

Characterization of metal corrosion by aqueous amino acid salts for the capture of CO₂

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Abstract—We investigated the absorption ability of potassium salts of amino acid solutions for carbon dioxide and compared the results with MEA. The corrosion and degradation behavior were investigated in a CO₂ absorption process using aqueous potassium salts of glycine and taurine. The experimental parameters varied were the concentration, amino acid type, temperature, CO₂ loading, piperazine, and the presence of corrosion inhibitors. The corrosion characteristics of carbon steel were measured with potassium glycinate and potassium taurate solutions over a wide range of concentrations (1.5 to 5.0 M) and temperatures (313.15 to 353.15 K). The corrosion rate was calculated using a weight loss method averaging the results of four specimens. The experimental results indicate that increases in the concentration of the aqueous amino acid salts, solution temperature, CO₂ loading, and piperazine concentration accelerate the corrosion rate. In addition, corrosion inhibitors were proven to be effective in controlling corrosion.

Key words: Carbon Dioxide, Amino Acid Salts, Corrosion, Rate Promoter, Corrosion Inhibitor

INTRODUCTION

Amine solutions have been widely used in processes to remove CO₂ from flue gases or other gas streams. However, the amine solutions generally undergo oxidative degradation [1] and must desorb a great deal of energy [2-4]. In addition, amine solutions have the problem of increasing corrosion in process equipment. For these reasons, amino acid salts are now being studied as new absorption solutions. Although more expensive, amino acid salts have several advantages in terms of their physical and chemical properties. The advantages of amino acid salts include resistance to oxidative degradation, higher surface tension, greater reactivity and CO₂ absorption capacity, and low volatility due to their ionic nature [5-7].

Van Holst et al. [8] measured physiochemical properties including density, viscosity, and solubility of various potassium amino acid salt solutions at 298 K. Zhang et al. [9] proposed a new technique for the absorption of CO₂. In their study, absorption was made by the synthesis reaction of tetrabutylphosphonium hydroxide (CH₃CH₂CH₂CH₂)₄P(OH) with amino acids including glycine, L-alanine, L-β-alanine, L-serine, and L-lysine [8]. Kumar et al. [10,11] proposed aqueous alkaline salts of amino acids as an alternative to alkanolamines. They studied crystallization during the absorption of CO₂ in aqueous potassium taurate solutions [10] and the thermodynamic characteristics [11].

The CO₂ capture solutions investigated in this work were aqueous potassium taurate and potassium glycinate solutions. The chemical structures of potassium glycinate and potassium taurate are shown in Figs. 1 and 2. Amino acids have the same functional groups as alkanolamines [8].

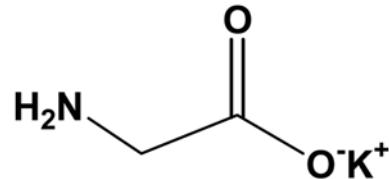


Fig. 1. Chemical structure of potassium glycinate.

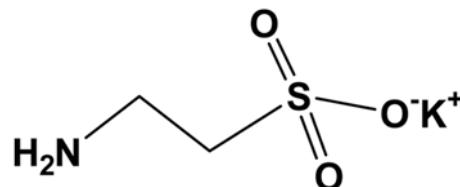


Fig. 2. Chemical structure of potassium taurate.

The most serious problem in CO₂ absorption processes is corrosion, which causes unplanned downtime, production losses, reduced equipment life, and even injury or death [12]. The cost of downtime in terms of production losses for a typical plant can vary between \$10,000 and \$30,000 per day [13,14]. In addition to production losses, management expenses are incurred to restore corroded systems and for treatments initiated to mitigate corrosion [15].

The goals of the present study are to establish the corrosion characteristics of CO₂ in amino acid solutions containing potassium salts and to investigate the effects of inhibitors, temperature, concentration, and CO₂ loading. The testing procedures used are based on the ASTM standard G1-90 (1999). The specimens used for corrosion testing in this study were carbon steel 1018.

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EXPERIMENTAL PROCEDURE

The experiments were performed in a corrosion reactor using a weight loss method for corrosion analysis. The experimental setup consisted of a 1 L flask corrosion cell, two condensers, a pH meter (Thermo Scientific Orion 3-Star Plus), a thermometer, a purge/vent tube, a water bath, and a glass cradle for the specimens. The glass cradles were used to support the specimens which, in contrast to hooks, provide multiple support sites.

1. Preparation of Aqueous Solutions

Potassium salts of amino acids are primarily used in a CCS process of TNO Corporation for CO₂ removal. Potassium salts of amino acids have three merits as components of a CO₂ capture solution: (1) the reaction rates of potassium salts of amino acids are fast, (2) the heat of vaporization of potassium salts of amino acids is low, and (3) the surface tension of potassium salts of amino acids is excellent. Due to these advantages, potassium salts of amino acids were chosen as the absorption solutions in these experiments.

Pure glycine and taurine do not react with carbon dioxide in aqueous solutions because the amine groups of glycine and taurine are quantized. Therefore, the potassium salt of the amino acid solution was prepared using a potassium hydroxide solution (J.T. Baker) at the concentration of the amino solutions. The reason for using potassium ions is that the reaction rate and absorption efficiency are excellent when potassium ions are added to other metals. The concentrations of the CO₂ capture solutions used in these experiments were between 1.5 and 5.0 M.

During the absorption of CO₂ in potassium glycinate solutions, precipitation did not occur at a concentration of 5.0 M. In the case of potassium taurate solutions, the concentrations of the CO₂ capture solution tested in this study varied from 2.0 to 3.0 M because precipitation occurs at a concentration of 5.0 M. To exactly measure the concentration of the prepared potassium salts of the amino acid, titration using 0.1 N H₂SO₄ was performed.

Before conducting the experiments, the absorbent solutions were saturated with CO₂. The CO₂ loading of the absorbent was analyzed with a titration method. The liquid samples were prepared as 2 ml amino acid absorbent solutions with absorbed CO₂, and 50 ml of BaCl₂ was added to 10 ml of NaOH [16]. After 24 hours, two drops of phenolphthalein indicator were added and then HCl was added until a pH of 8.0 was obtained. Next, two drops of methylorange indicator were added, and then HCl was added until a pH of 3.1 was reached [17]. When the CO₂ loading was measured, there was little change in the concentration.

2. Preparation of Specimens

The specimens used for corrosion experiments in this study were carbon steel 1018, which consists of C (0.14-0.20%), Mn (0.60-0.90%), P (0.030%), and S (0.035%) [18]. Carbon steel was chosen as it is widely used in the construction of equipment and piping in amine treating plants [19]. The specimens were cut into a rectangular shape with the following dimensions: 25.0 mm (0.9843 in.) width, 50.0 mm (1.9685 in.) length, and 1.0 mm (0.0393 in.) thickness. The specimens were prepared by wet grinding with 100 grit and 600 grit silicon carbide water-proof abrasive papers, degreasing with high purity methanol, and drying in a mechanical circulation oven, in accordance with the ASTM standard E3-80 [20]. After surface processing, the specimens were stored in silica gel and were

used in the experiment within 1 day. Four specimens were used in the experiments, and the corrosion rates were calculated as the average corrosion rate of the four specimens.

3. Experimental Procedure

The glycine, taurine, and MEA used in the experiments were purchased from Sigma Aldrich and had purities of over 98%, 98%, and 99%, respectively. A 45% KOH aqueous solution was purchased from J.T. Baker to make the potassium salt of amino acid solutions. Also, 99% pure piperazine was purchased from Acros Organics and was used as the reaction catalyst. 98% pure Na₂SO₃ and NaVO₃ were purchased from Alfa Aesar and used as corrosion inhibitors.

The volume of the CO₂ capture solutions used in the experiments was 1 L, and the experiment was started after reaching the desired temperature and CO₂ loading in the corrosion cell. Before putting specimens in the CO₂ capture solution, the masses of the specimens were measured with a precise balance. After 24 hours, the specimens were weighed again. Four specimens were used, and the corrosion rate was calculated as the average corrosion rate of the four specimens. The CO₂ loading was measured after 30 minutes, 12 hours, and 24 hours. The potassium salt of amino acid solution was held at a constant temperature by using a thermostat at 313.15 K and 353.15 K.

RESULTS AND DISCUSSION

1. Effect of Concentrations and Amino Acids Type

The effect of concentration on the corrosion behavior was investigated by conducting experiments in 1.5 M, 2.0 M, 2.5 M, 3.0 M, and 5.0 M solutions. The test conditions were a temperature of 353.15 K and a CO₂ loading of 0.62 for the MEA, potassium glycinate, and potassium taurate solutions. Under the CO₂ saturation condition, higher MEA concentrations generally caused higher corrosion rates (see Figs. 3 and 4). Higher MEA concentrations can cause higher corrosion rates because greater amounts of MEA molecules can absorb more CO₂ [21]. In addition, the dissolved CO₂ in the form of bicarbonate ions will result in iron dissolution, as shown in reaction 4-4. Therefore, increasing the concentration of bicarbonate ions causes

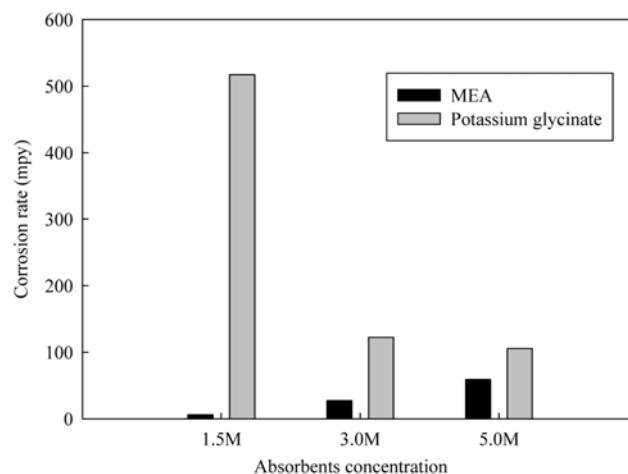


Fig. 3. Comparison of corrosion rates in MEA and potassium glycinate solutions systems at 353.15 K with $\alpha=0.62$.

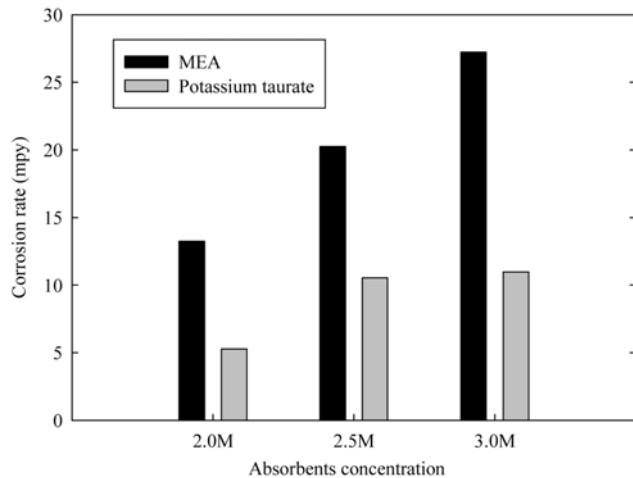


Fig. 4. Comparison of corrosion rates in MEA and potassium taurate solutions systems at 353.15 K with $\alpha=0.62$.

higher rates of iron dissolution and increases the corrosion rate [22].

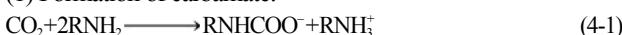
As the concentration of the potassium glycinate solutions increased, the corrosion rates tended to decrease. The reasons for the decrease in corrosion are the hydrolysis of carbamate (see reaction 4-2). The amount of bicarbonate ions which are made by the hydrolysis of carbamate is decreased because of restricted free water at high solution concentrations. Thus, the corrosion rate is reduced because the amounts of HCO_3^- (bicarbonate ion) and water which cause corrosion are decreased.

During the absorption of CO_2 in the aqueous potassium taurate solutions, precipitation occurs at high CO_2 loading.

The corrosion rate increased with an increase in the concentration of the potassium taurate solutions. This result is similar to the MEA results. The corrosion rate with the potassium taurate solutions is low compared to that with the MEA solutions. Because it has oxygen, nitrogen, and sulfur atoms, the double bond of the potassium taurate solutions provides corrosion inhibition on metal surfaces [22]. Therefore, the molecular structure of the potassium taurate solutions is effective in suppressing corrosion.

Corrosion mechanisms of carbon steel in amine solutions consist of the following steps:

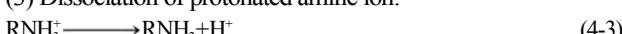
(1) Formation of carbamate:



(2) Hydrolysis of carbamate:



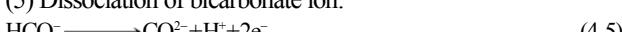
(3) Dissociation of protonated amine ion:



(4) Iron dissolution:



(5) Dissociation of bicarbonate ion:



2. Effect of Temperature

The absorption temperature has a significant effect on the corrosion rate in the CO_2 separation system. The experimental results at

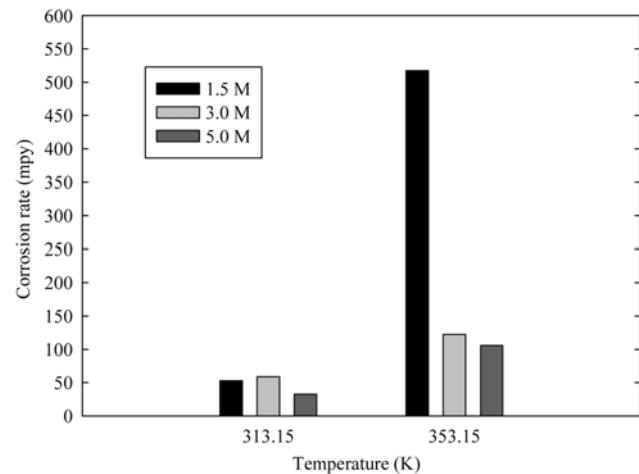


Fig. 5. Comparison of corrosion rates in potassium glycinate solutions systems with $\alpha=0.62$.

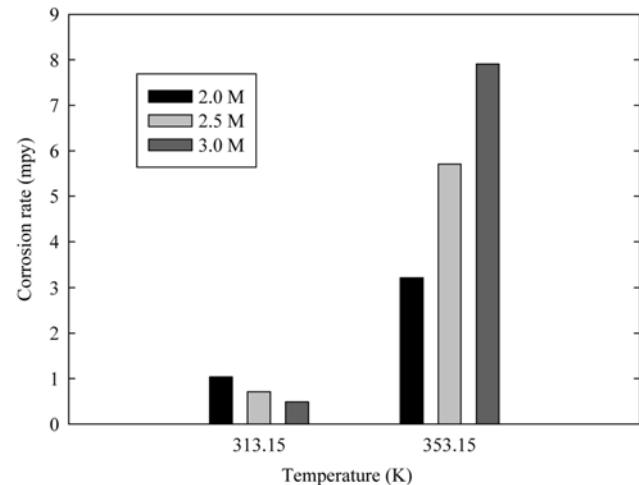


Fig. 6. Comparison of corrosion rates in potassium taurate solutions systems with $\alpha=0.35$.

different temperatures are shown in Figs. 5 and 6. The concentration of the potassium glycinate and potassium taurate solutions did not significantly affect the corrosion rate at 313.15 K. Increasing the solution temperature from 313.15 K to 353.15 K accelerated the rate of corrosion. In particular, the corrosion rate of the 1.5 M potassium glycinate solution was very fast at 353.15 K. The increasing corrosion rate was probably caused by the reaction of bicarbonate ions, as shown in reaction 4-4. The generation of bicarbonate ions gradually decreases as the potassium glycinate solution concentration increases because available water in the potassium salt of glycine solutions decreases (see reaction 4-2). The increased corrosion rates in the potassium taurate solutions at 353.15 K can be explained by a correlation between the equilibrium constant (K) and temperature [23]. To maintain equilibrium, more iron is dissolved into the solution, which subsequently generates more electrons for the oxidation reduction [24], thereby accelerating the corrosion process [21] so that the main metal corrosion occurs at high temperatures.

3. Effect of CO₂ Loading

The CO₂ loading is an important factor in determining the corrosion rate in the carbon dioxide absorption process. Typically, the corrosion rate increases with an increase in CO₂ loading. The reason is the increased presence of HCO₃⁻ (bicarbonate ion), which is a reaction product of CO₂ and amino acid absorbents. As mentioned previously, the reaction mechanism between potassium glycinate and potassium taurate solutions with carbon dioxide is shown in reactions 4-1 to 4-5.

The potassium glycinate solutions were saturated with carbon dioxide at a CO₂ loading of 0.62. However, the solutions were supersaturated by continuously supplying CO₂ during the experiments. Consequently, the corrosion rate did not change due to changes in the CO₂ loading (see Fig. 7). Thus, since the aqueous amino acid absorbents were saturated with carbon dioxide, additional CO₂ did not affect the corrosion rate.

The low CO₂ loading did not significantly affect the corrosion rate with the aqueous potassium salt of taurine system (see Fig. 8). However, the corrosion rate rapidly increased at a CO₂ loading of

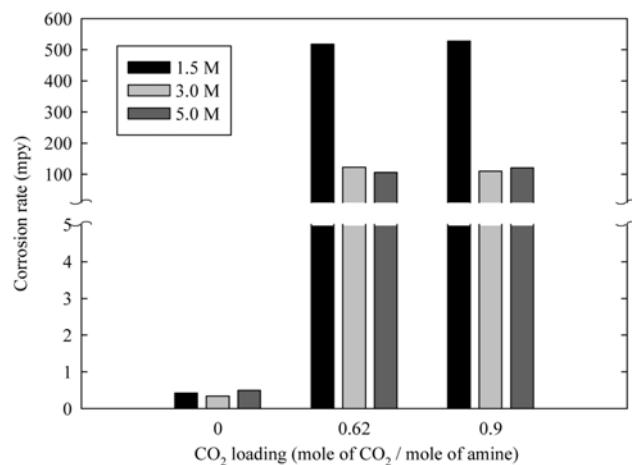


Fig. 7. Comparison of corrosion rates in potassium glycinate solutions systems at 353.15 K.

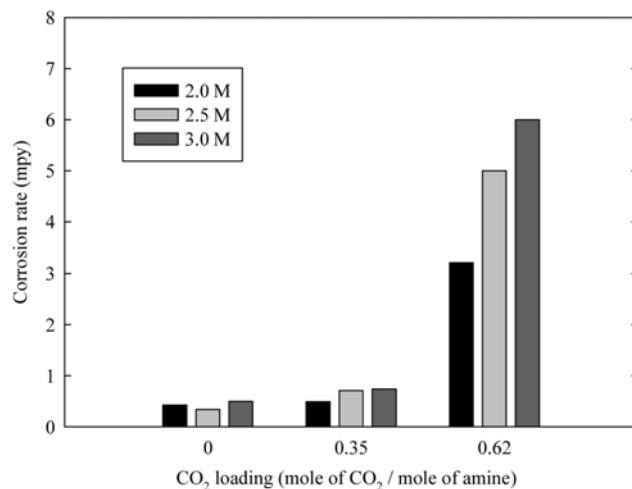


Fig. 8. Comparison of corrosion rates in potassium taurate solutions systems at 353.15 K.

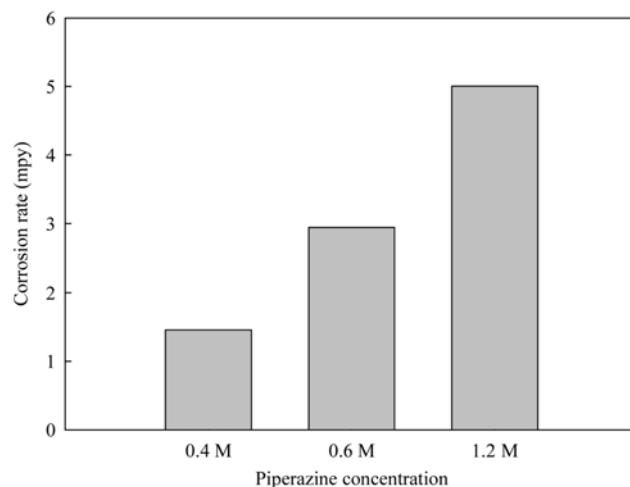


Fig. 9. Effect of piperazine on the corrosion rate in 2.0 M potassium taurate solutions at 353.15 K.

Table 1. Summary of corrosion inhibitor experiment results

| Inhibitor | Concentration (ppm) | Corrosion rate (mpy) | Effect inhibitor (%) |
|--|---------------------|----------------------|----------------------|
| Sodium sulfite (Na ₂ SO ₃) | 5 | 36.5957 | 92.9 |
| | 10 | 34.8289 | 93.3 |
| | 20 | 32.6387 | 93.7 |
| Sodium metavanadate (NaVO ₃) | 10 | 446.3895 | 13.7 |
| | 50 | 372.9968 | 27.9 |
| | 100 | 0.244248 | 99.9 |

0.62. Therefore, CO₂ loading at saturation can have the biggest influence on the corrosion rate.

4. Effect of Piperazine Addition

Piperazine, which is used in CO₂ removal processes as a promoter [25,26], is effective in increasing the absorption rate of CO₂ [26]. Lensen [27] investigated the influence of piperazine. Based on the results, piperazine is effective in combination with MDEA and aqueous potassium carbonate. This study reveals that the corrosion rate increases with an increase in the piperazine concentration (see Fig. 9), because when piperazine is added, the solutions can absorb more carbon dioxide [28]. Therefore, depending on the reaction mechanism between carbon dioxide and amino acid absorbents, the amount of HCO₃⁻ (bicarbonate ion), which is the cause of corrosion, increases and can promote corrosion.

5. Effect of Corrosion Inhibitors Addition

The corrosion inhibitors testing results are summarized in Table 1. The sodium metavanadate (NaVO₃) demonstrated excellent performance and was better than sodium sulfite (Na₂SO₃). In this study, the NaVO₃ achieves up to 99.9% protection, while the Na₂SO₃ inhibited corrosion up to 93.7%. The protection percentage increased as the concentration of corrosion inhibitor increased. The reason for this behavior is that increased quantities of corrosion inhibitors provide more effective protection and react with the existing dissolved oxygen to decrease the corrosion rate [29]. The concentrations of corrosion inhibitors were minimized in order to avoid precipitation of the insoluble inhibitors.

CONCLUSIONS

As new absorbents for carbon dioxide, potassium salts of glycine and taurine solutions were investigated in this study. The potential for utilizing potassium glycinate and potassium taurate solutions was evaluated, and their performances were compared to that of MEA, which is a conventional alkanolamine solution. We measured the corrosion rate with amino acid absorbent solutions at various concentrations and CO₂ loadings at different temperatures. The corrosion rate of the potassium glycinate solution decreased with an increase in the potassium salt of glycine concentration. The corrosion rate of the potassium taurate solution increased with an increase in the potassium salt of taurine concentration. We confirmed that the corrosion rate was higher at increased temperature, and the corrosion rate was the fastest with rich CO₂ loading. The corrosion rate increased when piperazines were added, which act as a reaction accelerator in the carbon dioxide absorption process. From the corrosion inhibitor experiment results, NaVO₃ was found to provide excellent corrosion inhibition effects, better than Na₂SO₃. From the results of this study, the potassium glycinate solution was beneficial at high concentration and adding NaVO₃ increased its potential as a CO₂ capture solution. The potassium taurate solution is advantageous at low concentration and, by adding piperazine, can have a greater ability to absorb carbon dioxide than MEA.

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