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Short Communication

Synergistic and antagonistic effects existing among polyacrylamide, phenyl phosphonate and Zn^{2+} on the inhibition of corrosion of mild steel in a neutral aqueous environment

Susai Rajendran[a,]*, B. V. Apparao[b], N. Palaniswamy[c]

[a]*Department of Chemistry, G.T.N. Arts College, Dindigul 624 005, India*
[b]*Department of Chemistry, Regional Engineering College, Warangal 506 004, India*
[c]*Central Electrochemical Research Institute, Karaikudi 630 006, India*

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Abstract

The corrosion rates of mild steel in neutral aqueous environment containing 60 ppm chloride in the absence and presence of polyacrylamide (PAA), phenyl phosphonate (PPA) and Zn^{2+} have been evaluated by the weight-loss method. The formulation consisting of 50 ppm PAA and 50 ppm Zn^{2+} and also the 50 ppm Zn^{2+}–300 ppm PPA system show synergistic effects (the inhibition efficiency of the latter is not decreased by addition of 50 ppm PAA) while the formulation consisting of 50 ppm PAA and 300 pmm PPA shows an antagonistic effect. The protective film has been analysed using X-ray diffraction measurements, FTIR and luminescence spectra. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyacrylamide and phenyl phosphonate; Corrosion inhibition; Synergistic and antagonistic effects; Mild steel; Neutral aqueous medium

1. Introduction

The adsorption behaviour of PAA on gold and mild steel from sulphuric acid and hydrochloric acid has been studied using cyclic voltammetry with simultaneous monitoring of the double layer capacity [1]. In acidic and neutral media, PAA has been used as a corrosion inhibitor for iron [2]. The synergistic inhibition effect of PAA and hexamethylenetetramine has been reported [1]. The present work (i) investigates the synergistic and antagonistic effects existing among PAA, phenyl phosphonate and Zn^{2+} by weight-loss method and (ii) examines the nature of the protective film by using X-ray diffraction data and Fourier transform infrared (FTIR) and luminescence spectra.

2. Experimental

2.1. Preparation of the specimens

The composition of the mild steel used in this study is given in Table 1.

Mild steel specimens 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.

2.2. Weight-loss method

Mild steel specimens, in triplicate, were immersed in 100 cm^3 of solution containing various concentrations of inhibitor in the absence and presence of Zn^{2+}, for a period of 7 days (168 h). The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion products were

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* Author to whom correspondence should be addressed. Fax: +91 451 32655.

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Table 1

S (%)	P (%)	Mn (%)	C (%)	Fe (%)
0.02 to 0.03	0.03 to 0.08	0.4 to 0.5	0.1 to 0.2	remainder

Table 2
Corrosion rates of mild steel in neutral aqueous environment (Cl^- 60 ppm) in the absence and presence of inhibitors and the inhibition efficiencies obtained by the weight-loss method

Inhibitor system: PAA + PPA + Zn^{2+}

Sl. No.	PAA (ppm)	PPA (ppm)	Zn^{2+} (ppm)	Corrosion rate, (mg/dm^2/day)	Inhibition efficiency (%)
1	0	0	0	15.54	–
2	50	0	0	7.30	53
3	50	0	50	5.40	65
4	50	300	0	14.92	4
5	50	300	50	0.72	95
6	0	300	50	0.78	95
7	0	300	0	6.53	58
8	0	0	50	19.11	–23

cleaned with Clarke's solution [3]. The percent inhibition efficiency (IE) was calculated using the relation, IE = $[(W_1-W_2)/W_1] \times 100$ where W_1 and W_2 are weight losses of mild steel in uninhibited and inhibited chloride solutions.

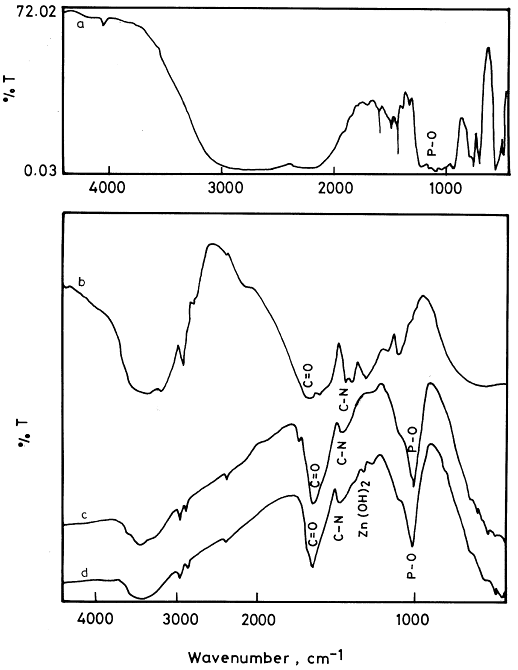

Fig. 1. FTIR spectra of PPA (a), PAA (b) and of mild steel surface immersed in various environments (c) and (d). (a) Pure PPA; (b) pure PAA; (c) Cl^- 60 ppm + PAA 50 ppm + PPA 300 ppm; (d) Cl^- 60 ppm + PAA 50 ppm + PPA 300 ppm + Zn^{2+} 50 ppm.

2.3. Surface examination study

The mild steel specimens were immersed in various test solutions for a period of 2 days. After 2 days, the specimens were taken out, rinsed with water and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

2.4. Fourier transform infrared (FTIR) spectra

FTIR spectra were recorded using a Perkin-Elmer 1600 FTIR spectrophotometer.

2.5. X-ray diffraction

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 ($\lambda = 1.5418$ Å) at a rating of 40 kV, 20 mA.

2.6. Luminescence spectra

Luminescence spectra of the film formed on the metal surface were recorded using an Hitachi 650-10 S fluorescence spectrophotometer equipped with a 150 W xenon lamp and an 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.

3. Results

3.1. Analysis of the results of the weight-loss method

Table 2 shows corrosion rates and inhibition efficiencies of mild steel in neutral aqueous environment containing 60 ppm chloride. 50 ppm polyacrylamide has an inhibition efficiency of 53%, while 50 ppm Zn^{2+} is found to be corrosive. The formulation consisting of 50 ppm PAA and 50 ppm Zn^{2+} has an inhibition efficiency of 65%.

The solution containing 300 ppm phenyl phosphonic acid (PPA) offers 58% inhibition. But the formulation consisting of 50 ppm PAA and 300 ppm PPA has only 4% inhibition.

The system consisting of 50 ppm Zn^{2+} and 300 ppm PPA has an inhibition efficiency of 95%. Addition of 50 ppm PAA does not reduce the inhibition efficiency of this system.

3.2. Analysis of the FTIR spectra

The FTIR spectra of phenyl phosphonic acid (PPA) and polyacrylamide (PAA) are given in Fig. 1(a) and (b). It is seen from the FTIR spectrum of the film formed on the surface of the metal specimen immersed in the environment containing 60 ppm Cl^-, 50 ppm PAA and 300 ppm PPA [Fig. 1(c)] that the P–O stretching frequency of PPA has shifted from 1080.3 to 1019.3 cm^{-1} suggesting that the oxygen atom of the phosphonic acid is coordinated to Fe^{2+}, resulting in the formation of a Fe^{2+}–PPA complex an the metal surface [4–8].

The C=O stretching frequency of PAA decreases from 1666.4 to 1634 cm^{-1} and the C–N stretching frequency increases from 1453.9 to 1464.2 cm^{-1}, suggesting that PAA is coordinated to Fe^{2+} through the oxygen atom and not through the nitrogen atom; the C–N bond acquires double bond character.

The FTIR spectrum of the film formed on the surface of the metal immersed in the environment containing 60 ppm Cl^-, 50 ppm PAA, 300 ppm PPA and 50 ppm Zn^{2+} is given in Fig. 1(d). The P–O stretching frequency of phenyl phosphonic acid decreases from 1080.3 to 1018.4 cm^{-1}. This suggests that the oxygen atom is coordinated to Fe^{2+} resulting in the formation of a Fe^{2+} PPA complex on the metal surface. The absorption at 1350 cm^{-1} corresponds to $Zn(OH)_2$ [9].

The C=O stretching frequency of polyacrylamide decreases from 1666.4 to 1641.4 cm^{-1} and the C–N stretching frequency increases from 1453.9 to 1465.7 cm^{-1}, suggesting that PAA is coordinated to Fe^{2+} through the oxygen atom and not through the nitrogen atom and the C–N bond acquires double bond character.

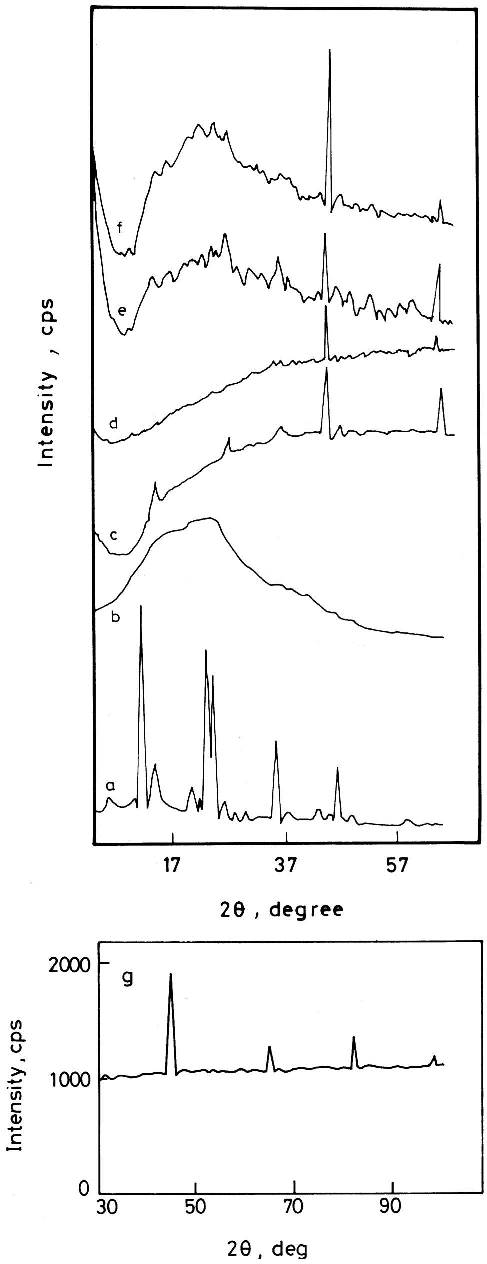

Fig. 2. XRD patterns of PPA (a), PAA (b) and of mild steel surface immersed in various environments (c), (d), (e) and (f). (a) Pure PPA; (b) pure PAA; (c) Cl^- 60 ppm + PAA 50 ppm; (d) Cl^- 60 ppm + PAA 50 ppm + Zn^{2+} 50 ppm; (e) Cl^- 60 ppm + PAA 50 ppm + PPA 300 ppm; (f) Cl^- 60 ppm + PAA 50 ppm + PPA 300 ppm + Zn^{2+} 50 ppm; (g) polished specimen not immersed in any solution.

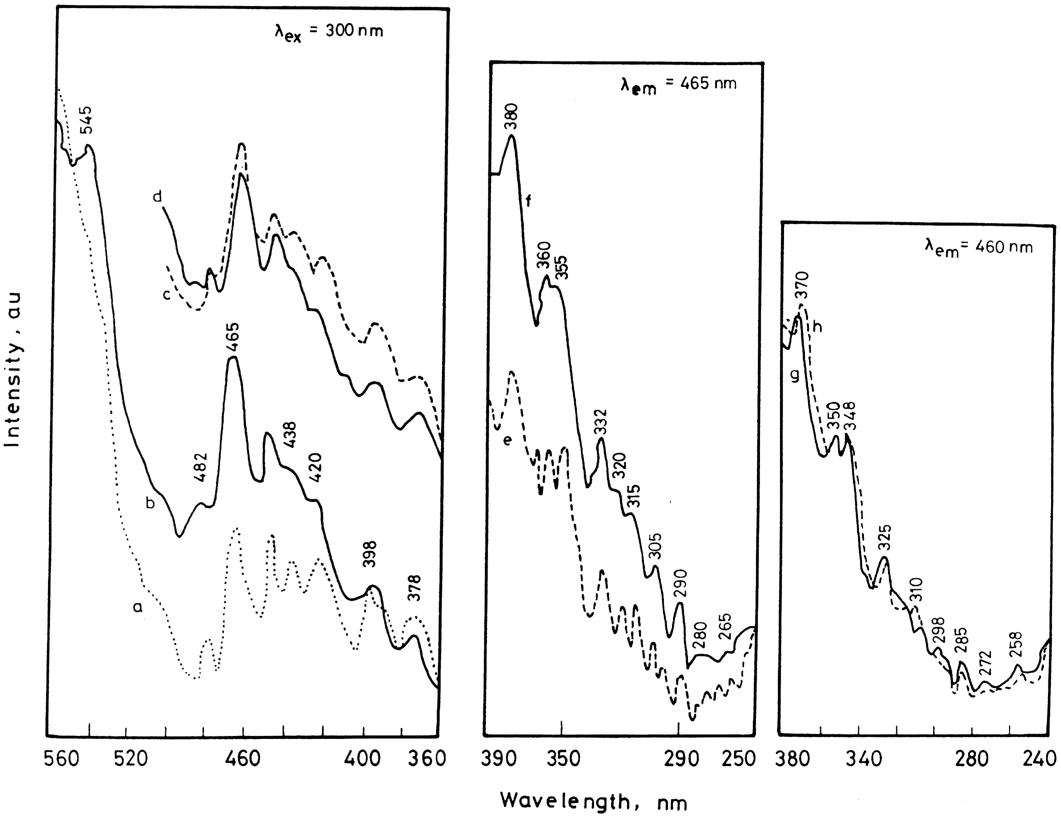

Fig. 3. Luminescence spectra of mild steel surface immersed in various environments. (a) and (e) Cl^- 60 ppm + PAA 50 ppm; (b) and (f) Cl^- 60 ppm + PAA 50 ppm + Zn^{2+} 50 ppm; (c) and (g) Cl^- 60 ppm + PAA 50 ppm + PPA 300 ppm; (d) and (h) Cl^- 60 ppm + PAA 50 + PPA 300 ppm + Zn^{2+} 50 ppm.

3.3. Analysis of the X-ray diffraction (XRD) patterns

The XRD pattern of phenyl phosphonic acid (PPA) [Fig. 2(a)] indicates its crystalline nature. The XRD pattern of polyacrylamide (PAA) [Fig. 2(b)] has no characteristic peaks. This indicates the amorphous nature of PAA.

The XRD pattern of the surface of the metal specimens immersed in various test solutions are given in Fig. 2(c) to (f). The XRD pattern of polished metal is given in Fig. 2(g). The peaks due to iron appear at $2\theta = 44.8°$, 65.1°, 88.4° and 99.0°. The XRD pattern of the surface of the metal immersed in the environment containing 60 ppm Cl^- and 50 ppm PAA [Fig. 2(c)] shows the presence of γ-FeOOH on the metal surface ($2\theta = 14.1°$, 36.0° and 46.8°) [10]. The peaks at $2\theta = 44.7°$ and 65.0° correspond to iron.

The XRD pattern of the film formed on the surface of the metal specimen immersed in the solution containing 60 ppm Cl^-, 50 ppm PAA and 50 ppm Zn^{2+} is given in Fig. 2(d). It indicates the presence of Fe_3O_4 ($2\theta = 62.4°$) on the metal surface [10]. The peaks at $2\theta = 44.7°$ and 65.0° are due to iron.

The XRD pattern of the film formed on the surface of the metal immersed in the environment consisting of 60 ppm Cl^-, 50 ppm PAA and 300 ppm PPA, given in Fig. 2(e), suggests that the film consists of γ-FeOOH ($2\theta = 36.2°$, 37.7° and 46.6°) [10]. The iron peaks appear at $2\theta = 44.4°$ and 64.8°. The peaks at $2\theta = 22.6°$, 24.0° and 26.7° indicate the presence of phosphonic acid [cf. Fig. 2(a)] on the metal surface [11] probably as a Fe^{2+}–PPA complex.

The XRD pattern of the film due to the environment consisting of 60 ppm Cl^-, 50 ppm PAA, 300 ppm PPA and 50 ppm Zn^{2+} [Fig. 2(f)] shows iron peaks at $2\theta = 44.8°$ and 65.0°. The peaks at $2\theta = 21.6°$, 24.2° and 26.8° suggest the presence of phenyl phosphonic acid [cf. Fig. 2(a)] on the metal surface [11] probably as a Fe^{2+}–PPA complex. The peaks due to oxides of iron such as α-FeOOH, γ-FeOOH and Fe_3O_4 are found to be absent. This indicates that the protective film is free from any oxides of iron.

3.4. Analysis of the luminescence spectra

The luminescence spectra of the films formed on the surface of the metal specimens immersed in various test solutions are given in Fig. 3. The emission spectrum given in Fig. 3(a) is due to the Fe^{2+}–PAA complex embedded in γ-FeOOH. The emission spectrum in Fig. 3(b) is due to the Fe^{2+}–PAA complex embedded in Fe_3O_4. It is interesting to note that the intensities of the peaks increase in the presence of Zn^{2+}. This indicates that, in the presence of Zn^{2+}, the formation of the Fe^{2+}–PAA complex is enhanced. This confirms the synergistic effect of the PAA–Zn^{2+} system. The emission spectra given in Fig. 3(c) and (d) are due to Fe^{2+}–PAA and Fe^{2+}–PPA complexes formed on the metal surface. The excitation spectra are given in Fig. 3(e) to (h).

4. Discussion

Weight-loss studies reveal that additions of Zn^{2+} to PAA alone and to PPA alone improve the inhibition efficiencies. Similar observations are made with the PAA–PPA system also, i.e. in the presence of Zn^{2+}, the above systems show synergistic effects in controlling corrosion of mild steel in neutral chloride medium. The anodic reactions are retarded by the formation of Fe^{2+}–polymer complexes. In the presence of Zn^{2+}, the cathodic reaction is also retarded (by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface). This is confirmed by an FTIR study which reveals the presence of Fe^{2+}–PAA complex, Fe^{2+}–PPA complex and $Zn(OH)_2$ on the metal surface. Further, luminescence spectra reveal that the intensities of the peaks are relatively higher in the presence of Zn^{2+}.

The PAA–PPA system shows an antagonistic effect. This may be due to the fact that the complex formed between PAA and PPA in solution has less tendency to break and to form their respective complexes with Fe^{2+} on the metal surface. The film formed on the metal surface is easily broken by the aggressive chloride ions, thus, leading to the antagonistic effect. Such an antagonistic effect between amino (trimethylene phosphonic acid) (ATMP) and PAA has been reported [12]. Similarly, the system consisting of 1-hydroxyethane-1,1-diphosphonic acid and PAA shows an antagonistic effect [13].

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