Inhibition effect of amino acid derivatives on the corrosion of brass in 0.6 M aqueous sodium chloride solution

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The inhibitive effects of three amino acids and their benzenesulphonyl derivatives against the corrosion of brass in 0.6 M aqueous sodium chloride solution have been studied using potentiodynamic polarization and electrochemical impedance spectroscopy. The amino acids used are glycine (I), L (-) aspartic acid (II) and L (-) glutamic acid (III) and their corresponding benzenesulphonyl derivatives IV, V and VI. The inhibition efficiency of these compounds increases in the order I< II< III for amino acids and the same trend is followed for benzenesulphonyl derivatives. Compound VI is found to be the best inhibitor. The inhibition efficiency of VI with 4 × 10^{-5} M concentration is the highest, which reaches 81.2- 85.5%. It has been observed that introduction of C_6H_5-SO_2- group increases the inhibition efficiency of the amino acids by 14-33% due to (a) higher molecular size (b) π - electron contribution of the benzene ring and (c) presence of more active adsorption sites.

Keywords: Corrosion inhibition, Brass, Polarization, Impedance, Amino acids

Due to various industrial applications and economic importance of brass, its protection against corrosion attracted much attention. One of the most important methods in corrosion protection is to use inhibitors. Due to restrictive inhibitor laws, inorganic corrosion inhibitors such as chromate or nitrites are replaced by organic compounds. Benzotriazole and its derivatives offer a good protection against corrosion of brass in aggressive environments, viz. 3- 3.5% NaCl solutions and sea water. But these compounds are toxic. Role and mechanism of corrosion prevention by most of the inhibitors are well known. It is now required to design new environment –friendly inhibitors.

Recently work has been initiated on the inhibition effect of amino acids on copper corrosion in acidic chloride solutions. Sulphonamides are of considerable importance for their physiological activity. It has been reported recently that compound containing –SO_2-NH- group is a good microbial corrosion inhibitor for mild steel in salty water environment.

Looking for environmentally acceptable corrosion inhibitors, amino acids viz. glycine (I), L (-) aspartic acid (II) and L(-) glutamic acid (III) have been chosen as starting materials. Further, sulphonamido derivatives of these acids may be biologically active as well as good chelating agents and corrosion inhibitors. These compounds may act as corrosion inhibitors and antifouling agents in marine environment. With this aim in view N-benzenesulphonyl glycine (IV), N-benzenesulphonyl L (-) aspartic acid (V) and N-benzenesulphonyl L (-) glutamic acid (VI) have been prepared. These molecules contain O, N, and S atoms and may function as chelating agents. These compounds may be good corrosion inhibitors for brass in chloride solution due to the presence of O, N and S atoms and π bonding effect of benzene nucleus. These sulphonamides are expected to be better inhibitors than the parent amino acids. If required the carboxyl group may be easily converted to amide, benzimidazole, benoxazole, imidazoline or hydroxypyrimidine containing hetero atoms to improve further their inhibition activity.

Two electrochemical techniques potentiodynamic polarization and electrochemical impedance spectroscopy have been used to study the effect of the addition of these compounds on the corrosion of brass in 0.6 M aqueous sodium chloride solution.

Experimental Procedure

Materials and Methods

The chemical composition of the commercial brass used in the present study was 59.8% Cu, 40.0% Zn and traces amount of Fe and Pb. The working electrode for potentiodynamic study and EIS
measurement was prepared from the brass rod from which only the circular cross-section (0.25 cm²) of rod was exposed. The brass sample was polished successively with (i) belt grinding polishing machine, (ii) metallographic emery paper of increasing fineness of up to 1200 grade and (iii) cloth polishing by Single Disc Polishing Machine CENSICO PMV-T 10-1. Then the samples were degreased with AR grade ethanol and acetone and rinsed with double distilled water prior to each experiment.

Amino acids were AR grade reagents and used as received. The ligands IV, V and VI were prepared by following usual procedure. Figure 1 shows the molecular structure of the investigated compounds. Analytical data of the sulphonamides are given in Table 1. The pH measurements were made with an Orion 420A Plus pH meter using 9157BN Triode pH electrode. The pH meter was calibrated with sodium hydrogen phthalate and borax buffer solution in water. Following solutions (50 mL) were titrated potentiometrically in water-methanol (1:1) at 30±0.5°C and μ= 0.25 (NaClO₄) against 0.150 M NaOH solution; (a) 0.01 M HClO₄, (b) 0.01 M HClO₄+ 0.02 M IV or V or VI (c) 0.01 M HClO₄+ 0.03 M IV or V or VI. The aggressive environment used was 0.6 M aqueous NaCl solution prepared from AR grade reagent and double distilled water. The pH of the solution was adjusted to 6.0. Oxygen content of the sodium chloride solution was 7.3 mg/L. All other reagents were of AR quality.

Potentiodynamic polarization study

The potentiodynamic polarization studies were carried out with polished and degreased brass specimens having an exposed surface area of 0.25 cm². The electrochemical measurements were carried out in a standard three-electrode electrochemical cell of volume 100 mL. The counter electrode was a platinised platinum plate with 1 cm² surface area, the reference electrode consisted of a commercial saturated calomel electrode with a Luggin capillary bridge and the working electrode was made up of brass. Polarization studies were carried out using potentiostat /galvanostat (ACM Instruments Gill AC) and the data obtained were analyzed using the software “ACM Instruments version 5”. The degreased working electrode was immersed in 0.6 M aqueous NaCl solution (pH=6) at 30±0.5°C. The inhibition efficiencies of the compounds were determined from corrosion current density using the Tafel extrapolation method.

AC impedance studies

AC impedance measurements were conducted at room temperature using “ACM Instruments Gill AC”. The instruments were controlled by the software “ACM Instruments version 5” between 1 m Hz and 100 kHz. An AC sinusoid voltage of ~ ±10 mV was applied at corrosion potential (Ecorr). The brass sample with an exposing surface area of 0.25 cm² was used as the working electrode. A three electrode electrochemical cell of volume 100 mL with a platinum plate electrode and a saturated calomel electrode was used.

![Chemical structures](image1)

Fig. 1—Chemical structures of the amino acids and their derivatives.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>% Yield</th>
<th>Eq.wt.</th>
<th>% N Found</th>
<th>pK values</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>80</td>
<td>214.9</td>
<td>6.43</td>
<td>3.80</td>
</tr>
<tr>
<td></td>
<td>(168)</td>
<td>(215.0)</td>
<td>(6.50)</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>50</td>
<td>136.2</td>
<td>5.00</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>(170)</td>
<td>(136.5)</td>
<td>(5.12)</td>
<td>5.34</td>
</tr>
<tr>
<td>VI</td>
<td>70</td>
<td>143.0</td>
<td>4.70</td>
<td>4.02</td>
</tr>
<tr>
<td></td>
<td>(132)</td>
<td>(143.5)</td>
<td>(4.87)</td>
<td>5.45</td>
</tr>
</tbody>
</table>

Table 1 — Analytical data of the sulphonamides
Results and Discussion

In general, the inhibition effect of the amino acid is due to the adsorption of its molecule on the metal surface.\(^{21}\) Inhibition efficiency depends on the number of adsorption sites in the molecule, molecular size and mode of interaction with the metal surface.\(^{22}\) The inhibition efficiency of these amino acids increases in the order I < II < III and the same trend is followed for sulphonyl derivatives (Tables 2 and 3). Compound II is better inhibitor than compound I due to the presence of more adsorption sites in the molecule and III is better inhibitor than II due to its larger molecular size and more basic character. Sulphonamido derivatives are better inhibitors than the corresponding amino acids due to the presence of \(\pi\) - electron of the benzene ring and introduction of electron rich group \(–\text{SO}_2\) in the derivatives. Hence the higher inhibition efficiency may be due to (a) higher molecular size (b) \(\pi\) - electron contribution of the benzene ring and (c) presence of more active adsorption sites.\(^{23}\) Inhibition efficiency is increased by 14-33% after introducing the \(\text{C}_6\text{H}_5\text{-SO}_2\)-group in the amino acids though the basic character of the compounds is decreased. The inhibition efficiency of all the reagents is highest in a solution with optimum concentration \((4 \times 10^{-5} \text{ M})\) of the inhibitor. This is due to higher surface coverage at this concentration. The inhibition efficiency of compound VI with \(4 \times 10^{-5} \text{ M}\) concentration is the highest, which reaches 81.2- 85.5%.

Potentiodynamic polarization study

The cathodic and anodic polarization curves of brass in 0.6 M aqueous NaCl solution with varying concentrations \((10^{-4} \text{ to } 10^{-6} \text{ M})\) of I, II, III, IV, V and VI were recorded and the curves with \(4 \times 10^{-5} \text{ M}\) concentration (highest inhibition efficiencies) are shown in Figs 2 and 3. The potentiodynamic polarization parameters are listed in Table 2. Inhibition efficiencies are calculated using the following equation

\[
\text{I.E.} = \left(1 - \frac{I_{\text{corr}}}{I_{\text{corr,blank}}}\right) \times 100
\]

Table 2 — Electrochemical parameters and inhibition efficiency values of various inhibitors for the corrosion of brass in 0.6 M NaCl solution

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>(E_{\text{corr}}) (mV) vs SCE</th>
<th>(I_{\text{corr}}) ((\mu\text{A/cm}^2))</th>
<th>I.E. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-301.8</td>
<td>6.14</td>
<td>–</td>
</tr>
<tr>
<td>I</td>
<td>-236.7</td>
<td>4.75</td>
<td>22.6</td>
</tr>
<tr>
<td>II</td>
<td>-221.8</td>
<td>3.52</td>
<td>42.6</td>
</tr>
<tr>
<td>III</td>
<td>-248.1</td>
<td>2.88</td>
<td>53.0</td>
</tr>
<tr>
<td>IV</td>
<td>-249.5</td>
<td>3.58</td>
<td>41.6</td>
</tr>
<tr>
<td>V</td>
<td>-268.3</td>
<td>1.51</td>
<td>75.5</td>
</tr>
<tr>
<td>VI</td>
<td>-280.3</td>
<td>1.15</td>
<td>81.2</td>
</tr>
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</table>

Table 3 — Impedance measurements and inhibition efficiency values of various inhibitors for the corrosion of brass in 0.6 M NaCl

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>(R_{\text{ct}}) (K ohm)</th>
<th>(C_{\text{dl}}) (F)</th>
<th>I.E. (\left(\frac{R_{\text{ct}}}{R_{\text{ct,blank}}}\right)) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.358</td>
<td>2.38 (\times) 10^{-4}</td>
<td>–</td>
</tr>
<tr>
<td>I</td>
<td>0.527</td>
<td>9.39 (\times) 10^{-4}</td>
<td>32.0</td>
</tr>
<tr>
<td>II</td>
<td>0.658</td>
<td>2.38 (\times) 10^{-5}</td>
<td>47.7</td>
</tr>
<tr>
<td>III</td>
<td>0.885</td>
<td>3.14 (\times) 10^{-5}</td>
<td>59.5</td>
</tr>
<tr>
<td>IV</td>
<td>0.713</td>
<td>1.45 (\times) 10^{-4}</td>
<td>49.7</td>
</tr>
<tr>
<td>V</td>
<td>1.726</td>
<td>1.10 (\times) 10^{-4}</td>
<td>79.2</td>
</tr>
<tr>
<td>VI</td>
<td>2.480</td>
<td>1.65 (\times) 10^{-4}</td>
<td>85.5</td>
</tr>
</tbody>
</table>

Fig. 2—Effect of amino acids on the polarization curve of brass in 0.6 M NaCl solution at 1 mV/s.

Fig. 3—Effect of benzenesulphonyl derivatives of amino acids on the polarization curve of brass in 0.6 M NaCl solution at 1 mV/s.
Inhibition efficiency = \[ \frac{I_{corr} - I_{corr\ (inh)}}{I_{corr}} \times 100 \]

where \( I_{corr\ (inh)} \) and \( I_{corr} \) are the corrosion current density value with and without inhibitor, respectively.

All reagents show relatively same behaviour against the polarization. Moreover, these inhibitors do not change the profile of the anodic and cathodic curves, indicating that the inhibitors merely block the reaction sites of copper surface without affecting the anodic and cathodic reaction mechanism. With increasing inhibitor concentration, no obvious trend is observed in the shift of \( E_{corr} \) values, suggesting that these compounds behave as mixed-type inhibitors.

**AC impedance studies**

The effects of varying concentrations (10\(^{-4}\) to 10\(^{-6}\) M) of I, II, III, IV, V and VI on the impedance behaviour of brass in 0.6 M NaCl solution were obtained and the curves showing highest inhibition efficiency (4 \( \times \) 10\(^{-5}\) M inhibitor concentration) are depicted in Figs 4 and 5. These curves show Nyquist plots of brass in presence of inhibitors and in absence of inhibitors. These plots reveal that the impedance response of the brass has significantly changed in the presence of these inhibitors. Various impedance parameters such as charge transfer resistance \( (R_{ct}) \), double layer capacitance \( (C_{dl}) \) and inhibition efficiency \( (IE) \) are given in Table 3. The charge transfer values are calculated from the difference in impedance at lower and higher frequencies as suggested by Haruyama et al.\(^{25}\). The percentage efficiency of corrosion of brass is calculated from \( R_{ct} \) as follows:\(^{26}\)

\[ IE = \left[ \frac{1}{R_{ct\ (inh)}} - \frac{1}{R_{ct\ (inh)}} / \frac{1}{R_{ct}} \right] \times 100 \]

where \( R_{ct\ (inh)} \) and \( R_{ct} \) are charge transfer resistance values with and without inhibitor respectively. The trend of increase in inhibition efficiency is same as in polarization study i.e. there is a good agreement between the results obtained from polarization and impedance studies (Tables 2 and 3).

The inhibition efficiencies of II and III are in the range of 47-60%. It is increased by 26-33% after introduction of \( C_6H_5-SO_2^- \) group. The inhibition efficiency may be further improved (90% and above) by converting \(-COOH\) groups to imidazoline and tetrahydropyrimidine groups.\(^{27}\)

**Conclusions**

From the results of the study the following conclusions can be drawn:

All investigated amino acids and their benzenesulphonyl derivatives have shown inhibiting properties for corrosion of brass in 0.6 M aqueous sodium chloride solution.

The corrosion inhibition efficiency of the amino acids increases in the following order I < II < III. Corresponding benzenesulphonyl derivatives follow the same order.

Benzenesulphonyl derivatives of the amino acids are better corrosion inhibitors due to the \( \pi \) electron contribution of the benzene ring and presence of more adsorption sites.

Significant improvement in the inhibition property of the amino acids is observed by introducing \( C_6H_5-SO_2^- \) group. Further improvement is possible if the carboxyl group is converted to benzimidazole, imidazoline or tetrahydropyrimidine group.

**Reference**

27 Ranjana & Nandi M M (unpublished work).