SYNERGISTIC EFFECT OF CITRATE ETHYLENE DIAMINE PHOSPHONIC ACID AND Zn$^{2+}$ ON THE INHIBITION OF CORROSION OF MILD STEEL IN LOW CHLORIDE MEDIA

J Matihyasaru, R Natarajan, N Palaniswamy and N S Rengaswamy

Central Electrochemical Research Institute, Karaikudi - 630 006, Tamil Nadu, INDIA

[Received: 13 September 1996 Accepted: 20 November 1996]

Synergistic effect of citrate ethylene diamine phosphonic acid (CEDPA) and Zn$^{2+}$ on the inhibition of corrosion of mild steel in water containing chloride ion of 60 ppm has been evaluated by weight loss, potentiostatic polarisation and electrochemical impedance spectroscopic methods. The weight loss studies have shown that neither the CEDPA nor Zn$^{2+}$ has any inhibitive action individually but when they are combined together because of synergistic effect they give higher inhibition efficiency with increase in concentration. An optimal critical concentration of 200 ppm of CEDPA and 80 ppm of Zn$^{2+}$ has been established to the maximum efficiency of 93 ± 2%. Potentiostatic polarisation studies have confirmed this system acts as a mixed inhibitor. X-ray diffraction technique, UV-VIS-NIR spectra and luminescence spectra have revealed that this synergistic effect is due to the formation of Fe$^{2+}$-CEDPA complex on the metal surface at a critical concentration ratio of 2.5:1.

Keywords: Corrosion inhibition, synergistic effect, luminescence, electrochemical impedance spectroscopy and Fe$^{2+}$-CEDPA complex.

INTRODUCTION

Studies on the synergistic effect of phosphonic acids with Zn$^{2+}$ ion as corrosion inhibitor for mild steel in low chloride media have been reported in the literature [1-7]. Even though several papers have discussed the use of aminotrimethylene phosphonic acid (ATMP) [8], 2-carboxylethyl phosphonic acid (2-CEPA) [9], hydroxy ethyl diphosphonic acid (HEDP) [10] as corrosion inhibitors with Zn$^{2+}$ in low chloride media, there is no report on the use of CEDPA as corrosion inhibitor in cooling water systems.

In this study, synergistic effect of CEDPA and Zn$^{2+}$ in corrosion inhibition of mild steel in low chloride media has been studied by weight loss and electrochemical methods. Besides the nature of the film formed on the surface of the metal has also been analysed by X-ray diffraction method, UV-Vis reflectance spectra and luminescence emission spectra.

EXPERIMENTAL

Materials

An aqueous solution of 60 ppm NaCl solution was used as a blank. The concentration of CEDPA used for the inhibition study was ranging from 50 ppm to 200 ppm. Zn$^{2+}$ ions were added to CEDPA in the form of zinc sulphate (ZnSO$_4$ .7H$_2$O). All the test solutions were adjusted to pH 7.00 ± 0.1.

For weight loss measurements and surface examination studies, mild steel specimens (0.02-0.03% S, 0.3-0.8% P, 0.4-0.5% Mn, 0.1-0.2% C and rest Fe) of the dimensions of 1 x 4 x 0.2 cm were used. The specimens were polished to mirror finish and degreased with trichloroethylene.

For electrochemical measurements, mild steel rod of the above composition encapsulated in teflon with an exposed area of 0.1963 cm$^2$ was used as working electrode. The steel surface was polished successively in 1/0 to 4/0 emery papers and degreased with trichloroethylene.
Weight loss measurements

The specimens were immersed in inhibitor solutions for a period of seven days. The corrosion inhibition efficiency was calculated from the change in weight loss.

Potentiostatic polarisation method

A three electrode cell assembly was used. The mild steel specimen was used as working electrode, platinum foil as counter electrode and saturated calomel a reference electrode formed the three electrodes. Polarisation studies were carried out using potentiostat (EG & G 173), Universal Programmer (EG & G 175) and X-Y recorder (Rikadenki ZOIT) at a sweep rate of 1 mV/sec.

Electrochemical impedance spectroscopy method

EIS measurements were performed with an A.C impedance system (PAR Model 6310). The impedance measurements were carried out between 0.1 Hz and 10 kHz with a perturbation amplitude of 10 mV with 5 data points per decade. The frequency sweep was initiated at high frequency and moved towards lower frequencies.

Surface examination studies

The polished mild steel specimens were immersed in solution with and without inhibitor for two days. After two days the specimens were taken out and washed with distilled water and dried. The dried specimens were used for surface examination studies.

X-ray diffraction technique

The XRD patterns of the film formed on the metal surface were recorded using a computer controlled X-ray powder diffractometer, JEOL JOX 8030 with CuKα (Ni filtered) radiation at a rating of 40 KV, 20 mA. The scan rate was 0.05-20° per step and the measuring time was 1s per step.

UV-visible NIR diffused reflectance spectra

UV-visible NIR diffused reflectance spectra of the film formed on the metal surface was recorded using Hitachi U-3400 spectrophotometer. The same instrument was used for recording UV-vis adsorption spectra of aqueous solutions.

Luminescence spectroscopy

Luminescence spectra of the film formed on the metal surface were recorded using Hitachi 650-10 S fluorescence spectrophotometer equipped with a 150 W xenon lamp and a Hamamatsu R 929 F photomultiplier tube. The emission spectra were corrected for the spectral response of the photomultiplier tube used.

RESULTS AND DISCUSSION

Weight loss method

Table I shows the results of corrosion rate measured by weight loss method for various combinations of CEDPA and Zn^{2+} at room temperature in 60 ppm chloride solution. CEDPA alone acts as an accelerator of corrosion of mild steel in chloride media. An increase in corrosion rate was observed with the increase of concentration of CEDPA. Similar effect was also observed in the case of addition of Zn^{2+} ions. Increase in concentration of Zn^{2+} ions accelerated the corrosion of steel. But a phenomenal change was observed in the combination of the two. The behaviour has been changed from corrosion accelerator to that of corrosion inhibitor. CEDPA:Zn^{2+} combination in the ratio 4:1 showed an inhibition efficiency of 60% whereas 2.5:1 ratio gave the maximum efficiency of 93 ± 2%; 2:1 ratio showed only 75% inhibition efficiency.

Potentiostatic polarisation method

The polarisation curves for the system 60 ppm Cl\textsuperscript{-}, and a combination of 200 ppm CEDPA+80 ppm Zn^{2+} are shown in Fig. 1. The corrosion parameter derived from the polarisation measurements are given in Table II. The combination shows an inhibition efficiency of 94%.

<table>
<thead>
<tr>
<th>TABLE I: Weight loss measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate of mild steel and inhibition efficiency</td>
</tr>
<tr>
<td>Conc of CEDPA (ppm)</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>100</td>
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<tr>
<td>150</td>
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<td>0</td>
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<td>0</td>
</tr>
</tbody>
</table>
**Table II: Polarisation studies**

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (µA/0.1963 cm²)</th>
<th>$b_c$ (mV)</th>
<th>$b_a$ (mV)</th>
<th>Inhibition efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-680</td>
<td>6.00</td>
<td>80.00</td>
<td>42.00</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>-650</td>
<td>0.39</td>
<td>62.00</td>
<td>42.00</td>
<td>94.00</td>
</tr>
</tbody>
</table>

$A = $ Blank (60 ppm chloride)

**Table III: Impedance measurements**

<table>
<thead>
<tr>
<th>System</th>
<th>$R_{ct}$ (kOhm cm²)</th>
<th>$C_{dl}$ (µF cm²)</th>
<th>Surface coverage efficiency %</th>
<th>Inhibition efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.611</td>
<td>1.018</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>16.659</td>
<td>0.013</td>
<td>0.987</td>
<td>90</td>
</tr>
</tbody>
</table>

$A = $ Blank (60 ppm Cl⁻)
Zn$^{2+}$ (5c) and a mixture of 200 ppm CEDPA+80 ppm Zn$^{2+}$ (5d) were shown in Fig. 5. A band at nearly 550 nm for the system 5a, 5b and 5c shows that the nature of the layer on the surface is semiconducting. This is due to the presence of iron oxides [14,15] on the surface of mild steel specimens immersed in 60 ppm Cl$^-$, 80 ppm Zn$^{2+}$ and 200 ppm CEDPA. But in the case of mild steel specimen immersed in 200 ppm CEPDA+80 ppm Zn$^{2+}$ mixture there is no such base line decrease at 550 nm. This proves that the individual systems 60 ppm Cl$^-$, 80 ppm Zn$^{2+}$ and 200 ppm CEDPA are corrosive.

**Analysis of UV luminescence spectra**

UV-visible luminescence emission spectra at λ-max 403 nm are shown in Fig. 6. The spectra for the surface immersed in CEDPA and Zn$^{2+}$ solutions are nearly the same while spectrum of the surface immersed in CEDPA+Zn$^{2+}$ combination is different from the other two. The peak at 595 nm for mixed system shows the presence of Fe$^{2+}$-CEDPA complex. This is confirmed by preparing Fe$^{2+}$-CEDPA complex also gave a peak at 595 nm. This indicates the presence of Fe$^{2+}$-CEDPA complex on the specimen immersed in a mixture of CEDPA+Zn$^{2+}$ solution.

**CONCLUSION**

* Maximum corrosion inhibition efficiency of 93% was achieved for mild steel immersed in 80 ppm Zn$^{2+}$ and 200 ppm for CEDPA mixture.
* The mixture of CEDPA+Zn$^{2+}$ formulations acts a mixed inhibitor.
* The complex formed on the surface of the metal was identified as Fe$^{2+}$-CEDPA.

![Fig. 3: UV-visible absorption spectra of solutions](image)

![Fig. 4: XRD patterns of surface films](image)
Fig. 5: UV-visible diffused reflectance spectra of mild steel specimens immersed in
a) 60 ppm Cl⁻  b) 200 ppm CEDPA  c) 80 ppm Zn^{2+}
d) 200 ppm CEDPA + 80 ppm Zn^{2+} + 60 ppm Cl⁻

Fig. 6: Luminescence spectra of mild steel immersed in
a) 60 ppm Cl⁻  b) 200 ppm CEDPA  c) 80 ppm Zn^{2+}
d) 200 ppm CEDPA + 80 ppm Zn^{2+} + 60 ppm Cl⁻
e) Luminescence spectra of Fe^{2+}-CEDPA complex

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