

# HIGH-EFFICIENCY CARBON CAPTURE WITH 2-METHYLIMIDAZOLE-WATER-PROPYLENE CARBONATE MIXTURE SOLVENT

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## ABSTRACT

Solvent absorption is currently the main decarbonization method, in which propylene carbonate (PC) washing is widely applied in virtue of its low material loss and simple process. In regard of the low solubility and selectivity to CO<sub>2</sub> of PC, traditional PC washing process is improved by adding 2-methylimidazole (2-mlm) and water as additives to PC. In this paper, firstly the miscible point of 2-mlm-water-PC three phase system as well as saturation point of 2-mlm were measured, so was the viscosity of mixture solvent. Next, the solubility of CO<sub>2</sub> in mixture solvents with different proportion was measured to make a comparison with that in pure PC, where temperature was in 298.15 and 308.15 K, pressure was in the range of 0.01-1.40 MPa. The heats of CO<sub>2</sub> absorption in these solvent mixtures were calculated using the Clausius-Clapeyron equation. Then the kinetic curves of pure PC and mixture solvents were measured, and solvent 2 (2-mlm 16.7 wt% + water 8.3 wt% + PC 75 wt%) showed a comparable absorption rate to that of pure PC and absorption balance can be achieved in a short time. Experimental results show that the mixture solvent possesses outstanding carbon capture capacity and is feasible to be applied in current PC washing process without any demand of equipment modification.

**Keywords:** CO<sub>2</sub> capture, PC washing process, absorption isotherm, absorption heat.

## 1. INTRODUCTION

As the main composition of greenhouse gas, CO<sub>2</sub> is widely accepted to be able to cause climate change, so it has become a global focus and a series of measures

have been proposed to reduce the emission of CO<sub>2</sub> [1]. Considering from energy resources, carbon resources, and environment, the emission control and development enhancement of CO<sub>2</sub> are subjects of great strategic significance [2]. By now, there have been CO<sub>2</sub> separation methods including cryogenic separation [3], absorption separation [4], membrane separation [5] adsorption separation [6], etc. Among the methods above, absorption separation has been widely applied in industry, including chemical [7] and physical [8] absorption separation processes. Chemical absorption separation is mainly suitable in the conditions of low CO<sub>2</sub> partial pressure and high purification degree requirement. However, all those chemical separation methods need to be heated in the solvent regeneration process, with a number of heat consumption, which means a high operation cost, as a cost of high purification degree. On the other hand, physical absorption separation is suitable for high CO<sub>2</sub> partial pressure. In physical separation, no reaction takes place between solvent and CO<sub>2</sub>, so in regeneration process, heat is unnecessary and low pressure desorption is enough, which means a lower total energy consumption than chemical absorption separation [9].

PC washing is a typical physical absorption method, which is applied in ammonia synthesis systems to remove CO<sub>2</sub>. This process has advantages including simple process, low equipment investment, high purification degree, etc. Some literatures have reported the ways to improve the PC process. In this paper, a novel improved PC washing process is proposed, in which 2-mlm and water is added to PC to improve the solubility and selectivity of solvent to CO<sub>2</sub>, and the appropriate 2-mlm-water-PC mixing solvent composition is suggested. The new solvent can be applied in the current PC washing system.

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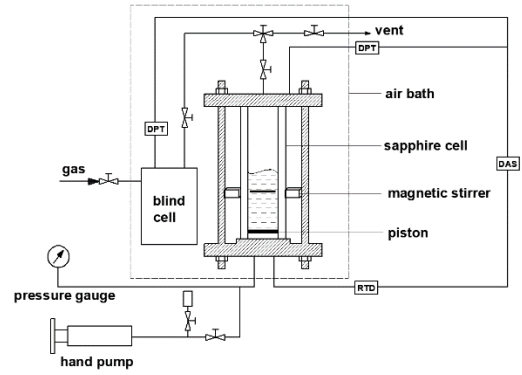
## 2. EXPERIMENTAL

### 2.1 Materials

Propylene carbonate and 2-methylimidazole used for preparing the mixture solvent were brought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Tap water was used. The CO<sub>2</sub> used in the experiments were brought from Beijing Ap Beifen Gases Industry Co., Ltd.

### 2.2 Experimental procedures

All the absorption/desorption experiments were conducted with the device illustrated as Fig. 1. It was also used in our previous works [10-12]. The whole rig consists of two parts—a blind cell and a sapphire cell, connected with pipes and valves. The blind cell is used to provide feed gas and has an effective volume ( $V_b$ ) of 126.4 cm<sup>3</sup>, while that volume for the sapphire cell is 72.5 cm<sup>3</sup>. And the maximum operating pressures of both cells are 20 MPa. The secondary platinum resistance thermometer (type-Pt100) and the calibrated Heise pressure gauge are connected to a computer to record the system temperature and pressure variation over time, whose accuracy are  $\pm 0.1$  K and  $\pm 0.01$  MPa respectively. Before the experiment, a certain mass of 2-mlm, water, and PC were weighed with a balance (with an accuracy of  $\pm 0.1$  mg), and then added into the sapphire cell to form solvent with stirring. The sapphire with solvent was then fixed back to the air bath. After that, the whole system including the blind cell and the sapphire cell with their connecting pipes were evacuated, and the magnetic stirrer in the solvent was kept working at the same time. Then a certain quantity of feed gas was charged into the blind cell, and the constant temperature bath was turned on. The experiment was started after the experimental temperature was set and then reached, and the pressure in the blind cell was recorded as  $P_0^b$  before the beginning of the experiment. As for the experiment procedure, firstly the valve between the two cells was turned on to make a certain quantity of feed gas enter the sapphire cell, where the residual pressure in the blind cell was recorded as  $P_1^b$ . Next, the magnetic stirrer in the solvent was turned on to increase the interface between the gas and solvent. When the pressure in the sapphire cell kept constant, the gas and liquid was considered to attain the equilibrium and a batch of experiment was finished, where the pressure in the sapphire cell was recorded as  $P_E$ .



**Fig. 1 Schematic diagram of experimental phase equilibrium separation apparatus: DPT, differential pressure transducer; DAS, data acquisition system; and RTD, resistance thermocouple detector.**

### 2.3 Data process

In this paper, the gas solubility in solvent is calculated by mass balance as below.

The total number of moles of the gas in the sapphire cell is calculated by:

$$n_t = \frac{p_0^b \times V^b}{Z_0 \times R \times T} - \frac{p_1^b \times V^b}{Z_1 \times R \times T}$$

where  $p_0^b$  and  $p_1^b$  are the initial pressure in the blind cell and the residual pressure in the blind cell after discharging gas into the sapphire cell, respectively;  $V^b$  is the volume of the blind cell;  $T$  is the experimental temperature;  $Z_0$  and  $Z_1$  are the compression factors calculated with Benedict-Webb-Rubin-Starling equation of state;  $R$  is the universal gas constant.

The volume of solvent and gas in the sapphire cell are respectively recorded as  $V_s$  and  $V_g$  in below:

$$V_s = h \times \pi \times r^2$$

$$V_g = V - V_s$$

where  $h$  is the height of the solvent;  $r$  and  $V$  are the inside radius and volume of the sapphire cell.

The number of moles in the gas phase of the sapphire cell after separation equilibrium is:

$$n_E = \frac{p_E \times V_g}{Z_E \times R \times T}$$

where  $p_E$  is the equilibrium pressure in the sapphire cell;  $Z_E$  is the coordinated compression factor in the sapphire cell.

The number of moles of absorbed gas in solvent is:

$$n = n_t - n_E$$

The solubility of gas in solvent is:

$$S_V = \frac{n}{V_s}$$

The desorption heat of gas in solvent is calculated with Clausius-Clapeyron Equation [13]:

$$Q = -R \times d(\ln p) / d(1/T)$$

where  $d(\ln p)/d(1/T)$  can be calculated by differentiating solubility curves of different concentration, so that the desorption heat of different solubility can be attained.

## RESULTS AND DISCUSSION

The 2-mlm aqueous solution is not completely miscible in PC, and its solubility is influenced by the introduction of PC, so the three-phase miscibility points were measured firstly. The saturation point of 2-mlm was measured as 2-mlm content increases. The 2-mlm-water-PC ternary phase diagram is shown in Fig.2. According to the diagram, mixture solvents in different composition were prepared and their viscosities at room temperature and atmospheric pressure were measured by using the capillary viscometer, which are listed in Table 1. Although the viscosity of mixture solvent are slightly higher than pure PC, they still remain in a lower level compared with 2-mlm-glycol-PC solvent [14]. The results indicate that compared with the traditional PC washing process, 2-mlm-water-PC solvent will not increase the load of liquid circling pumps in use.

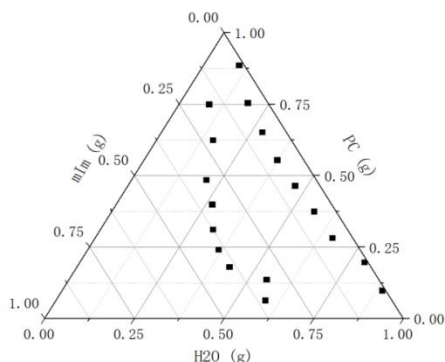


Fig. 2 mlm-water-PC three phase diagram

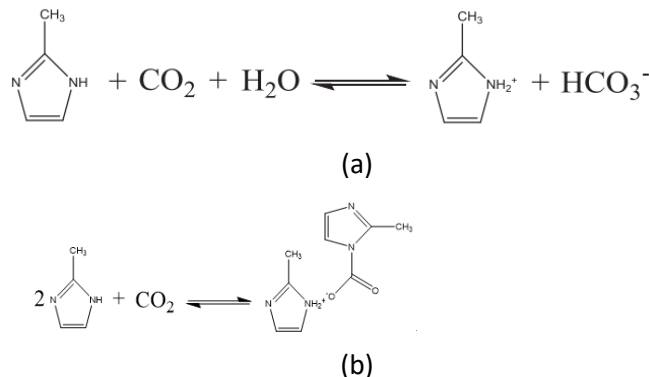
Table 1 compositions and viscosity of mixture solvents as well as of pure PC at 298.15 K.

Absorbent	Composition (wt%)			Viscosity (mPa.s)
	mlm	water	PC	
Pure PC	-	-	100	2.51
Solvent 1	30	35	35	3.17
Solvent 2	16.7	8.3	75	3.26
Solvent 3	9.1	9.1	81.8	2.74
Solvent 4	16.7	16.7	66.6	2.88

Fig. 3 illustrates the comparison of CO<sub>2</sub> solubility in pure PC and mixture solvent in different compositions,

which indicates higher solubility at different degrees in the mixture solvents than in pure PC. The 2-mlm content in solvent 1 is 30 wt%, which is the highest, and it has the most CO<sub>2</sub> solubility, with an absorption heat of 64 kJ/mol closing to chemical absorption. That is because of the chemical heat caused by the reaction between 2-mlm and CO<sub>2</sub> in the water, which can lead to increase the heat consumption in solvent desorption process. Solvent 2 and 3 have the same water/PC ratio of 1:9, and different 2-mlm contents, and their CO<sub>2</sub> solubility are similar. However, the desorption heat of solvent 2 is far less than that of solvent 3, where the former is 29 kJ/mol while the latter is 43 kJ/mol when the solubility of CO<sub>2</sub> is 1 mol/L. Solvent 2 and 4 have the same content of 2-mlm, and their water/PC ratio are 1:9 and 2:8 respectively. According to Fig.3 and 4, solvent 4 has a higher CO<sub>2</sub> solubility and desorption heat, whose reason lies in that 2-mlm is more easily combine with CO<sub>2</sub> in water, so CO<sub>2</sub> is more difficult to desorb from the solution. Results above indicate that when 2-mlm content is the same, a higher water content makes the CO<sub>2</sub> capture ability stronger, meanwhile with a more desorption heat.

The reason for the above phenomena is that the mechanisms of CO<sub>2</sub> capture by 2-mlm in solvent are discriminate, as shown in the following chemical reactions (a) and (b). With the addition of 2-mlm and water, the solubility of CO<sub>2</sub> in the solvent increases with the content of 2-mlm, and the desorption heat of the solvent has a great relationship with the water content. As shown, CO<sub>2</sub> absorption is dominated by strong chemical absorption with 2-mlm and water in the solvent, which leads to an increase in the solubility of CO<sub>2</sub>, and also has the drawback of the large heat absorption. However, when water accounts for a small amount, portion of 2-mlm and CO<sub>2</sub> produce weak chemical effects.[10]



When assuring the composition of solvent, it is necessary to strike the balance between solubility and

desorption. Compared with pure PC, at 0.6 MPa, 283.15 K, solvent 2 raises the CO<sub>2</sub> solubility by 34%.

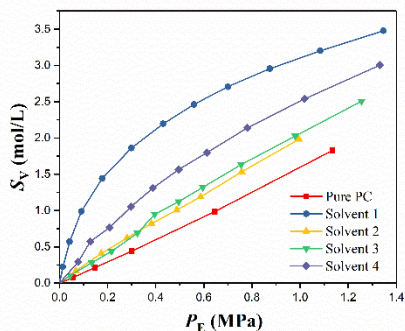


Fig. 3 Comparison of the CO<sub>2</sub> solubilities in pure PC and mixture solvent 1-4 at 298.15 K.

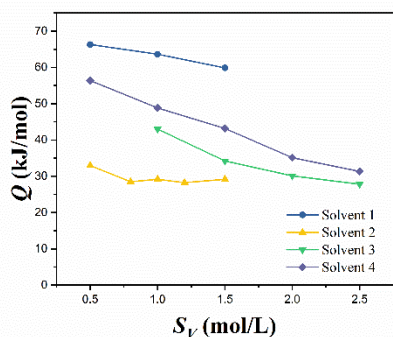


Fig. 4 Desorption heats of CO<sub>2</sub> in mixture solvents with different composition.

Fig. 5 illustrates the comparison of equilibrium time of pure PC and mixture solvent 1 and 2, all at 289.15 K and an initial pressure of 0.5 MPa. According to the figure, all the three solvent can reach equilibrium in a short time. Solvent 2 and pure PC have the same absorption rate in the early period, but pure PC reaches equilibrium in no more than 7 min because of its low solubility, while solvent 2 need 11 min. However, when the water and 2-mlm proportion are increased, the absorption rate will become lower, which makes the equilibrium time longer, as solvent 1 showed, 25 min is needed.

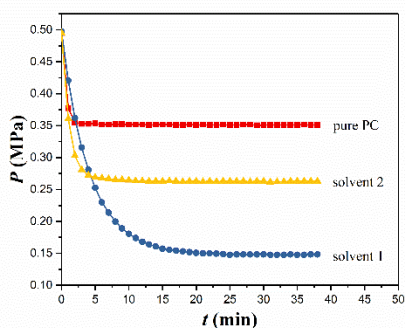


Fig. 5 Kinetic curves of CO<sub>2</sub> in pure PC, solvent 1 and solvent 2 at 298.15 K and initial pressure 0.5 MPa

## CONCLUSIONS

In this paper, a novel method to improve the traditional PC washing process is proposed, which is adding mlm and water into PC to form a mixing solvent. Furthermore, the viscosity, CO<sub>2</sub> solubility, absorption heat, and absorption rate of different mixing solvents are compared. Experimental results shows that compared with pure PC, at 0.6 MPa, 283.15 K, solvent 2 (mlm 16.7 wt% + water 8.3 wt% + PC 75 wt%) increases CO<sub>2</sub> solubility by 34%, and has the comparatively less sorption heat of 29 kJ/mol, as well as the similar absorption heat with pure PC. Study on the regeneration performance, corrosiveness, etc. of the circling solvent will be conducted in our later work.

## ACKNOWLEDGEMENT

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