Poly(Acrylic Acid) and Potassium Sodium Tartrate as Effective Corrosion Inhibitors for Mild Steel in Aqueous Environment

V. Dharmalingam1, P. Arockia Sahayaraj1.*, A. John Amalraj1, A. Angelin Prema2

1PG and Research Department of Chemistry, Periyar E.V.R College (Autonomous), Tiruchirappalli – 620 023, Tamilnadu, India.
2PG and Research Department of Physics, Periyar E.V.R College (Autonomous), Tiruchirappalli – 620 023, Tamilnadu, India.

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Abstract

The aim of the present work was to study the corrosion inhibition of mild steel using a ternary formulation. This new ternary inhibitor formulation, viz., Polyacrylic acid (PAA), with nickel ions and Potassium Sodium Tartrate (SPT) was used to protect mild steel from corrosion in a low-chloride environment. The weight loss studies showed that 93% inhibition efficiency was achieved with the ternary system consisting of 50 ppm Ni2+ ions, 200 ppm PAA, and 600 ppm SPT. Electrochemical methods (potentiostatic polarization and electrochemical impedance studies) and surface characterization techniques Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to ascertain the nature of the protective film and for explaining the mechanistic aspects of corrosion inhibition.

1. Introduction

Corrosion inhibitors are widely used as an economical method of corrosion control [1, 2]. Environmental restrictions imposed on heavy metal-based corrosion inhibitors oriented scientific researchers towards the study of non-toxic and environmentally friendly corrosion inhibitors [3]. The influence of several organic compounds containing polar functions such as nitrogen, oxygen, phosphorous or sulphur on the corrosion inhibition behavior of mild steel in aqueous solutions has been documented [4-8]. These groups of atoms or bonds facilitate electronic interactions between organic corrosion inhibitors and metal surface thereby aid adsorption of the inhibitors onto metal surface. The quest for eco-friendly compounds as corrosion inhibitors has shifted research focus to exploring potential application of polymers as corrosion inhibitors in the past few years.

The use of polymers as corrosion inhibitors has attracted considerable attention recently because: (1) they have low cost and are stable to metallic materials in aqueous media, (2) possession of multiple adsorption sites and (3) through their functional groups, they form complexes with metal ions, and on the metal surface, these complexes occupy a large area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution [9-13]. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen) that are regarded as centers of adsorption. Some polymers have been reported to inhibit the corrosion of mild steel in various aqueous media [14-17]. Recently, polyacrylic acid reported to be very effective corrosion inhibitors for the protection of mild steel in aqueous media to promote eco-friendly environment.

The aim of the present work is to determine the inhibitive effect of Polyacrylic acid (PAA), SPT and Ni2+ ions on the corrosion of mild steel in 60 ppm chloride medium by chemical and electrochemical methods. Surface characterization techniques (FT-IR, SEM and AFM) are also used to ascertain the nature of the protective film.

2. Experimental Methods

2.1 Materials

Polyacrylic acid (PAA), Nickel sulphate (NiSO4.6H2O), 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 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.

[Diagram of Polyacrylic acid (PAA) and Molecular structure of Potassium Sodium Tartrate (SPT)]

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 0.1 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, decreased with trichloroethylene and washed thoroughly with double distilled water and dried.

2.3 Weight Loss Measurements

Weight loss 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 the Mettler electronic balance, AE 240 model with a readability of 0.1 mg. Accuracy in weighing up to 0.0001g and its surface area measurement up to 0.1 cm². 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.

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

Where, m is the Loss in weight (mg), d is the Surface area of the specimen (dm²) and d is the Period of immersion (days). Inhibition efficiencies (IE) of the inhibitor were calculated by using the formula,

\[
\text{LE} = 100 \left[1 - \frac{\text{W}_{\text{inhibitor}}}{\text{W}_{\text{control}}} \right] \%
\]

Where, W₀ is the weight loss in the absence of inhibitor, Wᵢ is the weight loss in the presence of inhibitor.

2.4 Electrochemical Studies

Electrochemical impedance spectroscopic (EIS) studies and potentiostatic polarization studies were carried out using an electrochemical workstation CHI model 660A (USA) electrochemical analyzer. 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 Ecorr, 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 (Cdl), charge transfer resistance (Rct), corrosion current (Icorr), corrosion potential (Ecorr), anodic Tafel slope (βa) and cathodic Tafel slope (βc) were computed from the polarization curves and Nyquist plots. The IE values were calculated from potentiodynamic polarization measurements using the equation (3).

\[
\text{IE} (\%) = \left[\frac{\text{Icorr}_{\text{inhibitor}} - \text{Icorr}_{\text{control}}}{\text{Icorr}_{\text{control}}}\right] \times 100
\]

Where, Icorr and Icorr are the corrosion current densities in case of the absence and presence of the inhibitor respectively. From impedance measurements, the IE values were calculated from the following relation,

\[
\text{IE} (\%) = \left[\frac{R_{\text{ct}0} - R_{\text{ct}X}}{R_{\text{ct}0}}\right] \times 100
\]

Where, Rct0 and Rct are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

2.5 Surface 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 (FT-IR), Scanning electron microscopy (SEM) and 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 FT-IR spectra were recorded using Spectra 77 CX 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 VEGA 3-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 20 μm x 20 μm is evaluated for a set point of 20 nm and a scan speed of 10 mm/s. The three-dimensional topography of surface films gave various ruggedness parameters of the film.

3. Results and Discussion

3.1 Weight Loss Measurements

The weight loss 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, Ni²⁺ ions and SPT are given in Table 1. The inhibition efficiency was represented as a function of SPT concentration in Fig. 3.

<table>
<thead>
<tr>
<th>Concentration of SPT (ppm)</th>
<th>PAA (ppm)</th>
<th>SPT (ppm)</th>
<th>Weight loss (g)</th>
<th>IE (%)</th>
<th>Corrosion rate (mdd)</th>
<th>Surface Coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 ppm CI</td>
<td>50</td>
<td>300</td>
<td>0.0136</td>
<td>17.66</td>
<td>0.1298</td>
<td>60.01</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>400</td>
<td>0.0091</td>
<td>10.38</td>
<td>0.1411</td>
<td>55.01</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>600</td>
<td>0.0064</td>
<td>8.3446</td>
<td>0.5294</td>
<td>45.01</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>200</td>
<td>0.0047</td>
<td>6.1038</td>
<td>0.6544</td>
<td>35.01</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>300</td>
<td>0.0043</td>
<td>6.0259</td>
<td>0.7720</td>
<td>25.01</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>500</td>
<td>0.0020</td>
<td>2.5974</td>
<td>0.8529</td>
<td>15.01</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>600</td>
<td>0.0010</td>
<td>1.2987</td>
<td>0.9264</td>
<td>5.01</td>
</tr>
</tbody>
</table>

It can be seen from the results of the ternary formulations, that for lower concentration of 50 ppm Ni²⁺ and 200 ppm PAA with 600 ppm SPT, the maximum inhibition efficiency of only 93% is achieved. It is apparent that the inhibition efficiency increased with the increase in inhibitor concentration in the presence and absence of SPT. This behavior can be explained based on the strong interaction of the inhibitor molecule with the metal surface resulting in adsorption. The extent of adsorption increases with the increase in concentration of the inhibitor leading to increased inhibition efficiency. The maximum inhibition efficiency was observed at an inhibitor concentration of 600 ppm. Generally, inhibitor molecules suppress the metal dissolution by forming a protective film adsorbed to the metal surface and separating it from the corrosion medium.

3.1.1 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 (Fig. 4). When the pH is changed from 7 to 5 (addition of dil. H₂SO₄) the inhibition efficiency is altered very much lowered. When the pH is changed from 7 to 9 (addition of dil. NaOH) the inhibition efficiency is very much lowered, the system consisting of 50 ppm of Ni²⁺, 200 ppm of PAA and 600 ppm of SPT, the inhibition efficiency decreases from 93% to 46%. This is due to the fact at this pH when NaOH is added, Ni²⁺ is precipitated as Ni(OH)₂. Hence Ni²⁺ is not transported from the bulk of the solutions towards the metal surface. Hence inhibition efficiency decreases. However interestingly when pH is changed from 7 to 11, the inhibition efficiency decreases to some extent but still the system shows some inhibition efficiency. The reasons for this decrease in inhibition efficiency in more alkaline and acidic environments are explained under the mechanistic aspects.
3.2 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. 5, the linear relationships of C/θ versus C suggest that the adsorption of SPT on the mild steel is in well agreement with the Langmuir adsorption isotherm, which is expressed by the following equation.

$$ \frac{C}{\theta} = \frac{1}{K_{ads}} + C $$

Where, C is the concentration of inhibitor, θ is surface coverage on the metal surface and $K_{ads}$ is the equilibrium constant of adsorption process. The correlation coefficient ($R^2$ = 0.9819) was used to choose the isotherm that best fit experimental data.

3.2.2 Electrochemical Measurements

3.2.1 Potentiodynamic Polarization Studies

The potentiodynamic polarization studies were carried out to determine the kinetics of the cathodic and anodic reactions. Fig. 6. Shows the potentiodynamic polarization curves for mild steel electrodes in control solution at pH 7 in the absence and presence of inhibitor combinations. Electrochemical kinetic parameters, i.e., the corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), 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 60 ppm Cl\(^{-}\) medium, the corrosion potential ($E_{corr}$) is -598 mV/dec and the corrosion current is 129 µA/cm\(^2\). When 600 ppm SPT to 200 ppm of PAA and 50 ppm Ni\(^{2+}\) are added to 60 ppm Cl\(^{-}\) medium the corrosion potential is found to be -658 mV/dec and corrosion current is 7.83 µA/cm\(^2\). The corrosion current decreases from 129 µA/cm\(^2\) to 7.83 µA/cm\(^2\).

This shows that the formulation functions as a 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.

Table 2 Corrosion parameters of mild steel immersed in the absence and presence of inhibitor obtained from potentiodynamic polarization studies

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>$E_{corr}$ (mV/dec)</th>
<th>$I_{corr}$ (µA/cm(^2))</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$\beta_c$ (mV/dec)</th>
<th>θ (%)</th>
<th>LE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(^{2+})</td>
<td>PAA</td>
<td>SPT</td>
<td>Ni(^{2+})</td>
<td>PAA</td>
<td>SPT</td>
<td>Ni(^{2+})</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>112</td>
<td>25.40</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

3.2.2 Electrochemical Impedance Studies

Nyquist plots for mild steel immersed in 60 ppm of Cl\(^{-}\) solution at pH 7 in the absence and presence of formulations are shown in Fig. 7. The impedance parameters, charge transfer resistance ($R_t$), double layer capacitance ($C_d$) from the Nyquist plot values are shown in Table 3. When mild steel is immersed in 60 ppm Cl\(^{-}\) medium the $R_t$ value is found to be 112 (Ω cm\(^2\)). The $C_d$ value is 25.40 (µF/cm\(^2\)). When 600 ppm SPT to 200 ppm PAA and 50 ppm Ni\(^{2+}\) are added to 60 ppm Cl\(^{-}\) medium the $R_t$ value has increased from 112 to 807 (Ω cm\(^2\)) and the $C_d$ value has decreased from 25.40 to 0.50 (µF/cm\(^2\)). The increase in $R_t$ 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 behavior means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film.

Table 3 Corrosion parameters of mild steel immersed in the absence and presence of inhibitor obtained from electrochemical impedance studies

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>$R_t$ (Ω cm(^2))</th>
<th>$C_d$ (µF/cm(^2))</th>
<th>θ (%)</th>
<th>LE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(^{2+})</td>
<td>PAA</td>
<td>SPT</td>
<td>Ni(^{2+})</td>
<td>PAA</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>112</td>
<td>25.40</td>
</tr>
</tbody>
</table>
3.3 Surface Studies

3.3.1 Fourier Transform Infrared Spectroscopy

The FT-IR spectrum of pure PAA is shown in Fig. 9(a). The C=O stretching vibration at 1719 cm\(^{-1}\) and the broad absorption peak at 3448 cm\(^{-1}\) shows OH stretching vibration. The FT-IR spectrum of pure SPT is shown in Fig. 9(b). The C=O stretching frequency appears at 1604 cm\(^{-1}\) and OH stretching frequency appears at 3402 cm\(^{-1}\) respectively. The FT-IR spectrum of the film formed on the surface of the mild steel after immersion in the solution consisting of 60 ppm of Cl\(^{2-}\), 50 ppm of Ni\(^{2+}\), 200 ppm PAA and 600 ppm of SPT is shown in Fig. 9(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\(^{3+}\). This suggests that the O atom of the polyacrylic acid is coordinate to Fe\(^{3+}\) resulting in the formation of Fe\(^{3+}\)-PAA complex on the metal surface.

3.3.2 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. 10(a) show the metal surface 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.

3.3.3 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 2D and 3D AFM images of polished mild steel, 60 ppm Cl in mild steel and mild steel in 60 ppm Cl-solution containing 50 ppm of Ni\(^{2+}\), 200 ppm of PAA and 600 ppm of SPT, respectively are shown in Fig. 11(a-c). As can be seen from the AFM images, the surface is very clear for polished mild steel (Fig. 11a). Whereas in mild steel immersed in 60 ppm Cl (Fig. 11b) the surface is severely damaged by the solution. In (Fig. 11c) 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 a protective layer by adsorption of inhibitor molecules over the surface of mild steel. AFM data for mild steel is given in Table 4.

**Fig. 8** Impedance bode modules and bode phase angle plots of MS in a) 60 ppm Cl and b) 60 ppm Cl + 50 ppm Ni\(^{2+}\) + 200 ppm PAA + 600 ppm SPT

**Fig. 9** FT-IR Spectra of (a) Pure PAA (b) Pure SPT and (c) Surface film

**Fig. 10** SFM images of MS: (a) 60 ppm Cl and (b) 60 ppm Cl + 50 ppm Ni\(^{2+}\) + 200 ppm PAA + 600 ppm SPT

**Fig. 11** 2D and 3D AFM images of MS: (a) Polished mild steel (b) 60 ppm Cl and (c) 60 ppm Cl + 50 ppm Ni\(^{2+}\) + 200 ppm PAA + 600 ppm SPT
4. Mechanism of Protection

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

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \tag{5}$$

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

$$\text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 4\text{OH}^- \tag{6}$$

And the cathodic reaction is:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \tag{7}$$

![Fig. 12 Pictorial representation of mechanism of adsorption of inhibitors on MS surface](image-url)

When the environment containing 60 ppm Cl$^-$ ions/50ppm Ni$^{2+}$/200 ppm PAA/100 ppm SPT was prepared, a [Ni$^{2+}$/PAA-SPT] complex was formed in the solution. Besides this complex, the presence of free PAA, SPT and Ni$^{2+}$ ions. While the metal was immersed in this environment, the [Ni$^{2+}$/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.

$$[\text{Ni(II) · PAA · SPT}] + \text{Fe}^{2+}/\text{Fe}^{3+} \rightarrow [\text{Fe(II)/Fe(III)/Ni(II) · PAA · SPT}] \tag{8}$$

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

$$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \tag{9}$$

Thus, PAA, Ni$^{2+}$, and SPT play a very important role in the 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 weight loss measurements showed that the formulation consists yield good inhibition efficiency of 93%. The inhibitor system is effective in the pH range of 7.

The Langmuir adsorption isotherm suggests that inhibitor have strong tendency to adsorb spontaneously on the mild steel surface. The inhibitor formulation acts as a cathodic in nature. EIS measurements indicate that thickness of electric double layer increases due to adsorption of inhibitors at metal / electrolyte interfaces. The results of the SEM and AFM studied showed that the surface smoothness increases in the presence of inhibitor due to the formation of protective surface film.

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References