

Tungstate as a synergist to phosphonate-based formulation for corrosion control of carbon steel in nearly neutral aqueous environment

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Abstract. Synergistic inhibition of corrosion of carbon steel in low chloride aqueous medium using tungstate as a synergist in combination with *N,N*-bis(phosphonomethyl) glycine (BPMG) and zinc ions is presented. The synergistic action of tungstate has been established through the present studies. The new ternary inhibitor formulation is effective in neutral and slightly acidic as well as slightly alkaline media. Potentiodynamic polarisation studies inferred that the formulation functions as a mixed inhibitor. Impedance studies of the metal/solution interface revealed that the surface film is highly protective. Characterisation by X-ray photoelectron spectroscopy (XPS) of the surface film formed in presence of the inhibitor revealed the presence of iron, phosphorus, nitrogen, oxygen, carbon, zinc and tungsten in the surface film. The chemical shifts in the binding energies of these elements inferred that the surface film is composed of iron oxides/hydroxides, zinc hydroxide, heteropolynuclear complex [Fe(III), Zn(II)–BPMG] and WO_3 . Reflection absorption FTIR spectroscopic studies also supported the presence of these compounds in the surface film. Morphological features of the metal surface studied in the absence and presence of the inhibitor by scanning electron microscopy (SEM) are also presented. Based on all these results, a plausible mechanism of corrosion inhibition is proposed.

Keywords. Carbon steel; tungstate; corrosion inhibitor; synergistic effect; protective film; phosphonated glycine.

1. Introduction

Phosphonate-based formulations are well known as corrosion inhibitors for carbon steel in aqueous environments. Synergistic effect existing between phosphonic acids and zinc ions on corrosion control of carbon steel has been studied by several researchers.^{1–9} *N,N*-bis(phosphonomethyl) glycine (BPMG) is one among the phosphonic acids reported as corrosion inhibitors in combination with zinc ions.⁶ It was reported to be an environmentally friendly phosphonic acid⁶ and it can form complexes with metal ions like Fe^{2+} , Fe^{3+} and Zn^{2+} .^{10,11} In order to develop the inhibitor formulation containing relatively low concentration of BPMG, addition of one more synergist to the binary system, BPMG– Zn^{2+} ,

has been thought of in the present study. For this purpose, an inorganic compound namely sodium tungstate was chosen as the second synergist for the following reasons. Sodium tungstate possesses very low toxicity.¹² A few reports are available in literature stating that tungstate acts as a corrosion inhibitor for steel either alone¹³ or synergistically in combination with other compounds.¹⁴ The objectives of the present study are to investigate the synergistic action of tungstate in combination with BPMG– Zn^{2+} for corrosion control of carbon steel in nearly neutral aqueous solution and to study the inhibitive properties of the surface film formed by the ternary inhibitor system, BPMG– Zn^{2+} –tungstate. For all these studies, 200 ppm of sodium chloride solution has been chosen as control because of the following reason. The water used in cooling water systems is generally either demineralised water or unpolluted surface water. In either case, the aggressiveness of

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the water does not normally exceed that of 200 ppm of NaCl solution.

2. Experimental

2.1 Materials

For all the studies, the specimens taken from a single sheet of carbon steel of the following composition were chosen: C: 0.1–0.2%, P: 0.03–0.08%, S: 0.02–0.03%, Mn: 0.4–0.5% and the rest was iron. Prior to the tests, the specimens were polished to mirror finish with 1/0, 2/0, 3/0 and 4/0 grade 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 × 1.5 cm × 0.2 cm, were used while for electrochemical and surface analytical studies, the dimensions of the specimens were 1.0 cm × 1.0 cm × 0.1 cm. Electrochemical studies were carried out at an immersion period of 1 h and for the surface analytical studies, the immersion period was 7 days. *N,N*-bis(phosphonomethyl) glycine (BPMG) obtained from Aldrich Chemical Company Inc., USA, was used as such. The molecular structure of BPMG is shown in figure 1. Sodium tungstate (Na₂WO₄), zinc sulphate (ZnSO₄·7H₂O), sodium chloride and other reagents were analytical grade chemicals. All the solutions were prepared using triple distilled non-deaerated water. pH values of the solutions were adjusted using 0.01 N NaOH and 0.01 N H₂SO₄ solutions. An aqueous solution consisting of 200 ppm of sodium chloride has been used as the control throughout the studies.

2.2 Gravimetric measurements

For 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

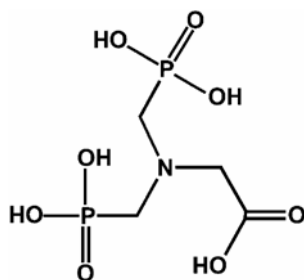


Figure 1. Molecular structure of BPMG.

concentrations, for a period of seven days. Then the specimens were reweighed after washing, degreasing and drying. Accuracy in weighing up to 0.01 mg and in surface area measured up to 0.1 cm², as recommended by ASTM G31, was followed.¹⁵ Inhibition efficiencies (IE_g) of the inhibitor formulations were calculated using the formula:

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

where $(CR)_O$ and $(CR)_I$ are the corrosion rates in the absence and presence of inhibitor respectively.

Gravimetric studies were carried out on the ternary system containing BPMG (20–30 ppm), Zn²⁺ (20–30 ppm) and tungstate (0–200 ppm) to establish minimum concentrations of both BPMG and Zn²⁺ in presence of tungstate for effective inhibition. The effect of pH on inhibition efficiency was determined in case of the effective ternary inhibitor formulations.

2.3 Electrochemical studies

Electrochemical impedance spectroscopic (EIS) studies and potentiodynamic polarisation studies were carried out using Electrochemical Workstation Model IM6e Zahner–elektrik, GmbH, Germany and the experimental data were analysed 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 cm² 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).

Polarisation curves were recorded in the potential range of –650 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. The ohmic drop compensation has been made 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 Tafel extrapolation method. The inhibition efficiencies (IE_p) were calculated from i_{corr} values using the equation¹⁶

$$IE_p (\%) = 100 [1 - (i'_{\text{corr}}/i_{\text{corr}})], \quad (2)$$

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 60 kHz to 10 mHz with 4 to 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,

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

where R_{ct} 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 films were carried out with Kratos analytical photoelectron spectrometer model AXIS 165 with monochromated Al K_{α} X-ray source (1486.6 eV) operated at 100 W and with a resolution of 0.1 eV. Analyser pass energy was 80 eV, with a step of 0.1 eV for the elements of interest namely Fe 2p, P 2p, N 1s, C 1s, O 1s, Zn 2p and W 4f.

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 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 sodium tungstate were recorded using 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° .

2.6 Surface analysis by scanning electron microscopy (SEM)

SEM images were recorded using FEI Quanta FEG 200 high resolution scanning electron microscope

for the specimens immersed in the control as well as in the inhibitor solution at two different magnifications.

3. Results and discussion

3.1 Gravimetric studies

The results of gravimetric studies using the binary system, BPMG-Zn²⁺, at various concentrations of both the constituents indicated that the minimum concentrations of BPMG and Zn²⁺ in the binary system are 40 ppm and 30 ppm respectively for inhibition efficiency (IE) > 90%. Before the addition of tungstate to the binary system, BPMG-Zn²⁺, the inhibitive effect of sodium tungstate alone was studied. The results of these studies indicated that sodium tungstate alone is not an effective inhibitor at low concentration levels. It was also reported in literature that sodium tungstate can be an effective inhibitor at the concentration of 300 ppm and it becomes more effective when the concentration exceeds 1200 ppm.¹⁷ When the possible binary combination of BPMG and tungstate is considered for gravimetric studies, it was inferred that this combination is not effective in corrosion control even at higher concentrations of both the components. As tungstate is being added to the binary formulation, BPMG-Zn²⁺, it is expected that the required minimum concentrations of BPMG and Zn²⁺ in the ternary inhibitor formulation are still lower than 40 ppm and 30 ppm respectively for an effective inhibition. Hence, the concentrations of both BPMG and Zn²⁺ are reduced by 10 ppm each and the formulations consisting of BPMG (30 ppm) + Zn²⁺ (20 ppm) + tungstate (20–200 ppm), are considered for the study of their IE . Figure 2 shows that none of these formulations showed an $IE > 90\%$. When the concentration of Zn²⁺, which plays very important role in phosphonate-based inhibitor formulations, is increased from 20 to 30 ppm, it has made the ternary inhibitor system effective in corrosion inhibition. Interestingly, the reduction in the concentration of BPMG from 30 to 20 ppm in the ternary formulation showed a very little effect on IE . Thus, in order to achieve an $IE > 90\%$, the required minimum concentrations of BPMG and Zn²⁺ are 20 ppm and 30 ppm respectively in presence of tungstate. While the binary system consisting of 20 ppm BPMG and 30 ppm Zn²⁺ accelerates corrosion, with the addition of tungstate,

the IE of the ternary formulation increased gradually with increase in concentration of tungstate reaching 99% at 200 ppm. It may be mentioned here that the molar ratio of BPMG/ Zn^{2+} /tungstate is 1.0 : 5.4 : 9.5 to exhibit excellent synergism. The role of each synergist is explained under mechanistic aspects of corrosion inhibition later in this paper.

The influence of pH on IE values of various compositions of the ternary system, BPMG- Zn^{2+} -tungstate, in the pH range from 5.0 to 9.0 is shown in figure 3. No adverse effect on the IE is observed with a decrease of pH from neutral to slightly acidic i.e. from pH 7.0 to 6.0. But on further decrease in pH from 6.0 to 5.0, the IE values are drastically decreased in case of all the ternary formulations. In the alkaline region, at the pH 8.0, the ternary formulations containing 200 ppm of tungstate are found to be effective. On further increase of pH to 9.0, the ternary inhibitor system is proved to be ineffective. From these results, it may be concluded that the ternary system, BPMG- Zn^{2+} -tungstate, is effective in the neutral and slightly acidic as well as slightly alkaline media.

3.2 Potentiodynamic polarisation studies

The potentiodynamic polarisation curves of carbon steel electrode in 200 ppm NaCl solution at pH 7 in the absence and presence of various inhibitor combinations are shown in figure 4. The Tafel parameters derived from these curves and the inhibition

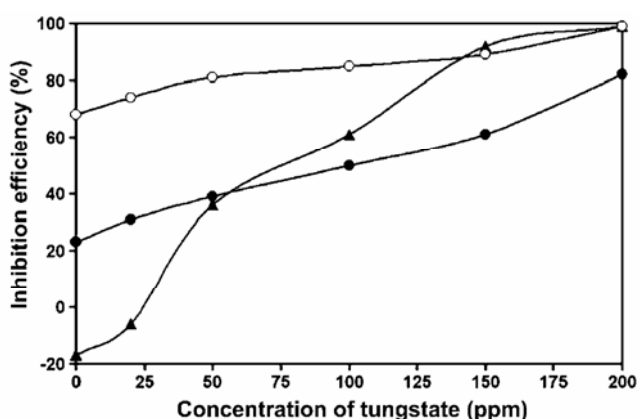


Figure 2. Corrosion inhibition efficiency of the ternary inhibitor formulations containing BPMG, Zn^{2+} and tungstate as a function of concentration of tungstate: —▲— BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate; —●— BPMG (30 ppm) + Zn^{2+} (20 ppm) + tungstate; —△— BPMG (20 ppm) + Zn^{2+} (20 ppm) + tungstate; —○— BPMG (30 ppm) + Zn^{2+} (30 ppm) + tungstate.

efficiency values (IE_p) are listed in table 1. The corrosion potential (E_{corr}) in case of the control is -323.4 mV vs SCE and the corresponding corrosion current density (i_{corr}) is $12.84 \mu A/cm^2$. From figure 4, it is clear that in case of all the inhibitor combinations studied, both the anodic and cathodic current density values are decreased when compared to the control. It is, thus, evident that all these formulations work as mixed type inhibitors. When the combination of 20 ppm BPMG and 30 ppm Zn^{2+} is con-

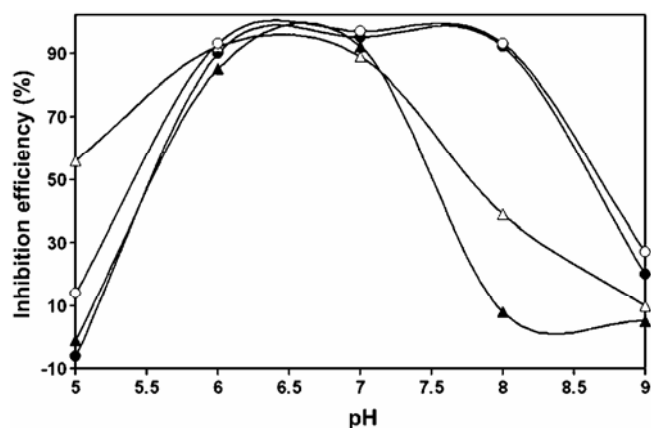


Figure 3. Corrosion inhibition efficiencies of the ternary inhibitor formulations as a function of pH —▲— BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate (150 ppm); —●— BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm); —△— BPMG (30 ppm) + Zn^{2+} (30 ppm) + tungstate (150 ppm); —○— BPMG (30 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm).

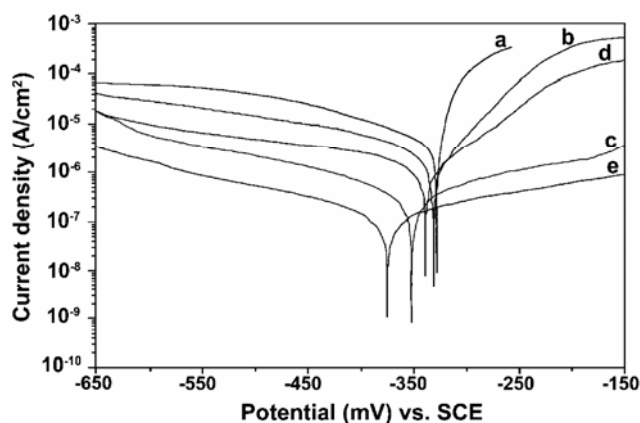


Figure 4. Potentiodynamic polarisation curves for carbon steel in various aqueous environments, (a) NaCl (200 ppm); (b) NaCl (200 ppm) + BPMG (20 ppm) + Zn^{2+} (30 ppm); (c) NaCl (200 ppm) + BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm); (d) NaCl (200 ppm) + BPMG (30 ppm) + Zn^{2+} (30 ppm); (e) NaCl (200 ppm) + BPMG (30 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm).

Table 1. Tafel parameters for carbon steel in 200 ppm NaCl environment in the absence and presence of inhibitor formulations.

Concentration (ppm)			Tafel parameters				
BPMG	Zn ²⁺	Tungstate	E_{corr} (mV vs SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/decade)	β_c (mV/decade)	IE_p (%)
0	0	0	-323.4	12.84	45	132	–
20	30	0	-330.8	7.11	54	112	44.62
20	30	200	-354.9	1.12	51	74	91.28
30	30	0	-341.5	5.93	57	98	53.81
30	30	200	-373.0	0.85	63	71	93.38

sidered, there is a slight shift of corrosion potential to cathodic side and the shift in cathodic Tafel slope is greater than the shift in anodic Tafel slope. The corrosion current density is decreased from 12.84 to 7.11 $\mu\text{A}/\text{cm}^2$, corresponding to an inhibition efficiency of only 44.62%. But, by the addition of 200 ppm of tungstate to the above formulation, E_{corr} is shifted to the extent of 31.5 mV towards cathodic side. The corrosion current density is decreased significantly to 1.12 $\mu\text{A}/\text{cm}^2$, corresponding to an inhibition efficiency of 91.28%. In case of the ternary formulation also, the shift in cathodic Tafel slope is higher than that in anodic Tafel slope. Similar results are obtained in case of the other ternary inhibitor formulation, BPMG (30 ppm) + Zn²⁺ (30 ppm) + tungstate (200 ppm), considered for the study by polarisation method. All these results indicate that the ternary inhibitor formulation retards both the anodic dissolution of carbon steel and oxygen reduction at cathodic sites in the corrosion inhibition process. Nevertheless, the effect on cathodic reaction is more pronounced. Similar phosphonate-based formulations were reported to be mixed inhibitors.^{2,8,9} Thus, the results of potentiodynamic polarisation studies infer the synergistic effect of tungstate as well as the synergistic effect of the ternary inhibitor formulation in corrosion control of carbon steel.

3.3 Electrochemical impedance studies

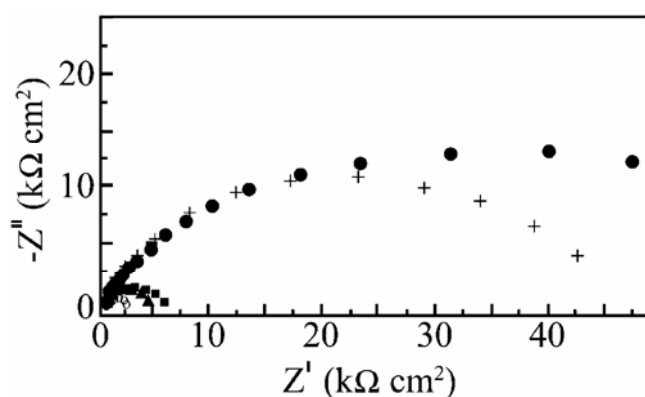
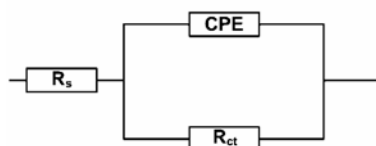
Nyquist plots for carbon steel immersed in 200 ppm of NaCl solution at pH 7 in the absence and presence of various formulations are shown in figure 5. In case of the control as well as in presence of various formulations, the Nyquist plots are found to be depressed semicircles instead of ideal semicircles and all the Nyquist plots are characterised by single time constant. The experimental data obtained from

these plots are fitted by the equivalent electrical circuit shown in figure 6. Such an equivalent circuit was also discussed by several researchers, who obtained similar depressed semicircles with single time constant.^{18–20} The charge transfer resistance (R_{ct}), constant phase element (CPE) and CPE exponent (n) obtained from the Nyquist plots and the calculated inhibition efficiency values (IE_i) are shown in table 2.

In the present study, in the presence of the control alone, a small semicircle with an R_{ct} value of 2575 Ω is observed. When the combination of 20 ppm of BPMG and 30 ppm of Zn²⁺ is considered in presence of the control, slight increase in R_{ct} is observed with a decrease in CPE value to the extent of only 4.5 $\mu\text{F}/\text{cm}^2$. But, on the addition of 200 ppm of tungstate to this binary formulation, 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 protective film on the metal surface. This result is supported by the significant decrease in CPE and an increase in n value. The value of R_{ct} in case of the ternary formulation is 44059 Ω , which is about ten times the R_{ct} value obtained in case of the binary combination of BPMG/Zn²⁺. The CPE value is found to decrease from 13.41 $\mu\text{F}/\text{cm}^2$ in case of the control to 2.83 $\mu\text{F}/\text{cm}^2$ in case of the ternary inhibitor formulation. This is because of the replacement of water molecules in the electrical double layer by the organic molecules having low dielectric constant.²¹ The value of n is considerably increased to 0.913 in presence of the ternary inhibitor system, suggesting the increase of homogeneity of the interface during inhibition. Similar results are obtained when the concentration of BPMG is increased from 20 to 30 ppm. All these results indicate that there is formation of a protective film in the presence of the

Table 2. Impedance parameters for carbon steel in 200 ppm NaCl environment in the absence and presence of inhibitor formulations.

Concentration (ppm)			Impedance parameters			
BPMG	Zn ²⁺	Tungstate	R_{ct} (Ω cm ²)	CPE (μ F/cm ²)	n	IE_i (%)
0	0	0	2,575	13.41	0.592	–
20	30	0	4,420	8.91	0.697	41.74
20	30	200	44,059	2.83	0.913	94.15
30	30	0	5,965	6.54	0.684	56.83
30	30	200	63,287	2.11	0.905	95.93

**Figure 5.** Nyquist plots for carbon steel in various aqueous environments, (○) NaCl (200 ppm); (▲) NaCl (200 ppm) + BPMG (20 ppm) + Zn²⁺ (30 ppm); (+) NaCl (200 ppm) + BPMG (20 ppm) + Zn²⁺ (30 ppm) + tungstate (200 ppm); (■) NaCl (200 ppm) + BPMG (30 ppm) + Zn²⁺ (30 ppm); (●) NaCl (200 ppm) + BPMG (30 ppm) + Zn²⁺ (30 ppm) + tungstate (200 ppm).**Figure 6.** The equivalent circuit used to fit the impedance spectra.

ternary inhibitor formulation. Several authors, who studied the inhibitory effects of phosphonate-based corrosion inhibitors, also reported that there is formation of a thick and less permeable protective film on the metal surface.^{2,4,8} They also concluded that the protective film consists of phosphonate-metal complexes. The impedance results of the present study also infer the synergistic action operating between BPMG, Zn²⁺ and tungstate. This inference is in agreement with the inferences drawn from gravimetric studies and potentiodynamic polarisation

studies. It may be noted that the inhibition efficiency values obtained from impedance studies are in agreement with those values obtained from polarisation studies. However, the inhibition efficiency values obtained from gravimetric studies are found to be slightly different from those obtained from electrochemical studies. This is due to different immersion periods used in these studies.

3.4 X-ray photoelectron spectroscopic studies

The XPS survey spectrum of the surface film formed in the presence of the inhibitor formulation, BPMG (20 ppm) + Zn²⁺ (30 ppm) + tungstate (200 ppm), is shown in figure 7. The survey spectrum of the surface film formed in the absence of any inhibitor and the deconvolution spectra of various elements present in the surface films formed in the absence as well as in the presence of the inhibitor formulation, are not shown here. However, the XPS deconvolution spectra of the elements namely P, N, Zn and W are given in the supporting information. The interpretation of all these spectra is done with the help of the data of the elemental binding energies reported in literature and also with the help of the reports published on the analysis of XPS spectra of the surface films.

The spectrum corresponding to the inhibitor system shows the Fe 2p_{3/2} peak at 712.0 eV. It indicates that Fe³⁺ is involved in the complex formation with BPMG apart from being present in the form of oxides/hydroxides like Fe₂O₃, Fe₃O₄, FeOOH, etc.^{22–24} However, these oxides/hydroxides of iron are present in very small quantities in the surface film formed by the inhibitor formulation as evident from the significant decrease in the intensity of Fe 2p_{3/2} peak in presence of the inhibitor. No peak is observed due to elemental iron in the case of control as well as inhibitor formulation. This result infers

the formation of thick films in both the cases. The film is non-protective in the case of control and highly protective in the presence of inhibitor molecules. The binding energy of Fe^{2+} state in iron oxides is reported to be around 708.5 eV.²⁵ The absence of any peak in this region in the present study also supports that iron does not exist in Fe^{2+} state. The XPS spectrum of phosphorus showed two P 2p peaks one each at 133.4 and 134.2 eV. The peaks are shifted from their characteristic elemental binding energies of 130.0 eV for P 2p_{3/2} and 131.0 eV for P 2p_{1/2}.²⁶ Based on the literature reports,^{4,7,27,28} the P 2p peaks observed in the present study suggest the presence of BPMG in the surface film in the form of complex with the metal ions. The XPS spectrum of the surface film in presence of the inhibitor shows the N 1s peak at 400.2 eV, which is shifted from the characteristic elemental binding energy of 398.0 eV.²⁶ The shift may be attributed to the presence of BPMG molecules in the surface film in the form of a complex with the metal ions. It was reported in literature²⁹ 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* reported that the peak at 399.9 eV could be attributed to the neutral imine (-N=) and amine (-N-H) nitrogen atoms.³⁰

The deconvolution spectrum of C 1s has three peaks one each at 284.6 eV, 285.5 eV and 288.4 eV. The presence of multiple peaks in the C 1s spectrum in case of the inhibitor can be attributed to various carbon environments present in BPMG. This inference is supported by several literature reports.^{7,19,31} In the XPS deconvolution spectrum of O 1s, a single peak of high intensity was observed at 531.5 eV. In the light of the results and interpretations reported in literature,^{4,8,25,32} the O 1s peak of high intensity

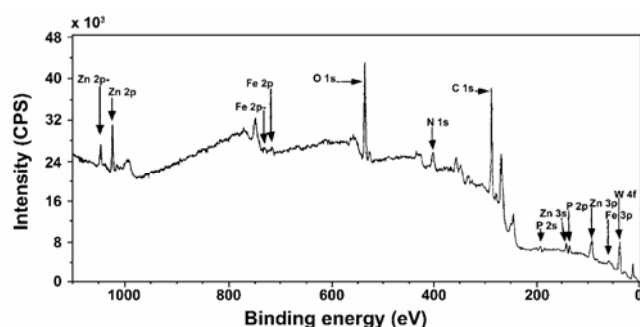


Figure 7. XPS spectrum of the surface film formed in presence of the inhibitor formulation, BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm).

observed in the present study may be interpreted as follows. The XPS of surface film shows that besides oxygen, there is presence of carbon, nitrogen, phosphorus, iron, zinc and tungsten in the surface film. That means BPMG is present on the surface, zinc is present as Zn^{2+} and the interpretation given above in case of Fe 2p indicates the presence of Fe_2O_3 , Fe_3O_4 and FeOOH. Hence, O 1s peaks can be ascribed to the presence of $\text{Zn}(\text{OH})_2$, Fe_2O_3 , Fe_3O_4 , FeOOH and oxygen of BPMG as well as tungsten oxide in the surface film.

The XPS deconvolution spectrum of zinc showed the Zn 2p_{3/2} peak at 1023.0 eV and the Zn 2p_{1/2} peak at 1046.0 eV. Zn 2p_{3/2} peak is normally interpreted. The high intensity of the Zn 2p_{3/2} peak may be ascribed to the presence of $\text{Zn}(\text{OH})_2$ in the surface film and also to the involvement of Zn^{2+} in the complex formation with BPMG. It was reported in literature that the Zn 2p_{3/2} peak at 1022.8 eV was due to the presence of $\text{Zn}(\text{OH})_2$ in the surface film.³³ Felhosi *et al* 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 HEDP and Zn^{2+} .⁴ In the XPS deconvolution spectrum of tungsten, the two peaks observed one each at 35.9 and 38.0 eV indicate the presence of tungsten in the surface film. The former peak corresponds to W 4f_{7/2} electron, which is shifted from characteristic elemental binding energy of 31.0 eV and the latter peak corresponds to W 4f_{5/2} electron, which is shifted from 33.6 eV.³⁴ The extent of shift is found to be very high in case of both the peaks. Such large shifts indicate that tungsten exists in the oxidation state of VI (in the form of WO_3) in the surface film. This interpretation in case of tungsten is also supported by literature reports.^{12,35} After consolidating all the inferences drawn from the XPS of individual elements present in surface film, it is suggested that the surface film in case of the ternary inhibitor system consists of mainly [Zn(II)-BPMG] complex, $\text{Zn}(\text{OH})_2$, WO_3 and small amounts of oxides/hydroxides of Fe(III). The complex may be chemisorbed on the metal surface and get attached to Fe(III) ions.

3.5 Interpretation of FTIR spectra

The reflection absorption FTIR spectra (not presented here) of the surface films formed on carbon steel in the absence and presence of the inhibitor are interpreted by comparing with the FTIR spectra of

pure BPMG and pure sodium tungstate (not presented here) as well as with the help of literature reports. In the FTIR spectrum of BPMG, multiple bands in the region, 900–1200 cm^{-1} were assigned to phosphonate group stretching frequencies. The peak at 1181 cm^{-1} can be assigned to $-\text{PO}_3$ antisymmetric (ν_{as}) stretching while the peak at 1080 cm^{-1} is assigned to symmetric (ν_{s}) stretching of $-\text{PO}_3$. The peak observed at 933.5 cm^{-1} can be attributed to the P–OH stretching vibrations. In case of the inhibited surface film, the antisymmetric and symmetric stretching vibrations, $\nu_{\text{as}}(\text{PO}_3)$ and $\nu_{\text{s}}(\text{PO}_3)$ are observed in the form of a band at 1170 cm^{-1} . This result can be interpreted in terms of interaction between $\text{P}-\text{O}^-$ present in the phosphonate with metallic species, viz. Zn(II) and Fe(III) to form P–O–Zn and P–O–Fe bonds. This interpretation was also given by several authors, who worked on corrosion inhibition of carbon steel by phosphonates.^{2,36,37} Carter *et al* found that FTIR spectra obtained with an organic phosphonate on a steel substrate are consistent with the phosphonate reaction on steel to produce a metal salt.³⁸ This also suggests that phosphonates are coordinated with metal ions resulting in the formation of [metal–phosphonate] complexes on the metal surface. A weak band observed around 1320 cm^{-1} indicates the presence of zinc hydroxide in the surface film formed by the inhibitor.^{36,39,40}

An intense band at 1732 cm^{-1} in the FTIR spectrum of BPMG is the characteristic of uncoordinated, protonated carboxylate carbonyl group in BPMG. The peak at 1700 cm^{-1} and at 1540 cm^{-1} in the reflection absorption FTIR spectrum of the surface film in case of the inhibitor system corresponds to the carbonyl group of BPMG in the surface film. The shifts in the stretching frequency are resulted due to the involvement of BPMG in the complex formation. A band at 1010 cm^{-1} in case of the inhibitor is due to C–N stretching vibration shifted from 1157 cm^{-1} observed in case of pure BPMG. The shift towards lower wave number indicates the formation of a coordinate bond between metal ions and phosphonate molecule. The peak observed at 925 cm^{-1} may be attributed to strong W–O bond of oxide of tungsten. Kolytyn *et al* observed a broad peak at a wave number less than 1000 cm^{-1} in the FTIR spectra of the prepared WO_3 nanoparticles.⁴¹ There are several bands in the region, 1200–400 cm^{-1} , in both the spectra of surface films. Many of these peaks imply the presence of various oxides and hydroxides of iron like Fe_3O_4 , FeOOH and Fe_2O_3 .^{27,31,36,42} A moderately intense and a broad

band formed at 3540.8 cm^{-1} , in case of the control, can be assigned to the presence of –OH group on the surface. This hydroxyl group may be in the form of FeOOH and/or $\text{Fe}(\text{OH})_3$.⁴³ Such peaks are observed in the spectra of the inhibited surface film also. These peaks can be assigned to the –OH group present in BPMG, to $\text{Zn}(\text{OH})_2$ and a small contribution of hydroxide of Fe(III) present in the inhibited film.

Thus, the reflection absorption FTIR spectrum of the surface film formed in presence of the inhibitor formulation infers the presence of [Zn(II)–BPMG] complex, $\text{Zn}(\text{OH})_2$, WO_3 and small amounts of oxides and hydroxides of Fe(III).

3.6 Surface analysis by SEM

Figure 8 shows the high resolution SEM images of the surfaces of carbon steel immersed for 7 days in the control in the absence and presence of the inhibitor, BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm). Figure 8a reveals that the surface is severely corroded and there is formation of different forms of corrosion products (iron oxides) on the surface in the absence of the inhibitor. The entire surface is covered by a scale-like black corrosion product, on which there is growth of another corrosion product appearing in the form of white clusters at several sites. A very few of such clusters are shown at sub-micron level in the Figure 8b. The morphological features of the inhibited surface are shown in figures 8c and d. The corrosion product deposits observed in case of the control are not present on the inhibited surface. It indicates that the penetration of Cl^- ions of the environment on to the substrate is controlled effectively through good surface coverage by the inhibitor film. The higher magnification (X5000) SEM image (figure 8d) of the inhibited surface contains some low depth inhomogeneities on the surface. But the closer look at such sites reveals that the inhomogeneities are due to the structural defects of the metal substrate and that these sites are also covered by the inhibitor film. Thus, the inhibitor film covers the entire metal surface. This observation also accounts for the high inhibition efficiency values obtained during the gravimetric studies of the inhibitor system. From the SEM analysis, it can be inferred that the surface film formed by the ternary inhibitor system exhibits good protective properties for carbon steel in low chloride media.

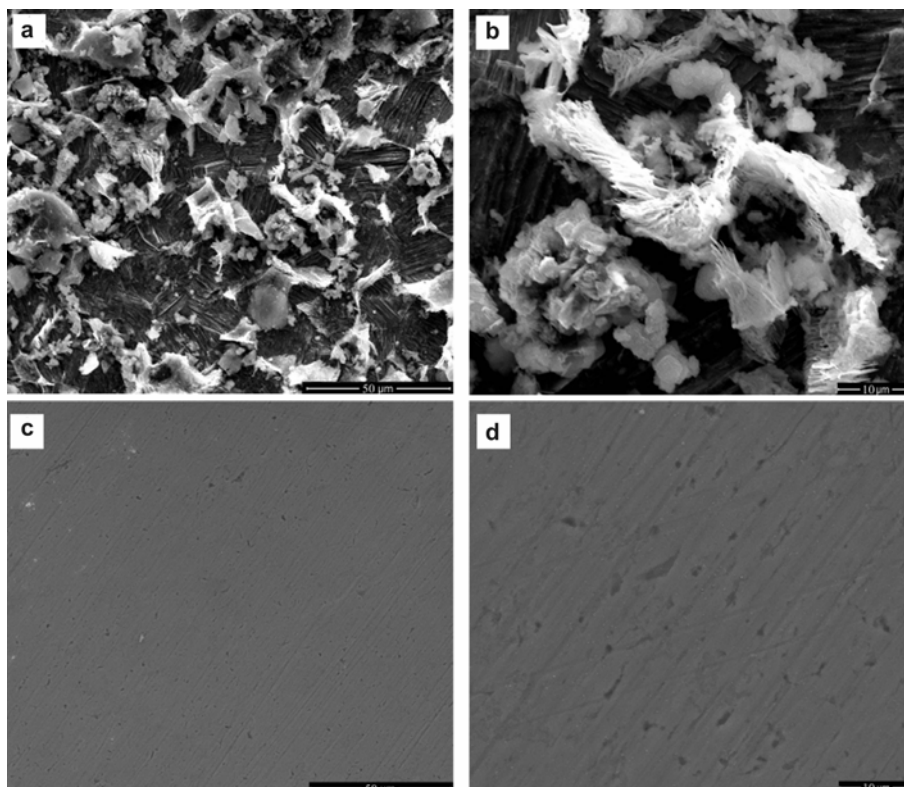


Figure 8. High-resolution SEM images of carbon steel surfaces after immersion in control in the absence and presence of the inhibitor, BPMG (20 ppm) + Zn^{2+} (30 ppm) + tungstate (200 ppm): (a) and (b) control, (c) and (d) inhibitor. (a) and (c) – magnification X1000, (b) and (d) – magnification X5000.

3.7 Mechanism of corrosion inhibition

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

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



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



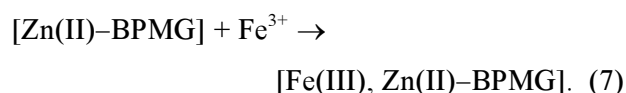
The corresponding reduction reaction at cathodic sites in neutral and alkaline media is



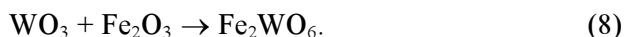
Fe^{3+} ions produced at anodic areas and OH^{-} ions produced at cathodic areas combine to form

$Fe(OH)_3$, $(Fe_2O_3 \cdot H_2O)$ which gets precipitated on the surface of the metal due to its very low solubility product.

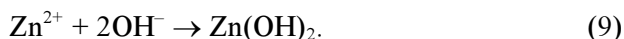
(ii) When BPMG, Zn^{2+} and tungstate are added to the aqueous solution, BPMG reacts with Zn^{2+} to form a complex, $[Zn^{2+}-BPMG]$. It diffuses to the metal surface and binds to $Fe(III)$ ions present on the surface. The cross-linkage and reorganisation of such complex ions on the surface will produce a polymeric network structure. The resulting polynuclear complex, $[Fe(III), Zn(II)-BPMG]$ covers the anodic sites and controls the corresponding anodic reaction.



Tungstate ions produce tungsten oxide (WO_3), which along with the iron oxides contributes to the protective nature of the surface film. For example, it is possible that WO_3 can react with Fe_2O_3 present on the surface to form iron tungstate.⁴⁴



(iii) Free Zn^{2+} 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 $\text{Zn}(\text{OH})_2$.



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

(iv) The inhibitor formulation is effective in the pH range, 6–8. At pH 9 and above, higher concentration of OH^- ions are available both in the bulk of the solution and on the surface. In such an environment, there is greater interference of OH^- ions in the complexation⁴⁵ leading to the formation of $[\text{Zn}(\text{II})\text{-BPMG-OH}]$ complex, which may not contribute to the formation of protective film on the metal surface. In acidic medium at $\text{pH} \leq 5$, the ligand will be in the protonated form and do not coordinate with $\text{Zn}(\text{II})$ as effectively as the deprotonated ligands. Secondly, enough amount of $\text{Zn}(\text{OH})_2$ will not be formed on the cathodic sites. Hence, the inhibitor is not effective at $\text{pH} \leq 5$.

(v) Thus, BPMG, Zn^{2+} and tungstate play 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_2O_3 , $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$, FeOOH , $\text{Zn}(\text{OH})_2$, WO_3 and a polynuclear complex, $[\text{Fe}(\text{III}), \text{Zn}(\text{II})\text{-BPMG}]$. Each of these constituents contributes itself to make the film highly protective.

4. Conclusions

- (i) The new ternary inhibitor formulation, BPMG– Zn^{2+} –tungstate, shows excellent synergistic effect in corrosion control of carbon steel in aqueous media.
- (ii) Synergistic effect of tungstate is well established through the present studies.
- (iii) The ternary formulation acts as a mixed type inhibitor controlling both the anodic and cathodic reactions.
- (iv) The metal/solution interface is modified significantly in presence of the inhibitor, inferring the formation of a dense and protective film on the metal surface.

- (v) The inhibitor formulation is effective in the neutral and slightly acidic as well as slightly alkaline media.
- (vi) Optimum amounts of each of the components of the inhibitor formulation are essential for an effective inhibition.
- (vii) The protective film consists of mainly $[\text{Zn}(\text{II})\text{-BPMG}]$ complex, $\text{Zn}(\text{OH})_2$, WO_3 and small amounts of oxides/hydroxides of $\text{Fe}(\text{III})$. Presence of optimum amounts of all these compounds is required to make the surface film protective.

Supplementary information

For supplementary information see www.ias.ac.in/chemsci website.

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