Reviewed papers

HEDP-Zn^{2+}: a potential inhibitor system for mild steel in low chloride media

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Keywords

Coatings, Corrosion inhibitors, Mild steel

Abstract

The inhibition efficiency of the HEDP-Zn^{2+} system, in a wider concentration range of Zn^{2+} and HEDP (10, 50, 100, 150, 200 and 300ppm), in controlling corrosion of mild steel immersed in low chloride medium (Cl^- = 60ppm) has been evaluated by weight-loss study. Synergism parameters have been calculated between HEDP and Zn^{2+}. The plot of C/θ vs. C gives a straight line. The HEDP-Zn^{2+} system functions as a mixed inhibitor. The protective film has been analysed by UV-visible reflectance spectra and X-ray diffraction.

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1-hydroxyethane-1, 1-diphosphonic acid (HEDP) has been widely used as corrosion inhibitor due to its scale inhibiting property, stability, ability to form complex with metal ions and low toxicity (Hatch, 1975; Good, 1983, Kuznetzov *et al.*, 1990; Kalman *et al.*, 1994; Konya *et al.*, 1992; Vanloyen and Zhocher, 1990; Terekhin *et al.*, 1990; Duprat and Moran, 1981; Wang *et al.*, 1989; Sekine and Hirakawa 1986; Veres *et al.*, 1992; Fang *et al.*, 1993; Rajendran *et al.*, 1997). The present work is undertaken:

(1) to evaluate the influence of a wider concentration range of Zn^{2+} (10, 50, 100, 150, 200, 300ppm), on the inhibition efficiency of a wider concentration range of HEDP (10, 50, 100, 150, 200, 300ppm);
(2) to determine the synergism parameter existing between Zn^{2+} and HEDP;
(3) to know the nature of the plot C/θ vs. C (where C is concentration of Zn^{2+}; θ is the surface coverage) for various concentration of HEDP;
(4) to study the polarization behaviour of HEDP-Zn^{2+} system; and
(5) to analyse the protective film by UV-visible reflectance spectra and X-ray diffraction.

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 $1.0 \times 4.0 \times 0.2$cm were polished to mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. For potentiostatic polarization 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 a mirror finish and degreased with trichloroethylene.

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.

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Potentiostatic polarization 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.

The UV-visible spectra

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

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 JDX 8030 with CuK_α (Ni-filtered) radiation (λ = 1.5418Å) at a rating of 40kV, 20mA. The scan rate was 0.05-20° per step and the measuring time was one second per step.

Results and discussion

The corrosion inhibition efficiencies (IE) of various concentrations of HEDP-Zn^{2+} system in controlling the corrosion of mild steel in a neutral aqueous environment containing 60ppm chloride are given in Table I. Corrosion rates are shown as a function of the inhibitor concentration in Figure 1.

It is seen from Table I that HEDP alone had low inhibition efficiency while Zn^{2+} alone was found to be corrosive. Interestingly, their combination had good inhibition efficiency, indicating a synergistic effect of HEDP and Zn^{2+}.

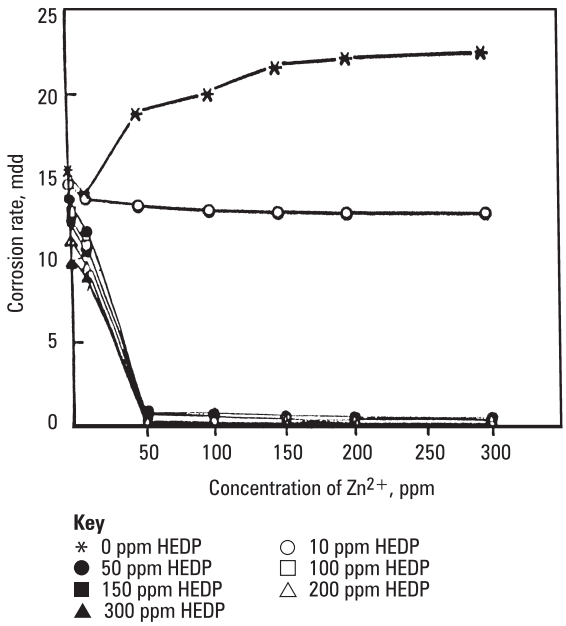
The formulation consisting of very low concentration of HEDP (50ppm) and very low concentration of Zn^{2+} (50ppm) offered very high corrosion inhibition efficiency (98 per cent).

The inhibition efficiency of the HEDP (50)-Zn^{2+} (50) system was not affected by further addition of either HEDP or Zn^{2+} to this system. This is very interesting because in some phosphonic acid-Zn^{2+} systems a decrease in IE is noticed when there is an increase in the concentration either of phosphonic acid or of Zn^{2+}. For example, in the phenyl phosphonic acid-Zn^{2+} system precipitation of phosphonic acid was observed (Rajendran *et al.*, 1995). In the present study various combinations of the HEDP-Zn^{2+} system remain as soluble complex in aqueous solution. This may be due to the presence of

Table I Corrosion inhibition efficiencies (%) offered by various concentrations of HEDP-ZN^{2+} system, to mild steel immersed in 60ppm chloride environment (synergism parameters given in parentheses)

HEDP (ppm)	Zn^{2+}(ppm) 0	10	50	100	150	200	300
0	–	10	–23	–35	–40	–43	–45
10	5	10	13	15	15	16	16
		(–4)	(8)	(10.3)	(11.7)	(11.7)	(12.3)
50	11	22	98	98	98	98	98
		(–4.3)	(2.5)	(3.7)	(4.2)	(4.5)	(4.7)
100	15	30	98	98	98	99	99
		(–4.3)	(3.5)	(5.2)	(5.9)	(6.3)	(6.6)
150	18	35	98	98	98	99	99
		(–4.4)	(4.2)	(6.3)	(7.2)	(7.6)	(8.0)
200	25	38	98	98	98	99	99
		(–5.8)	(5.9)	(8.9)	(10.1)	(10.8)	(11.3)
300	35	40	99	99	99	99	99
		(–7.9)	(8.3)	(12.5)	(14.2)	(15.3)	(16.0)

Figure 1 Corrosion rates of mild steel in neutral aqueous environment (Cl^- = 60ppm) as a function of concentration of the inhibitor



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hydroxyl group in HEDP which favours the solubility of the complex in aqueous solutions.

Synergism parameters

Synergism parameters were calculated using the relationship:

$$S_1 = (1 - I_{1+2})/(1 - I'_{1+2})$$

where

$I_{1+2} = (I_1 + I_2) - (I_1\ I_2)$;
I_1 = inhibition efficiency of substance 1;
I_2 = inhibition efficiency of substance 2;
I'_{1+2} = combined inhibition efficiency of substance 1 and substance 2.

The synergism parameters calculated for various systems consisting of various concentrations of HEDP and Zn^{2+} are given in Table I.

It is found that when the concentration of Zn^{2+} (as $ZnSO_4$) is very low (10ppm), very small inhibition efficiency is noticed and the synergism parameter is negative. But when the concentration of $Zn^{2+} \geqslant$ 50ppm, acceleration of corrosion is noticed and the synergism parameter is positive and greater than 1.

C/θ vs. C curves

Let the surface coverage be represented by θ:

$$\theta = \%\ IE/100 = (W_1 - W_2)/W_1$$

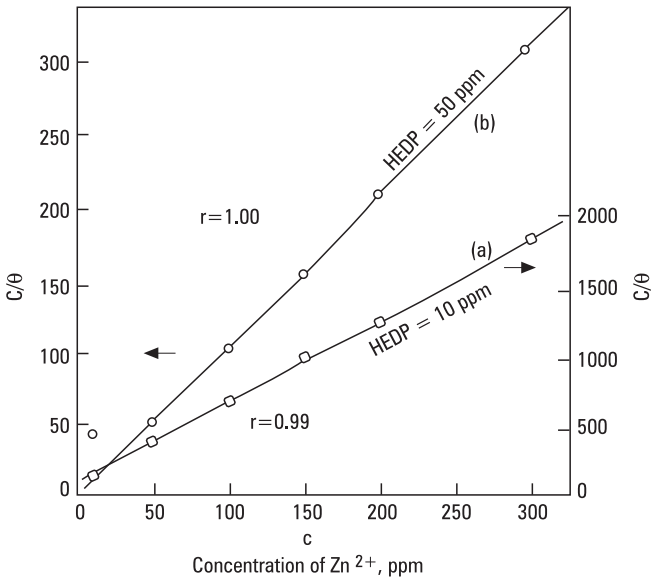
where

W_1 = weight loss in the absence of inhibitor;
W_2 = weight loss in the presence of inhibitor.

Let C represent the concentration of Zn^{2+}. When C/θ is plotted against C for various concentrations of HEDP, straight lines are obtained (Figure 2). When [HEDP] = 10ppm the straight line has correlation coefficient r = 0.99. When [HEDP] = 50ppm, the straight line has r = 1.00.

This represents an ideal protective film formed on the metal surface. Similar straight lines are obtained for other systems also, consisting of [HEDP] = 100, 150, 200 and 300ppm. It is interesting to note that the point corresponding to [Zn^{2+}] = 10ppm slightly deviates from the straight line. This suggests that very low concentrations of Zn^{2+} may be avoided for such systems.

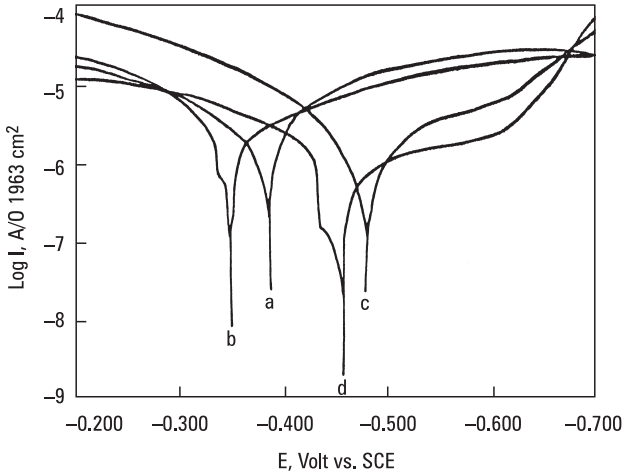
Figure 2 Plot of C/θ vs. C



Analysis of the results of the potentiostatic polarization study

The potentiostatic polarization curves of mild steel immersed in various neutral aqueous environments in the presence and absence of this inhibitor system are given in Figure 3. It is seen from Figure 3 that when 50ppm HEDP is added to 60ppm Cl^- environment the corrosion potential is shifted to positive region (from –389mV vs. SCE to –350mV vs. SCE). The addition of 50ppm Zn^{2+} shifts the corrosion potential to negative region (–489mV vs. SCE). Interestingly, the

Figure 3 Potentiostatic polarization curves of mild steel immersed in various environments



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

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formulation consisting of 50ppm HEDP and 50ppm Zn^{2+} shifts the corrosion potential to –470mV vs. SCE. It is found that this value of corrosion potential is between that of HEDP alone and of Zn^{2+} alone, though it is also negative, relative to the system in the absence of any inhibitor. These results suggest that, while HEDP alone acts as anodic inhibitor, the HEDP-Zn^{2+} combination functions as a mixed inhibitor controlling the anodic reaction by the formation of Fe^{2+}-HEDP complex and the cathodic reaction by the formation of $Zn(OH)_2$.

Analysis of the UV-visible reflectance spectra

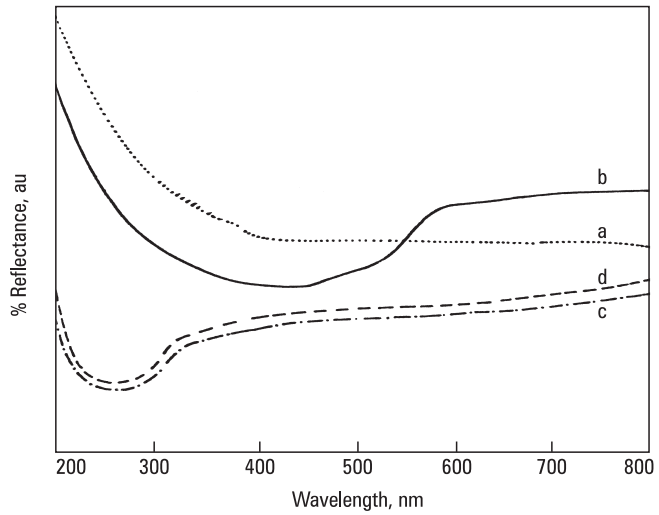
The UV-visible reflectance spectra of the films formed on the surfaces of metal specimens immersed in various test solutions are given in Figures 4a to d. The spectrum of the surface of the polished metal is given in Figure 4a. The spectrum of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^- shows wavelength transition at 550nm. The film has a band gap of (E_g = 1.239/0.55) 2.25eV corresponding to oxides of iron having semiconducting property.

The UV-visible reflectance spectra of the films formed on the surface of the metal specimens immersed in the environment consisting of 60ppm Cl^- and 50ppm HEDP, and also in the system 60ppm Cl^- + 50ppm HEDP + 50ppm Zn^{2+} are given in Figures 4c and d. They do not show any wavelength transition at 550nm, indicating the absence of any kind of oxides of iron on these metal surfaces. Further, absorption peak at 260nm indicates the presence of Fe^{2+}-HEDP complex on these metal surfaces.

Analysis of the X-ray diffraction patterns

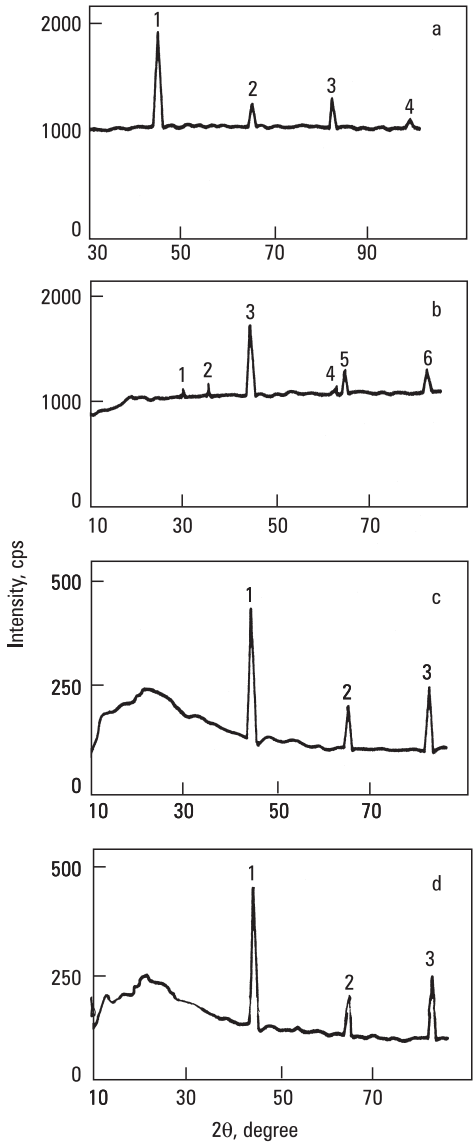
The X-ray diffraction (XRD) patterns of the films formed on the surfaces of the metal specimens immersed in various environments are given in Figure 5a to d.

Figure 4 UV-visible reflectance spectra of mild steel surface immersed in various environments



Key
(a) Polished metal not immersed in any solution
(b) Cl^- 60 ppm
(c) Cl^- 60 ppm + HEDP 50 ppm
(d) Cl^- 60 ppm + HEDP 50 ppm + Zn^{2+} 50 ppm

Figure 5 XRD pattern of mild steel surface immersed in various environments



Key
(a) Polished metal not immersed in any solution
(b) Cl^- 60 ppm
(c) Cl^- 60 ppm + HEDP 50 ppm
(d) Cl^- 60 ppm + HEDP 50 ppm + Zn^{2+} 50 ppm

The XRD pattern of the surface of the polished metal is given in Figure 5a. It shows iron peaks at $2\theta = 44.8^\circ$, 65.1°, 82.4° and 99.0°. The XRD pattern of the surface of the metal immersed in 60ppm Cl^- environment shows the peaks due to magnetite (Fe_3O_4) at $2\theta = 30.1^\circ$, 35.5° and 62.5° apart from the iron peaks at $2\theta = 44.7^\circ$, 65.0° and 82.4° (Figure 5b).

The XRD patterns of the surface of the metal specimens immersed in the environments consisting of 60ppm Cl^- and 50ppm HEDP and also in the system 50ppm Cl^- + 50ppm HEDP + 50ppm Zn^{2+} show the presence of iron peaks only, as in the case of polished metal (Figure 5c and d). It is inferred from this observation that the surfaces of the metal specimens, when immersed in the above systems, were as bright as the polished metal.

Conclusions

(1) HEDP-Zn^{2+} system is found to be a potential inhibitor system, in a wider concentration range of HEDP and Zn^{2+}, for mild steel in a low chloride medium (Cl^- = 60ppm).
(2) Synergism parameters existing between Zn^{2+} and HEDP have been evaluated.
(3) Plot of C/θ vs. C results in a straight line.
(4) HEDP-Zn^{2+} behaves as a mixed inhibitor.
(5) The protective film consists of Fe^{2+}-HEDP complex and $Zn(OH)_2$.

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