The corrosion inhibition performance of polyacrylic acid with Potassium Sodium Tartrate and Zn$^{2+}$ for corrosion control of mild steel in aqueous solution

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ABSTRACT. The goal of studying corrosion process is to find means of minimizing corrosion or prevent it from occurring. The use of inhibitors is one of the most popular methods for corrosion protection. A protective film has been formed on the surface of the mild steel in a neutral aqueous environment using a synergistic mixture of an eco-friendly inhibitor viz., Potassium Sodium Tartrate (SPT) along with polyacrylic acid (PAA) and Zn$^{2+}$ ions. The inhibiting effect of SPT, PAA and Zn$^{2+}$ ions have been investigated by gravimetric studies, Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The investigations revealed that SPT acts as an excellent synergist in corrosion inhibition. Optimum concentrations of all the three components of the ternary formulation are established by gravimetric studies. Potentiodynamic polarization studies inferred that this mixture functions as a cathodic inhibitor. EIS studies of the metal/solution interface indicated that the surface film is highly protective against the corrosion of mild steel. Surface characterization techniques (FTIR, SEM, AFM) are also used to ascertain the nature of the protective film. The mechanical aspect of corrosion inhibition is proposed.

1. INTRODUCTION

Corrosion is an electrochemical phenomenon and is accompanied by the flow of electrical current. One can minimize the rate and quantum of corrosion only by providing a suitable environment in which current cannot flow at interfaces. The best corrosion protection is to build a barrier separating the metal from its environment. Protection of mild steel from corrosion is a matter of practical importance. The most efficient corrosion inhibitors are organic compounds containing electronegative functional groups and $\pi$ electrons in their triple or conjugated double bonds [1]. The initial mechanism in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface [2-5]. The adsorption of the inhibitor on the metal surface can be facilitated by the presence of hetero atoms (such as N, O, P and S) as well as an aromatic ring. The inhibition of the corrosion of metals can also be viewed as a process that involves the formation of a chelate on the metal surface, which involves the transfer of electrons from the organic compounds to the surface of the metal and the formation of a coordinate covalent bond. In this case, the metal acts as an electrophile while the nucleophilic centre is in the inhibitor.

Polymers find applications as effective corrosion inhibitors for steel [6]. The use of polymers as corrosion inhibitors have drawn considerable attention recently due to their inherent stability and cost effectiveness. Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared with their monomer analogues [7]. Therefore, it is expected that the polymers will be better corrosion inhibitors.
The Literature reveals that a wide range of polymeric compounds have been successfully investigated as potential inhibitors for the corrosion of metals in aqueous media. Polymers such as polyvinylpyrrolidone [8,9], polyvinyl alcohol [10], poly (o-anisidine-co-metanilic acid) [12], polyanthranilic acid [13], Polyacrylic acid [14,15], Polyaniline[16].

In this paper, Polyacrylic acid was investigated as a promising corrosion inhibitor for mild steel. In the present work, the inhibitive effect with a new polymer inhibitor viz., Polyacrylic acid (PAA), SPT and Zn$^{2+}$ ions in controlling the corrosion of mild steel in neutral aqueous environment has been studied by the gravimetric studies. The corrosion inhibition was further investigated by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Surface analytical techniques, viz., Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Atomic force microscopy (AFM) were also used to investigate the nature of protective film formed on the metal surface. A suitable mechanism of inhibition of corrosion is proposed. For all these studies, aqueous solution of 60 ppm chloride has been chosen as control because the water used in cooling water systems is generally either demineralized water or unpolluted surface water.

2. EXPERIMENTAL

2.1. Materials

Polyacrylic acid (PAA), Zinc sulphate (ZnSO$_4$.7H$_2$O), Potassium Sodium Tartrate (SPT) and other reagents were analytical grade chemicals. The molecular structures of Polyacrylic acid and Potassium Sodium Tartrate are shown in Fig. 1 and 2 respectively. All the solutions were prepared by using double distilled water. pH values of the solutions were adjusted by using 0.01 N sodium hydroxide and 0.01 N sulphuric acid solutions. An aqueous solution consisting of 60 ppm of sodium chloride has been used as the control throughout the studies.

![Fig. 1. The molecular Structure of Polyacrylic acid (PAA)](image)

![Fig. 2. The molecular structure of Potassium Sodium Tartrate (SPT)](image)

2.2. Preparation of specimens

For all the studies, the specimens taken from a single sheet of mild steel of the following composition were chosen: C, 0.1-0.2%; P, 0.03-0.08%; S, 0.02-0.03%; Mn, 0.4-0.5% and the rest iron. For gravimetric measurements and surface analytical techniques, the polished specimens of the dimensions, 4 cm x 1.0 cm x 0.2 cm, were used while for other (electro chemical) studies, the dimensions of the specimens were 1.0 cm x 1.0 cm x 0.1 cm. Prior to all measurements, the specimens were polished successively using 1/0 to 6/0 emery papers, degreased with trichloroethylene and washed thoroughly with double distilled water and dried.
2.3. Gravimetric studies

Gravimetric experiments are the easiest way to find the corrosion rate (CR) and inhibition efficiency (IE). In all gravimetric experiments, the polished specimens were weighed and immersed in duplicate, in 100 ml control solution in the absence and presence of inhibitor formulations of different concentrations, for a period of seven days. Then, the specimens were reweighed after washing and drying. The weights of the specimens before and after immersion were determined by Mettler electronic balance, AE 240 model with a readability of 0.1 mg. Accuracy in weighing up to 0.0001 g and its surface area measurement up to 0.1 cm², as recommended by ASTM, was followed. Corrosion rates of mild steel in the absence and presence of various inhibitor formulations are expressed in mdd. The corrosion rate was calculated according to the following equation.

\[
\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of immersion (days)}} \quad (1)
\]

Where,

\[
m - \text{Loss in weight (mg)} \\
d - \text{Surface area of the specimen (dm}^2) \\
d - \text{Period of immersion (days)}
\]

Inhibition efficiencies (IE) of the inhibitor were calculated by using the formula

\[
\text{I.E} = 100 \left[1 - \frac{W_2}{W_1}\right] \% \quad (2)
\]

Where,

\[
W_1 = \text{Corrosion rate in the absence of inhibitor} \\
W_2 = \text{Corrosion rate in the presence of inhibitor.}
\]

2.4. Electrochemical studies

The versa STAT MC electrochemical analyzer make Princeton applied research was used to record Tafel polarization curve and impedance curve. The mild steel specimens used as working electrode while platinum and calomel electrodes were used as counter electrode and the reference electrode, respectively. Impedance measurements were carried out at E_{corr} potential at the range of 100 kHz to 10 mHz at amplitude of 10 mV. The impedance diagrams are given in Nyquist representation. The impedance and polarization parameters such as double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_{a}) and cathodic Tafel slope (β_{c}) were computed from the polarization curves and Nyquist plots. The IEp values were calculated from potentiodynamic polarization measurements using the equation (3).

\[
\text{IE}_{p} (%) = \left[\frac{I_{corr} - I'_{corr}}{I_{corr}}\right] \times 100
\]

Where, \(I_{corr}\) and \(I'_{corr}\) are the corrosion current densities in case of the absence and presence of the inhibitor respectively. From impedance measurements, the IE_{1} values were calculated from the following relation,

\[
\text{IE}_{1} (%) = \left[\frac{R_{ct(i)} - R_{ct(b)}}{R_{ct(i)}}\right] \times 100
\]

Where, \(R_{ct(b)}\) and \(R_{ct(i)}\) are the charge transfer resistance values in the absence and presence of the inhibitor respectively.
2.5. Surface examination studies

The mild steel specimens were immersed in various test solutions for a period of seven days. Then, they were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Atomic force microscopy (AFM).

2.5.1. Fourier transform infrared spectroscopy

The mild steel specimens were immersed in various test solutions for a period of seven days. On completion of the seventh day, the specimens were taken out and dried. The protective film formed on the metal specimens was scratched and mixed with KBr and pellets were obtained and the FTIR spectra were recorded using Spectrum RXI Spectrophotometer over a range of 4000 - 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

2.5.2. Scanning electron microscopy

The surface morphology of the formed layers on the mild steel surface after its immersion in control solutions containing 60 ppm chloride ions in the absence and in the presence of the inhibitor were carried out. After seven days, the specimens were taken out, washed with distilled water and dried. The SEM photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

2.5.3. Atomic force microscopy

The atomic force microscope was used for surface morphology studies. The protective films were examined with atomic force microscope (AFM) using A100 model, A.P.E research, Italy. The topography of the entire samples from a scanned area of 10 µm x 10 µm is evaluated for a set point of 20 nN and a scan speed of 10 mm/s. The three dimensional topography of surface films gave various roughness parameters of the film.

3. RESULTS AND DISCUSSION

3.1. Gravimetric studies

The gravimetric measurements were carried out to calculate the corrosion rate (CR) and inhibition efficiency (IE) for the mild steel in an aqueous solution containing 60 ppm chloride ions in the absence and presence of various inhibitor formulations consists in various amounts of PAA, Zn\(^{2+}\) ions and SPT are given in Table 1. The inhibition efficiency was represented as a function of SPT concentration in Fig. 3.

**Table 1**: Inhibition efficiency (IE) and Corrosion rate (CR) by gravimetric studies of mild steel in the presence of inhibitor

<table>
<thead>
<tr>
<th>SPT (ppm)</th>
<th>Weight loss (g)</th>
<th>IE (%)</th>
<th>Corrosion rate (mdd)</th>
<th>Surface Coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 ppm Cl(^{-})</td>
<td>0.0136</td>
<td>--</td>
<td>17.66</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>0.0098</td>
<td>27</td>
<td>12.72</td>
<td>0.2794</td>
</tr>
<tr>
<td>--</td>
<td>0.0111</td>
<td>18</td>
<td>14.41</td>
<td>0.1838</td>
</tr>
<tr>
<td>50</td>
<td>0.0058</td>
<td>57</td>
<td>7.53</td>
<td>0.5735</td>
</tr>
<tr>
<td>50</td>
<td>0.0044</td>
<td>68</td>
<td>5.71</td>
<td>0.6811</td>
</tr>
<tr>
<td>50</td>
<td>0.0029</td>
<td>79</td>
<td>3.76</td>
<td>0.7867</td>
</tr>
<tr>
<td>50</td>
<td>0.0021</td>
<td>84</td>
<td>2.72</td>
<td>0.8455</td>
</tr>
<tr>
<td>50</td>
<td>0.0005</td>
<td>96</td>
<td>0.6493</td>
<td>0.9632</td>
</tr>
<tr>
<td>50</td>
<td>0.0005</td>
<td>96</td>
<td>0.6493</td>
<td>0.9632</td>
</tr>
<tr>
<td>50</td>
<td>0.0005</td>
<td>96</td>
<td>0.6493</td>
<td>0.9632</td>
</tr>
</tbody>
</table>
The combination consists of 300 ppm PAA and 50 ppm Zn$^{2+}$ ions wherein the maximum inhibition efficiency of 99% is obtained. An effort has been taken to reduce the concentrations of the synergistic components viz., PAA and Zn$^{2+}$ ions. An environmentally friendly compound in the form of Potassium Sodium Tartrate (SPT) was chosen, added and the ternary system was studied. Further, the addition of SPT ions has not only increased the inhibition efficiency of mild steel, but also reduced environmental pollution because relatively lower concentrations of PAA and Zn$^{2+}$ were sufficient to achieve good inhibition efficiency. Moreover, SPT is cheaper. Hence, it was decided to fix the concentration of both Zn$^{2+}$ ions and PAA at levels below 200 ppm and vary the concentration of SPT in the range of 50 ppm to 175 ppm consisting of 6 different concentration systems. From the gravimetric studies, it is evident that for any protection to be established, a minimum concentration of each of the inhibitor constituent is necessary. It can be seen from the results of the ternary formulations, that for lower concentration of 50 ppm Zn$^{2+}$ and 200 ppm PAA with 50 ppm SPT, the maximum inhibition efficiency of only 68% is achieved. To achieve an inhibition efficiency of more than 90%, the required minimum concentration of PAA and Zn$^{2+}$ are 125 ppm respectively in presence of SPT. While the binary system consisting of 50 ppm Zn$^{2+}$ and 200 ppm PAA gives only 57% inhibition efficiency. With the addition of SPT, the inhibition efficiency of the ternary formulation increased gradually with increase in concentration of SPT (96%) at 125 ppm. By further increasing the concentration of SPT, the same trend of inhibition efficiency is observed. It is worth mentioning that on addition of SPT, the concentration of PAA was reduced from 500 ppm to 200 ppm and the concentration of Zn$^{2+}$ ions could be reduced from 70 ppm to 50 ppm to achieve good inhibition efficiency. In other words, the ternary systems were much more effective at very lower concentrations of PAA and Zn$^{2+}$. The combination of 50 ppm of Zn$^{2+}$, 200 ppm of PAA and 125 ppm of SPT was confirmed to be the best inhibitor system from the gravimetric data. A multi-coloured thin protective film was formed on the metal surface.

![Fig. 3. Inhibition efficiency as a function of concentration of SPT](image)

3.2. Effect of pH

The influence of pH on corrosion rate of mild steel in the presence of inhibitor system and the maximum inhibition efficiency obtained in the gravimetric measurements were studied. The effect of pH for the synergistic formulation consisting of PAA (200 ppm), Zn$^{2+}$ (50 ppm) and SPT (125 ppm) in the pH range of 5-11 is shown Fig. 4. The highest inhibition efficiency could be obtained in the pH range 5-7. But, when the pH is decreased from below 5 and on increasing pH range from 9-11, the inhibition efficiency is reduced to 45%. The reasons for decrease in inhibition efficiency in more alkaline and acidic environments are explained under the mechanistic aspects.
3.3.1. Potentiodynamic polarization studies

The potentiodynamic polarization studies were carried out to determine the kinetics of the cathodic and anodic reactions. Fig. 5(a) shows the potentiodynamic polarization curves for mild steel electrodes in control solution at pH 7 in the absence and presence of various inhibitor combinations. Electrochemical kinetic parameters, i.e., the corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), and anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$), obtained from extrapolation of the polarization curves are listed in Table 2. When mild steel is immersed in 60ppm Cl$^{-}$ medium, the corrosion potential ($E_{corr}$) is -598 mV/dec and the corrosion current is 12.9 $\mu$A/cm$^2$. When 125 ppm SPT to of 200 ppm PAA and 50 ppm Zn$^{2+}$ are added to 60ppm Cl$^{-}$ medium the corrosion potential is found to be -671 mV/dec and corrosion current is 1.0 $\mu$A/cm$^2$. The corrosion current decreases from 12.9 $\mu$A/cm$^2$ to 1.0 $\mu$A/cm$^2$.

![Fig. 4. Effect of pH](image)

This shows that the formulation functions as cathodic inhibitor controlling both anodic and cathodic processes but more predominantly cathodic process. This suggests indicate that protective film is formed on the metal surface.

![Fig. 5(a). Potentiodynamic polarization curves of mild steel in 60 ppm Cl$^{-}$ in the absence and Presence of SPT](image)
Table 2: Corrosion parameters of mild steel immersed in the absence and presence of inhibitor obtained by potentiodynamic polarization studies

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>$E_{corr}$ (mV/dec)</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$\beta_c$ (mV/dec)</th>
<th>$\theta$</th>
<th>I.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 ppm Cl$^-$</td>
<td>-598</td>
<td>12.9</td>
<td>192</td>
<td>198</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>60 ppm Cl$^-$ + 50 ppm of Zn$^{2+}$ + 200 ppm of PAA + 125 ppm of SPT</td>
<td>-671</td>
<td>1.0</td>
<td>162</td>
<td>185</td>
<td>0.92</td>
<td>92</td>
</tr>
</tbody>
</table>

3.3.2. Impedance spectroscopy (EIS) measurements

Nyquist plots for mild steel immersed in 60 ppm of Cl$^-$ solution at pH 7 in the absence and presence of various formulations are shown in Fig. 5(b). The impedance parameters, charge transfer resistance ($R_{ct}$), Double layer capacitance ($C_{dl}$) from the Nyquist plots and the calculated inhibition efficiency (IE$_i$) values are shown in Table 3. When mild steel is immersed in 60ppm Cl$^-$ medium the $R_{ct}$ value is found to be 342.17 (Ω cm$^2$). The $C_{dl}$ value is 27.00 (µF/cm$^2$). When 125 ppm SPT to of 200 ppm PAA and 50 ppm Zn$^{2+}$ are added to 60ppm Cl$^-$ medium the $R_{ct}$ value has increased from 342.17 to 1828.80 (Ω cm$^2$) and the $C_{dl}$ value has decreased from 27.00 (µF/cm$^2$) to 1.10 (µF/cm$^2$). The increase in $R_{ct}$ values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in 60 ppm Cl$^-$ medium. This behaviour means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film.

Fig. 5(b). AC impedance spectra curves of mild steel in 60 ppm Cl$^-$ in the absence and presence of SPT
Table 3: Corrosion parameters of mild steel immersed in the absence and presence of inhibitor obtained by AC impedance studies

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
<th>$\theta$</th>
<th>I.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 ppm Cl$^-$</td>
<td>342.17</td>
<td>27.00</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>60 ppm Cl$^-$ + 50 ppm of Zn$^{2+}$ + 200 ppm of PAA + 125 ppm of SPT</td>
<td>1828.80</td>
<td>1.10</td>
<td>0.81</td>
<td>81</td>
</tr>
</tbody>
</table>

3.4. Fourier transform infrared spectroscopy

The FTIR spectrum of pure PAA is shown in Fig.6.(a). The C=O stretching vibration at 1719 cm$^{-1}$ and the broad absorption peak at 3448 cm$^{-1}$ shows OH stretching vibration. The FTIR spectrum of pure SPT is shown in Fig.6.(b). The C=O stretching frequency appears at 1604 cm$^{-1}$. The FT-IR spectrum of the film formed on the surface of mild steel after immersion in the solution consisting of 60ppm of Cl$^-$, 50ppm of Zn$^{2+}$, 200ppm PAA and 125ppm of SPT is shown in Fig.6.(c). It is observed that the OH stretching frequency of PAA decreases from 3448 cm$^{-1}$ to 3409 cm$^{-1}$. This shift is caused by the electron cloud density from the O atom to Fe$^{2+}$. This suggests that the O atom of the polyacrylic acid is coordinate to Fe$^{2+}$ resulting in the formation of Fe$^{2+}$ - PAA complex on the metal surface.

![FTIR Spectra](image)

Fig. 6: FTIR Spectra of (a) pure PAA (b) pure SPT (c) surface film

The C=O stretching frequency of SPT has decreased from 1604 cm$^{-1}$ to 1589 cm$^{-1}$. This suggests that SPT has coordinate with Fe$^{2+}$ through oxygen atom resulting in the formation of Fe$^{2+}$ - SPT complex on the anodic sides of the metal surface. The peak at 1406 cm$^{-1}$ is due to Zn(OH)$_2$ on the cathodic sides of the metal surface. Thus FTIR spectral study leads to the conclusion that the protective film consists of Fe$^{2+}$ - PAA complex, Fe$^{2+}$ - SPT complex and Zn(OH)$_2$. 
3.5. Scanning electron microscopy

SEM analysis provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extend of corrosion of mild steel. Fig.7.(a) show the polished metal surface of mild steel before corrosion. Fig.7.(b) show the metal surface after immersion of 60 ppm Cl⁻ solutions. This shows the roughness of the metal surface by the corrosive environment and there is formation of different forms of corrosion products.

![Fig.7. SEM images of mild steel immersed in a). polished mild steel b). 60ppm Cl⁻ solution c). Inhibitor solution](image-url)

Fig.7.(b) show the metal surface immersion of 125 ppm SPT to of 200 ppm PAA and 50 ppm Zn²⁺ are added to 60ppm Cl⁻ medium gives metal surface incorporating into the passive film in order to block the active site present on the mild steel surface. comparative examination of these images, clearly suggest that the surface of mild steel is smoothened to a very large extent in the presence of the combined inhibitor system. This smoothening might be due to the adsorption of the inhibitor molecules on it and thus the surface is fully covered.

3.6. Atomic force micrographs

AFM is a dynamic tool to examine the surface morphology from nano to micro scale and has become a new choice to study the nature of protective layer formed over the surface of mild steel. The 3D AFM images of polished mild steel, 60ppm Cl⁻ in mild steel (blank) and mild steel in 60ppm Cl⁻ solution containing 50 ppm of Zn²⁺, 200 ppm of PAA and 125 ppm of SPT, respectively are shown in Fig.10(a-c). As can be seen from the AFM images, the surface is very clear for polished mild steel (Fig. 10.a) whereas in mild steel immersed in 60ppm Cl⁻ (Fig.10.b) the surface is severely damaged by solution. In (Fig.10.c) the surface is protected from attack by the protective layer formed by the inhibitor molecules. From the results, it is clear that, the inhibition of mild steel corrosion in inhibitor is mainly due to the formation of protective layer by adsorption of inhibitor molecules over the surface of mild steel. AFM data for mild steel is given in Table 4.
Fig. 10. 3D AFM images of mild steel surface. (a). Polished mild steel (b). 60ppm Cl⁻ solution (c). 60ppm Cl⁻ solution containing 50 ppm Zn²⁺ + 200 ppm PAA + 125 ppm SPT

Table 4: AFM parameters in different environments

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average Roughness (Ra) nm</th>
<th>Root-mean- square Roughness (Rq) nm</th>
<th>Maximum peak-to valley height (P-V) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished mild steel</td>
<td>143</td>
<td>215</td>
<td>1587</td>
</tr>
<tr>
<td>60ppm Cl⁻ solution</td>
<td>250</td>
<td>324</td>
<td>2587</td>
</tr>
<tr>
<td>60ppm Cl⁻ solution containing 50 ppm Zn²⁺ + 200 ppm PAA + 125 ppm SPT</td>
<td>169</td>
<td>279</td>
<td>1901</td>
</tr>
</tbody>
</table>

3.7. Adsorption isotherm

The efficiency of inhibitor molecules are related to their adsorption ability on the metal surface. An inhibitor reduces the corrosion rate by covering active centers on the metal surface. So, it is important to determine surface coverage ratio value (θ) for discussing the corrosion rate properly. Fig.11, the linear relationships of $\frac{C_{\text{inh}}}{\theta}$ versus $C_{\text{inh}}$ suggest that the adsorption of SPT on the mild steel are in well agreement with the langmuir adsorption isotherm, which is expressed by the following equation.

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}}$$

(5)
Where, $C_{\text{inh}}$ is the concentration of inhibitor, $\theta$ is surface coverage on the metal surface and $K_{\text{ads}}$ is the equilibrium constant of adsorption process. The correlation coefficient ($R^2 = 0.9946$) was used to choose the isotherm that best fit experimental data.

![Fig. 11. Langmuir adsorption isotherm on Mild steel surface of 60 ppm Cl$^-$ solution containing 50 ppm Zn$^{2+}$ + 200 ppm PAA + 125 ppm SPT](image)

3.8. Mechanism of protection

In order to explain all the experimental results, the following mechanism of corrosion inhibition can be proposed. Carbon steel undergoes initial corrosion to form Fe$^{2+}$ ions at anodic sites:

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (6)$$

Fe$^{2+}$ further undergoes oxidation in the presence of oxygen available in the aqueous solution:

$$\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}^{3+} + e^- \quad (7)$$

And the cathodic reaction is:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (8)$$

When the environment containing 60 ppm Cl$^-$ ions/50ppm Zn$^{2+}$/200ppm PAA/125ppm SPT was prepared, a [Zn$^{2+}$-PAA-SPT] complex was formed in the solution. Besides this complex, there is presence of free PAA, SPT and Zn$^{2+}$ ions. When the metal was immersed in this environment, the [Zn$^{2+}$-PAA-SPT] complex diffused from the bulk of the solution onto the surface of the metal and further complexes with Fe$^{2+}$/Fe$^{3+}$ ions available due to initial corrosion. Free PAA and SPT molecules diffuse from the bulk of the solution to the metal surface and form [Fe$^{2+}$/Fe$^{3+}$-PAA-SPT] complexes. These complexes fill the pores of the film formed on the surface and make it productive.

$$[\text{Zn(II)} - \text{PAA} - \text{SPT}] + \text{Fe}^{2+/3+} \rightarrow [\text{Fe(II)/Fe(III)/Zn(II)} - \text{PAA} - \text{SPT}] \quad (9)$$

Free Zn$^{2+}$ ions diffuse from the bulk of the solution to the metal surface and form Zn(OH)$_2$ at the local cathodic sites.

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (10)$$

Thus, PPA, Zn$^{2+}$, and SPT play a very important role in the synergistic effect controlling corrosion through the formation of a protective film on the metal surface.
4. CONCLUSION

All the results showed that the PAA has excellent inhibition properties for the corrosion of mild steel in aqueous medium. The gravimetric measurements showed that the formulation containing 50 ppm Zn$^{2+}$ ions and 200 ppm PAA and 125 ppm SPT yield good inhibition efficiency of 96%. The inhibitor system is effective in the pH range of 5-7. The inhibitor formulation acts as a cathodic in nature. Nyquist plots established that the inhibitors reduced the mild steel corrosion through their effective adsorption of inhibitive layer, which is further evidenced from SEM, AFM and FT-IR, Langmuir isotherm. The protective film may consist of [Fe (III)/Fe (II)/Zn (II)-PAA-SPT] complex, Zn(OH)$_2$, and hydroxides and oxides of iron. This multicomponent formulation consisting of PPA, Zn$^{2+}$ and SPT can be used as a potential inhibitor to prevent corrosion of mild steel in near and neutral aqueous media.

REFERENCES