Contributed papers

Analysis of protective film formed on surface of mild steel immersed in Chloride – HEDP-molybdate – Zn^{2+} environment

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Abstract

The inhibition efficiency of the formulation consisting of 1-hydroxyethane-1, 1-diphosphonic acid (HEDP), molybdate and Zn^{2+} in controlling the corrosion of mild steel in neutral aqueous environment containing 60ppm Cl^- has been evaluated by the weight-loss method. The formulation consisting of 50ppm HEDP, 300ppm molybdate and 10ppm Zn^{2+} has 97 per cent inhibition efficiency. The nature of the protective film has been analysed by using x-ray diffraction (XRD), FTIR and fluorescence spectra. The protective film is found to be fluorescent and to consist of Fe^{2+}–HEDP complex, $Fe_2(MoO_4)_3$ complex and $Zn(OH)_2$. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from the weight-loss method, polarisation study, XRD, FTIR, fluorescence and atomic absorption spectra.

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Among the various phosphonic acids used as corrosion inhibitors [1-23], 1-hydroxyethane-1, 1-diphosphonic acid (HEDP) has been extensively studied. Molybdates are among the most broadly applied inorganic inhibitors, chiefly because of their efficacy toward both ferrous and nonferrous metals and their very low order of toxicity [24]. Molybdates have been used along with phosphonic acids as corrosion inhibitors [4,9, 19-23]. The present study is undertaken:

(1) to evaluate the inhibition efficiency of the formulation consisting of HEDP, Zn^{2+} and molybdate (as sodium molybdate) in controlling the corrosion of mild steel immersed in neutral aqueous environment containing 60ppm Cl^-;
(2) to understand the nature of the protective film by using x-ray diffraction (XRD), FITR and fluorescence spectra; and
(3) to propose a suitable mechanism of corrosion inhibition based on the results obtained from the weight-loss method, polarisation study, XRD study, FTIR, fluorescence and atomic absorption 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 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.

Weight-loss method

Three mild steel specimens were immersed in 100ml of the solutions containing various

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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 ($\lambda = 1.5418Å$) at 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

The corrosion rates of mild steel immersed in the neutral aqueous environment containing 60ppm chloride, in the absence and presence of inhibitors, are given in Table I. The inhibition efficiencies of various formulations of inhibitors are also given in this table. It is observed from this table that the formulation consisting of 50ppm HEDP and 10ppm Zn^{2+} has an inhibition efficiency of only 22 per cent, whereas in the presence of 300ppm molybdate this inhibition efficiency increases from 22 per cent to 97 per cent. It is also seen from the table that the formulation consisting of 300ppm molybdate and 50ppm HEDP offers 95 per cent inhibition efficiency. This study reveals that a synergistic effect exits between HEDP and molybdate and also among HEDP, molybdate and Zn^{2+}.

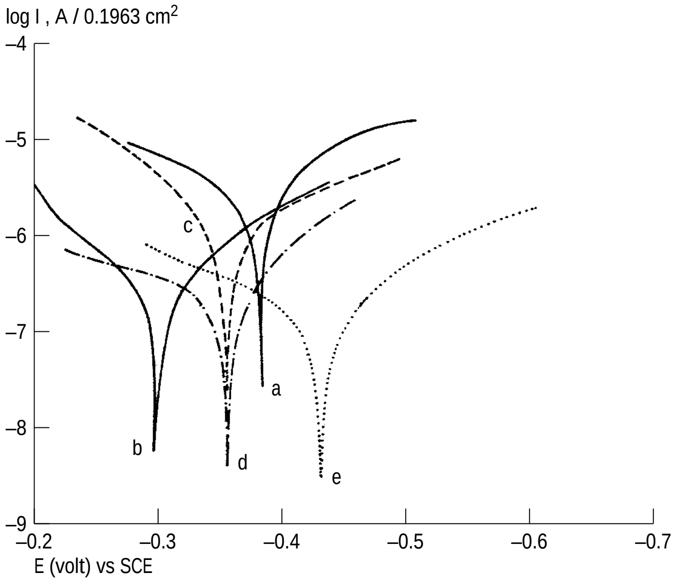
Analysis of the potentiostatic polarisation curves

The potentiostatic polarisation curves of mild steel in various environments are given in Figure 1. In the presence of 60ppm Cl^-, the corrosion potential is –389mV vs SCE. When 300ppm molybdate is added to the above environment, the potential is shifted to positive region (to –300mV vs SCE). When 10ppm Zn^{2+} is added, the potential is shifted to positive region (to –357mV vs SCE). The formulation consisting of 50ppm HEDP and 300ppm molybdate, shifts the potential to

Table I Corrosion rates of mild steel immersed in neutral aqueous environment (Cl^- = 60 ppm) in the absence and presence of inhibitors
Inhibitor system: HEDP + MoO_4^{2-} + Zn^{2+}

Sl. No.	HEDP (ppm)	Zn^{2+} (ppm)	MoO_4^{2-} (ppm)	Corrosion rate (mdd)	Inhibition efficiency (%)
1	0	0	0	15.54	-
2	50	0	0	13.83	11
3	50	10	0	12.12	22
4	100	10	0	10.88	30
5	150	10	0	10.10	35
6	200	10	0	9.63	38
7	300	10	0	9.32	40
8	50	10	300	0.47	97
9	50	0	300	0.78	95
10	0	10	0	13.99	10
11	0	0	300	3.11	80

Figure 1 Potentiostatic polarisation curves of mild steel in various environments



Key

(a) Cl^- 60 ppm
(b) Cl^- 60 ppm + MoO_4^{2-} 300 ppm
(c) Cl^- 60 ppm + Zn^{2+} 10 ppm
(d) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm
(e) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm + Zn^{2+} 10 ppm

–358mV vs SCE (positive region). However, the formulation consisting of 50ppm HEDP, 300ppm molybdate and 10ppm Zn^{2+}, shifts the potential to negative region (to –432mV vs SCE). Polarisation study, thus, reveals that HEDP-molybdate combination controls the anodic reaction predominantly whereas the HEDP-molybdate–Zn^{2+} formulation controls cathodic reaction predominantly.

Analysis of FTIR spectra

FTIR spectra of the films formed on the surface of the metal immersed in various environments are given in Figure 2. The FTIR spectrum of the film formed on the surface of the metal immersed in the formulation consisting of 60ppm Cl^-, 50ppm HEDP and 300ppm molybdate is given in Figure 2a. It is observed that the P-O stretching frequency of the phosphonic acid (HEDP) has shifted from 1,119cm^{-1} to 1022cm^{-1}. This suggests the HEDP has coordinated with Fe^{2+} through the oxygen atom resulting in the formation of $Fe2^+$–HEDP complex on the metal surface [8-20, 25-29]. It is also seen that the Mo-O frequency of molybdate has decreased from 818.1cm^{-1} to 760cm^{-1}. It suggests the formation of iron molybdate complex on the metal surface [19,20].

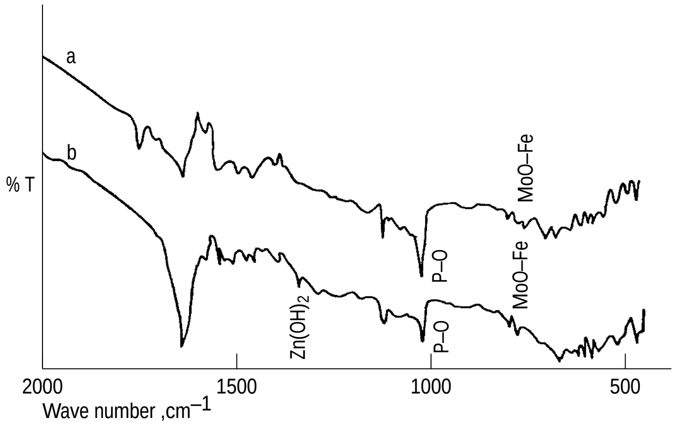
FTIR spectrum of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 50ppm HEDP, 300ppm molybdate and 10ppm Zn^{2+} is given in Figure 2b. It is observed that the P-O stretching frequency of HEDP has shifted from 1,119cm^{-1} to 1020cm^{-1}. This suggests the presence of Fe^{2+} –HEDP complex on the metal surface. The peak at 1353cm^{-1} is due to zinc hydroxide formed on the cathodic sites of the metal surface [8-20, 25-29]. Further, it is seen that the Mo-O frequency decreases from 818.1cm^{-1} to 780cm^{-1}. This suggests the formation of iron molybdate complex on the metal surface [19,20].

Analysis of x-ray diffraction

X-ray diffraction (XRD) patterns of surface of the metal immersed in various environments are given in Figure 3. The XRD pattern of the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 50ppm HEDP and 300 ppm molybdate is given in Figure 3a. The peaks at 21.4° and 66.2° are due to Fe2 (MoO_4) [30]. The peaks due to iron appear at 44.5°, 65.0° and 82.3°.

The XRD pattern of the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 50ppm HEDP, 300ppm molybdate and 10ppm Zn^{2+} is given in Figure 3b. The peaks due $Fe_2(MoO_4)_3$ appear at 21.9° and 66.6°. The peaks due to iron appear at 44.7°, 65.0° and 82.4°.

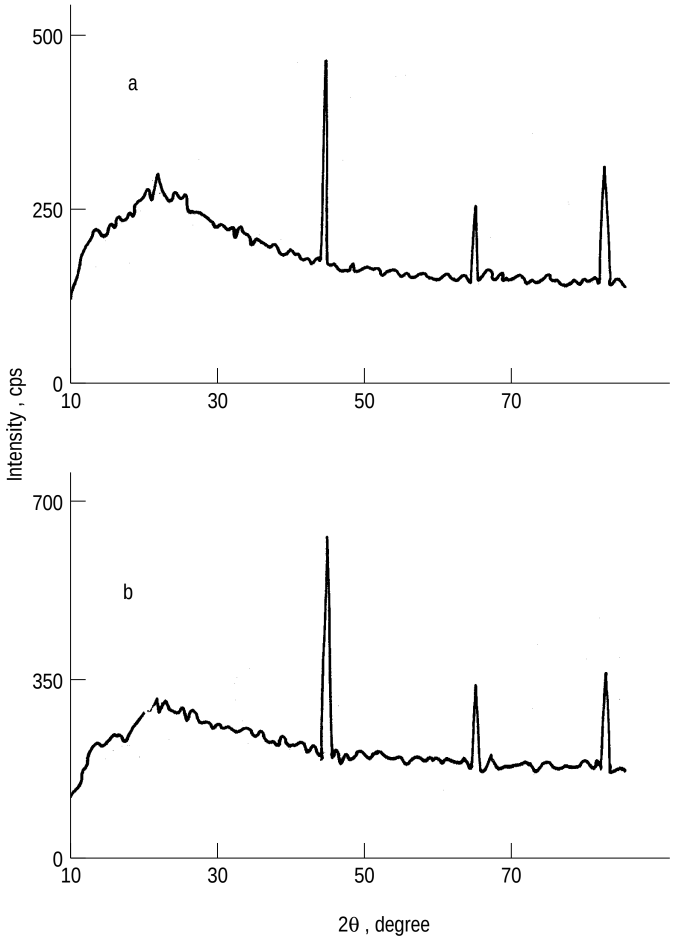
Figure 2 FITR spectra of the films formed on the surface of the metal immersed in various environments



Key

(a) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm
(b) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm + Zn^{2+} 10 ppm

Figure 3 XRD patterns of the films formed on the surface of the metal immersed in various environments

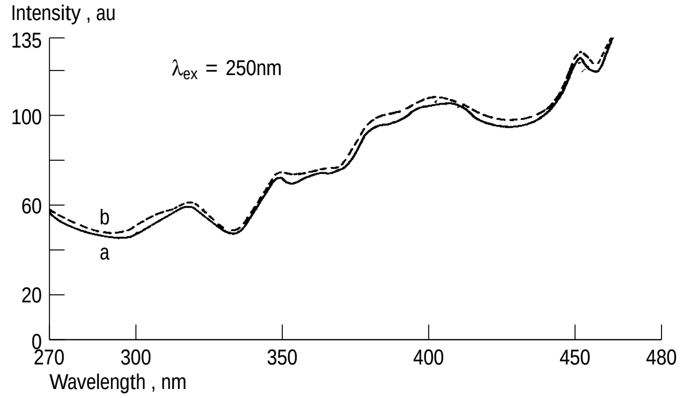


Key

(a) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm

(b) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm + Zn^{2+} 10 ppm

Figure 4 Flourescence spectra of the films formed on the surface of the metal immersed in various environments



Key

(a) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm

(b) Cl^- 60 ppm + MoO_4^{2-} 300 ppm + HEDP 50 ppm + Zn^{2+} 10 ppm

Analysis of fluorescence spectra

The fluorescence spectra (λ_{ex} = 250nm) of the films formed on the surface of the metal immersed in various environments are given in Figure 4. The fluorescence spectrum of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 50ppm HEDP and 300ppm molybdate is given in Figure 4a. Peaks appear at 315, 348, 400 and 450nm. The spectrum is, probably, due to Fe^{2+} –HEDP complex and $Fe_2(MoO_4)_3$ complex formed on the metal surface.

The fluorescence spectrum of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 50ppm HEDP, 300ppm molybdate and 10 ppm Zn^{2+} is given in Figure 4b. Peaks appear at the same positions as in the previous case. However, a small increase in intensity is observed. This suggests that the formation of Fe^{2+}–HEDP complex and $Fe_2(MoO_4)_3$ complex is slightly enhanced in the presence of Zn^{2+}. This is in agreement with results of the weight-loss method which reveals that the inhibition efficiencies are 95 per cent and 97 per cent in the absence and presence of Zn^{2+} respectively.

Analysis of the results of atomic absorption spectra

The amount of metal ions present in various test solutions in which mild steel specimens were immersed for a period of seven days is given in Table II. When mild steel was immersed in the environment consisting of 60ppm Cl^-, 50ppm HEDP and 300ppm molybdate, the test solution contained 66 ppm of iron and zero ppm of molybdate. This indicates that all the molybdate has diffused from the bulk of the solution towards the metal surface and deposited there, probably, as iron molybdate complex (as revealed by XRD study).

It is also observed from Table II that in the presence of Zn^{2+}, the amount of iron present in the test solution after seven days is less,

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)**	**MoO^{2-} (ppm)**	**Zn^{2+} (ppm)**	**Iron (ppm)**	**Zinc (ppm)**	**MoO^{2-}_4 (ppm)**
1	60	50	300	-	66	-	0
2	60	50	300	10	55	6	0

relative to the previous case (i.e. in the absence of Zn^{2+}). This suggests that the rate of dissolution of the protective film (iron complexes) formed on the metal surface is higher in the former case than in the latter case. It is seen from Table II that the amount of molybdate present in the test solution is found to be zero. This suggests that all molybdate has diffused from the bulk of the solution to the metal surface and deposited there as iron molybdate complex (as revealed by XRD study). It is also seen from Table II that out of 10ppm Zn^{2+} added to the environment 4ppm Zn^{2+} has diffused to the metal surface and deposited there as $Zn(OH)_2$ as confirmed by FTIR spectra.

Mechanism of corrosion inhibition

The results of the weight loss method reveal that the formulation consisting of 50ppm HEDP, 300ppm molybdate and 10ppm Zn^{2+} has 97 per cent inhibition efficiency. Polarisation study reveals that this formulation controls the cathodic reaction predominantly. FTIR spectrum suggests that the protective film consists of iron molybdate complex, Fe^{2+}–HEDP complex and $Zn(OH)_2$. XRD study reveals that the iron molybdate complex formed on the metal surface is $Fe_2(MoO_4)_3$.

Fluorescence spectrum reveals that the protective film is fluorescent. In order to explain all these observations in a holistic way, the following mechanism of corrosion inhibition is proposed.

(1) When the environment containing 60 ppm Cl^-, 50ppm HEDP, 300 ppm molybdate and 10ppm Zn^{2+} is prepared, there is formation of Zn^{2+}–HEDP complex and Zn^{2+}–MoO_4^{2-} complex in solution.

(2) When the metal is immersed in this environment, Zn^{2+}–HEDP complex and Zn^{2+}–MoO_4^{2-} complex diffuse from the bulk of the solution to the surface of the metal.

(3) On the surface of the metal, Zn^{2+}–HEDP complex is converted into Fe^{2+}–HEDP complex in the local anodic sites.

$$Zn^{2+}\text{–HEDP} + Fe^{2+} \Rightarrow Fe^{2+}\text{–HEDP} + Zn^{2+}$$

(4) Similarly, Zn^{2+}–MoO_4^{2-} complex is converted into iron molybdate complex, namely, $Fe_2(MoO_4)_3$.

$$3\ Zn^{2+}\text{–}MoO_4^{2-} + 2\ Fe^{2+} \Rightarrow Fe_2(MoO_4)_3 + 3\ Zn^{2+}$$

(5) The released Zn^{2+} forms $Zn(OH)_2$ in the local cathodic regions.

$$Zn^{2+} + 2\ OH^- \Rightarrow Zn(OH)_2 \Downarrow$$

(6) Thus the protective film consists of Fe^{2+}–HEDP complex, $Fe_2(MoO_4)_3$ complex and $Zn(OH)_2$.

Conclusions

(1) The formulation consisting of 50ppm HEDP, 300ppm molybdate and 10ppm Zn^{2+} has 97 per cent corrosion inhibition efficiency.
(2) This formulation controls the cathodic reaction predominantly.
(3) The protective film is found to be fluorescent and to consist of Fe^{2+}–HEDP complex, $Fe_2(MoO_4)_3$ complex and $Zn(OH)_2$.
(4) This formulation can be used in cooling water systems.

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