Synergistic inhibition of carbon steel by tertiary butyl phosphonate, zinc ions and citrate

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Abstract

Purpose – To develop a new corrosion inhibitor formulation for carbon steel in low chloride environments.

Design/methodology/approach – Corrosion inhibition efficiencies were evaluated by the weight loss method and by impedance measurement studies. The nature of the inhibition process was evaluated using potentiostatic polarization studies. The nature of the protective film was investigated using X-ray diffraction, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy. The concept of synergistic effect was used in the development of the new synergistic inhibitor formulation.

Findings – A new corrosion inhibitor formulation, containing tertiary butyl phosphonate (TBP), zinc ions and citrate, has been developed to control the corrosion of carbon steel in low chloride environments. This inhibitor formulation was found to offer a maximum inhibition efficiency of 96 per cent in a neutral pH test environment. It was interesting to observe that the binary system, consisting of higher concentrations of the TBP and zinc ions, offered only 79 per cent inhibition efficiency. The ternary system, consisting of relatively lower concentrations of the phosphonate, zinc ions and citrate offered a higher (96 per cent) efficiency. This ternary inhibitor system also was found to be efficient in acidic as well as basic environments in the pH range 5-8. The inhibitor combination was determined to function as a "mixed"-type inhibitor, though being predominantly cathodic. A plausible explanation of the mechanism of corrosion inhibition is proposed.

Practical implications – The ternary inhibitor formulations based on phosphonate, zinc ions and another environmentally friendly synergists like citrate will be quite useful for corrosion inhibition of carbon steel in cooling water systems as they contain relatively less concentrations of phosphonate and zinc ions.

Originality/value – The research paper presents the results of a new synergistic inhibitor formulation and also discusses the mechanistic aspects of corrosion inhibition.

Keywords Inhibitors, Zinc, Carbon, Steel

Paper type Research paper

Introduction

Phosphonates, in combination with Zn^{2+} ions, have long been used as corrosion inhibitors for carbon steel in aqueous environments (Sekine and Hirakawa, 1986; Rajendran et al., 1996; Gunasekaran et al., 1997). Ternary systems, containing organic additives such as tartrate, citrate and gluconate, in combination with Zn^{2+} and phosphonates, also have been used as corrosion inhibitors, either to improve the efficiency of corrosion inhibition, or to reduce the requirement for phosphonic acids, metal ions, or both. No work has been reported in the literature using tertiary butyl phosphonic acid as corrosion inhibitor for carbon steel in aqueous environments. This phosphonic acid, because of its bulky nature, was expected to cover large surface areas even at low concentrations. In the present work, the synergistic effect of tertiary butyl phosphonate (TBP), Zn^{2+}, and citrate; a three component inhibitor system, in controlling the corrosion of carbon steel was studied in an aqueous environments of 60 ppm chloride concentration, and at various pH values in the range 4-8, using weight loss method and electrochemical methods. Surface analytical techniques were used to investigate the nature of the surface film.

Experimental

Preparation of specimens

Carbon steel specimens (0.02-0.03 per cent S, 0.03-0.08 per cent P, 0.4-0.5 per cent Mn, 0.1-0.2 per cent C and balance iron), of dimensions 1.51 × 3.68 × 0.23 cm, were polished to a mirror finish, degreased with acetone, dried, and used for weight loss and surface examination studies. For potentiostatic polarisation tests and impedance measurements, carbon steel samples with an exposed cross-section of 0.5 cm diameter were encapsulated in Teflon for use as the working electrode. The surface of samples was polished to a mirror finish and was degreased with acetone prior to exposure in the test solution.

Weight loss method

Carbon steel specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor for a period of 7 days. The weights of the specimens before and after immersion were determined using a Mettler analytical balance.

Potentiostatic polarisation studies

These studies were carried out in a three-electrode cell assembly connected to BioAnalytical Systems (BAS-100 A) electrochemical analyser provided with iR compensation facility, using carbon steel as working electrode, platinum as counter electrode and saturated calomel electrode as the reference electrode.

Impedance studies

Impedance studies were carried out in a three-electrode cell assembly using computer controlled EG&G Princeton Applied Research Model 6310 system. Carbon steel was used as the working electrode, platinum as counter electrode and saturated calomel electrode as the reference electrode.

Surface examination studies

FTIR spectra

The FTIR spectra of pure tertiary butyl phosphonic acid and of the film formed on the surface of the metal specimen were recorded using Shimadzu 8201 PC FTIR spectrophotometer.

X-ray diffraction patterns

The X-ray diffraction patterns of polished carbon steel and of the surface film formed on the metal specimen were recorded using a computer-controlled X-ray powder diffractometer JEOL JDX 8030 with Cu K_{α} (Ni filtered) radiation (wavelength = 1.5418 A°) at a rating of 40 kv, 20 mA. The scan rate was 0.05-20° per step and measuring time was 1 s per step.

X-ray photoelectron spectroscopy

XPS data from the protective films formed on the surfaces of the steel specimens were recorded using an ESCA-LAB Mk 200 ×, manufactured by VG Scientific Limited, UK, with an aluminium K_{α} X-ray source for excitation and a hemispherical analyser, which was operated on a pass energy of 20 eV for data acquisition, giving analyser resolution of 0.4 eV.

Results

Weight loss studies

The weight loss studies showed that the maximum inhibition efficiency was only 79 per cent even at the concentrations of 75 ppm Zn^{2+} and 175 ppm phosphonate.

However, when citrate was combined with the relatively low concentrations of Zn^{2+} and phosphonate, the inhibition efficiency increased substantially. For example, inhibition efficiency increased from 23 to 96 per cent by adding 150 ppm of citrate to 50 ppm Zn^{2+} and 75 ppm of TBP. Table I shows the percentage inhibition efficiencies of the ternary system, Zn^{2+}/TBP/citrate.

It is also observed that the inhibition efficiencies were not adversely affected in the pH range 5-8 (inhibition efficiencies > 90 per cent). That means this inhibitor system works very well in this pH range. However, when the pH is reduced to 4, inhibition efficiency is found to be reduced to 83 per cent.

Table I Corrosion inhibition efficiencies of the ternary system

Cl⁻ (ppm)	Zn^{2+} (ppm)	TBP (ppm)	Citrate (ppm)	Corr. rate (mdd)	IE (per cent)
60	0	0	0	12.50	–
60	50	75	0	9.51	23.11
60	50	75	25	7.16	42.73
60	50	75	50	2.83	77.81
60	50	75	75	1.54	88.04
60	50	75	100	1.28	89.76
60	50	75	125	1.17	91.80
60	50	75	150	0.71	96.36
60	50	75	175	1.18	90.10
60	50	75	200	1.21	91.50

Potentiostatic polarisation studies

The potentiostatic polarisation curves of carbon steel immersed in various inhibitor combinations are shown in Figure 1.

It is seen from Figure 1 that 50 ppm Zn^{2+} alone and 150 ppm TBP alone shifted the corrosion potentials towards the cathodic side. The binary systems, viz., 50 ppm Zn^{2+}/ 50 ppm TBP, 50 ppm Zn^{2+}/75 ppm TBP, and 50 ppm Zn^{2+}/ 150 ppm TBP also were found to shift the corrosion potentials towards the cathodic side (Table II). Interestingly the ternary systems, viz., 50 ppm Zn^{2+}/50 ppm TBP/150 ppm citrate, and 50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate also shifted the corrosion potential more cathodic.

On comparing the shifts in the anodic and cathodic Tafel slopes for binary and ternary inhibitor systems, it was found that there is shift in both the anodic and the cathodic Tafel slopes, but shifts in cathodic Tafel slopes were greater than were those in anodic Tafel slopes. It can be inferred, therefore, that the inhibitor acted as a mixed inhibitor, predominantly cathodic in nature.

Figure 1 Polarisation curves of carbon steel immersed in various environments
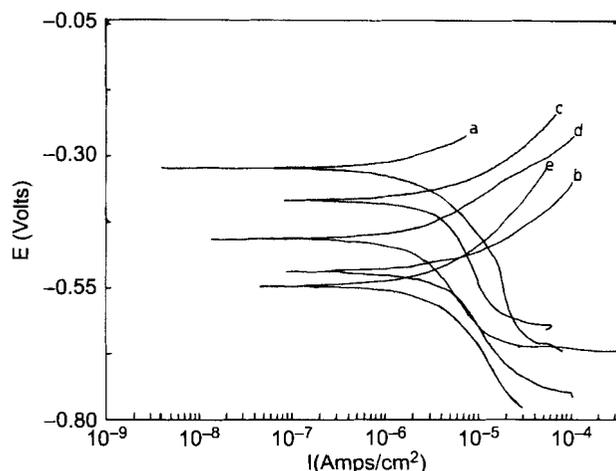
Notes: (a) 60 ppm Cl⁻; (b) 60 ppm Cl⁻/50 ppm Zn^{2+}; (c) 60 ppm Cl⁻/150 ppm TBP; (d) 60 ppm Cl⁻/50 ppmZn^{2+}/75 ppm TBP; (e) 60 ppm Cl⁻/50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate

Table II Corrosion parameters obtained by the potentiostatic polarisation method for carbon steel in neutral aqueous environment in the presence and absence of inhibitor

Cl⁻ (ppm)	Zn²⁺ (ppm)	TBP (ppm)	Citrate (ppm)	E_{corr} (mV)	I_{corr} $\mu A/cm^2$	b_a (mV/dec)	b_c (mV/dec)
60	0	0	0	−322	2.30	81	187
60	50	0	0	−573	3.20	78	220
60	0	150	0	−389	3.20	100	250
60	50	50	0	−457	1.80	87	182
60	50	75	0	−427	0.96	72	230
60	50	100	0	−399	0.77	72	250
60	50	150	0	−452	1.90	100	230
60	50	50	150	−500	1.08	73	160
60	50	75	150	−434	1.10	83	234
60	50	100	150	−492	6.80	120	250

Figure 2 XRD patterns of carbon steel surfaces

Notes: (a) Polished metal sample surface, (b) Surface of metal immersed in 60ppm Cl⁻/50 ppm/Zn²⁺/75ppm TBP/150ppm citrate

Impedance studies

Calculations from the impedance data using Bode plots show that the charge transfer resistance for Zn^{2+} alone was 1,048 ohm and for TBP alone was 1,756 ohm (Table III). The charge transfer resistances for the binary and ternary inhibitor systems were very high, i.e. 34,977 and 35,466 ohm, respectively. The calculated inhibition efficiencies were in good agreement with those obtained from the weight loss studies.

XRD patterns

An example XRD pattern from the surface of the polished metal samples is shown in the Figure 2(a). It shows characteristic iron peaks at $2\theta = 44.7, 64.8, 82.3°$.

The XRD pattern from the surface of the specimens immersed in an environment containing 60 ppm Cl⁻/50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate (Figure 2(b)) also showed the presence of characteristic iron peaks only. This result infers the absence of any oxides of iron, such as γ-FeOOH and Fe_3O_4, in the protective film (Favre and Landolt, 1993).

FTIR spectra

The FTIR spectrum of pure tertiary butyl phosphonic acid is shown in Figure 3(a). The various bands are assigned as follows: absorption bands due to the bending of O-P-O bonds

Table III Impedance parameters by the impedance method for carbon steel in neutral aqueous environment in the presence and absence of inhibitor

Cl⁻ (ppm)	Zn²⁺ (ppm)	TBP (ppm)	Citrate (ppm)	R_s (Ω)	R_t (Ω)	R_{ct} (Ω)	IE (per cent)
60	–	–	–	1,605	3,351	1,746	–
60	50	–	–	998	2,046	1,048	–
60	–	150	–	1,211	2,967	1,756	–
60	50	50	–	426	5,228	4,802	63
60	50	75	–	1,021	19,068	18,037	90
60	50	100	–	1,048	36,025	34,977	95
60	50	150	–	774	6,820	6,046	71
60	50	50	150	773	5,837	5,064	66
60	50	75	150	1,740	19,072	18,332	91
60	50	100	150	844	35,310	35,466	95

appear at 441 and 580 cm⁻¹. The P-O stretching frequency occurs at 1,080 cm⁻¹ (Silverstein *et al.*, 1981; Nakamoto, 1986; Cross, 1960). The FTIR spectrum of the surface film formed on the metal specimen immersed in the environment consisting of 60 ppm Cl⁻/50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate is shown in Figure 3(b). It is evident that the degree of stretching of the P-O bond decreased from 1,080 to 1,000 cm⁻¹. This observation suggests that the O-atom of the phosphonic acid is coordinated to metal ion. The band for carbonyl group was shifted from 1,715 to 1,580 cm⁻¹, suggesting the participation of the carbonyl group of the citrate ion in complex formation. This observation confirmed the formation of [Fe^{2+}-TBP-citrate] complex on the metal surface. The band at 1,320 cm⁻¹ was due to the presence of $Zn(OH)_2$ (Sekine and Hirakawa, 1986).

XPS pattern

XPS of the protective film formed on the surface of the carbon steel specimen immersed in the environment consisting of 60 ppm Cl⁻/50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate is shown in the Figure 4.

The XPS trace can be interpreted on the basis of data in the literature (Wagner *et al.*, 1978) for various elements exhibiting peaks at characteristic binding energy levels. The peaks at 284.4 and 531.4 eV were due to the $1s_{1/2}$ photoelectrons of carbon and oxygen, respectively. The peaks at 1,023 and 1,046 eV were due to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ photoelectrons, respectively. The peaks at 449 and 476 eV were the Auger peaks due to LMM transitions for zinc. A peak at 133 eV was due to $2p_{3/2}$ photoelectrons of P, and at 198.3 eV was due to the $2p_{3/2}$ photoelectrons of Cl. The peaks at 708 eV and 721 were attributed to the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ photoelectrons, respectively.

Discussion

Results from the potentiostatic polarisation studies infer that this ternary inhibitor system acts as a mixed inhibitor, though predominantly cathodic. It is well known that cathodic inhibitors are safer than the anodic inhibitors. The XRD pattern of the protective film corresponded to iron peaks only, and this indicated that oxides of iron were absent. The FTIR

Figure 3
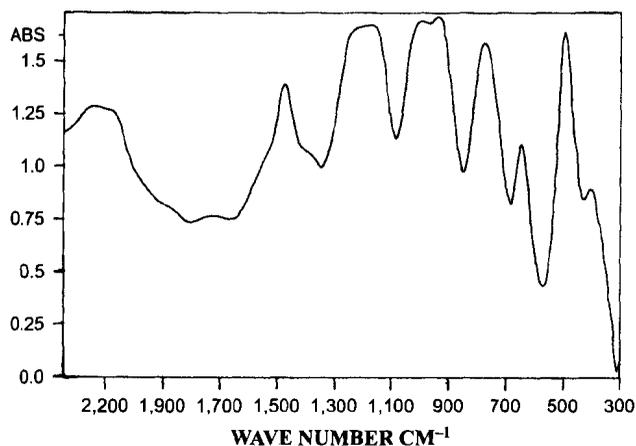
(a) FTIR Spectrum of pure TBP
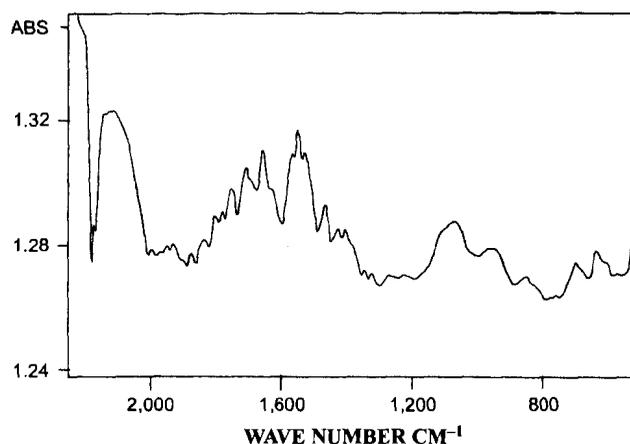
(b) FTIR Spectrum of the protective film on carbon steel surface

Figure 4 XPS of the protective film on carbon steel surface
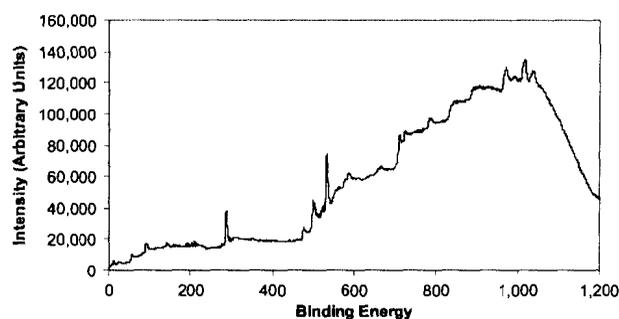
spectra indicated that zinc hydroxide and the [Fe^{2+}/Fe^{3+}-TBP-citrate] complex were present on the surface of the metal. The XPS clearly shows the presence of P, C, O, Fe, Zn and Cl. The presence of Zn can be interpreted due to Zn $(OH)_2$. The presence of Fe, O, P and C can be interpreted in terms of formation of [Fe^{2+}/Fe^{3+}-TBP-citrate] complex. Thus, the presence of the complex in the surface film is revealed by both FTIR spectra and XPS patterns. In view of these inferences, the following mechanism of corrosion inhibition can be proposed:
- When the environment containing 60 ppm Cl^-/50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate was prepared, a [Zn^{2+}-TBP-citrate] complex was formed in the solution. Besides this complex, there is presence of free TBP, citrate and Zn^{2+} ions.
- When the metal was immersed in this environment, the [Zn^{2+}-TBP-citrate] complex diffused from the bulk of the solution onto the surface of the metal and further complexes with Fe^{2+}/Fe^{3+} ions available due to initial corrosion.
- Free TBP and citrate molecules diffuse from bulk of the solution to the metal surface and form [Fe^{2+}/Fe^{3+}-TBP-citrate] complexes. These complexes fill the pores of the film formed on the surface and make it protective.
- Free Zn^{2+} ions diffuse from the bulk of the solution to the metal surface and form Zn $(OH)_2$ at the local cathodic sites.
- Thus, the corrosion is controlled by the protective film consisting of Zn $(OH)_2$ and metal – inhibitor complex, viz., [Fe^{2+}/Fe^{3+}-TBP-citrate].

- Formation of Zn $(OH)_2$ controls the cathodic reaction and formation of (metal – inhibitor) complexes controls the anodic reaction. Hence, the inhibition is under mixed control.

Conclusions

- The binary system consisting of 50 ppm Zn^{2+} and 75 ppm TBP had an inhibition efficiency of only 23 per cent. However, a ternary formulation consisting of 50 ppm Zn^{2+}/75 ppm TBP/150 ppm citrate was observed to achieve 96 per cent inhibition efficiency.
- The ternary formulation was effective in the pH range 5-8, which matched the pH range of the majority of cooling water systems.
- The inhibitor Zn^{2+}/TBP/citrate acted as a mixed inhibitor, though its predominant effect was on the cathodic reaction.
- The protective film on the metal surface consists of Zn $(OH)_2$ and Fe^{2+}/Fe^{3+}-TBP-citrate complex. Formation of metal – inhibitor complexes plays a significant role in controlling corrosion of carbon steel.

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