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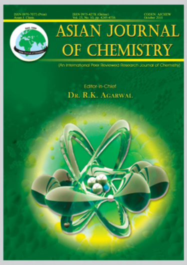

Carbon Dioxide Absorption into Aqueous Blends of Potassium Carbonate and Amine

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In this study, amines were added to aqueous K_2CO_3 solution as a promoter to improve absorption rate. The CO_2 equilibrium partial pressure (PCO_2^*) and the absorption rate were measured using vapour-liquid equilibrium (VLE) equipment at the 313, 333 and 353 K condition of flue gas. Results showed that K_2CO_3/ethylenediamine (EDA), K_2CO_3/diethylenetriamine (DETA), K_2CO_3/triethylenetetramine (TETA), K_2CO_3/tetraethylenepentamine (TEPA) solutions had CO_2 equilibrium partial pressure lower than that of monoethanolamine solution at 313 K. In addition, it was found that ethylenediamine was the most effective promoter to increase the absorption rate of aqueous K_2CO_3 solution.

Key Words: Carbon dioxide, Absorption, Potassium carbonate, Amine

INTRODUCTION

Carbon capture and storage (CCS) is the most promising technology in the mitigation technologies can be classified into three of greenhouse gas emissions from facilities of using large-scale fossil fuels. Carbon dioxide capture types: post-combustion, pre-combustion and oxyfuel combustion. Most existing post-combustion technologies are based on chemical absorption using amines. Acidic gas removal using single alkanolamine and blended alkanolamine solutions have been used in various chemical industries, such as ammonia production and natural gas purification of the alkanolamine solutions, aqueous monoethanolamine (MEA) solution has several advantages over the other alkanolamines. These advantages include low price and a high reaction rate with CO_2. However, primary amines, such as monoethanolamine, directly react with CO_2 to form carbamate and, thus, their regeneration requires high heat duty. Since chemical absorption forms strong bonds between absorbents and CO_2, large amount of energy are required to break these bonds. On the other hand, in tertiary amines, such as triethanolamine (TEA) and methyldiethanolamine (MDEA), hydrogen atoms are not bound to nitrogen atoms and thus they cannot directly react with CO_2. However, they do react in the form of bicarbonate [1-3]. Therefore, it is known that tertiary amines require lower heat duties for regeneration comparable to primary and secondary amines[4,5].

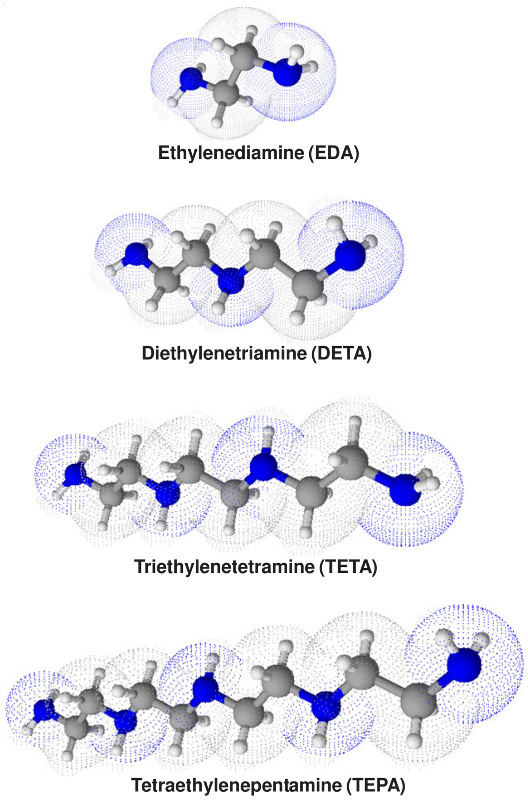
Recently, attention has been focused on the development of absorbents that can replace monoethanolamine. Many researchers have conducted diverse experiments and modeling studies to find appropriate substitutes[6-9]. Singh *et al.*[10,11] studied the relationship between the molecular structures and activities of various amines. They showed that increases in chain lengths between amines and other functional groups result in decreased absorption rates and increased absorption capacities. Puxty *et al.*[12] studied the absorption capacity and kinetics of 76 amines using isothermal gravimetric analysis and absorption apparatus. Through this study, they found four primary and secondary amines with initial absorption rates similar to those of monoethanolamine and excellent absorption capacity.

Absorption of CO_2 into potassium carbonate (K_2CO_3) solution is widely accepted for the removal of CO_2 from natural gas treatment and chemical processes. Aqueous potassium carbonate solution is an effective CO_2 absorbent at high temperatures and pressures, *e.g.*, the Benfield process. Although aqueous potassium carbonate solution is known to have low heat duty as it absorbs CO_2 in the form of bicarbonate, its absorption rates at low temperatures are low and $KHCO_3$ precipitates may be formed[13,14]. Many researchers have used amines as a promoter to compensate for these disadvantages. Laddha and Danckwerts[15] added monoethanolamine and diethanolamine to aqueous potassium carbonate solution and conducted experiments at 284 and 298 K and reported that diethanolamine had larger effects on incresing absorption rates than monoethanolamine. Cullinane and Rochelle[16,17] studied the CO_2 absorption rate, CO_2 solubility and speciation of aquoeus potassium carbonate solution with the addition of piperazine (PZ), which is a ring amine. To explain the equilibrium behaviour of the absorbents, they developed a rigorous thermodynamic model based on an electrolyte nonrandom two-liquid (ENRTL) model.

In this study, aqueous potassium carbonate solution mixed with ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) was used as an absorbent. Although many studies on the CO_2 absorption capacity and absorption rate of aqueous EDA, DETA, TETA and TEPA solutions have been published, few studies have been published on the CO_2 absorption characteristics of aqueous potassium carbonate solution mixed with these amines[18-21]. This study is intended to examine the absorption characteristics of various aqueous potassium carbonate solutions mixed with those amines through CO_2 absorption equilibrium experiments.

EXPERIMENTAL

Each amine absorbent was made into a 30 wt % aqueous solution and the blended K_2CO_3/amine absorbent was made into an aqueous K_2CO_3 15 wt %/amine 10 wt % solution. As reagents, monoethanolamine (99 %), potassium carbonate (99.5 %), ethylenediamine (99 %) and diethylenetriamine (98.5 %) (Samchun Chemical Co., Korea), triethylenetetramine (99 %) (Junsei Chemical Co., Japan) and tetraethylenepentamine (99 %) (Aldrich Co., USA) were used with any additional purification. The molecular structures of the amines were shown in Fig. 1. The amines have two primary amino groups. The number of secondary amino group in the diethanolamine, triethylenetetramine and tetraethylenepentamine are one, two, three, respectively. CO_2 (99.99 vol %) and N_2 (99.999 vol %) gases produced by Special Gas Co. in Korea were used.



Ethylenediamine (EDA)

Diethylenetriamine (DETA)

Triethylenetetramine (TETA)

Tetraethylenepentamine (TEPA)

Fig. 1. Molecular structures of ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine (blue: nitrogen, gray: carbon, white: hydrogen)

Experimental procedure: The CO_2 absorption capacity and absorption rates of absorbents were measured through equilibrium experiments conducted in vapour-liquid equilibrium experimental apparatus (Fig. 2). This apparatus consist of gas reservoir, reactor, pressure and temperature measuring instruments and a recorder. Most of the apparatus components were made of stainless steel to prevent corrosion damage. The internal volumes of the gas reservoir and reactor were made to hold 300.29 and 322.56 cm^3, respectively. The temperatures of gases and liquids in gas reservoir and reactor were measured by a K-type thermocouple and pressure of the gases was measured by a PTB pressure sensor from Synsys Ltd. The gas reservoir and the reactor were placed in a thermostatic water bath to maintain the required temperature.

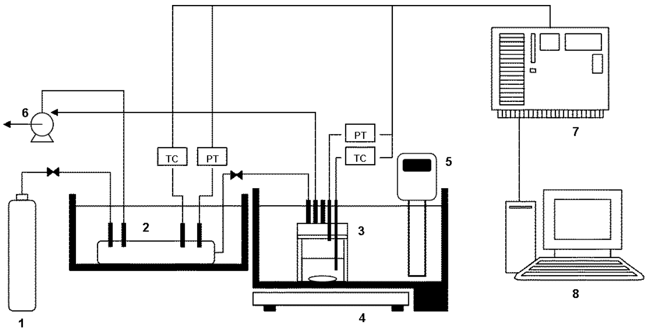


Fig. 2. Vapour-liquid equilibrium apparatus. (1. CO_2 gas, 2. Gas reservoir, 3. Reactor, 4. Magnetic stirrer, 5. Heating circulator, 6. Vacuum pump, 7. Pressure measuring instrument, 8. Recorder)

In this study, experiments were conducted under a broad range of temperatures (313, 333 and 353 K) and gas pressures (500 to 800 kPa). The reactor was filled with 100 mL of an absorbent and sealed; residual gases in the reactor were then removed using a vacuum pump. The injected CO_2 gas (99.99 %) was heated to 313 K in the gas reservoir and injected into the reactor. While the experiments were in progress, the reactor was stirred at 170 rpm in order to maximize areas of contact between the absorbent and CO_2.

When the temperatures of the gas reservoir and reactor reached the experimental temperature, the CO_2 injection valve was opened to inject CO_2 into the reactor. The pressure of CO_2 in the reactor was shown to decrease over time. The pressure in the reactor was measured every five seconds. When the temperature and pressure became constant, a state of equilibrium was determined and the pressure in that state was measured to calculate CO_2 equilibrium partial pressure. The pressure of the injected gas and pressure of the gas after the equilibrium were measured to calculate the moles of CO_2 absorbed in the absorbent. Since CO_2 reacts with the absorbents only in the closed reactor, the absorption rates can be calculated using pressure differences. In this study, subsequent to the original CO_2 injection, CO_2 was again injected into the reactor after equilibrium was reached to re-establish equilibrium.

RESULTS AND DISCUSSION

Amine-H_2O-CO_2 system: To examine the CO_2 absorption characteristics of aqueous solutions, their CO_2 absorption capacity and absorption rates were measured at 333 K. The

TABLE-1
SOLUBILITY OF CO_2 IN AQUEOUS EDA, DETA, TETA AND TEPA SOLUTIONS AT 333 K

EDA 30 wt %		DETA 30 wt %		TETA 30 wt %		TEPA 30 wt %	
α	$P_{CO_2}^*$ (kPa)	α	$P_{CO_2}^*$ (kPa)	α	$P_{CO_2}^*$ (kPa)	α	$P_{CO_2}^*$ (kPa)
0.084	2.158	0.150	2.354	0.207	0.883	0.258	0.098
0.167	2.354	0.296	2.354	0.409	3.236	0.513	0.098
0.250	2.354	0.440	2.354	0.609	3.432	0.767	0.230
0.330	2.354	0.583	2.354	0.808	3.432	1.019	1.863
0.412	3.040	0.725	3.236	1.006	4.217	1.270	2.942
0.493	4.119	0.867	3.825	1.201	6.276	1.520	5.982
0.573	5.394	1.006	4.903	1.392	15.298	1.752	32.166
0.654	7.257	1.146	8.140	1.544	106.206	1.932	145.237
0.734	7.257	1.279	24.321	1.683	189.268	2.089	240.557
0.815	11.768	1.385	134.449	1.750	400.504	2.168	426.100
0.891	27.753	1.455	302.633	1.790	561.333	2.253	505.239
0.946	167.498	1.499	465.228	1.819	660.380	2.282	646.945
0.980	353.138	1.529	583.104	1.842	723.927	2.316	703.529
1.002	503.572	1.551	665.970	1.862	753.936	2.339	753.151
1.020	598.990	1.571	710.198	–	–	–	–
1.027	700.097	1.579	764.036	–	–	–	–
1.038	733.832	–	–	–	–	–	–

α = CO_2 loading (mol CO_2/mol amine)

results are shown in Figs. 3 and 4. These graphs show that, as the number of amine group increases, the saturated CO_2 absorption capacity increases and the absorption rate decreases. The CO_2 absorption capacity refers to the CO_2 loading, which is expressed by the moles of CO_2 absorbed per mole of amine. Reviewing Fig. 3 and Table-1, it can be seen that the saturated CO_2 loadings of aqueous EDA, DEPA, TETA and TEPA solutions are shown to be 1, 1.6, 1.9 and 2.4, respectively. It is obvious that the CO_2 absorption capacity of the aqueous TEPA solution is the largest.

The CO_2 absorption reaction mechanism of the aqueous primary (RNH_2) or secondary (R_2NH) amine can be represented by the zwitterion (RNH_2^+ COO^- or $R_2NH^+COO^-$) formation reactions[22,23]. Dissolved CO_2 in aqueous amine solutions reacts rapidly and directly with amines to form the intermediates zwitterions. The zwitterions rapidly react with bases in the solution to be deprotonated, thereby forming carbamate.

$$CO_2 + RNH_2 \rightleftharpoons RNH_2^+COO^- \qquad (1)$$

$$RNH_2^+COO^- + B \rightleftharpoons RNHCOO^- + BH^+ \qquad (2)$$

where, B refers to bases, such as RNH_2, H_2O and OH^-. The carbamate formed as such again free amines and bicarbonate through hydrolysis.

$$RNHCOO^- + H_2O \rightleftharpoons RNH_2 + HCO_3^- \qquad (3)$$

As the formed carbamate becomes more stable, the degree of progression of the reaction, shown by equation (3), becomes smaller to extent of being ignorable and, thus, the overall reaction can be shown as follows:

$$CO_2 + 2RNH_2 \rightleftharpoons RNHCOO^- + RNH_3^+ \qquad (4)$$

Therefore, in case of monoethanolamine, which has high carbamate stability, the amount of CO_2 that can be absorbed by 1 mol of amine is limited to 0.5 mol. In this experiment, it was indicated that the CO_2 absorption capacity increased a slightly more in areas where CO_2 partial pressure was high so that more than 0.5 mol of CO_2 was absorbed per 1 mol of amine. In addition, it was shown that, in the case of aqueous ethylenediamine solution, 1 mol of CO_2 was absorbed per 1 mol of amine; this is because ethylenediamine is a diamine. The secondary amine group parts of DETA, TETA and TEPA have lower carbamate stability than primary amine group parts and, thus, the amounts of carbamate converted into bicarbonate are larger so that the absorption capacity increases further.

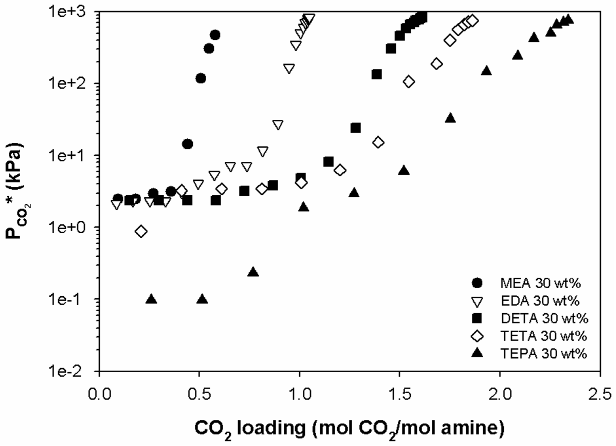


Fig. 3. CO_2 equilibrium into aqueous amine solutions at 333 K

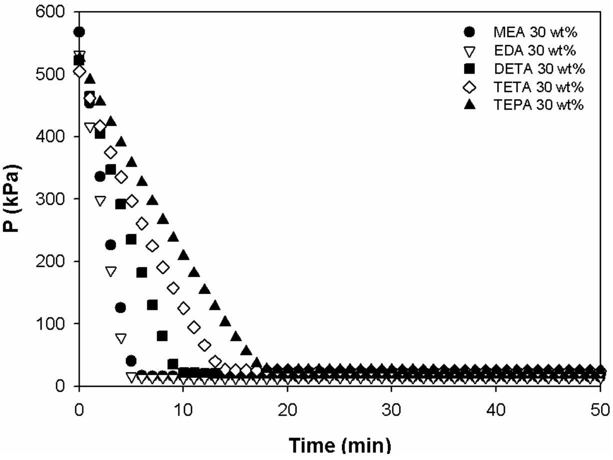


Fig. 4. CO_2 absorption rate into aqueous amine solutions at 333 K

K_2CO_3-Amine-H_2O-CO_2 system: To examine the CO_2 absorption characteristics of aqueous K_2CO_3 15 wt %/amine 10 wt % solutions relative to temperature, their CO_2 absorption capacity and absorption rates were measured at 313, 333 and 353 K. Figs. 5-7 show CO_2 equilibrium partial pressures under CO_2 loadings by temperature. It can be seen that, when CO_2 loading is low, points where vapour-liquid equilibrium curves cross each other occur and no tendency related to CO_2 loading appears but, when CO_2 loading is high, CO_2 equilibrium partial pressure increases as the number of amine groups increases, thus increasing the absorption capacity. Aqueous potassium carbonate solutions absorb CO_2 through the following reaction[24]:

$$K_2CO_3 + H_2O \Leftrightarrow 2K^+ + HCO_3^- + OH^- \quad (5)$$

$$CO_2 + OH^- \Leftrightarrow HCO_3^- \quad (6)$$

Therefore, the overall reaction equation can be shown as:

$$K_2CO_3 + H_2O + CO_2 \Leftrightarrow 2KHCO_3 \quad (7)$$

The formed bicarbonate can be hydrolyzed to form carbonate.

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \quad (8)$$

Therefore, it can be explained that aqueous K_2CO_3/amine solutions absorb CO_2 in forms of carbamate and bicarbonate/carbonate. In the case of aqueous potassium carbonate solutions, crystals may be formed if $KHCO_3$ formation increases due to their limited solubility. However, in case of the aqueous K_2CO_3 15 wt %/amine 10 wt % used in this study, no crystals were formed.

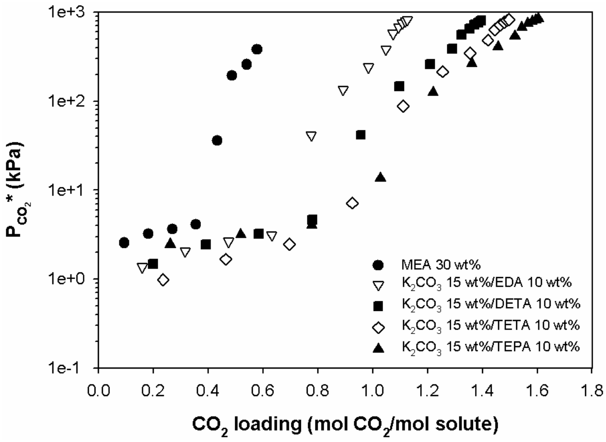


Fig. 5. CO_2 equilibrium into aqueous K_2CO_3/amine solutions at 313 K

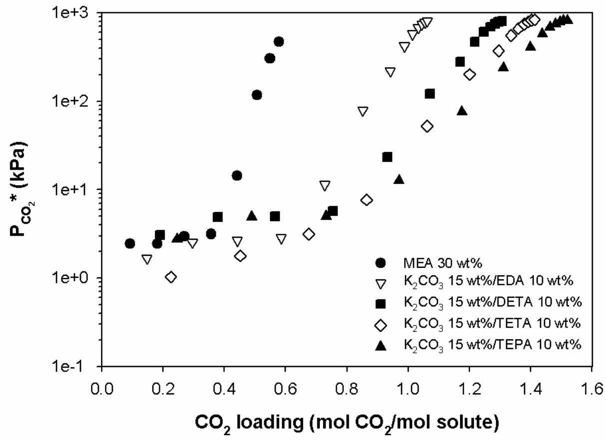


Fig. 6. CO_2 equilibrium into aqueous K_2CO_3/amine solutions at 333 K

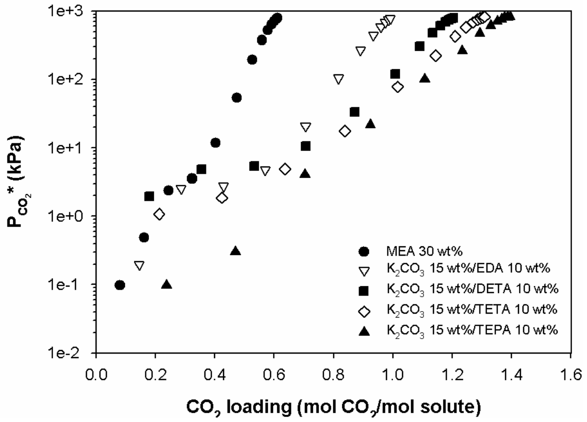


Fig. 7. CO_2 equilibrium into aqueous K_2CO_3/amine solutions at 353 K

Figs. 8-10 show CO_2 absorption rates by temperature. At all of the temperatures 313, 333 and 353 K, the absorption rate of aqueous potassium carbonate solutions increased the most when ethylenediamine was added. In particular, ethylenediamine showed absorption rates similar to those of monoethanolamine at 313 K. While the absorption rate of aqueous K_2CO_3/amine solution increased as the temperature increased, the CO_2 absorption capacity of the absorbent decreased. Therefore, when designing relevant processes, the CO_2 absorbing characteristics of absorbents relative to temperature, the solubility of K_2CO_3 and amines in water and the solubility of CO_2 in absorbents should be considered simultaneously.

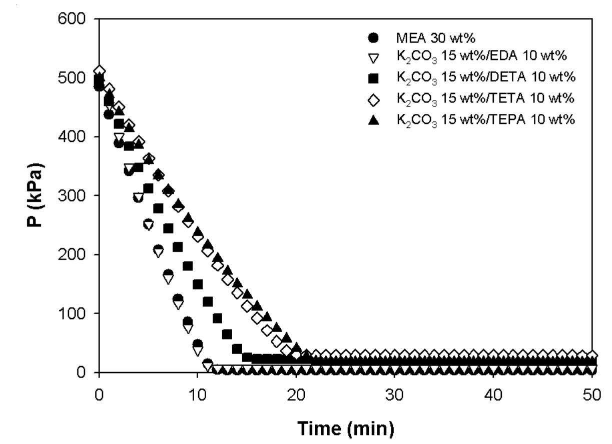


Fig. 8. CO_2 absorption rate into aqueous K_2CO_3/amine solutions at 313 K

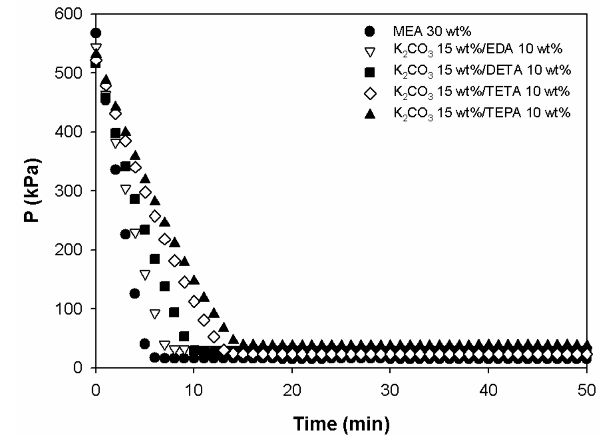


Fig. 9. CO_2 absorption rate into aqueous K_2CO_3/amine solutions at 333 K

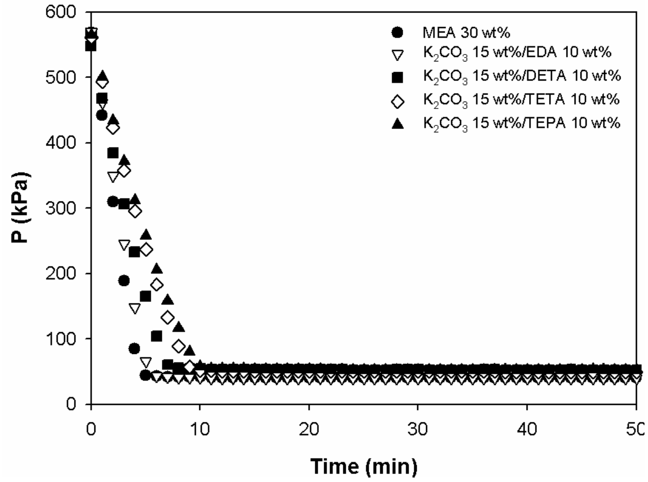


Fig. 10. CO_2 absorption rate into aqueous K_2CO_3/amine solutions at 353 K

Conclusion

To increase the CO_2 absorption rates of the aqueous K_2CO_3 solutions, the amines, EDA, DETA, TETA and TEPA were used as promoters. Gas-liquid absorption equilibrium experiments of aqueous K_2CO_3/amine solutions were conducted at 313, 333 and 353 K to measure their CO_2 loading capacity and absorption rates. Through these experiments, the CO_2 absorption characteristics of the aqueous K_2CO_3/amine solutions were studied. While the absorption rates of aqueous K_2CO_3/amine solutions increased as temperature increased, the CO_2 loading capacities of the absorbents decreased. It could be seen that in case of aqueous K_2CO_3/amine solutions, when CO_2 loading was low, points where vapour-liquid equilibrium curves crossed each other occurred and, thus, no tendency related to CO_2 loading appeared but, when CO_2 loading was high, the absorption capacity increased as the number of amine groups increased. Furthermore, while the absorption rates of aqueous K_2CO_3/amine solutions increased as temperature increased, the CO_2 absorption capacities of the absorbents decreased. The absorption rate of aqueous potassium carbonate solutions increased the most when ethylenediamine was added and, in particular, ethylenediamine showed absorption rate similar to that of monoethanolamine at 313 K.

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