The corrosivity of the cooling water in industries is increased by the content of chloride and dissolved oxygen. The pond waters used for recirculation contain 60-120 ppm of chloride ions. The use of corrosion inhibitors in cooling water systems reduce the frequency of maintenance and inspection shutdown which permit more extensive use of iron and carbon steels or low alloy steels.

Interphase inhibitors are effective for the protection of steel against corrosion in neutral low chloride solutions. They form weakly soluble compounds with the metal ions in solution, which precipitate on to the surface to form a three dimensional protective layer. Such inhibitors in the cooling water treatment are composed of phosphonic acids. Organophosphonic acids are used extensively to prevent the corrosion of mild steel in cooling waters. Synergistic inhibition was offered by phosphonic acids in the presence of metal cations.

The present work deals with the development of tartrate-based ethylene diamine phosphonic acid (TEDPA) and studies on the synergistic inhibition of this polymer in the presence of zinc ions by electrochemical methods and weight loss method.

**Experimental Procedure**

- Tartrate-ethylene diamine (TED) was prepared first. 0.1 M of tartaric acid was dissolved in 200 mL of distilled ethanol. 0.1 M of ethylene diamine in 200 mL of ethanol was added dropwise to this mixture with constant stirring. The white solid obtained was heated up to 140°C under nitrogen atmosphere for about an hour and cooled to 30°C. A change of colour from colourless to brownish yellow indicated the formation of tartrate-ethylene diamine polymer.

- Then tartrate-ethylene diamine phosphonic acid (TEDPA) polymer was obtained as follows: 0.1 M of tartrate ethylene diamine polymer and 0.2 M of phosphorous acid were dissolved in 200 mL acetic acid and refluxed under N₂ for 16 h. At the end of the distillation, a viscous brown coloured tartrate ethylene diamine phosphonic acid liquid (90% yield by weight) was obtained.

- Iron (II)-TEDPA polymer complex—To a neutral solution of TEDPA, dilute ferrous sulphate solution was added. The resulted residue was filtered, washed with distilled water and dried.

- Iron (III)-TEDPA polymer complex—Neutral ferric chloride solution was added slowly to dilute neutral TEDPA polymer solution. The residue was filtered, washed with distilled water and dried.

- Zinc (II)-TEDPA polymer complex—Dilute ZnSO₄ solution was added to neutral TEDPA polymer solution. The residue was filtered, washed with distilled water and dried.

Electrochemical measurements were carried out on 0.5 cm dia circular mild steel electrodes. The
electrode surfaces were polished successively in 1/0 to 4/0 emery papers and degreased with trichloroethylene. A three electrode cell assembly was used. The mild steel specimen was used as the working electrode, large platinum foil as counter electrode and saturated calomel electrode as reference electrode. The polarisation studies were carried out using EG & G PAR Model 1731 potentiostat in combination with Model 175 universal programmer and Rikadenki X-Y recorder. The test solution was prepared by dissolving sodium chloride in triple distilled water to maintain a concentration of 60 ppm of chloride.

Mild steel specimens of the composition 0.02-0.3%, 0.03-0.6% P, 0.4-0.5% Mn, 0.1-0.2% C and rest iron were used. The specimens of the dimensions 1x4x0.2 cm were used for weight change and surface examination studies.

Mild steel specimens in triplicate were immersed in 100 mL of the test solutions for a period of 7 days. The specimens were cleaned thoroughly to remove the film, dried and weighed. The changes in weights were recorded.

The percentage inhibition efficiency
\[ \frac{W_1 - W_2}{W_1} \times 100 \]

where \( W_1 \) and \( W_2 \) are weight losses of steel in uninhibited and inhibited chloride solutions.

The polished mild steel specimens were completely immersed in 60 ppm chloride solutions in the presence of inhibitor. After 3 days, the specimens were taken out, washed with distilled water and dried. From the dried specimens, the surface film was scratched carefully and the powder obtained was thoroughly mixed so as to make it uniform. FT-IR spectrum of the powder (KBr pellet) was recorded using Perkin Elmer 1600 FT-IR spectrometer.

Results and Discussions

Fig. 1 presents the variation of the percentage inhibition efficiency of mild steel in 60 ppm chloride solution with various concentrations of TEDPA and zinc ions. In the absence of polymer, addition of zinc ions accelerated the corrosion. This suggests that zinc ions react with the intermediate formed on iron dissolution and accelerated corrosion. Below 50 ppm of zinc ions the presence of the TEDPA accelerated corrosion. In the absence of zinc ions, at all concentrations TEDPA, acceleration of corrosion was seen. 50 ppm zinc ions and 50 ppm TEDPA polymer combination offered an inhibition efficiency of while 100 ppm TEDPA and 100 ppm zinc ions gave an efficiency of >95%.

Fig. 2 presents the typical polarisation curves for mild steel in 60 ppm chloride solutions and solutions containing \( \text{Zn}^{2+} \) ions and TEDPA polymers. The linear segments of the anodic and
Table 1—Parameters derived from polarisation curves for steel in 60 ppm chloride solutions at \( \text{pH} \) and 30°C

<table>
<thead>
<tr>
<th>System</th>
<th>Tafel slopes (mV/decade)</th>
<th>Corrosion current (( \mu \text{A} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anodic (±5)</td>
<td>Cathodic (±5)</td>
</tr>
<tr>
<td>(a) 60 ppm Cl(^-) solution</td>
<td>54</td>
<td>110</td>
</tr>
<tr>
<td>(b) 50 ppm Zn(^{2+}) ions + 100 ppm polymer</td>
<td>80</td>
<td>110</td>
</tr>
<tr>
<td>(c) 80 ppm Zn(^{2+}) ions + 100 ppm polymer</td>
<td>80</td>
<td>115</td>
</tr>
<tr>
<td>(d) 100 ppm Zn(^{2+}) ions + 100 ppm polymer</td>
<td>80</td>
<td>120</td>
</tr>
<tr>
<td>(e) 150 ppm Zn(^{2+}) ions + 100 ppm polymer</td>
<td>78</td>
<td>110</td>
</tr>
</tbody>
</table>

Cathodic polarisation curves were extrapolated to the corrosion potentials and the intersection points gave corrosion currents. The slopes of the anodic and cathodic linear segments of the polarisation curves gave anodic and cathodic Tafel slopes. Table 1 presents the parameters obtained from polarisation curves.

The cathodic Tafel Slopes were unaffected by the introduction of Zn\(^{2+}\) ions and polymer. The anodic Tafel slopes of 54±5 mV/decade changed to 80±5 mV/decade suggesting the participation of these species in the dissolution of steel.

The percentage inhibition efficiency is

\[
\text{I}_{\text{corr}} - \frac{I_{\text{corr}}'}{I_{\text{corr}}} \times 100
\]

where \( I_{\text{corr}} \), \( I_{\text{corr}}' \) are the corrosion currents in absence and presence of inhibitors.

More than 90% of inhibition was obtained in presence of inhibitors.

The FT-IR spectra of the tartrate-ethylene diamine polymer suggested that the TED polymer contains both trans and cis forms of amide linkages and possible structure of the polymer to be

![Chemical Structure of TEDP A Polymer](image)

The surface film formed on steel was obtained after immersing steel specimens in the solution of 60 ppm chloride containing 100 ppm TEDPA polymer and 100 ppm zinc ions. The FTIR spectra of the surface film confirmed the incorporation of Zn(OH)\(_2\) along with Iron TEDPA complex.

In presence of 60 ppm chloride solutions, the formation of chlorocomplex is due to

\[
\text{Fe}^{2+} + \text{M} \text{H}_2\text{O} + n\text{Cl}^- \rightarrow \text{Fe}\text{(OH)}\(_m\text{)(Cl)\(_n\text{)}^{2-n+m} + n\text{H}^+}
\]

and Zn\(^{2+}\) ions accelerated corrosion by reacting with the intermediate FeOH\(^+\) to form Zn(OH)\(_2\)

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

The inhibition observed in the presence of polymer may be due to blocking the diffusion of Fe\(^{2+}\) or FeOH\(^+\) and \( \text{H}^+ \) ions away from the surface film. The overall dissolution may occur as

\[
\text{Fe} + m \text{H}_2\text{O} + n\text{X}^- \rightarrow \text{Fe(OH)}\(_m\text{)}\text{X}^{2-n+m} + n\text{H}^+ + 2\text{e}^-
\]

where \( \text{X}^- \) is the anionic part of the polymer.

In the present study the observed synergistic inhibition may be due to the presence of Zn\(^{2+}\) ions which act as anchoring sites for the anionic part of the polymer to adsorb to form an impermeable layer on steel.

References
8 Kuznetsov Yu I & Rashkolykov A F, Zasch Met, 28 (1992) 249.