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Research Article

Corrosion Behaviour of Some Low Chromium-Molybdenum Steels in Sulphamic Acid

Hesham T.M. Abdel-Fatah1,*, Medhat M. Kamel2, Salah A. M. Rashwan2, Saad M. Abd El Wahaab3, Aliaa A. M. Hassan1

1 Central Chemical Laboratories, Egyptian Electricity Holding Company, Sabtia, Cairo, EGYPT.
2 Chemistry Department, Faculty of Science, Sues Canal University, Ismailia, EGYPT.
3 Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, EGYPT.

Abstract

In this study a series of experiments was carried out in 0.6 M sulphamic acid solution at different temperatures in order to investigate the effect of chromium and molybdenum content on the corrosion behaviour of low alloy steels (ASTM A213 grade T12 (1.0Cr-0.5Mo) and grade T22 (2.25Cr-1Mo) under stagnant conditions. The corrosion behaviour of both steels in 0.6M sulphamic acid solution in the absence and presence of Tryptophan (Trp) has been investigated using weight loss measurements, electrochemical impedance spectroscopy (EIS) and the new technique electrochemical frequency modulation (EFM). The results have revealed higher corrosion rates for the lower chromium and molybdenum content steel. Moreover, it was found that the inhibition efficiency increased with increasing inhibitor concentration, while a decrease was detected with the rise of temperature.

* Corresponding author
Hesham Tawfik M. Abdel-Fatah
E-mail: hesham_tm@yahoo.com
Tel/Fax: +20 2 22755341
Mobile: +20 12 22678654

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Introduction

Industrial acid cleaning is very important procedure applied chiefly to remove scale and other unwanted deposits from steam generating equipment and from chemical and petrochemical reaction vessels. Several solvents will effectively remove waterside deposits. Mostly, hydrochloric, sulfuric, sulphamic and citric acids are employed for such purpose [1,2].

There are little reports on the corrosion characteristics of different metal materials in sulphamic acid media. Only a few articles in the literature deal with this topic [3-6]. The present study therefore aims to filling this gap. Sulphamic acid has the advantage of being a crystalline solid, and compatible for use with stainless steels and low alloy steels.

Due to the corrosive effect of acid solutions on metal materials, corrosion inhibitors are commonly used to reduce this effect as an effective and economic corrosion control method [7,8]. The uses of corrosion inhibitors in specific applications such as the acid cleaning of steam generator components have been reviewed briefly [9].

Because of the issues of toxicity of substances like chromate inhibitors, there is an increasing interest in exploration and utilization of safer and environmentally friendly inhibitors, which are also known as green inhibitors [10-12].

Amino acids are from a class of organic compounds that are completely soluble in aqueous media, relatively cheap, easy to produce with high purity; non-toxic and considered as environmentally friendly compounds. These properties enhance their use as corrosion inhibitors for iron, steel and stainless steel [12-16].

Therefore, this study was designed to investigate the following: 1) The inhibition properties of Tryptophan on the corrosion behaviour of low alloy steels (T12 and T22) in sulphamic acid solutions. 2) The effect of chromium and molybdenum as alloying elements on the corrosion rate of T12 and T22 steels in sulphamic acid solutions at different temperatures. 3) The reliability of the EFM technique as an effective corrosion monitoring technique.

Experimental

Low Chromium-Molybdenum steels ASTM A213 grade T12 (1.0Cr-0.5Mo) and grade T22 (2.25Cr-1Mo) strips were used in the present study. Generally, low alloy steels are widely used as boiler tubes for heat exchangers and pressure vessels of power and petrochemical plants [17,18]. The chemical compositions of both alloys T12 and T22 were reported earlier [19].

All solutions were freshly prepared from analytical grade chemical reagents using ultrapure water.


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The experiments were conducted in stagnant aerated solutions at different temperatures 25, 40, and 60 °C ±1. Low alloy steel specimens of total exposed area of 4 cm² were used. The weight loss was determined by weighing the cleaned samples before and after immersion in sulphamic acid solutions at different immersion times and at different temperatures.

The electrochemical experiments were carried out using a three-electrode glass cell assembly, consisting of a steel electrode embedded in epoxy resins with an exposed area of 1 cm² as working electrode, a saturated calomel electrode as reference electrode, and a platinum foil 1 cm² as counter electrode. The working electrode was mechanically abraded with different grades (400, 600 and 1200) of silicon carbide papers, degreased with acetone in an ultrasonic bath, then rinsed with ultrapure water and finally dried before use.

The electrochemical impedance spectroscopy (EIS) measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open circuit potential in the frequency range between 15 kHz and 0.3 Hz. The electrochemical frequency modulation (EFM) is a new technique provides a new tool for electrochemical corrosion monitoring. The great strength of the EFM is the two causality factor (CF2 and CF3). The causality factor is calculated from the frequency spectrum of the current response. The idea behind this causality factor is that it can be used to check the validity of the EFM measurements. If the causality factors differ significantly from the theoretical values of 2 and 3, it can be deduced that the measurements are influenced by noise. If the causality factors are approximately equal to the predicted values of 2 and 3, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable. The features and theory of EFM technique were reported previously [20].

All Electrochemical experiments were carried out using Gamry PCI300/4 Potentiostat, EIS300 software, EFM140 software and Echem Analyst 5.21 for results plotting, graphing, data fitting & calculating.

**Results and Discussion**

**Effect of Temperature on the Corrosion Rate**

Electrochemical Frequency Modulation (EFM) Studies

Figure 1 shows the plots of the current as a function of frequency that were obtained by EFM for both alloys (T12 and T22) in 0.6 M sulphamic acid solution at 60 °C.

Table 1 shows the corrosion parameters such as \( I_{corr} \), \( \beta_0 \), \( \beta_c \), corrosion rate and the causality factors CF2 and CF3 of both steels in 0.6 M sulphamic acid solution at different temperatures.

It is obvious from Table 1 that, the corrosion current density \( (U_{corr}) \), and hence the corrosion rate of each sample increases with increasing temperature. The corrosion resistance of T22 steel is higher than that of T12 steel in this acid medium. Moreover, the causality factors CF2 and CF3 in Table 1 are close to the theoretical values 2.0 and 3.0, respectively, indicating that the measured data are reliable [5,20,21].

In order to evaluate the results of EFM technique as an effective corrosion monitoring technique, several traditional corrosion techniques were used to investigate the corrosion rates of low alloy steels in 0.6 M sulphamic acid solutions, weight loss and EIS measurements.

**Table 1 Corrosion rates of the two low alloy steels in 0.6 M sulphamic acid at different temperatures obtained from EFM technique**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( T^* ) (°C)</th>
<th>( \beta_0 ) (mV dec(^{-1}))</th>
<th>( \beta_c ) (mV dec(^{-1}))</th>
<th>CF2</th>
<th>CF3</th>
<th>( I_{corr} ) (µA cm(^{-2}))</th>
<th>CR (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T12</td>
<td>25</td>
<td>90.9</td>
<td>195.5</td>
<td>2.319</td>
<td>2.874</td>
<td>652.5</td>
<td>7.55</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>73.4</td>
<td>122.5</td>
<td>2.217</td>
<td>2.661</td>
<td>902.7</td>
<td>10.44</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>96.3</td>
<td>121.1</td>
<td>1.899</td>
<td>3.125</td>
<td>2171</td>
<td>25.11</td>
</tr>
<tr>
<td>T22</td>
<td>25</td>
<td>87.5</td>
<td>178.7</td>
<td>2.247</td>
<td>2.874</td>
<td>429.7</td>
<td>4.97</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>84.1</td>
<td>181.6</td>
<td>2.354</td>
<td>3.207</td>
<td>726.8</td>
<td>8.41</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>88.6</td>
<td>182.2</td>
<td>2.320</td>
<td>2.870</td>
<td>1649</td>
<td>19.08</td>
</tr>
</tbody>
</table>

*Temperature

**Weight Loss Measurements**

The weight losses of T12 and T22 steels in 0.6 M sulphamic acid solution were determined after 360 minutes of immersion at different temperatures. The corrosion rate in units of millimeters per year (mm/year) was calculated from the weight loss, time of exposure and original exposed surface area of the steel samples by the following formula [22,23];

\[
\text{Corrosion rate (mm/year)} = 3.16 \times \left( \frac{W}{DA_t} \right)
\]
where \( W \) is the weight loss in milligrams, \( D \) is the density in g/cm\(^3\) (\( D = 7.88 \)), \( A \) is the area in square inches (\( A = 0.62 \)) and \( t \) is the time of exposure in hours (\( t = 120 \)).

The values of corrosion rate for both steels T12 and T22 at different temperatures were presented in Figure 2. The weight losses of both steels obey the order: T12 > T22 and the rate of corrosion of each sample is enhanced with increasing the solution temperature.

![Figure 2](image1)

**Figure 2** Corrosion rates of T12 and T22 steels in 0.6 M sulphamic acid at different temperatures (associated from weight loss method)

**Electrochemical impedance spectroscopy (EIS) studies**

The corrosion of both steels T12 and T22 in 0.6 M sulphamic acid solution was investigated by EIS technique at different temperatures. Figure 3 - as an example - shows a typical set of Nyquist plots for T12 steel.

![Figure 3](image2)

**Figure 3** Nyquist plots of T12 steel in 0.6 M sulphamic acid at different temperatures

The determined values of charge-transfer resistance (\( R_{ct} \)) and double layer capacitance (\( C_{dl} \)) were listed in Table 2.

### Table 2 Corrosion rates of the two low alloy steels in 0.6 M sulphamic acid at different temperatures obtained from EIS technique

<table>
<thead>
<tr>
<th>Alloy</th>
<th>T (°C)</th>
<th>( C_{dl} ) (μF cm(^{-2}))</th>
<th>( R_{ct} ) (ohm.cm(^{-2}))</th>
<th>CR (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T12</td>
<td>25</td>
<td>453.1</td>
<td>40.68</td>
<td>7.67</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>877.5</td>
<td>23.7</td>
<td>9.74</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1686.5</td>
<td>11.29</td>
<td>23.90</td>
</tr>
<tr>
<td>T22</td>
<td>25</td>
<td>278.2</td>
<td>58.83</td>
<td>5.02</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>673.8</td>
<td>34.93</td>
<td>8.28</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1218.6</td>
<td>15.47</td>
<td>19.39</td>
</tr>
</tbody>
</table>

Generally, the corrosion current density (\( I_{corr} \)) can be calculated using the charge-transfer resistance (\( R_{ct} \)) based on the following Stern-Geary equation [24,25]:

\[
I_{corr} = \frac{1}{2.303} \times \left( \frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) \times \frac{1}{R_p}
\]

(2)

where \( I_{corr} \) is the corrosion current density (mA/cm\(^2\)), \( \beta_a \) is the anodic Tafel slope (mV/decade), \( \beta_c \) is the cathodic Tafel slope (mV/decade), and \( R_p \) is the polarization resistance (ohm.cm\(^2\)). Both Tafel slopes (\( \beta_a \) and \( \beta_c \)) were collected from EFM method.

The corrosion current density (\( I_{corr} \)) can be converted to corrosion rates in units of millimeters per year (mm/year) based on the following Faraday’s Law [24,25]:

\[
\text{Corrosion rate (mm/year)} = 3.15 \times 10^5 \left( \frac{M}{nFD} \right) \times I_{corr}
\]

(3)

where \( M \) is atomic mass of metal in g/mole (\( M = 55.85 \)), \( n \) is number of electrons involved of the corrosion reaction in mole (\( n = 2 \)), \( F \) is Faraday’s constant in coulombs/mole (\( F = 96500 \)), and \( D \) is density of metal in g/cm\(^3\) (\( D = 7.88 \)).

The calculated corrosion rate values obtained from the charge-transfer resistance (\( R_{ct} \)) were listed in Table 2. It is obvious from this table that the values of (\( R_{ct} \)) decreased, while the values of (\( C_{dl} \)) and corrosion rate increased with increase in the solution temperature. The corrosion rate of the two alloys in 0.6 M sulphamic acid as obtained from EIS obeys the following order: T12 > T22.

All results of corrosion rate obtained from the above three techniques; confirm that corrosion rate of T12 steel (1.0Cr-0.5Mo) is clearly higher than corrosion rate values of T22 steel (2.25Cr-1.0Mo) in 0.6 M sulphamic acid solutions at different temperatures. This is in high agreement with the common known fact that chromium (Cr) and molybdenum (Mo) improve corrosion resistance of steels [26,27]. The increased corrosion resistance due to the addition of Cr has been attributed to the Cr enrichment in the passive layer and a thickening of the passive film [28].

Many authors have suggested mechanisms for the beneficial influence of Mo [29-33]. It is proposed...
that the main effect of Mo was to decrease the rate of dissolution in active zones by formation and retention of molybdenum oxyhydroxide or molybdates at these sites. Other theories include; dissolving Mo from the substrate, into the solution, and then oxidized to molybdate, enrichment of Cr in the oxide layer by the selective dissolution of Mo and thickening of the passive film and stabilisation of the Cr oxides by the presence of Mo\(^{6+}\) forming an amorphous oxide film with a glassy structure. The produced results from weight loss and EIS measurements are compatible with those obtained from the EFM method.

**Effect of temperature on the inhibition efficiency**

EIS measurements

Table (3) shows the impedance parameters, the charge-transfer resistance (\(R_c\)) and the double layer capacitance (\(C_{dl}\)).

Inspections of these data indicate the following;

1) The charge-transfer resistance (\(R_c\)) increases, while the double layer capacitance (\(C_{dl}\)) decreases with the increase of inhibitor concentration. This may be the result of decreasing film capacitance due to increase in the surface coverage by the inhibitor molecules.

2) The values of (\(R_c\)) decrease, while the (\(C_{dl}\)) values increase with increase in the solution temperature.

The above results can be explained on the basis that the electrostatic adsorption of inhibitor species at the metal surface leads to form a physical protective film that retards the charge transfer process and therefore inhibits the corrosion reactions, leading to increase \(R_c\) values. Moreover, the adsorbed inhibitor species decrease the electrical capacity of the electrical double layer at the electrode/solution interface and, therefore, decrease the values of \(C_{dl}\) [34,35].

Since the electrochemical theory assumes that the reciprocal of charge-transfer resistance (1/\(R_c\)) is directly proportional to the corrosion rate, the inhibition efficiency (IE\%) was calculated using the following equation:

\[
IE\% = \left[1 - \left(\frac{R^o_{ct}}{R_{ct}}\right)\right] \times 100
\]  

(4)

where \(R^o_{ct}\) and \(R_{ct}\) are the charge-transfer resistance values in the absence and presence of inhibitor, respectively.

The calculated inhibition efficiencies obtained from EIS results were also presented in Table 3.

The values of IE\% increase with the increase of the inhibitor concentration, while decreasing with the increase of solution temperature.

**EFM measurements**

The calculated corrosion kinetic parameters at different concentrations of Trp in 0.6 M sulfamic acid solution (\(i_{corr}\), \(\beta_c\), \(\beta_a\), CF-2 and CF-3) at different temperatures were given in Table 4.

**Table 3** Electrochemical kinetic parameters obtained from EIS techniques for T22 in 0.6 M sulphamic acid in absence and presence of various concentrations of Trp at different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Trp Conc. (M)</th>
<th>(C_{dl}) ((\mu F.cm^2))</th>
<th>(R_c) (ohm.cm²)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.005</td>
<td>195.2</td>
<td>91.78</td>
<td>35.90</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>121.6</td>
<td>151.42</td>
<td>61.15</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>72.81</td>
<td>282.4</td>
<td>79.17</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>31.56</td>
<td>745.5</td>
<td>92.11</td>
</tr>
<tr>
<td>40</td>
<td>0.005</td>
<td>499.6</td>
<td>48.98</td>
<td>28.69</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>318.4</td>
<td>73.36</td>
<td>52.39</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>201.6</td>
<td>130.2</td>
<td>73.17</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>92.87</td>
<td>226.4</td>
<td>84.57</td>
</tr>
<tr>
<td>60</td>
<td>0.005</td>
<td>978.3</td>
<td>18.91</td>
<td>18.19</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>752.4</td>
<td>23.82</td>
<td>35.05</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>654.7</td>
<td>31.46</td>
<td>50.83</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>315.5</td>
<td>58.47</td>
<td>73.54</td>
</tr>
</tbody>
</table>

**Table 4** Electrochemical kinetic parameters obtained from EFM technique for T12 in 0.6 M sulphamic acid with various concentrations of Trp at different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Trp Conc. (M)</th>
<th>(\beta_c) (mV dec(^{-1}))</th>
<th>(\beta_a) (mV dec(^{-1}))</th>
<th>CF2</th>
<th>CF3</th>
<th>(i_{corr}) ((\mu A.cm^2))</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.005</td>
<td>88.3</td>
<td>192.7</td>
<td>1.973</td>
<td>3.140</td>
<td>380.1</td>
<td>41.75</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>84.6</td>
<td>191.2</td>
<td>1.735</td>
<td>2.856</td>
<td>280.4</td>
<td>57.03</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>93.3</td>
<td>199.4</td>
<td>1.953</td>
<td>2.875</td>
<td>140.0</td>
<td>78.54</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>75.7</td>
<td>190.7</td>
<td>1.851</td>
<td>2.851</td>
<td>73.12</td>
<td>88.79</td>
</tr>
<tr>
<td>40</td>
<td>0.005</td>
<td>72.5</td>
<td>118.5</td>
<td>2.156</td>
<td>3.281</td>
<td>589.6</td>
<td>34.68</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>79.8</td>
<td>125.4</td>
<td>1.846</td>
<td>2.856</td>
<td>419.2</td>
<td>53.56</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>80.6</td>
<td>123.5</td>
<td>2.264</td>
<td>3.211</td>
<td>261.4</td>
<td>71.04</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>78.9</td>
<td>118.4</td>
<td>1.895</td>
<td>2.886</td>
<td>145.3</td>
<td>83.90</td>
</tr>
<tr>
<td>60</td>
<td>0.005</td>
<td>91.5</td>
<td>115.3</td>
<td>1.894</td>
<td>3.101</td>
<td>1705.0</td>
<td>21.46</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>86.2</td>
<td>110.2</td>
<td>2.354</td>
<td>2.910</td>
<td>1248.0</td>
<td>42.51</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>98.4</td>
<td>125.5</td>
<td>2.089</td>
<td>3.128</td>
<td>904.8</td>
<td>58.32</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>111.5</td>
<td>132.2</td>
<td>1.991</td>
<td>2.901</td>
<td>621.2</td>
<td>71.39</td>
</tr>
</tbody>
</table>

From Table 4, the values of corrosion current density (\(i_{corr}\)) decreased in presence of Trp, which suggests that the rate of electrochemical reaction is reduced due to the formation of a barrier layer over the steel surface by the inhibitor. The values of \(\beta_a\) and \(\beta_c\) do not show any appreciable change indicating that the studied inhibitor in both acids is mixed type inhibitor [36]. The causality factors CF-2 and CF-3 are very close to the standard values 2.0 and 3.0 respectively, indicating that the measured data are reliable [3,20,21].
The inhibition efficiency (IE %) of Trp was calculated from the corrosion current density by using the following equation:

$$IE\% = \left[1 - \left(\frac{I_{corr}}{I_{corr}^o}\right)\right] \times 100$$ (5)

where $I_{corr}^o$ and $I_{corr}$ are the corrosion current densities for uninhibited and inhibited solutions respectively. The calculated values of inhibition efficiency (IE %) were also listed in Table 4. It can be seen that the inhibition efficiency decreases with temperature in the absence and presence of Trp.

Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between two processes at a particular temperature. With the increase of temperature, the equilibrium between the adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. This explains that the lower inhibition efficiency at higher temperature [37]. The obtained results show good agreement of corrosion kinetic parameters extracted from EFM and EIS methods.

**Surface Examinations**

The corrosion behaviour of the two alloys was further confirmed by Optical Microscope examinations of the electrode surface.

**Figures 4 and 5** represent the micrographs of the two low alloy steels T12 and T22 samples respectively, after 5 days immersion in 0.6 M sulphamic acid solutions in the absence and presence of 0.04 M Trp at 25°C.

The images of T12 and T22 steel samples after immersion in sulphamic acid solution are shown in Figures 4a and 5a respectively. It is observed that the localized attack in T12 steel was more intense than that in the case of T22 steel.

**Figure 4** Optical Micrographs (200X) of T12 steel surface after 6 days immersion in 0.6 M sulphamic acid solution in absence (a) and presence of 0.004 M Trp (b).

**Figure 5** Optical Micrographs (200X) of T22 steel surface after 6 days immersion in 0.6 M sulphamic acid solution in absence (a) and presence of 0.004 M Trp (b).

**Conclusion**

The results conducted by this study confirm the positive role of high chromium and molybdenum content on the corrosion behaviour of T12 and T22 steels in sulphamic acid solutions, which support the common known conclusion that chromium (Cr) and molybdenum (Mo) have a major role to improve the corrosion resistance of steels. Corrosion rate measurements reveal higher values with increasing solution temperature.

Tryptophan has shown good inhibitive properties for both T12 and T22 steels in 0.6M sulphamic acid solutions.

The obtained results at different experimental conditions are in good agreement. This is an indication that the EFM technique can be used efficiently for monitoring the corrosion rate.

**References**


