L-Aspartic Acid: An Efficient Water Soluble Inhibitor for
Corrosion of Carbon Steel in Aqueous Media

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Abstract

The corrosion and inhibition behaviors of carbon steel in the presence of L-aspartic acid and ZnSO₄ have been studied using gravimetric method and electrochemical techniques. The results obtained by various techniques are close and maximum inhibition efficiency is 90%. Synergistic parameters and statistical study of “F” test suggest that a synergistic effect exists between L-aspartic acid and Zn²⁺. The protective film on the metal surface was analyzed by FTIR spectra. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study, electrochemical study and surface analysis technique. The use of the inhibitor L-aspartic acid-Zn²⁺ system may find worthy application in cooling water system.

Keywords: Carbon steel, L-aspartic acid, ZnSO₄, synergistic effect, F-Test, FTIR spectra

1. Introduction

Carbon steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths, etc. Carbon steel rusts when in contact with any aqueous medium. The use of inhibitors is one of the best methods for protecting metals against corrosion. Corrosion is a chemical or electrochemical process in nature with four components which include: anode, cathode, electrolyte and some direct electrical connection between the anode and cathode. The adsorbed inhibitor then acts to slow corrosion process by either: increasing the anodic or cathodic polarization behavior or reducing the movement or diffusion of ions to the metallic surface. Corrosion inhibitors are used to prevent the effect of corrosion in such cases. The majority of well-known inhibitors are organic compounds containing heteroatom, such as O, N, S and multiple bonds [1]. Most of the organic compounds are not only expensive but also toxic to both human beings and environments [2] and therefore the use of hazardous chemical inhibitors is totally reduced because of environmental regulations. It is better to look for environmentally safe inhibitors. Many researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion [3-13]. This is due to the fact that amino acids are non-toxic, biodegradable, relatively cheap, and completely soluble in aqueous media and produced with high purity at low cost. Various amino acids have been used to inhibit the corrosion of metals and alloys [14-17]. Eco-friendly Inhibitor L-cysteine-Zn²⁺ System has been used to control corrosion of carbon steel in aqueous medium [6]. The corrosion of SS 316L has been inhibited by glycine, leucine, valine, and arginine [7]. Sivakumar et al. [8] used L-histidine to prevent corrosion on carbon steel. Cystein, glycine, glutamic acid, and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl [9]. Amino
acid such as DL-phenylalanine has been used to prevent corrosion of carbon steel [10]. The corrosion of brass in O2-free NaOH has been prevented by methionine [11]. Sahaya Raja et al. [12] have used glycine along with Zn2+ to prevent corrosion of carbon steel in well water. Synergistic and antagonistic effect of L-alanine for carbon steel in aqueous medium has been investigated [18]. Prathipa et al. [19] studied the corrosion inhibition of carbon steel using green inhibitor (L-alanine). Arginine-Zn2+ system has been used to inhibit corrosion of carbon steel [13, 20]. L-alanine as inhibitor for carbon steel in well water was studied [21].

Therefore, the aim of this research is to evaluate the inhibition efficiency of L-aspartic acid in controlling the corrosion of carbon steel in the absence and presence of Zn2+, to study the mechanistic aspects by potentiodynamic polarization study and alternating current (AC) impedance spectroscopy, to analyze the protective film on carbon steel by FTIR spectrophotometry and to propose a suitable mechanism for corrosion inhibition based on the results obtained from the study.

2. Materials and Methods

2.1. Determination of Corrosion Rate

The weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance-AY62. The corrosion rates (CR) were calculated using Equation 1.

\[
CR = \frac{\text{Loss in weight}}{\text{Surface Area of the specimen} \times \text{Period of the immersion}} \times 1000
\]

2.2. Electrochemical and Impedance Measurements

Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A).

2.3. Surface Characterization Studies

FTIR Spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. All solutions were prepared using well water collected from Seelapadi, Dindigul, Tamil Nadu, India. The study was carried out at room temperature (303K). The chosen environmental well water and its physicochemical parameters are given in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1870 µmhos/cm</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>1329 mg/L</td>
</tr>
<tr>
<td>Total hardness</td>
<td>510 mg/L</td>
</tr>
<tr>
<td>Total Alkalinity</td>
<td>410 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>55 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>69 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>210 mg/L</td>
</tr>
<tr>
<td>Potassium</td>
<td>60 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>712 mg/L</td>
</tr>
<tr>
<td>Sulphate</td>
<td>290 mg/L</td>
</tr>
</tbody>
</table>

3. Results and discussions

3.1. Analysis of the Weight Loss

CR of carbon steel immersed in well water in the absence and presence of inhibitor (L-aspartic acid) are given in Table 2. The inhibition efficiencies (IE) are also given in Table 2. It was observed that L-aspartic acid shows some IE. For example 50 mg/L of L-aspartic acid has 43% IE, as the concentration of L-aspartic acid increases, the IE decreases.

3.2. Influence of Zn2+ on the Inhibition Efficiencies of L-aspartic Acid

The influence of Zn2+ on the IE of L-aspartic acid is given in Table 2. It was observed that as the concentration of
L-aspartic acid increases, the IE decreases. Similarly, for a given concentration of L-aspartic acid, the IE increases as the concentration of Zn\(^{2+}\) increases. It was also observed that a synergistic effect exists between L-aspartic acid and Zn\(^{2+}\). For example, 5 mg/L of Zn\(^{2+}\) has 20% IE; 50 mg/L of L-aspartic acid has 43% IE. Interestingly, their combination has a high IE, specifically, 90%. In the presence of Zn\(^{2+}\), more amount of L-aspartic acid is transported towards the metal surface. Thus, the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn\(^{2+}\) and L-aspartic acid.

Anodic reaction: \(\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-\)
Cathodic reaction: \(\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-\)

Reaction of inhibitor system: \(\text{Fe}^{2+} + \text{Zn}^{2+} - \text{L}-\text{aspartic acid complex} \rightarrow \text{Fe}^{2+} - \text{L}-\text{aspartic acid complex} + \text{Zn}^{2+}\)
\(\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2\)

Table 2. Corrosion Rate of Carbon Steel Immersed in Well Water in the Presence and Absence of Inhibitor System at Various Concentrations and the Inhibition Efficiencies (IEs) Obtained by Weight Loss Method

<table>
<thead>
<tr>
<th>L-aspartic Acid (mg/L)</th>
<th>Zn(^{2+}) (0 mg/L)</th>
<th>Zn(^{2+}) (5 mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>IE (%) 0.0874</td>
<td>IE % 0.0699</td>
</tr>
<tr>
<td>50</td>
<td>43 0.0498</td>
<td>90 0.00874</td>
</tr>
<tr>
<td>100</td>
<td>39 0.0533</td>
<td>78 0.0192</td>
</tr>
<tr>
<td>150</td>
<td>35 0.0568</td>
<td>82 0.0157</td>
</tr>
<tr>
<td>200</td>
<td>32 0.0594</td>
<td>84 0.0139</td>
</tr>
<tr>
<td>250</td>
<td>27 0.0638</td>
<td>76 0.0209</td>
</tr>
</tbody>
</table>

3.3. Synergism Parameters (\(S_1\))

Synergism parameter (\(S_1\)) has been used to determine the synergistic effect existing between two inhibitors [22-24]. \(S_1\) was calculated using Equation 2.

**Synergism parameters (\(S_1\)) = \(1 - \theta_{1+2}/1 - \theta_{1+2}\)**

where \(\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2), \theta_1\) is the surface coverage by L-aspartic acid, \(\theta_2\) is the surface coverage by Zn\(^{2+}\), \(\theta_{1+2}\) is the surface coverage by both L-aspartic acid and Zn\(^{2+}\), and \(\theta\) (Surface coverage) = IE% / 100.

The \(S_1\) of L-aspartic acid-Zn\(^{2+}\) system are given in Table 3. For different concentrations of inhibitors, \(S_1\) approaches 1 when no interaction between the inhibitor compounds exists and when \(S_1 > 1\), it points to synergistic effects. In the case of \(S_1 < 1\), this gives an indication that the synergistic effect is not significant [23]. From Table 3, it was observed that the value of \(S_1\) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between L-aspartic acid and Zn\(^{2+}\) [24]. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn\(^{2+}\) ions to L-aspartic acid is due to the synergistic effect.

Table 3. Inhibition Efficiencies and Synergism Parameters for Various Concentrations of L-aspartic Acid-Zn\(^{2+}\) (5 mg/L) System, when Carbon Steel is Immersed in Well Water.

<table>
<thead>
<tr>
<th>L-aspartic acid (mg/L)</th>
<th>IE (%)</th>
<th>Surface Coverage ((\theta^\circ))</th>
<th>Zn(^{2+}) (mg/L)</th>
<th>IE (%)</th>
<th>Surface Coverage ((\theta^\circ))</th>
<th>Combined IE % ((I'_{1+2}))</th>
<th>Combined Surface Coverage ((\theta'_{1+2}))</th>
<th>Synergism Parameters ((S_1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>43</td>
<td>0.43</td>
<td>5</td>
<td>20</td>
<td>0.20</td>
<td>90</td>
<td>0.90</td>
<td>4.75</td>
</tr>
<tr>
<td>100</td>
<td>39</td>
<td>0.39</td>
<td>5</td>
<td>20</td>
<td>0.20</td>
<td>78</td>
<td>0.78</td>
<td>2.21</td>
</tr>
<tr>
<td>150</td>
<td>35</td>
<td>0.35</td>
<td>5</td>
<td>20</td>
<td>0.20</td>
<td>82</td>
<td>0.82</td>
<td>2.88</td>
</tr>
<tr>
<td>200</td>
<td>32</td>
<td>0.32</td>
<td>5</td>
<td>20</td>
<td>0.20</td>
<td>84</td>
<td>0.84</td>
<td>3.4</td>
</tr>
<tr>
<td>250</td>
<td>27</td>
<td>0.27</td>
<td>5</td>
<td>20</td>
<td>0.20</td>
<td>76</td>
<td>0.76</td>
<td>1.98</td>
</tr>
</tbody>
</table>

3.4 'F'-Test

To determine if the synergistic effect existing between L-aspartic acid and Zn\(^{2+}\) is statistically significant or not, F-test was used [19, 22-24]. The results are presented in Table 4. It was observed that the calculated F-value (20.17) is greater than the table value 5.32 for 8 degrees of freedom at a 0.05 level of significance. Hence, it could be concluded that the synergistic effect existing between L-aspartic acid and Zn\(^{2+}\) (5 mg/L) is statistically significant. Therefore, the synergistic effect existing between L-aspartic acid and Zn\(^{2+}\) (5 mg/L) is statistically significant.
3.5. Analysis of Potentiodynamic Polarization Study

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [6, 8, 10]. If a protective film is formed on the metal surface, the corrosion current value ($I_{corr}$) decreases. The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Figure 1. The corrosion parameters are given in Table 5. When carbon steel was immersed in well water the corrosion potential was -670 mV vs SCE. When L-aspartic acid (50 mg/L) and Zn$^{2+}$ (5 mg/L) were added to the system, the corrosion potential shifted to -640 mV vs SCE.

This suggests that a protective film is formed on the metal surface. Furthermore, the corrosion current decreases from $5.779 \times 10^{-7}$ A/cm$^2$ to $4.570 \times 10^{-7}$. Thus, polarization study confirms the formation of a protective film on the metal surface.

![Figure 1. Polarization Curves of Carbon Steel Immersed in Various Test Solutions](image)

a) Well Water (Blank); b) Well Water + L-aspartic Acid (50 mg/L) + Zn$^{2+}$ (5 mg/L)

3.6. Analysis of AC Impedance Spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface [11, 13]. If a protective film is formed on the metal surface, charge transfer resistance ($R_t$) increases; double layer capacitance value ($C_{dl}$) decreases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L-aspartic acid-Zn$^{2+}$) are shown in Figure 2 (Nyquist plot). The AC impedance parameters namely $R_t$ and $C_{dl}$ derived from Nyquist plot are given in Table 6. It was observed that when the inhibitors (L-aspartic acid (50 mg/L) +Zn$^{2+}$ (5 mg/L)) are added, the $R_t$ increases from 1197 Ω cm$^2$ to 11850 Ω cm$^2$. The $C_{dl}$ value decreases from $3.7357 \times 10^{-9}$ F/cm$^2$ to $4.1742 \times 10^{-10}$. These results prove that a protective film is formed on the metal surface.

<table>
<thead>
<tr>
<th>System</th>
<th>Nyquist plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water</td>
<td>$R_t$ (Ω cm$^2$)</td>
</tr>
<tr>
<td></td>
<td>1197</td>
</tr>
<tr>
<td>Well water + L-aspartic acid (50 mg/L) + Zn$^{2+}$ (5 mg/L)</td>
<td>11850</td>
</tr>
</tbody>
</table>

Figure 2. AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots) 
  a) Well water (Blank); b) Well water + L-aspartic acid (250 mg/L) + Zn$^{2+}$ (5 mg/L)

3.7. Surface Characterization Study

3.7.1. Analysis of FTIR Spectra

FTIR spectra have been used to analyze the protective film formed on the metal surface [19-25]. The FTIR spectrum of pure L-aspartic acid is shown in Figure 3 (a). The C=O stretching frequency of carboxyl group appears at 1650 cm$^{-1}$. The CN stretching frequency appears at 1088 cm$^{-1}$. The NH stretching frequency of the amine group appears at 3100 cm$^{-1}$ [26-30]. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 50 mg/L of L-aspartic acid and 5 mg/L Zn$^{2+}$ is shown in Figure 3 (b). The C=O stretching frequency has shifted from 1650 to 1620 cm$^{-1}$. The CN stretching frequency has shifted from 1088 to 1060 cm$^{-1}$. The NH stretching frequency has shifted from 3100 to 3290 cm$^{-1}$. This observation suggests that L-aspartic acid has coordinated with Fe$^{2+}$ through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe$^{2+}$- L-aspartic acid complex on the metal surface. The peak at 670 cm$^{-1}$ corresponds to Zn-O stretching. The peak at 3445 cm$^{-1}$ is due to OH- stretching. This confirms that Zn(OH)$_2$ is formed on the metal surface [19]. Thus, the FTIR spectral study leads to the conclusion that the protective film consist of Fe$^{2+}$- L-aspartic acid complex and Zn(OH)$_2$.

Figure 3. FTIR Spectra of (a) Pure L-aspartic Acid, (b) Film Formed on Metal Surface Immersion in Test Solution Containing 50 mg/L L-aspartic Acid + 5 mg/L Zn$^{2+}$
3.8. Mechanism of Corrosion Inhibition

The results of the weight-loss study show that the formulation consisting of 50 mg/L L-aspartic acid and 5 mg/L of Zn²⁺ has 90% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn²⁺ and L-aspartic acid. Polarization study reveals that this formulation acts as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe²⁺-L-aspartic acid complex and Zn(OH)₂. In order to explain these facts, the following mechanism of corrosion inhibition is proposed:

- When the solution containing well water, 5 mg/L of Zn²⁺ and 50 mg/L of L-aspartic acid is prepared, there is the formulation of Zn²⁺-L-aspartic acid complex in solution. When carbon steel is immersed in this solution, the Zn²⁺-L-aspartic acid complex diffuses from the bulk of the solution towards the metal surface.
- Zn²⁺-L-aspartic acid complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe²⁺-L-aspartic acid complex, which is more stable than Zn²⁺-L-aspartic acid.
- On the metal surface, Zn²⁺-L-aspartic acid complex is converted into Fe²⁺-L-aspartic acid and Zn²⁺ is released. Zn²⁺-L-aspartic acid+ Fe²⁺ → Fe²⁺-L-aspartic acid+ Zn²⁺
- The released Zn²⁺ combines with OH⁻ to form Zn(OH)₂. Zn²⁺ + 2OH⁻ → Zn(OH)₂↓
- Thus, the protective film consists of Fe²⁺-L-aspartic acid complex and Zn(OH)₂.

4. Conclusions

Weight loss study reveals that the formulation consisting of 50 mg/L of L-aspartic acid and 5 mg/L of Zn²⁺ has 90% inhibition efficiency, in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn²⁺ and L-aspartic acid system. Statistical study of F-test revealed that the synergistic effect existing between L-aspartic acid and Zn²⁺ is statistically significant. Polarization study reveals that L-aspartic acid system function as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectral study suggests that L-aspartic acid has coordinated with Fe²⁺ through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe²⁺-L-aspartic acid complex and Zn(OH)₂ is formed. Thus, the FTIR spectral study leads to the conclusion that the protective film consist of Fe²⁺-L-aspartic acid complex and Zn(OH)₂ on the metal surface thereby inhibiting the corrosion of carbon steel, which is protective in nature.

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REFERENCES


