Using Ethylthiazole-4-Carboxylate as Inhibitor for Copper Corrosion in 0.5 M HCL Acid

Dr. Raheem Aziz Hussein AL-Uqaily
IRAQ- AL-Muthanna University, College of Engineering, Chemical Engineering Department

Abstract: In this research was the study effect of ethylthiazole-4-carboxylate as inhibitor on copper corrosion in 0.5M HCl acid by using weight loss and polarization methods, results showed of decrease corrosion current density and corrosion rate with increasing inhibitor concentration of corrosion at 30 C and corresponding increase the efficiency of inhibition and surface coverage, the same way for the temperature of 40 and 50 C, where efficiency decreases depending on the temperature increase. Increase the inhibitor concentration, increased energy both activation, enthalpy and free of adsorption and decreased entropy energy, and this shows that the inhibitor has good energy to activate the process of adsorption and desorption be chemical type from good type inhibitor. Formation layer of film due found oxygen, nitrogen and sulphur molecules which have a crucial role to build the film.

Keywords: ethylthiaozole-4-carboxylate, copper, HCl ,weight loss ,polarization, corrosion.

1. INTRODUCTION

The copper and its alloys of metals used widely in the industry and is unable to remove hydrogen from the acidic solution due to the presence of oxygen which works on the dissolution of the metal [1].

In chemical industries, hydrochloric acid is widely used in the removal of salts and cleaning and pickling associated with dissolution of metal , so we use the corrosion inhibitors to reduce corrosion processes in many cases.[2,3]

Copper is characterized by being a good conductor of electricity and high thermal conductivity and good mechanical susceptibility, and is used widely in domestic and industrial water pipelines , heat exchangers , in the electronics industry , telecommunications etc.[4,5,6]

The study of several organic inhibitors such as thiazole derivatives that are interesting by the researchers, which contains a set of nitrogen, oxygen and sulfur, this kind of organic molecules can be adsorbed molecules of the solution and the metal interface and give good inhibition , as a result to prevent corrosion on the metal in the media acidic.[4,7,8]

Researchers [9] were examined in this study benzothiazole (BTH) and its substituent’s 2-methylbenzothiazole (MeBTH), 2-aminobenzothiazole (ABTH), 2-mercaptopbenzothiazole (MBTH) and 2-phenylbenzothiazole (PhBTH) have been utilized as corrosion inhibitors for а-brass in stirred 0.1 M HClO4 by using polarizations,weight loss and electrochemical impedance spectroscopy methods, where proved that the order of inhibition efficiency (% E) indicated the arrangement of inhibition efficiency was found to be BTH < MeBTH < ABTH < PhBTH < MBTH. The calculated values of thermodynamic factors followed this order thus creation of layers on surface of metal with action inhibitors were found to overpower on the corrosion rate were identified by various methods.

Investigators [10], were proved that the efficiency of the inhibitors increases with rise in inhibitor concentration but decreases with an increase in temperature and mixed type of the inhibitors action, The slopes of the anodic and cathodic tafel lines are nearly constant and independent of the inhibitor concentration, and the cathode is more polarized than the
anode. Follow the Temkin's adsorption isotherm , the adsorption of these compounds on C-steel surface have been calculated, where studied in 5-phenylazo-2-thioxo-thiazolidin-4-one and four of its derivatives as corrosion inhibitors for C-steel in 1 M sulphuric acid solution using weight-loss and galvanostatic polarization techniques.

2. EXPERIMENTAL WORK

In this study, using the method of loss of weight, and where we use samples of coupons with dimensions of 2.5 cm length of 0.1 cm width and thickness of 0.15 cm, prepares well samples of copper metal of polished, dried and weighed and immersed in a solution of 0.5 M hydrochloric acid with and without inhibitor corrosion "ethylthiaozole-4-carboxylate", it is then washed and dried and weighed again, and then calculate the corrosion rate and efficiency.

As well as the polarization method was used by computerized potentiostat and three poles, which consists of the sample pole, standard, platinum and placed inside the cell and be read both potential and current density at temperatures 30 ,40 and 50 C , thus inhibitors concentrations 50,100,150 and 200 ppm.

3. RESULTS AND DISCUSSION

Fig. 1 represents the curves anodic and cathodic between the relationship between potential and current density, we note carbon behavior in hydrochloric acid without and with the presence of concentrations of inhibitor corrosion at a temperature of 30 C , where the decrease corrosion current density with increasing inhibitor concentration of corrosion and in return increase the efficiency of inhibition , the same way for the temperature of 40 and 50 C here efficiency decreases depending on the temperature increase as in Fig. 2, 3 and 4, the polarization of the mixed type between the anodic and cathodic .

The inhibition efficiency was estimated agreeing to the follow rule: [11]

\[ E = \frac{I_{un} - I_{in}}{I_{un}} \]  \hspace{1cm} (1)

Where;

- \( I_{un} \) = corrosion current density without inhibitor, mA/cm\(^2\)
- \( I_{in} \) = corrosion current density with inhibitor, mA/cm\(^2\)

![Polarization curves for copper at various concentrations of ethylthiaozole-4-carboxylate in 0.5 M HCl at 30 C](Fig. 1)

---

Paper Publications
Fig. 2: Polarization curves for copper at various concentrations of ethylthiaozole-4-carboxylate in 0.5 M HCl at 40°C

Fig. 3: Polarization curves for copper at various concentrations of ethylthiaozole-4-carboxylate in 0.5 M HCl at 50°C

Table 1: Effect concentration of inhibitor on corrosion current density, corrosion potential and efficiency with various temperatures by using polarization method

<table>
<thead>
<tr>
<th>Conc. inhibitor (ppm)</th>
<th>$E_{corr}$, mV</th>
<th>Corrosion current density, $\mu$A/cm$^2$</th>
<th>Inhibition efficiency %</th>
<th>Surface coverage $\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-201</td>
<td>85 91 101</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>-184 (-203)</td>
<td>45 52 73</td>
<td>47.0 42.8 27.7</td>
<td>0.47 0.42 0.27</td>
</tr>
<tr>
<td>100</td>
<td>-176 (-190)</td>
<td>12 17 34</td>
<td>85.8 81.3 66.3</td>
<td>0.85 0.81 0.66</td>
</tr>
<tr>
<td>150</td>
<td>-167 (-185)</td>
<td>7 10 15</td>
<td>91.7 89.0 85.1</td>
<td>0.91 0.89 0.85</td>
</tr>
<tr>
<td>200</td>
<td>-152 (-162)</td>
<td>3 5 10</td>
<td>96.4 94.5 90.0</td>
<td>0.96 0.94 0.90</td>
</tr>
</tbody>
</table>
Table 2 illustrate effect inhibitor concentration on corrosion rate with various temperatures where that corrosion rate decreases with increasing inhibitor concentration at 30 C, in a similar manner at 40 and 50 C as shown in Fig.5, but to increase the corrosion rate. Thus, the efficiency increases with increasing inhibitor concentration at 30 C, while that efficiency decreases with increasing temperatures at 40 and 50 C, respectively.

**Table 2 : Effect concentration of inhibitor on corrosion current rate and efficiency with various temperatures using weight loss method.**

<table>
<thead>
<tr>
<th>Conc. of inhibitor ppm</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30˚C</td>
<td>40˚C</td>
</tr>
<tr>
<td>Blank</td>
<td>1.24</td>
<td>1.45</td>
</tr>
<tr>
<td>50</td>
<td>0.67</td>
<td>0.86</td>
</tr>
<tr>
<td>100</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>150</td>
<td>0.14</td>
<td>0.20</td>
</tr>
<tr>
<td>200</td>
<td>0.09</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Fig.4 : Relation between efficiency and inhibitor concentration in polarization method

Fig.5: effect inhibitor concentration on corrosion rate with various temperatures
Arrhenius' equation below is:

\[ k = A e^{-\frac{E_a}{RT}} \]  

(2)

Where, \( k \) is the rate of a reaction, \( T \) is absolute temperature, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, and \( R \) is the universal gas constant.

Kinetic parameters may be evaluated from the effect of temperature, such as enthalpy and entropy from an substitute formulation of Arrhenius equation is:[12]

\[ I_{corr} = \frac{RT}{Nh} e^{\frac{\Delta S}{R}} e^{\frac{\Delta H}{RT}} \]  

(3)

Where, \( h \) the Plank’s constant, \( N \) is the Avogadro’s number, \( \Delta S \) and \( \Delta H \) the entropy and enthalpy energies, respectively.

### Table 3: Effect inhibitor concentration on thermodynamics kinetic parameters \( E_a \), \( \Delta H \), \( \Delta S \), and \( \Delta G_{ads} \)

<table>
<thead>
<tr>
<th>Conc. of inhibitor ppm</th>
<th>( E_a ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (kJ/mol.K)</th>
<th>( \Delta G_{ads} ) (kJ/mol) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>27.01</td>
<td>19.56</td>
<td>-0.0877</td>
<td>45.69</td>
</tr>
<tr>
<td>50</td>
<td>82.03</td>
<td>70.22</td>
<td>-0.0902</td>
<td>97.09</td>
</tr>
<tr>
<td>100</td>
<td>179.62</td>
<td>167.96</td>
<td>-0.0956</td>
<td>196.44</td>
</tr>
<tr>
<td>150</td>
<td>128.85</td>
<td>117.13</td>
<td>-0.0972</td>
<td>146.09</td>
</tr>
<tr>
<td>200</td>
<td>206.94</td>
<td>191.35</td>
<td>-0.1014</td>
<td>221.56</td>
</tr>
</tbody>
</table>

### Fig. 6: Effect inhibitor concentration on inhibition efficiency for various temperatures

### Fig. 7: Relation between log I and 1/T for different inhibitors conc.
Fig. 7, represents Arrhenius plot Log C.R vs. 1/T without and with inhibitor where corrosion rate (C.R) is calculated by:

\[
(C.R) = \frac{87.6 \times w}{D \times a \times t}
\]

(4)

Where, \(C.R\) is corrosion rate (mmpy), \(w\) is weight loss (mg), \(D\) is alloy density (g/cm³), \(a\) is exposed area (cm²), \(t\) is exposure time (hr).[13]

\[\Delta G = \Delta H - T \Delta S\]

(5)

Where, \(\Delta G\) is free energy for adsorption.

Table 3 shows the effect of inhibitor corrosion thermodynamics kinetic parameters \(E_a, \Delta H, \Delta S,\) and \(\Delta G_{ads}\) were calculated from the Fig. 7 and 8 showed that whenever increase the inhibitor concentration ,increased energy both activation, enthalpy and free of adsorption and decreased entropy energy , and this shows that the inhibitor has good energy to activate the process of adsorption, and desorption be chemical type where that values activation energy more than 80 kJ / mol, and formation layer of film due found oxygen ,nitrogen and sulphur molecules which have a crucial role to build the film layer [14,15] ,while the decrease energy entropy mean decrease random and moving towards regularity and arrangement as shown in Fig.9.

Fig. 9: Structure of inhibitor "ethylthiazole-4-carboxylate"

4. CONCLUSIONS

In this research was the study effect of ethylthiazole-4-carboxylate as inhibitor on copper corrosion in 0.5M HCl acid by using weight loss and polarization methods, we note of following:

- Decrease corrosion current density and corrosion rate with increasing inhibitor concentration of corrosion at 30 C and corresponding increase the efficiency of inhibition and surface coverage, the same way for the temperature of 40 and 50 C ,where efficiency decreases depending on the temperature increase.
• Increase the inhibitor concentration, increased energy both activation, enthalpy and free of adsorption and decreased entropy energy, and this shows that the inhibitor has good energy to activate the process of adsorption, and desorption be chemical type from good type inhibitor.

• Creation layer of film due found oxygen, nitrogen and sulphur molecules which have a essential role to build the film.

REFERENCES


