Absorption rate of CO_2 in PZ promoted K_2CO_3 aqueous solutions

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Abstract. The absorption rate of CO_2 in piperazine (PZ) promoted potassium carbonate (K_2CO_3) aqueous solution were measured at normal pressure. The temperatures ranged from 323.2K to 343.2K. The mass fractions of PZ and K_2CO_3 respectively ranged from 0 to 0.03 and 0.2 to 0.3. The influences of the temperature and concentration on the absorption rate of CO_2 in K_2CO_3-PZ aqueous solutions were illustrated.

Introduction

In recent years there has been growing concern over the potential environmental impacts of anthropogenic greenhouse gas emissions [1]. Chemical absorption is proven to be a mature technology. Alkanolamines (MEA, DEA, MDEA, PZ, etc.) and potassium carbonate (K_2CO_3) have been widely used to capture CO_2 [2-6].

The K_2CO_3 process is an important chemical solvent technology to reduce CO_2 emissions. This process, also known as Benfield process, was developed for the synthesis of liquid fuel from coal [7]. K_2CO_3 aqueous solution is low cost, low toxic, easily regenerable, less corrosive, low degradable, and has high chemical solubility of CO_2. However, the reaction between CO_2 and potassium carbonate solution is not fast that is demonstrating the slow mass transfer in the liquid phase [8-10].

Piperazine (PZ) is considered to be an effective activator that can significantly enhance the absorption rate of CO_2 in amine aqueous solutions. It has greater capacity and higher reaction rates than MEA and the CO_2 reaction rates for PZ are shown to be 2-3 times faster than MEA [11, 12].

Previous work has identified PZ as an effective promoter of CO_2 absorption rates in K_2CO_3 aqueous solution. Cullinane and Rochelle [13-15] studied thermodynamics and kinetics of the aqueous K_2CO_3 solution promoted by PZ, and used an ENRTL model to predict the equilibrium partial pressure of CO_2, species distribution, and enthalpy. Kim et al.[16, 17] studied the equilibrium partial pressure of CO_2 and pressure changes in the vapor-liquid equilibrium (VLE) apparatus at 313, 333, and 353 K, and the mass fractions of PZ was 0.1 and the mass fractions K_2CO_3 of ranged from 0.15 to 0.2.

The main purpose of this work is to determine an appropriate addition of PZ to K_2CO_3 aqueous solution. To this end, we experimentally determined the absorption rate of CO_2 in K_2CO_3-PZ aqueous solution, and illustrated the influence of temperature and mass fraction.

Experimental

Materials. K_2CO_3 and PZ were purchased from Huaxin chemical Co., with mass purity≥ 99%. K_2CO_3 and PZ were used without further purification. CO_2 (99.99%), and N_2 (99.99%) gas was purchased from Jinglian Special Gases Co., Ltd, Baoding, China. Aqueous solutions of K_2CO_3-PZ were prepared by adding doubly distilled water. The uncertainly of the electronic balance is ±0.1 mg.

Apparatus and Procedure. The experimental setup consists of a high-pressure CO_2 tank, a high-pressure N_2 tank, two mass flow controllers (MFC), a mixed gas cylinder, an absorption bottle, a constant temperature water bath and a desiccator and a CO_2 analyzer (Advanced Gasmitter by Germany Sensors Europe GmbH, the accuracy is ±2%). The absorption bottle was immersed into the bath and the temperature of the water should be regulated within 0.1K. During the experiment, CO_2 and N_2 from the high-pressure tank are let into the two MFC which maintain a constant flow rate in a

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ratio of 1:2 into mixed gas cylinders. The gas mixture is then let into the absorption bottle and absorbed by the solution. The residual and unabsorbed gas is then flowed into the desiccator and then into the CO_2 analyzer. Both the data of gas concentration and flow rate were recorded by a computer. In all the experiments, the rotational speed of the magnetic stirrer is fixed at 1000 rpm. The schematic diagram for the measurements of saturated solubility and the absorption rate of CO_2 is shown in Fig.1.

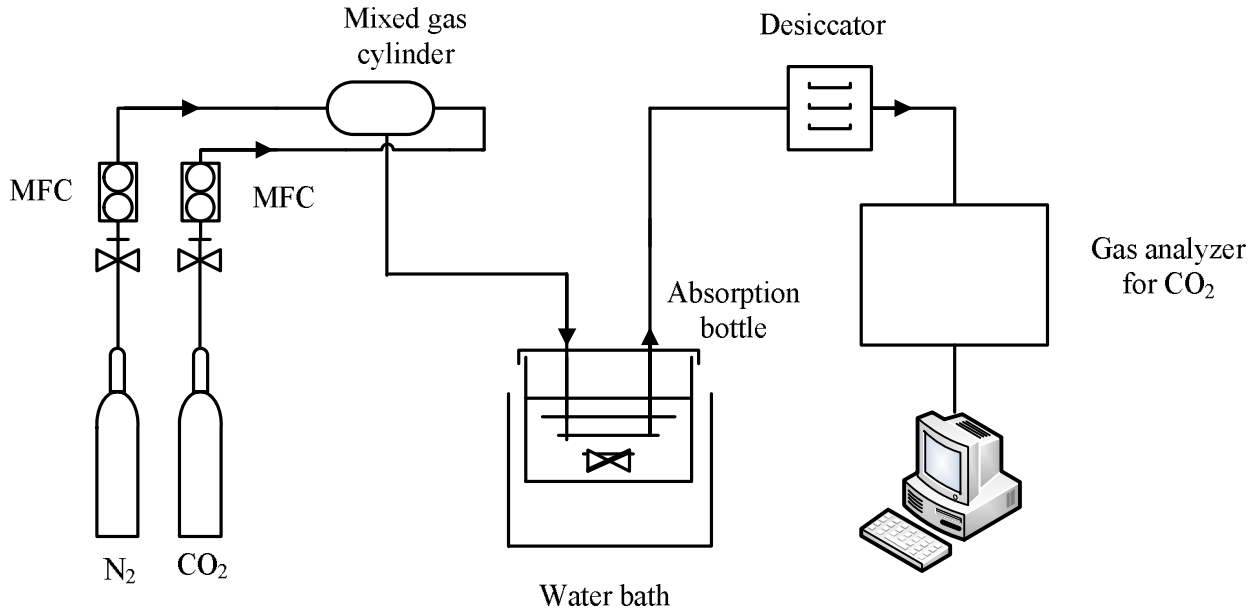

Fig 1. Schematic view of the experimental apparatus.

Results and Discussion

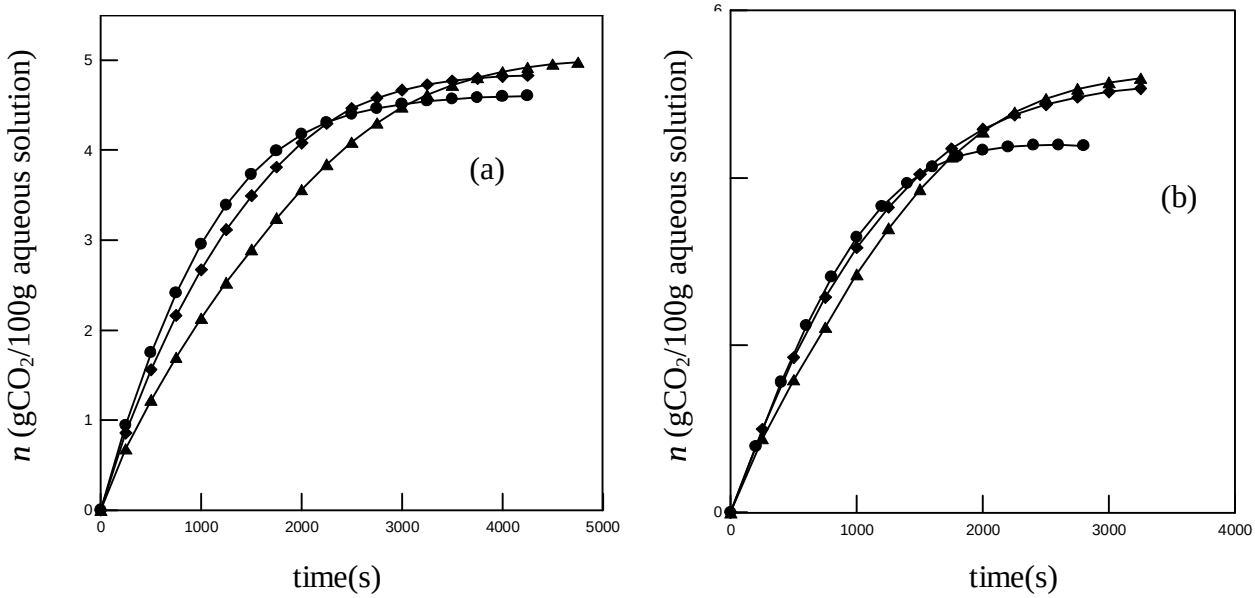

Fig 2. Effect of the temperature on the absorption rate of CO_2 in K_2CO_3-PZ aqueous solutions.(a) : w_{K2CO3}/w_{PZ} =0.20/0.01 ; (b) w_{K2CO3}/w_{PZ} =0.20/0.02. Symbols: ▲T=323.2K; ◆T=333.2K; ●T=343.2K. Lines: trend lines.

Fig.2 shows the influence of the temperature on the absorption rate of CO_2 in K_2CO_3-PZ aqueous solutions. One may find that the absorption rate of CO_2 increase with increasing temperature. With a further increase of the absorption time, the higher temperature led to less absorbed amount of CO_2.

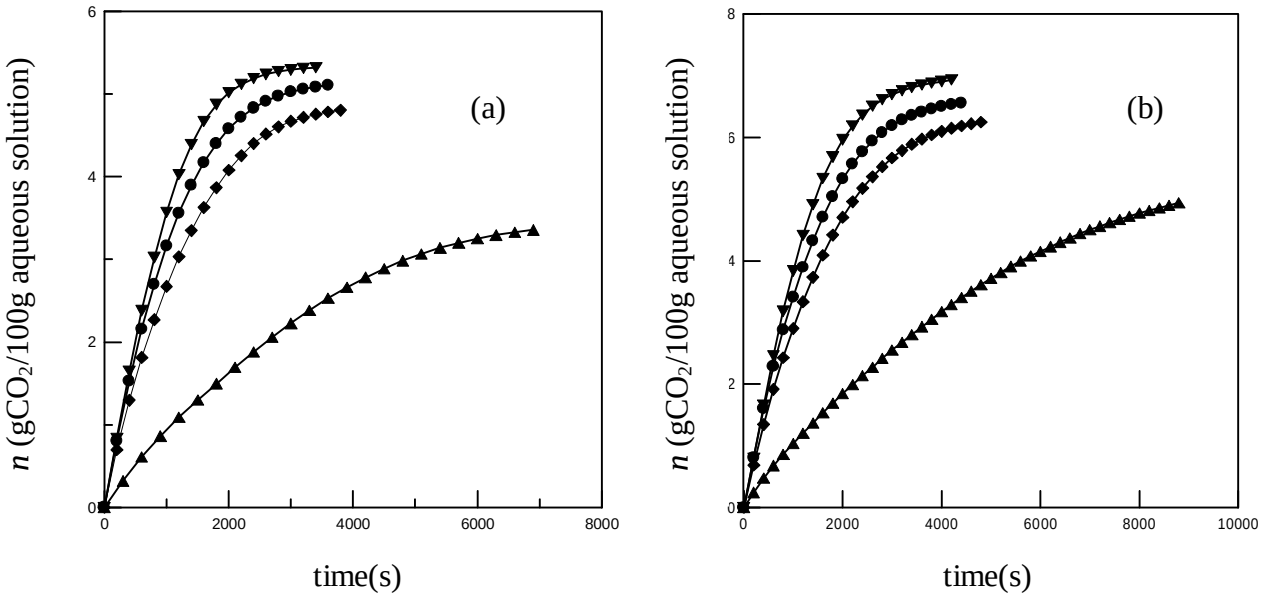

Fig 3. Effect of the mass fraction of PZ on the absorption rate of CO_2 in K_2CO_3-PZ aqueous solutions. (a) : w_{K2CO3}=0.20, T=333.2K ; (b) : w_{K2CO3}=0.30, T=343.2K. Symbols: ▲w_{PZ} =0； ◆w_{PZ} =0.01； ●w_{PZ} =0.02; ▼w_{PZ} =0.03. Lines: trend lines.

Fig. 3 shows the effect of the mass fraction of PZ on the absorption rate of CO_2 in K_2CO_3-PZ aqueous solutions. One may find that CO_2 is relatively slowly absorbed in K_2CO_3 aqueous solution, however, the absorption rate increases very significantly when the K_2CO_3 aqueous solution is promoted by PZ. Moreover, Fig.3 visually displays the influence of the addition of PZ on the absorption rate of CO_2 in K_2CO_3 aqueous solution. A small amount of PZ (w_{PZ}=0.01) can enhance the absorption rate, and the absorption rate increases with the increase of w_{PZ}.

To quantitatively show the effect of the addition of PZ on the absorption of CO_2 in K_2CO_3-PZ aqueous solutions, we followed Chowdhury et al.[18] 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 1.

Table 1 The absorption rate (R) of CO_2 in K_2CO_3-PZ aqueous solutions.

w_{K2CO3}	w_{PZ}	R [g/100g aqueous solution/min]		
		323.2K	333.2K	343.2
0.2	0	0.03	0.04	0.05
	0.01	0.12	0.17	0.19
	0.02	0.14	0.20	0.22
	0.03	0.22	0.23	0.24
0.3	0	0.02	0.03	0.05
	0.01	0.11	0.12	0.17
	0.02	0.14	0.15	0.21
	0.03	0.18	0.20	0.23

Conclusions

In this work, the absorption rate of CO_2 in PZ promoted K_2CO_3 aqueous solution was investigated. The effects of mass fraction and temperature on the absorption rate were studied. Our results show that the addition of small amount of PZ can significantly enhance the absorption of CO_2 in K_2CO_3 aqueous solution. The absorption rate of CO_2 increases with the increasing addition of PZ and temperature.

Acknowledgements

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