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Enhanced corrosion inhibition behavior of carbon steel in aqueous solution by Phosphoserine-Zn^{2+} system

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ABSTRACT

The corrosion inhibition effect of carbon steel in aqueous solution was using a synergistic mixture of an environmentally friendly inhibitor system phosphoserine (PS) and Zn^{2+} using gravimetric studies, potentiodynamic polarization, and electrochemical impedance studies. Potentiodynamic polarization studies showed that the inhibitor system is a mixed type inhibitor. Electrochemical impedance studies of the metal/solution interface indicated that the surface film is highly protective against the corrosion of carbon steel in the aqueous solution. X-ray photoelectron spectroscopic analysis of the protective film exhibited the presence of the elements viz., iron, phosphorus, nitrogen, oxygen, carbon, and zinc. The chemical shifts in the binding energies of these elements inferred that the surface film is composed of oxides/hydroxides of iron, $Zn(OH)_2$, and [Fe(II)/(III)-Zn(II)-PS] complex. Further, the surface examination techniques viz., FTIR, SEM, and AFM studies confirm the formation of an adsorbed protective film on the carbon steel surface. Based on the results obtained, a suitable mechanism of corrosion inhibition is presented.

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KEYWORDS
Carbon steel; corrosion inhibition; gravimetric; potentiodynamic polarization; electrochemical impedance; X-ray Photoelectron spectroscopy

1. Introduction

Carbon steel is an alloy of iron; it is extensively used in petrochemical, chemical, and metallurgical industries. Circulating cooling water system is extensively used in industrial processes and central air conditioning systems because of its high water upkeep efficiency and reduction of thermal pollution of receiving water compared to the ones through cooling water system.[1] In this system, carbon steel is widely used as most important materials. However, circulating cooling water system encounters three main problems such as corrosion, scaling, and microbial growth. To reduce or eradicate these problems, waters used in cooling circuits are treated with inhibitor formulations composed of corrosion inhibitors along with chemical reagents used to limit the scaling and fouling phenomena. Due to new protective laws concerning the environment, these compounds must be non-toxic and eco-friendly. More advanced treatments using organic compounds (e.g. phosphonates, polyacrylates, amines) have been used to develop corrosion protection, their principal advantage being their non-toxic nature. Phosphonate-based cooling water inhibitors

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offer protection by forming three-dimensional layers of the metal surfaces.[2] Most of the inhibitors used in cooling water nowadays are based on phosphonates, either alone or in combination with one or more other corrosion inhibitors.[3,4] Phosphonates give better inhibition efficiencies (IE) when used in combination with zinc salts. The use of organic phosphonic acids to protect carbon steel against corrosion has been the subject of various workers.[5,6] They have been commonly used as water treatment agents because of their low toxicity, high stability, and corrosion inhibition activity in neutral aqueous media.[7] It is well known that phosphonate/Zn^{2+} mixtures are important inhibitors to control corrosion of carbon steel in cooling water systems. Synergistic effect existing between phosphonic acids and zinc ions on the inhibition of metallic corrosion has been studied by a number of researchers.[4,8–10] Literature reports pointed to a synergistic action of Zn^{2+} and phosphonates which was explained on the basis of metal-phosphonate inhibiting films on the metallic surface.[10] Compounds with a phosphonic functional group are considered to be the mainly efficient chemicals for inhibiting the corrosion process and it is well known that short-chain-substituted phosphonic acids are good corrosion inhibitors for iron and low alloyed steels.[11,12]

In the present work, the inhibiting effect with a new organic inhibitor viz., phosphoserine (PS) and Zn^{2+} ions in controlling the corrosion of carbon steel alloy in a neutral aqueous environment containing low chloride has been studied by the gravimetric studies. The corrosion inhibition was further investigated by means of potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). Surface analytical techniques, viz., X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), and Atomic force microscopy (AFM) were used to investigate the nature of protective film formed on the metal surface. A plausible mechanism of inhibition of corrosion is proposed. For all these studies, aqueous solution of 60 ppm chloride has been chosen as control because the water used in cooling water systems is generally either demineralized water or unpolluted surface water. In either case, the aggressiveness of the water will never exceed that of 60 ppm of Cl^-.

2. Experimental

2.1. Materials

The specimens of carbon steel alloy of the following composition were chosen 0.02–0.03% S, 0.03–0.08% P, 0.4–0.5% Mn, 0.1–0.2% C and the rest iron. Prior to the tests, the carbon steel specimens of dimensions 3.5 cm × 1.5 cm × 0.2 cm were polished to a mirror finish with 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0 emery polishing papers, respectively, degreased with acetone, dried and used for gravimetric measurements, FTIR, and SEM. The specimens with dimensions 1.0 cm × 1.0 cm × 0.1 cm were used for electrochemical studies, XPS, and AFM analysis. PS purchased from Alderich Chemical Company Inc., USA, was used as such in the present study. The molecular structure of the PS is shown in Figure 1. Sodium chloride, zinc sulfate ($ZnSO_4{\cdot}7H_2O$), and other chemicals were analytical grade. All the solutions were prepared using triple distilled water.

2.2. Gravimetric measurements

The polished carbon steel specimens were weighed and immersed in triplicate, in 100 ml control solution in the absence and presence of inhibitor formulations of various concentrations,

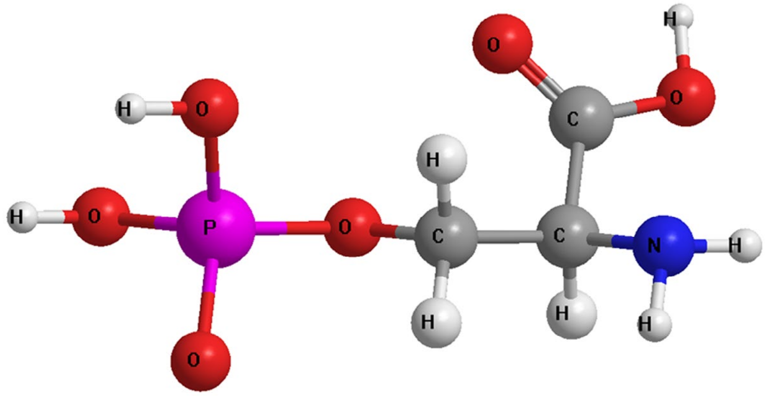

Figure 1. Molecular structure of PS.

for a period of 7 days. Then, the carbon steel specimens were reweighed after washing and drying. The weights of the carbon steel specimens before and after immersion were determined with Mettler balance AE 240 model. Accuracy in weighing up to 0.01 mg and its surface area measurement up to 0.1 cm^2, as suggested by ASTM, was followed. Corrosion rates (CR) of carbon steel in the absence and presence of PS and Zn^{2+} are expressed in mdd. The CR was calculated according to the following equation

$$\mathrm{CR(mdd)} = \left[\frac{\Delta W}{St}\right] \tag{1}$$

where ΔW (mg) is the weight loss, S (dm^2) is the surface area, and t (days) is the immersion period. IEs of the inhibitor were calculated using the formula

$$\mathrm{IE_g}(\%) = \left[\frac{\mathrm{CR_0} - \mathrm{CR_I}}{\mathrm{CR_0}}\right] \times 100 \tag{2}$$

where $\mathrm{CR_0}$ and $\mathrm{CR_I}$ are the CR of carbon steel specimens in the absence and presence of inhibitor, respectively.

2.3. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Inductively coupled plasma-optical emission spectrometer (ICP-OES) was used to analyze the gravimetric solutions. The collected gravimetric solutions were analyzed for Fe, Zn, and P present in the test solution after immersion of carbon steel in control and inhibitor solution for seven days was carried out using Optima 5300 DV, Perkin Elmer.

2.4. Electrochemical studies

The electrochemical experiments viz., potentiodynamic polarization and EIS, were carried out using CHI Electrochemical analyzer model 760 D with operating software CHI 760D. Conventional three-electrode system was used for potentiodynamic polarization and EIS studies. In this setup, polished carbon steel specimens with 1 cm^2 exposed surface area were used as working electrode, platinum electrode as an auxiliary electrode, and saturated calomel electrode (SCE) as a reference electrode. The reference electrode was placed close to the working electrode to minimize IR contribution. The three electrodes setup was immersed in control solution of volume 100 ml both in the absence and presence of various inhibitor formulations. This setup was kept at room temperature for 30 min and then electrochemical measurements were carried out.

The potentiodynamic polarization measurements were started from cathodic to anodic direction (OCP ± 200 mV) with a scan rate of 1 mV/s and the parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (b_a), and cathodic Tafel slope (b_c) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots. From I_{corr}, the inhibition efficiencies (IE_p) were calculated using the following relation,

$$IE_p(\%) = \left[\frac{I\text{corr} - I'\text{corr}}{I\text{corr}}\right] \times 100 \tag{3}$$

where I_{corr} and I'_{corr} are the corrosion current densities in case of control and inhibited solutions, respectively.

EIS measurements were carried out using ac signals of amplitude 10 mV peak to peak in the frequency range from 60 kHz to 10 mHz. The impedance parameters viz., charge transfer resistance (R_{ct}) and constant phase element (CPE) were obtained from the Nyquist plots. The inhibition efficiencies (IE_i) using R_{ct} were calculated using the equation,

$$IE_i(\%) = \left[\frac{R'_{ct} - R_{ct}}{R'_{ct}}\right] \times 100 \tag{4}$$

where R_{ct} and R'_{ct} are the charge transfer resistance values in the absence and presence of the inhibitor.

2.5. Surface examination studies

The carbon steel specimens were immersed in various test solutions for a period of seven days. Then, they were taken out and dried. The nature of the surface film formed on the carbon steel specimen was analyzed by XPS, FTIR, AFM, and SEM.

2.5.1. X-ray photoelectron spectroscopy

XPS measurements of the protective films were recorded on a Kratos AXIS 165 photoelectron spectrometer using Al K_α (1486.6 eV) excitation. Both the general survey spectrum and deconvolution spectra were recorded at four spots on each carbon steel specimen. The average of the four measurements is reported. The spectra were collected at an electron take-off angle of 90°. Analyzer pass energy was 80 eV, with a step of 0.1 eV for the elements of interest, namely Fe 2p, P 2p, N 1s, C 1s, O 1s, Zn 2p, and Cl 2p. The deconvolution spectra were corrected individually for each measurement set, based on a value of 285.0 eV for the C–C component of C 1s.

Table 1. IEs (%) and CR (mdd) of carbon steel in absence and presence of inhibitor system (PS–Zn^{2+}) by gravimetric studies.

PS (ppm)	Zn^{2+} (ppm)															
	0		10		20		50		75		100		125		150	
	CR	IE	CR	IE	CR	IE	CR	IE	CR	IE	CR	IE	CR	IE	CR	IE
0	13.30	–	14.79	−11	16.78	−26	17.55	−32	16.92	−27	17.72	−33	19.85	−49	17.72	−33
10	11.85	11	6.75	42	6.92	48	7.03	47	6.12	53	8.39	37	6.61	50	8.12	39
25	11.72	12	5.87	56	7.07	47	6.13	54	3.98	70	7.60	43	5.20	61	5.66	57
50	10.26	23	4.48	66	6.63	50	1.57	88	0.31	98	2.84	79	2.09	84	1.46	89
75	7.66	42	4.19	69	5.97	55	0.21	98	0.21	98	1.05	92	1.04	92	0.73	94
100	7.07	47	3.68	72	6.77	49	0.21	98	0.10	99	0.52	96	0.83	94	0.32	98
150	7.92	40	3.57	58	4.75	64	0.10	99	0.10	99	0.31	98	0.21	98	0.21	98
200	8.26	38	6.51	51	5.67	57	0.10	99	0.10	99	0.21	98	0.21	98	0.31	98
250	8.79	34	6.98	48	5.77	57	0.10	99	0.21	98	0.21	98	0.31	98	0.62	95

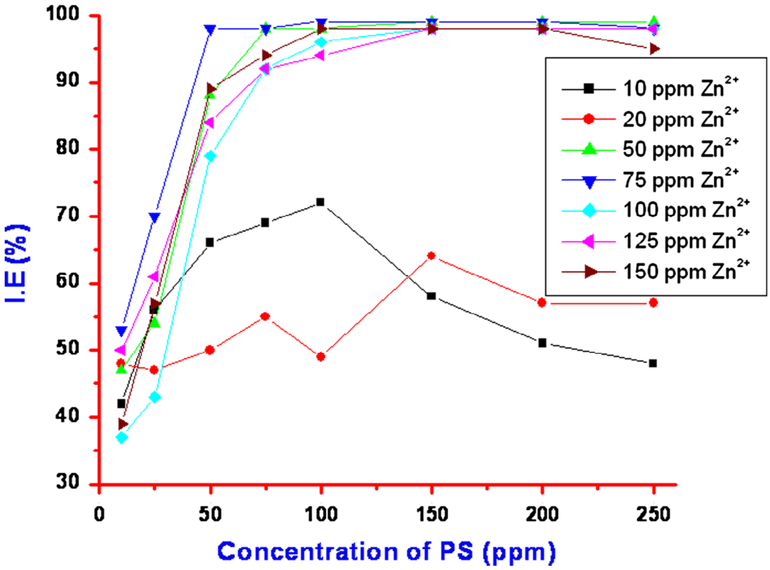

Figure 2. IE as a function of different concentration of PS.

2.5.2. Fourier transform infrared spectroscopy

FTIR was obtained with a resolution of 4 cm^{-1} over the range of 4000–400 cm^{-1} wave number using a JASCO 460 PLUS Spectrophotometer. The spectra of pure PS and the surface film formed on the carbon steel surface were made using the KBr pellet method.

2.5.3. Scanning electron microscopy

SEM has been used to examine the surface morphology. The surface features of carbon steel specimens were examined after exposure to solution after 7 days with and without inhibitor. The SEM photographs of the surfaces of the carbon steel specimens were recorded using the VEGA3 TESCAN model.

2.5.4. Atomic force microscopy

AFM images were carried out using NTEGRA PRIMA – NTMDT, Ireland. The topography of the entire samples for a scanned area of 10 μm × 10 μm is evaluated for a set point of 20 nN and a scan speed of 10 mm s^{-1}.

3. Results and discussion

3.1. Evaluation of corrosion inhibition

3.1.1. Gravimetric studies

The gravimetric measurements were carried out to calculate the CR and IEs for the carbon steel in an aqueous solution containing 60 ppm chloride in the absence and presence of various concentrations of the PS (10–250 ppm) and Zn^{2+} (10–150 ppm) for 7 days immersion period. IEs and CR are given in Table 1. The results of the gravimetric studies of the binary system PS–Zn^{2+} at various concentrations of both constituents are also shown in the Figure 2. Initially, carbon steel corroded in control solution and showed very high

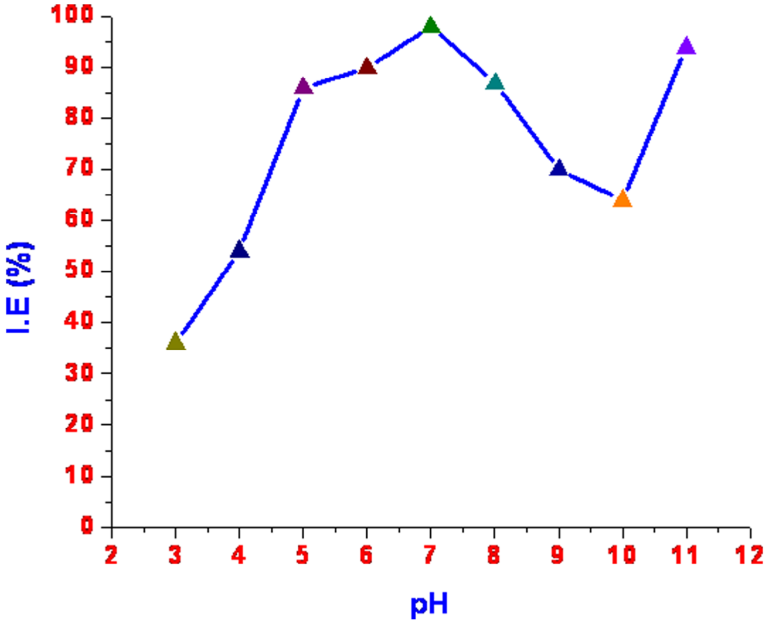

Figure 3. Effect of pH.

Table 2. The analysis results of the solution immersion by ICP-OES.

Sample	Fe (ppm)	IE ($M_i - M_f$)/M_i %		Zn (ppm)	P (ppm)
Control solution	M_i = 40.00	–	Before immersion of metal specimen	50.00	75.00
PS–Zn^{2+}	M_f = 2.00	95	After immersion of metal specimen for 7 days	3.76	2.50

CR with the heavy metal loss. The CR decreased and the IE increased appreciably by the addition of 50 ppm Zn^{2+} and 75 ppm PS and the efficiency reached up to 98%. It is evident from gravimetric results that PS by itself is a poor corrosion inhibitor. Also, zinc ions are found to be corrosive. The IE of phosphonic acids is improved by addition of Zn^{2+} ions.[3] Various concentrations of Zn^{2+} were added to PS for improving the corrosion efficiency. The formulation consists 10 ppm Zn^{2+} and 75 ppm PS shows an IE of 55% only. But, with increasing concentration of PS keeping Zn^{2+} constant at 10 ppm, the IE was found to decrease. On increasing concentration of Zn^{2+} from 20 ppm to 50 ppm, the IEs also increase to 72 and 98%, respectively. The combination containing of 50 ppm Zn^{2+} and 75 ppm of PS has achieved high IE of 98%. It is found that the value of IE was increased with an increase in the concentration of Zn^{2+}. After this concentration, no appreciable change in efficiency was observed. It can be interpreted that low concentrations of Zn^{2+} are insufficient to form a protective film with PS on the metal surface. At lower concentrations of Zn^{2+}, the PS is precipitated as PS–Zn^{2+} complex in the bulk of the solution. PS is not transported toward the metal surface. Only on increasing the concentrations of Zn^{2+}, the maximum efficiency (98%) is obtained. This is indicative of the strong synergistic effect of PS and Zn^{2+}. When 50 ppm of Zn^{2+} ions are added to PS, PS–Zn^{2+} complex is in solubilized form. It diffuses from the bulk of the solution to metal surface. The [Fe(III)/Fe(II)-PS-Zn^{2+}] complex is formed. A

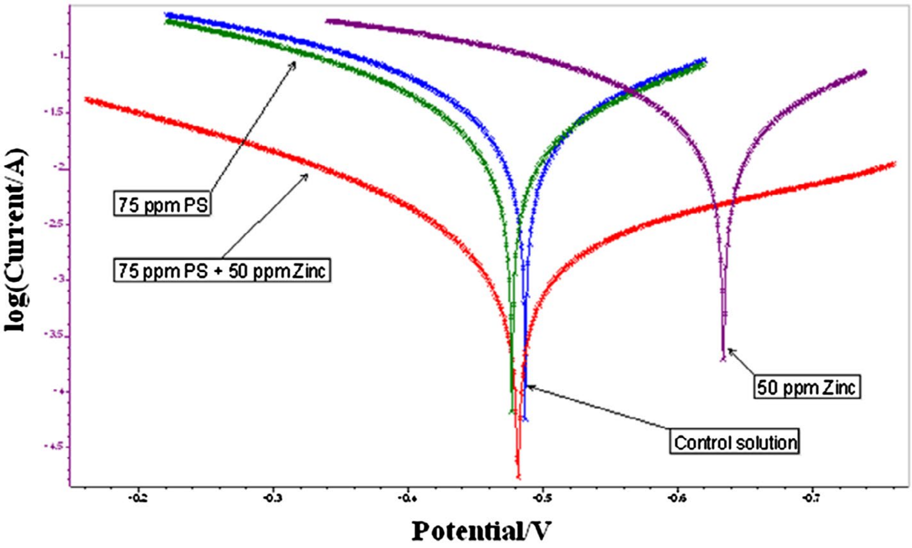

Figure 4. Potentiodynamic polarization curves of steel immersed in different test solutions.

Table 3. Corrosion parameters obtained by potentiodynamic polarization studies of carbon steel immersed in the absence and in the presence of inhibitor system.

Concentration (ppm)		Tafel parameters				
PS	Zn^{2+}	E_{corr} (mV/SCE)	I_{corr} (μA/cm^2)	β_a (mV/decade)	β_c (mV/decade)	IE$_p$ (%)
–	–	−487.62	22.68	209	212	–
75	–	−476.97	17.15	194	202	24
–	50	−633.83	23.30	208	209	–
75	50	−481.28	1.64	187	327	93

thin multicolor protective film was observed on the surface of carbon steel specimen after 7 days of immersion during the gravimetric studies.

3.1.2. Effect of pH

The inhibitor system containing 75 ppm PS and 50 ppm Zn^{2+} ions was selected for further studies at various pH ranges 3–11 because of its good IE. The effect of pH on the corrosion IE of 75 ppm PS and 50 ppm Zn^{2+} ions is shown in Figure 3. It can be seen from the results obtained that the IE decreases with increasing the pH from 7.0 to 9.0 in alkaline medium and also on decreasing the pH from 5.0 to 3.0. The highest IE could be obtained in the pH range 5.0–7.0. However, interestingly, the corrosion IE again increases from pH 10.0 to 11.0. This is due to formation of sodium zincate ((Na_2ZnO_2) over the metal surface, protecting the metal due to passivation. This inhibitor formulation is effective in the pH range 5.0–7.0 and also at pH 11.0.

3.2. Inductively coupled plasma-optical emission spectroscopy

The solution containing 60 ppm chloride, 75 ppm PS, and 50 ppm Zn^{2+} ions in which carbon steel specimens were immersed for 7 days was analyzed for Fe, Zn^{2+}, and P by ICP-OES.

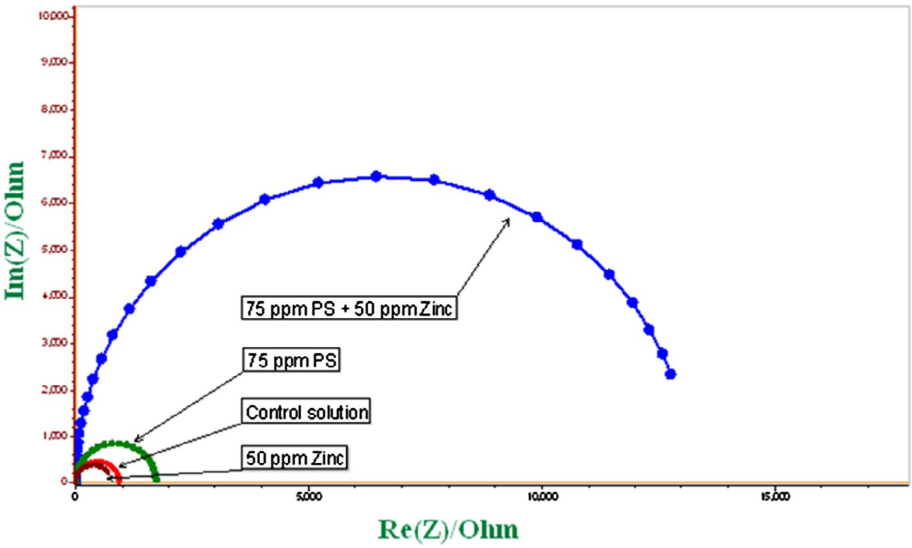

Figure 5. Nyquist plots of carbon steel immersed in different test solutions.

Inspection of obtaining results, given in Table 2, clearly shows that the concentration of iron in the solution without inhibitor was very high (40 ppm), the presence of the inhibitor solution has limited the passage of the iron in solution (2 ppm). Indeed, the obtained value of IE (95%) is in good agreement with that obtained using gravimetric measurements. The results show that out of 75 ppm of PS, 2.5 ppm of phosphorus is present in the solution and out of 50 ppm of Zn^{2+} ions, 3.76 ppm of Zn^{2+} ions is present in the solution. The results show that out of 50 ppm of Zn^{2+} ions, 46.24 ppm of Zn^{2+} ions have diffused from the bulk of the solution and adsorbed on the metal surface. The results show that it can be interpreted that the appreciable amount of phosphorous and Zn^{2+} ions have diffused from the bulk of the solution to the metal surface and incorporated in the protective film.

3.3. Electrochemical studies

3.3.1. Potentiodynamic polarization studies

The potentiodynamic polarization measurements have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions. Figure 4 shows the potentiodynamic polarization curves for carbon steel in control solution in the absence and the presence of different concentrations of inhibitor combinations. The values of the electrochemical parameters: corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c), and corrosion current density (I_{corr}) with and without inhibitor are summarized in Table 3. An examination of Table 3 shows that the corrosion potential (E_{corr}) in case of the control is −487.62 mV/SCE and the corresponding corrosion current density (I_{corr}) is 22.68 μA/cm^2. When PS was added to the control solution, the E_{corr} value is shifted to a more anodic side and its I_{corr} is reduced to 17.15 μA/cm^2. The anodic Tafel slope (β_a) for PS has been shifted more anodically (15 mV/decade) than the cathodic Tafel slope (β_c) (10 mV/decade). In the literature, it was reported that phosphonates in general are anodic inhibitors.[8] When 50 ppm of Zn^{2+} is added to the control, the corrosion potential is shifted to the

Table 4. A.C. impedance parameters obtained by A.C. impedance spectra of carbon steel immersed in the presence and absence of inhibitor system.

Concentration (ppm)		Charge Transfer Resistance	Constant phase element	Constant exponent	IE (%)
PS	Zn^{2+}	R_{ct} (Ω)	CPE (μF/cm^2)	n	
0	0	958	582	0.68	–
0	50	781	681	0.74	–
75	0	1748	392	0.86	45
75	50	13204	164	0.92	93

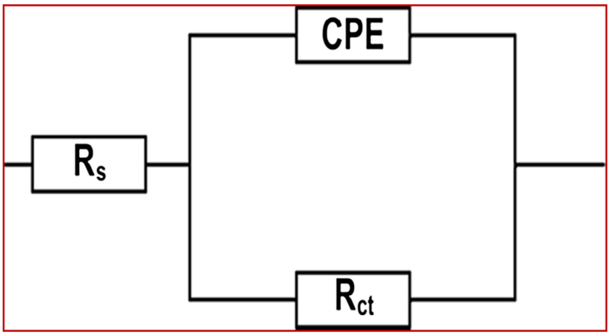

Figure 6. Nyquist plots are fitted by the equivalent electrical circuit.

cathodic side and the shift in cathodic Tafel slope is greater. Contrary to the result obtained in the case of PS, Zn^{2+} increased the rate of corrosion as implied by an increase in corrosion current density. In the presence of Zn^{2+}, the increase in I_{corr} leads to increase in CR.[11] The combination of 75 ppm PS and 50 ppm Zn^{2+}, the shift in cathodic Tafel slope (115 mV/decade) is greater than the shift in anodic Tafel slope shift (22 mV/decade). The E_{corr} value is shifted to −481.28 mV/SCE and its I_{corr} is significantly decreased from 22.68 μA/cm^2 to 1.64 μA/cm^2, corresponding to an IE of 93%. Thus, it is evident that this formulation acts as an effective mixed type inhibitor. Thus, the synergistic combination of 75 ppm PS and 50 ppm Zn^{2+} is proved to be an effective corrosion inhibitor for carbon steel. These results point out that the inhibitor formulation retards both the anodic dissolution of carbon steel and oxygen reduction at cathodic sites in the corrosion inhibition process. Similar type of inhibitor formulations was reported to be mixed inhibitors.[8,13] An important study related to the IE values are to be noted. If the IE values obtained from gravimetric studies (IE_g), potentiodynamic polarization (IE_p), and electrochemical impedance studies (IE_i) are compared, slight differences are observed. It is suggested that the IE values obtained from a variety of methods may not be strictly equal when the immersion times used in these methods are not the same.[14]

3.3.2. Electrochemical impedance studies

EIS provides more information on both the resistive and capacitive behaviors of the interface and makes it possible to evaluate the performance of the inhibitors. The corrosion behavior of carbon steel, in control solution at pH 7 in the absence and presence of various formulations was investigated by the EIS after 30 min of immersion. The obtained results are presented in Figure 5. The impedance parameters, charge transfer resistance (R_{ct}), constant phase element (CPE), and CPE exponent (n), obtained from the Nyquist plots and the calculated inhibition efficiency (IE_i) values are shown in Table 4. In case of the control as well as in the presence of inhibitor formulations, the Nyquist plots are established to be depressed semicircles instead of ideal semicircles. Li et al. [15] have observed this type of dispersed semicircles and reported that this kind of phenomenon is called the dispersing effect.

The simplest fitting is represented by an equivalent circuit (Figure 6), which is a parallel combination of the charge-transfer resistance (R_{ct}) and the constant phase element (CPE), both in series with the solution resistance (R_s) was used to evaluate the experimental EIS results. The equivalent circuit was also discussed by several authors, who obtained similar depressed semicircles with single time constant.[16–18] One constant phase element (CPE) is substituted for the capacitive element to give a more accurate fit,[19] where the capacitive loop obtained is a depressed semicircle rather than the regular one. Deviation from the ideal semicircle is usually attributed to frequency dispersion, to the roughness and inhomogeneity of the surface, and of resistance to mass transport.[20,21] The impedance of a CPE is described by the expression:

$$Z_{\mathrm{CPE}} = Y^{-1}(j\omega)^{-n} \tag{5}$$

where Y is the CPE coefficient, n is the CPE exponent (phase shift), ω the angular frequency ($\omega = 2\Pi f_{max}$, where f is the AC frequency), and j here is the imaginary unit. For $n = 0$, Z_{CPE} represents a resistance with $R = Y^{-1}$; for $n = -1$ an inductance with $L = Y^{-1}$, for $n = 1$, an ideal capacitor with $C = Y$ [22]. The value range of a real electrode of n is often between 0 and 1. The smaller value of n, the rougher the electrode surface and the more serious the corrosion of the electrode. The correction of the capacity to its real value is calculated from:

$$C_{\mathrm{dl}} = Y\left(\omega_{\max}\right)^{n-1} \tag{6}$$

where ω_{max} is the frequency at which the imaginary part component of the impedance (−Zi) is a maximum.

In the present study, the presence of the synergistic combination containing PS (75 ppm) and Zn^{2+} ions (50 ppm) has an R_{ct} value of 13,204 Ω, which is far higher than the corresponding values of the surface films obtained in the presence of the individual constituents, i.e. 1748 Ω for 75 ppm PS and 781 Ω for 50 ppm Zn^{2+} ions. The absence of the synergistic mixture is observed a small semicircle with an R_{ct} value of 958 Ω. Due to Zn^{2+} ions, CPE value increases with a slight increase in the value of n. By the addition of 75 ppm of PS to the control, the CPE value is decreased and n value is increased. These observations can be ascribed to the presence of organic inhibitor molecules in the double layer and control of the corrosion processes to some extent. The CPE value of the metal/solution interface was 164 μF/cm^2 in the presence of the synergistic combination containing 75 ppm PS and 50 ppm Zn^{2+} ions. The CPE value of the metal/solution interface is found to decrease from 582 μF/cm^2 in the case of the control to 164 μF/cm^2 in the presence of the inhibitor formulation. The high, CPE value is due to a large increase in the surface area caused by the presence of corrosion products on the metallic surface. It is well known that the capacitance is inversely proportional to the thickness of the double layer.[23] Decrease in the capacitance, which can result from a decrease in the local dielectric constant and/or an increase in the thickness

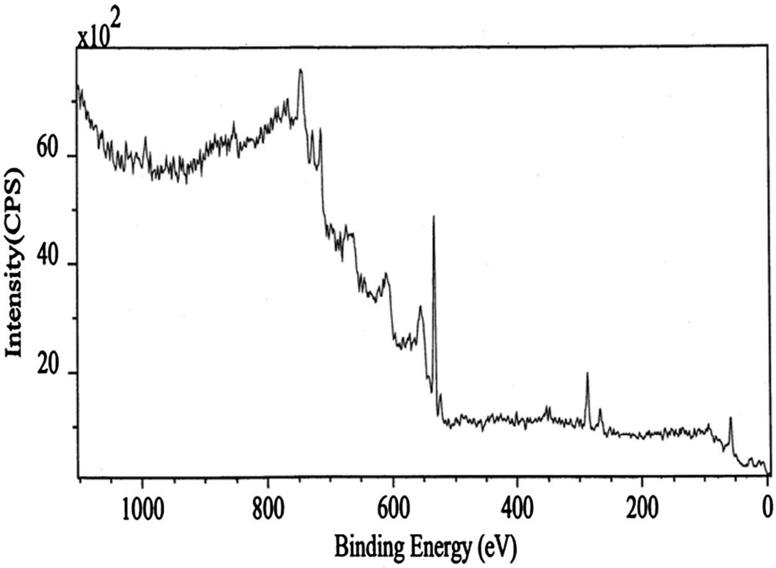

Figure 7. XPS spectrum of the general survey of the surface film formed on carbon steel surface immersed in control solution.

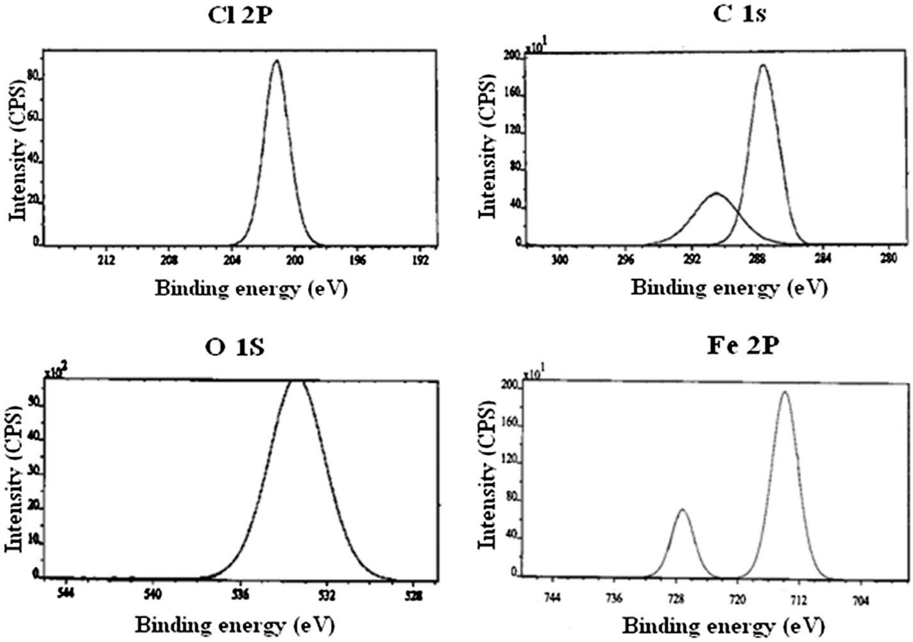

Figure 8. XPS pattern of the individual element in the surface formed on the carbon steel in control solution.

of the electrical double layer, strongly suggests that the inhibitor molecules adsorbed at the metal/solution interface.[21] The value of n is significantly increased to 0.92 in the presence of the inhibitor system, suggesting a decrease in the inhomogeneity of the interface during

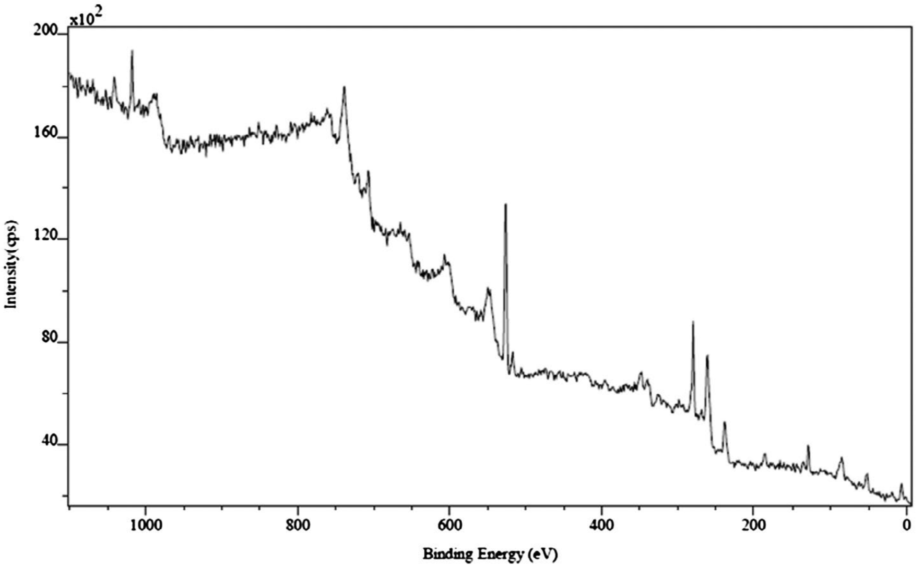

Figure 9. XPS spectrum of the general survey of the inhibited surface film (60 ppm Cl^- ions + 75 ppm PS + 50 ppm Zn^{2+} ions).

the inhibition process. These results indicated that there is formation of a non-porous and protective film in the presence of the binary inhibitor formulation. The IE obtained from electrochemical impedance studies is found to be 93%. This is in agreement with the inferences drawn from gravimetric studies and potentiodynamic polarization studies.

3.4. Surface examination studies

3.4.1. X-ray Photoelectron spectroscopy

XPS technique is the most broadly applicable surface analysis technique. It relies on measurements of the energy distribution of photon excited electrons from atoms in the surface region of the solid. XPS patterns of the protective films formed on the carbon steel surface immersed in an aqueous solution containing 60 ppm chloride (control solution) at neutral pH (pH 7.0) in the absence and the presence of the inhibitor formulations were recorded. The interpretation of all these spectra is done with the help of the data of the elemental binding energies reported in the literature and also with the help of the reports published on the analysis of XPS spectra of the surface films. X-ray photoelectron spectrum (general survey) of the protective surface film of carbon steel specimen immersed in control solution for a period of 7 days is given in Figure 7. The XPS deconvolution spectra of the individual elements for the control solution relating to chlorine, carbon, oxygen, and iron are shown in Figure 8. The two peaks at 287.5 and 290.4 eV correspond to C1s which appeared even in the absence of any inhibitor. These carbon peaks are due to residual carbon from oil vapors of the diffusion pump while recording the XPS spectrum with the instrument. These peaks are appearing due to surface contamination.[24–26] The presence of adsorbed water molecules is reported to show the peak at 533.2 eV.[27,28] However, there is the formation of a brown film consisting of oxides/hydroxides of iron on carbon steel surface. Therefore,

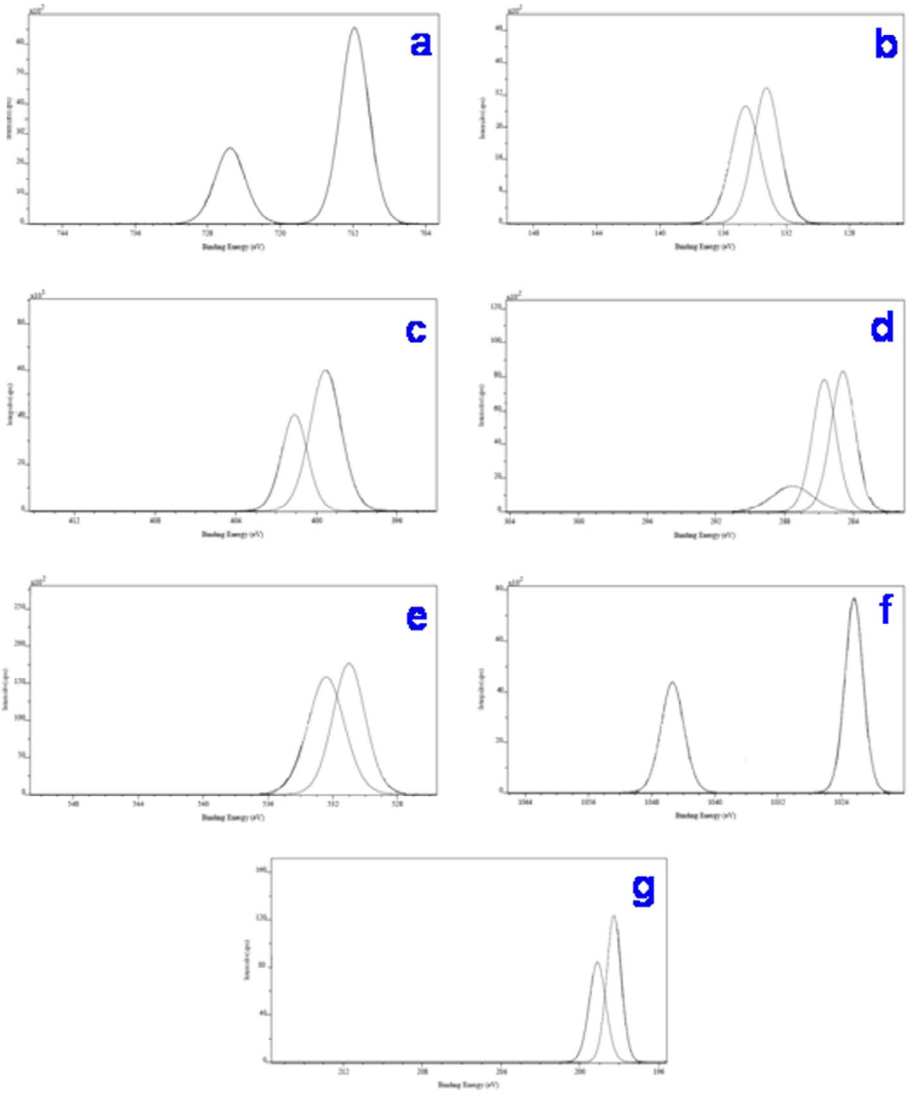

Figure 10. XPS deconvolution spectra of (a) Fe 2p (b) P 2p (c) N 1s (d) C 1s (e) O 1s (f) Zn 2p (g) Cl 2p.

the peak, which appeared due to O 1s at 533.4 eV in the present study, can be interpreted to occur due to the presence of iron only, adsorbed H_2O molecules and also oxides/hydroxides of iron. This interpretation can be seen along with the interpretation of the iron peak discussed below. The deconvolution spectrum of Fe 2p in the case of the control, two peaks appeared for iron, one at 713.9 eV and another at 727.1 eV. The former peak and the latter peak correspond to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The shifts in both the peaks from the corresponding binding energy values of elemental iron are quite important. The peak due to Fe $2p_{3/2}$ is interpreted for the determination of the chemical state of iron in the surface film. The peak of Fe $2p_{3/2}$ at 713.9 eV is the one shifted from 707.0 eV, the typical elemental binding energy of Fe $2p_{3/2}$.[29] Such a large shift of 6.9 eV, suggests that iron is present in Fe^{3+} state in the surface film. The peak at 713.9 eV can also be ascribed to the presence of γ-Fe_2O_3, Fe_3O_4, and FeOOH.[13,30] The peak at 727.1 eV corresponds to Fe 2p ½ which also indicates the presence of iron oxides. The chlorine $2p_{1/2}$ peak appeared at 201.11 eV indicates the presence of the lower amount of chlorine in the surface film.

The general survey of the XPS pattern of the surface film of carbon steel immersed in 60 ppm chloride ions, 75 ppm PS, and 50 ppm Zn^{2+} for a period of 7 days is also given in Figure 9. The XPS deconvolution spectra of the individual elements of iron, phosphorous, nitrogen, carbon, oxygen, zinc, and chlorine are given in Figure 10(a)–(e).

The XPS spectrum of Fe 2p in the case of the inhibitor formulation is shown in Figure 10(a). It shows two peaks, one with a lower binding energy value (711.82 eV) corresponding to Fe $2p_{3/2}$ electron and the other one with a higher binding energy value (725.55 eV) corresponding to Fe $2p_{1/2}$ electron. The peak due to Fe $2p_{3/2}$ is interpreted for the determination of the chemical state of iron in the surface film. The Fe $2p_{3/2}$ peaks at 711.82 eV has shifted from 707 eV for elemental iron. The Fe $2p_{1/2}$ peak has also shifted from 720 eV to 725.55 eV. Similar shifts were also observed by Felhosi et al. [27] and Karman et al. [28]. Thus, the Fe $2p_{3/2}$ peak obtained in the case of the inhibitor formulation implies the presence of oxides and hydroxides like Fe_2O_3, Fe_3O_4, and FeOOH and also involvement of Fe^{3+} in the complex formation with the inhibitor molecules. No peak is observed due to elemental iron in the case of both the control and the inhibitor formulation. This result implies the formation of thick films in both cases. The film is non-protective in the case of the control and highly protective in the presence of the inhibitor. If the intensities of Fe $2p_{3/2}$ peaks are compared, a large decrease in the intensity of the Fe $2p_{3/2}$ peak in the presence of the inhibitor formulation can be understood in terms of formation of protective film and consequently less corrosion of iron and less iron oxide. The binding energy of the $Fe2p_{3/2}$ state in iron oxides was reported to be around 708.5 eV.[31] The absence of any peak in this region in the present study also supports that iron does not exist in the Fe^{2+} state, but in Fe^{3+} state in the surface film. Paszternak et al., reported that the Fe $2p_{3/2}$ at 707 eV, Fe $2p_{1/2}$ at 719.5 eV, the mixture of Fe^{3+} and Fe^{2+} (Fe $2p_{3/2}$ at 711 eV and Fe $2p_{1/2}$ at 724 eV) and the phosphate and phosphonate have the M–O–P bonds attributed the presence of Fe(II) and Fe(III) phosphonates and confirmed the phosphonate layer formation on the passivated iron surface.[32]

The XPS spectrum of P 2p is shown in Figure 10(b). Two peaks of P $2p_{3/2}$ are observed, one at 133.30 eV and another at 134.62 eV. The shifts in the binding energy are noticed from 130 eV for the P $2p_{3/2}$ and 131 eV for P $2p_{1/2}$ elemental binding energy of phosphorous compounds and iron.[12,33,34] Labjar et al. [35] had studied ATMP-treated carbon steel surface by XPS spectra of P 2p and concluded that a binding energy of 133.5 eV was attributable to the phosphonates, the other peak was mainly attributed to $CH_2P(O)(OH)_2$.[36,37] Nakayama obtained a P 2p peak at 133.0 eV and attributed it to the presence of phosphate compounds.[24] Felhosi et al. [27] observed a P 2p peak at 132.1 eV in the XPS of the surface film formed on carbon steel when immersed in a solution containing Zn^{2+} and HEDP. They interpreted that this peak was due to the presence of [Zn-HEDP] complex in the surface film. Ochoa et al. [33] in their studies on the mixtures of salts of phosphono-carboxylic acids and fatty amines as inhibitors for corrosion of carbon steel reported the P 2p peak at 132.1 eV and interpreted that it was due to the presence of phosphonate group in the surface film. In the literature,[34] it was reported that the P 2p peak could be observed in the range of 132.9 to 133.8 eV, for iron or steels immersed in the solutions containing phosphonates, orthophosphates, or polyphosphates. In the light of these reports, the P 2p peaks observed in the present study suggest the presence of PS in the surface film in the form of a complex with Fe(III) and Zn (II).

Figure 10(c) shows the N 1s peak in the XPS spectrum of the surface film observed one at 399.55 eV and another at 401.08 eV. This peak is shifted from the characteristic elemental binding energy value of 398.0 eV for nitrogen.[29] This shift may be attributed to the presence of PS molecules in the surface film in the form of a complex with Fe(III) and Zn (II). It was reported in the literature that N 1s peak observed at 399.7 eV could be assigned to the presence of (=N–) in the molecule adsorbed on the metal surface.[38] Meneguzzi et al. [39] reported that the peak at 399.9 eV could be attributed to the neutral imine (–N =) and amine (–N–H) nitrogen atoms. Li et al. [23] reported that the peaks at 401.3 eV and 402.8 eV can be assigned to protonated amine. Therefore, the peak that appeared at 401.08 in the present study may be due to absorbed and complexes PS through nitrogen.

The C1s spectrum has three peaks, one is the most intense peak at 284.64 eV and other two are less intense peaks at 285.71 and 287.53 (Figure 10(d)). The presence of multiple peaks in the C 1s spectrum in the case of the inhibitor can be attributed to various carbon environments present in PS. The intensity of the C 1s peaks in the presence of the inhibitor is about twice as that of the peak in the case of control. This interpretation can be supported from studies reported in the literature.[16,25,26,33] Labjar et al. [35] had studied ATMP-treated carbon steel surface by XPS spectra of C 1s which showed three peaks and concluded that a binding energy of 284.7 eV was attributable to the C–H, the second peak may be assigned to the C–N bond in the ATMP ring at 286.7 eV, the last peak may be ascribed to the C–O or C–P in the ATMP ring at 288.9 eV.

In the O 1s spectrum, two peaks were observed at 531.04 eV and 532.42 eV (Figure 10(e)). The O 1s peak observed at 531.04 eV is due to O^{2-}, the presence of O^{2-} in the surface film may be in the form of oxides and hydroxides of Fe(III).[13,26] Karman et al. [28] studied the role of oxide layer formation during corrosion inhibition of mild steel in neutral aqueous media by a mixture of HEDP and Ca^{2+} ions. From the XPS studies, they interpreted that the peak at 531 eV is due to the presence of OH^- on the surface. Fang et al. [12] ascribed the O 1s peak observed at 531.3 eV to the complex formed between iron and phosphonate. Pech-Canul and Bartolo-Perez observed the O 1s peak at 531.3 eV, which was ascribed to OH^- from hydrous iron oxides and to the complex formed between iron and phsophonate group.[13] It was also mentioned in their study that such hydrous ferric oxides consist of $Fe(OH)_3$ and FeOOH. Felhosi et al. studied the effects of bivalent cations on the corrosion inhibition of steel by HEDP.[27] They mentioned that the O 1s peak at 531.4 eV is due to HO–Fe bond. Asami et al. observed O 1s peak at 531.5 eV in their study and attributed it to oxygen with a kind of Fe–O–H bond.[31] In the light of these results and interpretations reported in the literature, the O 1s peak of high intensity was observed at 531.04 eV. It may be interpreted as follows. The XPS of the surface film shows the presence of carbon, phosphorous, iron, and zinc. It means that PS is present on the surface, zinc is present as Zn^{2+}, and the interpretation given in the case of Fe 2p indicates the presence of Fe_2O_3, Fe_3O_4, and FeOOH. Hence, the O 1s peak observed in the inhibited surface films can be ascribed to the presence of $Zn(OH)_2$, Fe_2O_3, Fe_3O_4, FeOOH, and/or Fe $(OH)_2$ and oxygen of PS in the inhibited film.[12,13,25,40] The disappearance of the peak around 532.4 eV in the case of the inhibitor formulation indicates the absence of water molecules in the surface film, as they have been completely replaced by the inhibitor molecule.

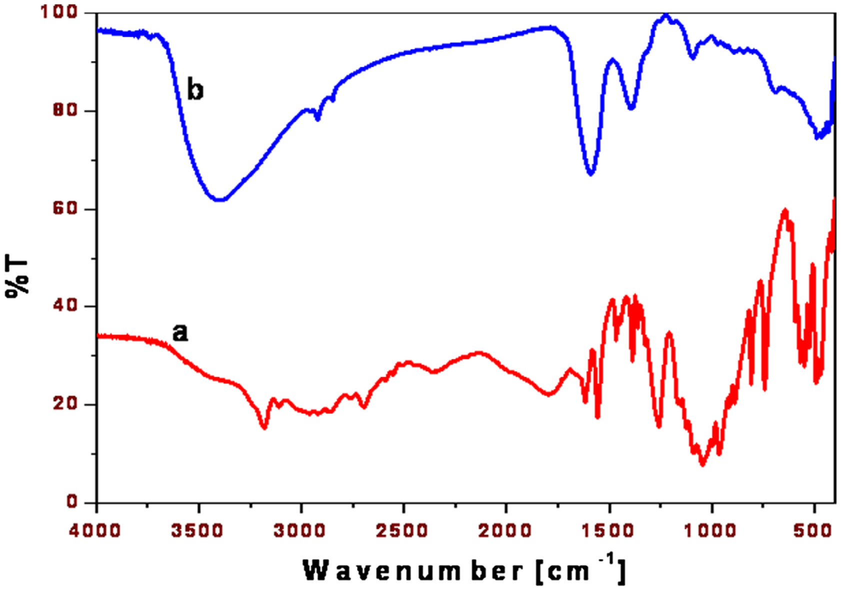

Figure 11. FT-IR Spectra of (a) pure PS (b) Surface film.

The XPS deconvolution spectrum of zinc is presented in Figure 10(f). The binding energy of Zn $2p_{3/2}$ is shifted from 1022 eV for elemental zinc to 1022.42 eV and binding energy of Zn $2p_{1/2}$ is shifted from 1044 eV to 1045.37. The Zn $2p_{3/2}$ peak is normally interpreted and ascribed to the presence of $Zn(OH)_2$ in the inhibited surface film and also to the involvement of Zn^{2+} in the complex formation with PS.[25]

The peak of Cl 2p appeared at the binding energy of 199.09 eV is shown in Figure 10(g). This indicates the decreased adsorption of chlorine, leading to higher resistance against localized corrosion. The present study also shows that the presence of small amounts of chlorine and subsequent absorption of aggressive ions on metal surfaces is decreased thereby allowing inhibitor molecules to cover the entire surface and protecting the metal.

After consolidating all the inferences drawn from the XPS of individual elements (Fe, P, N, C, O, Zn, and Cl) present in surface films, it is suggested that the surface film consists of mainly [Zn(II)-PS] complex, $Zn(OH)_2$, and small amounts of oxides/hydroxides of Fe(III) in the case of the inhibitor system. The complex may be chemisorbed on the metal surface and got attached to the Fe(III) ions.[41]

3.4.2. FT-IR Studies

The FT-IR spectrum of pure PS is shown in Figure 11(a). The stretching frequency made by the P=O band in the region 1380–1140 cm^{-1} and another band in the region 970–1188 cm^{-1}. The peak at 1261.22 cm^{-1} is assigned to P=O stretch of the ionic species and the other peak at 966.16 is assigned to P–OH group.[42] In the spectra of PS, the peak at 1155 cm^{-1} is related to the C–N stretch and the other peak at 1620 cm^{-1} is assigned to the bending of N–H. The band at 1795 cm^{-1} is ascribed to the stretching vibration C=O.

The FT-IR spectrum of 60 ppm Cl^-, 75 ppm PS, and 50 ppm Zn^{2+} ions (surface film) is shown in Figure 11(b). In this case, the inhibited surface film formed by the peak due

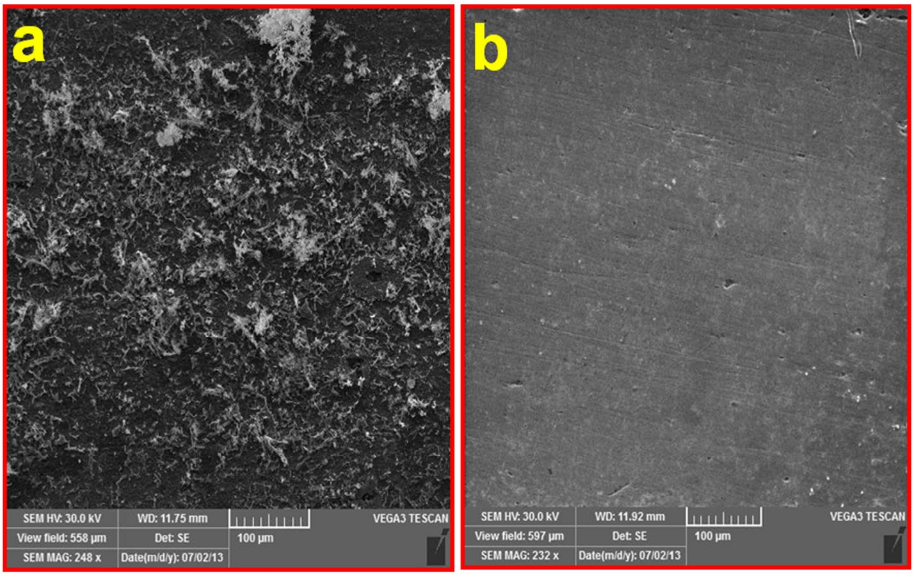

Figure 12. SEM images of carbon steel immersed in (a) control solution (b) presence of inhibitor.

to P=O is shifted from 1261 to 1094 cm^{-1}. The P-OH is stretching located at 966.16 cm^{-1} has disappeared. This result can be interpreted by interactions of free P–O^{-} present in the phosphonate with metallic species, viz., Fe(II) and Zn(II) to form P–O–Metal bonds. Carter et al. found that IR spectra obtained with an organic phosphate on a steel substrate are consistent with a reaction of the phosphate with the steel to produce a metal salt.[43] Gonzalez et al. found a similar band in the P-OH is stretching of the film formed in mild steel specimen by reflection absorption FT-IR spectroscopy and they interpreted the peak to be due to the formation P–O–M bond.[8] The peak at 1397 cm^{-1} indicates the presence of $Zn(OH)_2$ on the metal surface film.[11] An intense band at 1795 cm^{-1} in the FT-IR spectrum of PS is the characteristic of uncoordinated, a protonated carboxylate carbonyl group in PS. In the case of the inhibited surface film, this band is observed at 1593 cm^{-1}. It indicates the presence of PS molecules in the surface film. The shift in the absorption frequency is due to the involvement of the phosphonate in complexation with metal ions. A band at 1094 cm^{-1} is due to C–N stretching vibration shifted from 1155 cm^{-1} observed in the case of pure PS and the N–H is shifted from 1620 to 1632 cm^{-1}. The shift indicates the formation of a coordinate bond between metal ions and phosphonate molecule. The broad band of the OH stretching and bending mode of water or hydroxides within the protective film appeared at 3403 cm^{-1}. There are many weak bands in the region between 1200 and 400 cm^{-1} and a peak of high intensity appeared at 433.91 cm^{-1} implying the presence of ferric and ferrous oxides and hydroxide in the protective film.[24] The FT-IR spectra suggests that the protective film may consist of [Fe(II)/Zn(II)-PS], $Zn(OH)_2$ and small amounts of oxides and hydroxides of iron.

3.4.3. Scanning electron microscopy

SEM was applied to confirm that the protective film formed on the metal surface which can protect the metal from corrosion. SEM images of carbon steel surfaces that had been

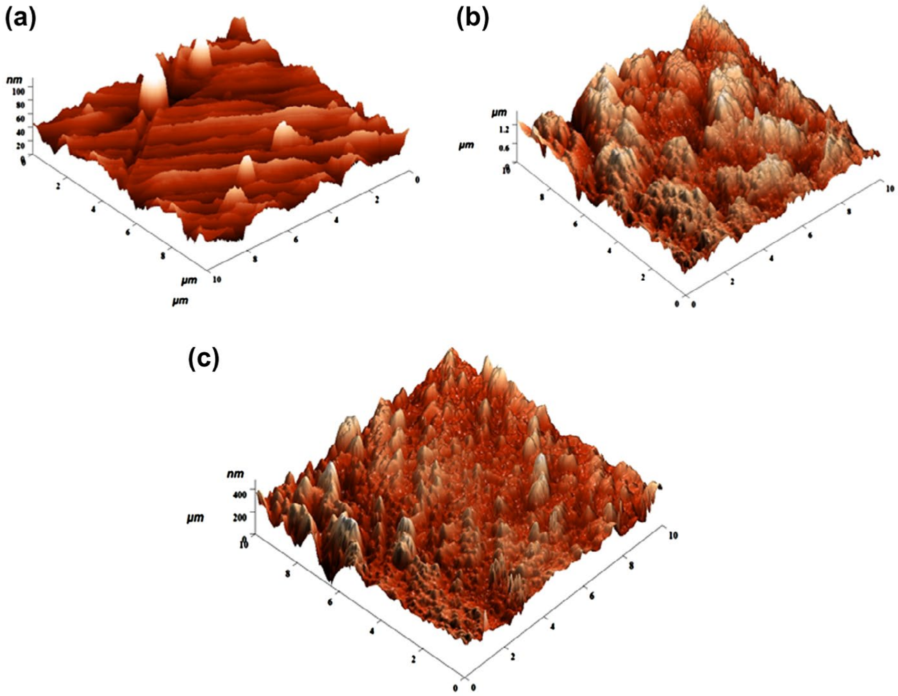

Figure 13. AFM topographical images of carbon steel surfaces after immersion in control in the absence and presence of the inhibitor system: (a) polished carbon steel (b) control (c) inhibitor system.

exposed to an environment containing 60 ppm Cl^- ions (i.e. control solution) and in the presence of the inhibitor, 75 ppm PS and 50 ppm Zn^{2+} for 7 days are shown in Figure 12. Figure 12(a) shows that the surface is strongly damaged and there is formation of different forms of corrosion products (iron oxides) on the surface in the absence of the inhibitor. The entire surface is covered by a scale-like black corrosion product on which there is growth of another corrosion product appearing in the form of white clusters at several sites. It further shows that the corrosion products appear very uneven and the surface layer is too rough. Figure 12(b) reveal that SEM images of polished carbon steel immersed in the inhibitor solutions are in better conditions having smooth surfaces. It is important to stress that when the inhibitor is present in the solution, the morphology of the carbon steel surface is quite different from the previous one. We noted the formation of a film, which is distributed in a random way on the whole surface of the metal. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to block the active site present on the carbon steel surface. Thus, the protective film covers the entire metal surface. This observation also accounts for the high IE values obtained during the gravimetric studies of the inhibitor system. This indicated that the inhibitor molecules hindered the dissolution of iron by forming a protective film on the carbon steel surface and thereby reduced the rate of corrosion. So, SEM analysis shows the protective nature of the surface film.[44]

3.4.4. Atomic force microscopy

AFM or scanning force microscopy is a very high resolution type of scanning probe and it is considered to be one of the most powerful methods to investigate the surface morphology.

AFM is a powerful technique to investigate the surface morphology at nano-scale to micro-scale and has become a new choice to study the influence of inhibitors on the generation and the progress of the corrosion at the metal-solution interface.[45] The topography of the surfaces recorded in 2D and 3D images was examined and surface roughness, root-mean-square roughness (RMS), mean roughness factor (R_a) was determined from the respective images. Figure 13(a) shows the AFM image of the polished metal surface, with a R_a value 6.83 and RMS value 9.47 nm when compared with other thin film coated surface values indicate the absence of iron oxides on the smooth surface. Figure 13(b) shows the AFM image of the polished surface immersed in 60 ppm Cl^- ions (control solution), with an increased R_a value 183.84 nm and RMS value 230.36 nm is indicating the formation of iron oxides. However, Figure 13(c) shows that the carbon steel immersed in inhibitor, 75 ppm PS and 50 ppm Zn^{2+} showed a decreased R_a value 38.22 nm and RMS value of 50.48 nm which indicates the formation of a protective film on the metal surface, most probably made of inhibitor molecules when compared to the control solution.

3.5. Mechanism of corrosion protection

A plausible mechanism of corrosion inhibition is proposed as follows:

Carbon steel undergoes initial corrosion to form Fe^{2+} ions at the anodic sites.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (7)$$

Fe^{2+} further undergoes oxidation in the presence of oxygen available in the aqueous solution.

$$Fe^{2+} \xrightarrow{[O_2]} Fe^{3+} + e^- \qquad (8)$$

The corresponding reduction reaction at the cathodic sites in neutral and alkaline media is

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^- \qquad (9)$$

Fe^{3+} ions produced at anodic areas and OH^- ions produced at cathodic area combine to form Fe $(OH)_3$. Apart from Fe $(OH)_3$, there is formation of other oxides and hydroxides like FeOOH, γ-Fe_2O_3, etc., on the metal surface before the formation of protective film.

When PS and Zn^{2+} ions are added to the aqueous solution, PS reacts with Zn^{2+} to form a [Zn(II)-PS] complex. This complex diffuses to the metal surface and reacts with Fe^{2+}/Fe^{3+} ions available at the anodic sites to form [Fe(II)/Fe(III)/Zn(II)-PS] complex which covers the anodic sites and controls the corresponding reaction at anodic sites.

$$[Zn(II)\text{ - }PS] + Fe^{2+}/Fe^{3+} \rightarrow [Fe(II)/\,Fe(III)/Zn(II)\text{ - }PS] \qquad (10)$$

Free Zn^{2+} ions which are available in the bulk of the solution diffuse to the metal surface and react with OH^- ions produced at the cathodic sites to form a precipitate of $Zn(OH)_2$. This precipitate gets deposited on the cathodic sites and controls the cathodic reaction.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \qquad (11)$$

Thus, PS and Zn^{2+} ions play a very important role in the synergistic effect in controlling corrosion through the formation of a protective film on the metal surface. Similar reports of complex formation have been observed in the literature.[4,11,14]

4. Conclusion

The present work shows an excellent synergistic inhibitive effect among PS and Zn^{2+} in corrosion control of carbon steel alloy. The binary system 75 ppm PS and 50 ppm Zn^{2+} is effective and has 98% IE. This inhibitor formulation is effective in the pH range 5.0–7.0 and also at pH 11.0. The inhibitor formulation acts as a mixed inhibitor predominantly cathodic in nature. In presence of the inhibitor, the charge transfer resistance is significantly increased. The double layer capacitance of surface film is markedly decreased. The protective film may consist of [Fe(II)/Fe(III)/Zn(II)-PS] complex, $Zn(OH)_2$, hydroxides, and oxides of iron. This formulation consisting of PS and Zn^{2+} can be used as a potential inhibitor to prevent the corrosion of carbon steel in near neutral aqueous media.

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