Contributed papers

Synergistic effect of 1-hydroxyethane-1, 1-diphosphonic acid and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment

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Keywords

Corrosion, Mild steel, Surface films

Abstract

The formulation consisting of 300ppm 1-hydroxyethane-1, 1-diphosphonic acid (HEDP) and 50ppm Zn^{2+} offered 99 per cent inhibition to the corrosion of mild steel immersed in neutral aqueous environment containing 60ppm chloride. This formulation functioned as a mixed inhibitor. The protective film was found to be luminescent and to consist of Fe^{2+}-HEDP complex and $Zn(OH)_2$.

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Introduction

The need to develop formulations free from chromates, nitrites and inorganic phosphorous compounds has stimulated research work on "Phosphonates as corrosion inhibitors". Phosphonates have been widely used as corrosion inhibitors due to their hydrolytic stabililty, ability to form complexes with metal ions and scale inhibiting property[1-14]. The present investigation is undertaken to:

(a) study the synergistic effect of sodium salt of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment containing 60ppm chloride, a situation commonly encountered in cooling water technology;
(b) understand the nature of the protective film formed on the metal surface, by using x-ray diffraction (XRD) measurement, FTIR and luminescence spectra; and
(c) propose a suitable mechanism of corrosion inhibition based on the results obtained from a polarisation study, XRD, FTIR, luminescence and atomic absorption spectra.

Experimental

Preparation of the specimens

Mild steel specimens (iron containing 0.02-0.03%S, 0.03-0.08%P, 0.4-0.5%Mn and 0.1-0.2%C) of the dimensions 1 × 4 × 0.2cm were polished to mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. For potentiostatic polarisation studies, mild steel rod encapsulated in Teflon was used as the working electrode. Its surface was polished to mirror finish and degreased with trichloroethylene.

Susai Rajendran is thankful to the University Grants Commission, India, for awarding a fellowship to the Executive Director, Sasha Industries Limited, Dindigul, to Mr Ranjit Soundarajan, the Correspondent, Professor S. Ramakrishnan, the Principal, and Professor P. Jayaram, HOD of Chemistry, GTN Arts College, Dindigul, Dr Kottaisamy, Dr R. Jegannathan, CECRI, Karaikudi and to Professor G.Karthikeyan of Gandhigram University for their help.

Anti-Corrosion Methods and Materials
Volume 46 · Number 1 · 1999 · pp. 23–28

ISSN 0003-5599

Weight-loss method

Three mild steel specimens were immersed in 100ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+}, for a period of seven days. The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240.

Potentiostatic polarisation study

This study was carried out in a three electrode cell assembly connected to a Bioanalytical system (BAS-100A) electrochemical analyser, provided with iR compensation facility, using mild steel as the working electrode, platinum as the counter electrode and saturated calomel electrode as the reference electrode.

Surface examination study

The mild steel specimens were immersed in various test solutions for a period of two days. After two days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

FTIR spectra

FTIR spectra were recorded using a Perkin-Elmer 1600 FTIR spectrophotometer.

X-ray diffraction technique

XRD patterns of the film formed on the metal surface were recorded using a computer controlled X-ray powder diffractometer, JEOL JDX 8030 with CuK_α (Ni-filtered) radiation (λ = 1.5418Å) at a rating of 40kV, 20mA.

Luminescence spectra

The luminescence spectra of the film formed on the metal surface were recorded using a Hitachi 650-10 S fluorescence spectrophotometer equipped with a 150W Xenon lamp and a Hamamatsu R 928F photomultiplier tube. The emission spectra were corrected for the spectral response of the photomultiplier tube used and the excitation spectra recorded were corrected for the beam intensity variation.

Estimation of iron and zinc present in test solutions

The amount of iron and zinc present in various test solutions was determined by using a fully automatic, computer-controlled atomic absorption spectrometer (model 906; make GBC – Australia), using air-acetylene flame.

Results and discussion

Analysis of the results of the weight-loss method

Corrosion rates of mild steel in neutral aqueous environment containing 60ppm chloride in the absence and presence of inhibitor at various concentrations obtained by the weight-loss method are given in Table I. The corrosion inhibition efficiencies of various HEDP-Zn^{2+} formulations are also given in this Table. It reveals that 300ppm HEDP alone had an inhibition efficiency of only 355 and 50ppm Zn^{2+} was found to be corrosive. But their combination offered 99 per cent inhibition efficiency. This suggests a synergistic effect of HEDP and Zn^{2+}. A thin interference film was observed on the surface of the metal, when it was immersed in the above environment during weight-loss experiment.

Analysis of the results of the potentiostatic polarisation study

The potentiostatic polarisation curves of mild steel immersed in various test solutions are given in Figure 1. It is seen from Figure 1 that addition of 300ppm HEDP to the solution containing 60ppm Cl^-, shifted the corrosion potential to the positive region (from –389mv vs SCE to –330mv vs SCE) while addition of 50ppm Zn^{2+} alone shifted the corrosion potential to the negative region (to –489mv vs SCE). However, the combination, consisting of 300ppm HEDP and 50ppm Zn^{2+} shifted the corrosion potential to –460mv vs SCE. It is found that this corrosion potential is intermediate between those of HEDP alone and Zn^{2+} alone, though it is also negative relative to the system in the absence of any inhibitor. It is inferred from these results that HEDP alone acted as an anodic inhibitor and the HEDP-Zn^{2+} combination functioned as a mixed inhibitor.

Analysis of FTIR spectra

The FTIR spectrum of HEDP is given in Figure 2a. The FTIR spectrum of the film carefully scratched from the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 300ppm HEDP and 50ppm Zn^{2+} is given in Figure 2b. It is observed that the P-O stretching frequency of HEDP had shifted from 1,119cm^{-1} to 1,046cm^{-1}. This

Table I Corrosion rates of mild steel in neutral aqueous environment (Cl^- = 60ppm) in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method. Inhibitor system: HEDP + Zn^{2+}

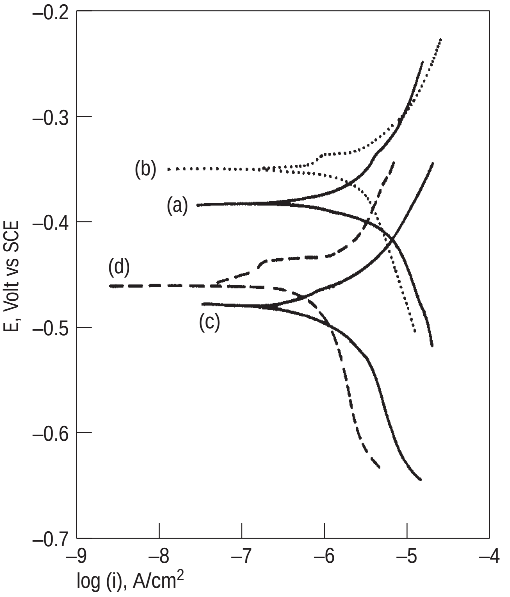
Sl. No.	Concn. of HEDP ppm	Concn. of Zn^{+2} ppm	Corrosion rate mdd	Inhibition efficiency %
1	0	0	15.54	–
2	10	0	14.76	5
3	50	0	13.83	11
4	100	0	13.21	15
5	150	0	12.74	18
6	200	0	11.66	25
7	300	0	10.10	35
8	300	10	9.32	40
9	300	50	0.16	99
10	300	100	0.15	99
11	300	150	0.14	99
12	300	200	0.12	99
13	300	300	0.11	99
14	0	50	19.11	–23

suggests that the O atom of the phosphonate group had coordinated with Fe^{2+}, resulting in the formation of an Fe^{2+}-HEDP complex on the metal surface. The peak at 1,360cm^{-1} is due to $Zn(OH)_2$[8-19].

Analysis of x-ray diffraction patterns

The x-ray diffraction (XRD) pattern of the surface of polished metal is shown in Figure 3a. The peaks due to iron appeared at 20 = 44.8°, 65.1°, 88.4° and 99.0°. The XRD pattern of the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 300ppm HEDP and 50ppm Zn^{2+} is given in Figure 3b. It showed the peaks due to iron only (20 = 44.4° and 64.9°). This suggests that the surface of the metal immersed in the above environment was as bright as the polished metal; the protective film was free from any oxides of iron[20]. Even though FTIR spectrum suggests the presence of an Fe^{2+}-HEDP complex on the metal surface, it was not detected by the XRD study. This may be due to the fact that the surface film was too thin to be detected by XRD technique.

Figure 1 Polarisation curves of mild steel immersed in various environments: (a) Cl^- 60ppm; (b) Cl^- 60ppm + HEDP 300ppm; (c) Cl^- 60ppm + Zn^{2+} 50ppm; (d) Cl^- 60ppm + HEDP 300ppm + Zn^{2+} 50ppm



Analysis of luminescence spectra

The luminescence spectrum (λ_{ex} = 440nm) of the Fe^{2+}-HEDP complex formed in aqueous

Figure 2 FTIR spectra: (a) HEDP; (b) surface film formed on the metal immersed in the environment consisting of 60ppm Cl^- + 300ppm HEDP + 50ppm Zn^{2+}

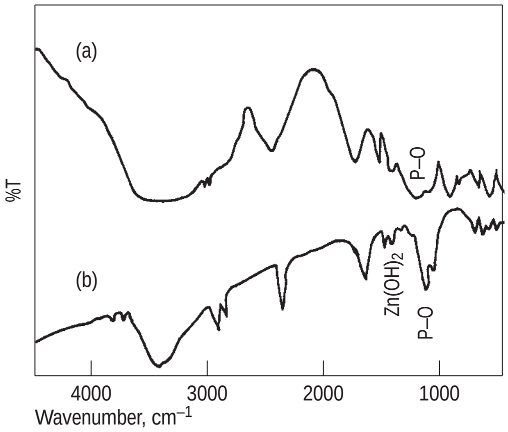


Figure 3 XRD patterns: (a) polished metal; (b) surface of the metal immersed in the environment consisting of 60ppm Cl^- + 300ppm HEDP + 50ppm Zn^{2+}

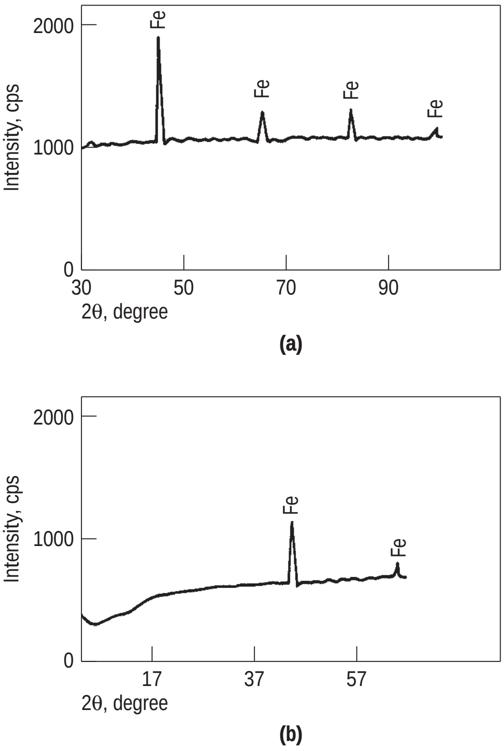
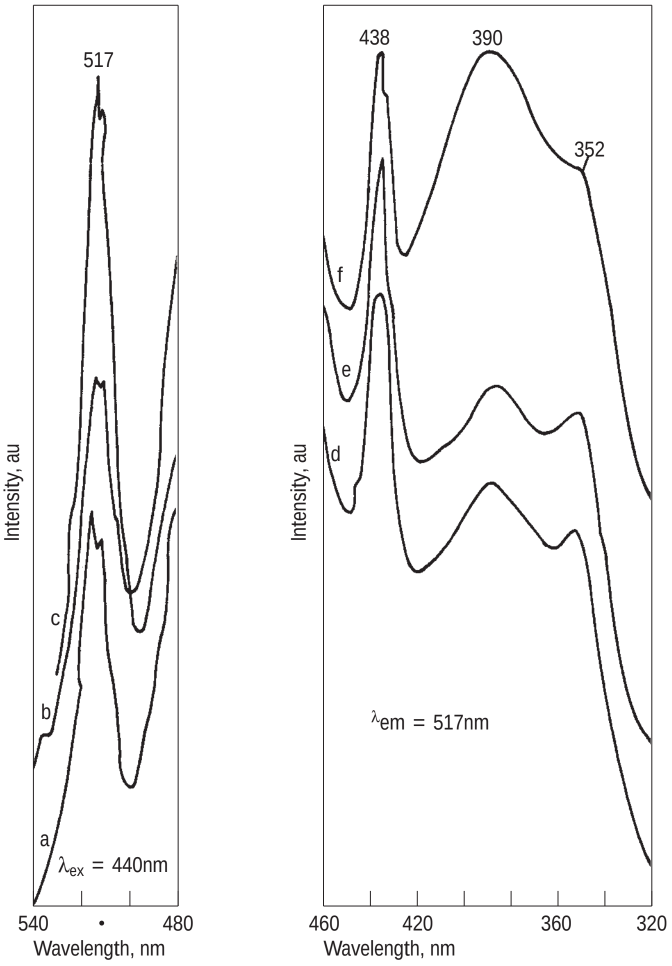


Figure 4 Luminescence spectra of various test solutions: (a) and (d) mild steel immersed in the environment consisting of 60ppm Cl^- + 300ppm HEDP + 50ppm Zn^{2+}; (b) and (e) solution containing 100ppm Fe^{2+} and 300 ppm HEDP; (c) and (f) mild steel immersed in the environment consisting of 60ppm Cl^- + 300ppm HEDP



solution containing 300ppm HEDP and 100ppm Fe^{2+} showed a peak at 517nm (Figure 4b). The luminescence spectra of the various test solutions in which mild steel specimens were immersed for a period of two days are given in Figures 4a and c. It is inferred from Figures 4a and c that Fe^{2+}-HEDP complex was present in the test solutions.

The luminescence spectrum (λ_{ex} = 300nm) of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 300ppm HEDP and 50ppm Zn^{2+} is given in Figure 5a. The peak at 520nm suggests the presence of Fe^{2+}-HEDP complex on the metal surface. The corresponding excitation spectrum (λ_{em} = 470nm) is given in Figure 5b).

Analysis of the results of the atomic absorption spectra

The results of the atomic absorption spectra of the test solutions in which mild steel specimens were immersed for seven days are given in Table II. It is observed that the amount of iron present in the environment containing 60ppm Cl^-, 300ppm HEDP and 50ppm Zn^{2+} is less than that present in the environment consisting of 60ppm Cl^- and 300ppm HEDP. This indicates that presence of Zn^{2+} had considerably reduced the dissolution of mild steel.

It is also inferred from Table II that out of 50ppm Zn^{2+}, 30ppm Zn^{2+} had diffused from the bulk of the solution towards the metal surface and deposited on it, probably as $Zn(OH)_2$, which is confirmed by FTIR spectrum.

Mechanism of corrosion inhibition

Analysis of the results of the weight-loss method shows that the formulation consisting of 300ppm HEDP and 50ppm Zn^{2+} offered an inhibition efficiency of 99 per cent. Results of the polarisation study show that this formulation functioned as a mixed inhibitor. The FTIR spectra show that Fe^{2+}-HEDP complex and $Zn(OH)_2$ were present in the film formed on the inhibited metal surface. The XRD patterns show that the protective film did not

Figure 5 Luminescence spectra of the film formed on the surface of the metal immersed in the environment containing 60ppm Cl^- + 300ppm HEDP + 50ppm Zn^{2+}: (a) emission spectrum (λ_{ex} = 300nm); (b) excitation spectrum (λ_{ex} = 470nm)

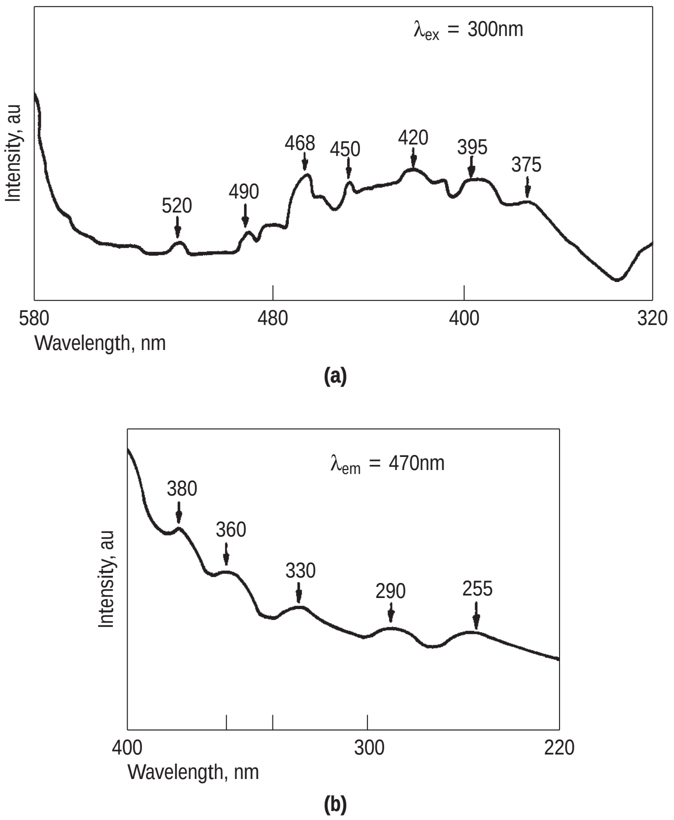


Table II Amount of metal ions present in various test solutions in which mild steel specimens were immersed for a period of seven days

	Environment			**Metal ions present after seven days**	
Sl. No.	**Cl^- (ppm)**	**HEDP (ppm)**	**Zn^{2+} (ppm)**	**Iron (ppm)**	**Zinc (ppm)**
1	60	300	–	280.00	–
2	60	300	50	66.46	20.00

contain any oxides of iron. The luminescence spectra confirm the presence of Fe^{2+}-HEDP complex in the protective film. Results of atomic absorption spectra reveal that dissolution of mild steel was reduced considerably by the presence of Zn^{2+} in the environment. In order to explain all these observations in a holistic way, the following mechanism of corrosion inhibition is proposed :

(1) When the environment containing 60ppm Cl^-, 300ppm HEDP and 50ppm Zn^{2+} is prepared, there is formation of Zn^{2+}-HEDP complex in solution.

(2) When the metal is immersed in this environment, the Zn^{2+}-HEDP complex diffuses from the bulk of the solution to the metal surface.

(3) On the surface of the metal, Zn^{2+}-HEDP complex is converted into Fe^{2+}-HEDP complex at the local anodic sites as the latter is more stable than the former.

$$Zn^{2+}\text{-HEDP} + Fe^{2+} \rightarrow Fe^{2+}\text{-HEDP} + Zn^{2+}$$

(This reaction takes place on the surface of the metal in the local anodic regions. Formation of Fe^{3+}-HEDP complex also to some extent cannot be ruled out.)

(4) The released Zn^{2+} ions on the surface will form $Zn(OH)_2$ in the local cathodic regions.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2{\downarrow}$$

(5) Thus the protective film consists of Fe^{2+}-HEDP complex and $Zn(OH)_2$.

Conclusions

The following conclusions are drawn:

(1) The formulation consisting of 300ppm HEDP and 50ppm Zn^{2+} offered 99 per cent inhibition to the corrosion of mild steel immersed in the neutral aqueous environment containing 60ppm Cl^-.

(2) This formulation functioned as a mixed inhibitor.

(3) This formulation may be used in cooling water systems.

(4) The protective film consisted of Fe^{2+}-HEDP complex and $Zn(OH)_2$.

(5) The protective film was found to be luminescent.

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