Indian Journal of Chemical Technology
Vol. 12, November 2005, pp. 629-634

Synergistic effect of NTMP, Zn^{2+} and ascorbate in corrosion inhibition of carbon steel

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Received 12 January 2005; revised received 15 August 2005; accepted 9 September 2005

Nitrilotris(methylenephosphonic acid) (NTMP) inhibits corrosion of carbon steel in presence of Zn^{2+} . However, in order to make the inhibitor more environment friendly, it is necessary to reduce the levels of Zn^{2+} or phosphonate or both by introducing an environment friendly organic salt as a second synergist. In this paper, the inhibitive action of ascorbate as a second synergist in the presence of relatively low concentrations of NTMP and Zn^{2+}, is presented. Addition of just 25 ppm of ascorbate to 20 ppm each of NTMP and Zn^{2+}, at pH=7, increased the inhibition efficiency markedly from 35 to 95%. In the pH range of 6-4, the concentration of ascorbate required to bring up the inhibition efficiency to 94%, is only 10 ppm. However, the alkaline region demanded relatively higher concentration of ascorbate. This ternary system is quite effective in a wide pH range, 4-10. This is the uniqueness of this new synergistic formulation. Potentiostatic polarization studies indicated that this synergistic formulation acts as a mixed inhibitor, predominantly cathodic in nature. A large increase in charge transfer resistance and also a decrease in double layer capacitance of the surface film, were observed from a.c. impedance studies. X-ray photoelectron spectrum of the surface film indicated the presence of the elements, *viz*., P, O, N, C, Zn and Fe in the film. The shifts in binding energies of these elements indicated the presence of oxides and hydroxides of iron and zinc as well as complexes of Fe(III) and Zn(II) with phosphonate and ascorbate. The reflection absorption FTIR spectrum of the surface film also supported the formation of insoluble complexes of phosphonate and ascorbate with metal ions as well as presence of $Zn(OH)_2$ on the metal surface. A suitable mechanism of corrosion inhibition is proposed, which corroborates all the above experimental results.

Keywords: Synergism, ascorbate, carbon steel, NTMP, corrosion inhibition

IPC Code: C23F11/00

Nitrilotris(methylenephosphonic acid) (NTMP) in combination with Zn^{2+} is a well-known inhibitor for corrosion of carbon steel in nearly neutral aqueous environment[1,2]. In view of the environmental guidelines restricting the concentration of Zn^{2+} in the industrial wastewaters, it is necessary to reduce the concentration of Zn^{2+} in the inhibitor formulations. For this purpose, the addition of a second synergist to NTMP – Zn^{2+} combination has been thought of and studies on environment friendly organic compounds like oxalic acid, phthalic acid anhydride as second synergist, have been reported[3,4]. In the present study, sodium ascorbate is chosen as a second synergist to NTMP – Zn^{2+} combination. It is an environment friendly organic compound containing five hydroxyl groups and one carboxyl ($-COO^-$) group in each ascorbate ion. This compound is known to form complexes with metal ions like Fe^{3+}. Its passivating properties have also been reported[5]. These properties of ascorbate favoured in selecting it as a second synergist. Results of weight-loss studies, potentiostatic polarization studies, A.C. impedance studies and surface examination studies, *viz*., X-ray photoelectron spectroscopic studies, Fourier Transform infrared spectroscopic studies of the inhibited surface film, have proved ascorbate as an excellent second synergist to the NTMP – Zn^{2+} system.

Experimental Procedure

Carbon steel specimens (0.1-0.2% C, 0.02-0.03% S, 0.04-0.05% P, 0.4-0.5% Mn and the balance iron) of the dimensions 3.5×1.5×0.2 cm were used for the weight-loss and reflection absorption FTIR spectroscopic studies. For surface examination studies by XPS, the same samples of dimensions 1 cm×1cm× 1mm, were used.

The polished and weighed carbon steel specimens in duplicate, were immersed in 100 mL solutions containing different concentrations of inhibitor and at different pH values, for a period of 7 days. Then the specimens were reweighed after washing, degreasing

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*For correspondence (E-mail: bva@nitw.ernet.in) with acetone and drying. Shimadzu AY 120 balance (accuracy, 0.1 mg), was used for weighing the specimens before and after immersion in various environments. Accuracy in weighing of 0.0001 g and in surface area measurement of 0.1 cm^2 as recommended by ASTM G31 of ASTM Standards[6] was followed. Period of immersion was measured accurately to 0.1 h in view of the lengthy immersion period (168 h). Under these conditions, the relative standard error in corrosion rate determination is of the order of 1% or less for an immersion period of 7 days[7].

Electrochemical studies were carried out using Solatron SI 1280 B electrochemical measurement system. Carbon steel rod encapsulated in teflon with an exposed cross section of 0.5 cm diameter, was used as working electrode. Saturated calomel electrode and platinum electrode were used as the reference and counter electrodes, respectively.

XPS studies were carried out with Kratos analytical photoelectron spectroscopy model AXIS 165 with Mg K_α radiation (1253.6eV) and resolution of 0.1 eV. The instrument has been calibrated by using Au foil for which the characteristic binding energy value of 4f electron is 84.1 eV. FTIR spectra were recorded using Shimadzu FTIR – 8201 PC spectrophotometer.

Results and Discussion

Weight-loss studies

Corrosion inhibition efficiency of the ternary system, NTMP (20 ppm) – Zn^{2+} (20 ppm) – ascorbate as a function of pH at various concentrations of ascorbate is presented in Fig. 1. Without any ascorbate and at such low levels of 20 ppm each of NTMP and Zn^{2+}, the system functions efficaciously at pH=4. With increase in pH from 4-7, the efficiency is drastically reduced. At pH=8, acceleration of corrosion is observed. By the addition of 25 ppm of ascorbate to this system consisting of 20 ppm each of NTMP and Zn^{2+}, at pH=7, the inhibition efficiency is increased from 35-95%. In fact, at pH=6, addition of ascorbate as less as 10 ppm makes the inhibitor formulation effective. However, the required concentration of ascorbate increases with increase in pH, reaching 75 ppm at pH=10. This formulation is very effective with 50 ppm of ascorbate in a wide pH range of 5-9, which includes the pH range of cooling water systems.

Potentiostatic polarization studies

The potentiostatic polarization curves are presented in Fig. 2. The corresponding corrosion parameters are listed in Table 1. In the case of ternary system con-

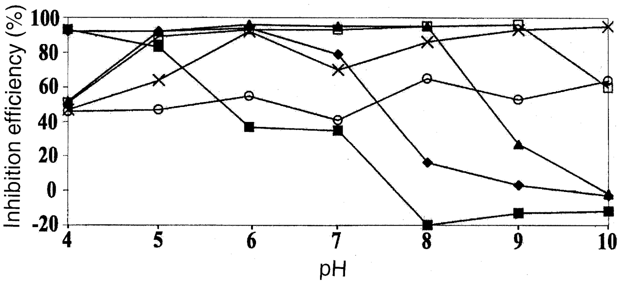

Fig. 1—Corrosion inhibition efficiency of the ternary system as a function of pH NTMP (20 ppm) + Zn^{2+} (20 ppm) + ascorbate (varying) [Ascorbate]: ■ 0 ppm ♦ 10 ppm ▲ 25 ppm □ 50 ppm x 75 ppm ○ 100 ppm

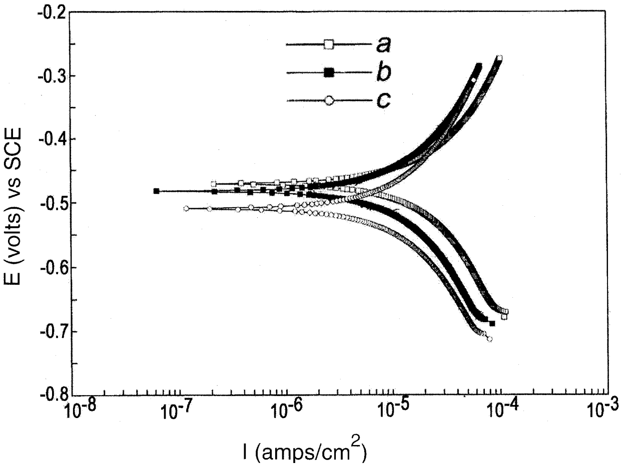

Fig. 2—Potentiostatic polarization curves for carbon steel in different aqueous environments. (a) Cl^- (60 ppm) (b) Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) (c) Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) + ascorbate (25 ppm)

Table 1—Corrosion parameters obtained from potentiostatic polarization studies

Environment	E_{corr} (mV)	I_{corr} (μA/cm^2)	b_a (mV/dec)	b_c (mV/dec)
Cl^- (60 ppm)	-468	6.97	93	112
Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm)	-473	3.91	65	111
Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) + ascorbate (25 ppm)	-516	2.74	81	53

taining 20 ppm of NTMP, 20 ppm of Zn^{2+} and 25 ppm of ascorbate, corrosion potential is shifted by 48 mV towards cathodic side. This shift is significant when compared with the shift of only 5 mV for the binary system containing 20 ppm of NTMP and 20 ppm of Zn^{2+}. There is a decrease in corrosion current by 4.23 $\mu A/cm^2$, which is also significant when compared with that of the binary system. In case of the ternary system, though there is a shift in both the anodic and cathodic tafel slopes, the shift in cathodic tafel slope is much higher. This clearly indicates that the ternary system acts as a mixed inhibitor, predominantly cathodic in nature.

A.C. impedance studies

Impedance data of carbon steel, immersed in various environments, in the form of nyquist plots are shown in Fig. 3. The plots are not perfect semicircles. Deviations from the ideal semicircles can be attributed to the inhomogeneties of the surface as well as due to mass transport process[8]. The impedance diagrams plotted in bode coordinates are shown in Fig. 4. The impedance parameters are listed in Table 2. An increase in charge transfer resistance by 615 Ω and the decrease in double layer capacitance by 253 μF in the presence of ternary inhibitor formulation, when compared with the blank solution, indicates that there is formation of a highly nonporous protective film in the presence of ternary inhibitor formulation and hence the observed inhibitive effect[9].

Table 2—Impedance parameters obtained from A.C. impedance studies

Environment	R_{ct} (Ω)	C_{dl} (μF)
Cl^- (60 ppm)	1535	309
Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm)	2288	214
Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) + ascorbate (25 ppm)	2150	56

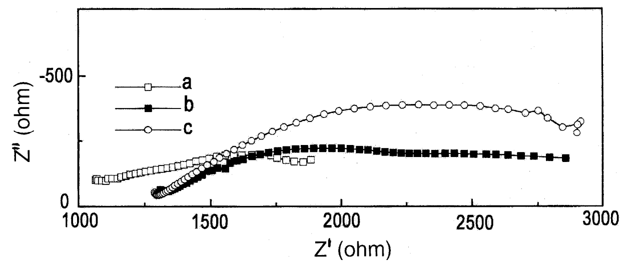

Fig. 3—Nyquist plots for carbon steel in different aqueous environments. (a) Cl^- (60 ppm) (b) Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) (c) Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) + ascorbate (25 ppm)

X-ray photoelectron spectra

The X-ray photoelectron spectrum (XPS) of the surface film in presence of inhibitor is shown in Fig. 5. The X-ray photoelectron spectra of individual elements namely P, O, N, C, Zn and Fe present in the surface film in presence of the ternary inhibitor system, are shown in Fig. 6.

The XPS of phosphorus (Fig. 6a) shows two broad peaks overlapped at a binding energy of 133.07 eV. These peaks are shifted from their characteristic binding energies of 133 eV for P $2p_{3/2}$ and 134 eV for P $2p_{1/2}$. In the literature, it was reported[10-12] that the binding energies for P 2p in the surface film on iron or steel immersed in the solutions containing phosphonates are in the range between 132.9 and 133.8 eV. Hence, the observed peaks at 133.07 eV can be

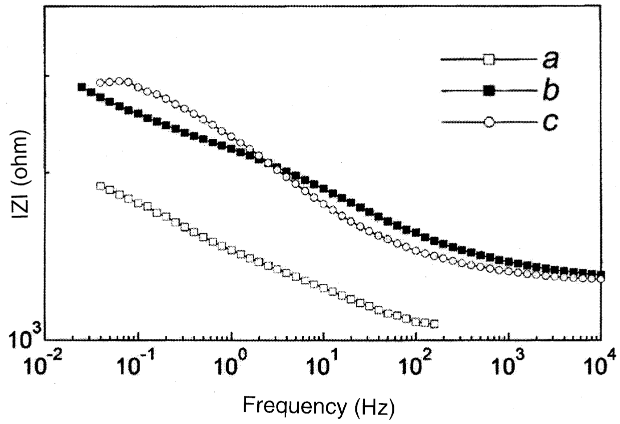

Fig. 4—Bode plots for carbon steel in different aqueous environments. (a) Cl^- (60 ppm) (b) Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) (c) Cl^- (60 ppm) + NTMP (20 ppm) + Zn^{2+} (20 ppm) + ascorbate (25 ppm)

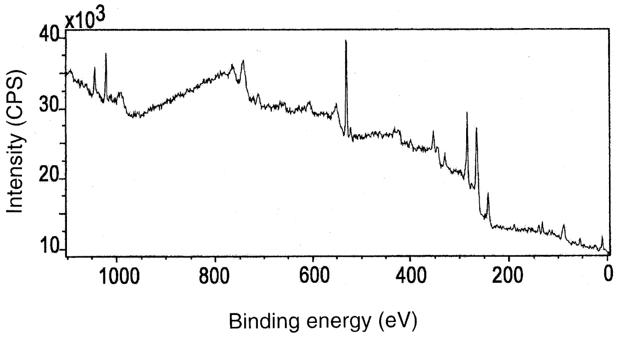

Fig. 5—X-ray photoelectron spectrum of the surface film on carbon steel in the presence of ternary inhibitor system

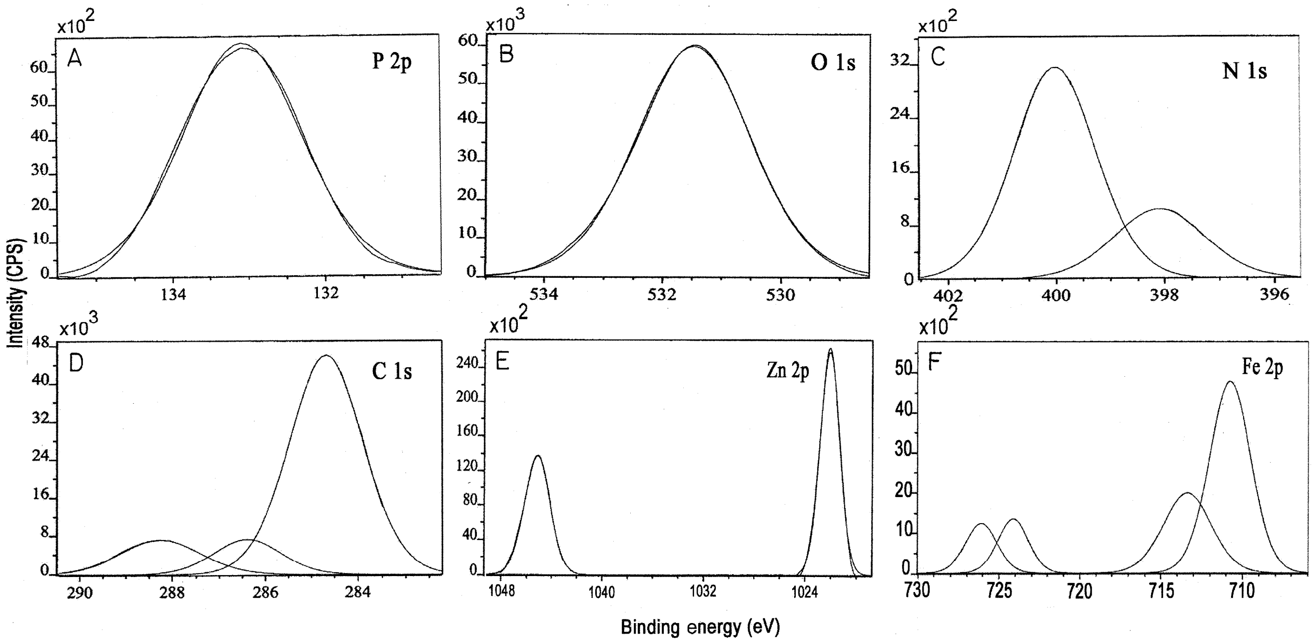

Fig. 6—X-ray photoelectron spectra of individual elements of the surface film in the presence of ternary inhibitor system. (a) P 2p (b) O 1s (c) N 1s (d) C 1s (e) Zn 2p and (f) Fe 2p

attributed to the presence of NTMP molecules on the surface, probably by the involvement in bond formation with the surface atoms.

The O 1s spectrum (Fig. 6b) shows two overlapped peaks at 531.5 eV shifted from 531.0 eV, which is characteristic binding energy value for elemental oxygen. Asami *et al.*[13] observed the O 1s peak at 531.5 eV and interpreted it due to the oxygen with a kind of Fe–O–H bond. This was supported by McIntyre & Zetaruk[14]. According to them, OH^- peak of α-FeOOH appears at 531.4 ± 0.2 eV. Fang *et al.*[15] reported that the O 1s peak observed at 531.3 eV can be attributed to the complex compound formed by oxygen of phosphonate group with iron. Hence, the O 1s peaks observed in the present studies can be attributed both to the presence of α-FeOOH on the surface and to the involvement of oxygen of NTMP in the complex formation with iron.

The N 1s peak (Fig. 6c) is shifted from 398 eV, characteristic binding energy for elemental nitrogen, to give two peaks, one at 398.1 eV and another one at 400 eV. In case of the former peak, the shift is negligible. The peak at 400 eV can be attributed to the NTMP molecules adsorbed on the metal surface. Ochoa *et al.*[16] reported that the N 1s peak observed at 400 eV is due to amine adsorbed on the metal surface.

The XPS of carbon (Fig. 6d) shows three peaks, one each at 284.7, 286.4 and 288.2 eV, respectively, shifted from 285 eV, characteristic binding energy for elemental carbon. The first peak is essentially accounted for by the presence of inhibitor molecules on the surface[16]. Meneguzzi *et al.*[17] have reported, that, the peak at 286.8 eV can be ascribed to carbon atoms coupled singly to oxygen atoms (C-O) or to nitrogen atoms (C–N, C=N). Hence, the peak observed at 286.4 eV in the present studies is due to the bond formed between either nitrogen of C-N in NTMP or oxygen of C-O in ascorbate or both with the metal. The peak observed at 288.2 eV may be due to different carbon environments present in ascorbate ion, other than the carbon of C-O involved in bond formation with the metal.

In the Zn 2p spectrum (Fig. 6e), the $2p_{3/2}$ peak is shifted to 1022.1 from 1021 eV, characteristic binding energy for the elemental Zn $2p_{3/2}$[18]. Aramaki[19] has reported a peak of Zn^{2+} (hydroxide) appearing at 1022.7 eV. Hence, the peak observed at 1022.1 eV in the present study indicates the presence of $Zn(OH)_2$ on the surface. This shift may also be due to the involvement of Zn(II) in the complex formation with inhibitor molecules. This is further supported by the shift of Zn $2p_{1/2}$ peak to 1045.1 eV from 1044 eV, characteristic binding energy for Zn $2p_{1/2}$[18].

In the Fe 2p spectrum (Fig. 6f), the peak due to $2p_{3/2}$ electron is shifted from 707 eV, characteristic binding energy of Fe $2p_{3/2}$ to give two peaks, one each at 710.8 and 713.4 eV. The peak of Fe $2p_{3/2}$ obtained at 710.4 eV, can be ascribed[20] to the presence of Fe^{3+}, with a small contribution of the Fe-phosphonate complex. Also, a peak at 711 eV is attributable[20] to FeOOH. Nakayama and Akira[21] reported that the peak at 711 eV is attributable to ferric compounds such as ferric oxides. Narmada[22] reported that Fe $2p_{3/2}$ peak was shifted from 707 to 713.9 eV and inferred that iron exists in its higher oxidation state of +3 in the surface film, in the form of $Fe_2O_3.H_2O$ or $Fe_3O_4.H_2O$. Hence, the two peaks observed at 710.8 and 713.4 eV in case of Fe $2p_{3/2}$ in the present studies can be attributed to the presence of Fe^{3+} in the surface film in the form of oxides/hydroxides, particularly Fe_2O_3, Fe_3O_4 and α-FeOOH. It can also be attributed to the involvement of Fe(III) in the complex formation with NTMP and ascorbate. The Fe $2p_{1/2}$ peak is shifted from 721 eV, characteristic binding energy, to give two peaks, one each at 724.1 and 726.1 eV. The peak of Fe $2p_{1/2}$ electron, observed at 724.1 eV is attributable[23] to Fe_2O_3 on the surface. The peaks observed in the case of Fe $2p_{1/2}$ electron in the present studies support the interpretation given above based on the shifts in the case of Fe $2p_{3/2}$ electron that iron exists in the Fe^{3+} state, in the form of oxides/hydroxides and involves in complex formation with phosphonate and ascorbate.

Thus, the XPS are supportive of the formation of $Zn(OH)_2$, oxides/hydroxides of iron, specifically, Fe_2O_3, Fe_3O_4 and α-FeOOH and complexes of Fe(III) and Zn(II) with NTMP as well as ascorbate, in the form of protective film on the metal surface.

FTIR spectra

The reflection absorption FTIR spectrum of the surface film in the presence of inhibitor is shown in Fig. 7. This spectrum shows a shift in P–OH stretching frequency to 1127 from 941 cm^{-1}, observed in case of pure NTMP (FTIR spectra of pure NTMP and pure ascorbic acid, recorded using the same instrument are not shown here). This result was interpreted[24] by interactions of free P–O^- with metallic species, *viz*., Zn(II) and Fe(III) to form P–O–metal bonds. The C=O stretching frequency for pure ascorbic acid is 1676 cm^{-1}, which is shifted to 1630 cm^{-1} in the spectrum of the surface film. This can be interpreted in terms of the involvement of ascorbate in the complex formation with Fe(III) and Zn(II). A small peak at 1321 cm^{-1} indicates the formation of $Zn(OH)_2$ on the surface[25]. A peak around 797 cm^{-1} indicates the presence of α-FeOOH in the surface film[26]. A broad band in the range of 3000-3600 cm^{-1} can be assigned to the presence of superficial adsorbed water and stretching mode of O–H in the ascorbate ion or in NTMP. Gunasekaran and Chauhan[27] reported that, broad bands in the range of 3000–3500 cm^{-1} can be assigned to the presence of adsorbed water, stretching mode of an O–H and/or N–H.

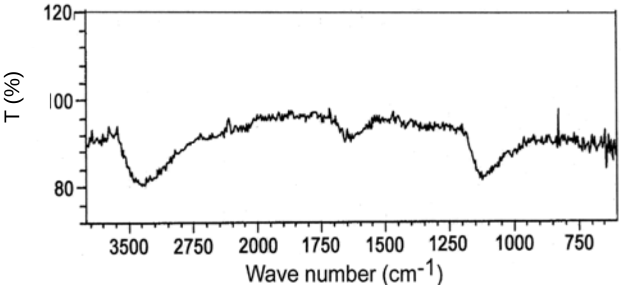

Fig. 7—Reflection absorption FTIR spectrum of the surface film in presence of ternary inhibitor system

Thus, the FTIR spectrum of the surface film indicates the involvement of NTMP and ascorbate in the complex formation with Fe(III) and Zn(II) as well as the presence of $Zn(OH)_2$ and α-FeOOH on the metal surface.

Mechanism of corrosion inhibition

In order to explain all the above results, the following mechanism of corrosion inhibition is proposed,

1 Before immersion of carbon steel in the aqueous environment consisting of Cl^-, NTMP, Zn^{2+} and ascorbate, there is formation of complexes, *viz*., Zn^{2+}-NTMP, Zn^{2+}-ascorbate, Zn^{2+}-NTMP-ascorbate. These complexes are in equilibrium with free Zn^{2+}, NTMP and ascorbate ions.

2 When carbon steel is immersed in this environment,

(i) There is diffusion of all the complexes mentioned above from the bulk of electrolyte to the metal surface and they complex further with Fe(III) available on the metal surface due to initial corrosion.

(ii) Free Zn^{2+} ions diffuse to the metal surface, combine with OH^- ions available at the cathodic sites due to oxygen reduction and form insoluble $Zn(OH)_2$. This controls the cathodic reaction.

3 The film formed on the surface of carbon steel consists of oxides/hydroxides of iron and zinc. It is also likely to comprise complexes of Fe(III) and Zn(II) with NTMP as well as ascorbate. XPS and reflection absorption FTIR spectrum of the

surface film suggest the formation of these complexes and the presence of $Zn(OH)_2$ in the surface film. These complexes fill the pores of the oxide/hydroxide film and make it nonporous and protective.

4 With increase in pH, the required concentration of ascorbate increases. Higher concentration of ascorbate is necessary to offset the effect of aggressive OH^- ions in destabilizing the protective film and to make the film stable at higher pH values.

Conclusion

From the results of the study the following conclusions can be drawn,

1 Ascorbate has an outstanding role as a second synergist in the NTMP-Zn^{2+}-ascorbate system to inhibit the corrosion of carbon steel.

2 The ternary system, NTMP (20 ppm) – Zn^{2+} (20 ppm) – ascorbate (5-75 ppm) is effective in a wide pH range such as 4-10.

3 The required concentrations of both NTMP and Zn^{2+} are reduced and ascorbate, which is environment friendly, is needed at very low concentrations. Thus, this new inhibitor formulation is more environment friendly.

4 Both NTMP and ascorbate form stable complexes with metal ions, *viz*., Fe(III) as well as Zn(II) on the metal surface.

5 The ternary system acts as a mixed inhibitor, predominantly cathodic in nature.

6 The protective film consists of α-FeOOH, Fe_2O_3, Fe_3O_4 and possibly complexes of Fe(III) and Zn(II) with NTMP as well as ascorbate.

Acknowledgement

One of the authors, Mr S Srinivasa Rao is grateful to the management and Principal of the V R Siddhartha Engineering College for sponsoring him for Ph. D. programme at NIT, Warangal.

References

1 Gonzalez Y, Lafont M C, Pebere N, Chatainier G, Roy J & Bouissou T, *Corros Sci*, 37 (1995) 1823.
2 Rajendran S, Appa Rao B V & Palaniswamy N, *Bull Electrochem*, 12 (1996) 15.
3 Kubicki J, Kuczkowska S & Falewicz P, *Kot J Pr Nauk Inst Technol Nawozow Miner*, 27 (1985) 123.
4 Falewicz P & Kuczkowska S, *Werkst Korros*, 43 (1992) 215.
5 Schumacher P D, *Proc Am Power Conf*, 46 (1984) 985.
6 ASTM Standard G31-72, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (Reapproved 1990), Annual Book of ASTM Standards, 0302 (Philadelphia, PA: ASTM, 1990).
7 Freeman R A & Silverman D C, *Corrosion*, 48 (1992) 463.
8 Juttner K, *Electrochim Acta*, 35 (1990) 150.
9 Bonnel A, Dabosi F, Deslovis C, Duprat M, Keddam M & Tribollet B, *J Electrochem Soc*, 130 (1983) 753.
10 Koudelka M, Sanchez J & Augustynski J, *J Electrochem Soc*, 129 (1982) 1186.
11 Moriarty B E, *Corrosion 89*, New Orleans Convention Center, New Orleans, Louisiana, Paper No.612, 1989.
12 Nakayama N, *Corros Sci*, 42 (2000) 1897.
13 Asami K, Hashimoto K & Shimodaira S, *Corros Sci*, 16 (1976) 35.
14 McIntyre N S & Zetaruk D G, *Anal Chem*, 49 (1977) 1521.
15 Fang J L, Li Y, Ye X R, Wang Z W & Liu Q, *Corrosion*, 49 (1993) 266.
16 Ochoa N, Baril G, Moran F & Pebere N, *J Appl Electrochem*, 32 (2002) 497.
17 Meneguzzi A, Ferreira C A, Pham M C, Delamar M & Lacaze P C, *Electrochim Acta*, 44 (1999) 2149.
18 Christie A B, in *Methods of Surface Analysis – Techniques and Applications*, edited by Walls J M (Cambridge University Press), 1989, 130.
19 Aramaki K, *Corros Sci*, 45 (2003) 451.
20 Pech-Canul M A & Bartolo-Perez P, *Surf Coat Technol*, 184 (2004) 133.
21 Nakayama N & Akira O, *Corros Sci*, 45 (2003) 2075.
22 Narmada P, *Corrosion Inhibition of Mild Steel and Copper in Aqueous Environment using Synergistic Formulations*, Ph.D. Thesis, National Institute of Technology, Warangal, India, 2004.
23 Moulder J F, Stickle W F, Sobol P E & Bomben K D, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Eden Prairie, Minnesota), 1995.
24 Gonzalez Y, Lafont M C, Pebere N & Moran F, *J Appl Electrochem*, 26 (1996) 1259.
25 Sekine I & Hirakawa Y, *Corrosion*, 42 (1986) 272.
26 Raymond Jasinski & Asfaha Iob, *J Electrochem Soc*, 135 (1988) 551.
27 Gunasekaran G & Chauhan L R, *Electrochim Acta*, 49 (2004) 4387.