Environmentally friendly ternary inhibitor formulation based on N,N-bis(phosphonomethyl) glycine

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Studies on an environmentally friendly ternary inhibitor formulation consisting of N,N-bis(phosphonomethyl) glycine (BPMG), with Zn^{2+} ions as primary synergist and ascorbate ions as secondary synergist to protect carbon steel from corrosion in low chloride environment are presented in this paper. Although the binary system, BPMG–Zn^{2+}, is an effective inhibitor, it demands relatively higher concentrations of both BPMG and Zn^{2+}. In the present study, ascorbate was added to lower the effective concentrations of BPMG and Zn^{2+}. The effect of addition of ascorbate is quite significant. While the binary system consisting of 20 ppm of BPMG and 30 ppm of Zn^{2+} accelerated corrosion of carbon steel, addition of just 25 ppm of ascorbate to the above system afforded an inhibition efficiency of 94%. The ternary inhibitor formulation is found to be effective in the pH range 5–11. The uniqueness of this system is that it has shown excellent inhibition efficiency even at pH 11, at which all the other phosphonate based formulations fail. This inhibitor system functions as a mixed inhibitor. The nature and composition of the protective film have been investigated by X-ray photoelectron spectra and Fourier transform infrared (FTIR) spectra. The mechanistic aspects of corrosion inhibition are discussed.

Keywords: Environmentally friendly, BPMG, Ascorbate, Carbon steel, Corrosion inhibition

Introduction

Phosphonates in combination with Zn^{2+} are widely used as corrosion inhibitors for protecting carbon steel in nearly neutral aqueous environments.[1-4] N,N-bis(phosphonomethyl) glycine (BPMG) in combination with Zn^{2+}, is found to be an effective corrosion inhibitor.[5] However, it does require relatively high concentrations of both BPMG and Zn^{2+}. It is of interest to explore whether the inhibition efficiency of this system may be improved at lower concentrations of BPMG and Zn^{2+} by adding an additional synergist, which also should be environmentally friendly. Sodium ascorbate was chosen as the second synergist for the following reasons. The ascorbate ion contains five hydroxyl groups and one carboxyl group and it forms complexes with Fe^{3+}. The present study proved ascorbate as an excellent second synergist to the BPMG–Zn^{2+} system. Results of corrosion inhibition studies in the BPMG–Zn^{2+}–ascorbate system using weight loss, potentiostatic polarisation, and AC impedance, as well as surface analytical studies using X-ray photoelectron spectroscopic (XPS), reflection absorption Fourier transform infrared (FTIR) spectroscopic of the inhibited surface film, are discussed in this paper.

Experimental

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 dimensions 3·5 × 1·5 × 0·2 cm were used for both the weight loss studies and reflection absorption FTIR spectroscopic studies. For surface examination studies by XPS, the same samples of the dimensions 1 × 1 × 0·1 cm were used. In the present work, an aqueous solution consisting of 60 ppm of chloride was used as the control.

Weight loss studies were carried out to observe the synergistic inhibition efficiency of the binary system, BPMG(0–100 ppm) + Zn^{2+}(0–100 ppm). Studies were also carried out on the ternary system containing BPMG(20–30 ppm), Zn^{2+}(20–30 ppm) and ascorbate(0–200 ppm) to establish minimum concentrations of both BPMG and Zn^{2+} for effective inhibition. During these studies, the inhibition efficiencies of ascorbate alone and of BPMG–ascorbate combination were also determined. Variation of the pH was also carried out in the case of the effective ternary inhibitor system. For all these studies, carbon steel specimens were polished finish with 2/0, 3/0 and 4/0 emery polishing papers and degreased with acetone. Then the specimens were weighed and immersed in duplicate, in

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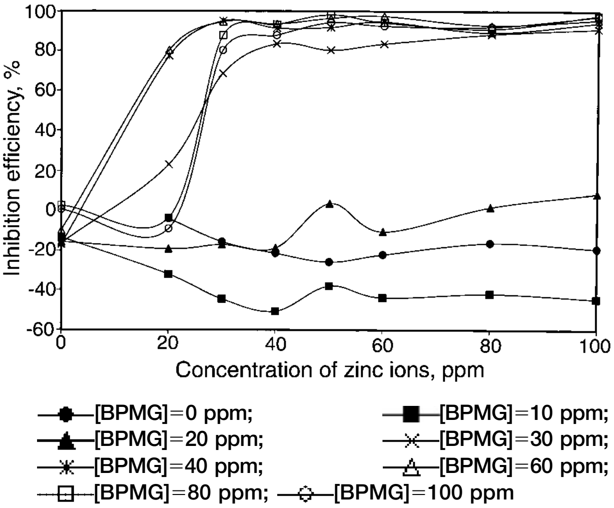


1 Inhibition efficiency as function of concentration of Zn^{2+} for binary system, BPMG+Zn^{2+}

100 mL solutions containing inhibitor formulations of different concentrations, for a period of seven days. The specimens were then reweighed after washing, degreasing and drying. A Shimadzu AY 120 balance, with an accuracy of 0·1 mg, was used for weighing the specimens before and after immersion in the various environments.

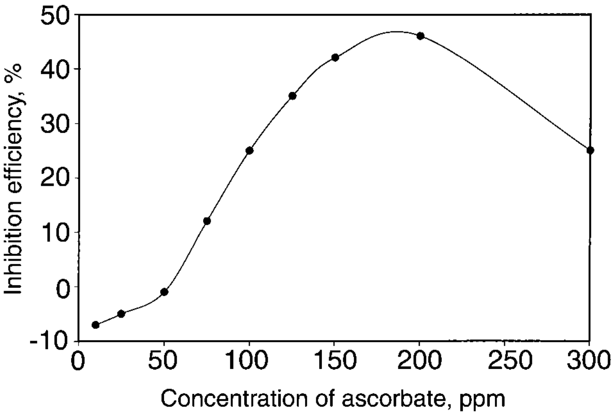
Both the potentiostatic polarisation and AC impedance measurements were carried out using Eco chemie B.Y. Auto lab PG STAT 20 electrochemical system. Carbon steel rod encapsulated in Teflon with an exposed cross-section of 0·5 cm diameter, was used as the working electrode. A saturated calomel electrode and a platinum electrode were used as the reference and counter electrodes respectively. The polarisation studies were carried out in the potential range of ±200 mV from OCP at a sweep rate of 1 mV s^{-1}. The corrosion parameters, i.e. corrosion potential, corrosion current, anodic and cathodic Tafel slopes were so obtained from these experiments. Impedance measurements were carried out over the frequency range of 10000 to 0·01 Hz and the Nyquist plots were recorded. The values of R_{ct}, constant phase element (CPE) and n were calculated from these plots using an appropriate equivalent circuit model.

Surface analysis was carried out by XPS using a Kratos analytical photoelectron spectrometer model AXIS 165 with Mg K_α radiation (1253·6 eV) and sensitivity of 0·1 eV. Fourier transform infrared spectra of pure BPMG and pure ascorbic acid, as well as reflection–absorption FTIR spectra of the inhibited surface film, were recorded using a Shimadzu FTIR 8201 PC spectrophotometer over the range 4000–500 cm^{-1}, with a resolution of 4 cm^{-1}. The average incident angle of beam onto the sample was fixed at 70° and the number of scans was fixed at 100.

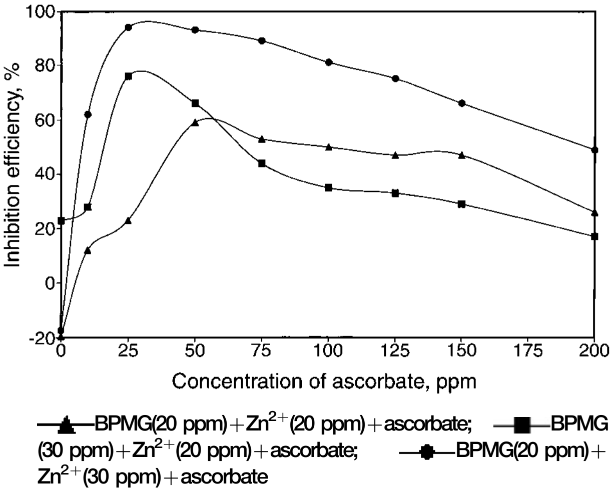
Results and discussion

Weight loss studies

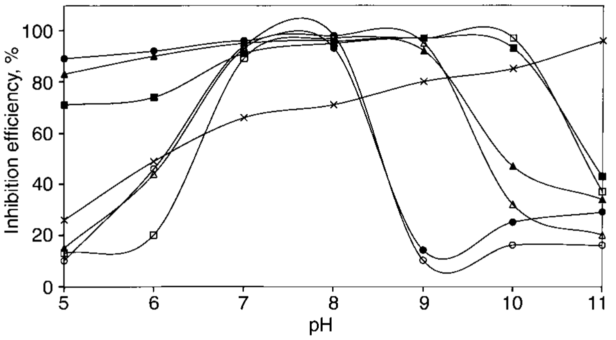
Figure 1 shows the results of weight loss studies using the binary system, BPMG–Zn^{2+}. The inhibition efficiency of binary formulations with a concentration of BPMG $\leqslant$20 ppm is not significant. In fact, some of these formulations aggravate the corrosion of carbon steel. Although the binary system containing 30 ppm of BPMG shows significant inhibition, the highest inhibition efficiency of 91% was obtained using the combination with 100 ppm of Zn^{2+}. Nevertheless, when the concentration of BPMG is increased to 40 ppm, an inhibition efficiency >90% was achieved at a relatively low concentration of Zn^{2+} such as 30 ppm. Thus, the minimum concentrations of BPMG and Zn^{2+} respectively in the binary system are 40 and 30 ppm for effective inhibition. Figure 2 presents the results of weight loss studies of ascorbate alone as an inhibitor. The inhibition efficiency increases gradually with increasing concentration of ascorbate, reaches the highest value of only 46% at 200 ppm and then decreases at 300 ppm of ascorbate. Thus, ascorbate alone does not function as an effective inhibitor even at higher concentrations. It was found from the results of weight loss studies of BPMG–ascorbate system (not shown here), that the inhibition efficiency of this system is not significant even when compared with that of ascorbate alone. Figure 3 shows the inhibition efficiency of the ternary system, BPMG+Zn^{2+}+ascorbate, as a function of concentration of ascorbate at different concentrations of BPMG and Zn^{2+}. In the case of all these ternary inhibitor formulations at pH 7, as the concentration of ascorbate is increased, the inhibition efficiency increases, reaches a maximum at an optimum concentration of ascorbate and then decreases. However, in order to achieve an inhibition efficiency >90%, the required minimum concentrations of BPMG and Zn^{2+}



2 Inhibition efficiency of ascorbate alone



3 Inhibition efficiency as function of concentration of ascorbate for ternary system

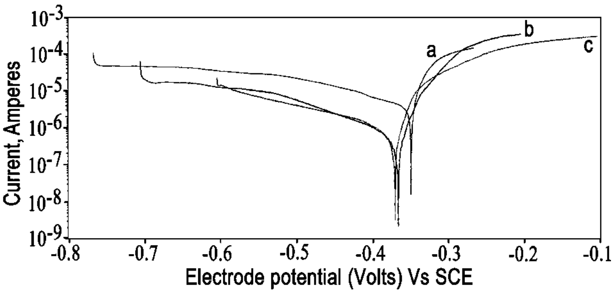


○ BPMG(20)+Zn^{2+}(30)+ascorbate(25); △ BPMG(20)+Zn^{2+}(30)+ascorbate(50); □ BPMG(20)+Zn^{2+}(30)+ascorbate(75); ● BPMG(30)+Zn^{2+}(30)+ascorbate(25); ▲ BPMG(30)+Zn^{2+}(30)+ascorbate(50); ■ BPMG(30)+Zn^{2+}(30)+ascorbate(75); × BPMG(20)+Zn^{2+}(30)+ascorbate(150)

4 Inhibition efficiency as function of pH for ternary system: numbers in brackets indicate concentrations in ppm

are 20 and 30 ppm respectively in the presence of ascorbate. The observed decrease in inhibition efficiency at higher concentrations of ascorbate can be explained as follows. In the synergistic inhibition, each of the three components namely BPMG, Zn^{2+} and ascorbate has its due role and to play one's own role, availability of optimum concentration of each of the species on the metal surface is essential. When the bulk concentration of ascorbate is far greater than that of BPMG and Zn^{2+}, more ascorbate is available at the metal surface, at the cost of the required optimum concentrations of BPMG and Zn^{2+} to manifest the highest possible synergism. It may be mentioned here that the molar ratio of BPMG:Zn^{2+}:ascorbate is 1 : 5·4 : 1·5 to exhibit excellent synergism. The role of each of the synergists is explained under mechanistic aspects of corrosion inhibition latter in this paper.

Figure 4 shows the results of weight loss studies by the ternary inhibitor system, BPMG(20–30 ppm)–Zn^{2+}(30 ppm)–ascorbate(25–150 ppm) as a function of pH. The ternary formulation, BPMG(20 ppm)–Zn^{2+}(30 ppm)–ascorbate(25 ppm) is effective at pH 7 and pH 8 only. This formulation is effective at higher pH values only with higher concentration of ascorbate. At pH 9, the required concentration of ascorbate for effective inhibition is 50 ppm while at pH 11, the required concentration of ascorbate is 150 ppm to show an inhibition efficiency of 96%. Higher concentrations of ascorbate are required at higher pH values to nullify the effect of OH$^-$ ions, which try to precipitate Zn^{2+} as Zn (OH)$_2$ in the bulk of the solution. This ternary system, BPMG(20 ppm)–Zn^{2+}(30 ppm)–ascorbate-(25–150 ppm) could not show effective inhibition in the acidic region, probably because there is an inadequate concentration of BPMG to form a stable protective film in acidic medium. Nevertheless, when the concentration of BPMG is increased from 20 to 30 ppm, the ternary system functions quite well in acid down to pH 5. Thus, the ternary formulation, BPMG(20–30 ppm)–Zn^{2+}(30 ppm)–ascorbate(25–150 ppm) is an excellent corrosion inhibitor for carbon steel in a wide pH range 5–11. It is interesting to note that in the pH range 5–8, good inhibition efficiency is obtained only at lower concentrations of ascorbate while in the pH range 9–11, good inhibition efficiency is achieved only at higher concentrations of ascorbate. This point is explained under mechanistic aspects of corrosion inhibition.



a Cl$^-$(60 ppm); *b* Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm); *c* Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm)+ascorbate(25 ppm)

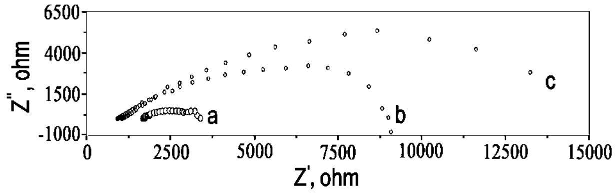
5 Potentiostatic polarisation curves for carbon steel in various aqueous environments

Potentiostatic polarisation studies

The potentiostatic polarisation curves are shown in Fig. 5. The corresponding corrosion parameters are listed in Table 1. In the presence of the ternary inhibitor system, BPMG(20 ppm)–Zn^{2+}(30 ppm)–ascorbate(25 ppm), the corrosion potential, E_{corr} is shifted from −350 to −371 mV in the cathodic direction. The corrosion current, I_{corr} is decreased from 6·16 μA cm^{-2} observed in the case of the control solution to 0·94 μA cm^{-2} in presence of the inhibitor. This significant reduction in corrosion current indicates the decrease in corrosion rate in presence of the inhibitor. Thus, the synergistic effect of the inhibitor formulation is inferred by potentiostatic polarisation studies. Both the anodic and cathodic Tafel slopes are shifted in presence of the inhibitor. Thus the ternary inhibitor system retards both anodic and cathodic partial reactions of the corrosion process. The shift in cathodic Tafel slope is higher than the shift in anodic Tafel slope. It is therefore inferred that the ternary inhibitor formulation acts as a mixed inhibitor, predominantly cathodic in nature. Pech-Canul and Chi-Canul[6] studied the inhibitive effect of N-phosphonomethyl glycine (NPMG) in presence of Zn^{2+} for corrosion of carbon steel by electrochemical techniques. They reported that NPMG/Zn^{2+} mixture acts as a mixed type inhibitor.

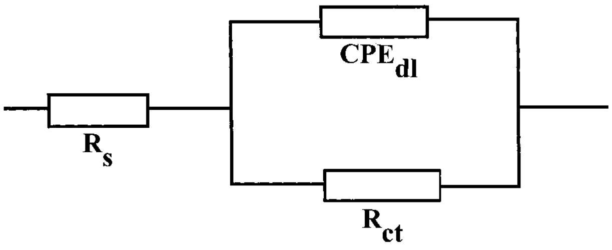
Table 1 Corrosion parameters obtained from potentiostatic polarisation studies at pH 7

Sample no.	Environment	E_{corr}, mV	I_{corr}, μA cm^{-2}	b_a, mV dec^{-1}	b_c, mV dec^{-1}
1	Cl$^-$(60 ppm)	−350	6·16	29	123
2	Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm)	−366	0·83	24	136
3	Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm)+ ascorbate(25 ppm)	−371	0·94	52	173



a Cl$^-$(60 ppm); *b* Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm); *c* Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm)+ascorbate(25 ppm)

6 Nyquist plots for carbon steel in various aqueous environments



7 Equivalent circuit used to fit impedance spectra

AC impedance studies

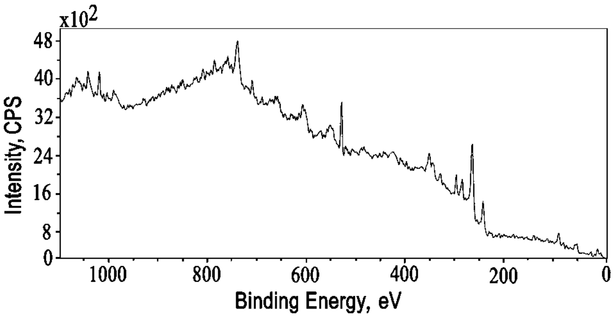
Figure 6 presents the Nyquist plots obtained in the presence and absence of the binary as well as ternary inhibitor formulations at pH 7. The impedance parameters obtained from these plots are shown in Table 2. The impedance spectrum for the carbon steel electrode was fitted by the equivalent circuit shown in Fig. 7.

In this circuit, R_s is the solution resistance between the working electrode and the reference electrode, R_{ct} is the charge transfer resistance for the corrosion reaction and CPE$_{dl}$ represents the double layer capacitance at the carbon steel/solution interface. Here a CPE is substituted for the capacitor to fit the depressed semicircle more exactly. The admittance and impedance of a CPE are, respectively defined as

$$Y_{CPE} = Y_o\,(j\omega)^n$$

$$\text{and } Z_{CPE} = (1/Y_o)(j\omega)^{-n}$$

where, Y_o is the modulus, ω is the angular frequency and n is the phase.[7,8] In the present study, R_{ct} in the control solution is 1306·1 Ω. In presence of the ternary inhibitor system, the R_{ct} value increased to 17 286·3 Ω, which indicates that formation of a protective film has occurred.[9] The observation is also supported by the decrease in CPE value from 8·738 μF in the case of the control solution to 1·096 μF observed in the case of the ternary inhibitor system. For a highly polished electrode, the value of n is always less than 1·0. The lower the value of n, the rougher is the electrode. In addition, the value of n is also related to the inherent physical and chemical heterogeneous nature of the solid surface,[10] the presence of a porous corrosion product layer,[11,12] the development of a solid corrosion product within the defects,[13] and finally to non-uniform distribution of the current density on the surface.[14] In the case of control solution, the value of n is 0·665 which slightly increased to 0·671 in presence of ternary inhibitor formulation.



8 X-ray photoelectron spectrum of surface film in presence of ternary system

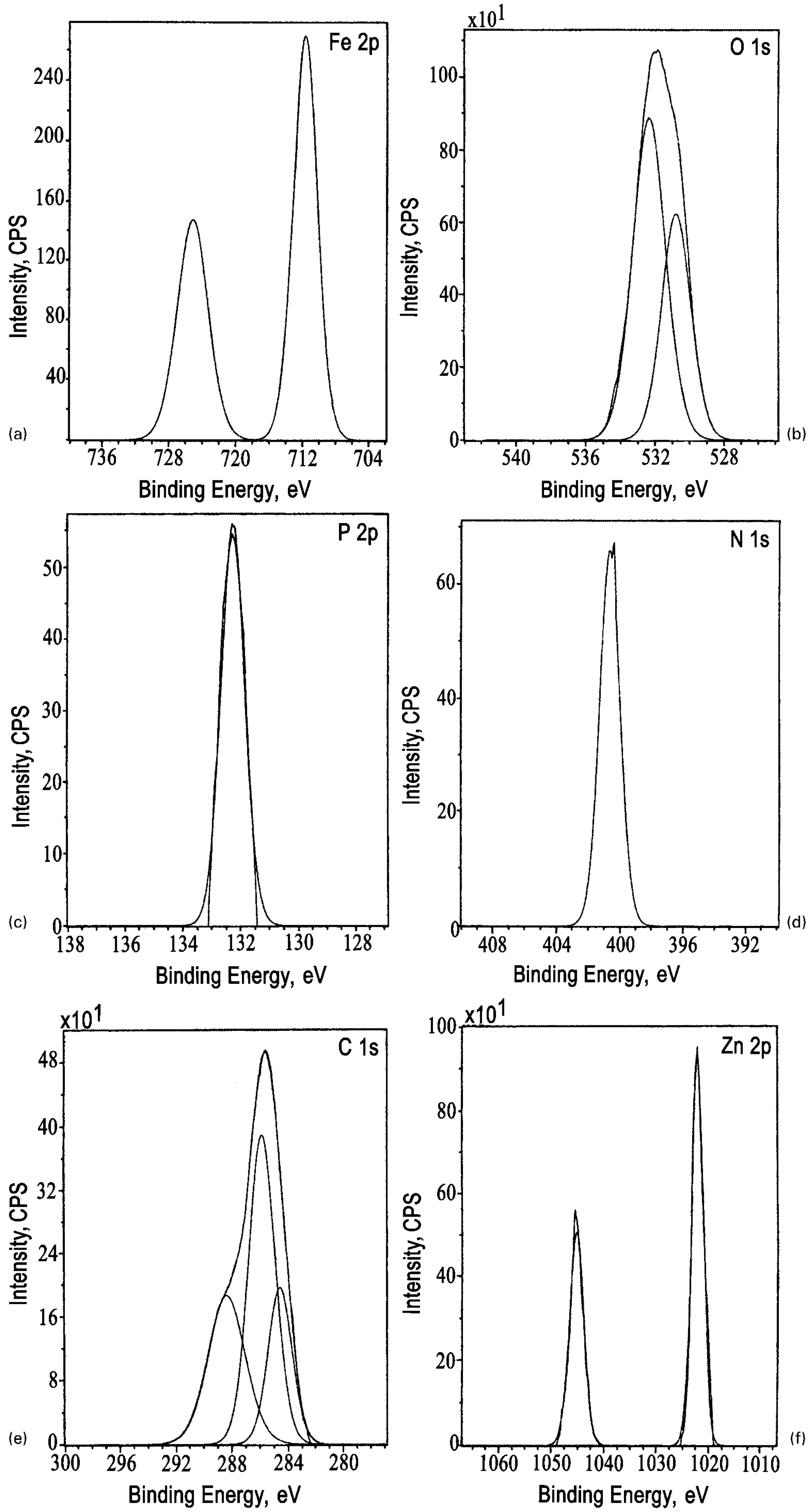
The Nyquist plots obtained in presence of the binary as well as the ternary inhibitor formulations, are characterised by a single time constant. Kalman *et al.*[4] studied the corrosion inhibition of carbon steel by HEDP. They obtained Nyquist plots with depressed semicircles and they interpreted them due to the formation of a three-dimensional (3D) inhomogeneous porous oxide layer at the metal surface. In the literature[6] the inhibitive effect of NPMG on the corrosion of carbon steel in neutral solutions was investigated using electrochemical techniques. They reported the fit parameters in their study. Based on these parameters, they interpreted that the 3D layer developed in the presence of the inhibitor was less permeable than that formed in the blank solution. Thus, all the observations in the impedance studies indicate that there is formation of a highly protective 3D film on the metal surface, which effectively controls the corrosion of metal surface in presence of the ternary inhibitor formulation.

Interpretation of X-ray photoelectron spectra

The XPS spectrum of the surface film in presence of the inhibitor formulation is shown in Fig. 8. The XPS spectra of the individual elements namely Fe, O, P, N, C and Zn present in the inhibited surface film in presence of the ternary inhibitor system, are shown in Fig. 9*a–f* respectively. The XPS of iron is shown in Fig. 9*a*. The peak due to Fe $2p_{3/2}$ electron is shifted from 707 eV, the characteristic binding energy of the Fe $2p_{3/2}$ electron in elemental iron,[15] to 711·7 eV. Thus there is a shift of 4·7 eV. The characteristic binding energy of Fe $2p_{1/2}$ electron is 721 eV,[16] which is shifted to 725·2 eV. In this case, there is a shift of 4·2 eV. Such large shifts in binding energy of Fe 2p electron indicate that iron exists in the +3 oxidation state in the surface film. Ochoa *et al.*[17] reported the Fe $2p_{3/2}$ peak at the binding energy of 711·8 eV and interpreted the shift due to the presence

Table 2 Impedance parameters obtained from AC impedance studies at pH 7

Sample no.	Environment	R_{ct}, Ω	CPE, μF	n
1	Cl$^-$(60 ppm)	1306·1	8·738	0·665
2	Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm)	9662·6	5·955	0·668
3	Cl$^-$(60 ppm)+BPMG(20 ppm)+Zn^{2+}(30 ppm)+ascorbate(25 ppm)	17 286·3	1·096	0·671

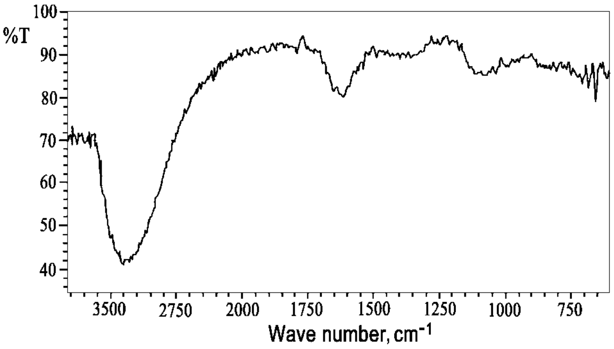


a Fe 2p; *b* O 1s; *c* P 2p; *d* N 1s; *e* C 1s; *f* Zn 2p

9 X-ray photoelectron spectra of individual elements of surface film in presence of ternary system

of iron oxide/hydroxide mixture on the metal surface. Nakayama and Akira[18] reported that the peak at 711·0 eV is attributable to ferric compounds such as ferric oxides. In the literature,[19] it was reported that the binding energy of Fe $2p_{3/2}$ electron in γ-Fe_2O_3 is 711·0±0·15 eV. A peak of Fe $2p_{3/2}$ at 710·4 eV was ascribed to the presence of Fe^{3+}, with a small contribution of Fe–phosphonate complex.[20] Narmada[16] reported that a peak obtained at 725·3 eV in the Fe $2p_{1/2}$ spectrum indicates the iron existing in the Fe^{3+} state in the form of oxides/hydroxides or [Fe(III)–inhibitor] complex. All these literature reports support that the shifts in the binding energies of both Fe $2p_{3/2}$ and Fe $2p_{1/2}$ electrons, are due to the presence of iron in the form of oxides/hydroxides, particularly γ-Fe_2O_3 or Fe_3O_4 or a combination of these. It may be noted that Fe(III) is also likely to be present in the form of complex with BPMG and ascorbate. The O 1s spectrum (Fig. 9*b*) shows two peaks, one at 530·8 eV and the other one at 532·4 eV, while the characteristic binding energy of O 1s is 531 eV.[21] Heuer and Stubbins[22] reported the O^{2-} peak of O 1s at 530·2 eV and interpreted that the O 1s peak is typical of iron oxides such as FeO, Fe_2O_3 and Fe_3O_4. Karman *et al.*[15] studied the role of oxide layer formation during corrosion inhibition of mild steel in neutral aqueous media by XPS. They interpreted the O 1s peak as O^{2-}/OH^- whose binding energies are $\sim$530 and $\sim$531 eV respectively. Aramaki reported a peak for O 1s electron at the binding energy of 532·6 eV. This peak was assigned to oxide/hydroxide and also due to formation of metal–inhibitor complex formed through oxygen atom.[23,24] Hence the two peaks obtained for O 1s in the present studies may be attributed to the presence of oxides/hydroxides of iron and also to the formation of a complex of metal with BPMG and ascorbate. The peak obtained at 532·4 eV can also be ascribed to the presence of adsorbed water in the surface film.[24,25]

The XPS spectrum for phosphorus is shown in Fig. 9*c*. It shows two peaks overlapped at a binding energy of 132·3 eV. These peaks are shifted from their characteristic binding energy values of 133 eV for P $2p_{3/2}$ and 134 eV for P $2p_{1/2}$.[21] These shifts suggest the involvement of phosphonate in the complex formation with Fe(III). Such shifts were also observed by several authors[26,27] in the study of interaction between phosphorous compounds and iron. Ochoa *et al.*[17] obtained a peak in the P 2p region at the binding energy of 132·1 eV and they interpreted it due to the interaction between phosphorous compound and iron. The N 1s spectrum (Fig. 9*d*) shows a peak at 400·7 eV, shifted from 398 eV, the characteristic binding energy of N 1s electron.[16] Ochoa *et al.*[17] reported that the N 1s peak observed at 400 eV is due to amine adsorbed on the metal surface. The peak observed in the present studies can be attributed to the chemisorbed and complexed molecules through nitrogen of BPMG. The XPS spectrum for carbon is shown in Fig. 9*e*. It shows three peaks, one each at 284·6, 285·9 and 288·4 eV, which are shifted from 285 eV, the characteristic binding energy for C 1s electron.[16] The first peak is essentially accounted for by the presence of inhibitor molecules on the surface.[17] The peaks observed at 285·9 and 288·4 eV may be due to different carbon environments present in both BPMG and ascorbate ion. The Zn 2p spectrum is shown in Fig. 9*f*. The peak corresponding to Zn $2p_{3/2}$ electron is shifted from its characteristic binding energy, 1021 eV (Ref. 28) to 1022·3 eV. Aramaki[29] reported that a peak of Zn^{2+}, due to its hydroxide, appeared at 1022·7 eV. Hence the peak observed at 1022·3 eV in the present studies may be interpreted as the presence of $Zn(OH)_2$. The characteristic binding energy of Zn $2p_{1/2}$ electron is 1044 eV.[28] This is shifted to 1045·3 eV. This shift in the binding energy of Zn $2p_{1/2}$ electron supports the above interpretation given in the case of the shift in the binding energy of Zn $2p_{3/2}$ electron.



10 Reflection absorption FTIR spectrum of surface film on carbon steel in presence of ternary system

Thus, the XPS spectra for the individual elements in the surface film are interpreted in terms of formation of $Zn(OH)_2$, oxides/hydroxides of iron in +3 oxidation state, particularly γ-Fe_2O_3, Fe_3O_4 and a complex of Fe(III) with BPMG and ascorbate in the form of a protective film on the metal surface.

Interpretation of FTIR spectra

The reflection absorption FTIR spectrum of the surface film formed in presence of the ternary inhibitor system, is shown in Fig. 10. This is compared with the FTIR spectra of pure BPMG and pure ascorbic acid in a KBr pellet (not shown here). The C=O stretching frequency in the case of pure BPMG is 1732 cm^{-1} and that in the case of pure ascorbic acid is 1676 cm^{-1}. These are shifted to give a band near 1623 cm^{-1} in the spectrum of the surface film. This can be interpreted in terms of the involvement of both BPMG and ascorbate in the complex formation on the metal surface. A broad band is observed around 3350 cm^{-1}, which can be assigned to the presence of O–H in the surface film.[30] The band obtained at 1100 cm^{-1} can be attributed to the C–N stretching frequency.[31] This indicates the involvement of nitrogen of C–N in BPMG in the complex formation with the metal. The band observed at 1100 cm^{-1} also includes P–OH stretching frequency. This result can be interpreted due to interaction of free $P–O^-$ present in the phosphonate with metallic species, namely, Fe(III) to form P–O–metal bonds.[32,33] A small peak at 1323 cm^{-1} indicates the formation of $Zn(OH)_2$ on the surface.[3] Thus, the reflection absorption FTIR spectrum of the surface film infers the presence of Zn $(OH)_2$ in the surface film and also the involvement of BPMG and ascorbate in the complex formation with Fe(III). Gunasekharan *et al.*[34] prepared pure complexes, namely, Fe^{3+}–2-CEPA, Fe^{3+}–2-CEPA–calcium gluconate and their FTIR spectra were compared with the corresponding reflection absorption FTIR spectra of the surface films formed in the presence of the respective inhibitor formulations. They found that the spectra of the complexes and of the surface films are similar. They interpreted that the changes in the positions of peaks of various functional groups in the FTIR spectra of the surface films are due to involvement of 2-CEPA and the organic additive in the complex formation with Fe(III).

Formation of complexes on metal surface

The XPS and reflection absorption FTIR spectrum of the surface film indicate the presence of Fe(III), BPMG and ascorbate in the surface film. They also infer the involvement of BPMG and ascorbate in the complex formation with Fe(III). This inference is further supported by several studies reported in literature. Popov *et al.*[35] published stability constants (log K_s) of NPMG with Fe^{2+}, Fe^{3+} and Zn^{2+}, which are given in Table 3. The log K_s value of [Fe(III)–NPMG] is far greater than that of [Fe(II)–NPMG] complex and that of [Zn(II)–NPMG] complex. The data for BPMG are not available in the literature. Because of the similarity between BPMG and NPMG, it is quite likely that the log K_s value of [Fe(III)–BPMG] complex is far greater than that of [Fe(II)–BPMG] complex and that of [Zn(II)–BPMG] complex. It is well known that ascorbate forms a highly stable complex with Fe(III).

Gunasekharan *et al.*[34] studied corrosion inhibition of mild steel in low chloride media using a formulation containing 2-carboxyethyl phosphonic acid (2-CEPA), Zn^{2+} and calcium gluconate. They characterised the surface film formed in the presence of the inhibitor, using UV luminiscence emission spectral studies. For this purpose, they prepared the pure metal complex, [Fe^{3+}–2-CEPA–calcium gluconate] and the UV luminiscence emission spectrum of this complex was compared with that of the surface film. They observed that the peaks in the spectrum of pure complex and that of surface film are at the same positions and inferred that the inhibitor film consists of [Fe^{3+}–2-CEPA–calcium gluconate] complex.

Kalman *et al.*[36] studied the inhibitive effect of NPMG using weight loss tests and Auger depth profiling of films formed on steel surface. One of their interpretations is that Ca^{2+} and Zn^{2+} ions form a passivating complex with NPMG, which protects the metal surface. In view of a very large value of log K_s for [Fe(III)–NPMG] complex, it is more likely that this complex is present on the metal surface rather than the [Zn(II)–NPMG] complex. The mechanism of inhibitive action of phosphonic acids as given by Kuznetsov[37] supports the view that [Fe(III)–phosphonate] complex is formed and Zn(II) is precipitated as zinc hydroxide on the metal surface.

Table 3 Stability constants[35] (log k_s) of various complexes of NPMG at 25°C

		log K_s		
		Equilibrium		
Sample no	Metal ion	M*+L†	M*+H+L†	M*+2L†
1	Fe^{2+}	6·9	12·8	11·2
2	Fe^{3+}	16·1	17·6	23·0
3	Zn^{2+}	8·7	–	11·7

*Metal ion.
†Ligand, NPMG.

The above literature reports and stability constants of complexes of phosphonates support the interpretation that there is formation of [Fe(III)–BPMG–ascorbate] complex on the metal surface.

Mechanistic aspects of corrosion inhibition

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

(i) carbon steel undergoes initial corrosion to form Fe^{2+} ions at the anodic sites

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

(ii) Fe^{2+} further undergoes oxidation in the presence of oxygen

$$Fe^{2+} \xrightarrow{[O_2]} Fe^{3+} + e^- \quad (2)$$

(iii) the corresponding reduction reaction at cathodic sites in neutral and alkaline medium is

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (3)$$

(iv) before the formation of protective film, there is formation of oxides of iron namely γ-Fe_2O_3 and Fe_3O_4 on the metal surface

(v) BPMG and ascorbate ions react with Zn^{2+} present in the bulk of the solution to form [Zn(II)–BPMG–ascorbate] complex and this complex diffuses to the metal surface. It reacts with Fe^{3+} available at the anodic sites to form hetero and polynuclear complex,[37] [Fe(III)–BPMG–ascorbate]. This is because the stability constant of the [Fe(III)–BPMG–ascorbate] is expected to be far greater than the [Zn(II)–BPMG–ascorbate] complex[35]

$$[Zn(II) - BPMG - ascorbate]\ complex + Fe^{3+} \rightarrow [Fe(III) - BPMG - ascorbate]\ complex + Zn^{2+} \quad (4)$$

(vi) Zn^{2+} ions released in the above reaction combine with OH^- ions present at the cathodic sites to form a precipitate of $Zn(OH)_2$ (Ref. 37)

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad (5)$$

(vii) thus, the ternary inhibitor system inhibits the corrosion by controlling both the anodic and cathodic reactions. A protective film is formed on the metal surface. It is inferred that the film consists of oxides of iron, namely, γ-Fe_2O_3, Fe_3O_4, $Zn(OH)_2$ and [Fe(III)–BPMG–ascorbate] complex

(viii) optimum bulk concentrations of BPMG, Zn^{2+} and ascorbate are needed to form the protective film, which is stable at a given pH value. At pH 7 and 8, the optimum concentrations of BPMG, Zn^{2+} and ascorbate respectively are in the molar ratio of 1 : 5·4 : 1·5. At pH 5 and 6, the ternary system functions effectively when the molar ratios of these three components are 1 : 5·4 : 1 and also 1 : 3·6 : 1. Thus, lower relative concentration of ascorbate is sufficient for its diffusion to the surface and for subsequent formation of

[Fe(III)–BPMG–ascorbate] complex. In the pH range 5–8, with increasing concentration of ascorbate, the inhibition efficiency slightly decreases. This is because, in this pH range, the concentration of OH^- is relatively less and hence relatively higher concentration of Zn^{2+} is required on the metal surface for the precipitation of $Zn(OH)_2$. When the bulk concentration of ascorbate is much higher than that required for the formation of [Zn(II)–BPMG–ascorbate] complex in the solution, free ascorbate reaches the metal surface at the cost of the required concentration of [Zn(II)–BPMG–ascorbate] complex. This reduces the required amounts of $Zn(OH)_2$ and [Fe(III)–BPMG–ascorbate] complex in the surface film to make it protective

(ix) above pH 8, the required concentration of ascorbate is higher for effective inhibition. The molar ratios of the three components namely BPMG, Zn^{2+} and ascorbate at pH values of 9, 10 and 11 respectively are 1 : 5·4 : 3, 1 : 5·4 : 6 and 1 : 5·4 : 9. At these pH values, higher concentrations of ascorbate are required for the formation of optimum amount of [Zn(II)–BPMG–ascorbate] complex in the solution, in the presence of relatively higher concentrations of OH^-, which favours the precipitation of Zn^{2+} as $Zn(OH)_2$ in the bulk of solution itself. Higher concentration of [Zn(II)–BPMG–ascorbate] complex in the bulk facilitates its diffusion to the metal surface and helps formation of the necessary amounts of $Zn(OH)_2$ and [Fe(III)–BPMG–ascorbate] complex on the metal surface

(x) The effectiveness of this ternary inhibitor formulation at higher pH of the environment is due to the stability of [Fe(III)–BPMG–ascorbate] complex formed on the metal surface and presence of optimum amounts of $Fe(OH)_3$ and $Zn(OH)_2$ in the surface film.

Conclusions

1. Ascorbate plays an excellent synergistic role in the BPMG–Zn^{2+}–ascorbate system to inhibit corrosion of carbon steel in low chloride environment.
2. The ternary system, BPMG–Zn^{2+}–ascorbate is effective in a wide pH range 5–11.
3. The inhibitor formulation acts as a mixed inhibitor, predominantly cathodic in nature.
4. It is inferred that both BPMG and ascorbate together form a stable hetero and polynuclear complex, [Fe(III)–BPMG–ascorbate] on the metal surface.
5. The protective film consists of ferric oxides and hydroxides, $Zn(OH)_2$ and hetero and polynuclear complex of Fe(III) with BPMG and ascorbate.

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References

1. Y. Gonzalez, M. C. Lafont, N. Pebere, G. Chatainier, J. Roy and T. Bouissou: *Corros. Sci.*, 1995, **37**, 1823–1837.
2. S. Rajendran, B. V. Appa Rao and N. Palaniswamy: *Bull. Electrochem.*, 1996, **12**, 15–19.
3. I. Sekine and Y. Hirakawa: *Corrosion*, 1986, **42**, 272–276.
4. E. Kalman, B. Varhegyi, I. Bako, I. Felhosi, F. H. Karman and A. Shaban: *J. Electrochem. Soc.*, 1994, **141**, 3357–3360.
5. B. V. Appa Rao and M. Venkateswara Rao: Proc. Eur. Corros. Cong., Nice, France, September 2004, Paper 238.
6. M. A. Pech-Canul and L. P. Chi-Canul: *Corrosion*, 1999, **55**, 948–956.
7. X. Wu, H. Ma, S. Chen, Z. Xu and A. Sui: *J. Electrochem. Soc.*, 1999, **146**, 1847–1853.
8. H. Ma, S. Chen, X. Chen, X. Chen, G. Li and X. Yang: *J. Serb. Chem. Soc.*, 1997, **62**, 1201–1212.
9. A. Bonnel, F. Dabosi, C. Deslovis, M. Duprat, M. Keddam and B. Tribollet: *J. Electrochem. Soc.*, 1983, **130**, 753–766.
10. E. Mccafferty: *Corros. Sci.*, 1997, **39**, 243–254.
11. M. Touzet, M. Cid, M. Puiggali and M. C. Petit: *Corros. Sci.*, 1993, **34**, 1187–1196.
12. J. R. Park and D. D. Macdonald: *Corros. Sci.*, 1983, **23**, 295–315.
13. U. Rammelt, G. Reinhard and K. Rammelt: *J. Electroanal. Chem.*, 1984, **180**, 327–336.
14. D. D. Macdonald and M. C. H. Mckubre: in 'Modern aspects of electrochemistry', (ed. J. O'M. Bockris *et al.*), Vol. 61; 1982, New York, Plenum Press.
15. F. H. Karman, I. Felhosi, E. Kalman, I. Cserny and L. Kover: *Electrochim. Acta*, 1998, **43**, 69–75.
16. P. Narmada: 'Corrosion inhibition of mild steel and copper in aqueous environment using synergistic formulaions', PhD thesis, National Institute of Technology, Warangal, India, 2004.
17. N. Ochoa, G. Baril, F. Moran and N. Pebere: *J. Appl. Electrochem.*, 2002, **32**, 497–504.
18. N. Nakayama and Akira Obuchi: *Corros. Sci.*, 2003, **45**, 2075–2092.
19. N. S. McIntyre and D. G. Zetaruk: *Anal. Chem.*, 1977, **49**, 1521–1529.
20. M. A. Pech-Canul and P. Bartolo-Perez: *Surf. Coat. Technol.*, 2004, **184**, 133–140.
21. D. Briggs and M. P. Seah (eds.): 'Practical surface analysis by Auger and X-ray photoelectron spectroscopy', 515; 1983, New York, John Wiley and Sons Ltd.
22. J. K. Heuer and J. F. Stubbins: *Corros. Sci.*, 1999, **41**, 1231–1243.
23. K. Aramaki: *Corros. Sci.*, 2003, **45**, 2361–2376.
24. K. Aramaki: *Corros. Sci.*, 2003, **45**, 1085–1101.
25. G. Gunasekaran and L. R. Chauhan: *Electrochim. Acta*, 2004, **49**, 4387–4395.
26. M. S. Eswaran and P. K. Mathur: *Corros. Sci.*, 1996, **38**, 1783–1790.
27. D. Schuetzle, R. O. Carter, J. Shyu, R. A. Dickie, J. Holubka and N. S. McIntyre: *Appl. Spec.*, 1986, **40**, 641–649.
28. A. B. Christie: in 'Methods of surface analysis – techniques and applications', (ed. J. M. Walls), 129; 1989, Cambridge, Cambridge University Press.
29. K. Aramaki: *Corros. Sci.*, 2003, **45**, 451–464.
30. L. J. Bellamy: in 'Advances in infrared group frequencies', (ed. Richard Clay), 94; 1968, Great Britain, The Chaucer press Ltd.
31. R. M. Silverstein, G. Clayton Bassler and T. C. Morrill: in 'Spectrometric identification of organic compounds', (ed. Jeannette Stiefel), 5th edn, 124; 1991, New York, John Wiley & Sons, Inc.
32. Y. Gonzalez, M. C. Lafont, N. Pebere and F. Moran: *J. Appl. Electrochem.*, 1996, **26**, 1259–1265.
33. S. Ramesh and S. Rajeswari: *Electrochim. Acta*, 2004, **49**, 811–820.
34. G. Gunasekharan, N. Palaniswamy, B. V. Appa Rao and V. S. Muralidharan: *Ind. Acad. Sci. (Chem. Sci.)*, 1996, **108**, 407–413.
35. K. Popov, H. Ronkkomaki and L. H. J. Lajunen: *Pure Appl. Chem.*, 2001, **73**, 1641–1677.
36. A. Shaban, E. Kalman and I. Biezo: *Corros. Sci.*, 1993, **35**, 1463–1470.
37. Y. I. Kuznetsov: Proc. Eur. Corros. Cong., Budapest, Hungary, September–October 2003, Paper 320.