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

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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]. Eventhough several papers have discussed the use of aminotrimethylene phosphonic acid (ATMP) [8], 2-carboxyethyl 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 ($ZnSO_4 . 7H_2O$). All the test solutions were adjusted to *p*H 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 CuK_α (Ni filtered) radiation at a rating of 40 KV, 20 mA. The scan rate was $0.05\text{-}20^0$ 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 phenominal 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^-, 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 I: Weight loss measurements
Corrosion rate of mild steel and inhibition efficiency

Conc of CEDPA (ppm)	Conc of Zn^{2+} (ppm)	Corrosion rate mdd (+0.01 mdd)	Inhibition efficiency % ± 2
0	0	20	—
50	0	20	- 1
80	0	21	- 4
100	0	22	- 8
150	0	22	-12
200	0	23	-16
200	50	8	60
200	80	1	93
200	100	5	75
200	150	6	70
0	100	24	-19
0	80	22	-11
0	50	21	- 4

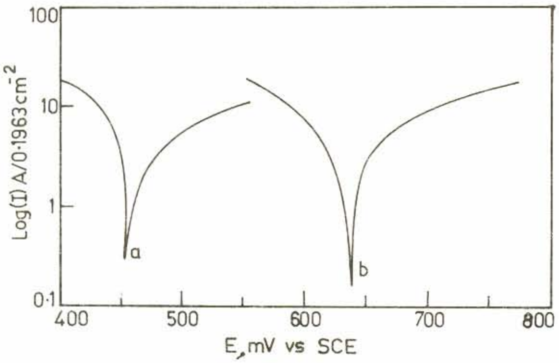

Fig. 1: Potentiostatic polarisation curves a) 60 ppm Cl^- b) 60 ppm Cl^- + 200 ppm CEDPA + 80 ppm Zn^{2+}

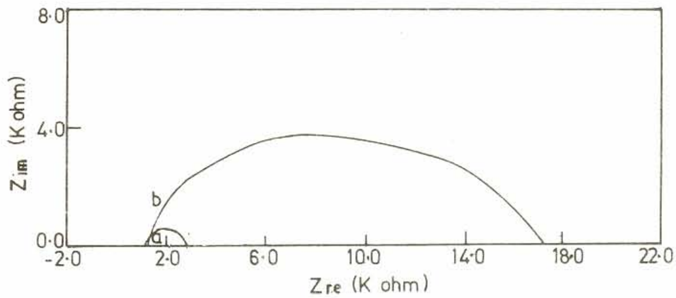

Fig. 2: Nyquist plots for mild steel in a) 60 ppm Cl^- b) 60 ppm Cl^- + 200 ppm CEDPA + 80 ppm Zn^{2+}

Electrochemical impedance spectroscopy method

The electrochemical impedance measurements of mild steel in 60 ppm Cl^-, and a mixture of 200 ppm CEDPA+80 ppm Zn^{2+} are shown in Fig. 2. The parameters derived from the Nyquist plots are given in Table III. The system comprising of 200 ppm CEPDA+80 ppm Zn^{2+} combination shows the highest value of R_{ct} [11] indicating that the combination is highly effective. The inhibition efficiency calculated based on the charge transfer resistance was also found to be 90%. The surface coverage (0) was calculated from the double layer capacitance C_{dl} value using the following equation.

$$\text{surface coverage } 0 = 1\text{-}C_{dli}/C_{dl}$$

where C_{dli} is the double layer capacitance with inhibitor and C_{dl} is the double layer capacitance without inhibitor. The system containing 200 ppm CEDPA+80 ppm Zn^{2+} showed a surface coverage of 0.98 indicates that the mild steel surface was completely covered by the complex.

Analysis of UV-vis absorption spectra

New peaks are observed at 300 nm, 260 nm and 210 nm for the solution containing Zn^{2+}+CEDPA and Fe^{2+} + CEDPA (Fig. 3). Increase in absorbance is also noticed in both the cases, but in the case of CEDPA and Zn^{2+} no such peaks are found. These observations indicate the formation of Zn^{2+}-CEDPA complex [8] and also Fe^{2+}-CEDPA complex in solution.

X-ray diffraction analysis

The XRD patterns of mild steel immersed in 60 ppm chloride, 200 ppm CEDPA, 80 ppm Zn^{2+} and a mixture of 200 ppm CEDPA+80 ppm Zn^{2+} solutions are given in Fig. 4. With specimens immersed in 60 ppm chloride solution, in addition to iron peaks (20 = 44.3, 64.6 and 82.0), peaks due to Fe_3O_4 occurs at 20 = 29.8 and 35.1 [12,13]. With the metal immersed in 200 ppm CEDPA, the peak due to τ-FeOOH occurs at 20 = 36.35 and the one at 20 = 71.2 and 77.8 is due to Fe_3O_4. With the metal immersed in 80 ppm Zn^{2+}, Fe_3O_4 peak occurs at 20 = 34.51, 59.96. For the mixed system, no additional peaks other than that of iron occur. This confirms that the mild steel surface was completely protected from corrosion.

Analysis of UV-vis reflectance spectra

The UV-visible diffused reflectance spectra were recorded using the surface of the mild steel specimens immersed in 60 ppm Cl^- solution (5a), 200 ppm CEDPA (5b), 80 ppm

TABLE II: Polarisation studies
Corrosion parameters of mild steel

System	E_{corr} mV	i_{corr} (μA/0.1963 cm^2)	b_c mV	b_a mV	Inhibition efficiency %
A	-680	6.00	80.00	42.00	—
B	-650	0.39	62.00	42.00	94.00

A = Blank (60 ppm chloride)

TABLE III: Impedance measurements
Corrosion parameters of mild steel

System	R_{ct} (kOhm cm^{-2})	C_{dl} (μF cm^{-2})	Surface coverage	Inhibition efficiency %
A	1.611	1.018	—	—
B	16.659	0.013	0.987	90

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.

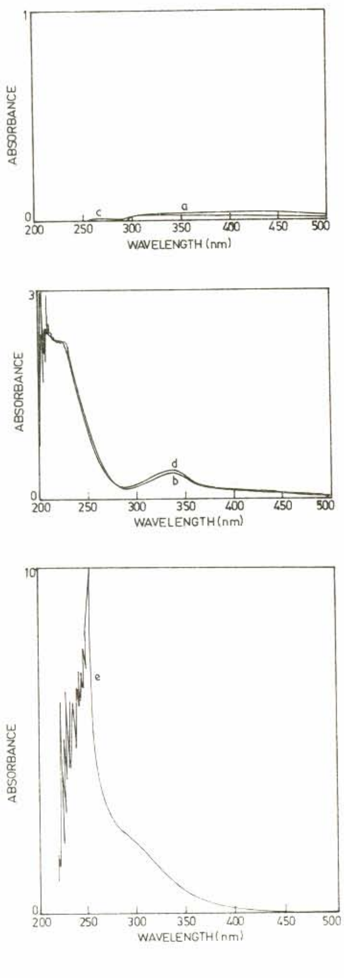

Fig. 3: UV-visible absorption spectra of solutions
a) 60 ppm Cl^- b) 200 ppm CEDPA c) 80 ppm Zn^{2+}
d) 200 ppm CEDPA + 80 ppm Zn^{2+}
e) 200 ppm CEDPA + 100 ppm Fe^{2+}

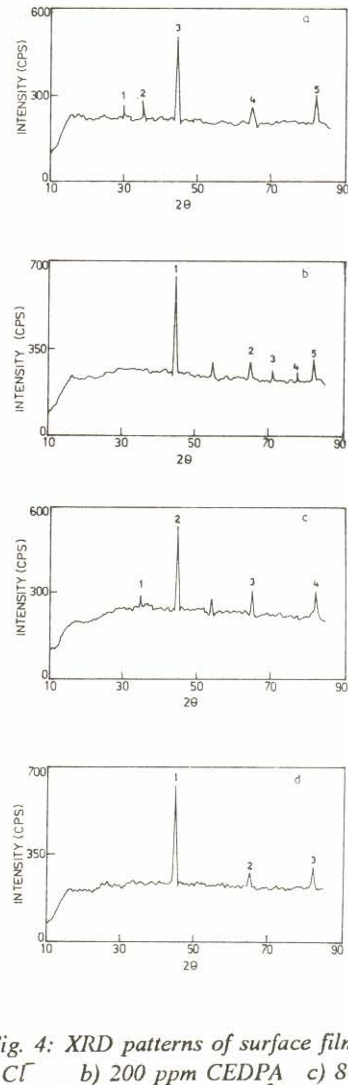

Fig. 4: XRD patterns of surface films
a) 60 ppm Cl^- b) 200 ppm CEDPA c) 80 ppm Zn^{2+}
d) 200 ppm CEDPA + 80 ppm Zn^{2+} + 60 ppm Cl^-

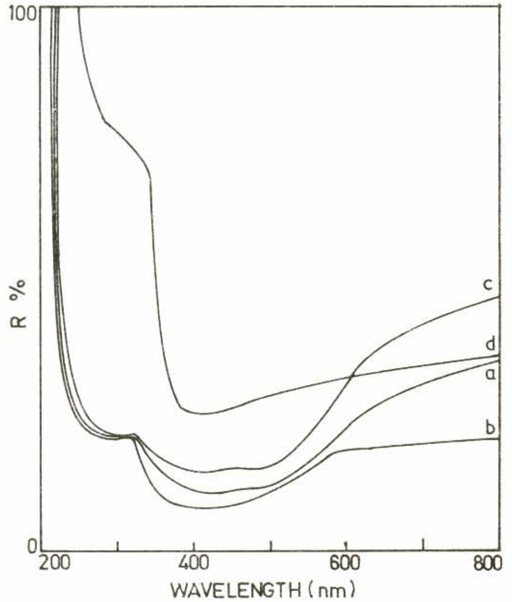

Fig. 5: UV-visible diffused reflectance spectra of mild steel specimens immersed in
a) 60 ppm Cl^- b) 200 ppm CEDPA c) 80 ppm Zn^{2+}
d) 200 ppm CEDPA + 80 ppm zn^{2+} + 60 ppm Cl^-

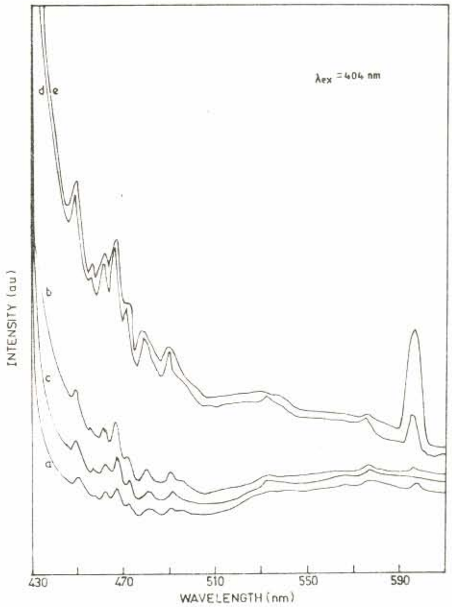

Fig. 6: Luminescence spectra of mild steel immersed in
a) 60 ppm Cl^- b) 200 ppm CEDPA c) 80 ppm Zn^{2+}
d) 200 ppm CEDPA + 80 ppm Zn^{2+} + 60 ppm Cl^-
e) Luminescence spectra of Fe^{2+}-CEDPA complex

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