Corrosion Protection of Stainless Steel by Organic Inhibitors in Phosphate Industries in 15% H$_2$SO$_4$

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Abstract
Phosphate industries use sulphuric acid during the manufacturing of fertilizers. This acid interacts with stainless steel to develop corrosion cell and it corrodes metal. Organic inhibitors 2-(aminomethyl)phenol and 2-(aminomethyl)benzenethiol were taken for corrosion control in 15% H$_2$SO$_4$ medium. Inhibitors anticorrosive effect studied at different temperatures and 10 mM concentration. The corrosion rate of metal absence and presence of inhibitors were determined gravimetric methods. The corrosion current density and inhibitors polarization effect was studied by potentiostat. Inhibitors’ corrosion protection activities like physisorption-chemisorption adsorption, thermal stability and surface films formation analysis can be done by activation energy, heat of adsorption, free energy, enthalpy and entropy. The experimental results of inhibitors surface coverage area and inhibition efficiency were exhibited strong bonding between inhibitors and base metal.

Keywords: Stainless steel; H$_2$SO$_4$; Inhibitors; Potentiostat; Surface adsorption

Introduction
Stainless steel is a very important metal for phosphate industry whereas H$_2$SO$_4$ produces hostile environment for surrounding material and it produces several forms of corrosion like galvanic, pitting, crevice, stress, intergranular embrittlement and blistering. Scientists and researchers were used different techniques for corrosion mitigation of materials like organic and inorganic coatings, use organic and inorganic inhibitors, composite materials coating, nano-coating and plasma coatings. Inorganic nanocoating of aluminum phosphate [1], zinc phosphate [2] and magnesium phosphate [3] in presence of DLC (diamond like carbon) filler were used as nanocoating materials in high temperature and acidic environment. Aliphatic and aromatic compounds [3-5] containing amino, hydroxyl and thiol functional groups were applied as corrosion protector in acidic medium. Polymeric coating [6-8] saved material for corrosion but this coating did not produce good results in long duration. Mixed types of organic inhibitors having cathodic [9-11] and anodic [12-15] polarization power used as an inhibitor in acidic condition. Plasma coating [16,17] provided corrosion resistance of metal at high temperature and strong acidic medium. Natural products [18,19] used as inhibitor which is ecofriendly with environment and these products has good inhibition properties.

Experimental
Stainless steel (5×3×0.01) square meter size of coupons made for experimental work. Its surface was sharpened with emery paper and samples were washed with double distilled water. Finally it was rinsed with acetone and dried with air dryer and kept into desiccator. Inhibition effect of 2-(aminomethyl)phenol and 2-(aminomethyl)benzenethiol were studied at 50°C, 60°C and 70°C temperatures and 10 mM concentration. The corrosion rate was calculated absence and presence of inhibitors by gravimetric method. Stainless steel (316) was used for this and its chemical composition analyzed in Bokaro Steel Plant Jharkhand, India.

The corrosion current and corrosion potential was determined with potentiostatic polarization by using an EG & G Princeton Applied Research Model 173 Potentiostat. A platinum electrode was used as an auxiliary electrode and a calomel electrode was used as reference electrode with stainless steel coupons.

\[
\text{IE} (%) = \left( 1 - \frac{K}{K_p} \right) \times 100
\]

Results and Discussion
The corrosion rates of stainless steel was calculated at 50°C, 60°C and 70°C temperatures and 10 mM concentration of inhibitors by equation 1 in presence of 15% H$_2$SO$_4$ solution absence and presence of inhibitors 2-(aminomethyl)phenol and 2-(aminomethyl)benzenethiol.

\[
K \text{(mmpy)} = 13.56 \frac{W}{D \cdot A \cdot t}
\]

Where W = weight loss of test coupon expressed in kg, A = Area of test coupon in square meter, D = Density of the material in kg/m$^3$.

The corrosion rates of stainless steel without and with inhibitors mentioned in Table 1. The result of Table noticed that corrosion rate of metal is increasing without inhibitors and its values are decreasing with inhibitor as above recorded temperatures and concentration. The graph between log K versus 1/T was looked in Figure 1 shown that the rate of corrosion enhanced at lower temperature to higher temperature and its values suppressed after addition of inhibitors.

The percentage inhibition efficiency and surface coverage area of inhibitors were determined using 2 and equation 3.

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The Corrosion of stainless steel in 15% H₂SO₄ at different temperatures and 10 mM concentration of inhibitors.

Table 1: The Corrosion of stainless steel in 15% H₂SO₄ at different temperatures and 10 mM concentration of inhibitors.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Temperature</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
<th>C (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IH(0)</td>
<td>Kₐ₀</td>
<td>0.139</td>
<td>0.208</td>
<td>0.241</td>
<td>0</td>
</tr>
<tr>
<td>log Kₐ₀</td>
<td>-0.856</td>
<td>-0.681</td>
<td>-0.617</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IH(I)</td>
<td>K</td>
<td>0.073</td>
<td>0.086</td>
<td>0.108</td>
<td>10mM</td>
</tr>
<tr>
<td>log K</td>
<td>-1.136</td>
<td>-1.065</td>
<td>-0.966</td>
<td></td>
<td></td>
</tr>
<tr>
<td>θ</td>
<td>0.474</td>
<td>0.586</td>
<td>0.551</td>
<td></td>
<td></td>
</tr>
<tr>
<td>log(θ/1-θ)</td>
<td>0.046</td>
<td>0.15</td>
<td>0.088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IE (%)</td>
<td>47.4</td>
<td>58.6</td>
<td>55.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IH(II)</td>
<td>K</td>
<td>0.037</td>
<td>0.043</td>
<td>0.078</td>
<td>10mM</td>
</tr>
<tr>
<td>log K</td>
<td>-1.431</td>
<td>-1.366</td>
<td>-1.107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>θ</td>
<td>0.733</td>
<td>0.793</td>
<td>0.676</td>
<td></td>
<td></td>
</tr>
<tr>
<td>log(θ/1-θ)</td>
<td>0.317</td>
<td>0.583</td>
<td>0.438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IE (%)</td>
<td>73.3</td>
<td>79.3</td>
<td>67.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These results were shown that inhibitors adhered with surface of base metal.

\[
\frac{d}{dt} (\log K) = \frac{E_a}{R T^2}
\]

where \( T \) is temperature in Kelvin and \( E_a \) is the activation energy of the reaction.

The heat of adsorption was calculated with help equation 5 and their values were mentioned in Table 2. The graph plotted between log \( (\theta/1-\theta) \) vs. \( 1/T \) was shown straight line in Figure 4 and its negative values indicated that inhibitors bind with metal by physical forces.

\[
\log (\theta/1-\theta) = \log (A . C) - \left(\frac{Q_{ads}}{R T}\right)
\]

where \( T \) is temperature in Kelvin and \( Q_{ads} \) heat of adsorption

Free energy was determined by equation 6 and its values were recorded in Table 3. Its values mentioned in Table 2 depicted that after addition of inhibitor exothermic reaction occurred.

\[
\Delta G = -2.303RT \left[\log C - \log \left(\frac{\theta}{1-\theta}\right) + 1.72\right]
\]
The observation of the results of Table 3, it was noticed that corrosion current increased without inhibitors and it reduced after addition of inhibitors. Figure 6 indicated that Tafel graph has plotted between electrode potential and corrosion current density in the absence and presence of inhibitors and this figure was shown that anodic potential, corrosion current density and corrosion rate increased without inhibitors but after addition of inhibitors these values decreased and inhibition efficiency increased.

**Conclusion**

Observation of results of inhibitors 2-(aminomethyl) phenol and 2-(aminomethyl) benzenethiol indicated that inhibition efficiency and surface coverage area at different temperatures in H2SO4 medium produced corrosion resistance effect for stainless steel. The inhibitors adhered with metal surface by physisorption-chemisorption adsorption. This adsorption phenomenon confirmed by activation energy, heat of adsorption, free energy, enthalpy and entropy. Potentiostat results for both inhibitors indicated that these inhibitors produced high polarization current and nullify the attack of H+ ions.

**Acknowledgement**

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**References**


**Table 3**: Potentiostatic Polarization values of stainless steel with inhibitors at 10 mM concentration.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>ΔE</th>
<th>ΔI</th>
<th>βa</th>
<th>βc</th>
<th>Icorr (mA)</th>
<th>K (mmpy)</th>
<th>C (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IH(0)</td>
<td>-725</td>
<td>72</td>
<td>111</td>
<td>63</td>
<td>2.14</td>
<td>0.561</td>
<td>0</td>
</tr>
<tr>
<td>IH(I)</td>
<td>-674</td>
<td>64</td>
<td>68</td>
<td>94</td>
<td>1.45</td>
<td>0.435</td>
<td>10</td>
</tr>
<tr>
<td>IH(II)</td>
<td>-521</td>
<td>51</td>
<td>44</td>
<td>75</td>
<td>1.01</td>
<td>0.305</td>
<td>10</td>
</tr>
</tbody>
</table>

The observation of results of Table 3, it was noticed that corrosion current increased without inhibitors and it reduced after addition of inhibitors. Figure 6 indicated that Tafel graph has plotted between electrode potential and corrosion current density in the absence and presence of inhibitors and this figure was shown that anodic potential, corrosion current density and corrosion rate increased without inhibitors but after addition of inhibitors these values decreased and inhibition efficiency increased.


