Electrochemical study on inhibitory effect of Aspirin on mild steel in 1 M hydrochloric acid


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Electrochemical study on inhibitory effect of Aspirin on mild steel in 1 M hydrochloric acid

B.M. Prasanna a, B.M. Praveen b,*, Narayan Hebbar b, T.V. Venkatesha c, H.C. Tandon d, S.B. Abd Hamid e

a Department of Chemistry, S.T.J. Institute of Technology, Ranebennur, Karnataka, India
b Department of Chemistry, Srinivas School of Engineering, Mukka, Mangalore, Karnataka, India
c Department of Chemistry, Kuvempu University, Shankaraghatta, Shimoga, Karnataka, India
d Department of Chemistry, Sri Venkateswara College, Dhaula Kuan, New Delhi, India
e Nanotechnology and Catalysis Research Centre (NANOCAT), University of Malaya, Kuala Lumpur 50603, Malaysia

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KEYWORDS
Aspirin;
Inhibitor;
Electrochemical measurements

Abstract Aspirin was investigated as a good corrosion inhibitor for mild steel in 1 M hydrochloric acid at a temperature region from 303 to 333 K. The computed inhibition efficiency increases by increasing the inhibitor concentration and decreases by increasing the temperature. The investigation was done by weight loss, electrochemical measurements such as Tafel polarization and electrochemical impedance spectroscopy. Inhibition effect is attributed to the adsorption of inhibitor on the surface of the mild steel. The Tafel method reveals that the Aspirin acts as a mixed type inhibitor. Activation parameters suggest that the adsorption process is exothermic in nature. SEM photographs of mild steel in the absence and presence of inhibitor visualize the adsorption layer on the surface of the mild steel.

1. Introduction

Corrosion is a destructive attack on metal and alloys by chemical or electrochemical reaction whenever it is exposed to a corrosive environment. The mild steel is one of the alloys of iron having good thermal and mechanical properties. So that the mild steel can be used in various industrial and structural applications like acid pickling, acid cleaning, acid descaling, and oil-well acidizing (Chauhan and Gunasekaran, 2007; Khaled, 2008). Acids are used to the removal of initial rust on the surface of the mild in various industrial processes, which gives an aggressive corrosive environment are more susceptible to corrosion (Obot, 2009). To avoid the metal dissolution through the attack of corrosion, it is controlled by various corrosion control techniques such as protective coatings, cathodic protection, and corrosion inhibitors. Among those, the use of corrosion inhibitors is the most convenient and practical method to control the corrosion. Corrosion inhibitors are heterocyclic organic molecules. Which consists of hetero atoms like Nitrogen, Sulfur, Oxygen and π-electrons in heterocyclic ring system in its structure are for its adsorption on the metal...
Inhibitory effect of Aspirin on mild steel

2. Experimental

2.1. Materials

Corrosion inhibition study of inhibitor was performed for mild steel (Composition: 0.35% C, 0.032% Mn, 0.028% P, 0.03% S and remaining Fe). This mild steel strips of dimensions of 6 cm x 1 cm x 0.1 cm were used for weight loss method, and the same strips with an exposed area of 1 cm$^2$ (remaining portion covered by the resin) were used for electrochemical studies. Therefore, the mild steel strips used for experiments were abraded with SiC abrasive papers grade no 100, 400, 1500 and 2000 respectively, then washed with acetone, dried at room temperature and kept apart from moisture. Corrosive media of 1 M HCl can be prepared by using Analytical grade HCl and distilled water for all the experiments.

2.2. Weight loss measurement

Mild steel strips with a dimension of 6 cm$^2$ were used for weight loss measurement. Mild steel strips were processed through an acid pickling (5% H$_2$SO$_4$) to the removal of preliminary rust and deposits and digressed by using acetone followed by double distilled water and then dried at room temperature. Different mild steel strips were weighed and immersed in the absence and presence of inhibitor in 1 M hydrochloric acid solution over an immersion period of 4 h at 303 K temperature. The weight difference was recorded before and after the immersion period.

2.3. Electrochemical measurements

The electrochemical measurement was carried out by using a three electrode system consisting of working electrode (mild steel strip), reference electrode (saturated calomel) and a counter electrode (platinum). The instrument used for the electrochemical analysis was carried out in atmospheric condition without stirring by using electrochemical system compactstat, El0800 from Ivium Technologies, Netherland.

For the Tafel polarization plots of potential Vs, the current was recorded, in the given potential range of $-0.28$ V to $-0.50$ V at a scan rate of 1 mV/s.

The electrochemical impedance spectra were recorded by using AC signals with amplitude 0.01 V/s at OCP in the frequency range from 100 kHz to 0.1 Hz.

2.4. Activation parameters

The variation of inhibition efficiency with elevated temperature was studied by activation parameters of the corrosion inhibition of mild steel. For this analysis, Tafel polarization data were used at a temperature range of 303–333 K in the absence and presence of various concentrations of Aspirin.

2.5. Scanning electron microscopic (SEM) studies

The surface analysis of the mild steel strip was recorded before and after the immersion in 1 M HCl in the absence and presence of Aspirin for about 4 h by using Scanning electron microscopy (JEOL JSM-840A model).

3. Result and discussion

3.1. Weight loss method

Weight loss measurement was studied for the corrosion of mild steel in the absence and presence of various concentrations of Aspirin in 1 M HCl for about the immersion period of 4 h at 303 K temperature. The corrosion rate ($v$) was calculated by using the following expression:

$$v = \frac{W^0 - W}{S T} \times 100$$

where $W^0$ and $W$ are the weights of the mild steel strips in the absence and presence of inhibitor in 1 M HCl respectively, $S$ and $T$ are the surface area of the steel strip and immersion time respectively. The inhibition efficiency ($\eta_v$) was calculated by using the following expression,

$$\eta_v = \frac{v^0 - v}{v^0} \times 100$$

where $v$ and $v_i$ are the corrosion rates of mild steel in the absence and presence of inhibitor in the bulk of the solution.
respectively. The values of corrosion rate ($\nu$) and inhibition efficiency ($\eta_i$) are reported in Table 1.

The results obtained by the weight loss measurement clear that the Aspirin effectively inhibits the corrosion of mild steel in 1 M HCl at elevated concentration. Whenever the inhibitor concentration ($C$) increases gradually the inhibition efficiency ($\eta_i$) of the corrosion of mild steel also increases due to the surface coverage by the Aspirin through the adsorption process. We found maximum inhibition efficiency 78.94% at 50 ppm of Aspirin in 1 M HCl solution for corrosion of mild steel at 303 K temperature.

3.2. Electrochemical Tafel polarization measurement

The electrochemical Tafel polarization plots for mild steel in the absence and presence of various concentrations of Aspirin in 1 M HCl solution at temperature range 303–333 K were recorded as shown in Fig. 2. The computed corrosion parameters by this method such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), Corrosion rate ($\nu$), Tafel Cathodic slope ($\beta_c$), Tafel anodic slope ($\beta_a$), and inhibition efficiency ($\eta_p$) are reported in Table 2. The inhibition efficiency was calculated by using the following relationship,

$$\eta_p = \frac{i_{corr} - i_{corr}'}{i_{corr}} \times 100 \quad (3)$$

where $i_{corr}$ and $i_{corr}'$ are corrosion current in the absence and presence of inhibitor respectively. A close examination of Fig. 2 and Table 2, reveals that Aspirin concentration increases including blank (1 M HCl), the following discussions were discussed,

- The corrosion potential ($E_{corr}$) of inhibited solutions decreases on the blank with the displacement of less than 85 mV. So this result indicates that the inhibitor acts as a mixed type (Ferreira et al., 2004), which retards both anodic (metal dissolution) as well as cathodic (hydrogen liberation) reaction.

- The decrease in corrosion current density ($i_{corr}$) and corrosion rate ($\nu$) is the indication of the inhibiting effect of Aspirin on the corrosion of mild steel in 1 M HCl which is attributed to the surface coverage through adsorption process.

- The displacement of Cathodic Tafel slope ($\beta_c$) and anodic Tafel slope ($\beta_a$) was not changed remarkably which, clearly shows that the Aspirin inhibits the corrosion through the adsorption process, without changing the mechanism of corrosion reaction (Prasanna et al., 2014b).

Table 1  Corrosion parameters for mild steel in the absence and the presence of various concentrations of Aspirin at 303 K by weight loss measurement.

<table>
<thead>
<tr>
<th>Corrosive medium of Aspirin C (ppm)</th>
<th>Corrosion rate $\nu$ (g/cm²/h)</th>
<th>Inhibition efficiency $\eta_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.380</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>0.260</td>
<td>31.57</td>
</tr>
<tr>
<td>20</td>
<td>0.225</td>
<td>40.78</td>
</tr>
<tr>
<td>30</td>
<td>0.142</td>
<td>62.63</td>
</tr>
<tr>
<td>40</td>
<td>0.122</td>
<td>67.89</td>
</tr>
<tr>
<td>50</td>
<td>0.080</td>
<td>78.94</td>
</tr>
</tbody>
</table>

Figure 2  Electrochemical Tafel polarization spectra for corrosion of mild steel in the absence and presence of Aspirin in 1 M HCl solution at (A) 303 K, (B) 313 K, (C) 323 K, (D) 333 K temperature.
3.3. Electrochemical impedance spectroscopy (EIS) measurement

The electrochemical measurement was carried out for the corrosion of mild steel in the absence and presence of various concentrations of Aspirin in 1 M HCl solution at 303–333 K temperature regions. Electrochemical impedance spectra were recorded as shown in Fig. 3. The EIS parameters such as polarization resistance ($R_p$), double layer capacitance ($C_{dl}$) and inhibition efficiency ($\eta_i$) were computed by fitting into an equivalent circuit as shown in Fig. 4 and reported in Table 3.

\[ \eta_i = \frac{R_p - R_p^0}{R_p} \times 100 \quad (4) \]

where $R_p$ and $R_p^0$ are polarization resistance values in the presence and absence of inhibitor. The formula evaluated the double layer capacitance values ($C_{dl}$) as follows,

\[ C_{dl} = \left( Q R_c^{1-n} \right)^{1/n} \quad (5) \]

where $Q$ is the constant phase element (CPE) ($Q = \frac{1}{\omega C}$), $\omega$ is angular frequency (rad/s), and $n$ is the CPE exponent that gives details about the degree of surface inhomogeneity.

Nyquist’s (Fig. 3) plots consist of a set of semicircles with a high-frequency capacitive loop and low-frequency inductive loop. While considering the EIS data obtained from Table 3 following discussions were listed as follows,

- The addition of the inhibitor, which increases the diameter of the semicircles represents increasing the polarization resistance ($R_p$), which controlled metal dissolution.
- The increasing the inhibitor concentration, the double layer capacitance ($C_{dl}$) value decreased due to the increasing the thickness of the double layer (Babic Samardzija et al., 2005) forms a passive film on the metal surface acts as a protective layer, which slowdowns the corrosion process.
- Inhibition efficiency increases, because of the adsorption of inhibitor over the metal surface. Inhibition efficiency increases by increasing the inhibitor concentration and decreases from 303 to 313 K and increases in the time interval 313–333 K.

**Table 2** Electrochemical Tafel polarization parameters for corrosion of mild steel in the absence and presence of Aspirin in 1 M HCl.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Inhibitor concentration (ppm)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ ($10^{-6}$ A cm$^{-2}$)</th>
<th>Corrosion rate (mpy)</th>
<th>$\beta_c$ mV/decade</th>
<th>$\beta_a$ mV/decade</th>
<th>Inhibition efficiency $\eta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 Blank</td>
<td></td>
<td>-0.389</td>
<td>116</td>
<td>1.975</td>
<td>-0.116</td>
<td>0.069</td>
<td>94.84</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.393</td>
<td>105</td>
<td>1.221</td>
<td>-0.098</td>
<td>0.080</td>
<td>98.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.391</td>
<td>58</td>
<td>1.061</td>
<td>-0.105</td>
<td>0.078</td>
<td>90.00</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-0.401</td>
<td>53</td>
<td>0.915</td>
<td>-0.114</td>
<td>0.069</td>
<td>54.31</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-0.383</td>
<td>37</td>
<td>0.648</td>
<td>-0.096</td>
<td>0.071</td>
<td>68.10</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.390</td>
<td>26</td>
<td>0.450</td>
<td>-0.112</td>
<td>0.068</td>
<td>77.58</td>
</tr>
<tr>
<td>313 Blank</td>
<td></td>
<td>-0.472</td>
<td>1014</td>
<td>14.600</td>
<td>-0.089</td>
<td>0.158</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.386</td>
<td>754</td>
<td>11.480</td>
<td>-0.094</td>
<td>0.134</td>
<td>25.64</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.384</td>
<td>661</td>
<td>10.150</td>
<td>-0.090</td>
<td>0.122</td>
<td>34.81</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-0.377</td>
<td>426</td>
<td>9.250</td>
<td>-0.107</td>
<td>0.087</td>
<td>57.98</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-0.373</td>
<td>290</td>
<td>7.800</td>
<td>-0.103</td>
<td>0.071</td>
<td>71.40</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.371</td>
<td>245</td>
<td>5.750</td>
<td>-0.092</td>
<td>0.097</td>
<td>75.83</td>
</tr>
<tr>
<td>323 Blank</td>
<td></td>
<td>-0.481</td>
<td>733</td>
<td>8.514</td>
<td>-0.104</td>
<td>0.156</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.457</td>
<td>542</td>
<td>6.298</td>
<td>-0.104</td>
<td>0.124</td>
<td>26.01</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.434</td>
<td>425</td>
<td>4.946</td>
<td>-0.097</td>
<td>0.116</td>
<td>41.89</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-0.410</td>
<td>378</td>
<td>4.397</td>
<td>-0.101</td>
<td>0.091</td>
<td>48.35</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-0.408</td>
<td>215</td>
<td>3.500</td>
<td>-0.096</td>
<td>0.113</td>
<td>70.57</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.432</td>
<td>213</td>
<td>2.476</td>
<td>-0.087</td>
<td>0.119</td>
<td>70.91</td>
</tr>
<tr>
<td>333 Blank</td>
<td></td>
<td>-0.400</td>
<td>283</td>
<td>4.590</td>
<td>-0.137</td>
<td>0.092</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.384</td>
<td>234</td>
<td>2.720</td>
<td>-0.110</td>
<td>0.080</td>
<td>17.25</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.377</td>
<td>198</td>
<td>2.301</td>
<td>-0.093</td>
<td>0.064</td>
<td>30.00</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-0.375</td>
<td>194</td>
<td>2.255</td>
<td>-0.104</td>
<td>0.076</td>
<td>31.44</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-0.377</td>
<td>164</td>
<td>1.735</td>
<td>-0.112</td>
<td>0.071</td>
<td>42.04</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.386</td>
<td>129</td>
<td>1.200</td>
<td>-0.094</td>
<td>0.076</td>
<td>54.41</td>
</tr>
</tbody>
</table>
Another reason for decreasing inhibition efficiency of Aspirin with increasing temperature is due to that the physical adsorption is the predominant mechanism rather than that of chemisorption.

3.4. Effect of temperature

The temperature is one of the important factors, which affects the corrosion of mild steel in the absence and presence of inhibitor in acid media. This effect of temperature with inhibition effect by inhibitor can be explained by activation energy \( E_a \) of the corrosion process. Tafel polarization data were fit to study the activation parameters. The relationship between corrosion rate \( m_{corr} \) with activation energy \( E_a \) and temperature can be explained by Arrhenius equation as follows (Ghasemi et al., 2013),

\[
\ln m_{corr} = \ln A - \frac{E_a}{RT}
\]

where \( m_{corr} \) is the corrosion rate, \( E_a \) is the apparent activation energy, \( R \) is the universal gas constant, \( T \) is the absolute temperature and \( A \) is the Arrhenius pre-exponential constant. The Arrhenius plot of \( m_{corr} \) against 1000/T is shown in Fig. 5. The computed activation parameters such as \( E_a \) and \( A \) are reported in Table 4.

It is clear that from Table 4, higher \( E_a \) values of inhibited solution than uninhibited solution indicate that the adsorption of inhibitor is of physical type (electrostatic), because it is closer toward threshold value of 80 kJ/mol. This adsorption process leads to an increase in activation energy and Arrhenius pre-exponential \( A \) factor in the presence of Aspirin, which retards the corrosion rate due to the increase in thickness of the double layer (Nataraja et al., 2012). The enthalpy of
activation \( \Delta H^* \) and entropy of activation \( \Delta S^* \) can be calculated by the following equation,

\[
\ln \frac{\nu_{corr}}{T} = \ln \left( \frac{R}{Nh} \right) + \frac{\Delta H^*}{R} - \frac{\Delta S^*}{R}
\]

where \( R \), \( h \), and \( N \) are the universal gas constant, plank’s constant and Avogadro number respectively. Plot a Transition graph of \( \ln \frac{\nu_{corr}}{T} \) as shown in the Fig. 6 set of straight lines were obtained in the plot with regression coefficient almost near to unity. The \( \Delta H^* \) value was calculated by using slope value \( (\Delta H^* = -\text{slope} \times R) \), and \( \Delta S^* \) is calculated (i.e. \( \Delta S^* = \text{intercept} - (R/Nh) \)). The calculated \( \Delta H^* \) and \( \Delta S^* \) values are reported in Table 4.

From the results obtained by Table 4, the positive sign of \( \Delta H^* \) value is an indication that the corrosion process is endothermic in nature. The entropy of activation \( (\Delta S^*) \) value is greater in free solution than that of inhibited solution, and also the value goes on increasing with the increase in Aspirin.

Table 4  Activation parameters for mild steel in 1 M HCl in the absence and presence of different concentrations of Aspirin.

<table>
<thead>
<tr>
<th>Inhibitor concentration (ppm)</th>
<th>Apparent activation energy ( (E_a^\nu) ) (kJ/mol)</th>
<th>Arrhenius pre-exponential constant (kJmol(^{-1}))</th>
<th>Enthalpy of activation ( (\Delta H^*) ) (kJmol(^{-1}))</th>
<th>Entropy of activation ( (\Delta S^*) ) (Jmol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>55.69</td>
<td>83.03 \times 10^4</td>
<td>53.20</td>
<td>-7.64</td>
</tr>
<tr>
<td>10</td>
<td>62.57</td>
<td>756.96 \times 10^8</td>
<td>60.77</td>
<td>-5.16</td>
</tr>
<tr>
<td>20</td>
<td>63.10</td>
<td>787.85 \times 10^8</td>
<td>60.60</td>
<td>-5.41</td>
</tr>
<tr>
<td>30</td>
<td>63.77</td>
<td>924.56 \times 10^8</td>
<td>61.33</td>
<td>-5.24</td>
</tr>
<tr>
<td>40</td>
<td>68.47</td>
<td>4269 \times 10^8</td>
<td>65.18</td>
<td>-3.99</td>
</tr>
<tr>
<td>50</td>
<td>70.29</td>
<td>59,998 \times 10^8</td>
<td>67.58</td>
<td>-3.47</td>
</tr>
</tbody>
</table>
concentration. These increasing values of $\Delta S^*$ show that the activated complex in the rate determining step represents a dissociation rather than an association which means that a decrease in disordering takes place going from reactants to the activated complex (Oguzie et al., 2008; Martínez and Metikos-Hukiovic, 2003; Karthikaiselvi and Subhashini, 2014).

3.5. Scanning electron microscopic (SEM) measurement

The surface morphology was studied by using Scanning electron microscopy for mild steel in the absence and presence of Aspirin in 1 M HCl solution at 303 K temperature. The SEM graphs for corrosion of mild steel in blank (1 M HCl) solution with an immersion period of 4 h at 303 K temperature have a large number of pits and cracks due to the attack of corrosion as shown in Fig. 7A. But SEM graph for mild steel immersed in the presence of Aspirin inhibitor with an optimum concentration at 50 ppm shows a uniform passive protective layer produced on the surface (Bammou et al., 2014) due to the adsorption process as shown in Fig. 7B.

The surface study by using SEM reveals that the mild steel surface was damaged in the absence of Aspirin in aggressive acid media, but in the presence inhibitor surface of the metal was protected due to the formation of a protective layer on the metal surface.

4. Conclusions

Aspirin acts as a good corrosion inhibitor for the corrosion of mild steel in 1 M HCl solution at temperature region 303–333 K. Inhibition efficiency of Aspirin increases with increasing the inhibitor concentration as on 10–50 ppm, but decreases with increasing temperature region 303–333 K. The Weight loss measurement shows that the Aspirin acts as a good inhibitor (inhibition efficiency around 80% at 303 K temperature) due to the decrease in corrosion rate. The electrochemical polarization measurement reveals that Aspirin acts as a mixed type inhibitor, which blocks the surface of the metal, which retards the corrosion process and EIS parameters, suggests that the inhibitor shows its inhibition effect due to the adsorption process. Activation parameters suggest that the corrosion process is endothermic in nature, and SEM photographs give a visual idea of the inhibition action of inhibitor due to the formation of the protective layer.

Conflict of interest

The authors declare no competing financial interest.

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![Graph](image1.png)

**Figure 6** Transition plot.

![Image](image2.png)

**Figure 7** (A) SEM micrographs of mild steel in the absence of Aspirin. (B) SEM micrographs of mild steel in the presence of the inhibitor.


