Research Article

A Novel Carbon Dioxide Desorption Phenomenon using an Aqueous Potassium Acetate Solution

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Abstract: A novel CO2 absorbent, 50–75 wt.% aqueous potassium acetate solution (AcK(aq)), which showed a CO2 absorption capacity of ~ 0.2 mol CO2/mol, and could almost immediately completely desorb CO2 on addition of 40 wt.% H2O at 30 °C was investigated. This novel phenomenon seemed contrary to the Le Chatelier’s principle because H2O is reactant in this system. After characteristics of products by FTIR and XRD diffraction pattern, the novel desorption behavior was attributed to the acid-base reaction between KH(CH3COO)2 and KHCO3 precipitates within the absorbent sludge. As H2O was added, both compounds re-dissolved and CO2 was released. A similar observation was made when the absorbent sludge was heated to temperatures above 60 °C, owing to an increase in solubility with temperature. The mechanism of CO2 captured and released by AcK(aq) was proposed in this study. This novel energy-saving CO2 absorption and desorption behavior reveals that AcK(aq) has a high potential for application in the commercial production process.

Keywords: carbon dioxide, carbon capture, absorption, desorption

1. Introduction

Reducing the negative effects of global warming via carbon dioxide capture and storage (CCS) is an important area of research. According to the analysis from NOAA’s Global Monitoring Lab, global average atmospheric carbon dioxide was 414.72 ppm in 2021 [1]. Many scientists have proposed exceptional and effective methods by which atmospheric or flue gas CO2 can be captured e.g., alkanolamine absorbents, including steric hindrance amines [2–5], have been used extensively owing to their ability to quickly absorb carbon dioxide, NOx, and SOx. For example, Aghel B et al. [6–9] reported that CO2 captured by monoethanolamine or/and diethanolamine microchannel reactor. They proposed that the mass transfer efficiency was determined based on the CO2 desorption percentage, volumetric liquid-side mass transfer coefficient (kLaV) and volumetric overall mass transfer flux (NCO2aV). The energy consumption per unit mass CO2 (R) is also a key point of CCU process. Unfortunately, during the absorbent regeneration process, a significant proportion of the alkanolamines is lost, and carcinogens such as nitrosamines may be produced [10–12] given that the desorption control conditions include high temperatures and pressures. Alternatively, metal hydroxides and carbonates, including potassium bicarbonate and sodium bicarbonate [13–17], have been employed as absorbents in CO2 capturing owing to their high stability and safety. However, their regeneration also requires high temperatures. Presently, ionic liquids (ILs) are becoming an important focus for research in the field of CCS owing to their appreciable chemical and high thermal stabilities as well as low vapor pressures [4,18,19]. However, they are expensive, and their structures can be destroyed via hydration reactions, by the humidity in flue gases.

Particularly, typical CO2 desorption processes are performed in high temperature ovens under high pressure. Therefore, the objective of this study was to explore the overall CO2 absorption/desorption mechanism as well as the behavior of highly concentrated aqueous solution of potassium acetate (AcK, CH3COOK(aq)) as a CO2 absorbent. A novel CO2 desorption method that can be employed at 30 °C and atmospheric pressure was discovered during laboratory experiments conducted in this study. High purity CO2 could be quickly desorbed...
from a CO₂-saturated AcK solutions by the addition of H₂O at room temperature. After CO₂ desorption, it was possible to regenerate the ultra-highly concentrated AcK aqueous solution (AcK(aq)) for reuse as a CO₂ absorbent. This is a novel phenomenon that has not been explored in previous CCS-related studies. The overall absorption and desorption behavior of the novel absorbent was in accordance with Eq. (1).

\[
\text{CH}_3\text{COOK(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)} \leftrightarrow \text{KHCO}_3\text{(aq)} + \text{CH}_3\text{COOH(l)} \quad (1)
\]

Interestingly, according to Eq. (1), the addition of water will not favor CO₂ desorption. Therefore, this phenomenon seems to be contrary to the Le Chatelier principle considering that according to Eq. (1), H₂O is a reactant. During the experiments conducted in this study, it was observed that CO₂ could be easily and quickly desorbed from AcK(aq) by the addition of H₂O at 30 °C. This novel CO₂ absorption/desorption system is very suitable for Power-to-Gas (P2G) systems [20] considering that high purity CO₂ gas desorbed at 30 °C can be used to significantly reduce energy consumption. Furthermore, in P2G systems, the AcK aqueous solution could also be used as an electrolyte for the electrolysis of water to obtain hydrogen. In other words, all the steps in the P2G system could be performed at room temperature.

2. Materials and Methods

All the chemicals used were analytical grade reagents, and they were used as supplied without any further purification. AcK (99.5 wt.%) was purchased from Sigma-Aldrich Co. Ltd., St Louis, MO, USA, while CO₂ (99 mol%) was purchased from Yunshan Co. Ltd., Yuanlin Chen, Changhua, Taiwan.

2.1. Absorption of CO₂

Aqueous solutions of AcK with different molalities (5, 10, 15, and 20 m) were prepared using AcK powder and deionized water. The CO₂ absorption experiments were performed at 30 °C in 1 h using a 300 mL bubbling reactor. The pure CO₂ gas was continuously supplied to the reactor at a flow rate of 50 mL/min using a flow controller, and the amount of CO₂ absorbed was determined using the weight method. The CO₂ absorption capacity of the aqueous AcK solutions was defined as the number of moles of CO₂/mole of AcK.

2.2. Desorption of CO₂

The CO₂-saturated AcK solutions were desorbed by adding 10–40 wt.% distilled water in room temperature and amounts of CO₂ released were detected using the water displacement method. Additionally, similar desorption experiments were performed at 60, 70, and 80 °C using hot water baths.

2.3. Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Frontier FTIR. The samples were mixed with KBr powder and pressed into tablets, and then analyzed over the range of 450 to 4000 cm⁻¹ with a spectrum resolution of 4 cm⁻¹. The spectra were averaged over 64 scans at 30 °C. X-ray diffraction (XRD) patterns were recorded using a Bruker D2 PHASER XRD with Cu Kα radiation operated at 40 kV and 40 mA. The diffraction angles were scanned within a 20 range of 20–80° at a scan speed of 4°/min.

3. Results

3.1. Behaviors of CO₂ Absorption

The variation of the pH and the CO₂ absorption capacity of the absorbent with time is shown in Figure 1. Initially, the 20 m AcK aqueous solution had a pH value of 10.5, which decreased with increasing CO₂ absorption. Particularly, after 20 min of absorption, there was an increase in the turbidity of the aqueous AcK solution owing to the formation of a precipitate in the aqueous AcK solution, and after 40 min of absorption, the precipitation process resulted in the formation of a sludge (AcK sludge) as shown in Figure 2. Finally, the pH value of the aqueous AcK solution decreased to 7.8, and the maximum CO₂ absorption capacity was approximately 21.3 mmol/mol AcK. However, the CO₂ absorption capacity of AcK(aq) increases with an increase in AcK(aq) concentration as shown in Table 1. After CO₂ absorption, some precipitations were present in the 15 m AcK(aq) and none in the 5 and 10 m AcK(aq). As the concentration of AcK(aq) was below 10 m, the amount of CO₂ absorption was too low to act as an absorbent.
Figure 1. Variation of pH and CO₂ absorption loading of 20 m AcK(aq) absorbent with absorption time at 30 °C and atmospheric pressure.

Figure 2. The turbidity and state of 20 m AcK aqueous after CO₂ absorption. (a) Initial state, (b) After 20 min, (c) After 30 min, and (d) After 40 min.
Table 1. Capacity of CO2 absorption at different AcK(aq) absorbent concentrations.

<table>
<thead>
<tr>
<th>[AcK] (m)</th>
<th>CO2 loading* (mole CO2/mole AcK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.206</td>
</tr>
<tr>
<td>15</td>
<td>0.142</td>
</tr>
<tr>
<td>10</td>
<td>0.089</td>
</tr>
<tr>
<td>5</td>
<td>0.005</td>
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* Absorption condition: [CO2]feed : 100%

Interestingly, CO2 desorption from the aqueous AcK solution was easily initiated by the addition of H2O as shown in the video included in the supplementary materials, i.e., within a short time, a large volume of CO2 was rapidly released from the AcK sludge as water was added, and the absorbent was restored to a transparent aqueous solution. The quantity of CO2 released depended on the amount of H2O added as shown in Figure 3. When 10 wt.% and 40 wt.% H2O were added, approximately 27 % and more than 85 % of CO2 were released from the AcK sludge, respectively. A significant volume of high purity CO2 could be released and collected from the absorbent by the addition of H2O at 30 °C. Based on Eq. 1, this particularly low energy consumption CO2 desorption behavior of AcK(aq) seemed to contradict the Le Chatelier’s principle. Considering that the H2O is a reactant in this equation, its addition would rather favor the forward reaction. This observation was very interesting. Thus, the AcK sludge was further analyzed to investigate the possible CO2 absorption/desorption mechanism of the aqueous AcK(aq) solution.

![Figure 3](image.png)

Figure 3. Variation of CO2 desorption ratio out of 20 m AcK sludge with time resulting from the addition of different amounts of H2O at 30 °C and atmospheric pressure.

3.2. Analysis of AcK Sludge

It is well established that the conversion of CO2 to bicarbonate (HCO3−) or carbonate (CO32−) depends on the pH of the aqueous solution. Given the high concentration of K+ in the AcK(aq) absorbent, the formation of all possible species, including KHCO3, K2CO3, AcK, and AcK sludge were investigated using FTIR and XRD analyses. Considering all the FTIR spectra shown in Figure 4, the characteristic peaks of AcK sludge at 1650, 1400, 1000, 832, and 700 cm−1 reveal that the AcK sludge contained large amounts of KHCO3. Additionally, the XRD diffraction pattern of AcK sludge also provided evidence that CO2 absorption by AcK(aq) was in accordance with Eq. (1), as shown in Figure 5. Based on the characteristic 2θ diffraction angles observed at 12°, 24.1°, 30.2°, 31.5°, and 34° (KHCO3, ICDD 01-0976), KHCO3 was the major constituent of the AcK sludge (AcK-CO2). Tiny 2θ diffraction angles characteristic of K2CO3 and AcK were also observed in the diffraction pattern of the AcK.
sludge. In addition to the characteristic peaks of KHCO₃, H₂CO₃, and AcK, some unknown peaks at 2θ = 14.4°, 22.1°, 32.4°, and 39.7° were also observed in the XRD diffraction pattern of the AcK sludge. After diffraction pattern data comparison, these peaks were attributed to potassium hydrogen diacetate (PHDA, CAS #4251-29-0, KH(CH₃COO)₂), which was formed as a result of the hydrogen bonding established between the excess acetic acid and potassium acetate, a conclusion that is consistent with the CO₂ absorption pattern of the AcK(aq) system. When the ultra-highly concentrated aqueous AcK solution absorbed CO₂, K⁺, and H₂O are consumed; thus, the amount of acetic acid increases according to Eq. (1). The acetic acid then reacted with potassium acetate to form PHDA, which salted out of the ultra-highly concentrated aqueous AcK solution as a solid sediment owing to a decrease in solubility due to saturation. Similarly, for the same reason, KHCO₃ also salted out of the ultra-highly concentrated absorbent as a solid sediment. Therefore, CO₂ desorption from AcK sludge as a result of the addition of H₂O can be explained as follows. In addition to PHDA, which is an acidic compound that is used as a food additive, the AcK sludge also contains basic compounds (KHCO₃ and K₂CO₃); thus, it behaves like an effervescent tablet. Both PHDA and KHCO₃ were possibly decomposed and reacted resulting in the rapid release of CO₂ as H₂O was added to the AcK sludge causing them to dissolve.

![Figure 4. FTIR spectra of K₂CO₃, KHCO₃, AcK, and AcK sludge (AcK-CO₂).](image-url)
3.3. Effect of the Temperature on CO₂ Desorption

The above mentioned results illustrate that CO₂ desorption out of AcK sludge can be achieved by the addition of H₂O to the AcK sludge owing to an solubility when solvent volume increases. Another method by which the solubility of PHDA and KHCO₃ could be increased was by heating the solution. Thus, the relationship between the ratio of desorbed CO₂ and the temperature of the AcK sludge was investigated. The results show that the...
percentage of CO₂ desorbed out of the AcK sludge obviously depended on temperature (Figure 6). At 60 °C, the percentage of CO₂ that desorbed from the AcK sludge was greater than 60 %, and at 80 °C, it was approximately 90 %, indicating that the addition of water to the AcK sludge could be replaced by heating the AcK sludge to bring about the thermal desorption of CO₂. Therefore, as an absorbent, AcK has potential for application in commercial plants. Notably, the CO₂ desorption temperature and pressure for AcK absorbents are much lower than those required for amine absorbents. These lower desorption temperature and pressure conditions represent a lower energy consumption and an eco-operation requirement.

4. Discussions

The mechanism of CO₂ absorption and desorption by AcK\textsubscript{aq} is created and presented in Figure 7, in which four stages of CO₂ capture mechanism are evidenced. Firstly, HCO₃\textsuperscript{-} and CO₃\textsuperscript{2-} are formed when CO₂ is dissolved in the aqueous AcK solution resulting in a rapid decrease in pH. During this stage, [HCO₃\textsuperscript{-}] will be higher than [CO₃\textsuperscript{2-}] owing to the pH that is below 9. Secondly, as [K\textsuperscript{+}] and [HCO₃\textsuperscript{-}] increase to reach the solubility of KHCO₃, and thus, it starts to precipitate causing the AcK\textsubscript{aq} absorbent to become turbid, and when it becomes saturated with CO₂, the sludge state is obtained. Thirdly, acetic acid will be formed within the AcK sludge given that the K\textsuperscript{+} is consumed by the CO₃\textsuperscript{2-}, and it will react with potassium acetate to form PHDA, which also precipitates out of the ultra-highly concentrated aqueous AcK solution as a solid sediment owing to a decrease in solubility brought about by saturation. Finally, as H₂O is added to the AcK sludge or as the AcK sludge is heated to temperatures above 60 °C, ultra-high purity CO₂ is released. When the CO₂ desorption results from the addition of H₂O, the final concentration of the absorbent is lower than its initial concentration. However, if thermal CO₂ desorption is employed, the concentration of the AcK\textsubscript{aq} absorbent typically remains unchanged.
Figure 7. Schematic presentation of the CO$_2$ absorption and desorption mechanism for AcK$_{\text{aq}}$ absorbent.

Summary, as an absorbent, AcK$_{\text{aq}}$ is a stable salt solution that does not result in the formation of secondary pollutants during CO$_2$ absorption and desorption. This novel desorption behavior was attributed to the dimer structure of KH(CH$_3$COO)$_2$, which was formed and precipitated within the AcK$_{\text{aq}}$. When water was added, the precipitated KH(CH$_3$COO)$_2$ and KHCO$_3$ re-dissolved and underwent an acid-base reaction that resulted in the release of high purity CO$_2$. This novel CO$_2$ absorption and desorption mechanism exhibited by AcK$_{\text{aq}}$ reveals that as a low-energy consumption CO$_2$ absorption/desorption system, AcK$_{\text{aq}}$ has a high potential for application in commercial production processes.

5. Conclusion

A novel CO$_2$ absorbent, AcK$_{\text{aq}}$, was explored in this study. The results showed that it could quickly and almost completely desorb CO$_2$ when 40 wt.% H$_2$O was added to it at 30 ℃ or when it was heated to temperatures above 60 ℃. This novel desorption behavior was attributed to the dimer structure of KH(CH$_3$COO)$_2$, which was formed and precipitated within the AcK$_{\text{aq}}$. When water was added, the precipitated KH(CH$_3$COO)$_2$ and KHCO$_3$ re-dissolved and underwent an acid-base reaction that resulted in the release of high purity CO$_2$. This novel CO$_2$ absorption and desorption mechanism exhibited by AcK$_{\text{aq}}$ reveals that as a low-energy consumption CO$_2$ absorption/desorption system, AcK$_{\text{aq}}$ has a high potential for application in commercial production processes. A pilot plant of the AcK$_{\text{aq}}$ absorption system is being constructed in the laboratory and further information will be published for the benefit of researchers and industry.

Author Contributions


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Conflicts of Interest
There is no conflict of interest for this study.

**Supplementary Materials**

Movie S1: The desorption of CO₂ by adding 40 wt.% water.

**References**


