Corrosion behaviour of carbon steel in river water in the presence of calcium propionate- Zn$^{2+}$ system

The inhibition efficiency of calcium propionate (CP)-Zn$^{2+}$ system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by mass-loss method. A synergistic effect is noticed between calcium propionate and Zn$^{2+}$. The formulation consisting of 50 ppm of calcium propionate and 50 ppm of Zn$^{2+}$ shows 91% inhibition efficiency (IE). At lower pH value IE decreases and in alkaline solution IE increases. Polarization study reveals that CP-Zn$^{2+}$ system controls cathodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe$^{2+}$-CP complex Zn(OH)$_2$ and Ca(OH)$_2$.

Key words: Corrosion inhibition, carbon steel, river water, synergistic effect

INTRODUCTION

The major problems in industrial use of the cooling water system are corrosion of the metal equipment, contamination of the circulating water system with microorganisms, and deposit formation that worsens the heat exchange. To solve the above problems complex treatment of the water is required including the use of the corrosion inhibitors and anti-deposit additives. Mixtures of inhibitors frequently provide better inhibition than either of the individual components. This was recognized by Speller [1] in the mid thirties, who reported the finding “compound films”, such as formed by phosphates chromate mixtures to be more effective than those of either alone.

Carboxylic acids, their salts and their derivatives have recently emerged as a new and potential class of corrosion inhibitors. Many carboxylates such as Salicylate [2], cinnamate [3], phenyl acetate [4], anthra- nilates [5], thio divalerate [6], adipate [7] and their derivatives have been used as inhibitors. Their inhibitive action results from the bonding of the anion to the metal surface through the excess electron on the O’ ion. Inhibitive anions such as benzoate, phthalate and other carboxylates stabilize the oxide film on iron surface [8,9]. Review of carboxylates as corrosion inhibitors have appeared from time to time. Mercer [10] reviewed carboxylates that provide protection to cast iron and non-ferrous metals.

The present work is undertaken: (i) to evaluate the inhibition efficiency of calcium propionate(CP) in controlling corrosion of carbon steel in a river (namely, Cuavery in Trichy, Tamilnadu, India) water, in the presence and absence of Zn$^{2+}$ (ii) to analyse the protective film by FTIR (iii) to make use of polarization study and AC impedance spectra to know the mechanistic aspects of corrosion inhibition.

EXPERIMENTAL

Preparation of the carbon steel specimens

Carbon steel specimens (0.026 % S, 0.06 % P, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass-loss and surface examination studies.

Mass- loss method

The weighed specimens in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions. After 3 days of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimens, corrosion rates and I.E. were calculated.

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

Where \(W_1\)=corrosion rate (mdd) in absence of inhibitor, \(W_2\)=corrosion rate (mdd) in presence of inhibitor.

Surface examination studies

The carbon steel specimens were immersed in various test solutions for a period of three days, the specimens were taken out, washed with distilled water and then dried. The nature of the film formed on the surface of metal specimens was analysed by FTIR spectra.
FTIR spectra

The film was carefully removed with sharp edged glass rod, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer.

Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm$^2$ area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements

A CHI electrochemical impedance analyzer (model 660 A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open-circuit potential. The real part ($Z'$) and imaginary part ($Z''$) of the cell impedance were measured in ohms at various frequencies ($f$). The values of the charge transfer resistance $R_t$ and the double layer capacitance $C_{dl}$ were calculated.

RESULTS AND DISCUSSION

Mass-loss method

The corrosion inhibition efficiencies of calcium propionate (CP)-Zn$^{2+}$ systems in controlling corrosion of carbon steel in Cauvery water, as determined by mass loss method, are given in Table-1. It is found from the table that CP is a poor inhibitor and 300 ppm of CP gives a maximum of 45% IE. Perusal of the table reveals that a combination of Zn$^{2+}$ and CP shows a better IE. For example, 50 ppm of Zn$^{2+}$ gives an IE of 50% and 300 ppm of CP gives 45%; but their combination offers an IE of 91%, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn$^{2+}$ and CP. The synergism may be due to the formation of complex between Zn$^{2+}$ and CP. Because of the complex formation with Zn$^{2+}$ the inhibitor molecules are readily transported from the bulk of the solution to the metal surface.

On the metal surface, Zn$^{2+}$-CP complex is converted into Fe$^{2+}$-CP complex on the anodic sites of the metal surface. Zn$^{2+}$ is released. This combines with OH$^-$ to form Zn(OH)$_2$ on the cathodic sites of the metal surface. Thus both the anodic reaction

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

and the cathodic reaction

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

are controlled effectively. This accounts for a synergistic effect between CP and Zn$^{2+}$.

Table 1 - Inhibition efficiency (%) of CP-Zn$^{2+}$ system in controlling corrosion of carbon steel in Cauvery river water.

<table>
<thead>
<tr>
<th>CP, ppm</th>
<th>Zn$^{2+}$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-- 28 33 41 50</td>
</tr>
<tr>
<td>50</td>
<td>8 49 74 89 91</td>
</tr>
<tr>
<td>100</td>
<td>14 42 71 85 87</td>
</tr>
<tr>
<td>150</td>
<td>24 39 66 82 84</td>
</tr>
<tr>
<td>200</td>
<td>30 45 64 77 79</td>
</tr>
<tr>
<td>250</td>
<td>43 46 63 72 78</td>
</tr>
<tr>
<td>300</td>
<td>45 43 67 70 71</td>
</tr>
</tbody>
</table>

FTIR spectral analysis

The FTIR spectrum of calcium propionate (CP in KBr) is shown in Fig.1a. The C=O stretching frequency of carboxyl group appears at 1579 cm$^{-1}$. The FTIR spectrum of the film formed on the metal surface after immersion in Cauvery water containing 50 ppm of CP and 50 ppm of Zn$^{2+}$ is shown in Fig.1b. It can be seen that the C=O stretching frequency of the carboxyl group has shifted from 1579 cm$^{-1}$ to 1590 cm$^{-1}$. This indicates that the oxygen atom of carboxyl group has coordinated with Fe$^{2+}$ resulting in the formation of Fe$^{2+}$-propionate complex on the anodic sites of the metal surface. The peak at 1352 cm$^{-1}$ is due to Zn(OH)$_2$ formed on the cathodic sites [11]. The band at 1505.6 cm$^{-1}$ is due to Ca(OH)$_2$ formed on the cathodic sites of the metal surface [12].

Fig 1: FTIR spectra of (a) calcium propionate and (b) Film formed on steel after immersion in well water containing 50 ppm CP & 50 ppm Zn$^{2+}$.
Analysis of the results of potentiodynamic polarization studies

The corrosion parameters of carbon steel immersed in river water in the absence and presence of inhibitor system are given in Table 2.

When carbon steel is immersed in river water, the corrosion potential ($E_{corr}$) is -463 mV vs SCE and the corrosion current is $1.556 \times 10^{-5}$ A/cm$^2$. When 50 ppm of Zn$^{2+}$ and 50 ppm of calcium propionate are added to river water the corrosion potential shifts to the cathodic side (-536 mV vs SCE). The corrosion current is $1.174 \times 10^{-5}$ A/cm$^2$. The cathodic slope is found to change from 276 to 492 mV/decade and the anodic slope from 217 to 184 mV/decade. The linear polarization resistance has increased from $3.643 \times 10^3$ to $4.963 \times 10^3$ $\Omega$cm$^2$. The increase in the value of $b_c$ is considerably more than that of $b_a$. This shows that the formulation controls the cathodic reaction predominantly. The increase in LPR value and decrease in corrosion current indicate that a protective film is formed on the metal surface [13].

Table 2 - Corrosion parameters of carbon steel in river water (Cauvery) in the presence and absence of inhibitor obtained by potentiodynamic polarization

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ mV vs SCE</th>
<th>$b_c$ mV/decade</th>
<th>$b_a$ mV/decade</th>
<th>LPR $\Omega$ cm$^2$</th>
<th>$I_{corr}$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>-463</td>
<td>327</td>
<td>217</td>
<td>$3.643 \times 10^3$</td>
<td>$1.556 \times 10^{-5}$</td>
</tr>
<tr>
<td>River water + 50 ppm CP + 50 ppm Zn$^{2+}$</td>
<td>-536</td>
<td>492</td>
<td>184</td>
<td>$4.963 \times 10^3$</td>
<td>$1.174 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Analysis of the results of AC impedance spectra

The AC impedance spectra of carbon steel immersed in various test solutions are shown in Fig.2.

The AC impedance parameters, namely, charge transfer resistance ($R_t$) and the double layer capacitance ($C_{dl}$) are given in Table 3.

When carbon steel is immersed in river water the $R_t$ value is found to be 1102 $\Omega$ cm$^2$. The $C_{dl}$ value is $8.2187 \times 10^{-9}$ F/cm$^2$. When 50 ppm of Zn$^{2+}$ and 50 ppm of calcium propionate are added, the $R_t$ value has increased from 1102 to 1697 $\Omega$ cm$^2$ and the $C_{dl}$ value has decreased from $8.2187 \times 10^{-9}$ to $5.3391 \times 10^{-9}$ F/cm$^2$. The increase in $R_t$ values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in river water. This behavior means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film [14].

Table 3 - Impedance parameters of carbon steel in river water in the absence and presence of inhibitor obtained by AC impedance spectra

<table>
<thead>
<tr>
<th>System</th>
<th>$R_t$ $\Omega$ cm$^2$</th>
<th>$C_{dl}$ F/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>1102</td>
<td>$8.2187 \times 10^{-9}$</td>
</tr>
<tr>
<td>River water + 50 ppm CP + 50 ppm Zn$^{2+}$</td>
<td>1697</td>
<td>$5.3391 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
The SEM pictures are shown in Fig. 4. In the absence of inhibitors pits are seen. But in the presence of inhibitors, barrier film is visible.

**Fig. 4**: SEM micrographs: a) Film formed on metal surface in presence of river water, b) Film formed on metal surface in presence of river water + 50 ppm CP + 50 ppm Zn²⁺

**CONCLUSIONS**

Corrosion behaviour of carbon steel in the absence and presence of calcium propionate and Zn²⁺ has been evaluated.

- The analysis of the results of mass-loss method shows that the formulations consisting of 50 ppm of Calcium propionate and 50 ppm of Zn²⁺ offers maximum IE of 91%.
- The results of polarization studies show that this formulation predominantly controls the cathodic reactions.
- SEM pictures reveal the presence of uniform complex layer on the metal surface.
- The AC impedance spectral studies reveal the formation of a film with higher resistance than that of the Cauvery water.
- FTIR spectra reveal that the protective film consists of Fe²⁺-propionate complex Zn(OH)₂ and Ca(OH)₂.

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**REFERENCES**


**List of reviewers**

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