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INVESTIGATION OF THE INHIBITING EFFECT OF ETHYL PHOSPHONIC ACID - Zn^{2+} SYSTEM

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The inhibiting effect of various combinations of ethyl phosphonic acid (EPA)-Zn^{2+} system in controlling corrosion of mild steel in neutral aqueous environment, containing 60 ppm Cl^- has been investigated by weight loss method. Polarisation study reveals that EPA-Zn^{2+} system functions as a mixed inhibitor. The nature of the protective film has been analysed by X-ray diffraction.

Keywords: Corrosion inhibition, phosphonic acid, steel, synergistic effect, synergism parameter.

INTRODUCTION

The need to develop inhibitor formulations free from chromates, nitrites and inorganic phospho rous compounds has stimulated research work on "Phosphonates as corrosion inhibitors" [1-10]. Phosphonates are sodium, potassium or ammonium salts of phosphonic acids. Studies on phosphonates as inhibitors in cooling water systems have gained considerable importance because of their ability to form complexes with metal ions, scale inhibiting property, hydrolytic stability and resistance to degradation by chlorine. The synergistic effect of ethyl phosphonic acid (EPA) and Zn^{2+} in low chloride media has been reported [7]. The present investigation is undertaken (i) to study the inhibiting property of various combinations of sodium salt of ethyl phosphonic acid (EPA)-Zn^{2+} system in controlling corrosion of mild steel in neutral aqueous environment, containing 60 ppm Cl^-, a situation commonly encountered in cooling water systems, (ii) to know whether this system functions as anodic, cathodic or mixed inhibitors and (iii) to study the nature of the protective film by X ray diffraction.

EXPERIMENTAL

Preparation of the specimens

Mild steel species (iron containing 0.02 to 0.03% S, 0.03 to 0.08% P, 0.4 to 0.5% Mn and 0.1 to 0.2% C) of the dimensions 1 x 4 x 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 100 ml of the solution 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 polarization study

This study was carried out in a three electrode cell assembly connected to a Bioanalytical system (BAS-100 A) 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 seven days. After seven days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by surface analysis technique.

X ray diffraction (XRD) 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 = 1.5418 Ä) at a rating of 40 kV, 20 mA.

RESULTS AND DISCUSSION

Analysis of the results of the weight loss study

Corrosion rates of mild steel in neutral aqueous environment containing 60 ppm chloride in the absence and presence of inhibitor at various concentrations have been measured by weight loss method. Corrosion rates, as a function of the inhibitor concentration are shown in Fig. 1. The corrosion inhibition efficiencies (IE) of the ethyl phosphonic acid (EPA)-Zn^{2+} system are given in Table I.

It is observed from these results that EPA by itself is a poor corrosion inhibitor. Also, Zn^{2+} is found to be corrosive (Table II). However, interestingly, EPA-Zn^{2+} combination offers good corrosion inhibition. This suggests a synergistic effect of EPA and Zn^{2+} combination. It is observed that the formulation consisting of 300 ppm EPA and 300 ppm Zn^{2+} offers 88% inhibition efficiency. This is found to be the maximum inhibition efficiency offered by this system.

C/ θ-C curves

Let θ represents surface coverage

$$\theta = \% \frac{IE}{100} = \frac{W_1 - W_2}{W_1} \qquad (1)$$

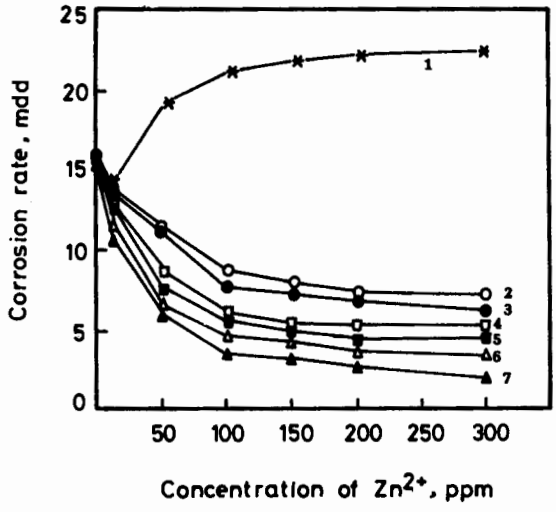

Fig. 1: Corrosion rate of mild steel in neutral aqueous environment (Cl^- = 60 ppm) as a function of concentration of the inhibitor
(1) 0 ppm EPA (2) 10 ppm EPA (3) 50 ppm EPA (4) 100 ppm EPA (5) 150 ppm EPA (6) 200 ppm EPA (7) 300 ppm EPA

TABLE I: Inhibition efficiencies (%) of various EPA-Zn^{2+} systems when mild steel is immersed in the environment containing 60 ppm Cl^-

EPA (ppm)	0	10	50	100	150	200	300
0	—	10	-23	-35	-40	-43	-45
10	5	12	25	44	48	52	53
50	5	15	27	50	52	55	62
100	7	14	45	61	65	65	65
150	3	15	30	62	68	70	70
200	2	25	58	70	70	78	79
300	2	30	60	78	78	82	88

where W_1 is weight loss in the absence of inhibition and W_2 is weight loss in the presence of inhibitor.

Let C represents the concentration of Zn^{2+}.

When C/ θ is plotted against C for various concentrations of EPA, straight lines are obtained. The straight line obtained when (EPA) = 150 ppm is given in Fig. 2.

Synergism parameters

Synergism parameters are calculated using the relationship

$$S_1 = \frac{I - I_{1+2}}{I - I'_{1+2}} \qquad (2)$$

$$I_{1+2} = (I_1 + I_2) - (I_1 I_2) \qquad (3)$$

where I_1 is IE of substance 1, I_2 is IE of substance 2 and I'_{1+2} is combined IE of substance 1 and substance 2

The synergism parameters calculated for various systems comprising of various concentrations of EPA and Zn^{2+} are given in Table II.

TABLE II: Synergism parameters for various EPA-Zn^{2+} systems

EPA (ppm)	Zn^{2+} (ppm) 10	50	100	150	200	300
10	-3.3	4.0	3.4	3.5	-3.5	3.5
50	-2.6	3.7	2.9	3.2	3.3	3.0
100	-2.7	3.3	3.6	3.8	4.1	4.3
150	-1.3	1.7	1.2	1.2	1.3	1.4
200	-0.4	0.4	0.5	0.6	0.6	0.6
300	-0.3	0.4	0.5	0.5	0.5	0.5

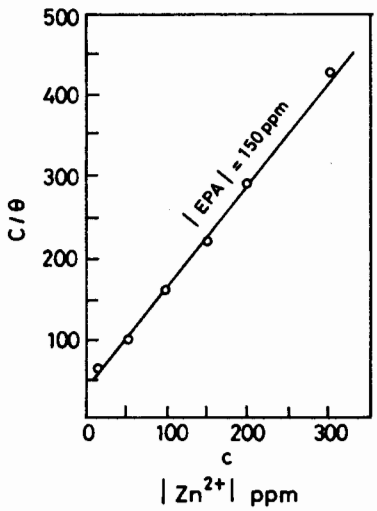

Fig. 2: C/θ vs C curve

Analysis of the results of potentiostatic polarisation study

Weight loss study revealed that the formulation consisting of 300 ppm EPA and 300 ppm Zn^{2+} had 88% IE. Potentiostatic polarisation study was carried out to know the nature of this inhibitor system whether anodic, cathodic or mixed.

The potentiostatic polarisation curves of mild steel immersed in various environments are given in Fig. 3. It is seen from Fig. 3 that 300 ppm of EPA alone shifts the corrosion potential to the positive side (from -389 mV vs SCE to - 375 mV vs SCE) while 300 ppm Zn^{2+} alone shifts the corrosion potential to the negative side (to -651 mV vs SCE). In the presence of 300 ppm EPA -300 ppm Zn^{2+} combination, the corrosion potential is shifted to -431 mV vs SCE. This potential is in between that of EPA alone and Zn^{2+} alone, though it is also cathodic (negative) relative to the system in the absence of any inhibitor. This suggests that this formulation functions as a mixed inhibitor, controlling both the anodic reaction.

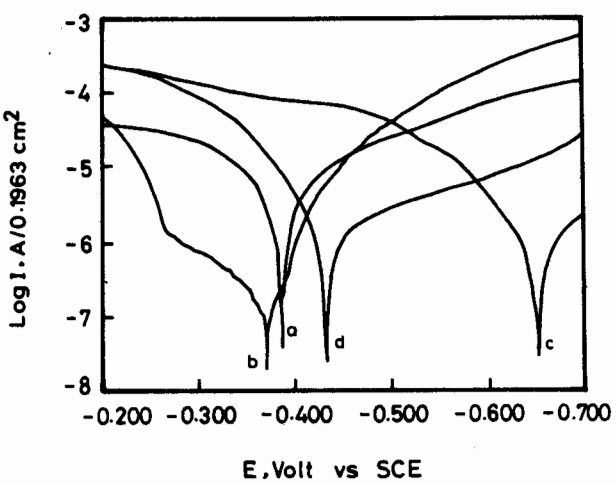

Fig. 3: Potentiostatic polarisation curves of mild steel immersed in various environments
(1) Cl^- 60 ppm (b) Cl^- 60 ppm + EPA 300 ppm
(c) Cl^- 60 ppm + Zn^{2+} 300 ppm
(d) Cl^- 60 ppm + EPA 300 ppm + Zn^{2+} 300 ppm

$$Fe \longrightarrow Fe^{2+} + 2e \quad (5)$$

and the cathodic reaction (generation of hydroxyl ions)

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^- \quad (6)$$

EPA transports Zn^{2+} to the metal surface, where EPA controls the anodic reaction by forming Fe^{2+} - EPA complex on the anodic sites. The released Zn^{2+} combines with OH^- generated on the cathodic sites and forms $Zn(OH)_2$ thus blocking the cathodic sites. Thus both the anodic and cathodic reactions are effectively controlled by the EPA-Zn^{2+} system.

Analysis of X ray diffraction patterns

The X ray diffraction (XRD) patterns of the films formed on the surfaces of the metal specimens immersed in various test solutions are given in Fig. 4. The various diffraction parameters such as glancing angle (2θ), interplanar spacing (d), intensity of peaks (I) and relative intensities of the peaks (I/I_0) are given in Table III.

In the case of the polished metal, the peaks due to iron appear at $2\theta = 44.8^0$, 65.1^0, 82.4^0 and 99.0^0 (Fig. 4a). The XRD patterns of the surface of the metal immersed in the environment consisting of 60 ppm Cl^- 300 ppm EPA, for a period of seven days, is given in Fig. 4b. The brown film formed on the surface is found to consist of α-FeOOH ($2\theta = 40.0^0$, 53.1^0) and γ-FeOOH ($2\theta = 14.5^0$, 36.8^0, 47.3^0, 60.9^0). The peaks due to iron appear at $2\theta = 65.5^0$ and 82.5^0.

The XRD patterns of the surface of the metal immersed in the environment consisting of 60 ppm Cl^-, 300 ppm EPA and 300 ppm Zn^{2+}, for a period of seven days is given in Fig. 4c. The surface was found to consist a very thin brown film (probably oxides of iron) and a very thin interference film (probably due to iron - EPA complex). The peaks due to only iron, comparable to that of the polished metal, appear at $2\theta = 65.5^0$ and 82.8^0, indicating the absence of

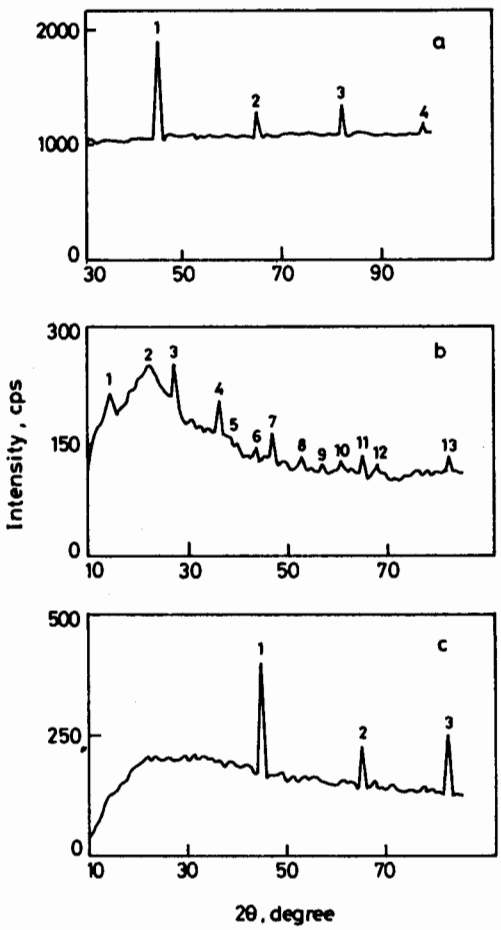

Fig. 4: XRD patterns of mild sttel surface immersed in various environments for seven days
(a) polished metal (b) Cl^- 60 ppm + EPA 300 ppm
(c) Cl^- 60 ppm + EPA 300 ppm + Zn^{2+} 300 ppm

oxides of iron. This may be due to the thinness of the iron oxide film.

CONCLUSION

- The present investigation leads to the following conclusions.
- Ethyl phosphonic acid and Zn^{2+} show a synergistic effect.
- The formulation consisting of 300 ppm EPA and 300 ppm Zn^{2+} functions as a mixed inhibitor.
- C/θ vs C plot gives a straight line.
- Synergism parameters have been calculated for various EPA- Zn^{2+} systems.

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TABLE III: XRD parameters of mild steel immersed in various environments

Environment	Peak no	Glancing angle 2θ degree	Inter planar spacing, d, Å	Intensity I, cps	Relative intensity I/I_0
A	1	44.80	2.021	1919	100
	2	65.10	1.432	1252	65
	3	88.40	1.169	1317	69
	4	99.00	1.013	1136	59
B	1	14.50	6.104	212	85
	2	22.30	3.983	250	100
	3	27.70	3.218	249	100
	4	36.80	2.440	203	81
	5	40.00	2.252	147	59
	6	43.80	2.065	145	58
	7	47.30	1.920	163	65
	8	53.10	1.723	130	52
	9	57.50	1.601	119	48
	10	60.90	1.520	125	50
	11	65.50	1.424	131	52
	12	68.20	1.374	119	48
	13	82.80	1.165	131	52
C	1	44.80	2.021	403	100
	2	65.40	1.432	233	58
	3	82.50	1.168	257	64

A = Polished metal
B = Polished metal + Cl^- 60 ppm + EPA 300 ppm
C = Polished metal + Cl^- 60 ppm + EPA 300 ppm + Zn^{2+} 300 ppm

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