Synergistic Effect of Diethylenetriamine Pentamethylene Phosphonic Acid (DTPMP) and Zn$^{2+}$ System on the Corrosion Inhibition of Mild Steel in Aqueous Environment
IV.1 Introduction

Metals acquire stability when their surfaces are isolated from the normal terrestrial environment. If this isolation is not achieved they undergo a process of embrittlement, suffer fatigue, transformed into oxides, which peel off or just dissolve away. Metals become unstable when they contact moist atmosphere containing carbon dioxide (Fig. IV.1) or sodium chloride suspension in marine atmosphere. The spontaneous instability or corrosion of metals or its alloys results from the charge transfer reactions at their interface between the metal and its electrolytic environment. The detrimental transformation of the bulk properties of a metal begins at its surface. According to local cell theory a corroding metal in moist air consists of separate sites for de-electronation and electronation reactions (Fig. IV.2a) due to heterogeneities on the surface or included impurities during slow equilibrium solidification of metals during metallurgical processes. However, homogeneous theory of corrosion emphasizes that corrosion is due to different electrodic (Fig. IV.2b) charge transfer reactions occurring simultaneously and in opposite directions at the surface. The consequences of corrosion are numerous and the effects of these on the safe, reliable and efficient operation of equipment are often more serious than the simple loss of a mass of metal.
The factors that can accelerate corrosion include: establishment of well-defined locations on the surface for the anodic and cathodic reactions, stimulation of these redox reactions by the aggressive ions such as $\text{Cl}^-$, $\text{SO}_4^{2-}$, etc. The use of corrosion inhibitors $^{8-15}$ is one of the most practical methods for the protection against corrosion. An inhibitor is a chemical substance which when added to the corrosive environment at an optimum concentration, significantly slow down the corrosion rate of metals. Anodic inhibitors caused pitting corrosion; therefore it
is ideal to use a mixture of cathodic and anodic inhibitors. This observation is referred as “synergism”. Mixture of inhibitors provides better inhibition than either of the individual components i.e., the mixture is synergistic.\textsuperscript{16-22}

Many organic inhibitors work by adsorption mechanism.\textsuperscript{23} The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes.\textsuperscript{24,25} Riggs\textsuperscript{26} proposed that the adsorption of organic inhibitors depends on the chemical nature of the inhibitor molecule, the environment, the nature of the metal surface and the electrochemical potential at the metal/solution interface. The relationship between the structure-corrosion inhibition\textsuperscript{27-29} and the effect of the substituents in related molecules such as aliphatic amines\textsuperscript{30}, thiophenes\textsuperscript{31}, azoles\textsuperscript{32}, etc., with inhibitive efficiencies has also been established in earlier works.

Interphase inhibitors are effective for the decrease of metal corrosion in neutral aqueous solutions by forming weakly soluble compounds with the metal ion existing in the solution, which precipitates on the surface to form a three-dimensional protective layer.\textsuperscript{33,34} Such inhibitors for cooling-water treatment technology in the last decades comprise different types of phosphonic acids.\textsuperscript{35,36} Phosphonates are sodium, potassium\textsuperscript{30} or ammonium\textsuperscript{37} salts of phosphonic acids. Several phosphonic acids have been used as corrosion inhibitors due to their ability to form complexes with metal ions and hydrolytic stability. In earlier studies HEDP\textsuperscript{38,39}, ATMP\textsuperscript{30}, NTMP\textsuperscript{30}, DTPMP\textsuperscript{30}, alkyl\textsuperscript{40} and arylphosphonic acids\textsuperscript{40} and polyphosphonic acids\textsuperscript{41} have been widely used for mild steel corrosion inhibition. Phosphonates when blended with certain metal cations\textsuperscript{42} and polymers\textsuperscript{43,44} reduce
the optimal inhibitor concentration needed for inhibition due to synergistic effects of components. Inspite of the great number of materials, which have been reported as corrosion inhibitors for mild steel, researchers continue to find out highly efficient inhibitors for specific applications e.g., cooling water systems.\textsuperscript{45} Carbon (mild) steel\textsuperscript{3,5} is known for its low cost, strength, easy fabricability and corrosion resistance. It is widely used in cooling water systems where water velocity, dissolved solids and continual aeration provide conditions for continued corrosion of mild steel.\textsuperscript{46}

Diethylenetriaminepentamethylene phosphonic acid (DTPMP) is a polyaminophosphonic acid like other amionopolyphates\textsuperscript{30} and it posses the following unique characteristics:

1. Molecular Formula: $\text{C}_9\text{H}_{28}\text{N}_3\text{O}_{15}\text{P}_5$
2. Molecular weight: 573.20

Structure of DTPMP

3. Physical state: amber viscous liquid
4. Specific gravity 1.40-1.45
5. Solubility in water: miscible
6. pH $< 2$ (1.0% sol)
7. Stability: stable under ordinary conditions
Applications

1. It forms complexes with zinc and other multivalent metal ions.

2. Corrosion inhibition: In the presence of other chemicals (synergists) it provides corrosion inhibition.

3. Antiscalant: By forming stable water-soluble complexes with polyvalent metal ions, it prevents undesired interaction by blocking normal reactivity of metal ions. It inhibits precipitation of typical scalants at substoichiometric inhibitor concentrations.

4. Hydrolytic stability: It resists decomposition in aqueous solutions even at elevated temperatures and extremes in pH.

5. Chlorine stability: It resists degradation by ppm levels of available chlorine.

The phosphonate chosen in the present work is sodium salt of DTPMP and the synergist is Zn$^{2+}$ ions. The environment chosen is an aqueous solution containing low concentration of chloride, say 60 ppm because in most of the industries demineralised water containing chloride concentration not exceeding 60 ppm is used as cooling water. In this chapter, the inhibition efficiency (IE) of diethylenetriaminepentamethylene phosphonic acid(DTPMP) in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl$^-\text{ in the absence and presence of Zn}^{2+}$ ions are presented. The influence of pH on the IE of the DTPMP-Zn$^{2+}$ system is also presented. The synergism parameters ($S_I$) calculated from surface coverage are given to show the synergistic effect exists between the phosphonic acid and Zn$^{2+}$ ions. The nano level protective films formed on the metal surface analyzed by potentiostatic methods, AFM, FTIR spectra, XRD
and Optical microscopic methods are presented to give an insight about the inhibitive action of the inhibitor. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight-loss method, the electrochemical method and different spectroscopic techniques.

IV.2 Results and Discussion

Synergistic effect of diethylenetriaminepentamethylenephosphonic acid (DTPMP)-Zn^{2+} system on the corrosion inhibition of mild steel in aqueous environment

IV.2.1 Weight-loss method

Weight loss method is widely used by many researchers in earlier works.\textsuperscript{3,5,30,47-49} Corrosion rates calculated for carbon steel in aqueous environment containing 60 ppm of chloride ion in the absence and presence of inhibitor DTPMP at various concentrations obtained by weight-loss method at different pH measurements are given in Tables IV.1-IV.8. The percentages of corrosion protection (Inhibition Efficiencies –IE) offered by DTPMP in controlling corrosion of carbon steel are also given in these tables.
Table IV.1. Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment \((\text{Cl}^- = 60 \text{ ppm})\) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: \((60 \text{ ppm Cl}^- + \text{DTPMP})\) at \(\text{pH} = 7\)

Immersion period: 7 days

<table>
<thead>
<tr>
<th>Conc. of DTPMP, ppm</th>
<th>Conc. of (\text{Zn}^{2+}), ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>18.00</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
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<td>15.30</td>
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<td>150</td>
<td>0</td>
<td>14.22</td>
<td>21</td>
</tr>
<tr>
<td>200</td>
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<td>24</td>
</tr>
<tr>
<td>250</td>
<td>0</td>
<td>12.96</td>
<td>28</td>
</tr>
</tbody>
</table>

mdd: Corrosion rate expressed in milligrams per square decimeter per day \((\text{mg/dm}^2\text{)(day)}\).

The corrosion rates and inhibition efficiencies (corrosion protection) calculated for carbon steel in aqueous environment using weight-loss method at different concentrations of DTPMP and constant concentration of Cl\(^-\) at pH 7 are given in the Table IV.1. It is found that at pH 7 DTPMP shows a slight increase in the IE. However, it decreases the corrosion rate of the metal with the increased concentration of DTPMP at ppm level. Taking an example the corrosion of heat exchanger tubes in industrial cooling water\(^{45}\), a typical corrosion rate in untreated water would be 210-260 mdd; the use of corrosion inhibitor could reduce this to less than 26 mdd. This reported fact in earlier works strongly support the studied inhibitor, which shows 16 mdd at 50 ppm concentration could
be an excellent inhibitor for cooling water systems. Horvath et al.\textsuperscript{30} have made an attempt to compare the inhibitive abilities of some amino polyphonates viz., ethylenediamine-$N,N,N',N''$-tetramethylenephosphonic acid (EDTMP), nitrilotrimethylenephosphonic acid (NTMP), DTPMP, etc., and reported that among these acids DTPMP showed an excellent IE due its molecular structure. IE increased with an increase in the number of amino and methylene phosphono groups.

DTPMP is an adsorption type organic corrosion inhibitor.\textsuperscript{30} Decrease in corrosion rate with the increase in inhibitor concentration may be due to the thin film of chemisorbed inhibitor on the metal surface. This layer gave protection against corrosion either by physically blocking the surface from the corrosive environment or by retarding the electrochemical processes. The amino (-NH$_2$), and phosphonate (-PO$_3$H$_2$) functional groups in DTPMP are capable of forming co-ordinate bonds with metal surface and reduce corrosion rates by chemisorption.

Hackerman et al.\textsuperscript{50} and other investigators\textsuperscript{52-54} have reported that there is a correlation between the absorbability of organic surface active substances and their inhibition action in aqueous solutions. It has been noted that adsorption of surface-active organic substances increases with their molecular weight and dipole moment. In organic compounds, suitable lone pair electrons for coordinate bonding occur in functional groups containing elements of Group V and VI of the periodic table. The tendency to stronger coordinate bond formation\textsuperscript{52,53} and hence stronger adsorption by the elements increases with decreasing electronegativity in the order O<N<S<Se\textsuperscript{54} and also depends on the nature of the functional groups containing
these elements. Organic molecules containing active electron–donor groups (CN\(^-\), -CNO\(^-\), -C = O, -CHO and -NH\(_2\)) are chemisorbed on the metal surface having incomplete d-orbitals. The electron density at the functional group, which is a direct consequence of adsorption, depends on the structure of the rest of the molecule\(^{30}\).

**Table IV.2.** Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment (Cl\(^-\) = 60 ppm) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: (60 ppm Cl\(^-\) + Zn\(^{2+}\)) at pH = 7

Immersion period: 7 days

<table>
<thead>
<tr>
<th>Conc. of DTPMP, ppm</th>
<th>Conc. of Zn(^{2+}) ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>10</td>
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<td>-16</td>
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</tr>
<tr>
<td>0</td>
<td>250</td>
<td>27.72</td>
<td>-54</td>
</tr>
</tbody>
</table>

The corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment in the absence of DTPMP and at different concentrations Zn\(^{2+}\) ions are given in Table IV.2. It is accepted that the protective action of cathodic filming inhibitors is due to the precipitation of insoluble material
produced by the reaction of the inhibitor and the alkali produced at the cathodes by such reaction as\textsuperscript{55-57}:

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\]

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

Zinc\textsuperscript{55-57} and calcium\textsuperscript{58-60} salts are the most common examples of cathodic filming inhibitors. A cathodic protective film of Zn(OH)\textsubscript{2} or Ca(OH)\textsubscript{2} is formed, respectively and protects the metal from corrosion. It is found from the Table IV.2 that the percentage of protection was actually negative, which indicates that the corrosion of mild steel was accelerated in that environment. This may be due to the prevention of formation of protective oxide films on the metal surface by the aggressive chloride ions made the environment more corrosive and thus increase corrosion rate. Further, hydrogen evolution in neutral water (pH = 7) medium is very slow, hence the amount of zinc hydroxide produced is not sufficient to protect cathodic sites from corrosion or the precipitate may be in solublished form in that environment. Negative IE is further confirmed by the observation of a thick brown rust scale on the metal surface and the solution turned reddish brown color even at 250 ppm level.

\section*{IV.2.2 Influence of Zn$^{2+}$ on the inhibition efficiency of DTPMP}

Phosphonates when blended with certain metal cations like Ca$^{2+}$, Mg$^{2+}$, Co$^{2+}$, Al$^{3+}$, Cr$^{3+}$, etc. reduce the optimal inhibitor concentration needed for inhibition due to synergistic effects of components. Predominantly Zn$^{2+}$ ions are used for elevating corrosion inhibition properties of phosphonic acids. Synergism\textsuperscript{18} (mixture of inhibitors often provides better inhibition than either of the individual
components) serves as the basis for all modern corrosion inhibitor formulations. Kalman et al.\textsuperscript{58} studied the N-phosphonoaminecarboxylic acids with and without zinc by potentiostatic and impedance spectroscopic methods. Corrosion inhibition efficiency of HEDP (1-Hydroxy ethane-1,1-diphosphonic acid) and zinc ion mixture was elaborately studied by many authors. Sekine and Hirakawa\textsuperscript{61} investigated the IE of HEDP with and without Zn\textsuperscript{2+} ions in 0.3% NaCl solution and proposed an adsorption model for the complex formation of HEDP with iron and Zn(OH)\textsubscript{2} precipitation in the inhibitor mixture for cathodic protection. Rajendran et al.\textsuperscript{65} investigated the synergistic effect of zinc ions with HEDP\textsuperscript{62}, 2-chloroethyphosphonic acid\textsuperscript{63}, ethylphosphonic acid\textsuperscript{64}, carboxymethyl cellulose-HEDP\textsuperscript{65} and proposed a suitable mechanism of corrosion. Earlier studies in literature strongly supported that the added zinc ions form insoluble complexes with phosphonic acid in aqueous environment and repair the porous oxide layer and prevent further corrosion by synergistic effect. Except a few, most of the phosphonates are not good corrosion inhibitors independently and hence the addition of metallic ions improved their ability.\textsuperscript{36,41}

The corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous solution at constant, Zn\textsuperscript{2+} and Cl\textsuperscript{−} concentrations and at different DTPMP concentrations by weight loss method are given in Table IV.3-IV.5.
Table IV.3. Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment (Cl⁻ = 60 ppm) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: (60 ppm Cl⁻ + DTPMP + 10 ppm Zn²⁺) at pH = 7

Immersion period: 7 days

<table>
<thead>
<tr>
<th>Conc. of DTPMP, ppm</th>
<th>Conc. of Zn²⁺, ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>18.00</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
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</tr>
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<td>-13</td>
</tr>
<tr>
<td>250</td>
<td>10</td>
<td>19.80</td>
<td>-10</td>
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</tbody>
</table>
Table IV.4. Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment ($Cl^- = 60$ ppm) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: ($60$ ppm $Cl^- +$ DTPMP + $25$ ppm $Zn^{2+}$) at pH = 7

Immersion period: 7 days

<table>
<thead>
<tr>
<th>Concn. of DTPMP, ppm</th>
<th>Concn. of $Zn^{2+}$, ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>18.00</td>
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<tr>
<td>250</td>
<td>25</td>
<td>7.02</td>
<td>61</td>
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</table>
Table IV.5. Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment \((\text{Cl}^- = 60 \text{ ppm})\) with and without corrosion inhibitor by weight-loss method.

Inhibitor system: \((60 \text{ ppm Cl}^- + \text{DTPMP} + 50 \text{ ppm Zn}^{2+})\) at pH = 7
Immersion period: 7 days

<table>
<thead>
<tr>
<th>Conc. of DTPMP ppm</th>
<th>Conc. of Zn(^{2+}), ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>18.00</td>
<td>-</td>
</tr>
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<td>50</td>
<td>21.91</td>
<td>-22</td>
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</tr>
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<td>1.80</td>
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</tr>
<tr>
<td>200</td>
<td>50</td>
<td>1.80</td>
<td>90</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>1.80</td>
<td>90</td>
</tr>
</tbody>
</table>

When 10 ppm of Zn\(^{2+}\) ions is added as synergists in the form of zinc sulphate, there is acceleration in corrosion rate indicated by the negative value -47%. This is due to the increase in the metal loss rate (corrosion rate) by aggressive Cl\(^-\) and SO\(_4^{2-}\) ions. Further, ferrous sulphate formed by the interaction of Fe\(^{2+}\) with SO\(_4^{2-}\) ions present in the electrolytic solution is in solublised form and does not form a stable protective layer on the metal surface. When 10 ppm of Zn\(^{2+}\) ions are added to different concentration of DTPMP, though there is a decrease in corrosion rate still the values are negative because at this lower concentration of Zn\(^{2+}\), DTPMP is precipitated as Zn\(^{2+}\)-DTPMP complex in the bulk of the solution and the formation
of coating of DTPMP might not occur on the carbon steel. There is a thick brown rust scale formed on the metal surface and the solution turned reddish brown color at 10 ppm level of \( \text{Zn}^{2+} \) ions with the increased concentration of DTPMP. Rajendran et al.\(^6\) has reported 40% IE for the formulation of 10 ppm \( \text{Zn}^{2+} \) and 300 ppm HEDP but with 50 ppm of \( \text{Zn}^{2+} \), 90% IE was achieved due to synergistic effect between zinc and phosphonate. Similarly the synergistic effect is noticed at 25 ppm of \( \text{Zn}^{2+} \) ions with different concentrations of the phosphonic acid (Table IV.4) and the \( \text{Zn}^{2+} \)-DTPMP complex is transported towards metal surface and enhances the protective effect.

It is seen from Table IV.1 that 50 ppm of DTPMP has only 11% IE and 50 ppm of \( \text{Zn}^{2+} \) ions is found to be corrosive indicated by the negative IE value \(-22\%\) (Table IV.5). However, the formulation consisting of 50 ppm of \( \text{Zn}^{2+} \) and 50 ppm of DTPMP has an inhibition efficiency (IE) of 89\% (Table IV.5). Further increase in IE, i.e., 90\% is achieved with the increase of DTPMP concentration. This indicates the synergistic effect of DTPMP and \( \text{Zn}^{2+} \) combination. A thin interference film is observed on the surface of the inhibited metal during the weight-loss experiment. Rajendran et al.\(^6\) has reported 95\% inhibition efficiency with 50 ppm of \( \text{Zn}^{2+} \) and 300 ppm of phenyl phosphonate and 95\% IE\(^6\) with the combination of 300 ppm of 2-Cl EPA (2-Chloroethylphosphonicacid) and 300 ppm of \( \text{Zn}^{2+} \). When 50 ppm of \( \text{Zn}^{2+} \) is added to DTPMP, the resultant complex of \( \text{Zn}^{2+} \)-DTPMP is in soluble form and thus diffuses towards the metal surface. On the anodic site, when \( \text{Fe}^{2+} \)-DTPMP complex is formed, \( \text{Zn}^{2+} \) is released. At the cathodic site, the formation of \( \text{OH}^- \) will occur in the presence of oxygen.
Thus the anodic reaction is the formation of Fe\(^{2+}\).

\[
{\text{Fe}} \rightarrow {\text{Fe}}^{2+} + 2{\text{e}}^- \quad (\text{anodic reaction})
\]

The cathodic reaction is the generation of OH\(^{-}\).

\[
{\text{O}_2} + 2\text{H}_2\text{O} + 4{\text{e}}^- \rightarrow 4\text{OH}^- \quad (\text{cathodic reaction})
\]

This accounts for the synergistic effect.\(^{68-71}\)

**IV.2.3 Influence of pH on the inhibition efficiency of DTPMP-Zn\(^{2+}\) system**

pH is a crucial factor for the determination of corrosion inhibition efficiency of phosphonic acids. The nature of pH selectivity of phosphonic acids depends on the metal, the composition of inhibitor, etc. Nitrogen containing phosphonic acids are effective at decreased pH (acidic levels). Vishnudevan and Natesan\(^{72}\) had reported the inhibitor efficiency of N-benzyldimethyl amine in 1 NHCl and H\(_2\)SO\(_4\) acids as 80% in 5 \times 10^{-3}M concentration of inhibitor. This inhibition efficiency on mild steel is dependent on concentration of inhibitor and also the efficiency increases with the increasing concentration of acids. Horvath and Kalman\(^{73}\) used DTPMP in acidic solutions. Raj *et al.*\(^{74}\) have reported 80% IE in neutral aqueous medium after 24 hours for DTPMP-Zn\(^{2+}\) system.
Table IV.6. Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment (Cl\(^-\) = 60 ppm) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: (60 ppm Cl\(^-\) + DTPMP + 50 ppm Zn\(^{2+}\)) at pH = 5
Immersion period: 7 days

<table>
<thead>
<tr>
<th>Conc. of DTPMP, ppm</th>
<th>Conc. of Zn(^{2+}), ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
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</table>

Table IV.7. Results of corrosion rates and inhibition efficiencies calculated for carbon steel in aqueous environment (Cl\(^-\) = 60 ppm) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: (60 ppm Cl\(^-\) + DTPMP + 50 ppm Zn\(^{2+}\)) at pH = 8
Immersion period: 7 days

<table>
<thead>
<tr>
<th>Conc. of DTPMP, ppm</th>
<th>Conc. of Zn(^{2+}), ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
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</thead>
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<td>50</td>
<td>14.70</td>
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</table>
Table IV.8. Results of corrosion rates and the inhibition efficiencies calculated for carbon steel in aqueous environment (Cl\(^-\) = 60 ppm) with and without corrosion inhibitor by weight–loss method.

Inhibitor system: (60 ppm Cl\(^-\) + DTPMP + 50 ppm Zn\(^{2+}\)) at pH =10

Immersion period: 7 days

<table>
<thead>
<tr>
<th>Concentration of DTPMP, ppm</th>
<th>Concentration of Zn(^{2+}), ppm</th>
<th>Corrosion rate, mdd</th>
<th>Inhibition Efficiency (IE), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>15.67</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>12.54</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>13.01</td>
<td>17</td>
</tr>
<tr>
<td>150</td>
<td>50</td>
<td>13.32</td>
<td>15</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>13.63</td>
<td>13</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>13.79</td>
<td>12</td>
</tr>
</tbody>
</table>

The results on the influence of pH on the DTPMP-Zn\(^{2+}\) system is given in Tables IV.5-IV.8. It is seen from Table IV.6 that when the pH is reduced from 7 to 5 (addition of dilute H\(_2\)SO\(_4\)) the inhibition efficiency is reduced very much. For example, the system consisting of 100 ppm of DTPMP and 50 ppm of Zn\(^{2+}\) has IE 90% at pH 7 (Table IV.5) and the IE is reduced to 29% at pH 5 (Table IV.6). When the pH is increased from 7 to 8 and then to 10 (addition of dilute NaOH) the IE is very much lowered when compared to IE at pH 7. This is due to the fact that, at pH 8 and 10 (when NaOH is added) Zn\(^{2+}\) is precipitated as Zn(OH)\(_2\). Hence Zn\(^{2+}\) is not able to transport DTPMP from the bulk of the solutions to the metal surface. This analysis shows that, in acidic and alkaline medium,
DTPMP-Zn\(^{2+}\) system does not show good IE. However, in neutral aqueous medium the same system shows a remarkable IE (Table IV.5).

**Figure IV.3.** Plots of Corrosion rates (C.R) of carbon steel in neutral aqueous environment against [DTPMP].

Inhibitor system DTPMP + Zn\(^{2+}\)

The plots of corrosion rates (C.R) against [DTPMP] at different pHs and different [Zn\(^{2+}\)] are shown in Fig. IV.3. It is noticed from the figure that at DTPMP-Zn\(^{2+}\) complex formed at pH 5 is not able to form protective layer because at this pH value cathodic hydrogen evolution reaction takes place in dilute sulphuric acid medium in a greater speed and the electrons released by the anodic metal
dissolution are consumed with the same speed and hence the corrosion rate 20.33 mdd is higher (Table IV.6) but when 50 ppm of Zn$^{2+}$ and different concentrations of DTPMP are added the corrosion rates decreased to 17 mdd and simultaneously IE increased because the protective layer of DTPMP-Zn$^{2+}$ complex controls the anodic reaction by adsorption on the active anodic sites. Fig. IV.4 shows the corrosion cell formed on a corroding metal surface.

![Corrosion cell](image)

**Figure IV.4.** Corrosion cell formed on heterogeneous surface of a metal.

In neutral aqueous medium i.e., at pH 7 the same system shows a remarkable IE (90%) and there is a decrease in the corrosion rate from 18 mdd to 2 mdd (Table IV.5). This is due to the fact that in neutral solution cathodic oxygen reduction is controlled and added Zn$^{2+}$ ions are able to form and transport DTPMP-Zn$^{2+}$ complex from the bulk of the solution to the metal surface. DTPMP itself can diffuse and adsorb on iron sheet and form DTPMP-Fe$^{2+}$ complex but it is less stable$^{33,58}$ and is formed insoluble form hence Zn$^{2+}$ ions are added as synergist at different pH values.

$$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$$
The added zinc ions form insoluble complexes with phosphonic acid and repair the protective porous oxide layer and prevent further corrosion. It is seen from Tables IV.7 and IV.8 the corrosion rate is almost same as 16 mdd in NaOH at pH 8 and 10 before adding inhibitors. But when 50 ppm of Zn$^{2+}$ and different concentrations of DTPMP there is no remarkable increase in IE because when NaOH is added Zn$^{2+}$ ion is precipitated as Zn(OH)$_2$ and so Zn$^{2+}$ ions are not available for complexation and transportation of the inhibitor to the metal surface. As a result there is increase in corrosion rate at pH 8 and pH 10. This analysis shows that, in acidic and alkaline medium, DTPMP-Zn$^{2+}$ system does not show good IE. But, the same system shows a remarkable IE in neutral aqueous medium.

**IV.2.4 Synergism parameters ($S_I$)**

The synergism parameter ($S_I$)$^{75-77}$ is calculated using the following relation.

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

Where $I_{1+2} = (I_1 + I_2) - (I_1 \times I_2)$

$I'_{1+2} = \text{combined inhibition efficiency of substance 1 and substance 2.}$
Table IV.9. Synergism parameters of (DTPMP + 50 ppm Zn\(^{2+}\)) inhibitor system is given below:

<table>
<thead>
<tr>
<th>Concn. of DTPMP, ppm</th>
<th>I.E. of DTPMP, I.</th>
<th>Concn. of Zn(^{2+}), ppm</th>
<th>I.E. of Zn(^{2+}), I.</th>
<th>Combined I.E. of I(<em>{1} + I</em>{2})</th>
<th>Synergism, (S_{I})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>11</td>
<td>50</td>
<td>-22</td>
<td>89</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>50</td>
<td>-22</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>150</td>
<td>21</td>
<td>50</td>
<td>-22</td>
<td>90</td>
<td>5</td>
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<td>200</td>
<td>24</td>
<td>50</td>
<td>-22</td>
<td>90</td>
<td>6</td>
</tr>
<tr>
<td>250</td>
<td>28</td>
<td>50</td>
<td>-22</td>
<td>90</td>
<td>7</td>
</tr>
</tbody>
</table>

It is observed from Table IV.9 that the negative value of C.R. at 50 ppm of Zn\(^{2+}\) is due to the acceleration of corrosion and the cation is unable to protect the metal surface from the corrosion in the absence of phosphonic acid inhibitor. The combined effect is synergistic.\(^{78}\) The synergism parameters are given in Table IV.9. The synergism parameters (\(S_{I}\)) calculated from surface coverage were found to be more than unity.\(^{79,80}\) This result clearly shows the synergistic effect between DTPMP and Zn\(^{2+}\).

IV.2.5 Analysis of the results of potentiostatic polarization study

The corroding piece of metal is described as a mixed electrode since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode\(^{57}\) is a complete electrochemical cell on one metal surface (Fig. IV.4).

Anodic process is mainly manifested by the metal dissolution reaction whereas in the case of cathodic process a number of reactions can occur. The most common electrochemical reactions in the corrosion of iron are thus:
Anodic reaction (corrosion) \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

Cathodic reactions:

- **Hydrogen evolution** \[ 2\text{H}^- + 2e^- \rightarrow \text{H}_2 \]
- **Oxygen reduction (neutral or basic solution)** \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]
- **Oxygen reduction (acid solution)** \[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]
- **Metal ion reduction** \[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \]
- **Metal deposition** \[ \text{Fe}^{3+} + 2e^- \rightarrow \text{Fe} \]

The above partial reactions can be used to interpret virtually all corrosion problems. In neutral aqueous medium OH\(^{-}\) formation is the major cathodic reaction and hence the overall reactions obtained by adding anodic reaction are:

\[ 2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^- \rightarrow 2\text{Fe(OH)}_2 \downarrow \]

Ferrous hydroxide precipitates from solution. However, this compound is unstable in oxygenated solutions and is oxidized to the ferric salt:

\[ 2\text{Fe(OH)}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Fe(OH)}_3 \downarrow \]

The final product is the familiar rust. The rust is precipitated as a result of secondary reactions it is porous and absorbent and encourages further corrosion. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film, which retards further corrosion then the surface is said to be passive. An example of such a process would be the production of an oxide film on iron in water, a reaction that is encouraged by oxidizing conditions.
\[2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_4 + 6\text{H}^- + 6\text{e}^-\]

The rates of the anodic and cathodic reactions must be equivalent according to Faraday’s law, being determined by the total flow of electrons from anode to cathode, which is called the corrosion current, \(I_{\text{corr}}\). A cathodic or anodic inhibitor affects the rate of cathodic or anodic partial process, respectively. The cathodic inhibitors reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reaction. They displace the corrosion potential in the negative direction and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate. Anodic inhibitors reduce the anode area by acting on the anodic sites and polarize the anodic reaction. They displace the corrosion potential in the positive direction and reduce the corrosion current, thereby retard anodic reaction and suppress corrosion rate. Mixed inhibitors affect both the cathodic and anodic reactions. Potential change in such a case is smaller and its direction is determined by the relative size of the anodic and cathodic effects.

The corrosion parameters of carbon steel in various test solutions are given in Table IV.10. The polarization curves are shown in Fig. IV.5. When carbon steel is immersed in an aqueous solution containing 60 ppm Cl\(^-\), the corrosion potential found to be \(-402\) mV vs. (SCE). When the inhibitor, DTPMP and Zn\(^{2+}\) is added the corrosion potential is shifted to more anodic side \(-179\) mV vs. (SCE). The increase in corrosion potential an the decrease in corrosion current indicate the inhibitive effect of this formulation i.e., \(I_{\text{corr}}\) value decreased from \(6.49 \times 10^{-6}\) A/cm\(^2\) to \(2.20 \times 10^{-6}\) A/cm\(^2\) (blank). This suggests that the formulation of 100 ppm DTPMP and 50 ppm of Zn\(^{2+}\) controls anodic reaction predominantly. The anodic (\(b_a\)) and cathodic (\(b_c\)) Tafel slopes\(^{81-83}\) are almost equal (\(b_a = 65\) mV and \(b_c = 63\) mV).
These results suggest that this formulation functions as a mixed inhibitor, equally controls both the anodic reaction (dissolution of metal) and cathodic reaction (generation of OH$^-$$^84$-$^87$). At the corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution and this point corresponds to the corrosion rate of the system expressed in terms of current density.

Nakayama and Obuchi$^88$ investigated that uric acid was adsorbed on to cathodic areas of the steel through coordination of nitrogen atoms and oxygen in the carbonyl group to the iron cations on the steel.

Morad$^40$ investigated the inhibiting action of propyl, propargyl, cyclopropyl, allyl, 1,3-dioxolan-2-ylmethyl, cinnamyl, tetrabutyl, substituted triphenylphosphoniumbromides and chlorides (PrTPhPBr, P$_g$TPhPBr, C$_p$TPhPBr, ATPhBr, DTPhPBr, CTPhPCl and TbuPBr) on the corrosion of mild steel in aerated acid solutions. He observed that all the studied phosphonium compounds behave as mixed type (little change in corrosion potential for e.g. b$_a$ value ranges between 20-23 mV dec$^{-1}$ and b$_c$ ranges between 23-26 mV dec$^{-1}$ for all the phohonium compounds) in aerated HCl solution. The constancy in b$_c$ values (50, mV dec$^{-1}$ in HCl, 75m mV dec$^{-1}$ in H$_2$SO$_4$ for all phosphonic acids alone indicate no change in the hydrogen evolution reaction (h.e.r.) or iron dissolution. The higher values of b$_a$ for all phosphonic acids in HCl suggests that the mechanism of dissolution is probably changed.

Similarly, Rajendran et al.$^89$ investigated that ethylphosphonic acid (EPA)-Zn$^{2+}$ combination in neutral aqueous medium shifts both the anodic and cathodic slopes of mild steel (b$_a$ = 30 mV vs SCE and b$_c$ = 28 mV vs. SCE ) equally to the extent of 28 mV dec$^{-1}$, indicating that this combination acts as a mixed
inhibitor. They retard the anodic reaction by forming iron–phosphonic acid complex and cathodic reaction by the formation of Zn(OH)_2 on the cathodic sites. Recently, Noor\textsuperscript{90} studied the inhibition of mild steel in phosphonic acid solution by some heterocyclic compounds and reported that this inhibitor system act as mixed type without changing the mechanism of the corrosion process.

**Table IV.10.** Corrosion parameters of carbon steel immersed in 60 ppm Cl\textsuperscript{−} environment by polarization method.

Inhibitor system: (60 ppm Cl\textsuperscript{−}+DTPMP+Zn\textsuperscript{2+}) at pH = 7

Immersion period: 7 days

<table>
<thead>
<tr>
<th>Concn. of Cl\textsuperscript{−}, ppm</th>
<th>Concn. of DTPMP, ppm</th>
<th>Concn. of Zn\textsuperscript{2+}, ppm</th>
<th>E\textsubscript{corr}, mV vs. SCE</th>
<th>b\textsubscript{c}, mV</th>
<th>b\textsubscript{a}, mV</th>
<th>I\textsubscript{corr}, A / cm\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td>-402</td>
<td>100</td>
<td>118</td>
<td>6.49 \times 10^{-6}</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>-179</td>
<td>65</td>
<td>63</td>
<td>2.20 \times 10^{-6}</td>
</tr>
</tbody>
</table>
Figure IV.5. Potentiostatic polarization curves recorded for carbon steel immersed in test solutions.
5(a). Cl\(^{-}\) 60 ppm.
5(b). Cl\(^{-}\) 60 ppm + 50 ppm Zn\(^{2+}\) + 100 ppm DTPMP.

IV.2.6 Analysis of the results of AC impedance spectra

Adsorption of a protective inhibitor on the metal surface causes a significant increase in the impedance of the corrosion system, thus causing an increase in the resistance to the charge-transfer process.\(^{1,6,8,9}\) Therefore the performance of an inhibitor can be determined by measurements of the corrosion system impedance. The degree of the corrosion protection can be determined by comparison of the impedance obtained with the presence and absence of the inhibitor in the environment. The AC impedance method is among the electrochemical techniques used to determine the charge-transfer resistance by measurements of the electrical components of the corrosion systems. Similar to the effect seen on the corrosion potential, the impedance of the steel corrosion system
was affected strongly by the presence of the inhibitors. A single semicircle curve (a) with low polarization resistance value (Table IV.11) is noticed for mild steel immersed in 60 ppm chloride solution (blank). For mild steel immersed in a mixture of inhibitor solution 100 ppm DTPMP and 50 ppm Zn\(^{2+}\), a distinct semicircle curve (b) with high polarization resistance is noticed.

The Nyquist plots\(^{91-93}\) for the corrosion behaviour of carbon steel in 60 ppm Cl\(^-\) medium in the absence and presence DTPMP and Zn\(^{2+}\) are shown in Fig. IV.6. and show only classic semicircles in the entire spectrum. The AC impedance parameters of carbon steel immersed in test solutions are given Table IV.11. When carbon steel is immersed in an aqueous solution containing 60 ppm of Cl\(^-\), the charge transfer resistance R\(_{ct}\) is calculated as 62.60 Ω cm\(^2\). The double layer capacitance C\(_{dl}\) is 1.61 \times 10^{-4} \mu F/cm\(^2\). When a mixture of 100 ppm of DTPMP and 50 ppm of Zn\(^{2+}\) inhibitor solution is added to the above solution, the R\(_{ct}\) value increases from 62.60 Ω cm\(^2\) to 561.25 Ω cm\(^2\). The C\(_{dl}\) value decreases from 1.61 \times 10^{-4} \mu F /cm\(^2\) to 0.45 \times 10^{-4} \mu F/cm\(^2\). These results suggest that a protective film is formed on the metal surface. Because corrosion kinetics (or corrosion rates) is dependent on the charge transfer between anode (oxidizing) and cathode (reducing)\(^{94}\), increase of the charge-transfer resistance means reduction of the corrosion rate. Corrosion kinetics of mild steel may probably shifts from the activation-controlled kinetics in the absence of inhibitor (62.6 Ω cm\(^2\)) to the diffusion-controlled mechanism\(^{95}\) (561.25 Ω cm\(^2\)) in the presence of inhibitor. This also indicates that the inhibitor protected mild steel from corrosion by forming a diffusion barrier film. As a result, the diffusion of corrosive species through the surface film of the inhibitor was a slow step and became the controlling process.
Table IV.11. AC impedance parameters of carbon steel immersed in chloride environment.

Inhibitor system: (60 ppm Cl⁻ + DTPMP + Zn²⁺) at pH = 7

<table>
<thead>
<tr>
<th>Concn. of Cl⁻, ppm</th>
<th>Concn. of DTPMP, ppm</th>
<th>Concn. of Zn²⁺, ppm</th>
<th>R&lt;sub&gt;ct&lt;/sub&gt;, Ω cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>C&lt;sub&gt;dl&lt;/sub&gt;, μF / cm&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td>62.60</td>
<td>1.61 × 10⁻⁴</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>561.25</td>
<td>0.45 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Figure IV.6. AC Impedance curves recorded for carbon steel immersed in test solution.

6(a). Cl⁻ 60 ppm.
6(b). Cl⁻ 60 ppm + 50 ppm Zn²⁺ + 100 ppm DTPMP.

Ashassisorkhabi and Nabaviamri<sup>96</sup> have studied the inhibition effects of diethanolamine (DEA), 3-aminopropanol (3-AP), 2-dimethylethanolamine (2-DEA), cyclohexylamine (CHA), N-methylcyclohexylamine (N-MCA) and dicyclohexylamine (DCHA) by electrochemical impedance spectroscopy (EIS). These compounds were dissolved in some petroleum/water corrosive mixtures.
containing acetic acid and NaCl. The best corrosion inhibition was obtained for the 4% of DEA, which is able to act as polarizing agent on the carbon steel surface and form protective adsorptive layer on the mild steel surface. Ajmal et al.\textsuperscript{97} studied the corrosion inhibiting behaviour of four nitrogen substituted thiobisformamidines-phenyl thiobisformamidines (PTBF), tolyl thiobisformamidines (TTBF), anisidyl thiobisformamidines (ATBF) and 4-chlorophenyl thiobisformamidines (CPTBF) for mild steel in 1 M 3 M and 5 M HCl by electro impedance spectroscopy and proposed a suitable mechanism of inhibition based on $R_{ct}$ and $C_{dl}$ values.

Morad\textsuperscript{40} studied the corrosion of mild steel in aerated acid solutions of HCl and H$_2$SO$_4$ and the inhibitive effect of some substituted phosphonium compounds. He observed that except in HCl solution-containing PgTPhPBr, the charge transfer process controls other inhibitive system processes. In HCl solution containing PgTPhPBr, the corrosion process was found to be under mixed charge transfer and diffusion controlled as indicated from the existence of Warburg impedance. These earlier works are in support to the inhibitive layer formation of DTPMP + Zn$^{2+}$ inhibitor system on the carbon steel in aqueous environment of this study.

IV.2.7 Analysis of FTIR spectra

Sekine and Hirakawa\textsuperscript{61} studied the effect of HEDP on the corrosion of mild steel in 0.3% NaCl by FTIR spectra and indicated the peaks at 1020 and 580 cm$^{-1}$ for the rust components Ferric hydroxide (γ-FeOOH) and magnetite (Fe$_3$O$_4$) respectively in blank solution. The absorption peaks at 1330 cm$^{-1}$ and 1150 cm$^{-1}$ in higher concentration of the HEDP indicator is believed to the absorption of the radicals, $-\text{P} = \text{O}$ and $-\text{P} = \text{O}$ (OH) from the phosphonic acid. Hence it is
suggested that HEDP could act as a rust-removing agent. Rajendran et al.\textsuperscript{65} investigated the influence of carboxymethyl cellulose (CMC) on the inhibition efficiency of 1-hydroxyethane-1,1-diphosphonic acid (HEDP)-Zn\textsuperscript{2+} system in controlling corrosion of mild steel immersed in a neutral aqueous environment containing 60 ppm Cl\textsuperscript{−} by FTIR spectra and the protective film consists of Fe\textsuperscript{2+}-HEDP complex, Fe\textsuperscript{2+}-CMC complex and Zn(OH)\textsubscript{2}.

Recently, Demadis \textit{et al.}\textsuperscript{98} investigated the protective layer formed by the inhibitor system amino-tris-methylene phosphonate (AMP) on mild steel in aqueous environment by FTIR spectra and suggested that the protective layer consists of Zn-AMP complex. Hence earlier studies from the literature revealed that phosphonic acids coordinated through phosphono oxygen atom and nitrogen atom of amino group with metal surface and synergistic complexes with additives like calcium and zinc cations. Thus FTIR spectra study is useful to suggest a probable mechanism for corrosion inhibition.\textsuperscript{64-67,99}

The FTIR spectrum recorded for pure DTPMP is shown in Fig. IV.7(a). The P-O stretching frequency appears at 1059 cm\textsuperscript{-1}. The C-N stretching frequency appears at 1111 cm\textsuperscript{-1}. The P-OH group absorbs at 3000 cm\textsuperscript{-1} and P(O)(OH) group\textsuperscript{100} at 3433 cm\textsuperscript{-1}. The absorption at 1344 cm\textsuperscript{-1} represents P=O stretching. The absorption bands due to the bending of O-P-O appear\textsuperscript{101} at 640 cm\textsuperscript{-1}, 575 cm\textsuperscript{-1} and 490 cm\textsuperscript{-1}. The bending vibration (δ, CH\textsubscript{2} scissoring) of aliphatic tertiary amine group CH\textsubscript{2}N- appears at 1458 cm\textsuperscript{-1}. The weak C-C stretching vibration appears at 951 cm\textsuperscript{-1}, 881 cm\textsuperscript{-1} and 737 cm\textsuperscript{-1}. The aliphatic -CH\textsubscript{2} group appears at 2927 cm\textsuperscript{-1}. The absorption at 1406 cm\textsuperscript{-1} results from the –CH\textsubscript{2} group absorption of -CH\textsubscript{2}P<. Thus diethylenetriaminepentamethylenephosphonic acid
(DTPMP) with molecular formula C₉H₂₈N₃O₁₅P₅ is characterized by the FTIR spectrum.

The FTIR spectrum of the film scratched from the surface of the metal immersed in the environment consisting of 100 ppm of DTPMP, 60 ppm of Cl⁻ and 50 ppm of Zn²⁺ is shown in Fig. IV.7(b). It is observed that P-O stretching frequency decreases from 1059 cm⁻¹ to 1036 cm⁻¹. The C-N stretching frequency decreases from 1111 cm⁻¹ to 1101 cm⁻¹. This suggests that the oxygen and nitrogen atoms of the phosphonic acid are coordinated to Fe²⁺ resulting in the formation of Fe²⁺-DTPMP complex on the anodic sites of the metal surface. The band at 1379 cm⁻¹ results from Zn(OH)₂. It is noteworthy to mention that the same Fe²⁺-DTPMP complex is formed on the metal surface in the presence and absence of Zn²⁺ but with differences in the corrosion inhibition efficiencies. In the absence of Zn²⁺ the film (Fe²⁺-DTPMP complex) is not able to protect the metal surface from corrosion due to the constant action of aggressive chloride ion. On the other hand, in the presence of Zn²⁺ and DTPMP, besides the formation of Fe²⁺-DTPMP complex at the anodic sites, there is formation of Zn(OH)₂ at the cathodic site, which controls the cathodic reaction.
Figure IV.7. FTIR spectra of DTPMP (a) and for the film formed on the carbon steel immersed in test solutions (a) and (b).
7(a). Pure DTPMP.
7(b). Mixture of Cl\(^-\) 60 ppm, 50 ppm Zn\(^{2+}\) and 100 ppm DTPMP.

IV.2.8 Analysis of optical micrographs

Giacomelli et al.\textsuperscript{104} studied the inhibitor effect of succinic acid on the corrosion-resistance of mild-steel by optical microscopic studies and established the protective layer formation from photographic images. The photomicrographs of mild steel specimens immersed in the presence and absence of inhibitor systems shown in Figs. IV.8(a-e). Fig. IV.8(e) shows the corrosion protection of carbon steel by the inhibitor system (60 ppm Cl\(^-\), 50 ppm Zn\(^{2+}\) and 100 ppm DTPMP).
Fig. IV.8(a) shows the surface due to atmospheric corrosion.

Fig. IV.8(b) shows the smooth surface on the polished metal piece.

Fig. IV.8(c) indicates the corrosion products spread on the surface by the aggressive Cl\(^-\) ions in the blank solution.

Fig. IV.8(d) shows partial removal of rusts by Zn\(^{2+}\) system.

Fig. IV.8(e) illustrates the metal surface exposed to the inhibitor system of 60 ppm Cl\(^-\), 50 ppm Zn\(^{2+}\) and 100 ppm DTPMP. The resultant metal surface was smooth and resembles a polished surface, due to the inhibitive action of phosphonic acid system.

**Figure IV.8.** Photomicrographs of mild steel specimens before and after immersion in the presence and absence of the inhibitor.

**Figure IV.8(a).** Unpolished metal surface before immersion.

**Figure IV.8(b).** Polished surface of mild steel before immersion.
Figure IV.8(c). Polished surface of mild steel after immersion in blank 60 ppm Cl\(^-\) solution.

Figure IV.8(d). Polished surface of mild steel after immersion in a mixture of 60 ppm Cl\(^-\) and 50 ppm Zn\(^{2+}\) solution.

Figure IV.8(e). Polished surface of mild steel after immersion in a mixture of 60 ppm Cl\(^-\), 50 ppm Zn\(^{2+}\) and 100 ppm DTPMP (inhibitor) solution.
IV.2.9 Analysis of atomic force micrographs (AFM)

The coated protective films on mild steel are examined with Atomic Force Microscope (AFM). The topography of all the samples for a scanned area of 5 nm × 5 nm (25 nm²) is evaluated for a set point of 10 nA and a scan speed of 10 mm/s. The three-dimensional (3D) images of topography in forward and reverse direction indicates many important parameters like roughness of metal surface (Rms) and potentiality of the metal. Zmax voltage indicates the conducting feature of thin films on the metal surface. The contact mode of operation used in this analysis is known as constant force, which enables to obtain a topographical image (hence the alternative name, height mode). Height image data given by AFM is three-dimensional. The usual method for displaying the data is to use a color mapping for height, black for low features and white for high features (Fig. IV.9). Popular choice of color scheme is shown on the left. Similar color mappings can be used for non-topographical information such as phase or potential. The Table IV.12 shows various AFM parameters obtained when the carbon steel surface immersed in different environments.

Atomic force microscopy provided direct insight into the changes in the surface morphology takes place at several hundred nanometers when topographical changes owing to the initiation of corrosion and formation of protective film on the metal surface in the presence and absence of the inhibitors, respectively. It is also used to determine the time-dependent thickness of protective film. The 2D and 3D AFM images of carbon steel specimens immersed in the presence and absence of inhibitor systems are shown in Figs. IV.9(a-e).
Fig. IV.9(a) shows roughness of polished metal surface and $Z_{\text{max}}$ value of 0.51 V. When compared with other thin film coated surfaces, the value indicates the absence of iron oxide on the smooth surface.

Fig. IV.9(b) indicates the 2D and 3D images of polished metal immersed in 60 ppm Cl$^-$ for a time duration of 10 min. The increased value of $Z_{\text{max}}$ of 1.14 V shows the formation of iron oxide on the surface of carbon steel.

Fig. IV.9(c) shows the 2D and 3D images of thin film on the metal surface of carbon steel, which was immersed in a mixture of 60 ppm Cl$^-$ and 50 ppm Zn$^{2+}$ solution with increased Rms value of 253 nm and $Z_{\text{max}}$ value of 0.78 V.

Figs. IV.9(d) and IV.9(e) shows the 2D and 3D images of carbon steel immersed in a mixture of 60 ppm Cl$^-$, 50 ppm Zn$^{2+}$ and 100 ppm DTPMP for 10 min. and 48 hrs duration. With the increase in immersion period, both parameters viz., Rms and $Z_{\text{max}}$ have also increased. The values of roughness (Rms) has increased from 180 nm to 234 nm and $Z_{\text{max}}$ has increased from 0.75 V to 0.95 V. These increased values strongly conclude the formation of protective film on the metal surface.
Table IV.12. AFM parameters of carbon steel immersed in neutral aqueous environment.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Period of immersion</th>
<th>AFM parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished metal</td>
<td>-</td>
<td>Rms, nm</td>
</tr>
<tr>
<td>Polished metal in 60 ppm Cl⁻</td>
<td>10 min</td>
<td>143.98</td>
</tr>
<tr>
<td>Polished metal immersed 60 ppm Cl⁻ and 50 ppm Zn²⁺</td>
<td>10 min</td>
<td>115.44</td>
</tr>
<tr>
<td>Polished metal immersed in a mixture 60 ppm Cl⁻, 50 ppm Zn²⁺ and 100 ppm DTPMP</td>
<td>10 min</td>
<td>115.44</td>
</tr>
<tr>
<td>Polished metal immersed in a mixture 60 ppm Cl⁻, 50 ppm Zn²⁺ and 100 ppm DTPMP</td>
<td>48 hrs</td>
<td>179.51</td>
</tr>
</tbody>
</table>

Figure IV.9. Atomic Force Micrographs (AFM) of mild steel specimens before and after immersion in the presence and absence of the inhibitor.

![AFM images](image)

Figure IV.9(a). 2D and 3D AFM images of polished metal surface.
Figure IV.9(b). 2D and 3D AFM images of polished metal surface after immersion in blank 60 ppm Cl\(^-\) solution.

Figure IV.9(c). 2D and 3D AFM images of polished metal surface after immersion in a mixture of 60 ppm Cl\(^-\) and 50 ppm Zn\(^{2+}\) solution.
**Figure IV.9 (d).** 2D and 3D AFM images of polished metal surface after immersion in a mixture of 60 ppm Cl$^-$, 50 ppm Zn$^{2+}$ and 100 ppm DTPMP (inhibitor) solution for 10 min.

**Figure IV.9(e).** 2D and 3D AFM images of polished metal surface after immersion in a mixture of 60 ppm Cl$^-$, 50 ppm Zn$^{2+}$ and 100 ppm DTPMP (inhibitor) solution for 48 hrs.
IV.3 Biocidal efficiency study

IV.3.1 Microbial corrosion- Introduction

Biological corrosion\textsuperscript{6} is the deterioration of a metal by corrosion processes that occur directly or indirectly as a result of activity of living organisms. These organisms include microforms such as bacteria and macro types such as algae and barnacles. These organisms have been observed to live and reproduce in mediums with pH values between 0 and 11 and temperatures between 30 and 180\textdegree F. Thus biological activity may influence corrosion in a variety of environments including soil, natural water and seawater, natural petroleum products, and oil emulsion-cutting fluids. Living organisms are sustained by chemical reactions i.e., organisms consume a reactant or food and eliminate waste products. These processes can affect corrosion behavior in the following ways:

1. By directly influencing anodic and cathodic reactions.
2. By influencing protective surface films.
3. By creating corrosive conditions.
4. By producing deposits.

These effects may occur singly or in combination, depending on the environment and the organism involved. Microorganisms\textsuperscript{110} include anaerobic (require oxygen for their metabolic processes, e.g., sulphate reducing bacteria) and aerobic (grow only on little or on oxygen, e.g., iron bacteria-crenothrix and leptothrix, sulphate oxidizing, thiosulphate oxidizing) type bacteria.

Hossain and Das\textsuperscript{111a} studied the kinetic and thermodynamics of microbial corrosion reaction on the surface of mild steel in 3\% NaCl solution and
found that adsorption of inhibitor molecules on the metal surface is exothermic but it is endothermic in the presence of bacteria. Increased activation energy shows that in the absence of bacteria corrosion is inhibited by the increased surface coverage of inhibitors. But when a bacteria named pseudomonas aeruginosa is added in the same medium, probably depleted the adsorbed inhibitors and uncovered the active sites to be accessed to the corrosive medium and thus accelerated the corrosion reaction.

The attachment of bacterial slime has probably hindered the transport of oxygen molecules to the metal surface and developed distinct anodic and cathodic areas that resulted localized corrosion by forming differential aeration cell. Microbial colonization of metals and alloys of industrial usage\textsuperscript{111b} takes place through the formation of biofilms made of bacteria, extracellular polymeric substances (EPS) and mainly water. These biological deposits can drastically modify the corrosion behavior of structural metals and alloys enhancing localized alterations in the type and concentrations of ions, pH, and oxygen levels. Problems due to biocorrosion and biofouling of industrial systems range from heavy microbiological contamination with consequent energy and efficiency losses to structural failures owing to corrosion. Cleaning procedures, most relevant biocides and other methods for prevention and control of biocorrosion like coatings, and cathodic protection are successively used in industries. Fouling and corrosion\textsuperscript{111c} are the two important operational discrepancies in heat exchangers and associated cooling water system pipelines. The problems include flow blockage of pipes, pipe punctures and unacceptable corrosion rates of the system components. For controlling fouling and corrosion, continuous addition of inhibitors as well as the addition of biocides every week or once in a fortnight is explored. Hence the phenomenon of studying the
effect of inhibitors and biocides is quite essential. Generally chlorine or hypochlorites are used as biocides in aqueous environments for the prevention of biofouling, microbial corrosion and or other microbial metabolic activities of microorganisms on metal surface, which directly influence corrosion process.\textsuperscript{112} Microheterogeneous systems are of two types: molecular aggregates composed of surfactants or lipids and organic or inorganic polymeric systems and supports.

The hydrocarbon chains align themselves to form an inner hydrophobic part while the polar head groups are located at the hydrocarbon-water interface. Depending on the nature of the head group these aggregates can be cationic, anionic or nonionic.

**Cationic**

CH$_3$(CH$_2$)$_{15}$N$^+$((CH$_3$)$_3$Br (N-cetyl-N,N,N-trimethylammoniumbromide, CTAB)

CH$_3$(CH$_2$)$_{15}$N$^+$C$_5$H$_5$ Cl$^-$ (N-cetylpyridiniumchloride, CPC)

**Anionic**

CH$_3$(CH$_2$)$_{11}$OSO$_3^-$Na$^+$, (SDS)

**Nonionic**

CH$_3$CH$_2$$_{12}$OCH$_2$CH$_2$)$_2$OH, (Brij 35)

Surfactants have also been used as corrosion inhibitors\textsuperscript{49,113} or in combination with other compounds such as organophonates\textsuperscript{114}, transcinnamaldehyde\textsuperscript{115} and 1-phenyl-2-propyne-1-ol\textsuperscript{116} to enhance their performance as inhibitors. Non-ionic surfactants are found to have marked inhibiting efficiency on iron in acidic media by adsorption on to its surface.\textsuperscript{117} The biocidal inhibitive effect of sodium dodecyl sulphate (SDS) anionic surfactant\textsuperscript{118} for mild steel in HCl have been reported. The present work is undertaken to evaluate the biocidal efficiency of two cationic surfactants CTAB and CPC in controlling corrosion of carbon steel immersed in a mixture of 60 ppm Cl$^-$, 50 ppm Zn$^{2+}$ and 100 ppm DTPMP inhibitor
solution by bioslyde method. In the present study N-cetyl-N,N,N-trimethylammonium bromide (CTAB)$^{119,120}$ and N-cetylpyridiniumchloride (CPC)$^{49,111(c),121(a)}$ are used as biocides.

**IV. 3.2 Determination of biocidal efficiency of the system**

The phosphonicacid-Zn$^{2+}$ formulation that offered the best corrosion inhibition efficiency was selected. The biocidal efficiency of N-cetyl-N,N,N-trimethylammoniumbromide (CTAB) and CPC in the presence of different inhibitor system are determined.

**Microbe detection device-Bactaslyde**

![Figure IV.10. Schematic representation of Bactaslyde usage procedure.](image)

1. Cut, open poly bag.
2. Bactaslyde.
3. Dip for 20-25 seconds, use a clean container to hold the test material.
4. The outer cover can be used to hold the test material.
5. Incubate in warm place.
Various concentrations of CTAB namely 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm are added to the formulation consisting of the inhibitor system, polished and degreased carbon steel specimens in triplicate were immersed in these environments for a period of 7 days. After 7 days, easy to use BACTASLYDE (tailor made bioslyde to detect bacterial growth in an incubated medium shown in Fig.IV.10) is dipped in each test solution containing phosphonic acid and synergists viz., Zn$^{2+}$, TSC, SG, SM and SPT for 20-25 seconds. The slydes are then incubated in a warm place for 24 hours to ensure rapid growth of microbial bacteria present in the inhibitor system, which causes microbial corrosion. After incubation the slydes are matched with density chart shown in Fig. IV.11 and the total viable heterotrophic bacterial colonies formed for each ml (CFU/ml-biological unit to count bacterial colonies) of the solution is counted and used for calculating biocidal inhibition efficiencies of the biocides CTAB and CPC. The corrosion
inhibition efficiencies of the formulations consisting of the inhibitor in the presence of various concentrations of CTAB are determined in the same way. Similarly the experiment is carried out with N-cetylpyridiniumchloride (CPC).

IV.3.3 Influence of DTPMP-Zn$^{2+}$ system on the biocidal efficiency of CTAB

The biocidal efficiency$^{42,122-125}$ of DTPMP-Zn$^{2+}$-CTAB system is given in Table IV.13. It is found that CTAB shows very good biocidal efficiency in a wide concentration range (i.e., 10 to 250 ppm). It seems that CTAB has biocidal activity as it aggregates together. The number of bacterial colonies formed as a function of concentration of CTAB in presence of DTPMP-Zn$^{2+}$-CTAB system is shown in Fig. IV.12. Mild steel widely used in the fabrication of cooling water pipes and heat exchanger tubes.$^{126,127}$ Fouling and microbial corrosion causes many problems and if the water used in these systems contain $1 \times 10^4$ CFU/ml then there is no problem of microbial corrosion. When 10 ppm of CTAB along with the inhibitor DTPMP-Zn$^{2+}$ is added unacceptable value of $2.4 \times 10^3$ CFU/ml is counted. 50 ppm CTAB in the same system has shown no sign of colonies in the system. It proves that a mixture of 60 ppm Cl$^-$, 100 ppm DTPMP, 50 ppm Zn$^{2+}$ and 50 ppm CTAB provides 100% biocidal efficiency. The 100% biocidal efficiency as evidenced by reported results in earlier works$^{122-128}$ proved that the cationic surfactant CTAB along with other organic and inorganic inhibitors may be applied as an excellent biocide in cooling water systems.
Table IV.13. Biocidal efficiencies of CTAB at various environments.

Inhibitor system: Carbon steel immersed in (DTPMP+Zn\(^{2+}\)+CTAB) at pH = 7

<table>
<thead>
<tr>
<th>Concen. of Cl(^-), ppm</th>
<th>Concen. of DTPMP, ppm</th>
<th>Concen. of Zn(^{2+}), ppm</th>
<th>Concen. of CTAB, ppm</th>
<th>Bulk bacterial count, CFU/ml</th>
<th>Biocidal Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0 \times 10^7</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>0</td>
<td>1.0 \times 10^5</td>
<td>99.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>10</td>
<td>1.0 \times 10^4</td>
<td>99.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>25</td>
<td>2.4 \times 10^3</td>
<td>99.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>100</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>150</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>200</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>250</td>
<td>Nil</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Figure IV.12** Number of colony forming units as a function of concentration of biocide CTAB.

CFU/ml: Biological unit to count number of bacterial colony forming units in one ml of an incubated sample solution.
IV.3.4 Influence of DTPMP-Zn$^{2+}$ system on biocidal efficiency of CPC

The biocidal efficiency of DTPMP-Zn$^{2+}$-CPC system is given in Table IV.14. It is found that CPC has very good biocidal efficiency in a wide concentration range (i.e., 10 to 250 ppm). It seems that CPC has biocidal activity as it aggregates together. The number of bacterial colonies formed as a function of concentration of CTAB in presence of DTPMP-Zn$^{2+}$-CPC system is shown in Fig. IV.13. When 10 ppm of CTAB along with the inhibitor DTPMP-Zn$^{2+}$ is added unacceptable value of $2.4 \times 10^3$ CFU/ml is counted. However, when 50 ppm CTAB of the same system has shown no sign of colonies in the system. It proves that a mixture of 60 ppm Cl$^-$, 100 ppm DTPMP-50 ppm Zn$^{2+}$-50 ppm CPC, provides 100% biocidal efficiency. The 100% biocidal efficiency is evidenced by reported results in earlier works$^{119,125}$ proved that the cationic surfactant CPC along with other organic and inorganic inhibitors may be used as an excellent biocide in cooling water systems.
Table IV.14. Biocidal efficiencies of CPC at various environments.

Inhibitor system: Carbon steel immersed in (DTPMP+Zn\textsuperscript{2+} + CPC) at pH = 7

<table>
<thead>
<tr>
<th>Conc. of Cl\textsuperscript{-}, ppm</th>
<th>Conc. of DTPMP, ppm</th>
<th>Conc. of Zn\textsuperscript{2+}, ppm</th>
<th>Conc. of CPC, ppm</th>
<th>Bulk bacterial count, CFU/ml</th>
<th>Biocidal Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0 × 10\textsuperscript{7}</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>0</td>
<td>1.0 × 10\textsuperscript{5}</td>
<td>99.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>10</td>
<td>2.6 × 10\textsuperscript{4}</td>
<td>99.00</td>
</tr>
<tr>
<td>.60</td>
<td>100</td>
<td>50</td>
<td>25</td>
<td>2.4 × 10\textsuperscript{3}</td>
<td>99.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>100</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>150</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>200</td>
<td>Nil</td>
<td>100.00</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>250</td>
<td>Nil</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure IV.13. Number of colony forming units as a function of concentration of biocide CPC.
IV.3.5 Comparative study of biocidal efficiencies of CTAB and CPC on mild steel in neutral aqueous medium of DTPMP-Zn$^{2+}$ inhibitor system

Ebenso$^{121(b)}$ investigated the synergistic effect of halides on the IE of 2-acetyphenthiazine on Al in H$_2$SO$_4$ and reported that bromide ions reduce the IE of the added inhibitor than chloride ions, which clearly indicates that the radii and the electronegativities of halides play a significant role in adsorption process. However, Oguzie$^{77}$ observed inhibition antagonism and synergism by halide ions on the inhibition effect of congored dye inhibitor on the corrosion of mild steel in H$_2$SO$_4$. CTAB and CPC, both the cationic biocides show 100% biocidal efficiency with the DTPMP-Zn$^{2+}$ inhibitor system.

IV.3.6 X-ray diffraction study

Surface evaluation technique by XRD analysis is used to determine the nature of protective film formed on the metal surface. Favre and Landolt$^{129}$ reported the possible and detailed composition of atmospheric rust formed on the mild steel in presence and absence of gallic acid and tannin inhibitor by XRD analysis. Santana et al.$^{130}$ carried out a detailed study on the nature of corrosion product formed on carbon steel exposed to marine atmosphere in the province of Las Palmas (The Canary islands, Spain) by XRD anaysis and reported the composition of rust as akagenite ($\beta$-FeOOH), lepidocrocite ($\gamma$-FeOOH), goethite ($\alpha$-FeOOH), magnetite (Fe$_3$O$_4$) and haematite (Fe$_2$O$_3$) which are typical in the case of carbon steel as seen in other studies. As the present study aims to find out the IE of phosphonates it is highly relevant to illustrate the anticorrosive nature of Delhi
Balasubramaniam\textsuperscript{131} reported the detailed rust characterization of the corrosion resistant of Delhi (India) iron pillar by XRD study and reported that the major constituent along with the amorphous $\alpha,\beta,\gamma$-iron oxyhydroxides and iron oxides is iron hydrogen phosphate hydrate ($\text{FePO}_4\cdot\text{H}_3\text{PO}_4\cdot4\text{H}_2\text{O}$) as shown in Fig. IV.14. The corrosion resistance of Delhi Iron Pillar is due to the environment and iron with its high P content conferring protection by the formation of the crystalline iron hydrogen phosphate. Rajendran \textit{et al.}\textsuperscript{125,132} reported the nature of protective film formed by HEDP-$\text{Zn}^{2+}$ inhibitor system by XRD analysis. Rajendran \textit{et al.}\textsuperscript{133,134} also investigated the anticorrosive protective layer formed on the carbon steel by EPA-$\text{Zn}^{2+}$ inhibitor system and CMPA, 2-CEPA-$\text{Zn}^{2+}$ inhibitor system by XRD analysis and indicated that the thin protective film contains only iron peaks and the peaks due to rusts are absent on the metal surface after immersion in the inhibitor systems.
Figure IV.1. Schematic representation of rust structure formed on mild steel, weathering steel and Delhi iron pillar.\(^{131}\)

**IV.3.7 Analysis of X-ray diffraction patterns**

The X-ray diffraction (XRD) patterns of the film formed on the surfaces of the carbon steel specimens immersed in various test solutions are shown in Fig. IV.15. The peaks due to the presence of usual corrosion products namely goethite (\(\alpha\)-FeOOH), lepidocrocite (\(\gamma\)-FeOOH), magnetite (Fe\(_3\)O\(_4\)) and the absence of these peaks in the inhibitor systems are shown clearly in these figures. The various diffraction parameters such as the glancing angle (2\(\theta\)), interplanar spacing
(d), intensity of the peaks (I) and the relative intensities of the peaks (I/I₀) are shown in Table IV.15.

**Table IV.15.** XRD parameters of carbon steel surface immersed in various Environments.
Inhibitor system: (DTPMP-Zn²⁺) at pH = 7

<table>
<thead>
<tr>
<th>Environment</th>
<th>Peak No.</th>
<th>Glancing angle, 2θ, Degree</th>
<th>Interplanar Spacing, d, Å</th>
<th>Intensity I, CPS</th>
<th>Relative Intensity, I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Unpolished Metal</td>
<td>1</td>
<td>13.72</td>
<td>6.44</td>
<td>6</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>14.79</td>
<td>5.98</td>
<td>8</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>33.35</td>
<td>2.68</td>
<td>10</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>36.65</td>
<td>2.45</td>
<td>6</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37.50</td>
<td>2.39</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>43.36</td>
<td>2.08</td>
<td>7</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>44.66</td>
<td>2.02</td>
<td>134</td>
<td>4191</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>64.95</td>
<td>1.43</td>
<td>25</td>
<td>709</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>69.31</td>
<td>1.35</td>
<td>15</td>
<td>453</td>
</tr>
<tr>
<td>(b) Polished metal</td>
<td>1</td>
<td>44.55</td>
<td>2.03</td>
<td>260</td>
<td>4952</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>64.89</td>
<td>1.43</td>
<td>49</td>
<td>933</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>73.60</td>
<td>1.28</td>
<td>20</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>78.45</td>
<td>1.21</td>
<td>14</td>
<td>147</td>
</tr>
<tr>
<td>(c) Polished metal in 60 ppm Cl⁻</td>
<td>1</td>
<td>30.90</td>
<td>2.89</td>
<td>15</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>35.59</td>
<td>2.51</td>
<td>13</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>37.13</td>
<td>2.41</td>
<td>10</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>44.76</td>
<td>2.02</td>
<td>348</td>
<td>5709</td>
</tr>
<tr>
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<td>706</td>
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<td></td>
<td>6</td>
<td>76.41</td>
<td>1.24</td>
<td>30</td>
<td>304</td>
</tr>
<tr>
<td>(d) Polished metal immersed in a mixture of 60 ppm Cl⁻, 50 ppm Zn^{2+} and 100 ppm DTPMP</td>
<td>1</td>
<td>44.72</td>
<td>2.02</td>
<td>360</td>
<td>6518</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>63.73</td>
<td>1.45</td>
<td>24</td>
<td>223</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>65.03</td>
<td>1.43</td>
<td>49</td>
<td>841</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>71.91</td>
<td>1.31</td>
<td>11</td>
<td>117</td>
</tr>
</tbody>
</table>
Figure IV.15 XRD patterns of carbon steel surface immersed in various environments.
15(a). Unpolished metal before immersion.
15(b). Polished metal before immersion.
15(c). Polished metal after immersion in blank (60 ppm Cl\textsuperscript{-}) solution.
15(d). Polished metal after immersion in a mixture of 60 ppm Cl\textsuperscript{-}, 50 ppm Zn\textsuperscript{2+} and 100 ppm DTPMP inhibitor solution.
The XRD pattern of the surface of unpolished metal is shown in Fig. IV.15(a). It contains peaks due to rust constituents $\gamma$-FeOOH ($2\theta = 13.72^\circ, 14.79^\circ, 37.50^\circ$ and $43.36^\circ$) and $\alpha$-FeOOH ($2\theta = 33.35^\circ$ and $36.65^\circ$). The peak due to iron appears at $2\theta = 44.66^\circ$, $64.95^\circ$ and $69.31^\circ$. In the case of polished metal, (XRD pattern shown in Fig. IV.15(b)) the peaks due to iron appear at $2\theta = 44.55^\circ$, $64.89^\circ$, $73.61^\circ$ and $78.46^\circ$. When the metal specimen immersed in 60 ppm Cl$^-$ solution (XRD pattern shown in Fig. IV.15(c)) peaks due to magnetite $^{130}$ (Fe$_3$O$_4$) appear at $2\theta = 30.91^\circ$, $35.60^\circ$ and $37.13^\circ$ appear in addition to iron peaks. This indicates that in the chloride environment, carbon steel specimen has undergone corrosion due to the aggressive chloride ions leading to the formation of magnetite. Thus peaks correspond to iron oxide/iron oxyhydroxides indicates that they are the major constituents of rust formed on the steel surface exposed in presence/absence of Cl$^-$ environment.

The XRD pattern of surface of the metal immersed in the solution containing 60 ppm Cl$^-$, 50 ppm Zn$^{2+}$ and 100 ppm DTPMP is shown in Fig. IV.15(d). The peaks due to iron appear at $2\theta = 44.73^\circ$, $65.04^\circ$, $63.73^\circ$ and $71.91^\circ$. The peaks due to oxides of iron such as $\alpha$-FeOOH, $\gamma$-FeOOH and Fe$_3$O$_4$ are found to be absent. The XRD pattern resembled that of the polished metal may be due to the thin protective film $^{133-135}$ formed by the DTPMP-Zn$^{2+}$ inhibitor system.

**IV.3.8 Mechanism of corrosion inhibition**

Results of the weight-loss method reveal that the formulation consisting of 60 ppm of Cl$^-$, 50 ppm of Zn$^{2+}$ and 100 ppm of DTPMP offers an inhibition efficiency of 90%. Polarization study shows that this formulation functions like a mixed inhibitor. AC impedance spectra indicate the presence of a
protective film on the metal surface. FTIR spectra reveal that the protective film consists of Fe$^{2+}$-DTPMP complex and Zn(OH)$_2$. Optical micrographic images and AFM images indicate the possibility of formation of protective layer on the metal surface and its surface morphology. XRD pattern of the protective film corresponds to the absence of peaks due to the usual rust components i.e., iron oxide/iron oxyhydroxides and the presence of iron peaks only. The biocidal efficiency of N-cetyl-N,N,N-trimethyl ammonium bromide(CTAB) and N-cetyl pyridinium chloride(CPC) with the DTPMP and Zn$^{2+}$ inhibitor system in controlling corrosion of carbon steel in aqueous environment containing copper Cl$^-$ has been investigated.

In order to explain all these observations in a holistic way, the following mechanism of corrosion inhibition is proposed.$^{30,62}$

1). When mild steel specimen is immersed in the neutral aqueous environment, the anodic reaction is

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

and the cathodic reaction is

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

2). When the formulation consisting of 60 ppm of Cl$^-$, 100 ppm of DTPMP and 50 ppm of Zn$^{2+}$ is used, the Zn$^{2+}$-DTPMP complex formed in solution at pH 7.

3). When carbon steel is immersed in this solution the Zn$^{2+}$-DTPMP complex diffuses from the bulk of the solution to the metal surface.

4). On the metal surface the Zn$^{2+}$-DTPMP complex is converted into Fe$^{2+}$-DTPMP complex on the local anodic sites as the latter is more stable than the former.$^{136}$
\[ \text{Zn}^{2+} \text{-DTPMP} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} \text{-DTPMP} + \text{Zn}^{2+} \]

(This reaction takes place in the anodic regions of the metal surface)

5). The released \( \text{Zn}^{2+} \) ions combine with \( \text{OH}^- \) ions forming \( \text{Zn(OH)}_2 \) precipitate on the local cathodic sites.

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \]

6). Thus the protective film consists of \( \text{Fe}^{2+}\text{-DTPMP} \) complex, \( \text{Zn(OH)}_2 \) and oxides of iron.\(^{14,114,130}\)
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