



Corrosion inhibition by strainless complexes

Susai Rajendran ^{a,*}, B.V. Apparao ^b, N. Palaniswamy ^c,
V. Periasamy ^d, G. Karthikeyan ^d

^a Corrosion Study Centre, Department of Chemistry, G.T.N. Arts College, Dindigul 624 005, India

^b Department of Chemistry, Regional Engineering College, Warangal 506 004, India

^c Corrosion Science and Engineering Division, Central Electrochemical Research Institute, Karaikudi 630 006, India

^d Department of Chemistry, Gandhigram Rural Institute, Deemed University, Gandhigram 624 302, Tamil Nadu, India

Received 14 January 2000; accepted 17 July 2000

Abstract

Introduction of a methylene group in the carbon chain of carboxymethyl phosphonic acid (CMPA) results in 2-carboxyethyl phosphonic acid (2-CEPA). The inhibition efficiency (IE) of these two phosphonic acids, in the absence and presence of Zn^{2+} , in controlling corrosion of carbon steel immersed in a neutral aqueous environment, containing 60 ppm Cl^- , has been evaluated by weight loss method. The IEs are measured as a function of immersion period, and compared. The protective film has been analysed by X-ray diffraction, Fourier transform infrared and luminescence spectra. A suitable mechanism of corrosion inhibition is proposed based on the results of weight loss study and various surface analysis techniques. The 2-CEPA– Zn^{2+} is found to offer better IE than the CMPA– Zn^{2+} system. This is due to the facts: (i) 2-CEPA keeps Zn^{2+} in a more solubilised form, (ii) larger size of Fe^{2+} –2-CEPA complex, which is more relaxed, strainless and more stable than Fe^{2+} –CMPA complex. The protective film is found to consist of Fe^{2+} –phosphonate complex and $\text{Zn}(\text{OH})_2$; it is found to be luminescent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carboxymethyl phosphonic acid; 2-Carboxyethyl phosphonic acid; Corrosion inhibitors; Carbon steel; Structure–inhibition correlation

* Corresponding author. Tel.: +91-451-431-299; fax: +91-451-433-822.

E-mail address: rmjoany@satyam.net.in (S. Rajendran).

1. Introduction

Several inhibitors such as chromates, molybdates, pertechnetates, nitrites, phosphates, silicates, carboxylates, tannins and phosphonates have been used in aqueous environments [1,2]. Among these inhibitors phosphonates have been widely used due to their ability to form metal complexes, scale inhibiting property, hydrolytic stability and non-toxic nature [3–14]. There is relationship between the size of the inhibitor and its inhibition efficiency (IE) [8,15]. The present work is undertaken (i) to study the influence of introducing a $-\text{CH}_2-$ group in the carbon chain of carboxymethyl phosphonic acid (CMPA), (ii) to analyse the protective film by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and luminescence spectra, and (iii) to propose a suitable mechanism of corrosion inhibition based on the results obtained from weight loss study and various surface analysis techniques.

2. Experimental

2.1. Preparation of the specimens

The composition of the carbon steel used in this study is given below.

S (%)	P (%)	Mn (%)	C (%)	Fe (%)
0.02–0.03	0.03–0.08	0.4–0.5	0.1–0.2	Remainder

Carbon steel specimens of the dimensions $1 \times 4 \times 0.2 \text{ cm}^3$ polished to mirror finish and degreased with trichloroethylene, were used for the weight-loss and surface examination studies.

2.2. Weight-loss method

Carbon steel specimens, in triplicate, were immersed in 100 cm^3 of solution containing various concentrations of inhibitor in the absence and presence of Zn^{2+} , for a known period (one or three days). The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion products were cleaned with Clarke's solution [16]. The percent IE was calculated using the relation, $\text{IE} = [(W_1 - W_2)/W_1] \times 100$, where W_1 and W_2 are weight losses of carbon steel in uninhibited and inhibited chloride solutions.

2.3. Surface examination study

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

2.4. Fourier transform infrared spectra

FTIR spectra (KBr) were recorded using a Perkin–Elmer 1600 FTIR spectrophotometer.

2.5. X-ray diffraction

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_α (Ni-filtered) radiation ($\lambda = 1.5418 \text{ \AA}$) at a rating of 40 kV, 20 mA.

2.6. Luminescence spectra

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

3. Results and discussion

3.1. Analysis of the results of the weight-loss method

The results of the weight-loss method are given in Table 1. The IEs of the phosphonic acids, namely, 2-CEPA, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{P}(\text{O})(\text{OH})_2$, and CMPA, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{P}(\text{O})(\text{OH})_2$, in the presence of Zn^{2+} , in controlling corrosion of carbon steel, immersed in the aqueous environment containing 60 ppm Cl^- are given in this table. Their IEs as a function of immersion period are also given in this table.

3.2. 2-CEPA– Zn^{2+} system

It is found from Table 1 that for a given concentration of Zn^{2+} (40 ppm), when the immersion period is one day, the IE increases from 90% to 99%, as the

Table 1

Inhibition efficiencies (%) of phosphonic acid (PA)– Zn^{2+} systems offered to carbon steel in aqueous environment ($\text{Cl}^- = 60 \text{ ppm}$; $\text{Zn}^{2+} = 40 \text{ ppm}$)

Concentration of PA (ppm)	Immersion period			
	CMPA		2-CEPA	
	1 day	3 day	1 day	3 day
25	83	68	90	–25
50	78	65	99	92
100	60	55	98	90
150	28	20	97	85
200	–13	–2.3	96	83

concentration of 2-CEPA is increased from 25 ppm to 50 ppm. However, further increase in the concentration of the phosphonic acid (PA) slightly lowers the IE. When the immersion period is three days, the formulation consisting of 40 ppm Zn^{2+} and 25 ppm 2-CEPA accelerates corrosion. A brown deposit is found on the metal surface. The acceleration in corrosion rate is due to the fact that PA is precipitated in the bulk of the solution as Zn^{2+} –2-CEPA complex. Addition of 50 ppm 2-CEPA to 40 ppm Zn^{2+} tremendously improves the IE from –25% to 92%. Further addition of PA slightly lowers the IE. In the absence of Zn^{2+} , 2-CEPA accelerates corrosion.

3.3. CMPA– Zn^{2+} system

When the immersion period is one day, the formulation consisting of 40 ppm Zn^{2+} and 25 ppm CMPA shows 83% IE. Further addition of PA lowers the IE. Similar observation is made, when the immersion period is three days. The formulation consisting of 40 ppm Zn^{2+} and 25 ppm CMPA has 68% IE. Further addition of CMPA to 40 ppm Zn^{2+} , lowers the IE. In the absence of Zn^{2+} , CMPA accelerates corrosion.

In, general, in the case of both the PAs, the IE decreases as the concentration of PA increases, for a given concentration of Zn^{2+} . This is due to the precipitation of Zn^{2+} –PA complex in the bulk of the solution. Similar observation has been made with amino (trimethylene phosphonic acid) [14].

It is found that, in the case of both the PAs, i.e., 2-CEPA and CMPA, the IE decreases as the period of immersion increases. This is due to the fact that as the period of immersion increases, the protective film formed on the metal surface gets ruptured by the aggressive chloride ion present in the environment.

3.4. Analysis of the FTIR spectra

The FTIR spectra (KBr) of the surface of carbon steel immersed in various solutions are given in Fig. 1. The FTIR spectrum of the film formed on the surface of the metal immersed in the solution containing 60 ppm Cl^- , 40 ppm Zn^{2+} and 25 ppm CMPA is given in Fig. 1(a). The P–O stretching frequency appears at 1059.9 cm^{-1} . The C=O stretching frequency of the carboxyl group appears at 1569.6 cm^{-1} . The band due to $\text{Zn}(\text{OH})_2$ appears at 1378.7 cm^{-1} [13,17–19]. These results suggest that CMPA is present in the film, probably as Fe^{2+} –CMPA complex. The coordination of CMPA to Fe^{2+} has taken place through O atom of phosphonic group and O atom of carboxyl group. The protective film consists of Fe^{2+} –CMPA complex, formed on the anodic sites of the metal surface, and $\text{Zn}(\text{OH})_2$ formed on the cathodic sites of the metal surface.

The FTIR spectrum of the film formed on the surface of the metal immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 100 ppm CMPA is given in Fig. 1(b). The band due to P–O stretching appears at 1055.5 cm^{-1} . The absorption

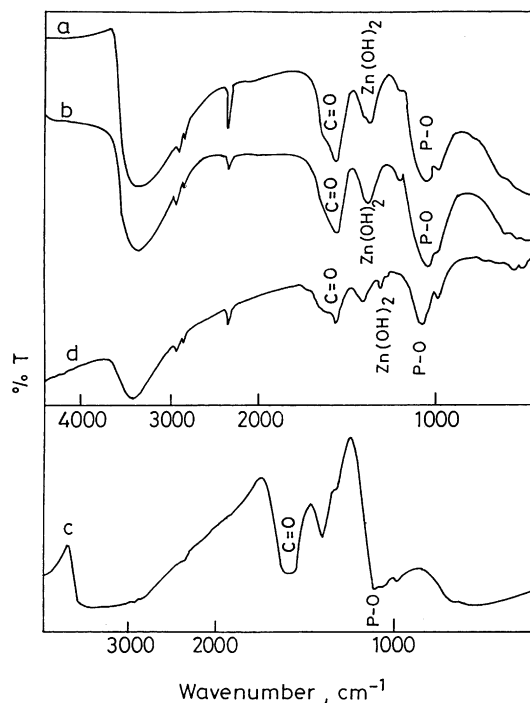


Fig. 1. FTIR spectra of film (KBr) formed on surface of carbon steel immersed in various environments: (a) Cl^- 60 ppm + Zn^{2+} 40 ppm + CMPA 25 ppm, (b) Cl^- 60 ppm + Zn^{2+} 40 ppm + CMPA 100 ppm, (c) Cl^- 60 ppm + Zn^{2+} 40 ppm + 2-CEPA 25 ppm, (d) Cl^- 60 ppm + Zn^{2+} 40 ppm + 2-CEPA 100 ppm.

due to C=O stretching of carboxyl group takes place at 1569.8 cm^{-1} . The band at 1386.4 cm^{-1} is due to $\text{Zn}(\text{OH})_2$. It is evident from these results that the protective film consists of Fe^{2+} –CMPA complex and $\text{Zn}(\text{OH})_2$.

The FTIR spectrum of the film formed on the surface of the metal immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 25 ppm 2-CEPA is given in Fig. 1(c). The absorption due to P–O stretching of the PA occurs at 1106.2 cm^{-1} . The band at 1569.7 cm^{-1} is due to C=O stretching of the carboxyl group. These results suggest the presence of Fe^{2+} –2-CEPA complex on the metal surface. It is interesting to note that the absorption band due to $\text{Zn}(\text{OH})_2$ is absent around 1350 cm^{-1} . Thus the protective film consists of Fe^{2+} –2-CEPA complex formed on the anodic sites of the metal surface. $\text{Zn}(\text{OH})_2$ is not formed on the cathodic sites of the metal surface.

The FTIR spectrum of the film formed on the surface of the metal immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 100 ppm 2-CEPA is given in Fig. 1(d). The absorption due to P–O stretching takes place at 1074 cm^{-1} . The C=O stretching frequency of the carboxyl group occurs at 1557.8 cm^{-1} . The band at 1325 cm^{-1} is due to $\text{Zn}(\text{OH})_2$. This study reveals that the protective film consists of Fe^{2+} –2-CEPA complex and $\text{Zn}(\text{OH})_2$.

3.5. Analysis of the X-ray diffraction patterns

The XRD patterns of the polished metal not immersed in any solution is shown in Fig. 2(a). The peaks due to iron appear at $2\theta = 44.8^\circ$, 65.1° , 88.4° and 99° . The XRD pattern of the film formed on the surface of the metal immersed in the solution

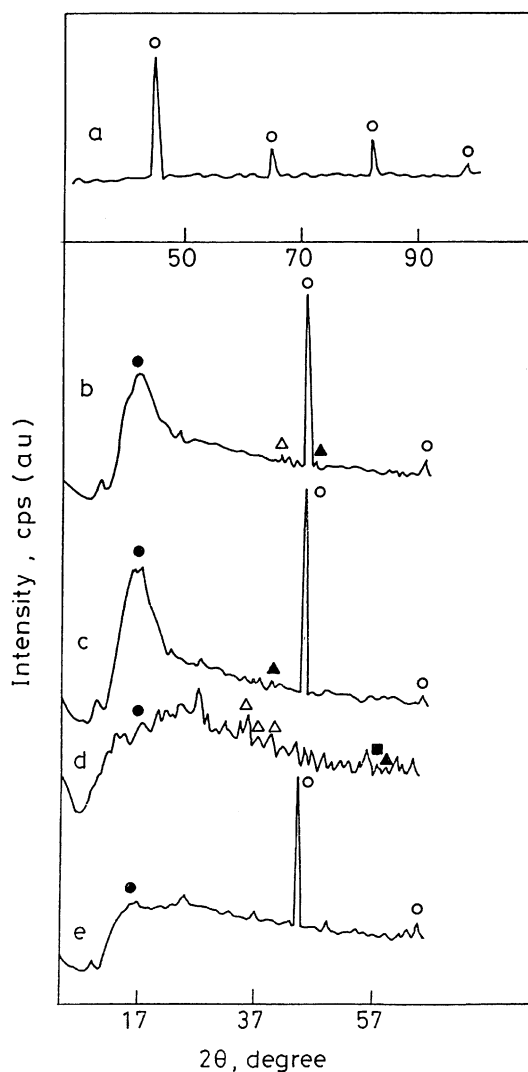


Fig. 2. XRD patterns of surface of carbon steel immersed in various environments: (○) Fe; (●) phosphonic acid; (Δ) α -FeOOH; (▲) γ -FeOOH; (■) Fe_3O_4 . (a) polished metal not immersed in any solution; (b) Cl^- 60 ppm + Zn^{2+} 40 ppm + CMPA 25 ppm; (c) Cl^- 60 ppm + Zn^{2+} 40 ppm + CMPA 100 ppm; (d) Cl^- 60 ppm + Zn^{2+} 40 ppm + 2-CEPA 25 ppm; (e) Cl^- 60 ppm + Zn^{2+} 40 ppm + 2-CEPA 100 ppm.

consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 25 ppm CMPA is given in Fig. 2(b). The film is found to consist of a very thin brown film and a thin interference film. The peak at $2\theta = 40.10^\circ$ suggests the presence of $\alpha\text{-FeOOH}$. The peak at $2\theta = 46^\circ$ indicates the presence of $\gamma\text{-FeOOH}$. The peaks due to iron appear at $2\theta = 44.5^\circ$ and 64.7° [8,20]. The peak around 17° is probably due to PA.

When the metal is immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 100 ppm CMPA, a thin brown film and a thin interference film are observed on the metal surface. The XRD pattern of this film is given in Fig. 2(c). The peak due to $\gamma\text{-FeOOH}$ appears at $2\theta = 39.3^\circ$. The iron peaks appear at $2\theta = 44.4^\circ$ and 65.1° . The peaks at $2\theta = 15^\circ$, 15.9° and 17.2° are probably due to PA.

When carbon steel is immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 25 ppm 2-CEPA, a brown film is formed on the metal surface Fig. 2 (d). This film consists of phosphonic acid ($2\theta = 16.8^\circ$), $\alpha\text{-FeOOH}$ ($2\theta = 33.9^\circ$, 39.1° and 41°), Fe_3O_4 ($2\theta = 35.1^\circ$, 43.4° and 57.4°) and $\gamma\text{-FeOOH}$ ($2\theta = 60.6^\circ$). Interference film is not observed on the metal surface.

When carbon steel is immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 100 ppm 2-CEPA a thin interference film is observed on the metal surface. No brown film is observed. The iron peaks appear at $2\theta = 44.4^\circ$ and 64.7° . The peak at 14.1° and peaks around 17° are due to PA (Fig. 2(e)).

3.6. Analysis of the luminescence spectra

The luminescence spectra of the film formed on the surface of the metal specimens immersed in various test solutions are given in Fig. 3. The luminescence spectrum of the film ($\lambda_{\text{ex}} = 300 \text{ nm}$) formed on the surface of the metal specimen immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 25 ppm CMPA is shown in Fig. 3(a). This spectrum is due to Fe^{2+} –CMPA complex entrained in iron oxide and $\text{Zn}(\text{OH})_2$ on the metal surface. The luminescence spectrum of the film ($\lambda_{\text{ex}} = 300 \text{ nm}$) formed on the surface of the metal specimen immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 100 ppm CMPA is shown in Fig. 3(b). This spectrum is due to Fe^{2+} –CMPA complex, embedded in iron oxide and $\text{Zn}(\text{OH})_2$ on the metal surface. It is interesting to observe that the peak intensities are higher in the former case than in the latter case. This suggests that more Fe^{2+} –CMPA complex is present on the metal surface, in the first case than in the second case. This is in agreement with the results of the weight loss method which reveal that in the former case the inhibition is higher (68%) than in the latter case (55%).

The luminescence spectrum of the film formed on the surface of the metal immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 25 ppm 2-CEPA is given in Fig. 3(c). This spectrum is due to Fe^{2+} –2-CEPA complex in the presence of iron oxides. The luminescence spectrum of the film formed on the surface of the metal specimen, immersed in the solution consisting of 60 ppm Cl^- , 40 ppm Zn^{2+} and 100 ppm 2-CEPA is given in Fig. 3(d). This spectrum is due to Fe^{2+} –2-CEPA complex in the presence of $\text{Zn}(\text{OH})_2$. It is interesting to note that the peak intensities are higher in the latter case than in the former case. This is in agreement with the

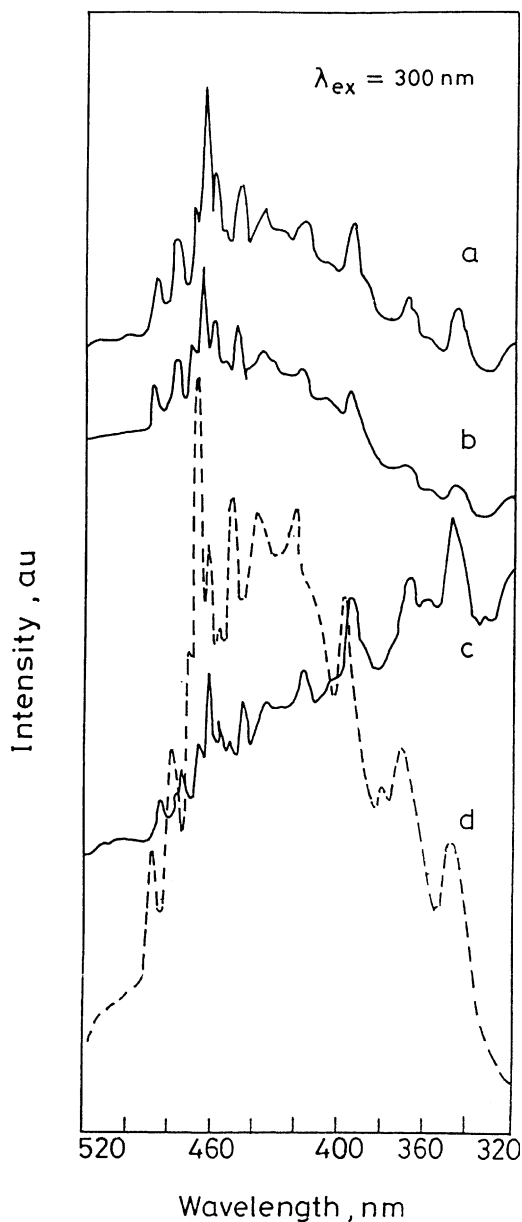


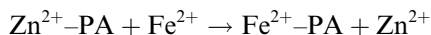
Fig. 3. Luminescence spectra of carbon steel surface, immersed in various environments: (a) Cl^- 60 ppm + Zn^{2+} 40 ppm + CMPA 25 ppm; (b) Cl^- 60 ppm + Zn^{2+} 40 ppm + CMPA 100 ppm; (c) Cl^- 60 ppm + Zn^{2+} 40 ppm + 2-CEPA 25 ppm; (d) Cl^- 60 ppm + Zn^{2+} 40 ppm + 2-CEPA 100 ppm.

results of the weight loss method which reveal that the former system is corrosive (IE = -25%) and the latter system has good IE (90%).

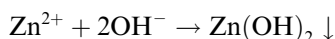
3.7. Mechanism of corrosion inhibition

The following mechanism of corrosion inhibition is proposed for PA–Zn²⁺ system.

1. When the solution consisting of 60 ppm Cl[−], phosphonic acid (PA) and Zn²⁺ is prepared, there is a formation of Zn²⁺–PA complex in solution.
2. When metal specimen is immersed in this solution, the Zn²⁺–PA complex diffuses towards the metal surface, from the bulk.
3. On the metal surface, Zn²⁺–PA complex is converted into Fe²⁺–PA complex on the anodic sites of the metal. Zn²⁺ is released.



4. The released Zn²⁺ combines with OH[−] and forms Zn(OH)₂ on the cathodic sites.



5. Thus the protective film consists of Fe²⁺–PA complex and Zn(OH)₂.

The bond formed between Zn²⁺ and PA in Zn²⁺–PA complex must be strong enough to carry the Zn²⁺–PA complex from the bulk of the solution to the metal surface and weak enough to break in the presence of Fe²⁺ and forms Fe²⁺–PA complex on the anodic sites metal surface.

In the present study, in general, 2-CEPA–Zn²⁺ system shows better IE than the CMPA–Zn²⁺ system. The main difference between 2-CEPA and CMPA is that the former contains one extra –CH₂– group. Both the phosphonic acids have one –COOH group and one –P(O)(OH)₂– group. It seems that 2-CEPA keeps the Zn²⁺–PA complex in more solubilised form than the CMPA. The transport of Zn²⁺ from the bulk of the solution towards the metal surface is more facilitated in the presence of 2-CEPA than in the presence of CMPA. This favours the formation of Zn(OH)₂ on the cathodic sites of the metal surface and thus retarding the cathodic reaction of generation of OH[−]. The Fe²⁺–2-CEPA complex formed on the anodic sites of the metal surface occupies a larger space than the Fe²⁺–CMPA complex. These two factors explain the better IE of the 2-CEPA–Zn²⁺ system. All these factors come into effect due to the introduction of one –CH₂– group into the carbon chain of CMPA.

Because of the presence of an additional –CH₂– group in 2-CEPA, the Fe²⁺–2-CEPA complex is more relaxed and strainless and more stable than Fe²⁺–CMPA complex.

4. Conclusions

(1) The 2-CEPA–Zn²⁺ system has better IE than the CMPA–Zn²⁺ system in controlling corrosion of carbon steel in neutral aqueous environment containing 60 ppm Cl[−].

(2) This is due to the following facts (i) 2-CEPA keeps Zn²⁺ in a more solubilised form which enables the retardation of the cathodic reaction by formation of

Zn(OH)_2 ; (ii) the larger size of Fe^{2+} –2-CEPA complex formed on anodic sites. (iii) The Fe^{2+} –2-CEPA complex is more relaxed and strainless and more stable than Fe^{2+} –CMPA complex.

Acknowledgements

S. Rajendran is thankful to the University Grants Commission, India, for awarding a fellowship; to the Executive Director, Sasha Industries Limited, Dindigul; to Mr. Ranjit Soundarajan, the Correspondent; Prof. L. George Joseph, the Secretary and Prof. P. Jayaram, the Principal, GTN Arts College, Dindigul; Mr. A.A. Joseph and Mr. M. Veluswamy, CECRI, Karaikudi, to Dr. R. Ramaraj, Madurai Kamaraj University and to Jay Bryson, The Goodyear Tire & Rubber Company, USA, for their help and encouragement.

References

- [1] A.D. Mercer, Proc. Seventh Europ. Sympos. Corros. Inhibitors, vol. 1, University of Ferrara, Italy, 1990, p. 449.
- [2] O. Lahodny-Sarc, F. Kapor, R. Halle, Eurocorr'99, Eurogress Aachen, 30 August–2 September, 1999.
- [3] G. Gunasekaran, N. Palaniswamy, B.V. Apparao, V.S. Muralidaran, Electrochim. Acta 49 (1997) 1427.
- [4] J.L. Fang, Y. Li, X.R. Ye, Z.W. Wang, Q. Liu, Corrosion 49 (1993) 266.
- [5] T. Horvath, E. Kalman, G. Kutsan, A. Rauscher, Br. Corros. J. 29 (1994) 215.
- [6] S. Rajendran, B.V. Apparao, N. Palaniswamy, Electrochim. Acta 44 (1998) 533.
- [7] S. Rajendran, B.V. Apparao, N. Palaniswamy, Proc. Eighth Europ. Sympos. Corros. Inhibitors, vol. 1, Ferrara, Italy, 1995, p. 465.
- [8] S. Rajendran, B.V. Apparao, N. Palaniswamy, Anti-Corros. Meth. Mater. 46 (1999) 284.
- [9] S. Rajendran, B.V. Apparao, N. Palaniswamy, Eurocorr'99, Eurogress Aachen, Germany, 30 August–2 September, 1999.
- [10] E. Kalman, B. Varhegyi, I. Bako, I. Felhosi, F.H. Karman, A. Shaban, J. Electrochem. Soc. 141 (1994) 3357.
- [11] S. Rajendran, B.V. Apparao, N. Palaniswamy, Proc. Environmental Degradation of Engineering Materials, Gdansk-Jurata, Poland, 19–23 September 1999.
- [12] S. Rajendran, B.V. Apparao, N. Palaniswamy, Bull. Electrochem. 13 (1997) 441.
- [13] S. Rajendran, B.V. Apparao, N. Palaniswamy, J. Electrochem. Soc. 48 (1999) 89.
- [14] S. Rajendran, Ph.D. Thesis, Gandhigram Rural Institute Deemed University, Tamil Nadu, India, 1996.
- [15] F.M. Donahue, K. Nobe, J. Electrochem. Soc. 112 (1965) 886.
- [16] G. Wranglen, Introduction to Corrosion and Protection of Metals, Chapman and Hall, London, 1985, p. 236.
- [17] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York, 1981, p. 166.
- [18] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1960, p. 168.
- [19] A.D. Cross, Introduction to Practical Infrared Spectroscopy, Butterworths, London, 1990, p. 73.
- [20] M. Favre, D. Landolt, Corros. Sci. 34 (1993) 1481.