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Corrosion inhibition by phosphonic acid $-Zn^{2+}$ systems for mild steel in chloride medium

S. Rajendran
B.V. Apparao and
N. Palaniswamy

The authors

S. Rajendran is based at the Corrosion Study Centre, Department of Chemistry, G.T.N. Arts College (Autonomous), Dindigul, Tamil Nadu, India.
B.V. Apparao is based in the Department of Chemistry, Regional Engineering College, Warangal, Andhrapradesh, India.
N. Palaniswamy is based in the Corrosion Science and Engineering Division, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India.

Keywords

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Abstract

The inhibition efficiencies of 2-carboxyethyl phosphonic acid (2 CEPA) – Zn^{2+} system and ethyl phosphonic acid (EPA) – Zn^{2+} system in controlling corrosion of mild steel in a neutral aqueous environment containing 60ppm Cl^- have been compared. Polarization study reveals that both the systems function as mixed inhibitors. The inhibition efficiencies of these systems decrease with period of immersion due to the dissolution of the protective film as the period of immersion increases. The 2 CEPA – Zn^{2+} system has a better inhibition efficiency than the EPA–Zn^{2+} system. This is due to the fact that the amount of Fe^{2+}– 2 CEPA complex present on the metal surface is higher than that of Fe^{2+}– EPA complex, as revealed by fluorescence spectra. The molecular size of the iron phosphonate complex exercises a greater influence than the electronic (inductive) effect of the substituent in controlling corrosion of mild steel in chloride environment.

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Introduction

Several phosphonic acids have been used as corrosion inhibitors due to their ability to form complexes with metal ions and hydrolytic stability (Airey *et al.*, 1988; Fang *et al.*, 1993; Kalman *et al.*, 1994; Kuznetzov and Bardasheva, 1988; Mathiyarasu *et al.*, 1997; Rajendran *et al.*, 1995; 1996; 1997; 1998a; 1998b; Varallyai *et al.*, 1990; Veres *et al.*, 1990). They have been used in combination with Zn^{2+}. The present study:

- compares the inhibition efficiencies (IE) of 2-carboxyethyl phosphonic acid (2 CEPA) $-Zn^{2+}$ system and ethyl phosphonic acid (EPA) $-Zn^{2+}$ system in controlling corrosion of mild steel in a neutral aqueous environment containing 60ppm Cl^-;
- investigates if there is any variation in the inhibition efficiency as the period of immersion is varied; and
- offers an explanation, if there is any variation in IE.

Experimental

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. For potentiostatic polarization studies, mild steel rod encapsulated in Teflon with an exposed cross-section of 0.5cm diameter was used as the working electrode. Its surface was polished to mirror finish and degreased with trichloroethylene.

Weight-loss method

Three mild steel specimens were immersed in 100ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+}, for a period of seven days. The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion

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products were cleaned with Clarke's solution (Wranglen, 1985). The per cent inhibition efficiency (IE) was calculated using the relation, IE = $[(W_1 - W_2)/W_1] \times 100$, where, W_1 and W_2 are weight losses of mild steel in uninhibited and inhibited chloride solutions.

Potentiostatic polarization study

This study was carried out in a three-electrode cell assembly connected to bioanalytical system (BAS – 100A) electrochemical analyser, provided with iR compensation facility, using mild steel as the working electrode, platinum as the counter electrode and saturated calomel electrode as the reference electrode. The scan rate was 1,000μV/second.

The uv-visible spectra

The uv-visible absorption spectra of solutions were recorded using Hitachi U-3400 spectrophotometer.

FTIR spectra

They were recorded in a Perkin Elmer 1600 FTIR spectrophotometer. A total of 16 scans were made. The resolving power was 4.0cm^{-1}.

Fluorescence spectra

The mild steel specimens were immersed in various test solutions for a period of seven days. After seven days, the specimens were taken out and dried. The emission and excitation spectra were recorded in a Hitachi F-4500 fluorescence spectrophotometer. The scan speed was 240nm/min. The slit was (EX/EM) 10.0nm/5.0nm; the PMT voltage was 700V and the response was auto shutter control.

The 3D fluorescence contour spectra were recorded by exciting the film formed on the metal surface, in the wavelength region of 250 to 600nm and recording the corresponding emission spectra for each wavelength of excitation continuously. The scan speed was 2,400nm/min; the slit was (EX/EM) 5.0nm/5.0nm; the PMT voltage was 700V and the response was auto shutter control.

Results and discussion

Weight loss method

The inhibition efficiencies of the systems consisting of various concentrations of 2-carboxyethyl phosphonic acid and 50ppm Zn^{2+} were determined. Similar experiments were carried out for ethyl phosphonic acid –Zn^{2+} systems also. The results are given in Table I. It is found that 2 CEPA – Zn^{2+} systems show better inhibition efficiency than the EPA – Zn^{2+} systems. In both cases, the inhibition efficiency decreases as the period of immersion increases (Figure 1). In the case of 2 CEPA – Zn^{2+} system, the inhibition efficiency was 99 per cent at the end of one day and it decreased to 98 per cent on the seventh day. The corresponding inhibition efficiencies are 95 per cent and 58 per cent respectively for the EPA – Zn^{2+} system. The reason for such a decrease in inhibition efficiencies is analysed by uv-visible absorption spectra.

uv-visible absorption spectra

The uv-visible absorption spectra of various test solutions are given in Figure 2. The spectrum of the solution containing iron-EPA complex prepared by mixing 100ppm Fe^{2+} and 200ppm EPA is given in Figure 2a. The absorption spectra of solution (Cl^- 60ppm + Zn^{2+} 50ppm + EPA 200ppm) in which mild steel specimens were immersed for a period of one day and seven days are given in Figures 2b and c respectively. It is found that the absorption is higher in the latter case. This is

Table I. Inhibition efficiencies of various inhibitor systems

Phosphonic acid (ppm)	Zn^{2+} (pm)	Inhibition efficiency (%) EPA	2 CEPA
25	50	16	20
50	50	27	90
100	50	45	96
150	50	50	97
200	50	58	98

Figure 1 Inhibition efficiency, obtained by weight-loss method, as a function of time

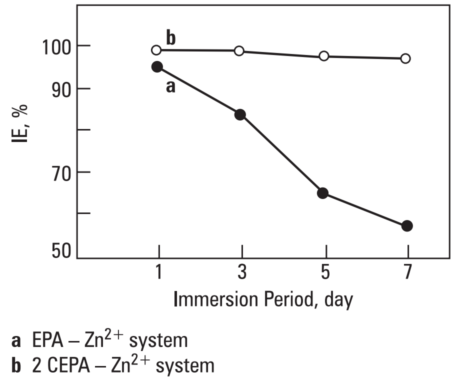
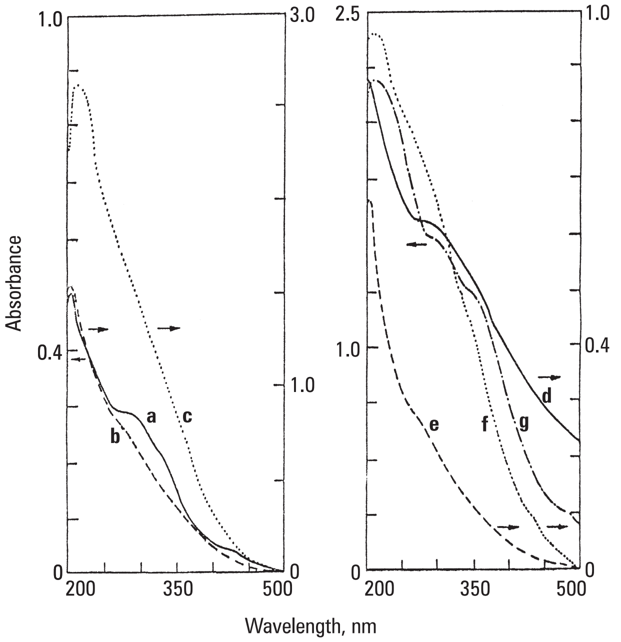


Figure 2 UV-visible absorption spectra of various test solutions



a Fe^{2+} 100 ppm + EPA 200 ppm
b Cl^- 60 ppm + Zn^{2+} 50 ppm + EPA 200 ppm (Immersion period 1 day)
c Cl^- 60 ppm + Zn^{2+} 50 ppm + EPA 200 ppm (Immersion period 7 days)
d Fe^{2+} 100 ppm + 2 CEPA 200 ppm
e Cl^- 60 ppm + Zn^{2+} 50 ppm + 2 CEPA 200 ppm (Immersion period 1 day)
f Cl^- 60 ppm ± Zn^{2+} 50 ppm + 2 CEPA 200 ppm (Immersion period 7 days)
g Cl^- 60 ppm + 2 CEPA 200 ppm (Immersion period 7 days)

due to the fact that, as the period of immersion increases, the amount of iron complex formed on the metal surface getting dissolved also increases.

The absorption spectrum of the solution containing iron-2 CEPA complex prepared by mixing 100ppm Fe^{2+} and 200ppm 2 CEPA is given in Figure 2d. The absorption spectra of solutions (Cl^- 60ppm + Zn^{2+} 0.50ppm + 2 CEPA 200ppm) in which mild steel specimens were immersed for a period of one day and seven days are given in Figures 2e and f respectively. It is observed that the absorption is higher in the latter case. This is due to the fact that as the period of immersion increases the rate of dissolution of the protective film (iron-2 CEPA complex) also increases.

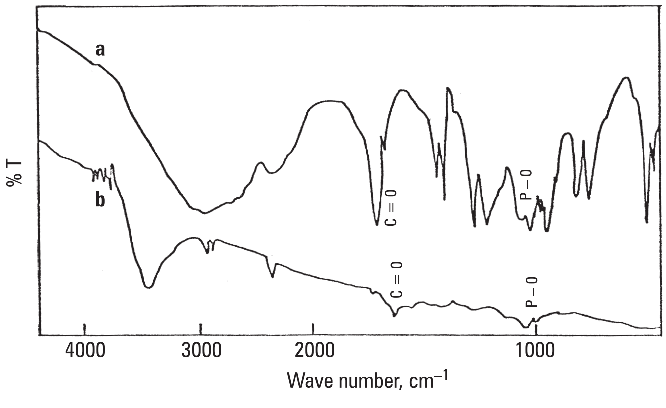
Comparison of Figures 2a and d reveals that absorbance value is higher for iron-2 CEPA complex than for iron-EPA complex. This indicates that the ability to form complex with iron is higher for 2 CEPA than for EPA.

Comparison of Figures 2b and e and also 2c and f reveals that absorbance values are higher for b and c than for e and f. This suggests that the amount of iron-EPA complex present in solution is higher than that of iron-2 CEPA complex. This in turn suggests that the protective film dissolves relatively faster in the former case (Zn^{2+} – 2 CEPA system) than in the latter case (Zn^{2+} – EPA system).

During weight loss study, it was found that the formulation consisting of 200ppm EPA offered 2 per cent inhibition efficiency (IE) to mild steel immersed in 60ppm Cl^- for a period of seven days. But the corresponding 2 CEPA system was found to be corrosive; the test solution was reddish brown in colour. It was expected that, in the absence of Zn^{2+}, and in the presence of 200ppm 2 CEPA only, the film formed on the mild steel surface dissolved completely; or the rate of diffusion of 2 CEPA from the bulk of the solution to the metal surface was lower than the rate of dissolution of metal resulting in the formation of Fe^{2+}/Fe^{3+} and diffusing towards the bulk of the solution. This results in the formation of iron-2 CEPA complex in solution. To confirm this, uv-visible absorption spectrum of the solution in which mild steel was immersed for seven days was recorded (Figure 2g). It is found that the absorbance value is higher (even after 1:1 dilution). This confirms that more iron-2 CEPA complex is present in the bulk of the solution.

The reddish brown solution was filtered. The FTIR spectrum of the residue is given in Figure 3b. The FTIR spectrum of pure 2 CEPA is given in Figure 3a. The P-O stretching frequency appears at 1,020cm^{-1} and the carboxyl group absorption band occurs at 1,715.8cm^{-1} (Cross, 1990; Nakamoto, 1986; Silverstein *et al.*, 1981). Comparison of this spectrum with that of the residue (Figure 3b) reveals that the P-O

Figure 3 FTIR spectra



a Pure 2 CEPA
b Residue of the solution in which mild steel was immersed in the environment Cl^- = 60 ppm and 2 CEPA = 200 ppm (7 days)

stretching frequency of phosphonic acid has decreased from $1,020cm^{-1}$ to $1,000cm^{-1}$. The C = O stretching frequency of the carboxyl group has decreased from $1,715.8cm^{-1}$. It is suggested that the phosphonic acid has coordinated through the oxygen atoms of phosphonic group and carboxyl group to Fe^{2+} resulting in the formation of iron-2 CEPA complex. Thus the presence of iron-2 CEPA complex in solution is confirmed.

Polarization curves

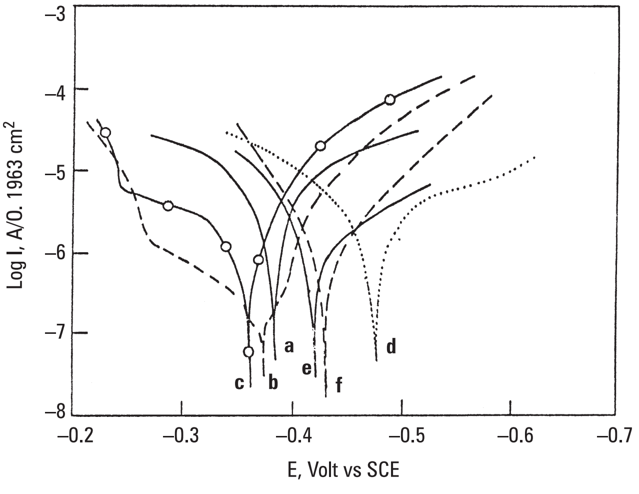
The polarization curves of mild steel immersed in various environments are given in Figure 4. Addition of 200ppm EPA to the environment containing 60ppm Cl^- shifts the corrosion potential from –389mV vs SCE to –380mV vs SCE (positive region); 200ppm 2 CEPA shifts the corrosion potential to more positive region (to –370mV vs SCE). This suggests that 2 CEPA retards the anodic reaction of metallic dissolution ($Fe \rightarrow Fe^{2+} + 2e^-$) more effectively than EPA. This is due to the fact that 2 CEPA is coordinated to Fe^{2+} through the carboxylate anion and the phosphonate anion, whereas it is only through the phosphonate anion in the case of EPA.

When 50ppm Zn^{2+} is added to the chloride environment, the corrosion potential is shifted to the negative region (to –489mV vs SCE) (Figure 4d). When 50ppm Zn^{2+} is added to 200ppm EPA the corrosion potential is shifted to –420mV vs SCE. When 50ppm Zn^{2+} is added to 200ppm 2 CEPA, the corrosion potential is shifted to –438mV vs SCE. These potentials are in between those of anodic and cathodic shifts. It is suggested that the EPA-Zn^{2+} system and also 2 CEPA – Zn^{2+} system function as mixed inhibitors. They retard the anodic reaction by forming Fe^{2+} – EPA complex and Fe^{2+} – 2 CEPA complex respectively and the cathodic reaction by the formation of $Zn(OH)_2$ on the cathodic sites.

Fluorescence spectra

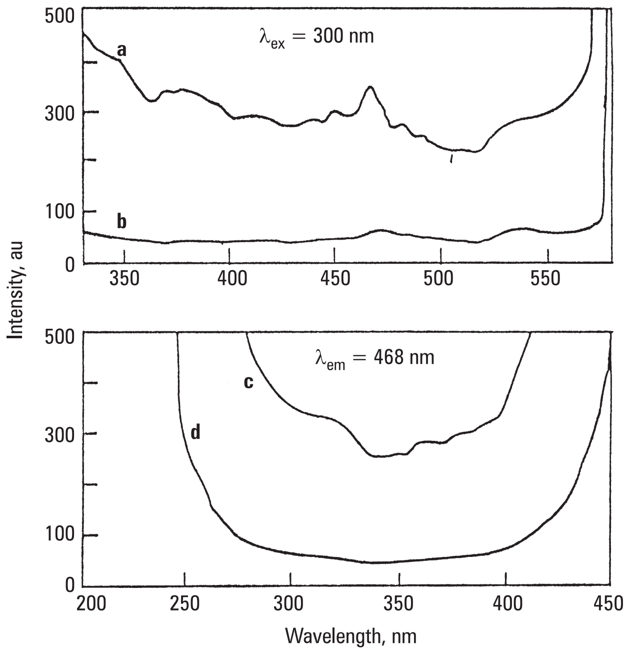
The emission spectrum (λ_{ex} = 300nm) of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 200ppm 2 CEPA and 50ppm Zn^{2+} is given in Figure 5a. A prominent peak appears at 468.5nm. The corresponding peak for the EPA system appears at 469nm (Figure 5b). It is found that the intensity of the peak is higher (341.6) in the former case and relatively lower (62.11) in the latter case. This confirms that the amount of Fe^{2+} – 2 CEPA complex present on the metal surface is higher than the amount of Fe^{2+} – EPA complex. This accounts for the higher inhibition efficiency (98 per cent) in the former case and lower inhibition efficiency (58 per cent) in the latter case.

Figure 4 Polarization curves of mild steel immersed in various environments



a Cl^- 60 ppm
b Cl^- 60 ppm + EPA 200 ppm
c Cl^- 60 ppm + 2 CEPA 200 ppm
d Cl^- 60 ppm Zn^{2+} 50 ppm
e Cl^- 60 ppm Zn^{2+} 50 ppm + EPA 200 ppm
f Cl^- 60 ppm Zn^{2+} 50 ppm +2 CEPA 200 ppm

Figure 5 Fluorescence spectra of surface of mild steel immersed in various environments



a and **c** Cl^- 60 ppm + 2 CEPA 200 ppm + Zn^{2+} 50 ppm
b and **d** Cl^- 60 ppm + EPA 200 ppm + Zn^{2+} 50 ppm

The excitation spectrum (λ_{em} = 468nm) of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 200ppm 2 CEPA and 50ppm Zn^{2+} is given in Figure 5c. Peaks appear at 317nm, 345nm and 361nm. The corresponding spectrum for the EPA system is given in Figure 5d. It is found that the intensity of spectrum is higher in the former case and lower in the latter case. Thus excitation spectra also confirm that the amount of Fe^{2+} – 2 CEPA complex formed on the metal surface is higher than the amount of Fe^{2+} – EPA complex formed on the metal surface, thus being in agreement with the results of the weight loss method.

3D fluorescence spectra

The 3D fluorescence contour of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 200ppm 2 CEPA and 50ppm Z^{2+} is given in Figure 6a. The emission spectrum (λ_{ex} = 300) derived from Figure 6a is given in Figure 6b. The emission peak appears at 460nm, with an intensity of 86.76. The excitation spectrum (λ_{ex} = 460nm) is given in Figure 6c.

The 3D fluorescence contour of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 200ppm EPA and 50ppm Zn^{2+} is given in Figure 7a. The emission spectrum (λ_{ex} = 300nm) derived from Figure 7a is given in Figure 7b. The emission peak appears at 470nm, with an intensity of 15.26. The excitation spectrum (λ_{em} = 470nm) is given in Figure 7c.

In Figures 6a and 7a the regions xx and yy are due to scattering. It is found that the other regions are more shaded in Figure 6a than in Figure 7a. This suggests that the intensity of the peaks are higher in the 2 CEPA – Zn^{2+} system than in the EPA – Zn^{2+} system; the amount of Fe^{2+} – 2 CEPA complex on the metal surface is higher than that of Fe^{2+} – EPA complex. This accounts for the higher inhibition efficiency of the 2 CEPA – Zn^{2+} system and lower inhibition efficiency of the EPA – Zn^{2+} system.

Comparison of Figures 6b and 7b reveals that the intensity of the emission spectrum is relatively higher in the 2 CEPA – Zn^{2+} system than in the EPA – Zn^{2+} system, thus supporting the results of the weight loss experiments.

Comparison of Figures 6c and 7c reveals that the intensity of the excitation spectrum is relatively higher in the 2 CEPA – Zn^{2+} system

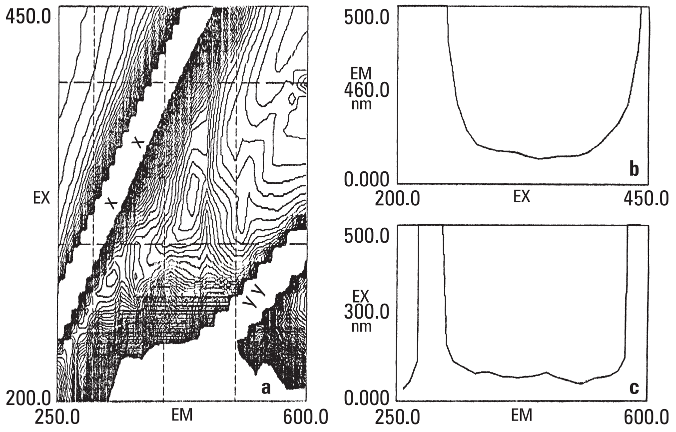


Figure 6 Fluorescence spectra of surface of mild steel immersed in the environment Cl^- 60ppm + 2 CEPA 200ppm + Zn^{2+} 50ppm

Sample :
Comment :
Data Mode : Fluorescence Scan Speed: 2400 nm/min
EX Start WL: 200.0 nm EX End WL: 450.0 nm Sampling Interval: 10.0 nm
EM Start WL: 250.0 nm EM End WL: 600.0 nm Sampling Interval: 10.0 nm
Contour Interval: 5.000 Slit (EX/EM): 5.0 nm/5.0 nm
PMT Voltage: 700 V Response: Auto
Shutter Control

a 3D contour
b Emission spectrum (λ_{ex} = 300 nm) derived from 3D contour
c Excitation spectrum (λ_{em} = 460 nm) derived from 3D contour

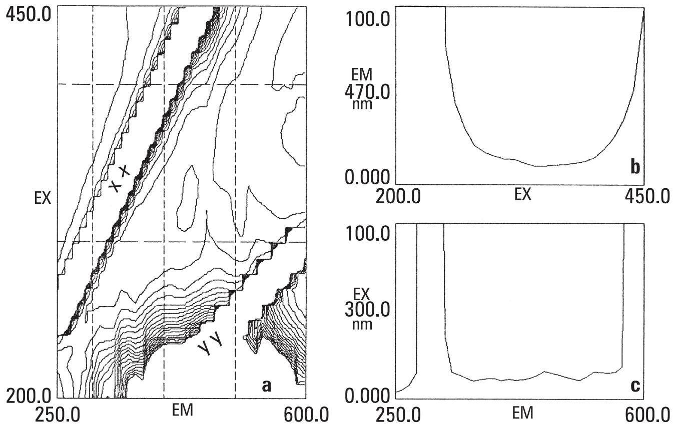


Figure 7 Fluorescence spectra of surface of mild steel immersed in the environment Cl^- 60ppm + 2 EPA 200ppm + Zn^{2+} 50ppm

Sample :
Comment :
Data Mode : Fluorescence Scan Speed: 2400 nm/min
EX Start WL: 200.0 nm EX End WL: 450.0 nm Sampling Interval: 10.0 nm
EM Start WL: 250.0 nm EM End WL: 600.0 nm Sampling Interval: 10.0 nm
Contour Interval: 5.000 Slit (EX/EM): 5.0 nm/5.0 nm
PMT Voltage: 700 V Response: Auto
Shutter Control

a 3D contour
b Emission spectrum (λ_{ex} = 300 nm) derived from 3D contour
c Excitation spectrum (λ_{em} = 470 nm) derived from 3D contour

than in the EPA – Zn^{2+} system, thus supporting the results of the weight loss experiments.

Mechanism of corrosion inhibition

The following mechanism of corrosion inhibition has been proposed for the phosphonic acid (PA) – Zn^{2+} system:

(1) When the environment consisting of chloride, phosphonic acid (PA) and Zn^{2+} is prepared, there is formation of Zn^{2+} – PA complex in solution.

(2) When mild steel is immersed in this solution, the Zn^{2+} – PA complex diffuses from the bulk towards the metal surface.

(3) On the metal surface, Zn^{2+} – PA complex is converted into Fe^{2+} – PA complex, on the anodic sites, thus retarding the anodic reaction:

$$Zn^{2+} - PA + Fe^{2+} \longrightarrow Fe^{2+} - PA + Zn^{2+}$$

(4) The released Zn^{2+} combines with OH^- and forms $Zn(OH)_2$ on the cathodic sites, thus retarding the cathodic reaction:

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow$$

(5) Thus, the protective film consists of Fe^{2+} – PA complex and $Zn(OH)_2$. This has been confirmed by FTIR spectra.

The bond formed between Zn^{2+} and PA to form Zn^{2+} – PA complex in solution is strong enough to carry the complex towards the metal surface and weak enough to break in the presence of Fe^{2+}, to form Fe^{2+} – PA complex.

The present study reveals that the order of inhibition efficiency of the two systems, in controlling corrosion of mild steel immersed in chloride environment, is as follows:

$$\underset{[2\ CEPA]}{Zn^{2+} - HOOC.CH_2CH_2P(O)(OH)_2} > \underset{[EPA]}{Zn^{2+} - CH_3CH_2P(O)(OH)_2}$$

This can be explained by considering EPA the electron withdrawing power (inductive effect) of carboxyl group present in 2 CEPA and the molecular size of the Fe^{2+} – 2 CEPA complex:

(1) 2 CEPA contains an electron withdrawing group, namely – COOH. Hence, the order of stability of the zinc complexes is:

$$Zn^{2+} - 2\ CEPA < Zn^{2+} - EPA.$$

For the same reason, the ease with which the zinc complex breaks, in the presence of Fe^{2+}, to form Fe^{2+} – PA complex is:

$$Zn^{2+} - 2\ CEPA > Zn^{2+} - EPA$$

(2) Another factor responsible for the observed order of inhibition efficiency is the molecular size of the Fe^{2+} – PA complex.
It is evident that Fe^{2+} – 2 CEPA complex is larger than the Fe^{2+} – EPA complex, and hence the observed order of inhibition efficiency.

If the concept of electron withdrawing power of – COOH is applied to Fe^{2+} – 2 CEPA complex and Fe^{2+} – EPA complex, then Fe^{2+} – 2 CEPA complex is less stable than the Fe^{2+} – EPA complex. Hence Fe^{2+} – 2 CEPA complex must offer lower inhibition efficiency than the Fe^{2+} – EPA complex. On the other hand, Fe^{2+} – 2 CEPA complex offers better inhibition efficiency. This confirms the fact that the molecular size of iron phosphonate complex plays a major role in retarding the corrosion of mild steel in chloride environment. The electronic (inductive) effect has a lesser influence (Table I).

Conclusions

The following conclusions are reached:

- The 2-carboxyethyl phosphonic acid (2 CEPA) – Zn^{2+} system has a better inhibition efficiency than the ethyl phosphonic acid (EPA) – Zn^{2+} system in controlling corrosion of mild steel in neutral aqueous environment containing 60ppm Cl^-.
- The molecular size of the iron phosphonate complex exercises a greater influence than the electronic (inductive) effect of the substituent in controlling corrosion of mild steel in chloride environment.
- The inhibition efficiency of these systems decreases as the immersion period increases, due to the dissolution of the protective films.
- The protective films are found to be luminescent.

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