

# “N,N-Bis(phosphonomethyl) Glycine, Zn<sup>2+</sup> and Tartrate” – A New Ternary Inhibitor Formulation for Corrosion Control of Carbon Steel

B. V. Appa Rao<sup>1</sup>, M. Venkateswara Rao<sup>2</sup>, S. Srinivasa Rao<sup>3,\*</sup>, B. Sreedhar<sup>4</sup>

<sup>1</sup>Department of Chemistry, National Institute of Technology, Warangal, 506004, India

<sup>2</sup>Department of Chemistry, Andhra Loyola College, Vijayawada, 520008, India

<sup>3</sup>Department of Chemistry, V. R. Siddhartha Engineering College, Vijayawada, 520007, India

<sup>3</sup>Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, 500007, India

**Abstract** Studies on inhibition of corrosion of carbon steel in aqueous environment using N,N-Bis(phosphonomethyl) glycine (BPMG), zinc ions and tartrate are presented. The investigations revealed that tartrate acts as an excellent synergist in corrosion inhibition. Optimum concentrations of all the three components of the ternary formulation are established by gravimetric studies. Potentiodynamic polarization studies indicate that the new ternary system is a mixed inhibitor. Results of the impedance studies show that a protective film is formed on the metal surface in presence of the inhibitor formulation. Analysis of the protective film using X-ray photoelectron spectroscopy (XPS) and reflection absorption Fourier transform infrared (FTIR) spectroscopy infer the presence of Zn(OH)<sub>2</sub>, oxides and hydroxides of iron and the inhibitor molecules in the surface film probably in the form of a complex, [Zn(II)-BPMG-tartrate]. A plausible mechanism of corrosion inhibition is proposed.

**Keywords** Corrosion Inhibitor, Carbon Steel, Phosphonated Glycine, Tartaric Acid, Synergism

## 1. Introduction

Carbon steel is an important material of construction for cooling water systems and heat exchangers in industries. In order to control corrosion of carbon steel in such systems, application of corrosion inhibitors is an effective practice. After the exit of formulations based on chromates, phosphates, etc., phosphonate based formulations are introduced and they have been in use as corrosion inhibitors since the past three decades [1-8]. Phosphonates in combination with zinc ions proved to be effective corrosion inhibitors for carbon steel [1-8]. However, they require higher concentrations of both phosphonate and zinc ions for an effective inhibition. An efficient technique to reduce the concentrations of both phosphonate and toxic zinc ions in the inhibitor formulations is to add a non-toxic organic/inorganic compound as a synergist. A few of such ternary inhibitor formulations containing phosphonate, zinc ions and organic/inorganic additive were reported in literature [9-13]. These reports suggest that the high inhibition efficiency exhibited by the ternary formulations

is due to synergism existing among the inhibitor components of the formulations.

In this background, the present study was carried out using an environmentally friendly organic compound namely tartaric acid as a synergist to the binary formulation containing N,N-Bis(phosphonomethyl) glycine (BPMG) and zinc ions for corrosion control of carbon steel. It was reported in a previous study that BPMG-Zn<sup>2+</sup> binary formulation acts as an effective corrosion inhibitor for carbon steel [8]. Tartaric acid is chosen as the synergist for the present study due to presence of two carboxyl groups and two hydroxyl groups in its structure, which provide complexing ability with metal ions. The main objective of the present study is to investigate the inhibitory effects of the new ternary inhibitor formulation containing BPMG, Zn<sup>2+</sup> and tartrate in corrosion inhibition of carbon steel in low chloride aqueous environment. Also, it is of interest to study the synergistic effect of tartrate in combination with BPMG and Zn<sup>2+</sup> on corrosion inhibition. For the present study, 200 ppm of NaCl solution has been chosen as control because of the following reason. 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 200 ppm of NaCl.

\* Corresponding author:

chemysri@yahoo.com (S. Srinivasa Rao)

Published online at <http://journal.sapub.org/ijmc>

Copyright © 2013 Scientific & Academic Publishing. All Rights Reserved

## 2. Experimental Section

## 2.1. Solutions and Specimens

For all the studies, the specimens taken from a single sheet of carbon steel of the following composition were chosen. C – 0.1 to 0.2 %, P – 0.03 to 0.08 %, S – 0.02 to 0.03%, Mn – 0.4 to 0.5 % and the rest iron. Prior to the tests, the specimens were polished to mirror finish with 1/0, 2/0, 3/0 and 4/0 emery polishing papers respectively, washed with distilled water, degreased with acetone and dried. For gravimetric measurements, the polished specimens of the dimensions, 3.5 cm x 1.5 cm x 0.2 cm, were used while for other studies, the dimensions of the specimens are 1.0 cm x 1.0 cm x 0.1 cm. BPMG (C<sub>4</sub>H<sub>11</sub>P<sub>2</sub>O<sub>8</sub>N) obtained from Aldrich Chemical Company Inc., USA was used in the present study. Zinc sulphate (ZnSO<sub>4</sub>.7H<sub>2</sub>O), potassium sodium tartrate tetrahydrate (C<sub>4</sub>H<sub>4</sub>NaK<sub>2</sub>O<sub>6</sub>.4H<sub>2</sub>O) and other reagents were analytical grade chemicals. All the solutions were prepared by using triple distilled water. The pH values of the solutions were adjusted by using 0.01 N NaOH and 0.01 N H<sub>2</sub>SO<sub>4</sub> solutions. An aqueous solution consisting of 200 ppm of NaCl has been used as the control throughout the study.

## 2.2. Gravimetric Measurements

In all the gravimetric experiments, the polished specimens were weighed and immersed in duplicate, in 100 mL control solution in the absence and presence of inhibitor formulations of different concentrations, for a period of seven days. Then the specimens were reweighed after washing, degreasing and drying. During the studies, only those results were taken into consideration, in which the difference in the weight-loss of the two specimens immersed in the same solution did not exceed 0.1 mg. Accuracy in weighing upto 0.01 mg and in surface area measured upto 0.1 cm<sup>2</sup>, as recommended by ASTM G31, was followed[14]. The immersion period of seven days was fixed in view of the considerable magnitude of the corrosion rate obtained in the absence of any inhibitor after this immersion period. The immersion period was maintained accurately upto 0.1 h in view of the lengthy immersion time of 168 h. Under these conditions of accuracy, the relative standard error in corrosion rate determinations is of the order of 2 % or less for an immersion time of 168 h[15].

Corrosion rates (CR) of carbon steel in the absence and presence of various inhibitor formulations are expressed in mmpy. Inhibition efficiencies (IE<sub>g</sub>) of the inhibitor formulations were calculated by using the formula,

$$IE_g (\%) = 100 [(CR)_o - (CR)_I] / (CR)_o \quad (1)$$

where (CR)<sub>o</sub> and (CR)<sub>I</sub> are the corrosion rates in the absence and presence of inhibitor respectively.

Gravimetric studies of the ternary formulations containing BPMG (20-30 ppm), Zn<sup>2+</sup> (20-30 ppm) and tartrate (0-150 ppm) were carried out at pH 7. The selected concentration ranges of both BPMG and Zn<sup>2+</sup> in these studies are based on the results of gravimetric studies of the binary inhibitor system, BPMG-Zn<sup>2+</sup>[8]. The influence of pH on inhibition efficiency of the ternary inhibitor formulation was also studied in the pH range, 5-9. Gravimetric experiments were

also conducted using the specimens covered by the protective film in the ternary inhibitor formulation, in order to decide the required minimum dosage of each of the components for maintenance of the protective film in the chosen corrosive environment.

## 2.3. Electrochemical Studies

Both the potentiodynamic polarization studies and electrochemical impedance spectroscopic (EIS) studies were carried out using the Electrochemical Workstation Model IM6e, Zahner-elektrik, GmbH, Germany and the experimental data were analyzed by using the Thales software. The measurements were conducted in a conventional three electrode cylindrical glass cell with platinum electrode as auxiliary electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode was carbon steel embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of 1 cm<sup>2</sup> was the only surface exposed to the electrolyte. The three-electrode set up was immersed in control solution of volume 500 mL both in the absence and presence of various inhibitor formulations and allowed to attain a stable open circuit potential (OCP). The pH values of the solutions were adjusted to 7.0 and the solutions were unstirred during the experiments.

Polarization curves were recorded in the potential range of –750 to –150 mV with a resolution of 2 mV. The curves were recorded in the dynamic scan mode with a scan rate of 2 mV s<sup>-1</sup> in the current range of –20 mA to +20 mA. The ohmic drop compensation has been made during the studies. The corrosion potential (E<sub>corr</sub>), corrosion current (I<sub>corr</sub>), anodic Tafel slope (β<sub>a</sub>) and cathodic Tafel slope (β<sub>c</sub>) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots. The inhibition efficiency (IE<sub>p</sub>) values were calculated from I<sub>corr</sub> values using the equation[16],

$$IE_p (\%) = [1 - (I'_{corr} / I_{corr})] \times 100 \quad (2)$$

where I<sub>corr</sub> and I'\_{corr} are the corrosion current densities in case of control and inhibited solutions respectively.

Electrochemical impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60 kHz to 10 mHz with 4 to 10 steps per decade. A sine wave, with 10 mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance (R<sub>ct</sub>), constant phase element (CPE) and CPE exponent (n) were obtained from the Nyquist plots. The inhibition efficiencies (IE<sub>i</sub>) were calculated using the equation,

$$IE_i (\%) = 100 [1 - (R_{ct} / R'_{ct})] \quad (3)$$

where R<sub>ct</sub> and R'\_{ct} are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

## 2.4. Surface Analysis By X-Ray Photoelectron Spectroscopy (XPS)

XPS measurements of the surface film was carried out with Kratos analytical photoelectron spectrometer (AXIS 165) with monochromated Al K<sub>α</sub> X-ray source (1486.6 eV) operated at 100 W. The spectra were collected at an electron

take-off angle of  $90^\circ$ . Analyser pass energy was 80 eV, with a step of 1 eV. Deconvolution spectra were recorded with analyser pass energy of 80 eV, with a step of 0.1 eV for the elements of interest namely Fe 2p, O 1s, P 2p, C 1s, N 1s and Zn 2p. Binding energies for 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.

### 2.5. Fourier Transform Infrared (FTIR) Spectroscopic Studies

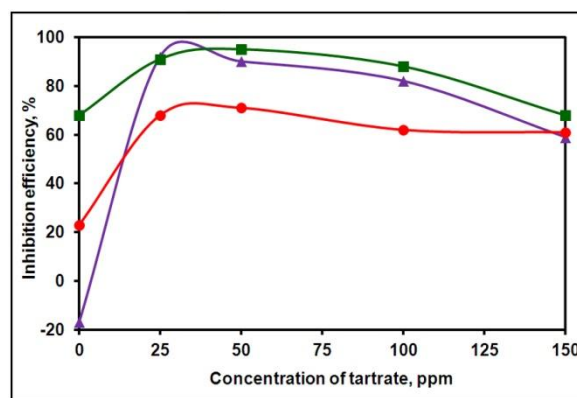
FTIR spectra were recorded using FTIR spectrophotometer from Thermo Electron Corporation, USA, model Nexus 670 with a resolving power of  $0.125\text{ cm}^{-1}$ . The detector is temperature stabilised DTGS (KBr window) and liquid nitrogen cooled MCT-A and the beam splitter is XT-KBr. FTIR spectra of pure BPMG and pure potassium sodium tartrate were recorded using the KBr pellet method. The reflection absorption FTIR spectra of the surface films were recorded in the wave number range of  $4000\text{--}400\text{ cm}^{-1}$ . The measurements were made at a grazing angle of  $85^\circ$ .

## 3. Results and Discussion

### 3.1. Gravimetric Measurements

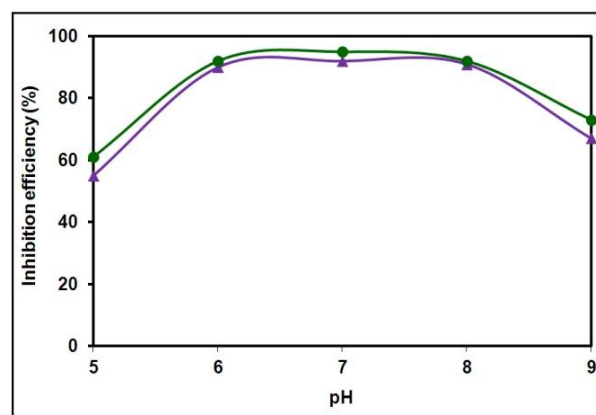
Figure 1 shows the inhibition efficiency of the ternary system, BPMG- $\text{Zn}^{2+}$ -tartrate, as a function of concentration of tartrate at different concentrations of BPMG and  $\text{Zn}^{2+}$ . From the figure, it can be observed that in case of all these ternary formulations at pH 7, as the concentration of tartrate is increased, the inhibition efficiency increases, reaches a maximum at an optimum concentration of tartrate and then decreases. In order to achieve an inhibition efficiency  $> 90\%$ , the required minimum concentrations of BPMG and  $\text{Zn}^{2+}$  are 20 ppm and 30 ppm respectively in presence of tartrate. While the binary system consisting of 20 ppm BPMG and 30 ppm  $\text{Zn}^{2+}$  accelerates corrosion, with the addition of just 25 ppm of tartrate, the inhibition efficiency of the ternary formulation is 92%. Further increase in the concentration of tartrate ions reduced the inhibition efficiency reaching 59% at 150 ppm of tartrate. In case of the binary system containing 30 ppm each of BPMG and  $\text{Zn}^{2+}$ , the inhibition efficiency is 68%, which is increased to 95% by the addition of 50 ppm of tartrate. On further increase in the concentration of tartrate, say to 100 ppm and 150 ppm, the inhibition efficiency is reduced to 88% and 68% respectively. From these results, it can be inferred that in case of the ternary system consisting of BPMG,  $\text{Zn}^{2+}$  and tartrate, the formulation containing optimum concentration of each of the components gives the highest inhibition efficiency. In other words, optimum amounts of each of the three components must be adsorbed on the surface of the metal, so that each one of them plays its own role in the formation of protective film either through complex formation or through formation of  $\text{Zn}(\text{OH})_2$  on cathodic sites, covering the entire metal surface. At higher concentrations

of tartrate ions viz., 100 ppm and above in the bulk of the solution, more tartrate is reaching the surface of the metal at the cost of the required optimum concentrations of BPMG and  $\text{Zn}^{2+}$  on the surface and therefore the necessary optimum concentration of BPMG and  $\text{Zn}^{2+}$  required for the formation of protective film, is not available on the surface. Hence, the decrease in inhibition efficiency is observed at concentrations of tartrate ions  $\geq 100$  ppm. It may be mentioned here that the molar ratio of BPMG :  $\text{Zn}^{2+}$  : tartrate is 1.0 : 5.4 : 2.0 to exhibit excellent synergism. The role of each synergist is explained under mechanistic aspects of corrosion inhibition.



**Figure 1.** Corrosion inhibition efficiency of the ternary inhibitor formulation containing BPMG,  $\text{Zn}^{2+}$  and tartrate as a function of concentration of tartrate, (●) BPMG (30 ppm) +  $\text{Zn}^{2+}$  (20 ppm) + tartrate, (▲) BPMG (20 ppm) +  $\text{Zn}^{2+}$  (30 ppm) + tartrate, (■) BPMG (30 ppm) +  $\text{Zn}^{2+}$  (30 ppm) + tartrate

The influence of pH on inhibition efficiencies of the two ternary inhibitor formulations namely, BPMG (20 ppm) +  $\text{Zn}^{2+}$  (30 ppm) + tartrate (25 ppm) and BPMG (30 ppm) +  $\text{Zn}^{2+}$  (30 ppm) + tartrate (50 ppm), in the pH range, 5.0 to 9.0 is shown in Figure 2.



**Figure 2.** Corrosion inhibition efficiencies of the ternary inhibitor formulations as a function of pH, (▲) BPMG (20 ppm) +  $\text{Zn}^{2+}$  (30 ppm) + tartrate (25 ppm), (●) BPMG (30 ppm) +  $\text{Zn}^{2+}$  (30 ppm) + tartrate (50 ppm)

There is decrease in inhibition efficiency of these formulations with a decrease of pH from neutral to acidic i.e. from pH 7.0 to 5.0. Similarly, increase in pH from 7.0 to 9.0, decreased the inhibition efficiency of both the ternary inhibitor formulations. From these results, it may be

concluded that the ternary system, BPMG-Zn<sup>2+</sup>-tartrate, is effective in the neutral as well as slightly acidic and slightly basic environments. Once, the protective film is formed on the metal surface in contact with the ternary inhibitor system consisting of BPMG (20 ppm), Zn<sup>2+</sup> (30 ppm) and tartrate (25 ppm), the concentrations of each of these components in the inhibitor could be even less in order to maintain the protective film. The results of gravimetric studies carried out in order to determine the minimum concentrations of the formulation for maintenance of the protective film are shown in Table 1. These results show that the inhibitor mixture containing only 10 ppm of BPMG, 10 ppm of Zn<sup>2+</sup> and 20 ppm of tartrate could maintain the protective film. The molar ratio of BPMG : Zn<sup>2+</sup> : tartrate in the maintenance dosage is 1.0 : 3.6 : 3.2.

**Table 1.** Results of Gravimetric Studies of the Inhibitor Formulations for Maintenance of the Protective Film

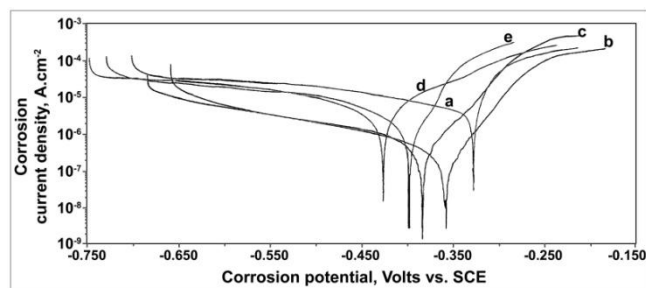
Inhibitor formulation for maintenance of the film, ppm			Corrosion rate, mmpy	Inhibition efficiency, %
BPMG	Zn <sup>2+</sup>	Tartrate		
-	-	-	0.08108	-
20	30	25	0.00636	92.16
20	25	25	0.00641	92.09
20	20	25	0.00640	92.10
20	15	25	0.00647	92.02
20	10	25	0.00705	91.30
20	5	25	0.02063	74.55
15	10	25	0.00721	91.10
10	10	25	0.00725	91.05
5	10	25	0.02778	65.73
10	10	20	0.00767	90.54
10	10	15	0.04530	44.13

### 3.2. Potentiodynamic Polarization Studies

The potentiodynamic polarization curves of carbon steel electrode in 200 ppm of chloride solution at pH 7 in the absence and presence of various inhibitor formulations are shown in Figure 3. The corrosion parameters are listed in Table 2. The Tafel potential ( $E_{\text{corr}}$ ) in case of the control solution is -328 mV vs. SCE. It is shifted to more cathodic side in case of all the inhibitor formulations considered for polarization studies. The corrosion current density ( $I_{\text{corr}}$ ) in case of the control solution is 12.84  $\mu\text{A}.\text{cm}^{-2}$ . In presence of all the inhibitor systems, the decrease in corrosion current is observed. The significant reduction in  $I_{\text{corr}}$  value in presence of the ternary inhibitor formulations indicates the decrease in corrosion rate in presence of the ternary inhibitor systems.

An examination of the Tafel slopes reveals that the addition of 20 ppm of BPMG, 30 ppm of Zn<sup>2+</sup> and 25 ppm of tartrate to the control solution shifts the anodic Tafel slope to an extent of 33  $\text{mV}.\text{dec}^{-1}$ , while the shift in cathodic Tafel slope is 46  $\text{mV}.\text{dec}^{-1}$ . Similarly, in presence of 30 ppm of BPMG, 30 ppm of Zn<sup>2+</sup> and 50 ppm of tartrate, the shift in anodic Tafel slope is 20  $\text{mV}.\text{dec}^{-1}$  and that in cathodic Tafel slope is 30  $\text{mV}.\text{dec}^{-1}$ . These shifts indicate that the ternary inhibitor system under study retards both the anodic and

cathodic partial reactions of the corrosion process and hence act as mixed type inhibitor. This is in agreement with several reports of literature indicating that phosphonate-based inhibitor formulations are mixed type inhibitors. Pech-Canul and Chi-Canul[17] investigated the inhibitive effect of N-phosphonomethyl glycine (NPMG) on the corrosion of carbon steel in neutral solutions using electrochemical techniques. From the results of polarization studies, they inferred that NPMG-Zn<sup>2+</sup> system acts as a mixed type inhibitor.



**Figure 3.** Potentiodynamic polarization curves for carbon steel in 200 ppm NaCl environment in the absence and presence of various inhibitor components, (a) Control (No inhibitor), (b) BPMG (20 ppm) + Zn<sup>2+</sup> (30 ppm), (c) BPMG (30 ppm) + Zn<sup>2+</sup> (30 ppm), (d) BPMG (20 ppm) + Zn<sup>2+</sup> (30 ppm) + tartrate (25 ppm), (e) BPMG (30 ppm) + Zn<sup>2+</sup> (30 ppm) + tartrate (50 ppm)

**Table 2.** Tafel Parameters for Carbon Steel in 200 ppm NaCl Environment in the Absence and Presence of the Inhibitor Formulations

Inhibitor formulation, ppm			Tafel parameters				$IE_p$ , %
BPMG	Zn <sup>2+</sup>	Tartrate	$E_{\text{corr}}$ , mV vs. SCE	$I_{\text{corr}}$ , $\mu\text{A}.\text{cm}^{-2}$	$\beta_a$ , $\text{mV}.\text{dec}^{-1}$	$\beta_c$ , $\text{mV}.\text{dec}^{-1}$	
-	-	-	-328	12.84	12	132	-
20	30	-	-358	12.30	32	80	4.20
30	30	-	-383	4.64	46	163	63.86
20	30	25	-427	1.93	45	86	84.97
30	30	50	-398	1.14	32	102	91.12

### 3.3. Electrochemical Impedance Studies

The impedance spectra in the form of Nyquist plots for carbon steel immersed in various environments at pH 7 are given in Figure 4. These plots are discussed to throw light on the nature of the protective film. The plots are depressed semicircles with the centre below the real axis. This kind of phenomenon is known as dispersing effect[18]. When the complex plane impedance contains a depressed semicircle with the centre below the real axis, which is characteristic for solid electrodes, it is often attributed to roughness and inhomogeneities of the solid surface[19]. It is also attributed to the distribution of active sites, adsorption of inhibitor molecules and formation of porous layers[20]. In such cases, the parallel network charge transfer resistance-double layer capacitance ( $R_{\text{ct}}-C_{\text{dl}}$ ) is a poor approximation especially for systems where an efficient inhibitor is present. Considering that the impedance of a double layer did not behave as an

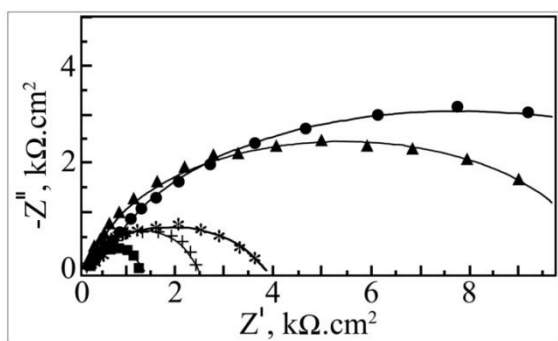
ideal capacitor in presence of the dispersing effect, a constant phase element (CPE) is substituted for the capacitor to fit the depressed semicircles more exactly[21].

The admittance and impedance of a CPE are, respectively defined as

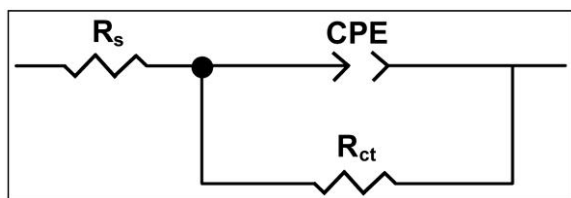
$$Y_{CPE} = Y_0 (j\omega)^n \text{ and}$$

$Z_{CPE} = A (j\omega)^{-n}$ , where  $Y_0$  is the modulus,  $\omega$  is the angular frequency,  $n$  is the CPE exponent and  $A$  is a proportional factor mathematically the reciprocal of modulus[22,23]. For a highly polished electrode, the value of  $n$  is close to 1.0. The lower the value of  $n$ , the rougher is the electrode. It can be seen that when  $n = 1$ , the element CPE is an ideal capacitor and  $A$  is equal to the capacitance,  $C$ .

Figure 4 indicates that the Nyquist plots are characterized by a single time constant. The experimental data obtained from these plots are fitted by the equivalent electrical circuit shown in Figure 5. Such an equivalent circuit was also discussed by several authors[22,23], who obtained similar depressed semicircles with a single time constant. The impedance parameters obtained from Nyquist plots and the inhibition efficiencies ( $IE_i$ ) calculated from these parameters are shown in Table 3.



**Figure 4.** Nyquist plots for carbon steel in 200 ppm NaCl environment in the absence and presence of various inhibitor components, (+) Control (No inhibitor), (■) BPMG (20 ppm) +  $Zn^{2+}$  (30 ppm), (\*) BPMG (30 ppm) +  $Zn^{2+}$  (30 ppm), (▲) BPMG (20 ppm) +  $Zn^{2+}$  (30 ppm) + tartrate (25 ppm), (●) BPMG (30 ppm) +  $Zn^{2+}$  (30 ppm) + tartrate (50 ppm), (lines represent fitted curves)



**Figure 5.** Equivalent circuit used to fit the impedance data

The value of  $R_{ct}$  in case of the control solution is 2575  $\Omega$ . In presence of the binary formulation namely BPMG (20 ppm) +  $Zn^{2+}$  (30 ppm), the value of  $R_{ct}$  is decreased while in case of the binary system containing BPMG (30 ppm) +  $Zn^{2+}$  (30 ppm), the value of  $R_{ct}$  is increased to 3830  $\Omega$ . Addition of tartrate to these binary systems increased the value of  $R_{ct}$  enormously to 12460  $\Omega$  and 21870  $\Omega$  respectively. The large increase in charge transfer resistance in presence of the ternary inhibitor formulations indicates that there is formation of an insulating protective film in presence of the

ternary inhibitor formulations. It also infers the synergistic effect operating between BPMG,  $Zn^{2+}$  and tartrate. Pech-Canul and Chi-Canul[17] investigated the inhibitive effect of N-phosphonomethyl glycine (NPMG) on the corrosion of carbon steel in neutral solutions using electrochemical techniques. They reported the fit parameters in their study. Based on these parameters, they interpreted that the 3D protective layer developed in presence of the inhibitor was less permeable than that formed in the blank solution.

**Table 3.** Impedance Parameters for Carbon Steel in 200 ppm NaCl Environment in the Absence and Presence of the Inhibitor Formulations

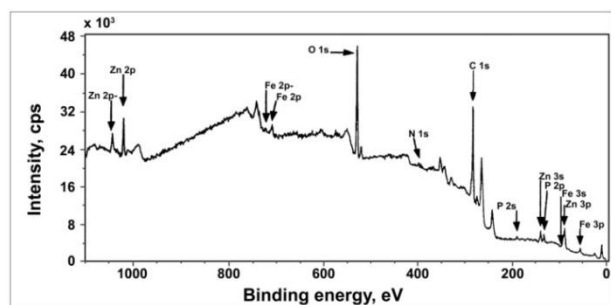
Inhibitor formulation, ppm			Impedance parameters			$IE_i$ , %
BPMG	$Zn^{2+}$	Tartrate	$R_{ct}$ , $\Omega.cm^2$	CPE, $\mu F.cm^{-2}$	n	
-	-	-	2575	13.41	0.592	-
20	30	-	1390	15.10	0.679	-
30	30	-	3830	10.09	0.811	32.76
20	30	25	12460	4.19	0.913	79.33
30	30	50	21870	3.75	0.922	88.22

The inference given above for the increase of charge transfer resistance is supported by the decrease in the value of CPE in presence of the ternary inhibitor formulations. The CPE value in case of the control solution is 13.41  $\mu F.cm^{-2}$ . In presence of the ternary inhibitor formulations, the CPE value is significantly decreased. The value of  $n$ , i.e., CPE exponent is found to be nearer to 1.0 in case of the ternary inhibitor systems. It indicates that the surface film formed in presence of these formulations is homogeneous. The increase in charge transfer resistance and decrease in CPE value in presence of the ternary inhibitor formulations indicate that there is formation of a highly protective surface film on the metal surface. It also infers that tartrate ions play an excellent role in the synergistic effect. A significant observation related to the inhibition efficiency values is to be noted. If the inhibition efficiency values obtained from gravimetric ( $IE_g$ ), polarization ( $IE_p$ ) and EIS ( $IE_i$ ) studies are compared, slight differences are observed. It is suggested that the inhibition efficiency values obtained from various methods may not be strictly compared when the immersion times used in these methods are not same.

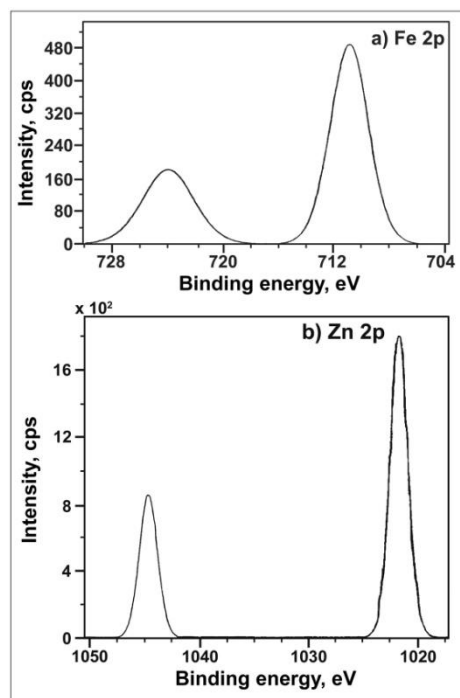
### 3.4. Interpretation of X-Ray Photoelectron Spectra

The X-ray photoelectron spectrum of the surface film formed on carbon steel immersed in the environment containing BPMG (20 ppm) +  $Zn^{2+}$  (30 ppm) + tartrate (25 ppm) is shown in Figure 6. The XPS spectrum shows binding energy peaks due to electrons of various elements present in the surface film. The corresponding computer deconvolution spectra of the individual elements are shown in Figures 7 and 8. The interpretation of all the spectra is done with the help of the data of the elemental binding energies reported in literature and also with the help of reports published on the

analysis of XPS spectra of the surface films formed on carbon steel.



**Figure 6.** XPS survey spectrum of the surface film formed in presence of the ternary inhibitor formulation



**Figure 7.** XPS deconvolution spectra of the elements in the surface film, a) Fe 2p and b) Zn 2p

The XPS spectrum of Fe 2p in case of the inhibitor formulation is shown in Figure 7a. It shows two peaks, one with lower binding energy value corresponding to Fe 2p<sub>3/2</sub> electron and the other one with higher binding energy value corresponding to Fe 2p<sub>1/2</sub> electron. The peak due to Fe 2p<sub>3/2</sub> is interpreted for the determination of chemical state of iron in the surface film. This peak is observed at 710.9 eV. The characteristic elemental binding energy of Fe 2p<sub>3/2</sub> electron is 707.0 eV[24]. That means the shift is to the extent of 3.9 eV. Such large shift suggests that iron is present in Fe<sup>3+</sup> state in the surface film. This shift may be ascribed due to the presence of iron in Fe<sup>3+</sup> state in the form of Fe(OH)<sub>3</sub>, FeOOH, γ-Fe<sub>2</sub>O<sub>3</sub> and [Fe(III)-BPMG-tartrate] complex [25-28]. The binding energy of Fe<sup>2+</sup> state in iron oxides is reported to be around 708.5 eV[29]. The absence of any peak in this region in the present study also supports that iron does not exist in Fe<sup>2+</sup>, but in Fe<sup>3+</sup> state in the surface film.

The XPS spectrum of zinc is presented in Figure 7b. The

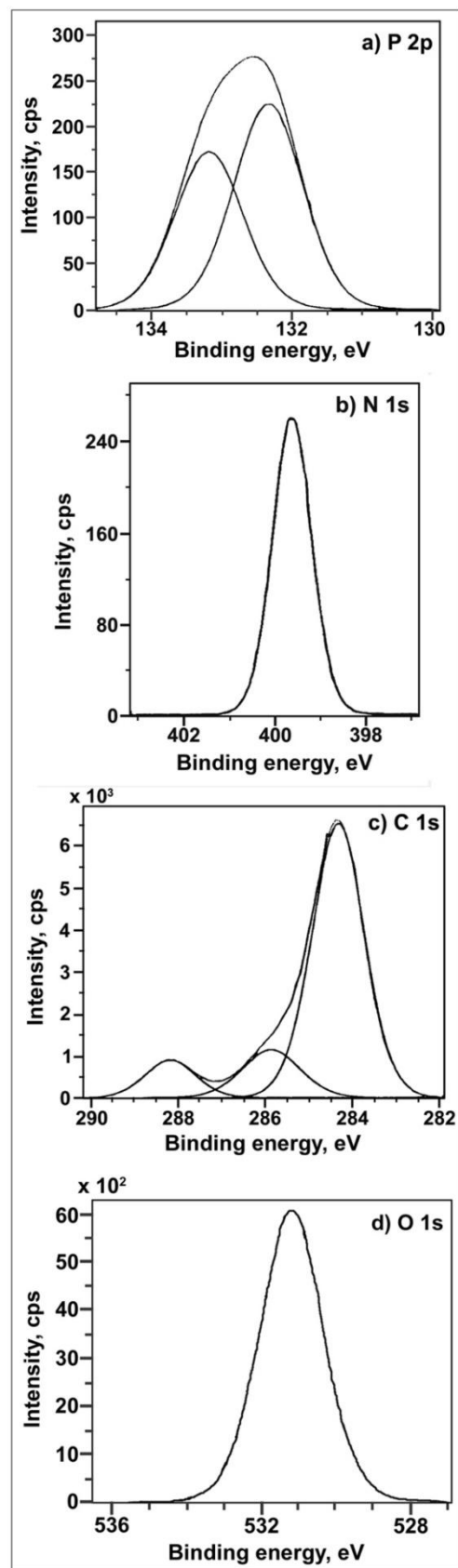
spectrum shows two peaks, one corresponding to Zn 2p<sub>3/2</sub> and the other one corresponding to Zn 2p<sub>1/2</sub>. It can be observed that the intensity of Zn 2p<sub>3/2</sub> peak is far greater than the intensity of Zn 2p<sub>1/2</sub> peak. Zn 2p<sub>3/2</sub> is normally interpreted. This peak is observed at 1021.7 eV. The high intensity peak of Zn 2p<sub>3/2</sub> may be ascribed to the involvement of Zn<sup>2+</sup> in the complex formation with BPMG as well as tartrate and also to the presence of Zn(OH)<sub>2</sub> in the surface film. It was reported in the literature by Aramaki [30,31] that the Zn 2p<sub>3/2</sub> peak at 1021.7 eV was due to the presence of Zn(OH)<sub>2</sub> in the surface film. Felhosi *et al.*[3] interpreted from the XPS analysis that there is formation of [Zn-HEDP] complex on the mild steel surface when immersed in a solution consisting of a mixture of Zn<sup>2+</sup> and 1-hydroxyethane-1,1-diphosphonic acid (HEDP).

The XPS spectrum of phosphorus is shown in Fig 8a. The figure shows two peaks, one corresponding to P 2p<sub>3/2</sub> and the other one corresponding to P 2p<sub>1/2</sub>. The peaks for P 2p<sub>3/2</sub> and P 2p<sub>1/2</sub> are observed at 132.3 and 133.2 eV respectively. These are shifted from their characteristic elemental binding energies of 130.0 eV for P 2p<sub>3/2</sub> and 131.0 eV for P 2p<sub>1/2</sub> [24]. Felhosi *et al.*[3] 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<sup>2+</sup> and HEDP. They interpreted this peak due to the presence of [Zn-HEDP] complex in the surface film. Ochoa *et al.*[32] 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 it due to the presence of phosphonate group in the surface film. In the literature[33], 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 BPMG in the surface film in the form of a complex with Fe (III) and Zn (II). Figure 8b shows the N 1s peak in the XPS spectrum of the surface film observed at 399.6 eV. This peak is shifted from the characteristic elemental binding energy value of 398.0 eV[24]. This shift may be attributed to the presence of BPMG molecules in the surface film in the form of a complex with Fe (III) and Zn (II). It was reported in the literature[34] 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. Meneguzzi *et al.*[36] reported that the peak at 399.9 eV could be attributed to the neutral imine (-N=) and an amine (-N-H) nitrogen atoms.

The XPS spectrum of the surface film for carbon is shown in Figure 8c. The spectrum contains three peaks of which one possesses high intensity relative to the other two peaks. The high intensity peak is observed at 284.3 eV. Ochoa *et al.*[32] in their studies on the mixtures of salts of phosphono-carboxylic acids and fatty amines as inhibitors for corrosion of carbon steel reported the C 1s peak at 284.5 eV. This signal was accounted for by the presence of the inhibitor molecules on the steel surface. BPMG consists of three different carbon environments namely C-C-OH, N-C-C

and N-C-P and tartrate ion also possesses two different carbon environments. Hence, the three peaks observed in case of carbon in the present study may be attributed to the presence of BPMG and tartrate in the surface film. Meneguzzi et al.[35] observed in their studies a less intense peak at 286.8 eV and ascribed it to C-O or C-N or C=N. The XPS spectrum of O 1s is presented in Figure 8d. The O 1s peak of very high intensity is observed at 531.2 eV. Karman et al.[7] studied the role of oxide layer formation during corrosion inhibition of mild steel in neutral aqueous media by a mixture of HEDP and  $\text{Ca}^{2+}$  ions. From the XPS studies, they interpreted that the peak at ~531 eV is due to the presence of OH<sup>-</sup> on the surface. Fang et al.[27] ascribed the O 1s peak observed at 531.3 eV to the complex formed between iron and phosphonate. Pech-Canul and Bartolo-Perez[26] observed the O 1s peak at 531.3 eV, which was ascribed to OH<sup>-</sup> from hydrous iron oxides and to the complex formed between iron and phosphonate group. It was also mentioned in their paper that such hydrous ferric oxides consist of  $\text{Fe}(\text{OH})_3$  and  $\text{FeOOH}$ . Felhosi et al.[3] studied the effects of bivalent cations on corrosion inhibition of steel by HEDP. They mentioned that the O 1s peak at 531.4 eV is due to HO-Fe bond. Asami et al.[29] observed O 1s peak at 531.5 eV in their study and attributed it to oxygen with a kind of Fe-O-H bond. In the light of these results and interpretations reported in literature, the O 1s peaks of high intensity observed in the present study may be interpreted as follows. The XPS spectrum of surface film (cf. Figure 6) shows that besides oxygen, there is presence of carbon, nitrogen, phosphorus, iron and zinc in the surface film. That means BPMG is present on the surface. Zinc is present as  $\text{Zn}^{2+}$ . The interpretation given above in case of Fe 2p indicates that iron is present in the form of  $\text{Fe}^{3+}$ . Hence, O 1s peak can be ascribed to the presence of  $\text{Fe}(\text{OH})_3$ ,  $\text{FeOOH}$ ,  $\text{Zn}(\text{OH})_2$  and oxygen of phosphonate and tartrate ion in the surface film.

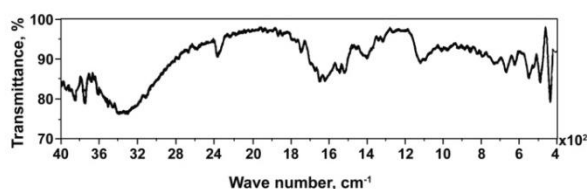
From the XPS spectrum (cf. Figure 6) of the surface film, it is clear that the intensity of Fe 2p peak is low when compared to that of Zn 2p. It can be explained as follows. In the surface film, iron exists as  $\text{Fe}^{3+}$  in the form of its oxides and hydroxides as well as in the form of complex with BPMG and tartrate. These  $\text{Fe}^{3+}$  ions are present on the surface due to initial corrosion. But after the formation of protective surface film, there is no further corrosion and hence the Fe 2p peak intensity is less. It is interesting to note that the intensity of Zn 2p peak is far greater than that of Fe 2p peak. Due to sufficient concentration of  $\text{Zn}^{2+}$  in the bulk of the solution, these ions diffuse to the metal surface and exist in the form of  $\text{Zn}(\text{OH})_2$  as well as in the form of complex with BPMG as well as tartrate. Hence the intensity of Zn 2p peak is very high. After consolidating all the inferences drawn from the XPS of the individual elements present in the surface film, it is suggested that the surface film consists of  $\text{Fe}(\text{OH})_3$ ,  $\text{FeOOH}$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Zn}(\text{OH})_2$  and [Fe(III),Zn(II)-BPMG-tartrate] hetero-polynuclear complex. These compounds and the complex all together make the film highly protective.



**Figure 8.** XPS deconvolution spectra of the elements in the surface film, a) P 2p, b) N 1s, c) C 1s and d) O 1s

### 3.5. Interpretation FTIR Spectra

The reflection absorption FTIR spectrum of the surface film formed on carbon steel in presence of the ternary inhibitor formulation, BPMG (20 ppm) + Zn<sup>2+</sup> (30 ppm) + tartrate (25 ppm), is shown in Figure 9. This spectrum is compared with the FTIR spectra of pure BPMG and pure potassium sodium tartrate tetrahydrate in KBr pellet. The spectra of pure compounds are not included in this paper. The reflection absorption FTIR spectrum of the surface film can be interpreted as follows. The peak due to P–OH stretching vibrations is observed at 1140 cm<sup>-1</sup>. This result can be interpreted due to interaction of free P – O present in the phosphonate with metallic species, viz., Fe(III) and Zn(II) to form P–O–Metal bonds [4,36]. Raman *et al.* [37] reported that a peak due to P–OH stretching vibrations appear in the range of 1100–1200 cm<sup>-1</sup> [38]. It infers that there is presence of BPMG in the surface film. The two peaks appeared at 1680 cm<sup>-1</sup> and 1520 cm<sup>-1</sup> in the spectrum of the surface film may be due to the carbonyl group of BPMG and due to carbonyl group of tartrate ions. These are shifted from 1732 cm<sup>-1</sup> and 1740 cm<sup>-1</sup> observed for carbonyl group of BPMG and carbonyl group of tartrate ion respectively in the spectra of pure compounds. The two peaks due to carbonyl groups in the spectrum of the surface film are observed to be at lower frequencies when compared to the corresponding peaks of pure compounds. It is therefore inferred that BPMG and tartrate ion are involved in complex formation with Fe(III) as well as Zn(II) and the presence of [Fe(III), Zn(II)–BPMG–tartrate] hetero-polynuclear complex is suggested. The small peak observed at 1320 cm<sup>-1</sup> is due to the presence of Zn(OH)<sub>2</sub> [39]. A broad band appeared around 3280 cm<sup>-1</sup> can be interpreted due to O–H stretching vibrations [40]. The hydroxyl group is present in BPMG, tartrate ions, Zn(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>. Hence this peak supports the presence of these compounds within the protective film. The peak at 2360 cm<sup>-1</sup> can be attributed to strong hydrogen bond, due to which the tartrate exists as a dimer or trimer [41]. In case of pure potassium sodium tartrate, this peak is observed at 2500 cm<sup>-1</sup>. The peaks observed at 570 cm<sup>-1</sup> and 630 cm<sup>-1</sup> in the spectrum of the surface film can be assigned to amorphous oxides of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> [42]. From the reflection absorption FTIR spectrum of the surface film, it is inferred that apart from [Fe(III), Zn(II)–BPMG–tartrate] hetero-polynuclear complex, the protective film consists of Zn(OH)<sub>2</sub> and oxides and hydroxides of iron (III).



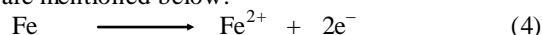
**Figure 9.** Reflection absorption FTIR spectrum of the surface film formed in presence of the ternary inhibitor formulation

### 3.6. Mechanism of Corrosion Inhibition

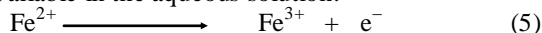
In order to explain all the experimental results, a plausible

mechanism of corrosion inhibition is proposed as follows:

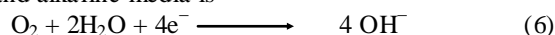
The mechanism of corrosion of carbon steel in nearly neutral aqueous media is well established. The well-known reactions are mentioned below.



Fe<sup>2+</sup> further undergoes oxidation in the presence of oxygen available in the aqueous solution.

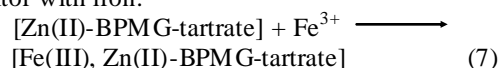


The corresponding reduction reaction at cathodic sites in neutral and alkaline media is

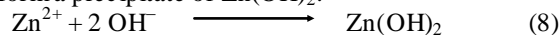


Fe<sup>3+</sup> ions produced at anodic areas and OH<sup>-</sup> ions produced at cathodic areas combine to form Fe(OH)<sub>3</sub>, (Fe<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O) which gets precipitated on the surface of the metal due to its very low solubility product.

When BPMG, Zn<sup>2+</sup> and tartrate ions are added to the aqueous solution, both BPMG and tartrate react with Zn<sup>2+</sup> to form a ternary complex, [Zn<sup>2+</sup>-BPMG-tartrate]. This complex diffuses to the metal surface and binds with Fe(III) ions available on the metal surface. A dense polymeric network structure is constituted on the surface by high degree of cross-linkage and reorganization. The polynuclear multiligand complex, [Fe(III), Zn(II)-BPMG-tartrate] covers the anodic sites and controls the anodic reaction of the corrosion process. Felhosi *et al.* [43] showed that iron can be passivated by simple immersion of it in aqueous solutions of 1,7-diphosphoheptane. The formation of protective layer by the phosphonate consists of a fast adsorption step and subsequent slower process, which is supposed to be due to the organization. According to the authors, this effect is due to the formation of self-assembling layer of complexes of the organic inhibitor with iron.



Free Zn<sup>2+</sup> ions are available in the bulk of the solution because of relatively higher molar concentration of Zn<sup>2+</sup> in the inhibitor mixture. These Zn<sup>2+</sup> ions diffuse to the metal surface and react with OH<sup>-</sup> ions produced at the cathodic sites to form a precipitate of Zn(OH)<sub>2</sub>.



The precipitate of Zn(OH)<sub>2</sub> gets deposited on the cathodic sites and controls the cathodic partial reaction of corrosion process.

The decrease in inhibition efficiency when the bulk concentration of tartrate is higher than the optimum value can be explained as follows. When the bulk concentration of tartrate is higher, the nature and composition of the complex, [Zn(II)-BPMG-tartrate] may be entirely different, with more tartrate than BPMG. Such a complex may not be protective. Secondly, higher concentration of free tartrate is available in the bulk of the solution. This free tartrate diffuses to the steel surface and gets chemisorbed on the metal surface. To that extent, the protective [Zn(II)-BPMG-tartrate] complex will not be available on the metal surface.

The ternary inhibitor formulation is effective in the pH range, 6–8. At pH 9, higher concentration of OH<sup>-</sup> ions are available both in the bulk of the solution and on the surface.



In such an environment, there is greater interference of OH<sup>-</sup> ions in the complexation[44] leading to the formation of [Zn(II)-BPMG-tartrate -OH] complex, which may not contribute to the formation of protective film on the metal surface. In acidic medium at pH 5, the ligands will be in the protonated form and do not coordinate with Zn(II) as effectively as the deprotonated ligands. Secondly, enough amount of Zn(OH)<sub>2</sub> will not be formed on the cathodic sites. Hence, decrease in inhibition efficiency is observed at pH 5.

Thus, BPMG, Zn<sup>2+</sup> and tartrate play a very important role in the synergistic effect in controlling corrosion through the formation of protective film on the metal surface. It is inferred that the film may consist of various oxides/hydroxides like Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>.H<sub>2</sub>O, FeOOH, Zn(OH)<sub>2</sub> and a polynuclear multiligand complex, [Fe(III), Zn(II)-BPMG-tartrate]. Each of these constituents contributes itself to make the film highly protective.

#### 4. Conclusions

Tartaric acid, a non-toxic organic compound is proved to be an excellent synergist in combination with BPMG and Zn<sup>2+</sup> for corrosion control of carbon steel in nearly neutral aqueous environment. The ternary formulation containing 20 ppm of BPMG and 30 ppm of Zn<sup>2+</sup> along with 25 ppm of tartrate is an effective corrosion inhibitor for carbon steel. Once the protective film is formed, a mixture of only 10 ppm each of BPMG and Zn<sup>2+</sup> and 20 ppm of tartrate will serve as the maintenance dosage. The ternary inhibitor system is thus relatively more environmentally friendly. The inhibitor system is effective in the pH range 6-8. The inhibitor formulation acts as a mixed type inhibitor. Electrochemical impedance studies indicated the significant modification of the metal/solution interface by the formation of dense protective film in presence of the inhibitor formulation. The protective film consists of mainly [Zn(II)-BPMG-tartrate] complex, Zn(OH)<sub>2</sub> and small amounts of oxides/hydroxides of Fe(III). Presence of optimum amounts of all these compounds is required at a given pH value to make the surface film protective.

#### REFERENCES

- [1] E. Kalman, B. Varhegyi, I. Bako, I. Felhosi, F. H. Karman, A. Shaban, "Corrosion inhibition by 1-Hydroxyethane-1,1-diphosphonic acid", The Electrochemical Society, Journal of The Electrochemical Society, vol.141, no.12, pp.3357-3360, 1994.
- [2] S. Rajendran, B. V. Appa Rao, N. Panaliswamy, "HEDP-Zn<sup>2+</sup>: A potential inhibitor system for mild steel in low chloride media", Emerald Publishers, Anti-Corrosion Methods and Materials, vol.47, no.2, pp.83-87, 2000.
- [3] I. Felhosi, Zs. Keresztes, F. H. Karman, M. Mohai, I. Bertoti, E. Kalman, "Effects of bivalent cations on corrosion inhibition of steel by 1-hydroxyethane-1,1-diphosphonic acid", The Electrochemical Society, Journal of The Electrochemical Society, vol.146, no.3, pp.961-969, 1999.
- [4] Y. Gonzalez, M. C. Lafont, N. Pebere, F. Moran, "A synergistic effect between zinc salt and phosphonic acid for corrosion inhibition of a carbon steel", Springer, Journal of Applied Electrochemistry, vol.26, no.12, pp.1259-1265, 1996.
- [5] G. Gunasekaran, N. Palaniswamy, B. V. Appa Rao, V. S. Muralidharan, "Enhanced synergistic inhibition by calcium gluconate in low chloride media. Part I. Kinetics of corrosion", Indian Academy of Sciences, Proceedings of Indian Academy of Sciences (Chemical Sciences), vol.108, no.4, pp.399-405, 1996.
- [6] G. Gunasekaran, N. Palaniswamy, B. V. Appa Rao, V. S. Muralidharan, "Enhanced synergistic inhibition by calcium gluconate in low chloride media. Part II. Surface film characterization", Indian Academy of Sciences, Proceedings of Indian Academy of Sciences (Chemical Sciences), vol. 108, no.4, pp.407-413, 1996.
- [7] F. H. Karman, I. Felhosi, E. Kalman, I. Cserny, L. Kover, "The role of oxide layer formation during corrosion inhibition of mild steel in neutral aqueous media", Elsevier Limited, Electrochimica Acta, vol.43, no.1-2, pp.69-75, 1998.
- [8] B. V. Appa Rao, M. Venkateswara Rao, S. Srinivasa Rao, B. Sreedhar, "Synergistic effect of N,N-Bis(phosphonomethyl) glycine and zinc ions in corrosion control of carbon steel in cooling water systems", Taylor & Francis, Chemical Engineering Communications, vol.198, no.12, pp.1505-1529, 2011.
- [9] G. Gunasekaran, R. Natarajan, N. Palaniswamy, "The role of tartrate ions in the phosphonate based inhibitor system", Elsevier Limited, Corrosion Science, vol.43, no.9, pp.1615-1626, 2001.
- [10] B. V. Appa Rao, S. Srinivasa Rao, M. Venkateswara Rao, "Environmentally friendly ternary inhibitor formulation based on N,N-Bis(phosphonomethyl) glycine", Maney Publishing, Corrosion Engineering Science and Technology, vol.43, no.1, pp.46-53, 2008.
- [11] G. Gunasekaran, R. Natarajan, B. V. Appa Rao, N. Palaniswamy, V. S. Muralidharan, "Polymer based phosphonic acid inhibitor for low chloride media", National Institute of Science Communication and Information Resources, Indian Journal of Chemical Technology, vol.5, no.2, pp.91-94, 1998.
- [12] B. V. Appa Rao, S. Srinivasa Rao, "Electrochemical and surface analytical studies of synergistic effect of phosphonate, Zn<sup>2+</sup> and ascorbate in corrosion control of carbon steel", Wiley-VCH Verlag GmbH & Co., Materials and Corrosion, vol.61, no.4, pp.285-301, 2010.
- [13] B. V. Appa Rao, M. Venkateswara Rao, S. Srinivasa Rao, B. Sreedhar, "Tungstate as a synergist to phosphonate-based formulation for corrosion control of carbon steel in nearly neutral aqueous environment", Indian Academy of Sciences, Journal of Chemical Sciences, vol.122, no.4, pp.639-649, 2010.
- [14] ASTM Standard G31-72, "Standard practice for laboratory immersion corrosion testing of materials (Reapproved 1990)", Annual Book of ASTM Standards, 0302, Philadelphia, PA:

- ASTM, 1990.
- [15] R. A. Freeman, D. C. Silverman, “Error propagation in coupon immersion tests”, NACE International, Corrosion, vol.48, no.6, pp.463-466, 1992.
- [16] M. Elachouri, M. S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert, E. Essassi, “Some nonionic surfactants as inhibitors of the corrosion of iron in acid chloride solutions”, NACE International, Corrosion, vol.52, no.2, pp.103-108, 1996.
- [17] M. A. Pech-Canul, L. P. Chi-Canul, “Investigation of the inhibitive effect of N-phosphono-methyl-glycine on the corrosion of carbon steel in neutral solutions by electrochemical techniques”, NACE International, Corrosion, vol.55, no.10, pp.948-956, 1999.
- [18] S. L. Li, H. Y. Ma, S. B. Lei, R. Yu, S. H. Chen, D. X. Liu, “Inhibition of copper corrosion with schiff base derived from 3-methoxysalicylaldehyde and O-phenyldiamine in chloride media”, NACE International, Corrosion, vol.54, no.12, pp.947-954, 1998.
- [19] K. Juttner, “Electrochemical impedance spectroscopy (EIS) of corrosion processes on inhomogeneous surfaces”, Elsevier Limited, Electrochimica Acta, vol.35, no.10, pp.1501-1508, 1990.
- [20] A. A. El Hosary, R. M. Saleh, A. M. Shams El Din, “Corrosion inhibition by naturally occurring substances – I. The effect of Hibiscus subdariffa (karkade) extract on the dissolution of Al and Zn”, Elsevier Limited, Corrosion Science, vol.12, no.12, pp.897-904, 1972.
- [21] F. Mansfeld, M. W. Kendig, W. J. Lorenz, “Corrosion inhibition in neutral, aerated media”, The Electrochemical Society, Journal of The Electrochemical Society, vol.132, no.2, pp.290-296, 1985.
- [22] G. Gunasekaran, L. R. Chauhan, “Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium”, Elsevier Limited, Electrochimica Acta, vol.49, no.25, pp.4387-4395, 2004.
- [23] M. S. Morad, “An electrochemical study on the inhibiting action of some organic phosphonium compounds on the corrosion of mild steel in aerated acid solutions”, Elsevier Limited, Corrosion Science, vol.42, no.8, pp.1307-1326, 2000.
- [24] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bamen, Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics, USA, 1995.
- [25] E. Kalman, F. H. Karman, I. Cserny, L. Kover, J. Telegdi, D. Varga, “The effect of calcium ions on the adsorption of phosphonic acid: a comparative investigation with emphasis on surface analytical methods”, Elsevier Limited, Electrochimica Acta, vol.39, no.8-9, pp.1179-1182, 1994.
- [26] M. A. Pech-Canul, P. Bartolo-Perez, “Inhibition effects of N-phosphono-methyl-glycine/Zn<sup>2+</sup> mixtures on corrosion of steel in neutral chloride solutions”, Elsevier Limited, Surface and Coatings Technology, vol.184, no.2-3, pp.133-140, 2004.
- [27] J. L. Fang, Y. Li, X. R. Ye, Z. W. Wang, Q. Liu, “Passive films and corrosion protection due to phosphonic acid inhibitors”, NACE International, Corrosion, vol.49, no.4, pp.266-270, 1993.
- [28] N. S. McIntyre, D. G. Zetaruk, “X-ray photoelectron spectroscopic studies of iron oxides”, Americal Chemical Society Publications, Analytical Chemistry, vol.49, no.11, pp.1521-1529, 1977.
- [29] K. Asami, K. Hashimoto, S. Shimodaira, “X-ray photoelectron spectrum of Fe<sup>2+</sup> state in iron oxides”, Elsevier Limited, Corrosion. Science, vol.16, no.1, pp.35-45, 1976.
- [30] Kunitsugu Aramaki, “Self-healing mechanism of a protective film prepared on a Ce(NO<sub>3</sub>)<sub>3</sub>-pretreated zinc electrode by modification with Zn(NO<sub>3</sub>)<sub>2</sub> and Na<sub>3</sub>PO<sub>4</sub>”, Elsevier Limited, Corrosion Science, vol.45, no.5, pp.1085-1101, 2003.
- [31] Kunitsugu Aramaki, “Effects of organic inhibitors on corrosion of zinc in an aerated 0.5 M NaCl solution”, Elsevier Limited, Corrosion Science, vol.43, no.10, pp.1985-2000, 2001.
- [32] N. Ochoa, G. Baril, F. Moran, N. Pebere, “Study of the properties of a multi-component inhibitor used for water treatment in cooling circuits”, Springer, Journal of Applied Electrochemistry, vol.32, no.5, pp.497-504, 2002.
- [33] M. Koudelka, J. Sanchez, J. Augustynski, “On the nature of surface films formed on iron in aggressive and inhibiting polyphosphate solutions”, The Electrochemical Society, Journal of the Electrochemical Society, vol.129, no.6, pp.1186-1191, 1982.
- [34] M. El Azhar, M. Traisnel, B. Mernari, L. Gengembre, F. Bentiss, M. Lagrenee, “Electrochemical and XPS studies of 2,5-bis(n-pyridyl)-1,3,4-thiadiazoles adsorption on mild steel in perchloric acid solution”, Elsevier Limited, Applied Surface Science, vol.185, no.3-4, pp.197-205, 2002.
- [35] A. Meneguzzi, C. A. Ferreira, M. C. Pham, M. Delamar, P. C. Lacaze, “Electrochemical synthesis and characterization of poly(5-amino-1-naphthol) on mild steel electrodes for corrosion protection”, Elsevier Limited, Electrochimica Acta, vol.44, no.12, pp.2149-2156, 1999.
- [36] S. Ramesh, S. Rajeswari, “Corrosion inhibition of mild steel in neutral aqueous solution by new triazole derivatives”, Elsevier Limited, Electrochimica Acta, vol.49, no.5, pp.811-820, 2004.
- [37] A. Raman, B. Kuban, A. Razvan, “The application of infrared spectroscopy to the study of atmospheric rust systems – I. Standard spectra and illustrative applications to identify rust phases in natural atmospheric corrosion products”, Elsevier Limited, Corrosion Science, vol.32, no.12, pp.1295-1306, 1991.
- [38] K. Aramaki, T. Shimura, “Prevention of passive film breakdown on iron in a borate buffer solution containing chloride ion by coverage with a self-assembled monolayer of hexadecanoate ion”, Elsevier Limited, Corrosion Science, vol.45, no.11, pp.2639-2655, 2003.
- [39] I. Sekine, Y. Hirakawa, “Effect of 1-hydroxyethylidene-1,1-diphosphonic acid on the corrosion of SS 41 steel in 0.3% sodium chloride solution”, NACE International, Corrosion, vol.42, no.5, pp.272-276, 1986.
- [40] R. M. Silverstein, G. C. Bassler, T. C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley & Sons, New York, 1981.
- [41] L. J. Bellamy, Advances in Infrared Group Frequencies, Recharad Clay (Ed.), The Chaucer Press Limited, Great Britain, 1968.

- [42] Shi Yu, Gan Moog Chow, "Carboxyl group ( $-\text{CO}_2\text{H}$ ) functionalized ferromagnetic iron oxide nanoparticles for potential bio-applications", RSC Publishing, Journal of Materials Chemistry, vol.14, no.18, pp.2781-2786, 2004.
- [43] I. Felhosi, E. Kalman, P. Poczik, "Corrosion protection by Self-Assembly", SpringerLink, Russian Journal of Electrochemistry, vol.38, no.3, pp.230-237, 2002.
- [44] V. Deluchat, J.-C. Bollinger, B. Serpaued, C. Caillet, "Divalent cations speciation with three phosphonate ligands in the pH-range of natural waters", Talanta, vol.44, no.5, pp.897-907, 1997.