Synergistic corrosion inhibition effect of carbon steel in sea water by propyl phosphonic acid - Zn²⁺ system

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ABSTRACT

Synergistic effect exists between the propyl phosphonic acid - Zn²⁺ system in controlling the corrosion of carbon steel immersed in sea water in the absence and presence of Zn²⁺. The formulation consisting of 250 ppm propyl phosphonic acid, 50 ppm of Zn²⁺ have 98% inhibition efficiency, A more stable and compact protective film formed on the metal surface. Polarization study reveals that the propyl phosphonic acid - Zn²⁺ system function as cathodic inhibitor. The FT-IR, SEM, EDAX and AFM analysis reveal that the protective film is formed on the metal surface.

Keywords: Propyl phosphonic acid, corrosion inhibition, carbon steel, FT-IR, SEM, EDAX and AFM.
1. INTRODUCTION

Corrosion is the gradual destruction of material, usually metal, by chemical reaction with its environment. Seawater is a complex natural electrolyte. Seawater contains many corrosive electrolytes such as sodium chloride, magnesium chloride, calcium chloride, etc.; hence, carbon steel immersed in seawater is corroded slowly because of chemical reactions between the metal and the electrolytes [1-3].

The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Seawater has been used as cooling fluid in various industries. Carbon steel is widely used in infrastructure in marine environments [4]. It is one of the major constituents in structural steel applications including body of a ship, offshore platforms, foundation piling, sheet piling, and coastal facilities. It is also used in industry where the metal is exposed to acid corrosion. So, it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in seawater. Inhibition of corrosion and scaling can be done by the application of inhibitors, which is one of the most practical and economic methods for protection against metallic corrosion [5,6]. Corrosion inhibitors disclose that most organic substances used as corrosion inhibitors can adsorb on the metal surface employed through hetero atoms such as nitrogen, oxygen, sulphur, and phosphorus, multiple bonds or aromatic rings and block the active sites decreasing the corrosion rate [15]. Several phosphonic acids have been used as corrosion inhibitor [7-11]. Phosphonic acids are organic compounds containing R-PO(OH)₂ or R-PO(OR)₂ groups. They are effective chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion.

Phosphonic acids are extensively used now-a-days due to their complex forming abilities, high stability under harsh conditions, and low toxicity [12,13]. The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents. Compounds with a phosphonic functional group are considered to be the most effective chemical for inhibiting the corrosion process and it is well known that short-chain-substituted phosphonic acids are good corrosion inhibitors for iron and low-alloyed steels [14].

An environmental friendly compound, propyl phosphonic acid, contains not only phosphono groups, but also propyl group, which can decrease corrosion. The present study aims a) to investigate the synergistic effect of the above mentioned inhibitors and Zn\(^{2+}\) systems on the inhibition of corrosion of carbon steel in sea water, b) to study the corrosion inhibition efficiency of the most effective synergistic system in propyl phosphonic acid and Zinc sulphate studied in the present work, in the presence of biocides such as (CTAB), c) to study the biocidal efficiency of the above said combination, d) to investigate the nature of the protective film, FTIR spectroscopy, scanning electron microscopy (SEM) and Energy dispersed x-ray (EDAX) and Atomic force microscopy (AFM) have been used. e) to propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

2. EXPERIMENTAL

2.1. Preparation of Specimen

Carbon steel specimen [0.0267 % S, 0.06 % P, 0.4% Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.2. Weight-Loss Method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn\(^{2+}\) for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke’s solution [16]. The inhibition efficiency (IE) was then calculated using the equation:

\[
IE = 100 \left[ 1 - \frac{W_2}{W_1} \right] \%
\]

where \(W_1\) is the weight loss value in the absence of inhibitor and \(W_2\) is the weight loss value in the presence of inhibitor.
2.3. Polarization Study

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

2.4. Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by various surface analysis techniques.

2.4.1. Fourier Transform Infrared Spectra (FT-IR)

The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The film formed on the metal surface was carefully removed and mixed thoroughly with KBr making the pellet.

2.4.2. Scanning electron microscopy and EDAX

The surface morphology of the formed layers on the carbon steel surface after its immersion in control solutions containing sea water in the absence and in the presence of the inhibitor were carried out. After one day, the specimens were taken out, washed with distilled water and dried. The SEM-EDAX photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

2.4.3 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 × 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 roughness parameters of the film.

3. RESULTS AND DISCUSSION

3.1. Weight-Loss Method

Table 1. Corrosion rates (CR) of carbon steel immersed in sea water containing in the
presence and absence of inhibitor system by weight loss method.

<table>
<thead>
<tr>
<th>PPA ppm</th>
<th>0 ppm of Zn$^{2+}$</th>
<th>25 ppm of Zn$^{2+}$</th>
<th>50 ppm of Zn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IE% CR(mm/y)</td>
<td>IE% CR(mm/y)</td>
<td>IE% CR(mm/y)</td>
</tr>
<tr>
<td>0</td>
<td>-- 0.1855 14</td>
<td>0.1590 22</td>
<td>0.1427</td>
</tr>
<tr>
<td>50</td>
<td>19 0.1485 64</td>
<td>0.0649 73</td>
<td>0.0519</td>
</tr>
<tr>
<td>100</td>
<td>27 0.1336 69</td>
<td>0.0591 84</td>
<td>0.0310</td>
</tr>
<tr>
<td>150</td>
<td>36 0.1130 76</td>
<td>0.0461 91</td>
<td>0.0184</td>
</tr>
<tr>
<td>200</td>
<td>44 0.1001 81</td>
<td>0.0371 95</td>
<td>0.0096</td>
</tr>
<tr>
<td>250</td>
<td>51 0.0921 86</td>
<td>0.0278 98</td>
<td>0.0037</td>
</tr>
</tbody>
</table>

Table 2. Influence of immersion period on the inhibition efficiency (IE) of PPA-Zn$^{2+}$ system

<table>
<thead>
<tr>
<th>System</th>
<th>Immersion Period (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Sea water CR (mm/yr)</td>
<td>0.1855</td>
</tr>
<tr>
<td>Sea water + PPA (250 ppm) + Zn$^{2+}$ (50 ppm) CR (mm/yr)</td>
<td>0.0037</td>
</tr>
<tr>
<td>IE (%)</td>
<td>98</td>
</tr>
</tbody>
</table>
Table 3. Influence of pH on the inhibition efficiency (IE) of PPA-Zn\(^{2+}\) system for a period of one day

<table>
<thead>
<tr>
<th>System</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
<th>pH 10</th>
<th>pH 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water CR (mm/yr)</td>
<td>0.2043</td>
<td>0.1962</td>
<td>0.1858</td>
<td>0.1996</td>
<td>0.1904</td>
</tr>
<tr>
<td>Sea water + PPA (250 ppm) + Zn(^{2+}) (50 ppm) CR (mm/yr)</td>
<td>0.0409</td>
<td>0.0255</td>
<td>0.0037</td>
<td>0.0200</td>
<td>0.0114</td>
</tr>
<tr>
<td>IE (%)</td>
<td>80</td>
<td>87</td>
<td>98</td>
<td>90</td>
<td>94</td>
</tr>
</tbody>
</table>

Table 1 gives values of the corrosion inhibition efficiencies and the corresponding corrosion rates of propyl phosphonic acid (PPA) - Zn\(^{2+}\) in controlling corrosion of carbon steel in seawater for a period of one day. The PPA alone has high rate of corrosion. The inhibition efficiency of PPA is improved by adding various concentrations of Zn\(^{2+}\). Similar observations have been made et al [17] where they have improved the inhibition efficiency of Na\(_3\)PO\(_4\) on EDTA by addition of Zn\(^{2+}\) ion [18] have improved the inhibition efficiency of heptane sulphonic acid by addition of Zn\(^{2+}\) ion. However, increasing the concentration of PPA as well as Zn\(^{2+}\), the maximum inhibition is achieved and the corrosion rate is decreased. It is found that 250 ppm of PPA and 50 ppm of Zn\(^{2+}\) has 98% inhibition efficiency. The inhibition efficiency increases with the increase of concentration of inhibitors. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of phosphonic acid with the increase of its concentration. It is generally assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media.

From Table 2 gives the IE decreases with the increase in the duration of immersion. For example the IE was found to be 98% for one day and decrease the IE to 78% on seventh day. This may due to the fact that as the period of immersion increases, the protective film formed on the metal surface namely, Fe\(^{2+}\)-PPA complex is broken by the aggressive chloride ions present in the sea water and hence the IE decreases.

From Table 3 gives the influence of pH on inhibition efficiency of PPA (250ppm) - Zn\(^{2+}\) (50ppm). It is found the inhibitor formulation system is highly effective at pH 7 and the
IE is 98%. The inhibition efficiency slightly decreases on lowering the pH to 3 and 5. At low pH 3 and 5, the protective film is broken by H\(^+\) ions of the acid and anion form of PPA is not available for zinc ions to react with it and may not able to form a stable complex in acidic medium, hence IE is reduced. When pH is increased by the addition of dil. NaOH solution (pH 10) the IE decreases. This is due to the when NaOH is added to the system Zn\(^{2+}\) ions are precipitate as Zn(OH)_2. Hence Zn\(^{2+}\) ions are unable to transport PPA from the bulk solution to the metal surface. When NaOH is added further (pH 12), Zn(OH)_2 is solubilised as sodium zincate and now PPA transport the metal surface, hence IE increases.

### 3.1.1. Synergism Parameter (S\(_I\))

**Table 4.** Synergism parameters for PPA - Zn\(^{2+}\) (25 ppm) system in carbon steel immersed in sea water for a period of one day

<table>
<thead>
<tr>
<th>PPA (ppm)</th>
<th>Zn(^{2+}) (ppm)</th>
<th>I(_1)</th>
<th>I(_2)</th>
<th>I(_I)</th>
<th>S(_I)</th>
<th>I.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>25</td>
<td>0.19</td>
<td>0.14</td>
<td>0.64</td>
<td>1.942</td>
<td>64</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>0.27</td>
<td>0.14</td>
<td>0.69</td>
<td>1.912</td>
<td>69</td>
</tr>
<tr>
<td>150</td>
<td>25</td>
<td>0.36</td>
<td>0.14</td>
<td>0.76</td>
<td>2.071</td>
<td>76</td>
</tr>
<tr>
<td>200</td>
<td>25</td>
<td>0.44</td>
<td>0.14</td>
<td>0.81</td>
<td>2.289</td>
<td>81</td>
</tr>
<tr>
<td>250</td>
<td>25</td>
<td>0.51</td>
<td>0.14</td>
<td>0.86</td>
<td>2.8013</td>
<td>86</td>
</tr>
</tbody>
</table>

**Table 5.** Synergism parameters for PPA-Zn\(^{2+}\) (50 ppm) system in carbon steel immersed in sea water for a period of one day

<table>
<thead>
<tr>
<th>PPA (ppm)</th>
<th>Zn(^{2+}) (ppm)</th>
<th>I(_1)</th>
<th>I(_2)</th>
<th>I(_I)</th>
<th>S(_I)</th>
<th>I.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>50</td>
<td>0.19</td>
<td>0.22</td>
<td>0.73</td>
<td>2.2011</td>
<td>73</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>0.27</td>
<td>0.22</td>
<td>0.84</td>
<td>3.2612</td>
<td>84</td>
</tr>
<tr>
<td>150</td>
<td>50</td>
<td>0.36</td>
<td>0.22</td>
<td>0.91</td>
<td>4.6970</td>
<td>91</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>0.44</td>
<td>0.22</td>
<td>0.95</td>
<td>8.3160</td>
<td>95</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>0.51</td>
<td>0.22</td>
<td>0.98</td>
<td>19.250</td>
<td>98</td>
</tr>
</tbody>
</table>
The values of synergism parameters are shown in Tables 4 and 5. Synergism Parameter \((S_I)\) has been calculated to know the synergistic effect existing between two inhibitors [19, 20]. The values of \(S_I > 1\) suggest a synergistic effect. \(S_I\) approaches 1 when no interaction exists between the inhibitor compounds. In case of \(S_I < 1\), the negative interaction of inhibitors prevails (i.e., corrosion rate increases). Synergism parameter is calculated using the relation.

\[
S_I = \frac{(1-I_{1+2})}{(1-I'_{1+2})}
\]

where \(I_1\) is the surface coverage of inhibitor (PPA), \(I_2\) is the surface coverage of inhibitor (Zn\(^{2+}\)) and \(I'_{1+2}\) is the combined surface coverage of inhibitors (PPA) and (Zn\(^{2+}\)).

### 3.2. Potentiodynamic Polarization Study

Polarization study has been used to detect the formation of protective film on the metal surface [21,22]. The polarization curves of carbon steel immersed in various test solutions are shown in Fig 1. It shows that there is a clear reduction of both anodic and cathodic currents in the presence of PPA Zn\(^{2+}\) compared with those for the blank solution. Hence, it is clear that the cathodic reaction (oxygen reduction) and the anodic reaction (iron dissolution) were inhibited. The electrochemical parameters such as corrosion potential \((E_{corr})\), Tafel slopes (anodic slope \(b_a\) and cathodic slope \(b_c\)), linear polarization resistance (LPR) and corrosion current \((I_{corr})\) values are given in Table 6.

**Table 6. Analysis of potentiodynamic polarization study**

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{corr}) (mV vs SCE)</th>
<th>(b_c) (mV/dec)</th>
<th>(b_a) (mV/dec)</th>
<th>LPR (Ω cm(^2))</th>
<th>(I_{corr}) (A/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water</td>
<td>–726</td>
<td>125.5</td>
<td>162.3</td>
<td>1.0756 \times 10^{-4}</td>
<td>3.80 \times 10^{-4}</td>
</tr>
<tr>
<td>Sea water + 250 ppm PPA + 50 ppm Zn(^{2+})</td>
<td>–789</td>
<td>156.7</td>
<td>183.0</td>
<td>1.6086 \times 10^{-4}</td>
<td>2.90 \times 10^{-4}</td>
</tr>
</tbody>
</table>
When carbon steel is immersed in seawater, the corrosion potential is -726 mV vs SCE. The formulation consisting of 250 ppm PPA + 50 ppm Zn\textsuperscript{2+} shifts the corrosion potential to -789 mV Vs SCE. It shows that the corrosion potential is shifted to more negative side. This indicates that the cathodic reaction is controlled predominantly.

The corrosion current density value and LPR value for seawater are 1.0756×10\textsuperscript{-4} Ω cm\textsuperscript{2} and 1.6086×10\textsuperscript{-4} Ω cm\textsuperscript{2}. For the formulation of 250 ppm PPA and 50 ppm Zn\textsuperscript{2+}, the corrosion current density value has decreased to 2.90×10\textsuperscript{-4} Α/cm\textsuperscript{2} and the LPR value has increased to 1.6086×10\textsuperscript{-4} Ω cm\textsuperscript{2}. The fact that the LPR value increases with decrease in corrosion current density indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface.

3.3. Fourier Transform Infrared Spectra (FT-IR)

FT-IR spectra have been used to analyze the protective film found on the metal surface [25,26]. The FTIR spectrum (KBr) of pure PPA is shown in Fig.2a. The P-O stretching frequency appears at 1148 cm\textsuperscript{-1}. The FTIR spectrum of the film formed on the metal surface shows characteristic peaks of the inhibitor.
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metal surface after immersion in seawater containing 250 ppm of PPA and 50 ppm of Zn$^{2+}$ is shown in Fig. 2b. The P-O stretching frequency has shifted from 1148 to 1190 cm$^{-1}$. It is inferred that oxygen atom of the phosphonate group has coordinated with Fe$^{2+}$ resulting in the formation of Fe$^{2+}$ - PPA complex formed on the anodic sites of the metal surface. The peak at 3432 cm$^{-1}$ is due to OH stretching. The band due to ZnO appears at 1369 cm$^{-1}$. These results confirm the presence of Zn(OH)$_2$ deposited on the cathodic sites of the metal surface. Thus, FT-IR spectral study leads to the conclusion that the protective film consists of Fe$^{2+}$ - PPA complex and Zn(OH)$_2$.

![FT-IR spectra of (a). Pure PPA (b). Surface film](image)

Fig.2. FT-IR spectra of (a). Pure PPA (b). Surface film

3.4. Scanning electron microscopy (SEM)

The scanning electron micrographs of carbon steel are shown in Fig 3. The SEM micrograph of polished carbon steel surface (control) is shown in Fig 3a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of carbon steel immersed in seawater is shown in Fig 3b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Fig 4c shows that the presence of 250 ppm of PPA and 50 ppm of Zn$^{2+}$ in seawater gives the formation of thick films on the carbon steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to

block the active site present on the carbon steel surface.[27-28]

Fig.3. SEM images of carbon steel surface (a). Polished metal (b). Sea water (c) Sea water+ 50 ppm of Zn\textsuperscript{2+} + 250 ppm PPA

3.5. Energy Dispersive X-ray Analysis (EDAX)

The energy dispersive spectroscopy (EDAX) of polished carbon steel (control) in figure 4a shows its composition. The EDAX spectrum of sea water environment is shown in figure 4b. This indicates the presence of C, Co, Mn and Fe along with Chloride on the metal surface. The EDAX spectrum of film formed on the surface of carbon steel after immersion in sea water environment containing 250 pm of PPA and 50 pm of Zn\textsuperscript{2+} is shown in figure 4c. This proves that the presence of phosphorous, Zinc and oxygen atom of above mentioned Inhibitor system along with compositon of carbon steel. This indicates that oxygen atom of functional group of PPA has coordinated with Fe\textsuperscript{2+}, resulting in the formation of Fe\textsuperscript{2+} - PPA complex on the anodic sites of metal surface and Zn(OH)\textsubscript{2} formed on the cathodic sites of metal surface[29].
3.6. Atomic Force Microscopy (AFM)

The value of Ra, Rq and P-V height for the polished carbon steel surface (reference sample) are 3.99 nm, 3.26 nm and 34.23 nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth. Figure 5a displays the non-corroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The average roughness, rms roughness and P-V height values for the carbon steel surface immersed in sea water environment are 38.9 nm, 28.8 nm and 181.8 respectively. These data suggests that carbon steel surface immersed in sea water environment has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and was due to the corrosion of carbon steel. Figure 5b displays corroded metal surface with few pits. The presence of 250 ppm of PPA, 50 ppm of Zn$^{2+}$ in sea water environment in figure 5c reduces the Rq from 38.9
nm to 30 nm and the average roughness is significantly reduced to 28.8 nm when compared with 3.26 nm of carbon steel surface immersed in sea water[30].

Fig.5. 2D &3D AFM images of carbon steel surface (a). Polished carbon steel (b) Sea water (c). Sea water + 50 ppm Zn$^{2+}$ + 250 ppm PPA

Table.8. AFM parameters in different environments

<table>
<thead>
<tr>
<th>Environment</th>
<th>Root-mean- square Roughness (nm)</th>
<th>Average Roughness (nm)</th>
<th>Maximum peak-to valley height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Polished carbon steel</td>
<td>3.99</td>
<td>3.26</td>
<td>34.23</td>
</tr>
<tr>
<td>b) Sea water</td>
<td>38.9</td>
<td>28.8</td>
<td>181.8</td>
</tr>
<tr>
<td>c) Sea water+ 50 ppm Zn$^{2+}$ + 250 ppm PPA</td>
<td>30</td>
<td>19.21</td>
<td>69.52</td>
</tr>
</tbody>
</table>

3.7. Mechanism of corrosion inhibition

In order to explain the above results, the following mechanism of corrosion inhibition is proposed: When carbon steel is immersed in sea water, the anodic reaction is,

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

The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions,

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

When the formulation consists of 250 ppm of PPA and 50 ppm Zn$^{2+}$ in seawater, there is formation of PPA – Zn$^{2+}$ complex in solution.

When carbon steel is immersed in this environment, the PPA – Zn$^{2+}$ complex diffuses from the bulk of the solution to the metal surface. The PPA – Zn$^{2+}$ complex is converted into PPA Fe$^{2+}$ complex on the anodic sites of the metal surface, the stability of Fe$^{2+}$ – PPA complex is higher than the corresponding Zinc complex.

$$\text{Zn}^{2+} + \text{PPA} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{PPA} + \text{Zn}^{2+}$$

The released Zn$^{2+}$ combines with OH- to form Zn(OH)$_2$ on the cathodic sites of the metal surface.

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

The protective nature of the film is due to the presence of metal inhibitor complex and Zinc hydroxide. Formation of the metal inhibitor complex fills the pores of the otherwise porous film and makes it a protective film.

Thus, the protective film consists of Fe$^{2+}$ – PPA complex and Zn(OH)$_2$.

4. CONCLUSION

Synergistic effect exists between the propyl phosphonic acid - Zn$^{2+}$ system in controlling the corrosion of carbon steel immersed in sea water in the absence and presence of Zn$^{2+}$. The formulation consisting of 250 ppm propyl phosphonic acid, 50 ppm of Zn$^{2+}$ have 98% inhibition efficiency. A more stable and compact protective film formed on the metal surface. Polarization study reveals that the propyl phosphonic acid - Zn$^{2+}$ system function as cathodic inhibitor and there is increase in LPR value and decrease in corrosion current [31-37]. The FT-IR, SEM, EDAX and AFM analysis reveal that the protective film is formed on the metal surface.
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