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Role of Zn^{2+} in the inhibition of corrosion of mild steel by 1-hydroxyethane-1, 1-diphosphonic acid

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50 ppm sodium salt of 1-hydroxyethane-1, 1-diphosphonic acid (HEDP) offered only 11% inhibition efficiency (IE) to corrosion of mild steel immersed in neutral aqueous environment containing 60 ppm chloride. When 50 ppm Zn^{2+} is added to 50 ppm HEDP, the IE increased to 98%. The influence of Zn^{2+} on the corrosion -inhibition by HEDP is discussed based on the results obtained from UV-visible, FTIR and luminescence spectra. Presence of Zn^{2+} facilitates the transport of HEDP from the bulk of the solution to the metal surface; both the anodic reaction and cathodic reaction are controlled effectively.

Phosphonic acids have been extensively used as corrosion inhibitors due to their hydrolytic stability, ability to form complexes with metal ions and scale inhibiting property[1-20]. Several reports have discussed the use of 1-hydroxyethane-1, 1-diphosphonic acid (HEDP) as corrosion inhibitor[3,6,14-20]. Sekine and Hirakawa investigated the effectiveness of HEDP as corrosion inhibitor by measuring weight losses and polarization curves of SS41 Steel in 0.3% NaCl. They observed that in concentrations lower than 50 ppm of HEDP, the corrosion of SS41 steel was inhibited in accordance with the Langmuir adsorption isotherm of HEDP on the steel. In concentrations greater than 50 ppm of HEDP, the iron complex of HEDP developed, and the inhibition effect was decreased[15]. Kalman *et al.*,[20] have investigated the impedance spectra of carbon steel in the presence of HEDP in neutral, 0.5 mol dm^{-3} aqueous $NaClO_4$ solutions. The concentration of inhibitor was changed in the range of 10^{-5} to 10^{-2} mol dm^{-3}. Results of the investigations showed that at low concentrations, HEDP inhibits carbon steel corrosion by a precipitation mechanism forming insoluble iron complexes and repairing the porous oxide layer formed on the metal surface. Increasing HEDP concentration beyond the optimal value decreases its corrosion inhibition efficiency due to the dissolution of the oxide layer. The present work aims (a) to study the influence of addition of Zn^{2+} to a given concentration of HEDP on the inhibition of corrosion of mild steel in neutral aqueous environment containing 60 ppm chloride, a situation commonly encountered in cooling water system, (b) to understand the nature of the protective film formed on the metal surface by using FTIR and luminescence spectra and (c) to propose a mechanism of corrosion inhibition based on the results obtained from UV-visible, FTIR and luminescence spectra.

Experimental Procedure

Preparation of the specimens

Mild steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of the dimensions 1×4×0.2 cm were polished to mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

Weight-loss method

Mild steel specimens, in triplicate, were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} (as $ZnSO_4.7H_2O$) for a period of seven days. 60 ppm of Cl^- was introduced by dissolving of NaCl in triple distilled water. The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion inhibition efficiency (IE) was calculated using the equation:

$$IE = 100\ [1 - (W_2 / W_1)]\ \%$$

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Table 1—Corrosion rates of mild steel in neutral aqueous environment ($Cl^- = 60$ ppm) 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	50	0	13.83	11
3	50	10	12.12	22
4	50	50	0.37	98
5	50	100	0.35	98
6	50	150	0.31	98
7	50	200	0.29	98
8	50	300	0.25	98
9	0	50	19.11	-23

where W_1 = Corrosion rate in the absence of inhibitor, W_2 = Corrosion rate in the presence of inhibitor.

The UV-visible spectra

The UV-visible absorption spectra of aqueous solutions were recorded using a Hitachi U-3400 spectrophotometer. Aqueous solutions containing 50 ppm of HEDP, 50 ppm of Zn^{2+} (as $ZnSO_4.7H_2O$), and 100 ppm of Fe^{2+} (as $FeSO_4.7H_2O$) were used for recording the UV-visible absorption spectra.

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 FTIR spectra

The FTIR spectra were recorded using a Perkin-Elmer 1600 FTIR spectrophotometer. The FTIR spectrum of pure HEDP was recorded by KBr pellet method. The FTIR spectrum of the protective film was recorded, by carefully removing the film, mixing it with KBr and making the pellet.

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 928 F photomultiplier tube. The emission spectra were corrected for the spectral response of the photomultiplier tube used and the excitation spectra recorded were corrected for variation in the beam intensity.

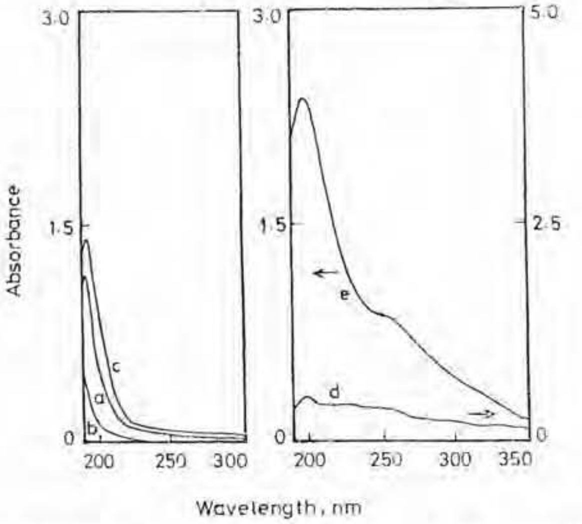

Fig 1—UV-visible absorption spectra of solutions. (a) HEDP 50 ppm; (b) Zn^{2+} 50 ppm; (c) HEDP 50 ppm + Zn^{2+} 50 ppm; (d) Fe^{2+} 100 ppm; (e) HEDP 50 ppm + Fe^{2+} 100 ppm

Results and Discussion

Analysis of the results of the weight-loss method

Corrosion rates of mild steel in neutral aqueous environment containing 60 ppm chloride in the presence and absence of the inhibitor system consisting of various concentrations of HEDP and Zn^{2+}, obtained by weight-loss method are given in Table 1. The corrosion inhibition efficiencies of the system HEDP-Zn^{2+} are also given in this Table.

It is evident from these results that 50 ppm HEDP has an inhibition efficiency of 11 percent only while 50 ppm Zn^{2+}, without HEDP is found to be corrosive. However, the formulation consisting of 50 ppm HEDP and 50 ppm Zn^{2+} offers an inhibition efficiency of 98 percent. This clearly shows the synergistic effect of HEDP and Zn^{2+} combination. A thin interference film is observed on the surface of the metal, when it is immersed in the above environment during weight-loss experiment.

Analysis of the UV-visible absorption spectra

The UV-visible absorption spectra of the various test solutions are given in Fig. 1. The aqueous solution containing 50 ppm HEDP has a peak at 192 nm. An increase in the value of absorbance is noticed in the absorption spectrum of the solution consisting of 50 ppm HEDP and 50 ppm Zn^{2+} (as

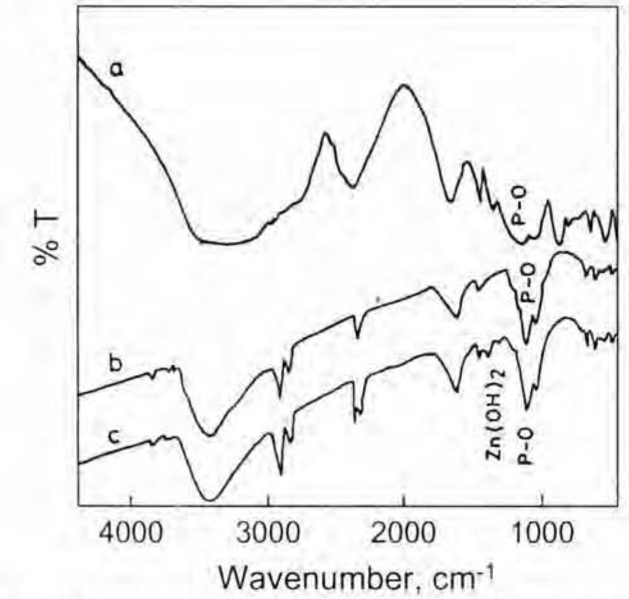

Fig 2—FTIR spectra of HEDP (a) and of mild steel surface immersed in various environments (b,c) pure HEDP; (b) Cl^- 60 ppm + HEDP 50 ppm; (c) Cl^- 60 ppm + HEDP; (d) 50 ppm + Zn^{2+} 50 ppm

$ZnSO_4.7H_2O$). This indicates the possibility of formation of Zn^{2+}-HEDP complex in solution. The electronic spectrum of the solution consisting of 50 ppm HEDP and 100 ppm Fe^{2+} (as $FeSO_4.7H_2O$) shows two peaks one at 198 nm and the other at 252 nm. There is an increase in the value of absorbance also when compared to either of the species. From these results, it is inferred that a complex is formed between Fe^{2+} and HEDP in solution.

Analysis of the FTIR spectra

The FTIR spectrum of pure HEDP is given in Fig. 2a. The FTIR spectrum of the film scratched from the surface of the metal immersed in the environment consisting of 60 ppm Cl^- and 50 ppm HEDP is given in Fig. 2b. It is found that the P-O stretching frequency of HEDP decreases from 1119 cm^{-1} to 1047.1 cm^{-1}. This shift is caused by the decrease of electron cloud density of the P-O bond[4,8]. Due to the shift of the electron cloud density from O atom to Fe^{2+}, it is suggested that the O atom of the phosphonic acid is coordinated to Fe^{2+} resulting in the formation of Fe^{2+}-HEDP complex on the metal surface[8,21-25].

The FTIR spectrum of the film scratched from the surface of the metal immersed in the solution containing 60 ppm Cl^-, 50 ppm HEDP and 50 ppm Zn^{2+} is given in Fig. 2c. It is observed that the P-O stretching frequency has decreased from 1119 cm^{-1} to 1047.6 cm^{-1}. This indicates the formation of Fe^{2+}-HEDP complex on the metal surface. The band at 1357.1 cm^{-1} is due to $Zn(OH)_2$[8,21-25].

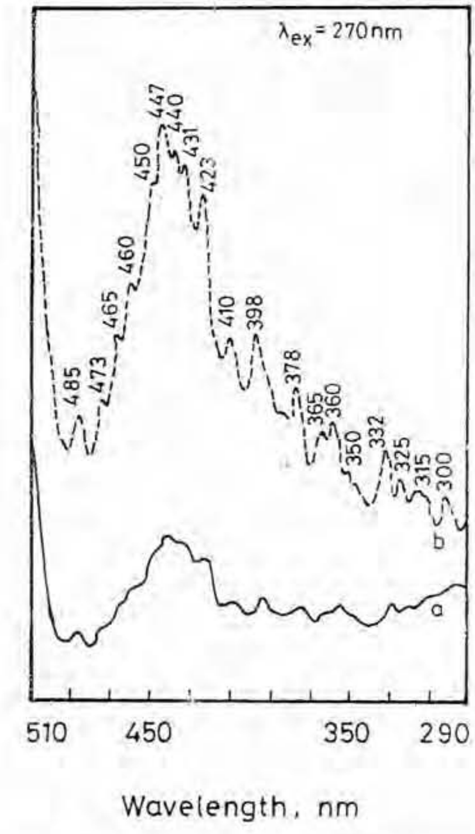

Fig 3—Luminescence spectra of mild steel surface immersed in various environments (a) Cl^- 60 ppm + HEDP 50 ppm; (b) Cl^- 60 ppm + HEDP 50 ppm + Zn^{2+} 50 ppm

Analysis of the luminescence spectra

The emission spectrum (λ_{ex} = 270 nm) of the film formed on the surface of the metal immersed in aqueous solution consisting of 60 ppm Cl^- and 50 ppm HEDP is given in Fig. 3a. It is observed that the intensity of the peaks increases upon addition of 50 ppm Zn^{2+} to the above environment (Fig. 3b). This clearly indicates that the formation of Fe^{2+} - HEDP complex on the metal surface is enhanced by the presence of Zn^{2+} in the environment.

Influence of Zn^{2+} on corrosion inhibition by HEDP

HEDP by itself functions as a poor inhibitor. In the presence of Zn^{2+} its inhibition efficiency is tremendously improved. This may be explained by the fact that, HEDP, when present alone, controls the anodic reaction (Fe ----------> Fe^{2+} + $2e^-$) only by forming Fe^{2+}-HEDP complex on the metal surface.

This film is easily broken by the aggressive chloride ions. Further, Fe^{2+}-HEDP complex dissolves. In the presence of Zn^{2+}, HEDP forms Zn^{2+}-HEDP complex (in solution) which diffuses from the bulk of the solution to the metal surface. Thus, presence of Zn^{2+} facilitates the transport of HEDP towards the metal surface. Now, not only the anodic reaction but also the cathodic reaction ($2\ H_2O + O_2 + 4e^- \text{------>} 4\ OH^-$) is controlled by formation of $Zn(OH)_2$. This accounts for the improved inhibition efficiency of the HEDP – Zn^{2+} system. This is confirmed by FTIR study which reveals the presence of Fe^{2+} - HEDP complex and $Zn(OH)_2$ on the metal surface. Luminescence spectra reveal that in the presence of Zn^{2+}, there is an increase in the intensities of the peaks due to Fe^{2+} - HEDP complex. This suggests that the formation of Fe^{2+}-HEDP complex is facilitated by the presence of Zn^{2+}.

In the case of some phosphonic acid -Zn^{2+} systems, when various concentrations of Zn^{2+} are added to a given concentration of phosphonic acid, a decrease in inhibition efficiency is noticed due to the precipitation of phosphonic acid -Zn^{2+} complex. This type of behaviour has been observed in phenyl phosphonic acid -Zn^{2+} system[8,12] and also with ATMP -Zn^{2+} system[9]. But in the present system an interesting observation is made. It is observed that when 50 ppm Zn^{2+} is added to 50 ppm HEDP, the IE is enhanced from 11% to 98%. Further addition of Zn^{2+} (100, 150, 200 and 300 ppm) does not decrease the I.E. of the system. This suggests that at these concentrations also, HEDP and Zn^{2+} form soluble complex in solution, which facilitates the transport of HEDP and Zn^{2+} to the metal surface. Thus, it is found that the HEDP -Zn^{2+} system functions as an efficient inhibitor system in a wider concentration range of Zn^{2+}.

Conclusions

(i) The formulation consisting of 50 ppm HEDP and 50 ppm Zn^{2+} offered 98% inhibition efficiency to the corrosion of mild steel immersed in neutral aqueous environment containing 60 ppm chloride.

(ii) The presence of Zn^{2+} facilitates the transport of HEDP from the bulk of the solution to the metal surface.

(iii) HEDP-Zn^{2+} system controls both the anodic and cathodic reactions.

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

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

(vi) This formulation may find application in cooling water system.

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