

# Solubility of Carbon Dioxide in Four Mixed Solvents

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A constant-volume method was used to measure the solubility of carbon dioxide in four mixed solvents at different temperatures and pressures. The mixed solvents are 2,3-butanedione + propylene carbonate, 2,3-butanedione + *N*-methyldiethanolamine (MDEA) + water, ethylene carbonate + MDEA + water, and acetoacetamide + MDEA + water. The data are compared with literature data for the solubility of carbon dioxide in pure propylene carbonate or a mixed solvent of MDEA + water.

## 1. Introduction

The solubility of gases in liquids is a fundamental properties for the design of gas absorption and stripping columns and gas–liquid and gas–liquid–solid reactors in the chemical industry. In addition, solubility results over a wide range of temperature are useful for studying the solution properties in the chemical, biochemical, environmental protection, and energy industries.

However, the removal of acid gases from refinery and natural gases using mixed solvents continues to be of interest, and carbon dioxide capture by the solvent absorption method becomes increasingly important with people's increasing awareness of environment problems. Gas solubility data plays an important role in the process of absorbent selection in these two fields. However, there has been little reported data on gas solubility in mixed solvents.

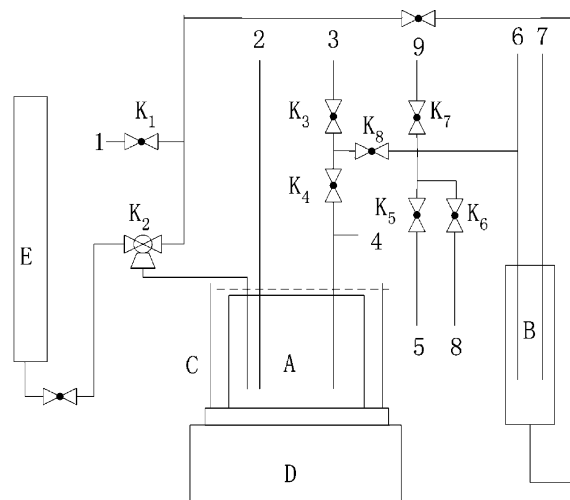
The widely used solvent for the absorption of carbon dioxide is *N*-methyldiethanolamine (MDEA). Although the aqueous MDEA solution has improved properties against degradation and corrosion, an activator such as piperazine<sup>1</sup> is necessary to increase the absorption rate. More efficient absorption of carbon dioxide is still interesting, especially with regard to decreasing the cost of capture of carbon dioxide for environment protection.

In this work, some new compounds are studied as the activator: 2,3-butanedione, ethylene carbonate, and acetoacetamide. The solubility of carbon dioxide in a mixed solvent of propylene carbonate with ethylene carbonate and in an aqueous solution of 48 mass % MDEA with these suggested activators was measured at 298.15 K and 303.15 K and a partial pressure of carbon dioxide up to 0.4 MPa.

## 2. Experimental Section

**2.1. Apparatus.** The gas solubility measurement apparatus used in this work was based on the constant-volume method and is similar to that described by Chen et al.<sup>2</sup> According to other researchers' work,<sup>3–9</sup> minor modifications were made in this work. The principle of the constant-volume method is to bring a measured quantity of a solute gas into contact with a measured quantity of gas-free solution, agitate until equilibrium is established, and measure the quantity of the remaining gas. The gas solubility in the solvent is then calculated from the material balance.

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**Figure 1.** Schematic diagram of the apparatus: A, absorption cell; B, gas storage cell; C, water bath connected to a temperature controller; D, magnetic stirring system; E, solvent input buret; K<sub>1</sub> to K<sub>7</sub>, valves; 1, waste solution and gas output; 2, digital temperature transducer; 3, connection to vacuum pump; 4, digital pressure transducer; 5, CO<sub>2</sub> gas input; 6, digital pressure transducer; 7, digital temperature transducer; 8, N<sub>2</sub> gas input.

A schematic diagram of the equilibrium apparatus is shown in Figure 1. The apparatus comprises an absorption cell A, a gas cell B, a water bath C, a magnetic stirrer D, a sampling buret E, and a degassing system F. In Figure 1, line 1 leads to a waste storage tank, lines 2 and 7 connect to temperature transducers, line 3 connects to a vacuum pump, lines 4 and 6 connect to pressure transducers, line 5 connects to a carbon dioxide cylinder, and line 8 connects to a nitrogen cylinder. The volume of absorption cell A is 83 cm<sup>3</sup>, and it is immersed in water bath C whose temperature was regulated to within 0.1 K by a temperature controller. The temperature of absorption cell A and gas cell B was measured by platinum resistance temperature transducers and displayed by digital meters. The pressures of cells A and B were measured by pressure transducers and also displayed by digital meters. Users can conveniently obtain the temperature and pressure of both A and B by using the transducers, so this set of equipment can be used to measure the absorption rate. The measurement error of the liquid volumes is 0.05 mL.

**2.2. Materials.** Carbon dioxide and nitrogen are from the Beijing Praxair Company and have purities of 99.95% and 99.5%, respectively. 2,3-Butanedione is from Acros Organics with a purity of more than 99.0%. Ethylene carbonate and acetoacetamide are both from Fluka Organics and have purities of 97.0% and 98.0%, respectively. Propylene carbonate and MDEA are both from the Beijing Chemical Reagents Company with purities of 99.0% and 97.0%, respectively. Gas chromatography was used to check the purities of all of the above components. All components were used without further purification.

**2.3. Experimental Procedure.** The volumes of absorption cell A and gas cell B were measured by determining the mass of water used to fill the cells. A mixed solvent of known composition was first boiled under reflux at atmospheric pressure. The change in solvent composition during the degassing operation was less than 0.7%, and air contamination was less than 0.005% based on the chromatography analysis.

The gas leakage of the apparatus was checked, and then the apparatus was pumped to vacuum. The temperature control system was turned on, and the temperature of absorption cell A was set.

About 10 mL of mixed solvent from titration buret E was fed to absorption cell A with the help of the vacuum in cell A, and the exact volume of solvent was recorded through the scale of titration buret E with an error of 0.05 mL. After more than 1 h of equilibration, the pressure and temperature of absorption cell A were recorded, and this pressure was used as the saturated vapor pressure of the mixed solvent at the equilibrium temperature.

The magnetic stirring apparatus was turned on and set at a constant rotation speed.

Gas cell B was charged with carbon dioxide, and the temperature and pressure of B were recorded. The valve from cell A to cell B was opened, and carbon dioxide was added to cell A. After 10 minutes, the temperature and pressure of B were recorded again.

After the pressure of cell A did not change for 2 h, the system was considered to be at equilibrium, and then temperature and pressure of absorption cell A were recorded.

Then the gas solubility at this carbon dioxide partial pressure was calculated according to the material balance as shown in following section.

**2.4. Data Processing.** The total amount of gas charged into absorption cell A is calculated from

$$\Delta n = n_1 - n_2 \quad (1)$$

where  $n_1$  is the amount of gas in gas cell B before the gas-charging step and  $n_2$  is the amount of gas in gas cell B after the gas-charging step.

The absorbed amount of gas is calculated from

$$n_g = \Delta n - n^E \quad (2)$$

where  $n^E$  is the residual amount of gas in the gas phase of absorption cell A while the phase equilibrium is being established.

The amount of solvent added to cell A is calculated from

$$n_1 = \frac{\Delta V \rho}{M} \quad (3)$$

where  $\Delta V$  is the volume of the solvent,  $\rho$  is the density of the solvent, and  $M$  is the mean molecular weight of the solvent.

**Table 1. Mole Fraction Solubility of CO<sub>2</sub> in Water at  $P_{\text{CO}_2} = 1.0$  atm**

T/K	$10^4 x_{\text{CO}_2}$	$\pm 10^4 \delta x_{\text{CO}_2}$
303.15	5.2	1.0
308.15	4.3	1.0
313.15	3.8	1.0
318.15	3.3	1.0

**Table 2. Mole Fraction Solubility of CO<sub>2</sub> in Propylene Carbonate**

T/K = 298.15			T/K = 303.15		
$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm \delta x_{\text{CO}_2}$	$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm \delta x_{\text{CO}_2}$
55.3	0.0056	0.0001	70.1	0.0061	0.0001
100.8	0.0102	0.0004	103.6	0.0088	0.0003
137.2	0.0136	0.0006	119.8	0.0101	0.0004
149.5	0.0150	0.0007	190.5	0.0160	0.0008
249.5	0.0249	0.0012	252.1	0.0213	0.0011
370.5	0.0362	0.0022	315.4	0.0262	0.0013
439.5	0.0451	0.0026	414.8	0.0352	0.0021

The equilibrium partial pressure  $P_{\text{CO}_2}$  can be calculated from

$$P_{\text{CO}_2} = P_A - P^S(1 - x_{\text{CO}_2}) \quad (4)$$

where  $P_A$  is the pressure of absorption cell A while phase equilibrium is being established and  $P^S$  is the saturated vapor pressure of the mixed solvent at the equilibrium temperature. Then, the solubility of carbon dioxide in the solvent expressed in mole fraction was calculated from

$$x = \frac{n_g}{n_g + n_1} \quad (5)$$

In the case of physical absorption, because the total pressure  $P$  was nearly 1 atm and  $x_{\text{CO}_2} \ll 1$ , eq 4 can be simplified to

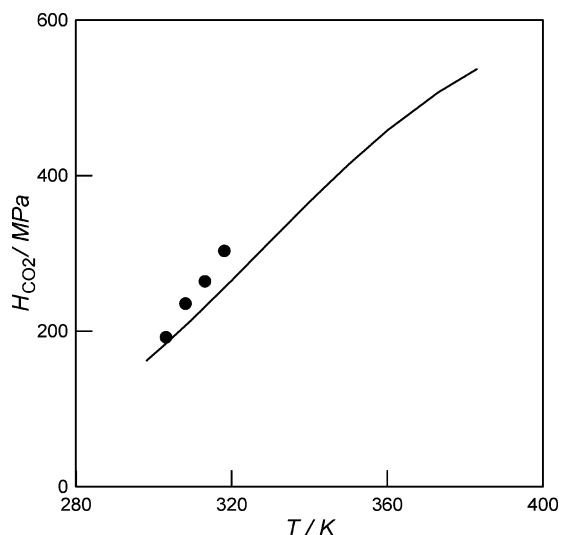
$$P_{\text{CO}_2} + P_A - P_S \quad (6)$$

whereas in the case of chemical absorption, iterative computation is needed to obtain the experimental results.

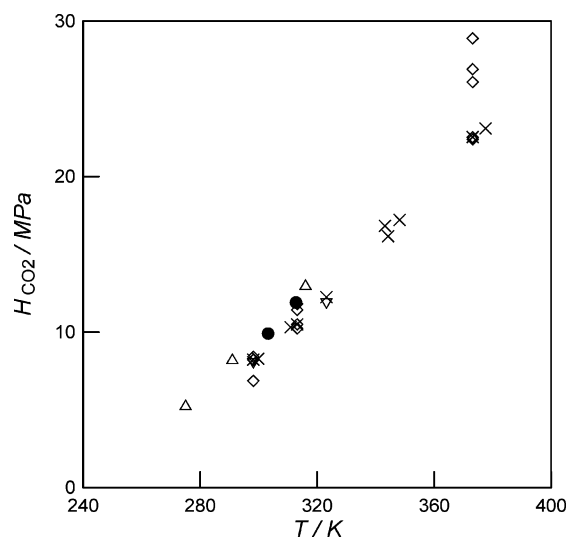
No correction for vapor-phase nonideality was included.  $n_1$ ,  $n_2$ , and  $n^E$  are all calculated by an equation of state from the data of  $PVT$ , and a perfect gas equation is adopted in this paper.

### 3. Results

**3.1. Reliability of Apparatus.** The solubility of CO<sub>2</sub> in water and propylene carbonate was measured at different temperatures and pressures to verify the laboratory techniques used and to ensure that analytical equipment was operated correctly. Results are listed in Tables 1 and 2. As shown in Figure 2, measured Henry's constants of CO<sub>2</sub> in water are in the range of (200 to 500) MPa, and experimental deviations are around 10% with literature correlation results<sup>10</sup> and became larger with increasing temperature. That means that the experimental method cannot be used to measure the system with a small solubility of less than 0.0005 or with a high Henry's law constant larger than 200 MPa. But as shown in Figure 3, measured Henry's law constants of CO<sub>2</sub> in propylene carbonate are in good agreement with literature data<sup>11–14</sup> because of the larger solubility, so the experimental method used in this work is valid for the measurement of gas solubility larger than 0.0005 or a Henry's law constant smaller than 200 MPa.



**Figure 2.** Henry's constant of CO<sub>2</sub> in water: ●, this work; ○, correlation of Carroll et al.<sup>10</sup>



**Figure 3.** Henry's constant of CO<sub>2</sub> in propylene carbonate: ●, this work; ×, Mantor et al.;<sup>11</sup> ▽, Murrieta-Guevara et al.;<sup>12</sup> ◇, Murrieta-Guevara et al.;<sup>13</sup> Δ, Blanchard et al.<sup>14</sup>

The uncertainties of the measured solubilities consist of measurement errors for temperature, pressure, and volume. The uncertainties for measured temperature, pressure, and volume are  $u(T)/T = 0.1/298.15 = 0.00033$ ,  $u(P)/P = 0.002$ , and  $u(x) = n_g/(n_g + n_1)(V)/V = 0.05/10.0 = 0.005$ . On the basis of the method for the estimation of uncertainties, the overall uncertainty of the measured solubility of CO<sub>2</sub> is

$$\frac{u(x)}{x} = \sqrt{\left(\frac{u(n_g)}{n_g}\right)^2 + \left(\frac{u(n_g + n_1)}{n_g + n_1}\right)^2} = \sqrt{\frac{u(n_1)^2 + u(n_2)^2 + u(n^E)^2}{n_g^2} + \frac{u(n_1)^2 + u(n_2)^2 + u(n^E)^2 + u(n_1)^2}{(n_g + n_1)^2}} \quad (7)$$

in which  $u(n_1)$ ,  $u(n_2)$ , and  $u(n^E)$  can be estimated as

$$\frac{u(n_1)}{n_1} = \frac{1}{R} \sqrt{\left(\frac{u(P_1)}{P_1}\right)^2 + \left(\frac{u(V_1)}{V_1}\right)^2 + \left(\frac{u(T_1)}{T_1}\right)^2} \quad (8)$$

**Table 3.** Mole Fraction Solubility of CO<sub>2</sub> in 5 Mass % 2,3-Butanedione + Propylene Carbonate

T/K = 298.15			T/K = 303.15		
$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$	$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$
45.5	0.0052	0.0001	60.0	0.0063	0.0001
96.9	0.0104	0.0004	106.3	0.0111	0.0003
153.2	0.0172	0.0008	158.2	0.0163	0.0006
211.7	0.0234	0.0012	206.8	0.0213	0.0009
270.5	0.0303	0.0017	268.7	0.0280	0.0014
346.0	0.0388	0.0024	340.5	0.0351	0.0019
			361.8	0.0370	0.0021

**Table 4.** Mole Fraction Solubility of CO<sub>2</sub> in 5 Mass % 2,3-Butanedione + 48 Mass % MDEA + Water

T/K = 298.15			T/K = 303.15		
$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$	$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$
2.1	0.0071	0.0001	4.1	0.0136	0.0001
4.6	0.0148	0.0002	8.6	0.0254	0.0002
6.3	0.0264	0.0004	13.9	0.0354	0.0003
10.3	0.0365	0.0006	19.9	0.0453	0.0005
16.9	0.0469	0.0009	32.2	0.0572	0.0007
31.3	0.0608	0.0012	50.5	0.0676	0.0009
69.2	0.0760	0.0016	91.9	0.0787	0.0011
171.0	0.0885	0.0020	121.0	0.0822	0.0012
185.6	0.0909	0.0022	173.5	0.0868	0.0013
249.6	0.0930	0.0024	216.3	0.0893	0.0015
			274.3	0.0917	0.0016

**Table 5.** Mole Fraction Solubility of CO<sub>2</sub> in 5 Mass % Ethylene Carbonate + 48 Mass % MDEA + Water

T/K = 298.15			T/K = 303.15		
$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$	$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$
7.9	0.0166	0.0001	8.6	0.0129	0.0001
22.9	0.0369	0.0004	16.3	0.0269	0.0002
78.6	0.0756	0.0010	30.7	0.0441	0.0004
166.4	0.0901	0.0014	55.8	0.0618	0.0006
			74.0	0.0694	0.0008
			96.4	0.0765	0.0010
			126.0	0.0828	0.0011
			181.4	0.0899	0.0013
			265.4	0.0965	0.0015

whereas  $u(n_1)$  is estimated as

$$u(n_1) = \frac{\rho}{M} u(V_1) \quad (9)$$

The estimated uncertainties are also included in the tables containing the experimental results.

**3.2. Experimental Results.** The solubility of carbon dioxide in a mixed solvent of 5 mass % 2,3-butanedione + propylene carbonate and the results are shown in Table 3.

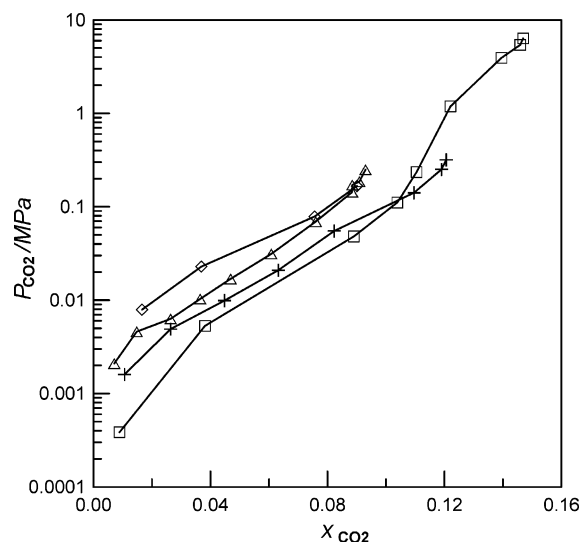
The results show that the solubility of carbon dioxide in 5 mass % 2,3-butanedione + propylene carbonate increases with increasing CO<sub>2</sub> partial pressure and decreases with increasing temperature. The measured solubility values are in reasonable agreement with Henry's law. This indicates that both 2,3-butanedione and propylene carbonate are physical solvents.

The Henry's law constants for carbon dioxide in the 5 mass % 2,3-butanedione + propylene carbonate solvent are 8.98 MPa at 298.15 K and 9.66 MPa at 303.15 K. They are almost the same as those in pure propylene carbonate, as shown in Figure 2.

The solubility of carbon dioxide in three mixed solvents—5 mass % 2,3-butanedione + 48 mass % MDEA + water, 5 mass % ethylene carbonate + 48 mass % MDEA + water, and 5 mass % acetoacetamide + 48 mass % MDEA + water—was measured, and the results are shown in Tables 4 to 6.

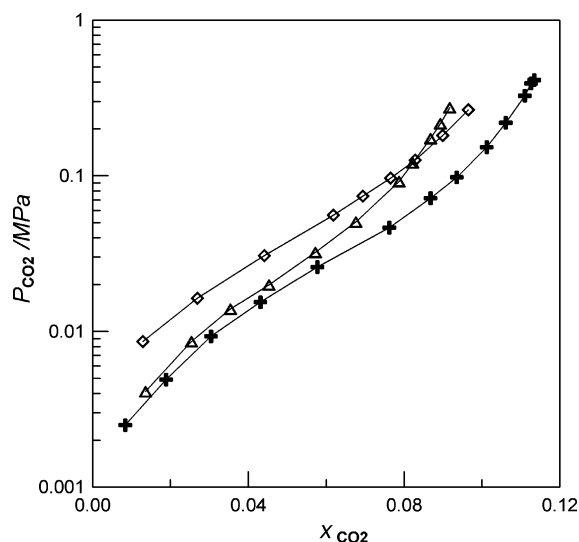
**Table 6. Mole Fraction Solubility of CO<sub>2</sub> in 5 Mass % Acetoacetamide + 48 Mass % MDEA + Water**

T/K = 298.15			T/K = 303.15		
$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$	$P_{\text{CO}_2}/\text{kPa}$	$x_{\text{CO}_2}$	$\pm\delta x_{\text{CO}_2}$
1.6	0.0106	0.0001	2.5	0.0084	0.00001
4.9	0.0264	0.0002	4.9	0.0189	0.0002
9.9	0.0448	0.0005	9.3	0.0304	0.0003
20.9	0.0632	0.0008	15.4	0.0431	0.0005
55.0	0.0823	0.0012	25.9	0.0577	0.0007
141.3	0.1096	0.0017	46.4	0.0762	0.0010
251.2	0.1190	0.0020	71.8	0.0868	0.0013
317.5	0.1206	0.0022	97.8	0.0935	0.0015
			152.7	0.1012	0.0017
			219.0	0.1061	0.0018
			326.7	0.1110	0.0020
			392.5	0.1126	0.0021
			412.2	0.1134	0.0022

**Figure 4.** Solubility of CO<sub>2</sub> in mixed solvents at 298.15 K:  $\Delta$ , 5 mass % 2,3-butanedione + 48 mass % MDEA + water;  $\diamond$ , 5 mass % ethylene carbonate + 48 mass % MDEA + water; +, 5 mass % acetoacetamide + 48 mass % MDEA + water;  $\square$ , 48.5 mass % MDEA + water, Jou et al.<sup>15</sup>

The solubility of carbon dioxide in all three aqueous mixed solvents increases with increasing CO<sub>2</sub> partial pressure and decreases with increasing temperature. At lower CO<sub>2</sub> partial pressure, CO<sub>2</sub> solubility increases rapidly with increasing pressure, and the difference in gas solubility between 298.15 K and 303.15 K is not obvious because of the experimental uncertainty in the range of low pressure. At higher CO<sub>2</sub> partial pressure, CO<sub>2</sub> solubility increases slowly with increasing pressure, and the difference in gas solubility between 298.15 K and 303.15 K becomes obvious.

In Figure 4, the solubility data of carbon dioxide in three aqueous mixed solvents at 298.15 K are plotted together with similar data in aqueous 48.5 mass % MDEA.<sup>15</sup> The data at 303.15 K are plotted in Figure 5. In Figure 4, one can see that the solubility in these mixed solvents is one-half to one-third less than that in the aqueous solution of 48.5 mass % MDEA, except for the situation in 5 mass % acetoacetamide + 48 mass % MDEA + water with the partial pressure of CO<sub>2</sub> higher than 0.1 MPa. The mixed solvent of acetoacetamide + MDEA + water is the best one in these three mixed solvents based on the solubility data, and the feasibility of these mixed solvents in the absorption of CO<sub>2</sub> will finally be justified from the kinetic data measured and published later.

**Figure 5.** Solubility of CO<sub>2</sub> in four mixed solvents at 303.15 K:  $\Delta$ , 5 mass % 2,3-butanedione + 48 mass % MDEA + water;  $\diamond$ , 5 mass % ethylene carbonate + 48 mass % MDEA + water; +, 5 mass % acetoacetamide + 48 mass % MDEA + water.

#### 4. Conclusions

The solubility of carbon dioxide in four mixed solvents has been measured at different temperatures and pressures in this work. The solubility of carbon dioxide in 5 mass % 2,3-butanedione + propylene carbonate is similar to that in pure propylene carbonate. The solubility of carbon dioxide in three aqueous MDEA mixed solvents is one-half to one-third less than that in the aqueous MDEA solution with the exception of acetoacetamide + MDEA + water at a partial pressure of carbon dioxide larger than 0.1 MPa. The mixed solvent acetoacetamide + MDEA + water shows a potential in the absorption of carbon dioxide at high partial pressure. The actual possibility of these mixed solvents absorbing carbon dioxide will be justified with the kinetic data measured later.

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