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Synergistic effect of 2-chloroethyl phosphonic acid and Zn^{2+}

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Keywords

Corrosion inhibitors, Steel

Abstract

2-chloroethyl phosphonic acid (2-Cl EPA) and Zn^{2+} show a synergistic effect in controlling corrosion of carbon steel in a neutral aqueous environment containing 60 ppm Cl^-. The protective film consists of Fe^{2+}–2–Cl EPA complex and $Zn(OH)_2$; it is found to be uv-luminescent.

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Introduction

Use of inhibitors is an old remedy to combat the new challenges in the field of corrosion in cooling water systems. Phosphonic acids are the inhibitors which have been widely used, due to their stability, ability to form complexes with metal cations and scale inhibiting properties (Fang *et al.*, 1993; Kalman *et al.*, 1993; Kuznetzov *et al.*, 1987; Niess *et al.*, 1985; Rajendran *et al.*, 1995, 1998a, 1998b, 1999). Bis (2-chloroethyl) phosphonate and bis (2-chloroethyl) vinyl phosphonate have been used in corrosion inhibiting rubber compounds for steel surfaces (Niess *et al.*, 1985). The present study investigates the synergistic effect of sodium salt of 2 chloroethyl phosphonic acid (2 Cl EPA) and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment containing 60ppm Cl^-, a situation commonly encountered in cooling water technology, by weight loss method, and examines the protective film by x-ray diffraction, fourier trans form infrared (FTIR) and luminescence spectra.

Experimental

Preparation of the specimens

Mild steel specimens (0.02 to 0.03% S, 0.03 to 0.08% P, 0.4 to 0.5% Mn, 0.1 to 0.2% C and the rest iron) of the dimensions $1.0 \times 4.0 \times 0.2$cm were polished to mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

Weight-loss method

Mild steel specimens, in triplicate, were immersed in 100ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+}, for seven days. The weights of the specimens

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before and after immersion were determined using a Mettler balance, AE-240. The corrosion products were cleaned with Clarke's solution (Wranglen, 1985).

Surface examination study

The mild steel specimens were immersed in various test solutions for a period of three days. After three days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

FTIR spectra

These spectra were recorded in a Perkin Elmer-1600 spectrophotometer.

X-ray diffraction technique

The XRD patterns of the film formed on the metal surface were recorded using a computer controlled x-ray powder diffractometer, JEOL JDX 8030 with CuK$_\alpha$ (Ni-filtered) radiation (λ = 1.5418 Å) at a rating of 40 kV, 20 mA. The scan rate was 0.05-20° per step and the measuring time was one second per step.

Luminescence spectra

The luminescence spectra of the film formed on the metal surface were recorded using a Hitachi 650-10 S fluorescence spectrophotometer equipped with a 150W Xenon lamp and a Hamamatsu R 928 F photomultiplier tube. The emission spectra were corrected for the spectral response of the photomultiplier tube used.

Results and discussion

Weight-loss method

The inhibition efficiencies (IE) of 2-chloroethylphosphonic acid (2 Cl EPA) in controlling corrosion of carbon steel immersed in an aqueous solution containing 60ppm Cl^-, a situation commonly encountered in cooling water technology, in the presence and absence of Zn^{2+}, are given in Table I. It is found that 2 Cl EPA is not a good inhibitor. Zn^{2+} is found to be corrosive. However, their combination shows better inhibition efficiency. For example, the formulation consisting of 300ppm 2 Cl EPA and 300 ppm Zn^{2+} shows 95 per cent IE. This suggests a synergistic effect between 2 Cl EPA and Zn^{2+}. During the weight-loss experiment, a thin interference film was observed on the mild specimens.

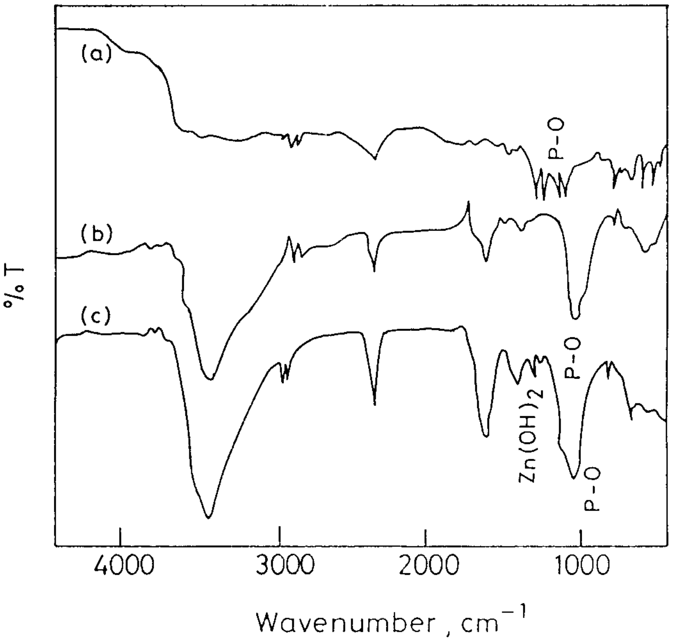
Table I Corrosion rates of mild steel in neutral aqueous environment (Cl^- = 60ppm) in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight-loss method
Inhibitor system : 2 Cl EPA + Zn^2+

2 Cl EPA (ppm)	Zn^{2+} (ppm)	Corrosion rate (mg/dm^2/day)	Inhibition efficiency (%)
0	0	15.54	–
10	0	14.92	4
50	0	14.61	6
100	0	12.74	18
150	0	14.61	6
200	0	14.45	7
300	0	14.30	8
10	300	11.30	27
50	300	8.08	48
100	300	8.08	48
150	300	8.24	47
200	300	1.55	90
300	300	0.78	95
0	300	22.53	–45

FTIR spectra

The FTIR spectrum of 2 Cl EPA is shown in Figure 1a. The FTIR spectrum (KBr) of the film formed on the surface of the metal specimen immersed in the solution containing 60ppm Cl^- and 300ppm 2 Cl EPA is shown in

Figure 1 FTIR spectra of 2-Cl EPA (a) and of carbon steel surface immersed in various environments (b, c)



(a) Pure 2-Cl EPA
(b) Cl^- 60 ppm + 2-Cl EPA 300 ppm
(c) Cl^- 60 ppm + 2-Cl EPA 300 ppm + Zn^{2+} 300 ppm

Figure 1b. The P-O stretching frequency of the phosphonic acid decreases from 1,115.9cm^{-1} to 1,058.1cm^{-1}. This shift is caused by the decrease of electron density of the P-O bond. Owing to the shift of electron density from O atom to Fe^{2+}, it is suggested that O atom of the phosphonic acid is coordinated to Fe^{2+}, resulting in the formation of Fe^{2+}–2 Cl EPA complex, on the anodic sites of the metal surface, thus retarding the anodic reaction of dissolution of metal.

The FTIR spectrum (KBr) of the film formed on the surface of the metal immersed in the solution containing 60ppm Cl^-, 300ppm 2 Cl EPA and 300 ppm Zn^{2+} is given in Figure 1c. The P-O stretching frequency decreases from 1,115.9 to 1,078.5cm^{-1}. This suggests that the O atom of phosphonic acid is coordinated to Fe^{2+}, resulting in the formation Fe^{2+}–2 Cl EPA complex on the anodic sites of the metal surface. The band at 1,340cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface, thus controlling the cathodic reaction of generation of OH^-.

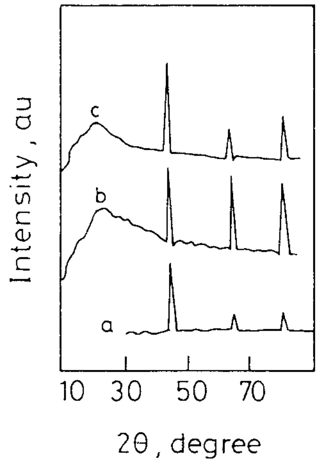
In the absence of Zn^{2+}, anodic reaction only is controlled. In the presence of Zn^{2+} both anodic reaction and cathodic reaction are controlled. This accounts for the synergistic effect between 2 Cl EPA and Zn^{2+}.

X-ray diffraction (XRD)

The XRD pattern of the polished metal not immersed in any solution shows iron peaks only (2θ = 44.8°, 65.1°, 82.4° and 99.0°) (Figure 2a). The XRD pattern of the film formed on the surface of the metal immersed in the solution containing 60ppm Cl^- and 300ppm 2 Cl EPA shows iron peaks at 2θ = 45.0°, 65.4° and 82.7° (Figure 2b). The peak at 2θ = 16° is due to Fe-O coordination (Rajendran *et al.*, 1998b). This suggests the presence of iron phosphonate comple on the metal surface.

The XRD pattern of the film found on the surface of the metal specimen immersed in the solution containing 60ppm Cl^-, 300ppm EPA and 300 ppm Zn^{2+} shows iron peaks at 2θ = 44.6°, 65.0° and 82.4° (Figure 2c). The peak at 2θ = 16.2° is due to Fe-O coordination. This suggests the presence of iron phosphonate complex on the metal surface (Rajendran *et al.*, 1998b).

Figure 2 XRD pattern of carbon steel surface immersed in various environments



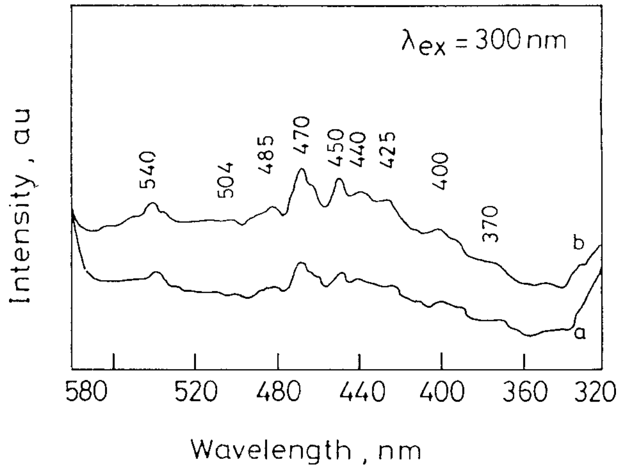
(a) Polished Metal
(b) Cl^- 60 ppm + 2-Cl EPA 300 ppm
(c) Cl^- 60 ppm + 2-Cl EPA 300 ppm + Zn^{2+} 300 ppm

The uv-luminescence spectra

The uv-luminescence spectrum (λ_{ex} = 300nm) of the film formed on the surface of the metal immersed in the solution containing 60ppm Cl^- and 300ppm 2 Cl EPA is shown in Figure 3a. This spectrum is due to Fe^{2+}–2 Cl EPA complex present on the metal surface. The peak at 470nm is due to Fe-O coordination (Rajendran *et al.,* 1995, 1998a, 1998b). This confirms the presence of iron phosphonate complex on the metal surface.

The uv-luminescence spectrum (λ_{ex} = 300nm) of the film formed on the surface of the metal immersed in the solution containing 60ppm Cl^-,

Figure 3 Luminescence spectra of carbon steel surface immersed in various environments



(a) Cl^- 60 ppm + 2-Cl EPA 300 ppm
(b) Cl^- 60 ppm + 2-Cl EPA 300 ppm + Zn^{2+} 300 ppm

300ppm 2 Cl EPA and 300 ppm Zn^{2+} is shown in Figure 3b. This spectrum corresponds to Fe^{2+}–2 Cl EPA, entrailed in $Zn(OH)_2$. The peak at 470nm is due to Fe-O coordination (Rajendran *et al.*, 1995, 1998a, 1998b). This confirms the presence of iron phosphonate complex on the metal surface.

It is observed that the intensities of the peaks are slightly higher for the 2 Cl EPA – Zn^{2+} system. This suggests that more iron phosphonate complex is formed on the metal surface when carbon steel is immersed in the 2 Cl EPA–Zn^{2+} system. This accounts for the synergistic effect of this formulation and confirms that phosphonates function as transporters of Zn^{2+}, from the bulk to the metal surface.

Conclusions

- 2 Cl EPA – Zn^{2+} system shows a synergistic effect in controlling corrosion of carbon steel in a neutral aqueous environment containing 60ppm Cl^-.
- The protective film consists of Fe^{2+} – 2 Cl EPA complex and $Zn(OH)_2$
- The protective film is found to be uv-fluorescent.

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