

# Analysis of a New Phosphonate-based Surface Film on Carbon Steel for Protection from Corrosion

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**Abstract**—Electrochemical and surface analytical studies of the surface film formed by a formulation containing Nitrilotris(methylenephosphonic acid) (NTMP)–Zn(II)–uric acid (UA) on carbon steel are presented. This new ternary formulation was selected for the study in view of its effectiveness as corrosion inhibitor in low chloride aqueous environment, as inferred by gravimetric studies. According to the results of potentiodynamic polarization studies, the formulation acts as a mixed type inhibitor. Impedance parameters like charge transfer resistance and constant phase element of the metal/solution interface are found to be significantly changed in presence of the inhibitor formulation, indicating the protective nature of the surface film. X-ray photoelectron spectroscopic studies (XPS) show the presence of the elements namely iron, zinc, phosphorous, nitrogen, carbon and oxygen in the protective film. Based on the XPS deconvolution spectra of these elements, it is inferred the presence of a complex [NTMP-Zn(II)-UA] along with zinc hydroxide and oxides/hydroxides of iron. This inference is further supported by the FTIR spectral analysis. Scanning electron microscopic images and atomic force microscopic images of the inhibited and uninhibited surfaces indicate the formation of a surface film on the metal in presence of the inhibitor formulation. Based on all these results, a plausible mechanism of corrosion inhibition is proposed.

**Keywords**–phosphonate; electrochemical; corrosion inhibition; carbon steel; XPS; FTIR

## I. INTRODUCTION

Phosphonate–Zn<sup>2+</sup> systems are prominent inhibitors for corrosion control of carbon steel in cooling water systems. Synergistic effect existing between phosphonic acids and zinc ions on inhibition of corrosion of carbon steel has been studied by several researchers [1-6]. Although phosphonate–Zn<sup>2+</sup> formulations are highly effective in corrosion control of carbon steel, they require higher levels of both Zn<sup>2+</sup> and phosphonate. But, the disposal of zinc salts in wastewaters at higher levels has become unacceptable [7]. Owing to these strict environmental restrictions on industrial wastewater disposal, research has been progressed in the direction to minimize the concentration of Zn<sup>2+</sup> in the inhibitor formulations. An effective method to handle this task is to add another non-toxic component of either organic or inorganic nature, which can synergistically act along with phosphonate and Zn<sup>2+</sup> and bring about effective corrosion inhibition at relatively lower concentrations of zinc ions. A few of such ternary inhibitor formulations were reported in literature [8-9]. The authors of the present study have considered a new non-toxic organic compound namely, uric acid as a new synergist to the combination of Nitrilotris(methylenephosphonic acid) (NTMP) and zinc ions for corrosion control of carbon steel. Through their study based on gravimetric measurements, they observed that uric acid acts as an excellent synergist to the combination of NTMP and zinc ions. In the present study, the protective film formed on carbon steel by immersing in the aqueous solution containing the above ternary inhibitor formulation was analyzed by electrochemical and surface analytical studies. The main objective of the present study is to analyze the surface film formed on carbon steel by the inhibitor formulation containing NTMP, Zn<sup>2+</sup> and uric acid using electrochemical and surface analytical studies. The entire study was conducted using 200 ppm of NaCl as the control at pH = 7.0. The study is confined to carbon steel.

## II. EXPERIMENTAL

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 – 0.04 to 0.07 %, S – 0.03 to 0.04 %, Mn – 0.3 to 0.5 % and the rest iron. Prior to the tests, the specimens were polished to mirror finish with emery polishing papers respectively, washed with distilled water, degreased with acetone and dried. NTMP (C<sub>3</sub>H<sub>12</sub>NO<sub>9</sub>P<sub>3</sub>), Zinc sulphate (ZnSO<sub>4</sub>.7H<sub>2</sub>O), uric acid (C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O<sub>3</sub>) and other reagents were analytical grade chemicals. An aqueous solution consisting of 200 ppm of NaCl has been used as the control throughout the study. 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. Polarization curves were recorded in the potential range of  $-1000$  to  $+200$  mV with a resolution of 2 mV. 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. XPS measurements of the surface films were carried out with Kratos analytical photoelectron spectrometer model AXIS 165 with monochromated Al K X-ray source (1486.6 eV) operated at 100 W. FTIR spectra were recorded using FTIR spectrophotometer from Thermo Electron Corporation, USA, model Nexus 670. Scanning electron microscopy (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. AFM topographical images were realised using Dimension 3100 (Nanoscope-IV) Atomic Force Microscope in contact mode with commercial  $\text{Si}_3\text{N}_4$  cantilever.

### III. RESULTS AND DISCUSSION

#### A. Potentiodynamic polarisation studies

Potentiodynamic polarisation curves of carbon steel immersed in control in the absence and presence of various inhibitor formulations are shown in Fig. 1. The corresponding Tafel parameters are listed in Table 1. Corrosion current density ( $I_{\text{corr}}$ ) values are found to be less in case of all the tested formulations. However, lowest value of  $I_{\text{corr}}$  is recorded in presence of the ternary inhibitor system, corresponding to an inhibition efficiency of 86.29 %. It indicates that the ternary formulation is able to effectively control corrosion of carbon steel. Corrosion potential ( $E_{\text{corr}}$ ) is found to be shifted in the cathodic direction to the extent of 40 mV vs. Ag/AgCl in presence of the inhibitor system. Further, the shift in cathodic Tafel slope is greater than that in the anodic Tafel slope. Hence, the ternary formulation is a mixed inhibitor, predominantly cathodic in nature.

#### B. Impedance studies

Results of impedance measurements recorded in the form of Nyquist plots are shown in Fig. 2. The corresponding impedance parameters are listed in Table 2, which were obtained by fitting the impedance data to the equivalent circuit shown in Fig. 3. The charge transfer resistance of the interface is  $2.232 \text{ k } \Omega \text{ cm}^2$  in case of the control. It is enormously increased to  $14.29 \text{ k } \Omega \text{ cm}^2$  in presence of the ternary inhibitor. Constant phase element of the double layer ( $\text{CPE}_{\text{dl}}$ ) is decreased from  $71.08 \mu\text{F/cm}^2$  in case of the control to  $8.29 \mu\text{F/cm}^2$  in presence of the inhibitor. These results indicate that there is significant modification of interface at the metal surface in presence of the inhibitor formulation. The film resistance is also found to be more in presence of the inhibitor. The significant decrease in  $\text{CPE}_{\text{film}}$  and increase in  $n_{\text{film}}$  also support that there is formation of a protective film on the surface in presence of the inhibitor formulation.

#### C. Surface analysis by X-ray photoelectron spectroscopy (XPS)

The XPS survey spectrum of the surface film formed on carbon steel in presence of the ternary inhibitor formulation is shown in Fig. 4. The corresponding deconvolution spectra of the elements namely Fe, Zn, P, N, C and O (not shown here) are considered for the interpretation. The Fe  $2p_{3/2}$  peak is observed at 711.1 eV. Zn  $2p_{3/2}$  peak is observed at 1022.1 eV and Zn  $2p_{1/2}$  at 1045.2 eV. Two P 2p peaks are observed one at 132.9 eV and another at 134.2 eV. The deconvolution spectrum of N 1s has two peaks one each at 398.2 eV and 400.0 eV. C 1s spectrum has peaks at 284.6 eV, 286.3 eV and 288.5 eV. O 1s spectrum shows one peak at 531.2 eV and another peak at 532.7 eV. The shifts in the binding energy values of electrons of these elements from their characteristic binding energies and the literature reporting the XPS analysis of the phosphonate-based surface films on carbon steel have directed to the following inferences. Iron is present as ferric ion in the complex formed by the inhibitor molecules namely NTMP and UA. Zinc is present as  $\text{Zn}^{2+}$  in the form of both complex as well as  $\text{Zn}(\text{OH})_2$ . Presence of NTMP and UA in the surface film is confirmed by the P 2p, N 1s, O 1s and C 1s deconvolution spectra. Based on the XPS analysis, it can be concluded that the protective film consists mainly of  $[\text{Zn}(\text{II})\text{-NTMP-UA}]$  complex,  $\text{Zn}(\text{OH})_2$  and small amounts of oxides/hydroxides of Fe(III).

#### D. Surface analysis by Fourier transform Infrared (FTIR) spectroscopy

FTIR spectrum of surface film on carbon steel immersed in the inhibitor formulation is shown in Fig. 5. The peak due to P=O is shifted from  $1002 \text{ cm}^{-1}$  to  $1055$  and  $1118 \text{ cm}^{-1}$ . The P-OH stretching located at  $930 \text{ cm}^{-1}$  in case of the pure NTMP is not observed in the FTIR of the surface film. These results can be interpreted in terms of interaction between  $\text{P-O}^-$  present in the phosphonate with metallic species, viz., Zn(II) and Fe(III) to form P-O-Zn and P-O-Fe bonds. This inference 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 in the spectrum around  $1336 \text{ cm}^{-1}$  indicates the presence of zinc hydroxide in the surface film. In case of the inhibited specimen, the C=O stretching frequency is observed by multiple absorption bands at  $1631$ ,  $1716$  and  $1734 \text{ cm}^{-1}$ . The small absorption band at  $1456 \text{ cm}^{-1}$  in the FTIR spectrum of the surface film indicates the C=C stretching of the uric acid molecules. The bands at  $2853$  and  $3430 \text{ cm}^{-1}$  in the FTIR of surface film indicate the N-H stretching of uric acid. The band at  $2924 \text{ cm}^{-1}$  in the FTIR of the surface film indicates the C-H stretching of uric acid. Presence of these bands in the surface film indicates the existence of inhibitor molecules, viz., NTMP and uric acid in the surface film. The shifts in the stretching frequencies of various functional groups present in the

inhibitor molecules are resulted due to the involvement of these molecules in the complex formation. The broad and intense band at  $3430\text{ cm}^{-1}$  is contributed by the  $-\text{OH}$  group present in NTMP,  $\text{Zn}(\text{OH})_2$  and possibly traces of ferric hydroxide present in the inhibited film. Thus, the FTIR spectrum of the surface film formed in presence of the inhibitor formulation infers the presence of  $[\text{Zn}(\text{II})\text{-NTMP-UA}]$  complex,  $\text{Zn}(\text{OH})_2$  and small amounts of oxides and hydroxides of  $\text{Fe}(\text{III})$ .

E. Surface morphological and topographical studies

Fig. 6 shows the high resolution SEM images of carbon steel surface immersed in control in the absence and presence of the inhibitor formulation, NTMP (40 ppm) +  $\text{Zn}^{2+}$  (15 ppm) + UA (20 ppm). Fig. 6a 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. Fig. 6b shows the morphological features of the inhibited surface. The inhibited surface does not contain the corrosion products observed in case of the control alone. Instead, the surface is completely covered by a uniform protective film. From the SEM analysis it can be inferred that the inhibitor film exhibits good protective properties for carbon steel in low chloride media. Fig. 7 shows the AFM topographical images of the surfaces of carbon steel immersed for 7 days in the control in the absence and presence of the inhibitor formulation. A severely corroded surface topography (Fig. 7a) with high surface roughness is observed after immersion in the control in the absence of the inhibitor. The microstructure of the surface shows several smaller and larger corrosion product deposits. In presence of the inhibitor formulation, the surface is found to possess a homogeneous topography (Fig. 7b) with low dispersion in height and without any predominant peak structure. The enormous decrease in roughness in case of the inhibitor system, infers greater smoothness and homogeneity of the surface film produced by the inhibitor formulation and the absence of any corrosion product deposits. The results of the surface topographical studies strongly support the inferences drawn above in the electrochemical studies, in favour of the protective nature of the surface film produced by the inhibitor formulation.

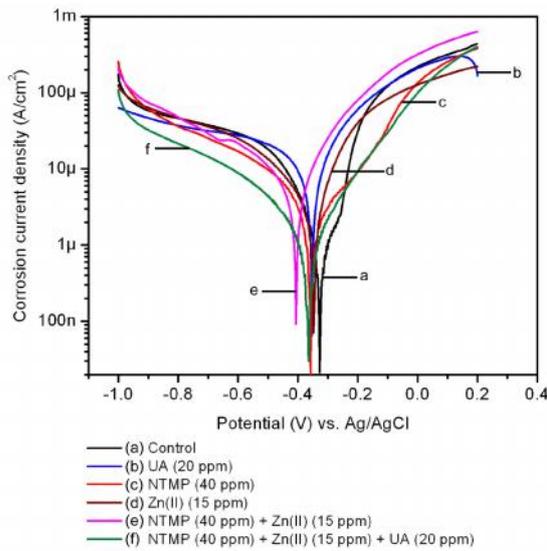


Figure 1. Potentiodynamic polarisation curves for carbon steel in various aqueous environments

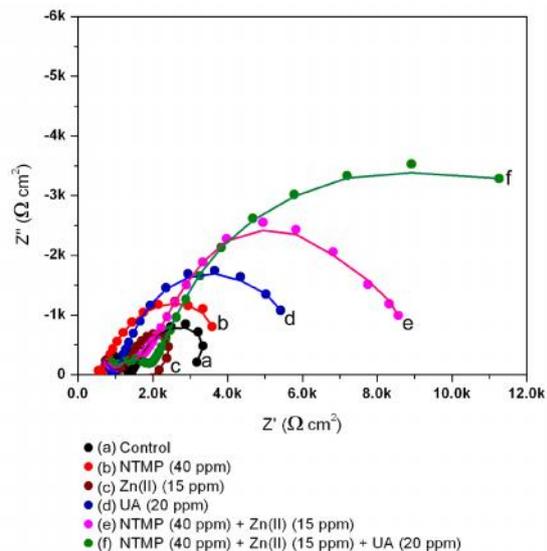


Figure 2. Nyquist plots for carbon steel in various aqueous environments

TABLE I. TAFEL PARAMETERS FOR CARBON STEEL IN CONTROL SOLUTION IN THE ABSENCE AND PRESENCE OF VARIOUS INHIBITOR FORMULATIONS

Concentration (ppm)			Tafel parameters				Inhibition efficiency, $\text{IE}_p$ (%)
NTMP	$\text{Zn}^{2+}$	UA	$E_{\text{corr}}$ (mV) vs. Ag/AgCl	$I_{\text{corr}}$ ( $-\text{A cm}^{-2}$ )	$a$ ( $\text{mV dec}^{-1}$ )	$c$ ( $\text{mV dec}^{-1}$ )	
0	0	0	-325.8	12.33	234	711	-
40	0	0	-358.2	6.03	193	659	51.09
0	15	0	-347.9	8.83	252	605	28.38
0	0	20	-353.1	9.91	221	613	19.63
40	15	0	-407.3	6.05	184	524	50.93
40	15	20	-366.1	1.69	203	389	86.29

TABLE II. IMPEDANCE PARAMETERS FOR CARBON STEEL IN CONTROL SOLUTION IN THE ABSENCE AND PRESENCE OF VARIOUS INHIBITOR FORMULATIONS

Concentration (ppm)			Impedance parameters						Inhibition efficiency, IE <sub>i</sub> (%)
NTMP	Zn <sup>2+</sup>	UA	R <sub>ct</sub> (k cm <sup>2</sup> )	CPE (μF/cm <sup>2</sup> )	n	R <sub>film</sub> (k cm <sup>2</sup> )	CPE <sub>film</sub> (nF/cm <sup>2</sup> )	n <sub>film</sub>	
0	0	0	2.232	71.08	0.732	1.332	5.896	0.624	–
40	0	0	3.653	34.95	0.731	0.346	6.197	0.652	38.90
0	15	0	1.588	54.75	0.679	0.854	15.92	0.542	–40.55
0	0	20	5.673	24.59	0.685	0.894	5.184	0.759	60.65
40	15	0	8.421	21.44	0.732	1.532	6.254	0.690	73.49
40	15	20	14.29	8.29	0.852	2.303	2.651	0.839	84.38

F. Mechanism of corrosion inhibition

When NTMP, Zn<sup>2+</sup> and UA are added to the aqueous solution, both NTMP and UA react with Zn<sup>2+</sup> to form a ternary complex, [Zn<sup>2+</sup>-NTMP-UA]. 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 heteroleptic complex, [Fe(III), Zn(II)-NTMP-UA] covers the anodic sites and controls the anodic reaction of the corrosion process [10].

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.

Thus, NTMP, Zn<sup>2+</sup> and UA 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 heteroleptic complex, [Fe(III),Zn(II)-NTMP-UA]. Each of these constituents contributes itself to make the film highly protective.

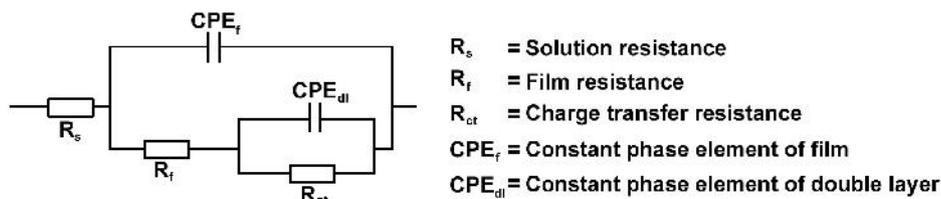


Figure 3. Electrochemical equivalent circuit used to fit the impedance data

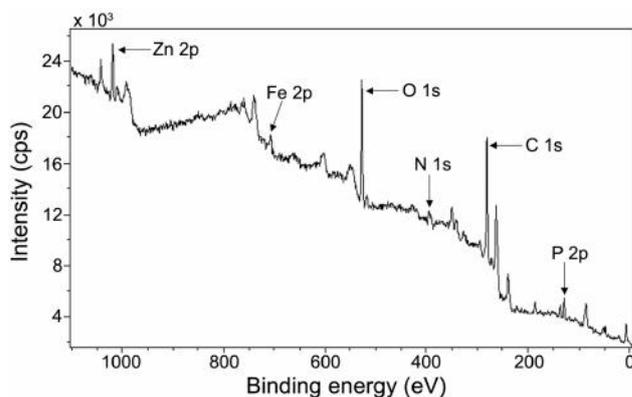


Figure 4. XPS survey spectrum of the surface film formed in presence of the inhibitor formulation

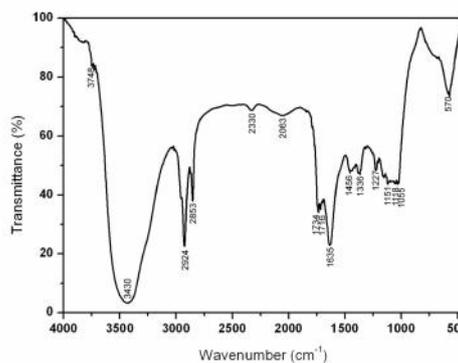


Figure 5. FTIR spectrum of the surface film formed in presence of the inhibitor formulation

IV. CONCLUSIONS

The surface film formed on carbon steel by NTMP, zinc ions and uric acid, is found to be highly protective against corrosion of carbon steel in low-chloride aqueous environment. The inhibitor formulation acts as a mixed type inhibitor controlling both the anodic and cathodic reactions. Significant modification of the metal/solution interface occurs through the formation of a protective film in presence of the inhibitor formulation. The protective film consists of mainly [Zn(II)-NTMP-UA] 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 to make the surface film protective.

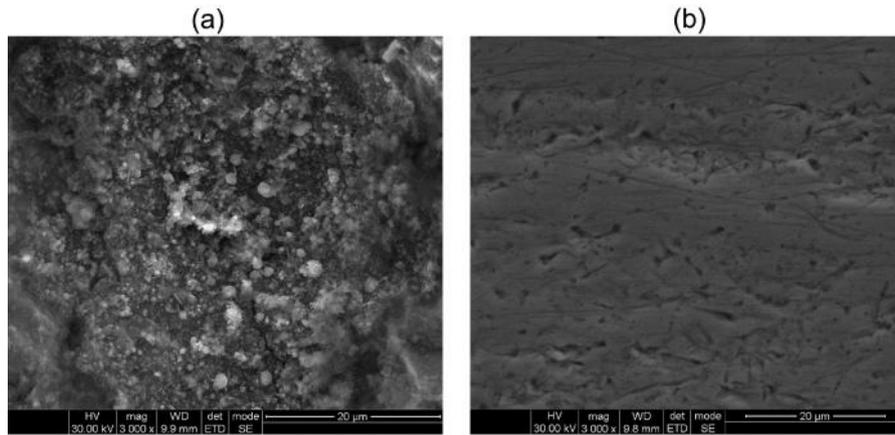


Figure 6. High resolution SEM images of surface film on carbon steel in control (a) in the absence and (b) in presence of the inhibitor formulation

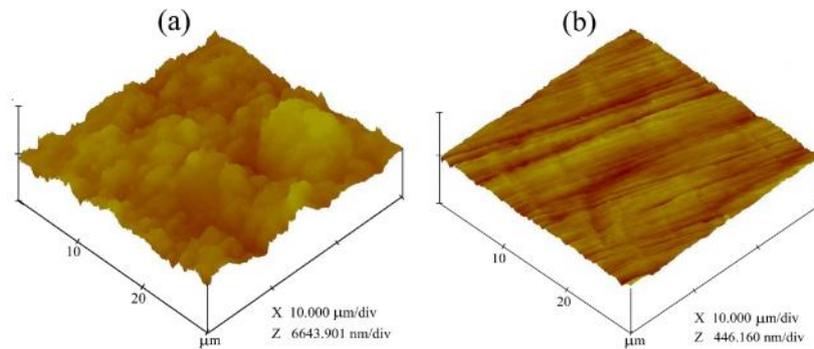


Figure 7. AFM images of surface film on carbon steel in control (a) in the absence and (b) in presence of the inhibitor formulation

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