Mechanism of inhibition of corrosion of mild steel by polyacrylamide, phenyl phosphonate and Zn^{2+}

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Keywords

Corrosion, Corrosion inhibitors, Mild steel

Abstract

The formulation consisting of 50ppm polyacrylamide (PAA), 300ppm phenyl phosphonic acid (PPA) and 50ppm Zn^{2+} has 95 per cent inhibition efficiency in controlling corrosion of mild steel in a neutral aqueous environment, containing 60ppm Cl^-, a situation commonly encountered in cooling water systems. A discussion of mechanistic aspects of corrosion inhibition is based on the results obtained from a potentiostatic polarization study, UV-visible, FTIR and luminescence spectra. The protective film is found to be luminescent and to consist of Fe^{2+}–PAA complex, Fe^{2+}–PPA complex and $Zn(OH)_2$.

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Polyacrylamide (PAA) strongly adsorbs on silver and titanium[1] and gold and iron[2] from neutral aqueous solutions. In acidic and neutral media, PAA has been used as a corrosion inhibitor for iron[3]. PAA, containing a thiomalic acid group in its backbone, has been used as an inhibitor to prevent corrosion of mild steel in acid medium[4]. The synergistic effect of PAA and hexamethylenetetramine has been reported[5]. Synergistic, antagonistic and biocidal effects of amino (trimethylene phosphonic acid), PAA and Zn^{2+} on the inhibition of corrosion of mild steel in a neutral aqueous environment have been studied[6]. In the present work, the inhibitive effect of PAA, phenyl phosphonic acid (PPA) and Zn^{2+} in controlling the corrosion of mild steel in a neutral aqueous environment containing 60ppm Cl^- has been studied using the weight-loss method. A suitable mechanism of corrosion inhibition has been proposed based on the results obtained from potentiostatic polarization study, FTIR, UV-visible and luminescence spectra.

Experimental

Preparation of the specimens

Mild steel specimens (0.02 to 0.03 per cent S, 0.03 to 0.08 per cent P, 0.4 to 0.5 per cent Mn, 0.1 to 0.2 per cent C and the rest iron) 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 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 mirror finish and degreased with trichloroethylene.

Weight-loss method

Mild steel specimens, in triplicate, were immersed in 100cm^3 of solution containing various concentrations of the inhibitor in the

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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 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, washed with water and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

FTIR spectrum

FTIR spectrum was recorded using a Perkin-Elmer 1600 FTIR spectrophotometer (Multiple Internal Reflection Technique).

UV-visible spectra

UV-visible reflectance spectra were recorded using a Hitachi U-3400 spectrophotometer. The same instrument was used for recording UV-visible absorption spectra of aqueous solutions also.

Luminescence spectra

Luminescence spectra of the film formed on the metal surface were recorded using a Hitachi 65-10 S fluorescence spectrophotometer equipped with a 150 W 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 the beam intensity variation.

Results and discussion

Analysis of the results of the weight-loss method

Corrosion rates of mild steel in a neutral aqueous environment containing 60ppm chloride in the absence and presence of inhibitors obtained by the weight-loss method are given in Table I. The corrosion inhibition efficiencies of various systems are also given in Table I.

Table I Corrosion rates of mild steel in a 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+})

	Concentration of				
Sl. no.	PAA, ppm	PPA, ppm	Zn^{2+}, ppm	Corrosion rate, mdd	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

It is found that the system consisting of 50ppm Zn^{2+} and 300ppm PPA has an inhibition efficiency of 95 per cent. This shows a synergistic effect of PPA and Zn^{2+}. It is interesting to note that addition of 50ppm PAA does not reduce the inhibition efficiency of this system.

Analysis of the potentiostatic polarization study

The potentiostatic polarization curves of mild steel immersed in various test solutions are given in Figure 1. It is seen from Figure 1 that when 50ppm PAA is added to the solution containing 60ppm Cl^-, the corrosion potential is shifted from – 389 mv vs. SCE to – 329 mv vs. SCE (positive shift) while 50ppm Zn^{2+} alone shifts the corrosion potential towards negative region (to –489 mv vs. SCE). However, the PAA–Zn^{2+} combination has a corrosion potential value intermediate between those of PAA alone and of Zn^{2+} alone, though it is also negative (–400 mv vs. SCE) relative to the system in the absence of any inhibitor.

These results suggest that while PAA alone functions as an anodic inhibitor, the PAA–Zn^{2+} combination acts as a mixed inhibitor.

It is also inferred from Figure 1 that 300ppm PPA acts as an anodic inhibitor (E_{corr} = –307mV vs. SCE).

The formulation consisting of 300ppm PPA and 50ppm PAA also functions as anodic inhibitor (E_{corr} = –311 mV vs. SCE). The formulation consisting of 300ppm PPA and 50ppm Zn^{2+} acts as a mixed inhibitor (E_{corr} = –430 mV vs. SCE). Addition of 50ppm PAA

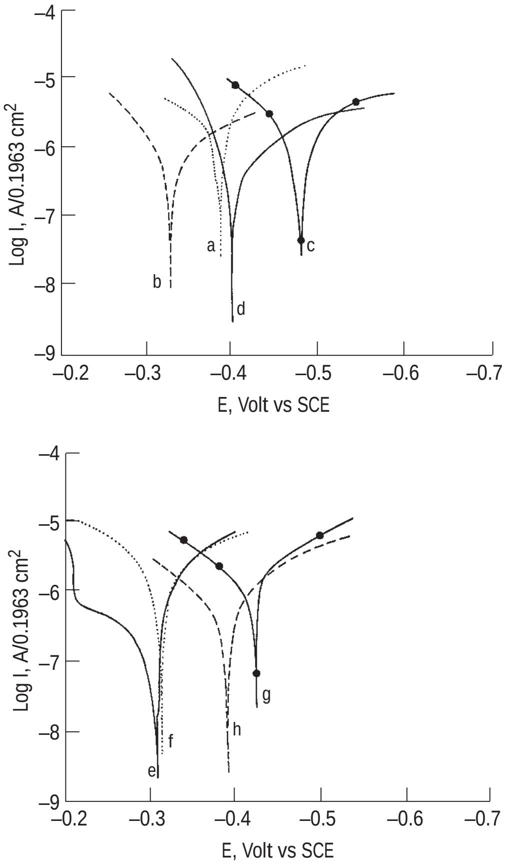


Figure 1 Potentiostatic polarisation curves of mild steel immersed in various environments: (a) Cl^- 60ppm; (b) Cl^- 60ppm + PAA 50ppm; (c) Cl^- 60ppm + Zn^{2+} 50ppm; (d) Cl^- 60ppm + PAA 50ppm + Zn^{2+} 50ppm; (e) Cl^- 60ppm + PPA 300ppm; (f) Cl^- 60ppm + PPA 300ppm + PAA 50ppm; (g) Cl^- 60ppm + PPA 300ppm + Zn^{2+} 50ppm; (h) Cl^- 60ppm + PPA 300ppm + PAA 50ppm + Zn^{2+} 50ppm

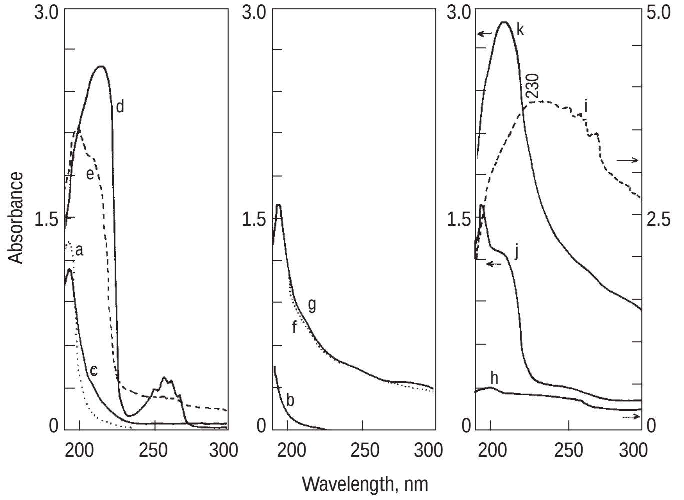


Figure 2 UV-visible absorption spectra of solutions: (a) PAA 50ppm; (b) Zn^{2+} 50ppm; (c) PAA 50ppm + Zn^{2+} 50ppm; (d) PPA 300ppm; (e) PPA 300ppm + PAA 50ppm; (f) PAA 50ppm + Fe^{2+} 100ppm; (g) PAA 50ppm, + Fe^{2+} 100ppm + Zn^{2+} 50ppm; (h) Fe^{2+} 100ppm; (i) PPA 300ppm + Fe^{2+} 100ppm; (j) PPA 300ppm + Fe^{2+} 100ppm + Zn^{2+} 50ppm; (k) PPA 300ppm + Fe^{2+} 100ppm + Zn^{2+} 50ppm + PAA 50ppm

to the above system shifts the corrosion potential to –398 mV vs. SCE. This potential is negative relative to PAA alone or PPA alone or PAA–PPA system. However, it is positive relative to that when Zn^{2+} is used alone. These observations suggest that the formulation consisting of 50ppm PAA, 300ppm PPA and 50ppm Zn^{2+} acts as a mixed inhibitor.

Analysis of UV-visible absorption spectra of solutions

The UV-visible absorption spectra of various test solutions are given in Figure 2. The UV-visible absorption spectrum of an aqueous solution containing 50ppm PAA has an absorbance at 192nm (Figure 2a). The UV-visible absorption spectrum of an aqueous solution containing 50ppm Zn^{2+} is given in Figure 2b. The UV-visible absorption spectrum of the solution containing 50ppm PAA and 50ppm Zn^{2+} (Figure 2c) shows a decrease in the intensity of absorbance at 192nm and an increase in absorbance in the region of 210 to 250nm. This indicates the formation of a complex between PAA and Zn^{2+} in solution.

The UV-visible absorption spectrum of the solution containing 300ppm PPA (Figure 2d) shows peaks at 213nm, 252nm, 258nm, 268nm and 270nm. The absorption spectrum of the solution consisting of 300ppm PPA and 50ppm PAA (Figure 2e) shows shift in the position of λmax.

There is a decrease in the absorbance also. The peaks in the region of 252 to 270nm have almost disappeared. These observations suggest the formation of a complex between PPA and PAA in solution.

It is interesting to note that the absorption spectrum of the solution containing 50ppm PAA, 50ppm Zn^{2+} and 100ppm Fe^{2+} is almost identical with that of the solution containing 50ppm PAA and 100ppm Fe^{2+} (Figures 2f and 2g). This suggests that PAA prefers Fe^{2+} to Zn^{2+} in complex formation.

The UV-visible absorption spectrum of the solution containing 300ppm PPA and 100ppm Fe^{2+} has a peak at 230nm (Figure 2i). There is an increase in absorbance also. This indicates the formation of Fe^{2+}–PPA complex in solution.

It is observed from Figure 2j that PPA forms complexes with the cations (Zn^{2+} and Fe^{2+}) present in the solution, preferably with Fe^{2+}. It further reveals that the nature of the complex differs from that formed by this system in the presence of PAA (Figure 2k). It is seen from Figure 2k that PAA and also PPA form complexes with the cations (Fe^{2+} and Zn^{2+}) present in the solutions, preferably with Fe^{2+}.

Analysis of the FTIR spectrum

The FTIR spectrum of the film formed on the surface of the metal immersed in the environment containing 60ppm Cl^-, 50ppm PAA, 300ppm PPA and 50ppm Zn^{2+} is given in Figure 3. It is noted that the P-O stretching frequency of phenyl phosphonic acid decreases from 1,080.3cm^{-1} to 1,018.4cm^{-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 1,350cm^{-1} corresponds to $Zn(OH)_2$[7-9].

It is also inferred from the spectrum that the C=O stretching frequency of polyacrylamide decreases from 1,666.4cm^{-1} to 1,641.4cm^{-1} and the C-N stretching frequency increases from 1,453.1cm^{-1} to 1,465.7cm^{-1}. It is learned from these observations 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.

Analysis of the UV-visible reflectance spectra

The UV-visible reflectance spectra of the surface of the metal specimens immersed in various test solutions are given in Figure 4. The reflectance spectrum of the surface of the metal immersed in solution containing 60ppm Cl^- and 50ppm PAA (Figure 4a) shows wavelength transition at 550nm indicating the presence of oxides of iron[10-13], with a band gap of $E_g = 1.239/0.55 = 2.25$ eV, having semiconducting property [14-17]. The peak at 320nm, probably, corresponds to Fe^{2+} – PAA complex.

Figure 3 FTIR spectrum of the surface of the metal immersed in the environment containing Cl^- 60ppm + PAA 50ppm + PPA 300ppm + Zn^{2+} 50ppm

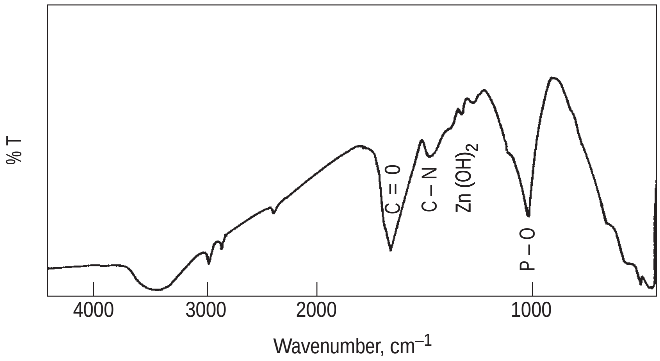
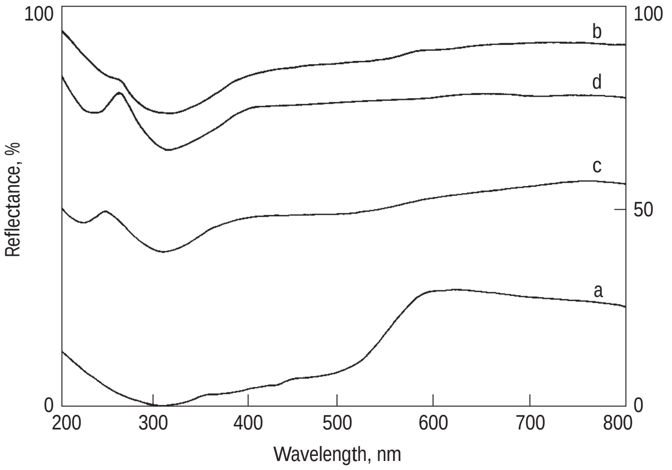


Figure 4 UV-visible reflectance spectra of mild steel surface immersed in various environments: (a) Cl^- 60ppm + PAA 50ppm; (b) Cl^- 60ppm + PAA 50ppm + Zn^{2+} 50ppm; (c) Cl^- 60ppm + PAA 50ppm + PPA 300ppm; (d) Cl^- 60ppm + PAA 50ppm + PPA 300ppm + Zn^{2+} 50ppm



The UV-visible reflectance spectrum of the surface of the metal specimen immersed in the solution containing 60ppm Cl^- 50ppm PAA and 50ppm Zn^{2+} (Figure 4b) shows a peak at 320nm, probably due to Fe^{2+}–PAA complex. The wavelength transition at 550nm indicates the presence of oxides of iron[10-13] having semiconducting property[14-17].

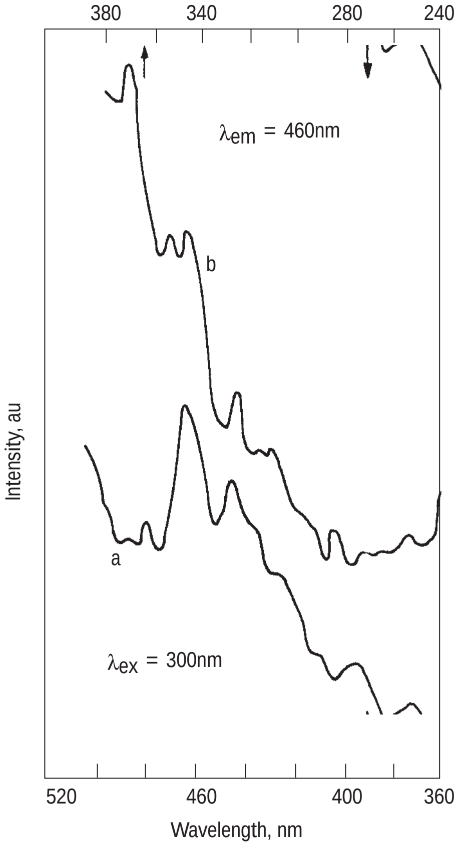
It is seen from the wavelength transition at 550nm in Figure 4c, that oxides of iron[10-13] having semiconducting property[14-17] are formed on the surface of the metal specimen, when it is immersed in the environment consisting of 60ppm Cl^-, 300ppm PPA and 50ppm PAA. The peak at 320nm is due to Fe^{2+}–PAA complex and the peak at 230nm is due to Fe^{2+}–PPA complex.

The UV-visible reflectance spectrum of the surface of the metal immersed in the solution containing 60ppm Cl^-, 300ppm PPA, 50ppm PAA and 50ppm Zn^{2+} shows peaks at 320nm and 230nm, probably due to Fe^{2+}–PAA complex and Fe^{2+}–PPA complex respectively. There is no wavelength transition at 550nm. This indicates the absence of any oxides of iron on the metal surface.

Analysis of the luminescence spectra

The emission spectrum ($\lambda_{ex} = 300$nm) of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 300ppm PPA, 50ppm PAA and 50ppm Zn^{2+} is given in Figure 5a. The corresponding excitation spectrum ($\lambda_{em} = 460$nm) is given in Figure 5b.

Figure 5 Luminescence spectra of mild steel surface immersed in the environment consisting of Cl^- 60ppm + PAA 50ppm + PPA 300ppm + Zn^{2+} 50ppm



Mechanism of inhibition of corrosion

The results of the weight-loss method reveal that the formulation consisting of 50ppm PAA, 300ppm PPA and 50ppm Zn^{2+} has an inhibition efficiency of 95 per cent. The polarization study suggests that this formulation acts as a mixed inhibitor. The UV-visible absorption spectra of solutions show that PAA prefers the formation of Fe^{2+}–PAA complex to Zn^{2+}–PAA complex in the presence of both the cations. The FTIR spectra indicate that the protective film consists of Fe^{2+}–PAA complex, Fe^{2+}–PPA complex and $Zn(OH)_2$. The UV-visible reflectance spectra also show the presence of Fe^{2+}–PAA complex and Fe^+–PPA complex in the protective film. The luminescence spectra suggest that the protective film is luminescent. In order to explain all these observations, in a holistic way, the following mechanism of inhibition of corrosion has been proposed:

(1) When mild steel specimen is immersed in the neutral aqueous environment, the anodic reaction is
$$Fe \rightarrow Fe^{2+} + 2e^-$$
and the cathodic reaction is
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
(2) When the environment consisting of 60ppm Cl^-, 50ppm PAA, 300ppm PPA and 50ppm Zn^{2+} is prepared, there is formation of Zn^{2+}–PAA complex and Zn^{2+}–PPA complex in solution.
(3) When the metal is immersed in this environment, the Zn^{2+}–PPA complex and Zn^{2+}–PAA complex diffuse from the bulk of the solution to the surface of the metal.
(4) On the surface of the metal, Zn^{2+}–PAA complex is converted into Fe^{2+}–PAA complex in the local anodic sites, since the latter is more stable than the former:
$$Zn^{2+}\text{–PPA} + Fe^{2+} \rightarrow Fe^{2+}\text{–PPA} + Zn^{2+}$$
(5) Similarly, Zn^{2+}–PPA complex is converted into Fe^{2+}–PPA complex in the local anodic sites:
$$Zn^{2+}\text{–PPA} + Fe^{2+} \rightarrow Fe^{2+}\text{–PPA} + Zn^{2+}$$
(Formation of Fe^{3+}–PAA complex and also Fe^{3+}–PPA complex to some extent cannot be ruled out.)
(6) The released Zn^{2+} ions on the metal surface form $Zn(OH)_2$ in the local cathodic regions:
$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$$
(7) Thus, the protective film consists of Fe^{2+}–PAA complex, Fe^{2+}–PPA complex and $Zn(OH)_2$.

Conclusions

The following points are concluded:

(1) The solution containing 50ppm polyacrylamide (PAA) has an inhibition efficiency of 53 per cent. The protective film consists of Fe^{2+}–PAA complex and oxides of iron. It is found to be semiconducting.
(2) The formulation consisting of 50ppm PAA and 50ppm Zn^{2+} offers 65 per cent inhibition efficiency. This indicates the synergistic effect of PAA and Zn^{2+}. The protective film consists of Fe^{2+}–PAA complex and oxides of iron. This film is found to be semiconducting.
(3) The formulation, consisting of 50ppm PAA, 50ppm Zn^{2+} and 300ppm PPA, has an inhibition efficiency of 95 per cent. The protective film consists of Fe^{2+}–PAA complex, Fe^{2+}–PPA complex and $Zn(OH)_2$. This film is found to be luminescent and not semiconducting.
(4) The above formulation functions as a mixed inhibitor controlling both anodic reaction of metallic dissolution and cathodic reaction of generation of hydroxylions.

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