueous MDEA 20 wt% solutions. In addition, the TGA curve of KIER-C3 has the characteristics of MEA, AMP and MEA because KIER-C3 reacts with CO_2 and forms the bicarbonate as well as the carbamate. The DSC curves for increase of the CO_2 loading of KIER-C3 are different from the curves of other amines. KIER-C3 is a diamine, so thatthe regeneration takes place on the two nitrogen atoms, respectively. The regeneration heat of aqueous amine solutions was decreased in the order MEA>AMP>KIER-C3>MDEA. The regeneration heat of aqueous KIER-C3 solution was 57.259-36.289 kJ/mol-CO_2, so it was about 19.733-30.418 kJ/mol-CO_2 lower than that of aqueous MEA.

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