Contributed papers

Synergistic and biocidal effects of 1-hydroxyethane -1, 1-diphosphate, Zn^{2+} and polycrylamide on the inhibition of corrosion of mild steel in neutral aqueous environment

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Abstract

The formulation consisting of 300ppm 1-hydroxyethane-1, 1-diphosphonic acid (HEDP), 50ppm polyacrylamide (PAA) and 50ppm Zn^{2+} offered 99 per cent corrosion inhibition and 99 to 99.9 per cent biocidal inhibition to mild steel in neutral aqueous environment containing 60ppm Cl^-, a situation commonly encountered in cooling water systems. The nature of the protective film formed on the metal surface was analysed using X-ray diffraction, Uv-visible reflectance, FTIR and luminescence spectra. The film was found to be luminescent and to consist of Fe^{2+} -HEDP complex, Fe^{2+} -PAA complex and $Zn(OH)_2$.

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Phosphonic acids are noted for their hydrolytic stability, ability to form complexes with metal cations and scale inhibiting properties, so they have been widely used as corrosion inhibitors (Fang *et al.*, 1993; Gunasekaran *et al.*, 1997; Hatch and Ralston, 1972, Rajendran *et al.*, 1995; 1996a; 1996b; 1997a; 1997b; 1998; Sekine and Kirakawa, 1986). 1-hydroxyethane-1, 1-diphosphonic acid (HEDP) is one on the phosphonic acids that has been extensively studied. The present work is undertaken to formulate a system which can offer maximum corrosion inhibition efficiency and maximum biocidal efficiency, to mild steel in neutral aqueous medium containing 60 ppm Cl^-, a situation commonly encountered in cooling water systems. HEDP, Zn^{2+} and polyacrylamide have been used for this purpose. This work also aims to understand the nature on the protective film formed on the metal surface, be using X-ray diffraction, Uv-visible reflectance, FTIR and luminescence spectra.

Experimental

Preparation of the specimens

Mild steel specimens (iron containing 0.02 to 0.03 per cent S, 0.03 to 0.08 per cent P, 0.4 to 0.5 per cent Mn, and 0.1 to 0.2 per cent C) of the dimensions $1 \times 4 \times 0.2$cm polished to mirror finish and degreased with trichloroethylene, were used for the weight-loss and surface examination studies. For potentiostatic polarisation studies, a mild steel rod encapsulated in teflon with an exposed cross-section of 0.5cm diameter was used as the working electrode. Its surface was polished to mirror finish and degreased with trichloroethylene.

Weight-loss study

Mild steel specimens, in triplicate, were immersed in 100cm^3 of solution containing various concentrations of inhibitor in the

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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 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.

UV-visible reflectance spectra

UV-visible reflectance spectra were recorded using a Hitachi U-3400 spectrophotometer.

X-ray diffraction technique

XRD patterns on 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

Luminescence spectra on 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 on the photomultiplier tube used, and the excitation spectra recorded were corrected for the beam intensity variation.

Determination of the biocidal efficiency of the system

The biocidal efficiency of the system was determined using Zobell medium and calculating the number of colony forming units per ml, using a bacterial colony counter.

Results and discussion

Analysis of the results of the weight loss study

The corrosion rates on mild steel immersed in the neutral aqueous environment (Cl^- = 60ppm) in the presence and absence of the inhibitor are given in Table I. The inhibition efficiencies and biocidal efficiencies on various systems are also given in this Table. It reveals that 300ppm HEDP offered only 35 per cent inhibition efficiency and 50ppm Zn^{2+} was found to be corrosive. However, the formulation consisting on 300ppm HEDP and 50ppm Zn^{2+} offered 99 per cent inhibition efficiency. This suggests a synergistic effect on HEDP and Zn^{2+}. The results further suggest that the formulation consisting of 300ppm HEDP, 50ppm Zn^{2+} and 50ppm polyacrylamide (PAA) had 99 per cent corrosion inhibition efficiency and 99 to 99.9 per cent biocidal efficiency. It is interesting to note that addition on PAA did not reduce the corrosion inhibition efficience on the HEDP-Zn^{2+} system.

Analysis of potentiostatic polarisation curves

The polarisation curves on mild steel in various environments are given in Figure 1. Addition of 50ppm PAA to the solution containing 60ppm Cl^- shifted the corrosion potential from –389mV vs SCE to –323mV vs SCE. Addition of 300ppm HEDP shifted the corrosion potential to –330mV vs SCE while addition on 50ppm Zn^{2+} shifted the corrosion potential to –489mV vs SCE. The formulation consisting of 300ppm HEDP, 50 ppm Zn^{2+} and 50ppm PAA shifted the corrosion potential to –691mV vs SCE. these results suggest that HEDP alone and also PAA alone acted as anodic inhibitors; Zn^{2+} alone controlled the cathodic reaction predominantly; the formulation consisting of HEDP, PAA and Zn^{2+} controlled the cathodic reaction predominantly.

Analysis of FTIR spectra

The FTIR spectra on PAA and HEDP are given in Figures 2(a) and (b). the FTIR spectrum on the film scratched from the surface on the metal immersed in the environment consisting of 60ppm Cl^-,

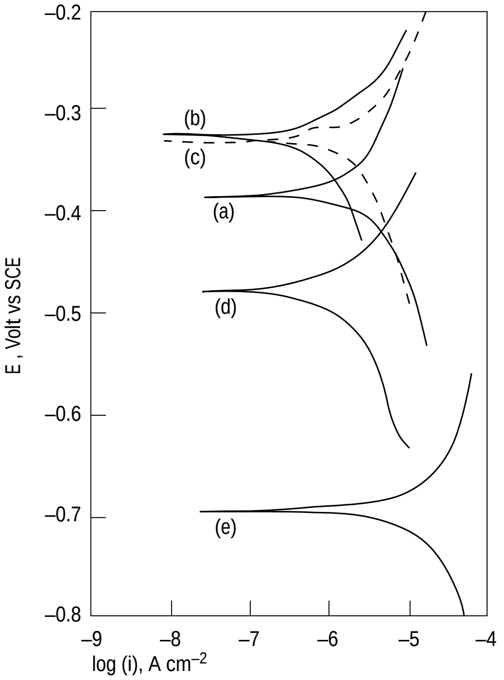
Table I Corrosion rates, inhibition efficiencies and biocidal efficiencies obtained when mild steel is immersed in 60ppm Cl^- environment, in the absence and presence of inhibitors

HEDP (ppm)	Zn^{2+} (ppm)	PAA (ppm)	Corrosion rate (mdd)	I.E. (percent)	Colony forming units/ml	Biocidal efficiency (percent)
0	0	0	15.54	–	10^8	–
300	0	0	10.10	35	–	–
300	10	0	9.32	40	–	–
300	50	0	0.16	99	10^6	99
300	100	0	0.15	99	–	–
300	50	50	0.19	99	10^5 to 10^6	99 to 99.9
0	50	0	19.11	–23	–	–

300ppm HEDP, 50 ppm PAA and 50ppm Zn^{2+} is given in Figure 2(c). The spectrum reveals that the P-O stretching frequency of HEDP has shifted from 1,119cm^{-1} to 107cm^{-1}. This suggests that the O atom on the phosphonic acid (HEDP) has coordinated with Fe^{2+}, resulting in the formation of Fe^{2+}–HEDP complex on the metal surface. The band at 1357.1 cm^{-1} corresponds to $Zn(OH)_2$, deposited on the cathodic sites (Fang *et al.*, 1996; Horner and Horner, 1976; Rajendran *et al.*, 1995; 1996a; 1996b; 1997a; 1997b; Sekine and Kirakawa, 1986).

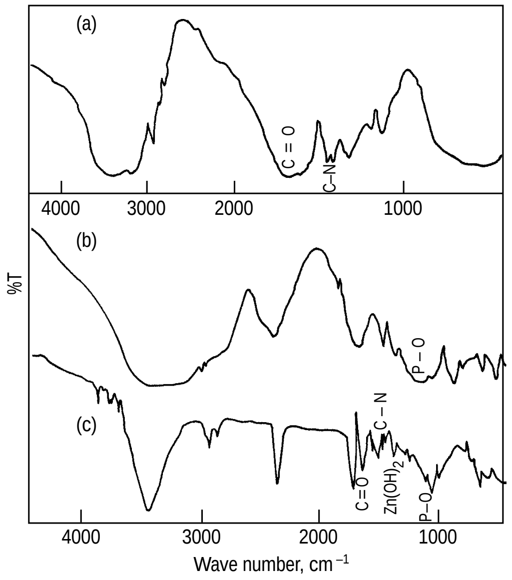
The spectrum also reveals that the C = O stretching frequence on PAA has decreased from 1,666.4cm^{-1} to 1,652.1cm^{-1}; the C-N stretching frequence has increased from 1453.9 cm^{-1} to 1476.2 cm^{-1}. These results suggest that PAA has coordinated with Fe^{2+} through the carbonyl oxygen atom and not through the N atom; the C-N bond acquired double bond character (Rajendran *et al.*, 1997b).

Figure 1 Potentiostatic polarisation curves of mild steel in various environments



Key
(a) Cl^- 60 ppm
(b) Cl^- 60 ppm + PAA 50 ppm
(c) Cl^- 60 ppm + HEDP 300 ppm
(d) Cl^- 60 ppm + Zn^{2+} 50 ppm
(a) Cl^- 60 ppm + PAA 50 ppm + HEDP 300 ppm + Zn^{2+} 50 ppm

Figure 2 FTIR spectra



Key
(a) PAA
(b) HEDP
(c) Film formed on the surface of the metal immersed in the environment containing Cl^- 60 ppm + HEDP 300 ppm + PAA 50 ppm + Zn^{2+} 50 ppm

Analysis of UV-visible reflectance spectra

The UV-visible reflectance spectra on the surface of the metal immersed in various environments are given in Figure 3. The reflectance spectrum on the surface on the metal immersed in the environment containing 60ppm Cl^-, 50ppm PAA and 50ppm Zn^{2+} is given in Figure 3(a). The peak at 320nm is probably due to Fe^{2+}-PAA complex formed on the metal surface.

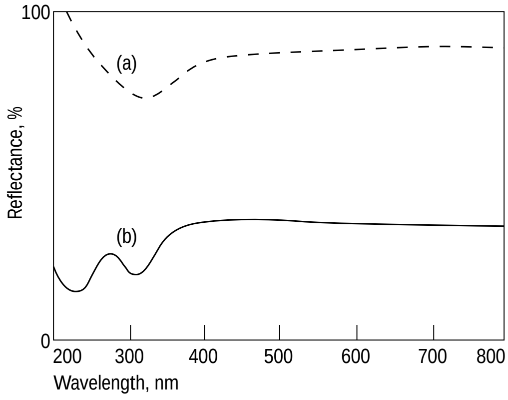
The reflectance spectrum on the surface on the metal immersed in the environment consisting on 60ppm Cl^-, 50ppm PAA, 300ppm HEDP and 50ppm Zn^{2+} is given in Figure 3(b). The peak at 320nm is due to Fe^{2+}–PAA complex and the one at 230nm is due to Fe^{2+}–HEDP complex formed on the metal surface.

Analysis of XRD patterns

The XRD pattern on the surface of the polished metal is given in Figure 4(a). The peaks due to iron appear at 2θ = 44.8°, 65.1°, 82.4°, and 99.0°. The XRD pattern on the film formed on the surface on the metal immersed in the environment consisting of 60ppm Cl^-, 300 ppm HEDP, 50ppm PAA and 50ppm Zn^{2+} is given in Figure 4(b). It shows the peaks due to iron only (2θ = 44.7° and 65.0°). This suggests that:

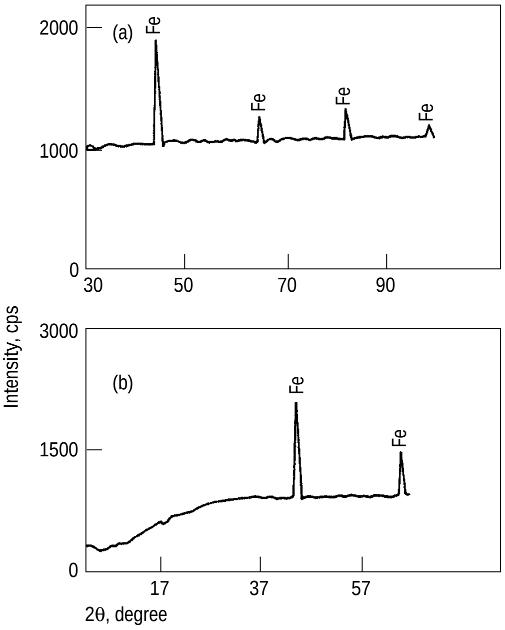
(1) the surface on the metal was as bright as the polished metal;
(2) the protective film was very compact and extremely thin; and
(3) the surface on the metal was free from oxides of iron such as α–FeOOH, T-FeOOH and Fe_3O_4 (Favre and Landolt, 1993).

Figure 3 UV-visible reflectance spectra of the film formed on the surface of metal immersed in various environments



Key
(a) Cl^- 60 ppm + PAA 50 ppm + Zn^{2+} 50 ppm
(b) Cl^- 60 ppm + PAA 50 ppm + Zn^{2+} 50 ppm + HEDP 300 ppm

Figure 4 XRD patterns of the film formed on the surface of metal immersed in various environments



Key
(a) Polished metal
(b) Cl^- 60 ppm + PAA 50 ppm + Zn^{2+}50 ppm + HEDP 300 ppm

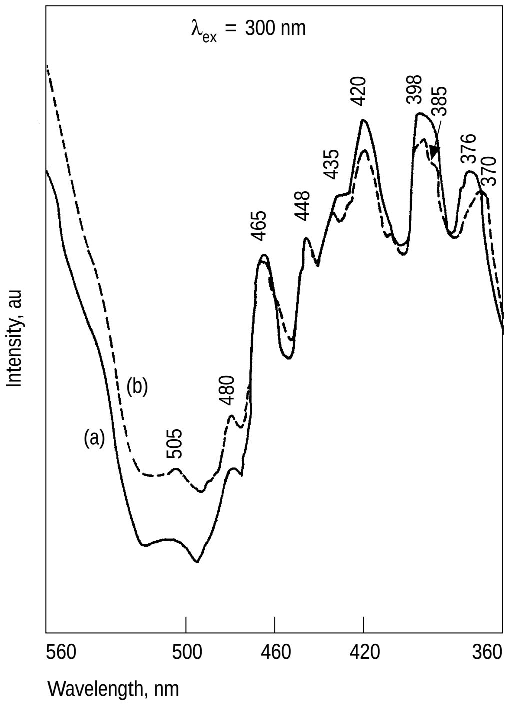
Analysis of luminescence spectra

The luminescence spectra (λ = 300nm) of the surface on the metal immersed in various environments are given in Figures 5(a) and (b). These spectra are, probably, due to Fe^{2+}-HEDP complex and Fe^{2+}-PAA complex formed on the metal surface. The excitation spectra (λ = 420nm) of the film formed on the surface on the metal immersed in various environments are given in Figures 5(c) and (d). The peaks at 230nm and 320nm confirmed the presence of Fe^{2+}-HEDP complex and Fe^{2+}-PAA complex on the metal surface.

Mechanism of corrosion inhibition

The results of the weight loss method reveal that the formulation consisting of 60ppm Cl^-, 300ppm HEDP, 50ppm PAA and 50ppm Zn^{2+} had 99 per cent corrosion inhibition efficiency and 99 to 99.9 per cent biocidal efficiency. Polarisation study suggests that this formulation controlled the cathodic reaction predominantly. Analysis on FTIR spectra suggests that the protective film consisted of Fe^{2+}-HEDP complex, Fe^{2+}-PAA complex

Figure 5a Luminescence spectra of the film formed on the surface of the metal immersed in various environments



and $Zn(OH)_2$. The Uv-visible reflectance spectra and luminescence spectra confirm the presence of Fe^{2+}-HEDP complex and Fe^{2+}-PAA complex on the metal surface. The XRD pattern suggests that the surface of the metal was as bright as the polished metal. In order to explain all these observations in a holistic way, the following mechanism on corrosion inhibition is proposed:

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

(2) Now, when the metal is immersed in this environment, Zn^{2+}-HEDP complex and Zn^{2+}-PAA complex diffuse from the bulk on the solution to the metal surface.

(3) On the metal surface, Zn^{2+}-HEDP complex is converted into Fe^{2+}-HEDP complex on the anodic regions, thus controlling the anodic reaction.
Zn^{2+} -HEDP + Fe^{2+} ⇒ Fe^{2+} -HEDP + Zn^{2+}

(4) Similarly, Zn^{2+}-PAA complex is converted into Fe^{2+}-PAA complex on the anodic regions, thus controlling the anodic reaction.
Zn^{2+}– PAA + Fe^{2+} ⇒ Fe^{2+} – PAA + Zn^{2+}

(5) The released Zn^{2+} combines with OH^- $Zn(OH)_2$ is deposited on the cathodic sites, thus controlling the cathodic reaction.
$Zn^{2+} + 2\,OH^- \Rightarrow Zn(OH)_2 \Downarrow$

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

Conclusions

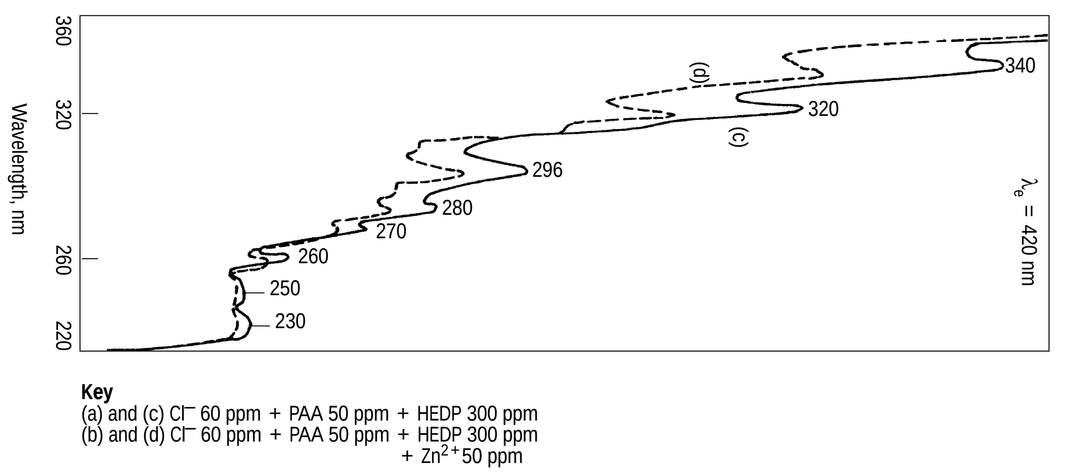
(1) The formulation consisting of 300ppm HEDP, 50ppm PAA and 50ppm Zn^{2+} had 99 per cent corrosion inhibition efficience and 99 to 99.9 per cent biocidal efficiency.

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

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

(4) The above formulation controlled the cathodic reaction predominantly.

Figure 5b Luminescence spectra of the film formed on the surface of the metal immersed in various environments



(5) The above formulation may find application in cooling water systems.

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