



Corrosion Inhibition of Carbon Steel by Polyacrylamide

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Abstract

The inhibition efficiency (IE) of Polyacrylamide (PAA) in controlling corrosion of carbon steel in ground water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm PAA and 50 ppm Zn^{2+} has 98% IE. It is found that the inhibition efficiency (IE) of PAA increases by the addition of Zn^{2+} ion. A synergistic effect exists between PAA and Zn^{2+} . The mechanistic aspects of corrosion inhibition have been studied using polarization study. Also FTIR spectra reveal that the protective film consists of Fe^{2+} – PAA complex and $Zn(OH)_2$. The scanning electron microscopy (SEM) study confirms the protection of carbon steel surface by strong adsorption of PAA. A suitable mechanism for corrosion inhibition is proposed based on the results from the above studies.

Keywords: Corrosion inhibition, polyacrylamide, carbon steel, synergistic effect, ground water

Introduction

Corrosion is the destruction of metals and alloys by chemical and electrochemical reactions with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using appropriate preventive techniques like metallic coating, anodic protection, cathodic protection and using inhibitors, etc. Inhibitors imparts very good role in the process of corrosion inhibition. The organic inhibitors containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus, etc shows better corrosion inhibition by forming protective film on the metal surface. The order of corrosion inhibition efficiency of the compounds containing heteroatoms follows, $O < N < S < P^{1-4}$. Application of polymers as corrosion inhibitors have been attracted several researchers⁵⁻⁷. Corrosion inhibition by conducting polymer has been studied⁸. The studies on corrosion inhibition of Polyacrylamide grafted with fenugreek mucilage⁹ and polyvinylpyrrolidone have been reported¹⁰. The corrosion inhibition studies of mild steel¹¹, aluminium¹² and zinc¹³, etc in various aqueous environment have been studied.

The aim of the present study was to investigate synergistic corrosion inhibition for the Polyacrylamide (PAA) and Zn^{2+} combination to carbon steel in ground water collected from Yadava College at Madurai, Tamil Nadu, India. The physico-chemical parameters¹⁴ of the ground water taken in the present study have been given in table 1. The corrosion inhibition efficiency was calculated using weight loss and polarization studies. The protective film formed on the metal surface characterized using surface morphological studies such as Fourier Transform Infrared spectra (FTIR) and scanning electron microscopy (SEM).

Table-1
Physico-Chemical Parameter of Ground Water

Parameters	Value
pH	7.3
Total Hardness as $CaCO_3$	460 ppm
Calcium	32 ppm
Magnesium	91 ppm
Nitrate	8 ppm
Chloride	270 ppm
Fluoride	0.8 ppm
Sulphate	100 ppm
Phosphate	0.46 ppm

Material and Methods

Preparation of the specimens: Carbon steel specimen (0.026% S, 0.06% P, 0.4% Mn and 0.1% C and rest Fe) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

Weight – Loss Method: Carbon steel specimens in triplicate were immersed in 100 mL of the ground water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for 3 days. The corrosion product cleaned with Clark's solution¹⁵. The parameter of the marine media is given in Table 1. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY 210 model. Then the inhibition efficiency was calculated using the equation (1)

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

Where, W_1 and W_2 are Corrosion rate in the absence and presence of inhibitor respectively.

The corrosion rate (CR) was calculated using the formula (2)

$$CR = [(Weight\ loss\ in\ mg) / (Area\ of\ the\ specimen\ in\ dm^2 \times Immersion\ period\ in\ days)]\ mdd \dots\dots(2)$$

Potentiodynamic Polarization Study: Polarization study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant $1\ cm^2$ area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing iR compensation. The corrosion parameters such as Tafel slopes (anodic slope b_a and cathodic slope b_c), corrosion current (I_{Corr}) and corrosion potential (E_{Corr}) values were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at E_f (s) was zero and quiet time (s) was 2.

Surface Examination Study: The carbon steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by surface analysis technique, FTIR spectra and SEM.

FTIR spectra: The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with potassium bromide (KBr), so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin–Elmer– 1600 spectrophotometer.

Scanning electron microscopy (SEM): The carbon steel specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by scanning electron microscopy (SEM) using HITACHI S-3000H SEM.

Results and Discussion

Analysis of results of weight loss study: The calculated inhibition efficiencies (IE) and corrosion rates (CR) of PAA in controlling corrosion of carbon steel immersed in ground water both in the absence and presence of Zn^{2+} ion are given in table 2 and also shown in figure 1. The IE's of the PAA- Zn^{2+} systems as a function of concentrations of PAA are shown in Fig.1. The calculated value indicates the ability of PAA to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Zn^{2+} ion. PAA alone shows some IE. But the combination of 250 ppm PAA and 50 ppm Zn^{2+} shows 98% IE. This suggests a synergistic effect exists between PAA and Zn^{2+} ion¹⁶.

Analysis of Polarization curves: The potentiodynamic polarization curves of carbon steel immersed in ground water in the absence and presence of inhibitors are shown in figure 2. The corrosion parameters such as corrosion potential (E_{Corr}), Tafel slopes (anodic slope b_a and cathodic slope b_c), linear polarization resistance and corrosion current (I_{Corr}) values were calculated and are given in table 3. When carbon steel was immersed in ground water the corrosion potential was -680 mV vs SCE (Saturated calomel electrode). When PAA (250 ppm) and Zn^{2+} (50 ppm) were added to the above system the corrosion potential shifted to the cathodic side -698 mV vs SCE. This indicates that the PAA- Zn^{2+} system control the cathodic reaction predominantly. Further, the LPR value increases from 18820.2 ohm cm^2 to 29682.6 ohm cm^2 ; the corrosion current decreases from 2.016×10^{-6} A/ cm^2 to 1.471×10^{-6} A/ cm^2 . Thus, polarization study confirms the formation of a protective film on the metal surface. However the shift is not very much. Therefore it is concluded, that the system functions as a mixed type inhibitor. The anodic reaction is controlled by the formation of Fe^{2+} - PAA confirms on the anodic sites. The cathodic reaction (generation of OH^-) is controlled by formation of $Zn(OH)_2$ on the cathodic sites on the metal surface. Thus anodic reaction and cathodic reaction are controlled. This accounts for synergistic effect^{17, 18}.

Table-2
Inhibition efficiencies (IE %) and Corrosion rates (CR) obtained from PAA - Zn^{2+} systems, when carbon steel immersed in ground water

PAA ppm	Zn^{2+} ppm									
	0		5		10		25		50	
	CR mdd	IE %	CR mdd	IE %	CR mdd	IE %	CR mdd	IE %	CR mdd	IE %
0	15.15	---	14.09	7	13.64	10	13.33	12	12.88	15
25	14.39	5	6.82	55	9.06	40	7.58	50	3.03	80
50	12.45	18	5.30	65	6.06	60	5.30	65	2.73	82
75	11.36	25	4.55	70	3.64	76	3.64	76	2.42	84
100	9.85	35	3.79	75	3.03	80	1.82	88	1.52	90
125	8.75	42	2.27	85	2.73	82	1.52	90	0.91	94
250	7.85	48	2.12	86	1.82	88	0.91	94	0.30	98

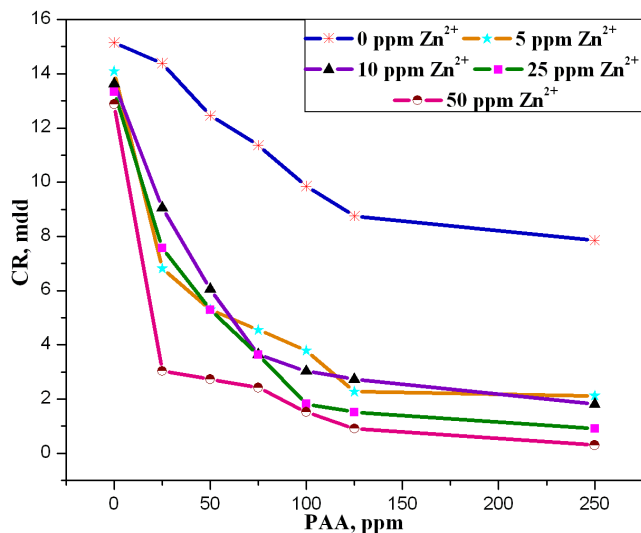


Figure-1
Corrosion rates (CR) of carbon steel immersed in various test solutions

Table-3
Corrosion parameters of carbon steel immersed in ground water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

System	E _{corr} mV vs SCE	b _c mV/decade	b _a mV/decade	I _{corr} A/cm ²	LPR ohm cm ²
Ground Water	-680	172	177	2.016 x 10 ⁻⁶	18820.2
Ground Water + PAA (250 ppm) + Zn ²⁺ (50 ppm)	-698	177	212	1.471 x 10 ⁻⁶	29682.6

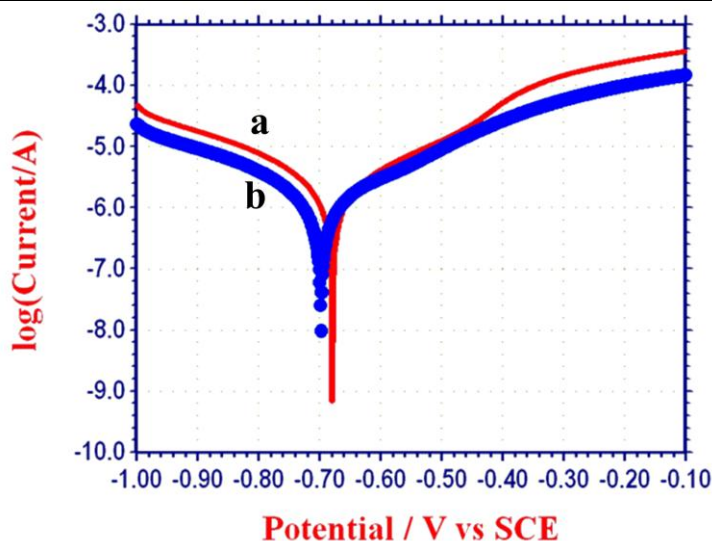


Figure-2
Polarization curves of carbon steel immersed in various test solutions (a) Ground water (blank)
(b) Ground water + PAA (250 ppm) + Zn²⁺ (50 ppm)

Analysis of FTIR spectra: FTIR spectra have been used to analyze the protective film formed on the metal surface¹⁹. The structure of pure PAA is shown in figure 3. The FTIR spectrum (KBr) of pure PAA is shown in figure 4(a). The N-H stretching and deformation frequencies appear at 3442 cm^{-1} and 1641 cm^{-1} respectively. The C=O stretching frequency appears at 1650 cm^{-1} . The C-N stretching frequency appears at 1021 cm^{-1} . The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing ground water, 250 ppm of PAA and 50 ppm Zn^{2+} is shown in figure 4(b). The N-H stretching frequency has shifted from 3442 cm^{-1} to 3445 cm^{-1} . The N-H deformation frequency has shifted from 1641 cm^{-1} to 1645 cm^{-1} . The C=O stretching frequency has shifted from 1650 cm^{-1} to 1623 cm^{-1} . This observation suggest that PAA has coordinated with Fe^{2+} through the nitrogen atom of N-H group resulting in the formation of Fe^{2+} - PAA complex on the anodic sites of the metal surface. The peak at 1384 cm^{-1} is due to Zn-O stretching. The OH stretching frequency appears at 3442 cm^{-1} . This confirms that $\text{Zn}(\text{OH})_2$ is formed on the cathodic sites of metal surface²⁰⁻²². Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+} -PAA complex and $\text{Zn}(\text{OH})_2$.

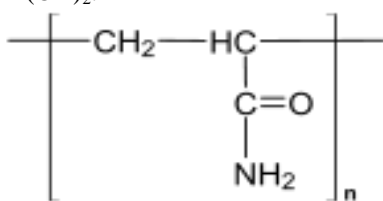


Figure-3
Structure of polyacryl amide

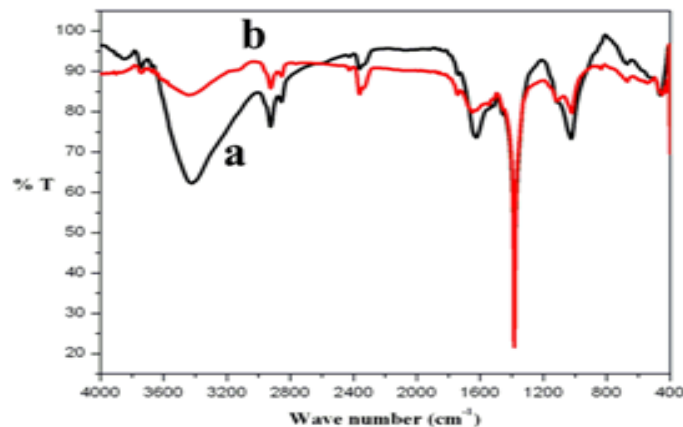


Figure-4
FTIR spectra (a) Pure PAA (b) Film formed on the metal surface

Scanning Electron Microscopy (SEM): SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined. The SEM micrograph (X 1000) of a polished carbon steel surface (control) in figure 5(a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrograph (X 1000) of carbon steel specimen immersed in the ground water for one day is shown in figure 5(b) and figure 5(c) respectively.

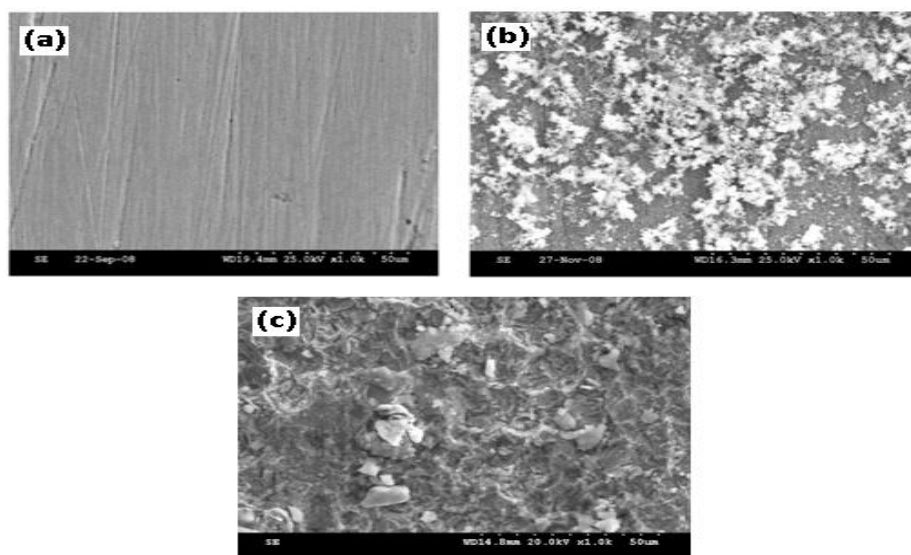


Figure-5
SEM micrographs of carbon steel surface (Magnification – X 1000)
(i) Polished Carbon steel (control) (ii) Carbon steel immersed in ground water (iii) Carbon steel immersed in ground water containing PVA (250 ppm) and Zn^{2+} (50 ppm)

The SEM micrograph of carbon steel surface immersed in ground water is shown in figure 5(b). This shows the roughness of the metal surface which indicates the corrosion of carbon steel in ground water. The figure 5(c) indicates that in the presence of 250 ppm PAA and 50 ppm Zn^{2+} mixture in ground water, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface. In the presence of PAA and Zn^{2+} , the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel²³⁻²⁹.

Mechanism of corrosion inhibition: With these discussions, a mechanism is proposed for the corrosion inhibition of carbon steel immersed in ground water by 250 ppm PAA and 50 ppm Zn^{2+} system: When the formulation consisting of 250 ppm of PAA and 50 ppm of Zn^{2+} in ground water there is a formation of PAA – Zn^{2+} complex in solution. When carbon steel is immersed in this solution PAA – Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface. PAA – Zn^{2+} complex is converted into PAA – Fe^{2+} complex on the anodic sites of the metal surface with the release of Zn^{2+} ion,

$Zn^{2+} - PAA + Fe^{2+} \rightarrow Fe^{2+} - PAA + Zn^{2+}$
The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface,
 $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$

Thus the protective film consists of $Fe^{2+} - PAA$ complex and $Zn(OH)_2$. In near neutral aqueous solution the anodic reaction is the formation of Fe^{2+} . This anodic reaction is controlled by the formation of PAA – Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH^- . It is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

$Fe \rightarrow Fe^{2+} + 2e^-$ (Anodic reaction) $Fe^{2+} + Zn^{2+} - PAA \text{ complex} \rightarrow Fe^{2+} - PAA \text{ complex} + Zn^{2+}$
 $O_2 + 2OH^- + 4e^- \rightarrow 4OH^-$ (Cathodic reaction) $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$ This accounts for the synergistic effect of PAA – Zn^{2+} system.

Conclusion

The inhibition efficiency (IE) of Polyacrylamide (PAA) in controlling corrosion of carbon steel immersed in ground water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm PAA and 50 ppm Zn^{2+} has 98% corrosion inhibition efficiency. Polarization study reveals that PAA – Zn^{2+} system controls the cathodic reaction predominantly. FTIR spectra reveal that the protective film consists of $Fe^{2+} - PVA$ complex and $Zn(OH)_2$. The SEM micrographs confirm the formation of protective layer on the metal surface.

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