The Inhibiting Effect of Non Toxic 4-Amino antipyrine and 4,6-Dimethyl-1H-pyrazolo[3,4-b]pyridin-3-amine on Mild steel Corrosion in Sulphuric acid

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Potentiodynamic polarization, electrochemical impedance, weight loss, and scanning electron microscopy (SEM) techniques are used to study the inhibiting effect of 4-amino antipyrine (AAP) and the prepared 4,6-dimethyl-1H-pyrazolo[3,4-b]pyridin-3-amine (PP) in order to decrease the dissolution of mild steel in 0.5 M H₂SO₄. The results indicate that increasing inhibitors concentration increases the efficiency of inhibition and increasing the temperature decreases the efficiency of inhibition. The AAP compound was seen to retard the rate of corrosion of mild steel more effective than PP compound. The adsorption of the AAP inhibitor on the mild steel surfaces obeys both of Langmuir and Temkin isotherms while PP inhibitor obeys only Langmuir isotherm. Studies of the scanning electron microscopy established the corrosion protection property of AAP and PP to be through adsorption on sites on the mild steel surface which are active. Also, mixed action of the inhibitors effect is showed from the results. The theoretical assumptions show proper agreement with most of experimental data. Temperature studies are occurred to find the thermodynamic parameters of inhibition and to suggest the isotherm of the adsorption processes.

Keywords: Mild steel, Corrosion Inhibitor, Potentiodynamic polarization, Adsorption isotherms and EIS

1. INTRODUCTION

Many researches focused on protecting Mild steel from corrosion in various aggressive environments. The low price of Mild steel allows it to be broadly used in many applications [1]. Actually corrosion cannot be prevented completely but attempts have been made to decrease it. One of the best vital methods to minimize corrosion is using inhibitors. In past, most of these inhibitors are inorganic, such as chromate and phosphate, which are toxic compounds. The new trend in using
inhibitors is focused on replacing toxic inorganic inhibitors by new environment friendly organic compounds such as N-heterocyclic synthetic compounds [2-7]. \(\pi\)-electrons and heteroatoms such as nitrogen, oxygen and sulphur present in inhibitors molecules are important in the adsorption of their molecules on the metal surface [8]. Some of the synthetic compounds containing pyrazole moiety have been used as effective inhibitors for corrosion of mild steel in aqueous media [9-12]; it forms stable complexes with many transition metals via their adsorption. The adsorption of any inhibitor on a metal or alloy surface is governed by the metal/alloy nature, the adsorption mode and the chemical structure of the inhibitor. Sulphuric acid is from the common acids used for various industrial requests such as acid pickling, descaling, in oil wells etc. Schiff bases were used also as good inhibitors for mild steel corrosion in sulphuric acid [13, 14]. Pyrozolo pyridine had been used to control the corrosion of steel in HCl solution and their adsorption mechanism was examined [15, 16].

Our objective in the present work is to find out the influence of 4-aminoantipyrine (AP) and the lab prepared pyridine pyrozole (PP) as green inhibitors of corrosion of mild steel in 0.5 M \(\text{H}_2\text{SO}_4\) solution. The temperature dependency of the corrosion efficiencies of inhibition helped in achieving the apparent energies of activation of the corrosion process in absence and presence of inhibitors. From the other purpose of the current work is to check the experimental data with several adsorption isotherms, to calculate the standard free energies of the adsorption process and knowing the mode of adsorption.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of PP

The starting material 4,6-dimethyl-1H-pyrazolo[3,4-b]pyridin-3-amine (1) was prepared according to the reported method [17, 18] as shown in the following scheme which involves the preparation of cyanoacetamide which was reacted with acetyl acetone under basic condition to afford the 4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile. The latter compound was chlorinated, through its treatment with phosphoryl chloride to afford the 2-chloro-4,6-dimethylnicotino-nitriile and then the chloro derivative was reacted with hydrazine hydrate under reflux in ethanol, to give the starting material pyrazolopyridine derivative (1) as the following scheme.
2.2. Weight loss measurements:

Mild steel specimen in triplicate was polished using a variety of grade emery paper then washed in acetone then with distilled water and dried. The samples were weighed and followed by immersing 0.5M H₂SO₄ as a medium in different concentration of inhibitors (APP and PP) for 4 hr at room temperature (25 ± 2 °C). Then the specimen was removed, rinsed in double distilled water, acetone, dried and weighed. The average loss in weight was determined for each sample. The percentage of inhibition efficiency (IE%) was calculated using the formula:

\[ IE\% = \frac{W_o - W_i}{W_o} \times 100 \]  

(1)

Where, \( W_o \) and \( W_i \) (in gm) are the weight loss observed in the absence and presence of inhibitors.

2.3. Electrochemical measurements

Electrochemical studies were carried out in a three-electrode conventional glass cell with mild steel of 0.5 cm² surface area as a working electrode in 0.5 M H₂SO₄ using Autolab potentiostat/galvanostat PGSTAT302N connected to a computer. The potential of the working electrode was measured against Ag/AgCl reference electrode (\( E^o = 0.203 \text{V vs. SHE} \)) and pure Pt-foil used as counter electrode. Before each experiment, the working electrode was polished using a variety of grade emery paper then washed in acetone then with distilled water and quickly immersed in the test solution 0.5 M H₂SO₄ with and without inhibitor at 25 °C until a steady-state was reached (after ~15 min). The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from −700 mV to 0 mV with potential scan rate of 1 mV s⁻¹. To study the temperature effect, the same procedure of polishing the working electrode was happened and it was immersed in 0.5 M H₂SO₄ with and without selected inhibitor concentration at different temperature. The corrosion parameters i.e. corrosion current density \( i_{corr} \) and corrosion potential \( E_{corr} \) were evaluated from the intersection of the linear anodic and cathodic branches of the Tafel plots. The inhibition efficiency (IE%) was calculated from the corrosion current density by using this formula:

\[ IE\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \]  

(2)

Where \( i_{corr} \) and \( i'_{corr} \) are the corrosion current density in the absence and presence of inhibitors. The electrochemical impedance spectroscopy (EIS) of the electrode surface after immersion in 0.5 M H₂SO₄ with and without inhibitor has been carried out with an Ac voltage amplitude of 10 mV using an electrochemical impedance system. The frequency range used in the study was 0.02–10⁵ Hz. The values of the equivalent circuit parameters were analyzed by using the Equivalent Circuit program written by Boukamp [19]. All the electrochemical impedance measurements were carried out at open circuit potential.
2.4. Surface examination:

The surface morphology of the mild steel specimen specimens after 3 days of immersion in 0.5M H₂SO₄ without and with inhibitors (10 mM) AP and (5 mM) PP are performed on scanning electron microscope JEOL-JSM-5600 equipped with an energy dispersive X-ray spectrometer OXFORD Link-ISIS-300.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization study

Curves of potentiodynamic polarization of mild steel after immersion in 0.5 M H₂SO₄ solution in absence and presence of different concentration of inhibitors (AAP & PP) are shown in Fig. 1a,b.

![Figure 1a](image1.png)

![Figure 1b](image2.png)

**Figure 1.** Polarization curves of mild steel corrosion in 0.5 M H₂SO₄ in presence and absence of different concentrations of inhibitors (a) AAP (b) PP.
The associated corrosion parameters such as cathodic and anodic Tafel slopes ($\beta_c$, $\beta_a$), corrosion potential ($E_{corr}$), and corrosion current density ($i_{corr}$) are presented in Table 1.

It can be seen that the values of $i_{corr}$ are decreased with increasing the concentration of the inhibitors due to the restriction of both the anodic dissolution and cathodic reaction. Compared with the blank, there are shift of $\beta_a$, $\beta_c$ values also the shift of corrosion potential ($E_{corr}$) towards positive direction in the presence of inhibitor indicate that the role of inhibitor is blocking the available active sites in the surface [20]. Adsorbing inhibitor molecules on the mild steel surface leads to suppress both the anodic and cathodic reaction and confirm that they are mixed-type corrosion inhibitors [21].

**Table 1.** The Corrosion parameters obtained from polarization curves of Mild steel in 0.5 M $\text{H}_2\text{SO}_4$ in the absence and presence of different concentrations of AAP and PP at 25 °C.

<table>
<thead>
<tr>
<th>Type of soln.</th>
<th>[Inhibitor], mM</th>
<th>$\beta_a$, mV/dec</th>
<th>$\beta_c$, mV/dec</th>
<th>$E_{corr}$, mV</th>
<th>$i_{corr}$, A/cm$^2$</th>
<th>IE% Elect.</th>
<th>IE% Wt. Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>251</td>
<td>108</td>
<td>-580</td>
<td>3.04 x $10^{-3}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AAP</td>
<td>1.25</td>
<td>183</td>
<td>52</td>
<td>-564</td>
<td>7.72 x $10^{-4}$</td>
<td>74.6</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
<td>142</td>
<td>56</td>
<td>-532</td>
<td>3.75 x $10^{-4}$</td>
<td>87.7</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>112</td>
<td>103</td>
<td>-539</td>
<td>3.11 x $10^{-4}$</td>
<td>89.8</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>138</td>
<td>46</td>
<td>-480</td>
<td>2.38 x $10^{-4}$</td>
<td>92.2</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>335</td>
<td>45</td>
<td>-399</td>
<td>5.73 x $10^{-4}$</td>
<td>98.1</td>
<td>91</td>
</tr>
<tr>
<td>PP</td>
<td>1.25</td>
<td>135</td>
<td>78</td>
<td>-548</td>
<td>9.48 x $10^{-4}$</td>
<td>68.8</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>146</td>
<td>48</td>
<td>-467</td>
<td>4.94 x $10^{-4}$</td>
<td>83.7</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>108</td>
<td>49</td>
<td>-468</td>
<td>3.14 x $10^{-4}$</td>
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<td>139</td>
<td>40</td>
<td>-456</td>
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<td>92.2</td>
<td>78</td>
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<td>10.0</td>
<td>142</td>
<td>33</td>
<td>-446</td>
<td>2.62 x $10^{-4}$</td>
<td>92.1</td>
<td>79</td>
</tr>
</tbody>
</table>

**3.2. Weight loss measurements**

![Figure 2](image-url)  
**Figure 2.** Relation between mass loss ($\Delta m$) and different concentration of inhibitors in 0.5 M $\text{H}_2\text{SO}_4$ at 25 °C.
Weight loss data of Mild steel in 0.5 M H₂SO₄ in absence and presence of various concentrations of inhibitors (AAP & PP) at 25 °C were obtained and the relation between the loss in mass of the mild steel samples (Δm) and the inhibitors concentration were presented in Fig. 2. It is clear that the loss in mass decreases with the increase of inhibitor concentration but appears nearly the same for PP concentrations more than 5 mM. Equation (1) is used to calculate the inhibition efficiencies (IE%) which listed in Table 1. The listed values show an increase in IE% with the increase in the inhibitor concentrations indicating passivation process. This is attributed to the adsorbed inhibitor complex on the mild steel/solution interface forming a protective barrier on the mild steel surface [22]. From Table 1 we can see that the values of inhibition efficiency of AAP are higher than that of PP. This is due to the molecular structure of inhibitor, surface state and surface excess charge of the metal [23]. The inhibition efficiencies obtained from electrochemical measurements and weight loss show similar behavior with little difference in the inhibition efficiencies because weight loss tests were carried out for longer immersion time 4 hours while the electrochemical tests were carried out after steady state reaching (≈ 15 min). So, IE% values from weight loss tests show lower values in comparing with electrochemical values.

3.3. Effect of Temperature

Studying the effect of temperature on the corrosion of mild steel in 0.5 M H₂SO₄ in absence and presence of different concentration of inhibitors is very complicated. This is due to many changes happen on the metal surface such as quick etching, the decomposition, desorption and rearrangement of inhibitors [24]. Temperature ranges from 298 to 328 K is used to study the effect of temperature on the corrosion current density (i_corr) in absence and presence of the best concentration of inhibitor (10 mM AAP and 5 mM PP) in 0.5 M H₂SO₄ as shown in Fig 3 a, b (polarization curves for 10 mM AAP is used as sample). The parameters of corrosion such as cathodic and anodic Tafel slopes (β_c, β_a), corrosion potential (E_corr), and corrosion current density (i_corr) are itemized in Table 2.
Figure 3. (a) The relation between corrosion current density and selected concentration of inhibitors (10 mM AAP) as a function of temperature. (b) Arrhenius plot of mild steel corrosion in 0.5 M of H₂SO₄.

It is obvious that, as the temperature increases, \( i_{\text{corr}} \) increases which happens as a result of decreasing the adsorption of inhibitor molecules on the mild steel surface with increasing the temperature. Arrhenius equation expresses the dependency of corrosion current density \( i_{\text{corr}} \) on temperature as the following [25]:

\[
\frac{d \log i_{\text{corr}}}{d \left( \frac{1}{T} \right)} = \frac{E_a}{R}
\]

Where \( R \) is the gas constant (8.314 J/mol.K) and \( E_a \) is the apparent activation energy.

Table 2. The Corrosion parameters obtained from polarization curves of Mild steel in 0.5 M H₂SO₄ in absence and presence of 0.01 M AAP, 0.005 M PP at different temperature.

<table>
<thead>
<tr>
<th>Type of soln.</th>
<th>Temp. K</th>
<th>( i_{\text{corr}} ) A/cm²</th>
<th>( \beta_a ) mV/dec</th>
<th>( \beta_c ) mV/dec</th>
<th>( R_p ) Ohm</th>
<th>( E_{\text{corr}} ) mV</th>
<th>Corrosion rate mm/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>298</td>
<td>3.04x10⁻³</td>
<td>251</td>
<td>108</td>
<td>27.9</td>
<td>-580</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>5.01x10⁻³</td>
<td>239</td>
<td>176</td>
<td>21.7</td>
<td>-525</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>6.76x10⁻³</td>
<td>216</td>
<td>114</td>
<td>15.0</td>
<td>-514</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>9.99x10⁻³</td>
<td>265</td>
<td>128</td>
<td>21.4</td>
<td>-530</td>
<td>45</td>
</tr>
<tr>
<td>10mM AAP</td>
<td>298</td>
<td>57.7x10⁻⁶</td>
<td>335</td>
<td>45</td>
<td>293</td>
<td>-399</td>
<td>0.67</td>
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<tr>
<td></td>
<td>308</td>
<td>316x10⁻⁶</td>
<td>141</td>
<td>45</td>
<td>104</td>
<td>-490</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>505x10⁻⁶</td>
<td>171</td>
<td>70</td>
<td>38.4</td>
<td>-552</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>602x10⁻⁶</td>
<td>182</td>
<td>93</td>
<td>44.4</td>
<td>-526</td>
<td>7.0</td>
</tr>
<tr>
<td>5mM PP</td>
<td>298</td>
<td>3.14x10⁻⁵</td>
<td>108</td>
<td>49</td>
<td>118.2</td>
<td>-468</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>762x10⁻⁵</td>
<td>125</td>
<td>57</td>
<td>22.5</td>
<td>-487</td>
<td>8.8</td>
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<tr>
<td></td>
<td>318</td>
<td>935x10⁻⁵</td>
<td>207</td>
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<td>22.0</td>
<td>-477</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>1.23x10⁻⁴</td>
<td>177</td>
<td>98</td>
<td>22.5</td>
<td>-498</td>
<td>14.2</td>
</tr>
</tbody>
</table>
The slope of the straight line of the plotted log \( i_{\text{corr}} \) versus \( 1/T \) (Fig 3b) is used to calculate the values of \( E_a \) for mild steel in the temperature range 298-328 K, in absence and presence of optimum concentration of inhibitors. The increase of \( E_a \) for inhibited solution which is evaluated 28 KJ/mol for AAP and 15.2 KJ/mol for PP inhibitor but in absence of them is 13.9 KJ/mol. It is obvious that \( E_a \) for the inhibited solution is higher than that for uninhibited solution indicating that more energy barrier is required for the corrosion reaction to occur [26] and informing the electrostatic character of the inhibitor’s adsorption on the mild steel surface (physisorption) [27].

3.4. Adsorption isotherm:

Applying the experimental data to the known adsorption isotherm equations to get the information about the interaction between inhibitor molecules and Mild steel surface was happened by calculating the degree of surface coverage, \( \theta \), at different concentrations of the AAP and PP inhibitors from the corresponding electrochemical polarization measurements according to [28]:

\[
\theta = \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}}
\]

The obtained values of \( \theta \) were fitted to various isotherms including Temkin, Langmuir, Frumkin, …etc. The Langmuir isotherm, Eq.( 5 ) was verified for both inhibitors [29]:

\[
K_{\text{ads}} C = \frac{\theta}{1-\theta}
\]

Where \( C \) is the concentration of inhibitor, \( \theta \) is the surface coverage, and \( K_{\text{ads}} \) is the equilibrium constant of adsorption. Plotting of \( C/\theta \) versus \( C \) shows the best fit and gives a straight line with slope equal unity according to rearranged Langmuir isotherm equation:

\[
\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C
\]

The equilibrium constant of adsorption \( K_{\text{ads}} \) is calculated from the intercept of the straight line of the relation of \( \frac{C}{\theta} \) with \( C \) as shown in Fig.4a, \( K_{\text{ads}} \) related to the standard free energy of adsorption (\( \Delta G_{\text{ads}}^o \)) by the relation [29, 30]:

\[
\Delta G_{\text{ads}}^o = -RT \ln(55.5 K_{\text{ads}})
\]

Where \( T \) is the absolute temperature, the value of 55.5 is the concentration of water in solution in mol/L, and \( R \) is the gas constant (8.314 J/mol.K). The calculated \( K_{\text{ads}} \) values for inhibitors AAP and PP at 298 °K are 2x10³ and 2272 M⁻¹, respectively and \( \Delta G_{\text{ads}}^o \) values for inhibitors AAP and PP are -28.78 and -29.1 KJ/mole, respectively. Plotting of \( \theta \) versus \( \log C \) according to rearranged Temkin isotherm Eq.( 8 ) fits properly and a straight line is shown with AAP inhibitor only.

\[
\theta = \frac{2.303 \log K_{\text{ads}}}{2a} - \frac{2.303 \log C}{2a}
\]

The attractive parameter (\( a \)) is calculated from the slope of the straight line and have a negative value (-4.95) indicating the presence of repulsion on the adsorbed molecules [31]. The equilibrium constant of adsorption \( K_{\text{ads}} \) is calculated from the intercept of the straight line of the relation of \( \theta \) with
logC as shown in Fig. 4b, the standard free energy of adsorption (ΔG^o_{ads}) is calculated according to the relation (7) and were found to be 1046 M⁻¹ and -39.2 KJ/mole, respectively. The high K_{ads} values are attributed to more and stronger adsorbed layer formed on mild steel surface [32, 33]. The negative values of ΔG^o_{ads} indicated that the adsorption of both inhibitors on Mild steel surface and the stability of the adsorbed film are spontaneous [34]. The values of ΔG^o_{ads} up to -20 KJ/mole are agree with physical adsorption and the values around -40 KJ/mole indicates the presence of chemisorption [35].

![Graph](image)

**Figure 4.** (a) The relation between C/θ and C for selected concentration of inhibitors (b) The relation between θ and logC for selected concentration of AAP.

### 3.5. Electrochemical impedance measurements:

EIS has been used to typify the interface properties of electrodes. Simulated and experimental impedance plots for Mild steel electrode after 15 min of immersion in 0.5 M H₂SO₄ without and with different concentration of inhibitors at open circuit potential are shown in Fig (5 a, b). Each Bode plot shows a resistive region at high and low frequencies, a capacitive region at intermediate frequencies.
The bode plots shape for the inhibited mild steel doesn't change from that of uninhibited Mild steel. Which indicates that the inhibitor doesn't change the corrosion mechanism of Mild steel in 0.5 M H₂SO₄ solution [36]. The impedance, Z, of the alloy increases as the concentration of the inhibitor increases. The impedance data were analyzed using a simple equivalent circuit, Rₛ(RċQ), it shown in Fig. 5c.

Figure 5. Bode plots of Mild steel in 0.5M H₂SO₄ at 25°C in the absence and presence of different concentrations of inhibitors (a) AAP (b) PP (c) Equivalent circuit model used for fitting of impedance
Based on the proposed circuit, the simulated spectra agreed reasonably well with the experimental curves. It is a simple circuit which can be used to represent the electrode reaction such as metal deposition or metal dissolution; it consists of a resistor, $R_s$, representing the solution resistance in series to a parallel combination of $R_{ct}$ and $Q$ representing the charge transfer resistance and the constant phase element CPE, respectively. $Q$ is used instead of the capacitor to show good fit of the double layer capacitor $C_{dl}$ on the equivalent circuit [19]: The impedance of a CPE is defined as follows [37]:

$$Z_{CPE} = \frac{1}{Y_o(j\omega)^n}$$

Where $Y_o$ is the modulus, $j$ is the imaginary root, $\omega$ is the angular frequency, and $n$ is the phase. The values of the parameters obtained with the fitting procedure for Mild steel in uninhibited and inhibited solutions are reported in Table 3.

### Table 3. Equivalent circuit parameters after 15 min of immersion of Mild steel in 0.5M H$_2$SO$_4$ in the absence and presence of different concentrations of AP and PP at 25°C.

<table>
<thead>
<tr>
<th>Type of soln.</th>
<th>[Inhibitor], mM</th>
<th>$R_s$, $\Omega$</th>
<th>$R_{ct}$, $\Omega$ cm$^2$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$Y_o$, $\mu\Omega^{-1}$ cm$^{-2}$</td>
</tr>
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<td>Blank</td>
<td>0</td>
<td>2.9</td>
<td>23.8</td>
<td>935</td>
</tr>
<tr>
<td>AP</td>
<td>1.25</td>
<td>3.1</td>
<td>42.4</td>
<td>807</td>
</tr>
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<td></td>
<td>2.50</td>
<td>3.1</td>
<td>59</td>
<td>562</td>
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<td>5.00</td>
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<td>10.0</td>
<td>3.0</td>
<td>120</td>
<td>170</td>
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</tbody>
</table>

Retardation of corrosion reaction of mild steel with increasing the inhibitors concentration is observed which represented by increasing $R_{ct}$. The adsorption of inhibitor molecules on the corroding surface is the reason for this retardation which is verified by the decrease in the CPE values as well as the capacitive behavior [38]. The impedance results agree with the results observed by polarization and weight loss measurements which indicate the ability of AAP and PP to decrease the corrosion of mild steel in 0.5 M H$_2$SO$_4$ solution.

### 3.6. Scanning electron microscopy (SEM):

The SEM micrographs of the mild steel surfaces after 72 hours of immersion in 0.5 M H$_2$SO$_4$ solution without and with addition of 10 mM AAP and 5 mM PP are given in Fig. 6(a-c). In the absence of the inhibitor, a very rough corroded and porous surface with a large number of micro pits is observed (Fig. 6a).
Figure 6. SE micrograph of Mild steel surface after 72 hours of immersion in 0.5 M H$_2$SO$_4$ (a) in absence of inhibitors (b) in presence of 10 mM AAP (c) in presence of 5 mM PP
Figure 7. EDX analysis of Mild steel surface after 72 hours of immersion in 0.5 M H$_2$SO$_4$ (a) in absence of inhibitors (b) in presence of 10 mM AAP (c) in presence of 5 mM PP

In the presence of 10 mM AAP and 5 mM PP, a smooth surface with much less corroded area is observed which confirm adsorption of the inhibitor on the active sites of the mild steel surface (Fig. 6b, c). In the EDX spectrum Fig 7(a) of uninhibited mild steel, the presence of iron peaks proves the dissolution of iron without the formation of any protective film on the mild steel surface. While the EDX spectra (Fig. 7b, c) of the inhibited mild steel show the appearance of N peak and O peak beside
the Fe peak.

This also reveals that AAP and PP is adsorbed on the mild steel surface and their percentage atomic contents are listed in Table 4. The sulphur peak proves adsorption of sulphate ions from solution on the surface.

Table 4. The composition of Mild steel surface after 72 hours of immersion in 0.5 M H₂SO₄ in absence and presence of 10 mM AAP and 5 mM PP

<table>
<thead>
<tr>
<th></th>
<th>O K</th>
<th>S K</th>
<th>Fe K</th>
<th>N K</th>
<th>C K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At%  Wt%</td>
<td>At%  Wt%</td>
<td>At%  Wt%</td>
<td>At%  Wt%</td>
<td>At%  Wt%</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>80.31</td>
<td>94.99</td>
<td>-</td>
</tr>
<tr>
<td>10 mM AAP</td>
<td>31.36</td>
<td>26.78</td>
<td>1.63</td>
<td>5.1</td>
<td>34.66</td>
</tr>
<tr>
<td>5 mM PP</td>
<td>18.97</td>
<td>42.89</td>
<td>2.16</td>
<td>5.73</td>
<td>47.04</td>
</tr>
</tbody>
</table>

3.7. Mechanism of corrosion inhibition

Mild steel dissolution decreased by adsorbing AAP and PP molecules on its surfaces and the adsorption can be explained as follows: In acidic solutions, Fe dissolves from the alloy surface leaving negative charges on the surface which interacted with the -NH₂ group of the inhibitors which attains positively charged due to its protonation. As well as, the adsorption of the protonated inhibitor through electrostatic interactions may occur with the adsorbed sulfate ions. The electron pairs on the oxygen and nitrogen atoms of the AAP and PP molecules could interact with metal surface. The π-electrons of the heterocyclic on inhibitor molecules can be also adsorbed on the vacant d-orbitals of iron surface by donor–acceptor interactions.

The values of inhibition efficiencies in case of using AAP as inhibitor is higher than the values of inhibition efficiencies in case of using PP as inhibitors due to the presence of two strong electrodonating groups (-NH₂ and -O) which have more ability to absorb on the metal surface [39] and one weak donating group (-CH₃) in the AAP structure while PP structure contains only one strong electrodonating group (-NH₂) and two weak electrodonating groups (-CH₃).

4. CONCLUSION

AAP and PP showed good inhibition efficiency for the corrosion of mild steel in 0.5 M H₂SO₄. The value of inhibition efficiency of AAP is seen to increase with increasing the inhibitor concentration while it shows an optimum level at 5.0 mM PP and then remains nearly constant for PP concentration more than 5.0 mM. Impedance measurements indicate that, the charge transfer resistance is increased while the double layer capacitance is decreased with increasing the inhibitors concentration. The group substituents are played a role in the inhibition process. Results obtained from electrochemical measurements and weight loss are in good agreement. The adsorption of AAP obeys Langmuir and Temkin isotherms while the adsorption of PP obeys only Langmuir isotherm.
References


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