Absorption Rate of CO_2 in DEA Promoted K_2CO_3 Solution at High Temperatures

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Keywords: Absorption rate; DEA; K_2CO_3; CO_2

Abstract. The absorption rates of CO_2 in diethanolamine (DEA) promoted potassium carbonate (K_2CO_3) solution at normal pressure with temperature ranging from 343.2K to 363.2K were investigated. The mass fractions of DEA and K_2CO_3 respectively ranged from 0 to 0.02, and 0.35 to 0.40. The results revealed the effects of DEA concentration and temperatures on the absorption rate of CO_2.

Introduction

The utilization of grand amount of fossil fuel causes large emission of CO_2 concentration in the atmosphere, which has destructively affected global climate through the so-called "greenhouse effect"[1-3]. Carbon capture and storage (CCS) is one of promising routes to reduce CO_2 emissions from fossil fuel-fired power plants[4].

Over the past years, numerous methods have been proposed for post-combustion CO_2 capture[5-7]. Some of the commercially used methods are chemical absorption, physical absorption and membrane separation. Potassium carbonate(K_2CO_3) and amines like monoethanolamine (MEA), diethanolamine(DEA) and N-methyldiethanolamine(MDEA), can remove acid gas constituents from sour gas streams for a large-scale implementation. K_2CO_3 has a number of advantages over the amine-based solvents, including low cost, low toxicity, characteristic of refractory, and so on. One of the most important advantages is that the absorption can occur at high temperatures, making regeneration process more efficient and economical[8]. The biggest challenge associated with using K_2CO_3 as a solvent is that it has a low rate of reaction, resulting in poor CO_2 mass transfer[9-13], thus promoters were often added to the solvent to improve the CO_2 mass-transfer rates.

The concept of the addition of amine to carbonate system to enhance CO_2 absorption has been known for a long time[14, 15]. The hot potassium carbonate process, also known as the Benfiled process, has been used commercially for treating acid gas streams for many years[16-18]. It has been well known that small amount of certain organic or inorganic additives can enhance the absorption rate significantly[19]. Moreover, due to its thermal stability, K_2CO_3 is able to serve as absorbent at high temperatures. The solubilities of both K_2CO_3 and potassium bicarbonate ($KHCO_3$) get much higher at high temperatures, which enables the use of high concentrated K_2CO_3 aqueous solution as absorbent. Compared with the Benfield process, the absorption process using high concentrated K_2CO_3 aqueous solutions at high temperatures is expected to achieve larger absorption amount of CO_2 and higher reaction rate[20, 21] and reduce the pre-cooling energy requirements[22]. However, the absorption rate of CO_2 in DEA-K_2CO_3 solution at high temperatures have not been well documented so far.

The main purpose of this work is to determine an appropriate addition of DEA to high concentrated K_2CO_3 aqueous solution at high temperatures, so that the high absorption rate can be achieved. To this end, the absorption rate of CO_2 in series of DEA-K_2CO_3 aqueous solution were measured at temperatures ranging from 343.2K to 363.2K, and the influence of the mass fraction of DEA on absorption rate was demonstrated.
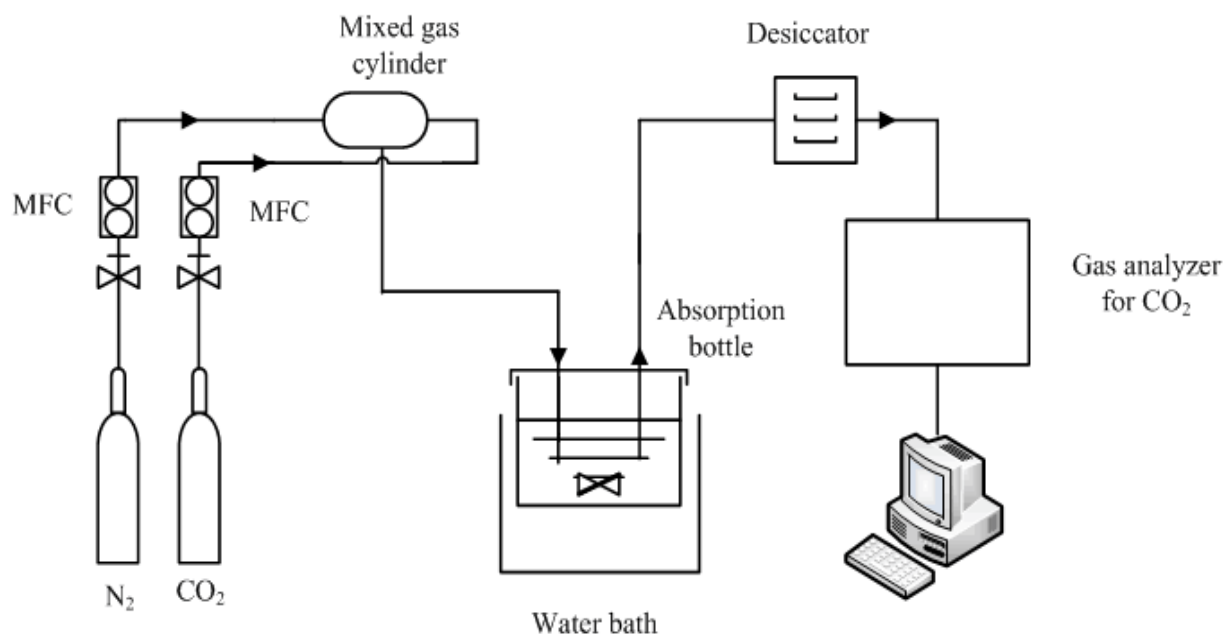
Experimental

Materials

Both K_2CO_3 and DEA were purchased from Huaxin Chemical Co. The sample description is shown in Table 1. They were used without further purification. Aqueous solutions of K_2CO_3–DEA were prepared by adding doubly distilled water. The uncertainty of the electronic balance is ±0.1 mg.

Table 1. Sample description

Chemical	CAS NO.	Purity (in mass fraction%)	Molecular(Da)
DEA	111-42-2	99.0	138.21
K_2CO_3	584-08-7	99.0	105.14

Apparatus and Procedure
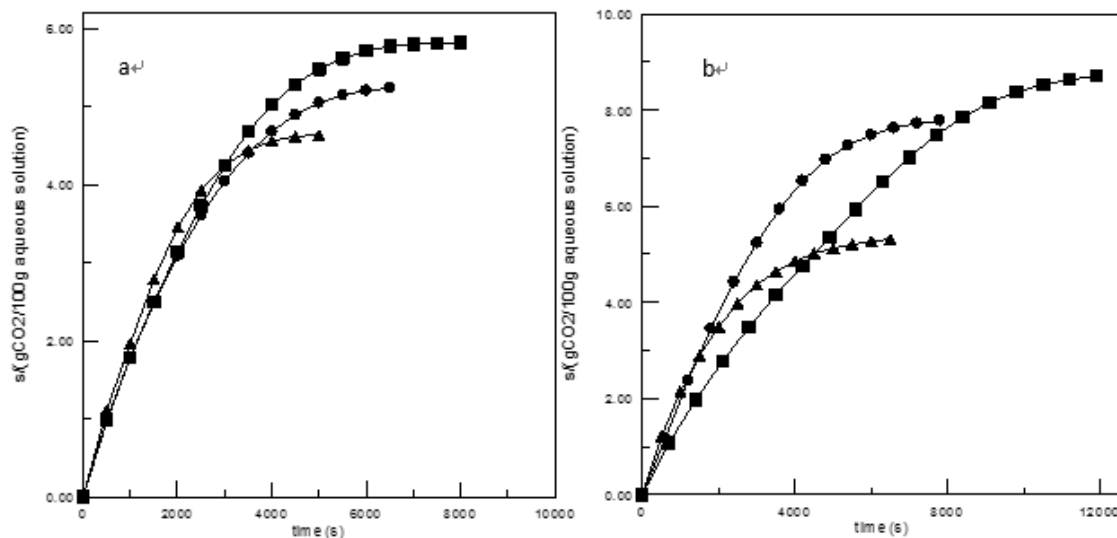
The absorption performance of aqueous solutions was measured by the system composed of one high-pressure CO_2 tank, one high-pressure N_2 tank, two mass flow controllers (MFC), one mixed gas cylinder, one absorption bottle, one constant temperature water bath, one desiccator and one CO_2 analyzer(Advanced Gasmitter by Germany Sensors Europe GmbH, the accuracy is ±2%). The schematic diagram for the experiment is shown in Fig.1. The absorption bottle was immersed into the thermostatic bath and the temperature of the solution can be regulated within 0.1K. During the experiment, CO_2 and N_2 from high-pressure tanks were respectively inlet into MFC to maintain constant flow rate($CO_2$100ml·min^{-1}, $N_2$200ml·min^{-1}) and then into the mixed gas cylinder,absorption bottle and absorbed by the solution. The residual and unabsorbed gas firstly flowed into the desiccator and then into the CO_2 analyzer. The gas concentration was measured by the CO_2 analyzer. Both the data of gas concentration and flow rate were recorded by the computer. In all the experiments, the rotational speed of the magnetic stirrer is fixed as 1000 rpm.

**Figure 1.** The schematic diagram of the experiment.

Results and Discussion

Fig.2 illustrates the influence of temperature on the absorption rate of CO_2. With the increase of temperature, the absorption rate increases. The higher is the temperature, the faster is the absorption rate.

Figure 2. The influence of temperature on the absorption rate of CO_2 in K_2CO_3-DEA aqueous solutions.Symbols: ■T=343.2K●T=353.2K▲T=363.2K, a. w_2/w_1=0.01/0.35; b. w_2/w_1=0.01/0.40.

Fig. 3 illustrates the influence of the mass fraction of DEA on the absorption rate of CO_2. One finds from this figure that without DEA promotion, CO_2 is very slowly absorbed by K_2CO_3 aqueous solution. When the K_2CO_3 aqueous solution is promoted by DEA, the absorption rate increases very significantly, e.g., the saturated absorption corresponding to w_2=0.02 is achieved nearly 5 times faster than that corresponding to w_2=0.
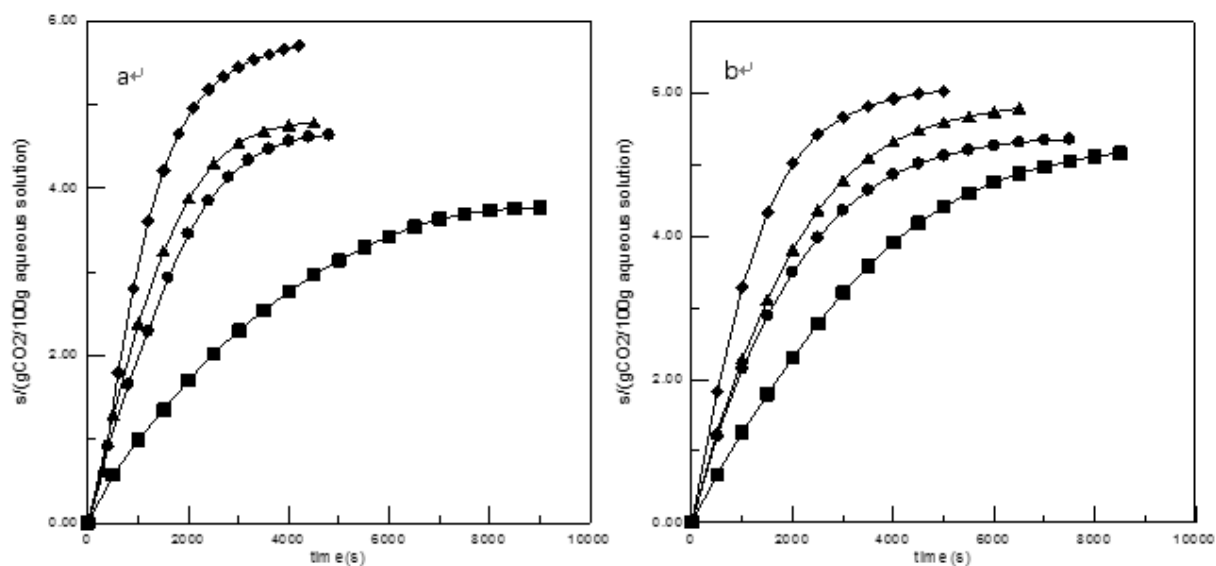
Figure 3 The influence of mass fraction of DEA on the absorption rate of CO_2 in K_2CO_3-DEA aqueous solution at 363.2K. Symbols: a. ■w_2/w_1=0.00/0.35; ●w_2/w_1=0.01/0.35; ▲w_2/w_1=0.015/0.35; ◆w_2/w_1=0.02/0.35; b.■w_2/w_1=0.00/0.40; ●w_2/w_1=0.01/0.40; ▲w_2/w_1=0.015/0.40; ◆w_2/w_1=0.02/0.40

To quantitatively show the effect of the addition of DEA on the absorption of CO_2 in K_2CO_3-DEA aqueous solutions, we followed Chowdhury et al.[23] and defined the absorption rate (R, g CO_2/100g aqueous solution/min) as the gradient of the loading-time curve at 50% of the saturated loading. The absorption rates under different concentrations and temperatures were listed in Table 2.

Table 2. the absorption rates(R) in K_2CO_3 (1)-DEA (2) aqueous solutions

w_1	w_2	R/ [gCO$_2$/100g aqueous solution/min]		
		343.2K	353.2K	363.2K
0.35	0	0.05	0.04	0.05
	0.010	0.10	0.10	0.14
	0.015	0.11	0.18	0.14
	0.020	0.15	0.21	0.19
0.40	0	0.05	0.04	0.07
	0.010	0.07	0.11	0.11
	0.015	0.11	0.20	0.13
	0.020	0.17	0.22	0.20

One finds from this table that the absorption rate of CO_2 increases with the increase of the mass fraction of DEA. The addition of very small amount of DEA can significantly enhance the absorption of CO_2 in K_2CO_3 aqueous solution at high temperatures.

Conclusions

In this study, the absorption rates of CO_2 in K_2CO_3-DEA aqueous solution was measured. The effects of mass fraction and temperature on the absorption rate were studied. Our results show that the addition of DEA into K_2CO_3 aqueous solution can significantly increase the absorption rate. Moreover, the absorption rate of CO_2 increases with the increase of temperature.

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