Inhibitive properties of a phosphonate-based formulation for corrosion control of carbon steel

M. Prabakaran · S. Ramesh · V. Periasamy

Received: 2 July 2012/Accepted: 5 October 2012 © Springer Science+Business Media Dordrecht 2012

Abstract The aim of the present work was to study the corrosion inhibition of carbon steel using a ternary formulation. This new ternary inhibitor formulation, viz., 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), with zinc ions and silicate ions was used to protect carbon steel from corrosion in a low-chloride environment. The gravimetric studies showed that 96 % inhibition efficiency was achieved with the ternary system consisting of 50 ppm PBTC, 50 ppm Zn²⁺ ions, and 10 ppm silicate ions. Out of 0.310 mmol of Zn²⁺ ions, 0.218 mmol was diffused from the bulk of the solution to the metal surface, as revealed from the studies of the solutions by atomic absorption spectroscopy (AAS). Electrochemical methods (potentiostatic polarization and electrochemical impedance spectroscopy) and surface characterization techniques [Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), and atomic force microscopy (AFM)] were used to ascertain the nature of the protective film and for explaining the mechanistic aspects of corrosion inhibition.

Keywords Corrosion inhibition · Carbon steel · PBTC · Zinc ions · Silicate

Introduction

Corrosion inhibitors are widely used as an economical method of corrosion control [1, 2]. Environmental restrictions imposed on heavy metal-based corrosion inhibitors oriented scientific researchers towards the study of non-toxic and environmentally friendly corrosion inhibitors [3]. Phosphonic acids have been extensively used as corrosion inhibitors due to their hydrolytic stability, ability to

Department of Chemistry, Gandhigram Rural Institute—Deemed University, Gandhigram 624302, Tamil Nadu, India e-mail: drsramesh_56@yahoo.com

Published online: 27 October 2012

M. Prabakaran · S. Ramesh (⊠) · V. Periasamy

form complexes with metal ions, and scale-inhibiting property [4-10]. Phosphonatebased formulations are well known as corrosion inhibitors for carbon steel in aqueous environments [11–19]. Against this background, a new ternary inhibitor formulation with relatively low concentrations of both phosphonate and Zn^{2+} in the presence of an inorganic salt has been proposed. The use of 2-phosphonobutane-1.2.4-tricarboxylic acid (PBTC) as a corrosion inhibitor has been reported in the literature [20–22]. For this purpose, an inorganic salt, namely, silicate in the form of sodium silicate, was chosen as the second synergist for the following reasons. Silicate is an environmentally friendly compound that has been historically used for water supplies as a corrosion inhibitor [23] and a good synergistic co-inhibitor with molybdate in cooling waters [24]. The compound is highly attractive in terms of non-toxicity, low cost, and availability [25, 26]. The inhibitive properties and synergistic effect of PBTC, Zn^{2+} , and silicate ions, a three-component inhibitor system in controlling the corrosion of carbon steel, was studied in an aqueous environment containing 60 ppm chloride using a gravimetric method and electrochemical methods. Surface analytical techniques were also used to investigate the nature of the surface film and a suitable mechanism of corrosion inhibition is proposed.

Experimental part

Material

The molecular structure of PBTC is shown in Fig. 1. The tested compound, namely, PBTC obtained from Dequest, USA, as 50 wt% in H_2O ($C_7H_{11}O_9$), was used without further purification.

Preparation of the specimens

Carbon steel specimens (0.026 % S; 0.035 % P; 0.548 % Mn; 0.104 % C; and the remainder iron) with dimensions of $1.5 \times 3.5 \times 0.2$ cm were polished to a mirror finish, degreased with acetone, and used for the gravimetric studies and surface examination studies.

Fig. 1 Structure of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)



2-Phosphono butane-1, 2, 4-tricarboxylic acid

Methods

Gravimetric studies

Carbon steel specimens in triplicate were immersed in 100 mL of the test solutions of 60 ppm chloride in aqueous environment medium containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} ions (as $ZnSO_4 \cdot 7H_2O$) for a period of 7 days. The weights of the specimens before and after immersion were determined using a Mettler Balance AE240 model. The inhibition efficiency (IE) was then calculated using the equation:

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

where W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor.

Atomic absorption spectroscopy (AAS)

The analysis of Zn^{2+} present in the aqueous solutions after immersion of the carbon steel in inhibitor containing PBTC, Zn^{2+} ions, and silicate ions for 7 days was carried out using a PerkinElmer Atomic Absorption Spectrophotometer, model AA100.

Electrochemical studies

Electrochemical impedance spectroscopic (EIS) studies and potentiostatic polarization studies were carried out using an electrochemical workstation CHI model 760D electrochemical analyzer and the experimental data were analyzed by using EC-Lab software. The measurements were conducted in a conventional threeelectrode cylindrical glass cell with a platinum electrode as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was carbon steel embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of 1 cm^2 was the only surface exposed to the electrolyte. The three-electrode setup was immersed in control solution of volume 100 mL both in the absence and in the presence of various inhibitor formulations and allowed to attain a stable open circuit potential (OCP). Polarization curves were recorded in the potential range of ± 200 mV from the OCP at a sweep rate of 1 mV/s. The ohmic drop compensation was taken into account during the studies. The corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) were obtained by the Tafel extrapolation method. The inhibition efficiencies (IE_p) were calculated from i_{corr} values using the equation:

$$\mathrm{IE}_{\mathrm{p}}(\%) = 100 \left[1 - \left(i_{\mathrm{corr}}' / i_{\mathrm{corr}} \right) \right] \tag{2}$$

where i_{corr} and i'_{corr} are the corrosion current densities in case of the control and inhibitor solutions, respectively.

Impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 0.01 to 10,000 Hz with 4–10 steps per decade. The charge transfer resistance (R_{ct}), constant phase element (CPE), and CPE exponent (n) were

obtained from Nyquist plots. The inhibition efficiencies (IE_i) were calculated using the equation:

$$IE_{i} (\%) = 100 \left[1 - \left(R_{ct} / R'_{ct} \right) \right]$$
(3)

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

Surface characterization studies

The nature of the film formed on the surface of the metal specimen was analyzed by various surface analytical techniques.

Fourier transform infrared (FT-IR) spectra

The carbon steel specimens were immersed in various test solutions for a period of 7 days. On completion of the 7th day, the specimens were taken out and dried. The protective film formed on the metal specimens was scratched and mixed with KBr and pellets were obtained and the FT-IR spectra were recorded using a Jasco 460 Plus Spectrophotometer over a range of 400–4,000 cm⁻¹, with a resolution of 4 cm⁻¹.

Scanning electron microscopy (SEM)

The polished carbon steel specimens were immersed in solutions containing 60 ppm chloride ions in the absence and in the presence of the inhibitors. After 7 days, the specimens were taken out, washed with distilled water, and dried. The SEM photographs of the surfaces of the specimens were obtained using a Hitachi S-3000H model scanning electron microscope with a resolution of 3.5 nm.

Atomic force microscopy (AFM)

The polished carbon steel specimens were immersed in solutions containing 60 ppm chloride ions in the absence and in the presence of the inhibitors. After 7 days, the specimens were taken out, washed with distilled water, and dried. The coated protective films were examined with a NanoSurf easyScan 2 atomic force microscope. The topography of all the samples for a scanned area of 5 μ m × 5 μ m (25 μ m²) is evaluated for a set point of 20 nN and a scan speed of 10 mm/s. The three-dimensional (3D) images of the topography in forward and reverse scanning gives information about the roughness of the metal surface (Rms) and the ΔZ value indicates the conducting nature of thin films on the metal surface.

Results and discussion

Gravimetric studies

The inhibition of corrosion of carbon steel by phosphonic acids can be explained in terms of adsorption on the metal surface [27–29]. Phosphonic acids can be adsorbed



Fig. 2 Inhibition efficiency as a function of the concentration of silicate ions

on the carbon steel surface by the interaction between lone pairs of electrons of nitrogen, oxygen, and phosphorus atoms of the inhibitor and the metal surface. This process is facilitated by the presence of vacant orbitals of low energy in iron atoms, as observed in the transition metals [30, 31].

Studies on the corrosion inhibition of carbon steel using Zn^{2+} ions, PBTC, and organic additives have been reported in the literature [20]. An attempt has been made to use an inorganic salt, viz., silicate, in combination with Zn^{2+} ions and PBTC for the synergistic effect and was evaluated by gravimetric studies. For this ternary system, it was decided to study both the Zn^{2+} ions and PBTC at 50 ppm and less at three different concentration levels (10, 25, and 50 ppm) in combination with silicate ions. The silicate ion concentration was kept at five times the proposed Zn^{2+} ions and PBTC concentration, i.e., up to 250 ppm at eight different concentration levels (10, 25, 50, 75, 100, 150, 200, and 250 ppm). Thus, all three components were studied at three concentration levels each, making possible 72 different inhibitor combinations for evaluation. In the present study, an environmentally friendly inorganic compound, viz., silicate, is introduced. The corrosion rate of carbon steel in a neutral aqueous environment containing 60 ppm chloride ions was studied in the absence and in the presence of the inhibitor formulations containing various amounts of PBTC, Zn^{2+} ions, and silicate ions, and the inhibition efficiency as a function of the concentration of silicate ions obtained from the gravimetric studies is shown in Fig. 2. The results of the gravimetric studies show that the ternary combinations afforded reasonable to excellent inhibition efficiency, except at the 100 ppm concentration of Zn²⁺ ions (maximum 83 % inhibition efficiency). It is evident that, for any protection to be established, a minimum concentration of each of the inhibitor constituents is necessary. Clearly, 10 ppm of Zn^{2+} ions is insufficient and a minimum concentration of 20 ppm or above of Zn^{2+} ions is required to achieve inhibition efficiency. Similarly, a PBTC concentration of 25 ppm or above is required in order to establish similar protection levels. The binary system containing 50 ppm Zn^{2+} ions and 10 ppm silicate afforded an inhibition efficiency of 11 %. On addition of just 50 ppm of PBTC to 50 ppm Zn^{2+} ions and 10 ppm silicate ions, the inhibition efficiency tremendously increased to 96 % (data not shown). The optimum concentration of each of the three components is essential to protecting the carbon steel by forming an insoluble film. At lower concentrations, PBTC and Zn^{2+} ions with varying silicate concentration did not afford good inhibition efficiency. Utilizing the combination consisting of 50 ppm PBTC, 50 ppm Zn^{2+} ions, and 10 ppm silicate ions, an inhibition efficiency of 96 % is obtained. The anodic reaction is controlled by the formation of Fe²⁺–PBTC complex and Fe²⁺–silicate complex on the sites of the metal surface. The cathodic reaction is controlled by the formation of Zn(OH)₂ on the cathodic sites of the metal surface.

Atomic absorption spectroscopy (AAS)

The solution containing 60 ppm chloride, 50 ppm PBTC, 50 ppm Zn^{2+} ions, and 10 ppm silicate ions in which carbon steel specimens were immersed for 7 days was analyzed for Zn^{2+} ions by AAS. The results reveal that 0.218 mmol of Zn^{2+} ions was diffused from the bulk of the solution to the metal surface (Table 1).

Electrochemical studies

Potentiostatic polarization studies

The potentiostatic polarization curves of carbon steel electrode in solution containing 60 ppm Cl⁻ at pH 7 in the absence and presence of various inhibitor combinations are shown in Fig. 3. The Tafel parameters derived from these curves and the inhibition efficiencies are listed in Table 2. For the control solution, the values for the corrosion potential and corrosion current of -487.62 mV versus SCE and 22.68 μ A/cm² are obtained. When PBTC alone was added to control, the current potential shifted to the negative side and its *i*_{corr} value was reduced to 12.70 μ A/cm². The anodic Tafel (β_a) slope for PBTC was shifted more anodically (89 mV/decade) than the cathodic Tafel (β_c) slope (9 mV/decade). Similar observations have been reported in the literature [32, 33]. In the case of the addition of Zn²⁺ ions to the control, there was no significant change in corrosion potential, but, however, there was change in the corrosion current density, which lead to an increase in the corrosion rate [34]. For a binary combination each of 50 ppm PBTC and Zn²⁺, the corrosion potential was shifted to -501.77 mV versus

Table 1	Analysis	of the	solution	for	zinc	ions
---------	----------	--------	----------	-----	------	------

[Zn ²⁺] present in solution (100 mL) before	[Zn ²⁺] present in solution (100 mL) after immersion
immersion of the metal specimen (mmol)	of the metal specimen for 7 days (mmol)
0.310	0.092



Fig. 3 Potentiostatic polarization curves of carbon steel immersed in various test solutions

Concentration (ppm)		Tafel parameters					
PBTC	Zn ²⁺	Silicate	$E_{\rm corr}$ (mV vs. SCE)	$I_{\rm corr}$ (μ A/cm ²)	β_a (mV/decade)	$\beta_{\rm c}$ (mV/decade)	IE _p (%)
0	0	0	-487.62	22.68	209	212	_
50	-	-	-633.83	12.70	298	221	44
-	50	-	-633.83	23.30	228	209	-
50	50	-	-501.77	4.23	273	202	81
50	-	10	-593.07	13.61	230	244	40
-	50	10	-634.38	11.48	222	288	49
50	50	10	-578.01	1.57	157	148	93

 Table 2
 Corrosion parameters of carbon steel immersed in the absence and in the presence of inhibitor obtained by potentiostatic polarization studies

SCE and its corrosion current density was also reduced to $4.23 \ \mu\text{A/cm}^2$ when compared to the control. The other two possible binary combinations, viz., 50 ppm PBTC with 10 ppm silicate and 50 ppm Zn²⁺ with 10 ppm silicate, also shifted the corrosion potential to more the cathodic side and decreased the corrosion current densities, and corresponding inhibition efficiencies of 40 and 49 % were obtained. It is interesting to note that an addition of 10 ppm silicate to each of 50 ppm PBTC and Zn²⁺ afforded the maximum inhibition efficiency of 93 %, which corroborates with the results obtained in the gravimetric studies. The corrosion potential of the ternary combination is shifted to an extent of 91 mV versus SCE in the cathodic direction and its corresponding *i*_{corr} value is also largely reduced to 1.57 μ A/cm². Moreover, in the ternary combination, the cathodic Tafel slope shifted more



Fig. 4 Nyquist plots of carbon steel immersed in various test solutions

(64 mV/decade) when compared to the anodic Tafel slope (52 mV/decade). Since both cathodic and anodic Tafel slopes were shifted, it can be interpreted that this ternary combination acts as a mixed inhibitor that is predominantly cathodic in nature. Similar phosphonate-based formulations have been reported as mixed inhibitors in the literature [32, 35, 36].

Electrochemical impedance studies

Nyquist plots for carbon steel immersed in control solution at pH 7 in the absence and presence of various formulations are shown in Fig. 4. In case of the control as well as in the presence of inhibitor formulations, the Nyquist plots are found to be depressed semicircles instead of ideal semicircles. Li et al. [37] observed this type of dispersed semicircles and reported that this kind of phenomenon is called the dispersing effect. All the Nyquist plots obtained in the present study are characterized by a single time constant. The experimental data obtained from these plots are fitted by the equivalent electrical circuit shown in Fig. 5. Such an equivalent circuit has also been discussed by several researchers [38-40], who obtained similar depressed semicircles with a single time constant. 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 3. Charge transfer resistance (R_{ct}) and the nonideal capacitance (CPE) are the two important parameters related to corrosion processes at the metal-solution interface. The former is directly related to the rate of corrosion reaction at the interface, while the latter is related to the structure of the electrical double layer at the interface. During corrosion inhibition by the adsorption of inhibitor molecules, the high R_{ct} values can be obtained due to the slower corroding





 Table 3
 AC impedance parameters of carbon steel immersed in the presence and absence of inhibitor obtained by AC impedance spectra

Concentration (ppm)		Charge transfer	Constant phase	Constant	IE (%)	
PBTC	Zn^{2+}	Silicate	resistance, $R_{\rm ct}$ (Ω)	element, CPE (µF/cm ²)	exponent, n	
0	0	0	129	55.1	0.91	_
50	0	0	232	44.4	0.92	44
0	50	0	118	58.7	0.94	_
50	50	0	1,472	22.4	0.97	91
50	0	10	258	41.1	0.93	50
0	50	10	233	49.4	0.94	45
50	50	10	2,102	30.7	0.98	94

system [41, 42]. Consequently, the decrease in CPE can result from the decrease of the local dielectric constant and/or from the increase of the thickness of the electrical double layer, which suggests an adsorption of the inhibitor molecules on the metal surface [43]. Hence, for an effective inhibition process, there will be an increase in R_{ct} and a decrease in CPE. However, there are inhibition processes that are associated with increases in capacitance values. This can be interpreted as being due to the replacement of water molecules in the interface by ionic inhibitor species and/or due to oxides/hydroxides of metal formed due to initial corrosion. Bonnel et al. [44] studied the corrosion of carbon steel in a neutral chloride solution by the impedance technique. They obtained high capacitance values in their studies and ascribed them to the existence of a layer of inner corrosion products.

In the present study, for the control alone, a small semicircle with an $R_{\rm ct}$ value of 129 Ω is observed. A similar semicircle is also obtained when 50 ppm of Zn²⁺ was added to the control. Due to Zn²⁺ ions, $R_{\rm ct}$ decreased and the CPE value increased with a slight increase in the value of *n*. These changes are due to the replacement of water molecules in the interface by zinc ions, which resulted in the increased rate of corrosion. By the addition of 50 ppm of PBTC to the control, a single and slightly depressed semicircle with high $R_{\rm ct}$ value is obtained. The capacitance value decreased and the *n* value increased. These observations can be attributed to the presence of organic inhibitor molecules in the double layer and the control of 50 ppm of Zn²⁺ is considered in the presence of the control, a large depressed semicircle is observed from high-frequency to low-frequency regions in the Nyquist plot, indicating that the charge transfer resistance becomes dominant in the corrosion processes due to the presence of a protective film on the metal surface.

This result is supported by the significant decrease in CPE and an increase in *n* value. The semicircle obtained in the presence of PBTC/Zn²⁺ represents an R_{ct} value of 1,472 Ω , which is greater than that observed in the case of the control. The CPE value at the metal-solution interface is found to decrease to 22.4 μ F cm⁻² in the case of the control from 55.1 μ F cm⁻² in the case of the binary inhibitor formulation. In the case of the other two binary inhibitor formulations, PBTC $(50 \text{ ppm}) + \text{silicate} (10 \text{ ppm}) \text{ and } Zn^{2+} (50 \text{ ppm}) + \text{silicate} (10 \text{ ppm}), \text{ the } R_{\text{ct}}$ value increased and the CPE value decreased. The value of R_{ct} in case of the ternary formulation is manifold increased to 2,102 Ω when compared to the other binary formulations. The CPE value is found to decrease from 55.1 μ F cm⁻² for the control to 30.7 μ F cm⁻² in case of the ternary inhibitor formulations. This is because of the replacement of water molecules in the electrical double layer by the organic molecules having low dielectric constants [45]. The value of n is considerably increased to 0.98 in the presence of the ternary inhibitor system, suggesting a decrease of the inhomogeneity of the interface during inhibition. These results indicate that there is formation of a non-porous and protective film in the presence of the ternary inhibitor formulation. The inhibition efficiency obtained from impedance studies is found to be 93.86 %. Several authors who have studied the inhibitory effects of phosphonate-based corrosion inhibitors have also reported that there is the formation of a thick and less permeable protective film on the metal surface [32, 35, 46]. They also concluded that the protective film consists of phosphonate-metal complexes. The results also imply the synergistic action operating between PBTC, Zn^{2+} , and silicate. This is in agreement with the inferences drawn from gravimetric studies and potentiostatic polarization studies.

Fourier transform infrared (FT-IR) spectra

The FT-IR spectrum of pure PBTC is given in Fig. 6a. The stretching frequency mode of the P=O bond gave rise to a strong band in the region $1,380-1,140 \text{ cm}^{-1}$ and another band in the region $970-1,188 \text{ cm}^{-1}$. The peak that appeared at $1,200 \text{ cm}^{-1}$ is assigned to the P=O group and the other peak at 926.3 cm^{-1} is assigned to the P=OH group [47, 48].

The FT-IR spectrum of pure silicate is given in Fig. 6b. The FT-IR spectrum of the surface film of the carbon steel specimen when immersed in the environment containing 60 ppm Cl⁻ ions, 50 ppm PBTC, 50 ppm Zn²⁺ ions, and 10 ppm silicate ions is shown in Fig. 6c. The P=O stretching frequency of PBTC was shifted from 1,200 to 1,076 cm⁻¹. The carbonyl group in PBTC was also shifted from 1,716 cm⁻¹ (in pure PBTC) to 1,570 cm⁻¹. These shifts suggest the involvement of the P=O group and the carbonyl group of PBTC in complex formation between the metal and PBTC [49, 50]. The P–OH stretch of 926.3 cm⁻¹ disappeared. This can be interpreted in terms of an interaction of P⁺–O⁻ with the metal ions to form P–O–M bonds. The peak at 1,076 cm⁻¹ corresponds to the P=O group and it indicates the participation of the P=O group in [Fe(II)–PBTC–silicate] complex formation. The peak at 1,312 cm⁻¹ is due to Zn(OH)₂ [10, 11, 52]. The broad band of the OH stretching and bending modes of water or hydroxides within the protective film



Fig. 6 Fourier transform infrared (FT-IR) spectra of: \mathbf{a} pure PBTC, \mathbf{b} pure silicate, \mathbf{c} surface film in the presence of inhibitor

appeared at 3,407 cm⁻¹. There are many weak bands in the region between 1,200 and 400 cm⁻¹. The peak at 465 cm⁻¹ implies the presence of ferric and ferrous oxide and hydroxide in the protective film [14, 53]. The Si–O stretching vibrations appeared at 992 cm⁻¹ (pure silicate). The Si–O stretching frequency shifted from 992 to 1,076 cm⁻¹. This shift in the stretching frequency of silicate is due to the involvement of complex formation with phosphonate and zinc ions, and also with Fe²⁺/Fe³⁺ ions. So, the FT-IR spectra suggest that the protective film may consist of [Fe(II)/Fe(III)–PBTC–silicate] complex, [Zn(II)–PBTC–silicate] complex, Zn(OH)₂, and small amounts of oxides and hydroxides of iron.

Scanning electron microscopy (SEM)

SEM analysis was carried out for characterizing the inhibitive film formed on the carbon steel surface. SEM images of carbon steel surfaces that had been exposed to an environment containing 60 ppm Cl^- ions (i.e., control solution) and in the presence of the inhibitor, 50 ppm PBTC, 50 ppm Zn^{2+} ions, and 10 ppm silicate ions for 7 days are shown in Fig. 7. The SEM pattern of the specimen immersed in the absence of the inhibitor exhibits corrosion and also the presence of different forms of iron oxides. It can be seen that the surface of the carbon steel immersed in the inhibitors showed a smooth surface and there are no observations of pits and cracks, indicating that the aggressive Cl^- ions have not penetrated because of the good surface coverage by the



Fig. 7 Scanning electron microscopy (SEM) images of: a 60 ppm Cl⁻, b 60 ppm Cl⁻ + 50 ppm PBTC + 50 ppm Zn²⁺ + 10 ppm silicate

inhibitive film. This protective film formed on the substrate also corroborates the high inhibition efficiency values obtained with gravimetric studies. So, SEM analysis shows the protective nature of the surface film.

Atomic force microscopy (AFMs)

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



Fig. 8 Atomic force microscopy (AFM) images of the polished metal surface: \mathbf{a} normal image, \mathbf{b} 3D image, \mathbf{c} cross section analysis

surface morphology. This technique has been used to investigate the influence of the inhibitor in the corrosion inhibition process at the metal–solution interface and is used to study the surface morphology both qualitatively and quantitatively. AFM is used mainly for measuring three-dimensional topography. The images of AFM are shown in Figs. 8, 9, and 10. The parameters obtained from the AFM for the carbon steel immersed in different environments is shown in Table 4. Figure 8 shows the AFM images and cross section analysis of the polished metal surface, with an Rms value 12 nm and ΔZ value of 7.15 nm, and Fig. 9 shows the AFM images and cross section analysis of the polished surface in 60 ppm Cl⁻ ions, with an increased Rms value of 95 nm and ΔZ value of 579.2 nm, indicating the formation of iron oxides. However, Fig. 10 shows that the carbon steel immersed in inhibitor, 50 ppm PBTC, 50 ppm Zn²⁺, and 10 ppm silicate, showed an increased Rms value of 152.5 nm, which indicates the formation of a protective film on the metal surface, most probably made of inhibitor molecules [54] when compared to



Fig. 9 AFM images of the polished metal surface immersed in 60 ppm Cl^- ions: **a** normal image, **b** 3D image, **c** cross section analysis

the polished metal surface. These increased values strongly imply the formation of an inhibitive film by the addition of Zn^{2+} ions along with the phosphonic acid inhibitor system on the metal surface. Further, these results are confirmed by the clearly visible differences among the optical cross section analysis. The metal surface was covered with a protective layer, thereby, forming a barrier against attack by aggressive ions from the corrosive environment. Similar observations have been reported in the literature [35, 55].

Mechanism of protection

In order to explain all the experimental results, a plausible mechanism of corrosion inhibition is proposed as follows:

1. The mechanism of corrosion of carbon steel in neutral aqueous media is well established. The well-known reaction is shown below:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$



Fig. 10 AFM images of the polished metal surface immersed in 60 ppm $Cl^- + 50$ ppm PBTC + 50 ppm $Zn^{2+} + 10$ ppm silicate: **a** normal image, **b** 3D image, **c** cross section analysis

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

$$\mathrm{Fe}^{2+} \xrightarrow{\mathrm{[O_2]}} \mathrm{Fe}^{3+} + \mathrm{e}^{-}$$

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

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

 Fe^{3+} ions produced at anodic areas and OH^- ions produced at cathodic areas combine to form $Fe(OH)_3$, $(Fe_2O_3 \cdot H_2O)$, which gets precipitated on the surface of the metal due to its very low solubility product.

2. When PBTC, Zn²⁺, and silicate ions are added to the aqueous solution, both PBTC and silicate ions react with Zn²⁺ to form a multiligand complex [Zn(II)– PBTC–silicate]. This complex diffuses to the metal surface and reacts with Fe²⁺/Fe³⁺ ions available at the anodic sites to form a [Fe(II)/Fe(III)/Zn(II)–

Environment	Period of immersion	AFM parameters		
		Rms value (nm)	ΔZ value (nm)	
Polished metal	_	12	7.15	
Polished metal $+$ 60 ppm Cl ⁻	7 days	95	579.2	
Polished metal + 60 ppm Cl^- + 50 ppm PBTC + 50 ppm Zn^{2+} + 10 ppm silicate	7 days	52	152.5	

Table 4 Atomic force microscopy (AFM) parameters in different environments

PBTC-silicate] polynuclear multiligand complex, which covers the anodic sites and controls the corresponding reaction at anodic sites:

$$\begin{split} & [Zn(II)-PBTC-silicate] + Fe^{2+}/Fe^{3+} \\ & \rightarrow [Fe(II)/Fe(III)/Zn(II)-PBTC-silicate] \end{split}$$

3. Free Zn²⁺ ions 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:

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

The precipitate of $Zn(OH)_2$ gets deposited on the cathodic sites and controls the cathodic partial reaction of the corrosion process.

4. Thus, PBTC, Zn²⁺, and silicate play a very important role in the synergistic effect in controlling corrosion through the formation of a protective film on the metal surface. It is inferred that the film may consist of various oxides/ hydroxides, such as Fe₂O₃, Fe₃O₄·H₂O, FeOOH, Zn(OH)₂, and a polynuclear complex [Fe(II)/Fe(III)/Zn(II)–PBTC–silicate]. Each of these constituents itself makes the film highly protective. Similar reports of complex formation have been observed in the literature [5, 16, 20, 52].

Conclusions

The corrosion rates of carbon steel immersed in a Cl^- ion environment in the absence and presence of PBTC, Zn^{2+} , and silicate ions have been evaluated. The inhibitive properties and also the synergistic effect of phosphonate-based formulations are studied. The present study leads to the following conclusions:

- The results of the gravimetric studies results indicate that the formulation consisting of 50 ppm of PBTC, 50 ppm of Zn²⁺, and 10 ppm of silicate afforded 96 % inhibition efficiency.
- Analysis of the solution for Zn^{2+} by atomic absorption spectroscopy (AAS) indicates that an amount of Zn^{2+} ions was diffused from the bulk of the solution to the metal surface.
- Polarization studies reveal that this formulation functions as a mixed inhibitor predominantly cathodic in nature.

- AC impedance spectra reveal the presence of a protective film on the metal surface.
- Fourier transform infrared (FT-IR) spectral data appear to indicate that the protective film may consist of [Fe²⁺/Fe³⁺–PBTC–silicate], [Zn²⁺–PBTC–silicate] complex, and Zn(OH)₂.
- The protective film formation is also confirmed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies.

Acknowledgments M. Prabakaran is grateful to the University Grants Commission (UGC) for the fellowship under Research Fellowship in Science for Meritorious Students. The authors thank the Coordinator, UGC Special Assistance Programme (UGC-SAP), Gandhigram Rural Institute, for his help and also thank the authorities of Gandhigram Rural Institute for the encouragement.

References

- 1. Q.-J. Xu, Z. Lu, G.D. Zhou, J. East China Univ. Sci. Technol. 29, 493 (2003)
- 2. Q.-J. Xu, Z. Lu, G.D. Zhou, Acta Chim. Sinica 59, 950 (2001)
- 3. D. Choi, S. You, J. Kim, Mater. Sci. Eng. A 335, 228 (2002)
- H. Amar, J. Benzakour, A. Derja, D. Villemin, B. Moreau, T. Braisaz, Appl. Surf. Sci. 252, 6162 (2006)
- 5. G. Gunasekaran, R. Natarajan, N. Palaniswamy, Corros. Sci. 43, 1615 (2001)
- S. Rajendran, B.V. Appa Rao, N. Palaniswamy, V. Periasamy, G. Karthikeyan, Corros. Sci. 43, 1345 (2001)
- N. Labjara, M. Lebrini, F. Bentiss, N.-E. Chihib, S. El Hajjaji, C. Jamab, Mater. Chem. Phys. 119, 330 (2010)
- 8. N. Nakayama, Corros. Sci. 42, 1897 (2000)
- 9. J. Telegdi, M.M. Shaglouf, A. Shaban, F.H. Karman, I. Betroti, M. Mohai, E. Kalman, Electrochim. Acta 46, 3791 (2001)
- G. Gunasekaran, N. Palaniswamy, B.V. Appa Rao, V.S. Muralidharan, Electrochim. Acta 42, 1427 (1997)
- 11. H. Amar, T. Braisaz, D. Villemin, B. Moreau, Mater. Chem. Phys. 110, 1 (2008)
- 12. H. Amar, T. Braisaz, D. Villemin, B. Moreau, J. Electroanal. Chem. 558, 131 (2003)
- S. Rajendran, B.V. Appa Rao, V. Periasamy, G. Karthikeyan, N. Palaniswamy, Anti-Corros. Methods Mater. 45, 109 (1998)
- 14. K. Aramaki, T. Shimura, Corros. Sci. 45, 2639 (2003)
- 15. B.V. Appa Rao, S. Srinivasa Rao, M. Venkateswara Rao, Corros. Eng. Sci. Technol. 43, 46 (2008)
- 16. B.V. Appa Rao, K. Christina, Indian J. Chem. Technol. 13, 275 (2006)
- G. Gunasekaran, R. Natarajan, B.V. Appa Rao, N. Palaniswamy, V.S. Muralidharan, Indian J. Chem. Technol. 5, 91 (1998)
- 18. I. Felhosi, E. Kalman, Corros. Sci. 47, 695 (2005)
- 19. G. Gunasekaran, B.I. Dubey, J. Rangarajan, Def. Sci. J. 55, 51 (2005)
- 20. B.V. Appa Rao, S. Srinivasa Rao, Mater. Corros. 60, 1 (2009)
- 21. R. Ashcraft, G. Bohnsack, R. Holm, R. Kleinstueck, S. Storp, Mater. Perform. 27, 332 (1988)
- 22. G. Bohnsack, K.H. Lee, D.A. Johnsona, E. Buss, Mater. Perform. 25, 32 (1986)
- 23. E.P. Katsanis, W.B. Esmonde, R.W. Spencer, Mater. Perform. 25, 19 (1986)
- 24. J.R. Chen, H.Y. Chao, I.J. Yang, J.C. Oung, F.M. Pen, Surf. Sci. 247, 352 (1991)
- 25. S.T. Amaral, I.L. Muller, Corrosion 55, 17 (1999)
- 26. V.S. Saji, S.M.A. Shibili, Anti-Corros. Methods Mater. 49, 433 (2002)
- 27. I. Ahamad, M.A. Quraishi, Corros. Sci. 52, 651 (2010)
- 28. P. Lowmunkhong, D. Ungthararak, P. Sutthivaiyakit, Corros. Sci. 52, 30 (2010)
- 29. A.K. Singh, M.A. Quraishi, Corros. Sci. 52, 152 (2010)
- 30. G.E. Badr, Corros. Sci. 51, 2529 (2009)
- 31. V.S. Sastri, Corrosion Inhibitors: Principles and Applications (Wiley, New York, 1998)
- 32. Y. Gonzalez, M.C. Lafont, N. Pebere, J. Appl. Electrochem. 26, 1259 (1996)

- 33. X.H. To, N. Pebere, N. Pelaprat, B. Boutevin, Y. Hervaud, Corros. Sci. 39, 1925 (1997)
- 34. S. Rajendran, B.V. Appa Rao, N. Palaniswamy, Bull. Electrochem. 17, 171 (2001)
- 35. M.A. Pech-Canul, P. Bartolo-Perez, Surf. Coat. Technol. 184, 133 (2004)
- 36. S. Rajendran, B.V. Appa Rao, N. Palaniswamy, Anti-Corros. Methods Mater. 46, 23 (1999)
- 37. S.L. Li, H.Y. Ma, S.B. Lei, R. Yu, S.H. Chen, D.X. Liu, Corrosion 54, 947 (1998)
- 38. G. Gunasekaran, L.R. Chauhan, Electrochim. Acta 49, 4387 (2004)
- 39. M.S. Morad, Corros. Sci. 42, 1307 (2000)
- 40. A. Alagta, I. Felhosi, J. Telegdi, I. Bertoti, E. Kalman, Corros. Sci. 49, 2754 (2007)
- 41. K. Babic-Samardzija, C. Lupu, N. Hackerman, A.R. Barron, A. Luttge, Langmuir 21, 12187 (2005)
- 42. K.F. Khaled, Electrochim. Acta 48, 2493 (2003)
- 43. E. Machnikova, K.H. Whitmire, N. Hackerman, Electrochim. Acta 53, 6024 (2008)
- 44. A. Bonnel, F. Dabosi, C. Deslovies, M. Duprat, M. Keddam, B. Tribollet, J. Electrochem. Soc. 130, 753 (1983)
- 45. C.T. Wang, S.H. Chen, H.Y. Ma, N.X. Wang, J. Serb. Chem. Soc. 67, 685 (2002)
- I. Felhosi, Zs. Keresztes, F.H. Karman, M. Mohai, I. Bertoti, E. Kalman, J. Electrochem. Soc. 146, 96 (1999)
- N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd edn. (Academic Press, New York, 1993)
- 48. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn. (Wiley, New York, 1986)
- 49. G. Gunasekaran, N. Palaniswamy, B.V. Apparao, Bull. Electrochem. 12, 59 (1996)
- 50. S. Rajendran, B.V. Apparao, N. Palaniswamy, Anti-Corros. Methods Mater. 47, 294 (2000)
- 51. R.O. Carter III, C.A. Gierogak, R.A. Dickie, Appl. Spectrosc. 40, 649 (1986)
- 52. I. Sekine, Y. Hirakawa, Corrosion 42, 272 (1986)
- 53. A. Raman, B. Kuban, A. Razvan, Corros. Sci. 32, 1295 (1991)
- 54. P. Manjula, E.-J. Chem. 6(3), 887 (2009)
- 55. J. Li, D.J. Meier, J. Electroanal. Chem. 454, 53 (1998)