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Ternary inhibitor system containing phosphonate, molybdate and Zn^{2+} in corrosion control of carbon steel

B V Appa Rao* & K Christina

Department of Chemistry, National Institute of Technology, Warangal 506 004, India

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With the objective of developing a new environmental friendly inhibitor formulation for corrosion of carbon steel in nearly neutral aqueous environments, phosphonic acid *viz*., N-(2-hydroxyethyl) imino-bis(methylphosphonic acid) [HEIBMPA] was chosen as the inhibitor. Zn^{2+} was chosen as the first synergist. A maximum inhibition efficiency of 99.3% was obtained with the binary system containing 70 ppm HEIBMPA and 80 ppm Zn^{2+}. Molybdate ion, which is inorganic in nature but environmental friendly, was used as the second synergist. The binary inhibitor formulation containing relatively low concentrations, *viz*., 30 ppm HEIBMPA and 40 ppm Zn^{2+} offered an inhibition efficiency of only 23%. To the above combination, when 200 ppm molybdate was added, the inhibition efficiency was found to increase to 95%. The potentiostatic polarization studies revealed that this ternary inhibitor system controlled the anodic reaction predominantly. A large increase in the polarisation resistance (R_p) value indicated the formation of a non-porous protective film on the metal surface. The reflection absorption FT-IR spectrum and X-ray photoelectron spectra of the film suggested that the film consisted of [Fe(III)-HEIBMPA-molybdate] complex, [Fe(III), Zn(II)-HEIBMPA-molybdate]complex, oxides and hydroxides of iron and $Zn(OH)_2$. A plausible mechanism of inhibition of corrosion is proposed, which explains all the above experimental results.

Keywords: N-(2-hydroxyethyl)imino-bis(methylphosphonic acid), Molybdate, Corrosion inhibition

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In the past, efficient corrosion inhibition treatments of cooling water systems to protect carbon steel were based on inorganic inhibitors such as chromates, nitrites and polyphosphates. But the use of chromates and nitrites is restricted due to their high toxicity and stringent environmental regulations. Hence, the focus shifted during the last three decades to non-toxic or relatively less toxic systems. Among these, phosphonic acids attracted a lot of attention. Phosphonic acids are the inhibitors, which have been widely used due to their stability, ability to form complexes with metal ions and scale inhibiting properties[1]. The chief advantage of use of a phosphonic acid is that it eliminates calcium phosphate deposition on the metal surface and the associated problems[2]. In an effort to develop a new environmentally friendly inhibitor formulation, a new phosphonic acid *viz.,* N-(2-hydroxyethyl) imino-bis(methylphosphonic acid) [HEIBMPA] was chosen in the present study. Zn^{2+} was used as the first synergist. In an attempt to reduce the concentrations of both Zn^{2+} and HEIBMPA, addition of a second synergist was envisaged. The second synergist chosen is molybdate ion, which is inorganic in nature, but environmental friendly[3,4]. Results of several experiments have shown that the minimum required concentrations of HEIBMPA and Zn^{2+} are 30 ppm and 40 ppm respectively in order to provide significant improvement of inhibition efficiency by the addition of molybdate. Studies on the ternary inhibitor system containing 30 ppm of HEIBMPA, 40 ppm of Zn^{2+} and molybdate at different concentrations in the range of 50-300 ppm, are presented in this paper.

Experimental Procedure

Preparation of specimens

Carbon steel specimens (carbon, 0.38, sulphur, 0.01, phosphorous 0.02, manganese 1.06% and rest iron) of the dimensions 1.5 × 3.5 × 0.2 cm, were polished to mirror finish, degreased with acetone and used for weight-loss and FTIR studies. For XPS studies, carbon steel specimen of 1.0 × 1.0 × 0.1 cm, prepared in a similar way was used.

Weight-loss studies

Carbon steel specimens in duplicate were immersed in 100 mL of the solutions containing different concentrations of molybdate in the presence of 60 ppm Cl^-, 40 ppm Zn^{2+} and 30 ppm HEIBMPA, and at different *p*H values for a period of seven days.

Then the specimens were reweighed after washing, degreasing with acetone and drying. The weights of the specimens before and after immersion were determined with Mettler electronic balance, with a readability of 0.1 mg.

Potentiostatic polarisation studies

Potentiostatic polarisation measurements were made using a three electrode cell assembly with an electrochemical system (Model 1280 B, Solatron, UK). Carbon steel specimen encapsulated in teflon with an exposed cross-section of 0.5 cm diameter polished to mirror finish and degreased with acetone was used as the working electrode. Saturated calomel electrode (SCE) was used as the reference electrode and platinum wire was used as the counter electrode. The polarization studies were made in the potential range of ±200 mV from the open circuit potential at a sweep rate of 1 mV/s.

Surface examination studies

The mild steel specimen were immersed in various test solutions for a period of five days. Then, they were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by FTIR and X-ray photoelectron spectra (XPS).

FTIR Spectra

The reflection absorption FTIR spectrum was recorded on a Shimadzu FTIR 8201 PC IR spectrophotometer in the range of 4000-500 cm^{-1}, with a resolution of 4 cm^{-1}.

X-ray photoelectron spectra (XPS)

The XPS patterns of the protective film were recorded using ESCA Kratos, model AXIS–155, with Mg Kα radiation and sensitivity of 0.1 eV.

Results and Discussion

Weight-loss studies

In an effort to reduce the concentrations of both the synergistic components, *viz.*, HEIBMPA and Zn^{2+}, molybdate was added as a second synergist. The variation of inhibition efficiency (I.E.). as a function of concentration of molybdate is shown in Fig. 1. It is evident that the inhibitor formulation containing 30 ppm HEIBMPA and 40 ppm Zn^{2+} offered an I.E. of only 23%. To the above combination when 50 ppm of molybdate is added, the I.E. increases to 59.7%. As the concentration of molybdate is further increased, the I.E. increases and maximum value of 95% is obtained by the addition of 200 ppm of molybdate. When the concentration of molybdate is further increased beyond 200 ppm, I.E. decreases. Thus, maximum inhibition efficiency is offered by the system consisting of 30 ppm HEIBMPA, 40 ppm Zn^{2+} and 200 ppm molybdate. It is worth mentioning here that the molybdate ion at concentrations greater than 50 mg/L, in the presence of oxygen, is capable of passivating boiler metal[5]. The I.E. of the binary system, ATMP-MoO_4^{2-} has been reported to be 32% and that of the ternary system[6], ATMP-Zn^{2+}-MoO_4^{2-} as 96%.

In the present study the synergism may be attributed to the complex forming ability of HEIBMPA-Zn^{2+}-MoO_4^{2-} in the solution and to the formation of [HEIBMPA-Fe^{3+}-MoO_4^{2-}] complex on the metal surface, besides formation of ferric oxides and $Zn(OH)_2$ on the metal surface.

Studies on the effect of *p*H on I.E. of the inhibitor formulation consisting of 30 ppm HEIBMPA, 40 ppm Zn^{2+} and molybdate (100-300 ppm) were carried out. Figure 2 depicts the I.E. as a function of *p*H. It is evident from the results that maximum I.E. is offered

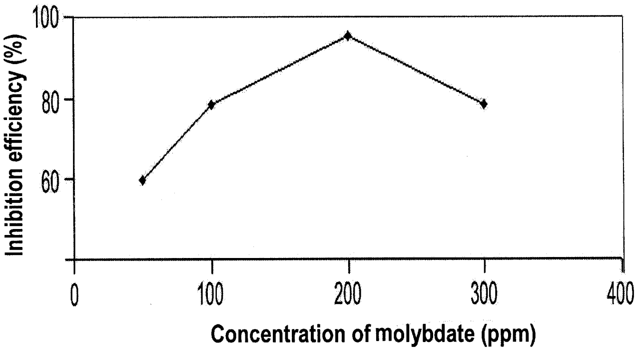

Fig. 1—Corrosion inhibition efficiency of the inhibitor system containing HEIBMPA (30 ppm)+Zn^{2+}(40 ppm) as a function of concentration of molybdate

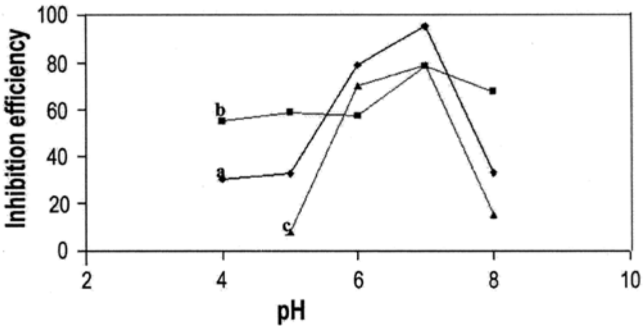

Fig. 2—Corrosion inhibition efficiency of the ternary inhibitor system containing HEIBMPA (30 ppm), Zn^{2+}(40 ppm) and molybdate, as a function of *p*H. [Molybdate]: a) 200 ppm b) 100 ppm c) 300 ppm

at *p*H=7. The I. E. decreased both in the acidic region as well as in the alkaline region. A plausible explanation is that the protective film is stable in neutral medium and the stability of the film is decreased in acidic and alkaline media.

Potentiostatic polarization studies

The potentiostatic polarization curves of carbon steel immersed in various neutral aqueous solutions, in the absence and presence of ternary inhibitor system, HEIBMPA-Zn^{2+}-MoO_4^{2-} are shown in Fig. 3. The parameters obtained from the polarization studies are given in Table 1. The curve 'a' of Fig. 3 represents the potentiostatic polarization curve of carbon steel immersed in neutral aqueous environment containing 60 ppm Cl^- only. The E_{corr} of carbon steel immersed in this solution is –407.2 mV versus SCE. Curve 'b' represents the potentiostatic polarization curve of carbon steel immersed in 60 ppm Cl^- and 200 ppm molybdate. The E_{corr} value for this system is –280.0 mV versus SCE. The shift in the E_{corr} value is towards anodic potential side, i.e., from –407.2 to –280.0 mV. It is reported by Qian and Turgoose[7] that the corrosion potential is raised by the addition of molybdate to Cl^- ions. This indicates the effect on the anodic reaction. Curve 'c' denotes the potentiostatic polarization curve of carbon steel immersed in 60 ppm Cl^-, 30 ppm HEIBMPA and 40 ppm Zn^{2+}. It is found that the E_{corr} value is shifted towards cathodic side and the shift is from –407.2 to –420.5 mV versus SCE. The anodic tafel slope is shifted from 170 to 212 mV/dec. The cathodic tafel slope is shifted from 150 to 235 mV/dec. The shifts in anodic and cathodic tafel slopes are 42 and 85 mV/dec, respectively.

Curve 'd' represents the potentiostatic polarization curve of carbon steel immersed in 60 ppm Cl^-, 30 ppm HEIBMPA, 40 ppm Zn^{2+} and 200 ppm molybdate. The shift in the E_{corr} value is from –407.2 to –287.8 mV versus SCE. The shift is towards anodic side. The shift in the anodic tafel slope is from 170 to 387 mV/dec. The shift in the cathodic tafel slope is from 150 to 275 mV/dec. As much greater shift is observed in the anodic tafel slope when compared to the shift in the cathodic tafel slope, this indicates that addition of 200 ppm molybdate to the system environment has greater effect on the anodic reaction of the metal surface. This ternary inhibitor system acts as a mixed inhibitor, predominantly anodic in nature. Rajendran *et al.* [8] also investigated the mode of inhibitive action of Zn^{2+}-MoO_4^{2-} system in low and high Cl^- ion concentrations. It is reported that at low concentrations of Cl^- *viz.*, 60 ppm, the Zn^{2+}-MoO_4^{2-} system (300 and 50 ppm, respectively) acts as a mixed inhibitor, while at high chloride concentration such as 3550 ppm, the same system (0.0025 M of each of the components) acts as a cathodic inhibitor.

A.C. impedance studies

The bode plots of mild steel specimens immersed in various solutions are given in Fig. 4. The impedance parameters calculated from the bode plots are given in Table 2. From the data, it is observed that the polarization resistance (R_p) value for the mild steel immersed in 60 ppm chloride is 135 ohms. The R_p value for the specimen immersed in 60 ppm Cl^- and 200 ppm molybdate, is 317 ohms. The polarization

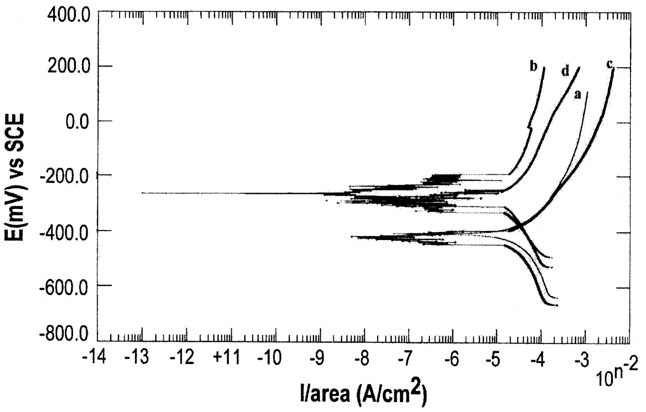

Fig. 3—Potentiostatic polarization curves of carbon steel immersed in various environments at neutral *p*H (a) Cl^-(60 ppm) (b) Cl^-(60 ppm) + molybdate (200 ppm) (c) Cl^-(60 ppm) + Zn^{2+}(40 ppm)+HEIBMPA(30 ppm) (d) Cl^-(60 ppm) + Zn^{2+}(40 ppm)+HEIBMPA(30 ppm) + molybdate (200 ppm)

Table 1—Corrosion parameters obtained from potentiostatic polarization studies

Cl^- conc. (ppm)	Zn^{2+} conc. (ppm)	HEIBMPA conc. (ppm)	Molybdate conc. (ppm)	E_{corr} mV vs SCE	b_a (mV/dec)	b_c (mV/dec)
60	-	-	-	-407.2	170	150
60	-	-	200	-280.0	212	195
60	40	30	-	-420.5	212	235
60	40	30	200	-287.8	387	275

Table 2—Impedance parameters obtained by A.C. impedance method

Cl^- conc. (ppm)	Zn^{2+} conc. (ppm)	HEIBMPA conc. (ppm)	Molybdate conc. (ppm)	R_Ω (ohms)	R_p+R_Ω (ohms)	R_p (ohms)	I.E. (%)
60	-	-	-	437	572	135	-
60	-	-	200	97	415	317	-
60	40	30	-	415	685	270	-
60	40	30	200	85	662	577	77

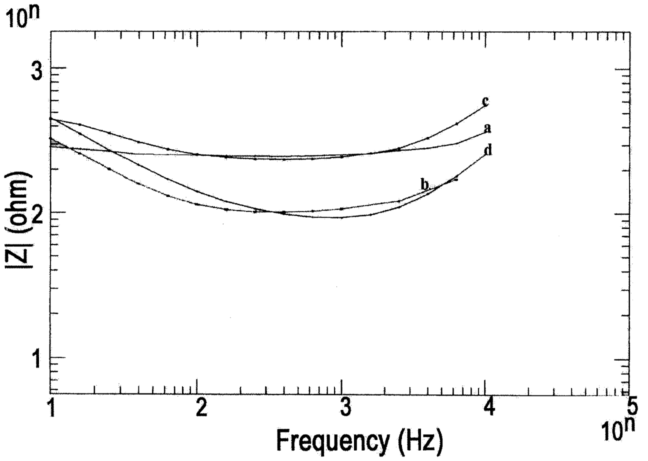

Fig. 4—Bode plots of carbon steel immersed in various environments at neutral *p*H (a) Cl^-(60 ppm) (b) Cl^-(60 ppm) + molybdate(200 ppm) (c) Cl^-(60 ppm) + Zn^{2+}(40 ppm)+HEIBMPA(30 ppm) (d) Cl^-(60 ppm) + Zn^{2+}(40 ppm)+HEIBMPA (30 ppm) + molybdate (200 ppm)

resistance increased from 135 to 270 ohms when the specimen is immersed in 60 ppm Cl^-, 30 ppm HEIBMPA and 40 ppm Zn^{2+}. The R_p value is further increased to 577 ohms when the metal is immersed in the solution consisting of 60 ppm Cl^-, 30 ppm HEIBMPA, 40 ppm Zn^{2+} and 200 ppm molybdate. The I.E. calculated after an immersion period of 30 min is 77%. Such an increase in R_p value confirms the formation of a non-porous protective film on the metal surface.

X-ray photoelectron spectra (XPS)

The X-ray photoelectron spectrum of the film formed on the mild steel surface immersed in 60 ppm Cl^-, 30 ppm HEIBMPA, 40 ppm Zn^{2+} and 200 ppm molybdate is given in Fig. 5 and the XPS of the individual elements are given in Fig. 6 (a-h).

The spectra are interpreted based on the shift in the binding energy of each element namely, iron, phosphorous, oxygen, nitrogen, carbon, zinc and molybdenum from its characteristic elemental binding energy taken from the literature[9,10].

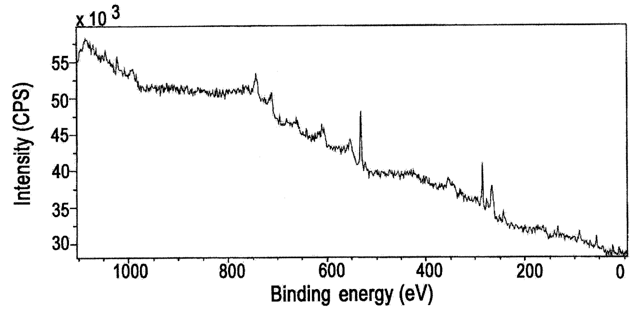

Fig. 5—X-ray photoelectron spectra of the surface film formed on carbon steel when immersed in the environment containing 60 ppm Cl, 40 ppm Zn^{2+}, 30 ppm HEIBMPA and 200 ppm molybdate

Two peaks, one at 711.0 eV and the other at 724.8 eV appeared in the XPS spectrum for iron. These two peaks indicate that the Fe $2p_{3/2}$ is shifted from 707 to 711 eV and the Fe $2p_{1/2}$ has shifted from 721.0 to 724.8 eV. The peak at 711.0 eV is attributable to ferric compounds[11] such as oxides. It is reported[5] that in presence of oxygen, molybdate converts Fe_2O_3 into Fe_3O_4. In the present study, the shift in the binding energy is due to Fe^{3+} state of iron in the form of oxides or hydroxides. Fe^{3+} is also involved in the formation of a complex with inhibitor molecules.

The XPS exhibited a peak at 135 eV, which indicated that the elemental peak of phosphorous, P $2p_{3/2}$ is shifted from 133 to 135 eV. It can be inferred that the shift is due to co-ordinate bond formation between metal ions i.e., Fe^{3+} and possibly Zn^{2+} with phosphonate group of HEIBMPA.

The XPS exhibited two peaks for O 1s electron. The first peak is seen at 531.8 eV and the second peak is at 533.1 eV. These are the peaks, shifted from 531.0 eV, which is the characteristic binding energy of elemental oxygen. It is reported by Ochao *et al.*[12] that a peak at 531.6 eV corresponds to the binding energy of OH^- ions and the other peak at 533.2 eV is often associated with the presence of H_2O molecules adsorbed on the oxide. In the present study, the two peaks may be due to the formation of OH^- ions, adsorbed H_2O molecules and also due to the

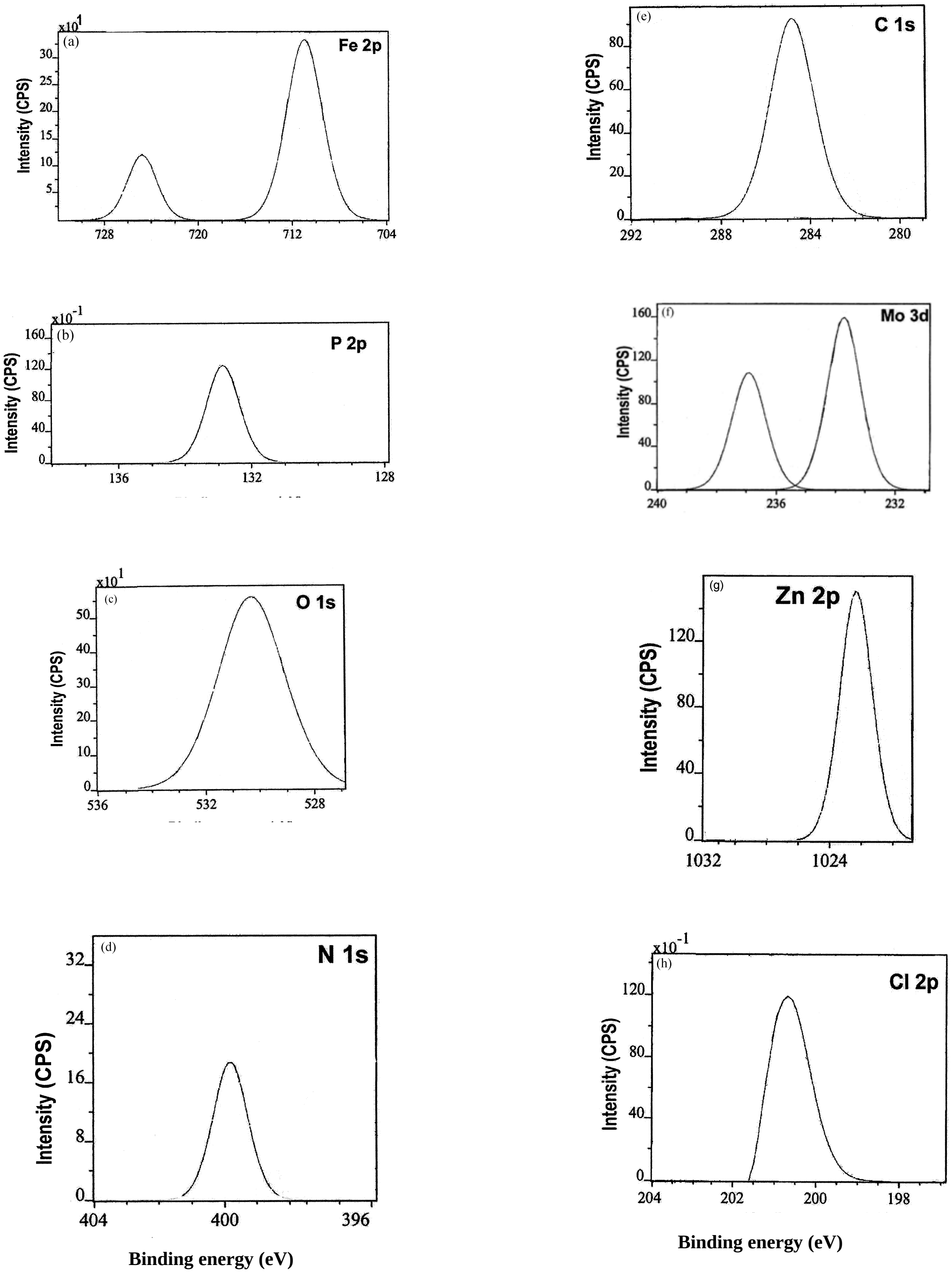

Fig. 6—X-ray photoelectron spectra of individual elements of the surface film in the presence of ternary inhibitor system (a) Fe 2p (b) P 2p (c) O 1s (d) 1s (f) Mo 3d (g) Zn 2p (h) Cl 2p

formation of a co-ordinate bond between metal ion and oxygen of HEIBMPA.

The characteristic binding energy for elemental nitrogen is 398.0 eV. A peak in the XPS of the surface film is exhibited at 401.4 eV. That means, the shift is from 398.0 to 401.4 eV. It is reported[13] that the peaks at 401.3 and 402.8 eV can be assigned to protonated amine. Therefore, the peak at 401.3 eV in the present study may be due to adsorbed and complexed HEIBMPA through nitrogen. The characteristic binding energy for elemental carbon is 285.0 eV. But in the XPS of the surface film, three peaks are exhibited at 286.4, 288.4 and 290.5 eV, respectively. It is reported by Meneguzzi *et al.*[14] that the peak at 286.8 eV can be ascribed to carbon atoms coupled singly to oxygen atoms or to nitrogen atoms. The peak at 286.4 eV in the present study is due to the bond formed between nitrogen of C-N group of phosphanate and the metal. The other two peaks at 288.4 and 290.5 eV are due to the other two carbons present in the phosphonate.

The XPS of the surface film also exhibited two peaks for molybdenum. The characteristic binding energy for elemental Mo $3d_{5/2}$ is 232.2 eV and the value for Mo $3d_{3/2}$ is 235.4 eV. These peaks are shifted to 233.7 and 236.9 eV, respectively in the surface film. As reported earlier[15] the presence of MoO_4^{2-} in the film on steel protects the metal from further corrosion, whilst the presence of MoO_2 does not do so. But the surface film formed on the metal in the presence of the ternary inhibitor system is quite protective giving an I.E. of 95%. This indicates the formation of MoO_4^{2-} on the surface of mild steel in the present inhibitor system. The shifts in the two peaks are interpreted due to the presence of MoO_4^{2-} in the surface film.

The Zn $2p_{3/2}$ peak is shifted from 1021.0 to 1022.4 eV. It is reported[16] that this peak due to Zn $2p_{3/2}$ at 1022.7 eV is due to $Zn(OH)_2$ layer. The peak of Cl 2p appeared at the binding energy of 200.7 eV. However, the intensity is very small. Therefore, there a is very small amount of adsorbed Cl^- on the metal surface before the formation of protective film. From the XPS, it is evident that the binding energies of all the elements present in the surface film are shifted from their elemental binding energy values. Therefore, it is suggested that there is a co-ordinate bond formed between metal ion i.e., Fe^{3+} and possibly Zn^{2+} with the elements, oxygen, nitrogen and phosphorus of HEIBMPA and also molybdate ion to form metal-inhibitor complexes. Besides these complexes, there is formation of oxide and hydroxide of iron and also zinc hydroxide.

Hence, the protective film may consist of ferric oxide and hydroxide, [Fe(III)-HEIBMPA-molybdate] complex, [Fe(III), Zn(II)-HEIBMPA-molybdate] complex and $Zn(OH)_2$.

Reflection absorption FTIR spectrum

The reflection absorption FTIR spectrum of surface film of carbon steel in the presence of ternary inhibitor system is given in Fig. 7. A peak present at 1093 cm^{-1} is due to the stretching vibrational frequency of P-OH group of phosphonic acid. It is reported[17,18] that P-OH stretching frequencies of different phosphonic acids occur in the range of 1100 to 1200 cm^{-1}. This shift towards lower wave number indicates the formation of a co-ordinate bond between metal ion and P-OH group of the phosphonic acid. Nakayama[19] studied the corrosion inhibition of mild steel, using NTMP in saturated $Ca(OH)_2$ solutions. It was suggested that peaks between 900-1200 cm^{-1} are due to functional groups included in phosphonates such as P-OH. In the reflection absorption FTIR spectrum of the surface film of carbon steel, the N-H stretching vibration peak is exhibited at 3330 cm^{-1}, which is also another evidence for the presence of HEIBMPA. The peak at 1323 cm^{-1} corresponds to $Zn(OH)_2$ formed on the cathodic sites of the metal surface. The Mo-O frequency for pure molybdate is present at 818 cm^{-1}. Rajendran *et al.*[6] reported that Mo-O frequency shifts from 818 to 800 cm^{-1}. In the present study, a small peak is observed at 800 cm^{-1}. This may be due to the participation of molybdate ion in complex formation. From the FTIR spectrum it is interpreted that a complex is formed between

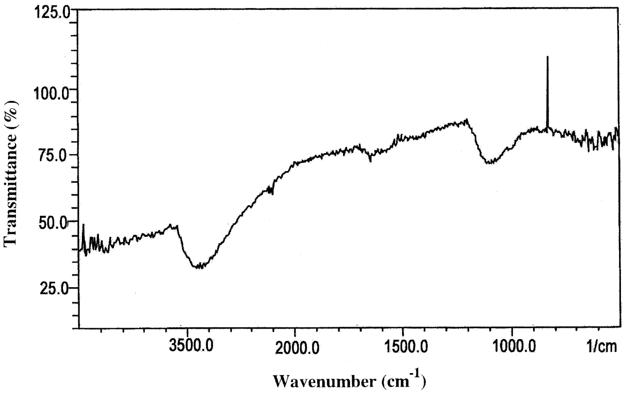

Fig. 7—Reflection absorption FTIR spectrum of the surface film in the presence of ternary inhibitor system

phosphonate, metal ion and molybdate ion. Thus, the reflection absorption FTIR spectrum also suggests that the protective film may consist of [Fe(III)-HEIBMPA-molybdate] complex, [Fe(III), Zn(II)-HEIBMPA-molybdate] complex and $Zn(OH)_2$.

Mechanistic aspects of corrosion inhibition

The results of the weight-loss studies showed that the formulation consisting of 30 ppm HEIBMPA, 40 ppm Zn^{2+} and 200 ppm MoO_4^{2-} has an I.E. of 95%. The potentiostatic polarization studies revealed that this system controlled the anodic reaction predominantly, though the cathodic reaction is also controlled. The reflection absorption FTIR spectrum and X-ray photoelectron spectra indicate that the protective film consists of [Fe(III)-HEIBMPA-molybdate] complex, [Fe(III), Zn(II)-HEIBMPA-molybdate] complex, oxide and hydroxide of iron and $Zn(OH)_2$. A plausible mechanism of corrosion inhibition involves the following steps,

1. In neutral aqueous medium, the anodic reactions due to corrosion of carbon steel are as follows.

$$Fe \longrightarrow Fe^{2+} + 2e^{--} \qquad \ldots (1)$$

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

The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad \ldots (3)$$

2. When the environment consisting of 60 ppm Cl^-, 30 ppm HEIBMPA, 40 ppm Zn^{2+} and 200 ppm MoO_4^{2-} is prepared, there is formation of [Zn^{2+}-HEIBMPA-molybdate] complex in solution.
3. When the metal is immersed in this environment, the [Zn^{2+}-HEIBMPA-molybdate] complex diffuses from the bulk of the solution to the surface of the metal.

a) On the surface of the metal, the [Zn^{2+}-HEIBMPA-molybdate] complex further complexes with Fe^{3+} ions available due to initial corrosion.

b) The free HEIBMPA molecules and molybdate ions also diffuse from the bulk of the solution to the metal surface and form [Fe(III)-HEIBMPA-molybdate] complex.

c) The free Zn^{2+} ions also diffuse from the bulk of the solution to the metal surface and react with the released OH^- ions on the cathodic sites and form an adherent film of $Zn(OH)_2$.

d) The Fe^{3+} ions formed as per the Eq. (2) also react with OH^- and form hydrated ferric oxides

$$Fe^{3+} + OH^- \longrightarrow Fe(OH)_3 \qquad \ldots 4(a)$$

$$Fe^{3+} + OH^- + \frac{1}{2}O_2 \longrightarrow \gamma\text{-}FeOOH \qquad \ldots 4(b)$$

Thus there is formation of hydroxides of iron *viz*., $Fe(OH)_3$ and γ - FeOOH.

e) The protective nature of the film is due to the presence of oxides and hydroxides of iron, metal-inhibitor complexes and zinc hydroxide. Formation of the metal-inhibitor complexes fills the pores of the otherwise porous film and makes it a protective film.

Conclusions

1) The concentrations of both Zn^{2+} and HEIBMPA could be reduced successfully by adding molybdate as a second synergist. The ternary system, which has less concentration of Zn^{2+} is more environmental friendly.
2) Molybdate ion is proved to be effective as second synergist. But, the required concentration of molybdate is as high as 200 ppm. The ternary inhibitor system, HEIBMPA-Zn^{2+}-molybdate functions as a mixed inhibitor, predominantly anodic in nature.
3) In any phosphonate-Zn^{2+} binary system, the concentration of Zn^{2+} can be reduced by adding a suitable non-toxic compound as second synergist. Thus, more environmental friendly inhibitor formulations can be developed.

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