

CORROSION INHIBITION BY CARBOXYMETHYL CELLULOSE-1-HYDROXYETHANE- 1,1-DIPHOSPHONIC ACID-Zn²⁺ SYSTEM

S RAJENDRAN¹, R M JOANY², B V APPARAO³ AND N PALANISWAMY⁴

1 Corrosion Study Centre, Dept of Chemistry, G T N Arts College (Autonomous), Dindigul 624 005. INDIA

2 PSNA College of Engineering and Technology, Dindigul

3 Department of Chemistry, Regional Engineering College, Warangal 506 004. Andhra Pradesh. INDIA

4 Corrosion Science and Engg Divn, Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 09 March 2001

Accepted: 10 October 2001]

Influence of carboxymethyl cellulose (CMC) on the inhibition efficiency of 1-hydroxyethane-1,1-diphosphonic acid (HEDP)- Zn²⁺ system in controlling corrosion of mild steel immersed in a neutral aqueous environment containing 60 ppm Cl⁻ has been evaluated by weight loss study. The formulation consisting of 10 ppm Zn²⁺ and 300 ppm HEDP has 40% inhibition efficiency (IE). Addition of 10 ppm CMC improves the IE from 40% to 50%, addition of 50 ppm CMC improves the IE to 80%. Further, addition of CMC (≥ 100 ppm) lowers the IE, since the resistance to the rate of diffusion of the inhibitors from the bulk of the solution towards the metal surface increases. The protective film has been analyzed by X ray diffraction (XRD) and FTIR. The protective film consists of Fe²⁺- HEDP complex, Fe²⁺-CMC complex and Zn(OH)₂. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from polarization study, XRD and FTIR spectra.

Keywords: Carboxymethyl cellulose, corrosion inhibitor, mild steel, phosphonic acid and X ray diffraction.

INTRODUCTION

Several phosphonic acids have been used as corrosion inhibitors as substitutes for toxic chromates, polyphosphates and nitrites [1-6]. Our previous study revealed that the formulation consisting of 50 ppm HEDP and 50 ppm Zn²⁺ offered 98% inhibition efficiency (IE) to mild steel immersed in a neutral aqueous environment containing 60 ppm Cl⁻ [4]. The present work is undertaken (i) to evaluate the IE of HEDP in the presence of a lower concentration of Zn²⁺ (10 ppm), (ii) to investigate the influence of carboxymethyl cellulose (CMC) on the IE of the HEDP-Zn²⁺ system, (iii) to examine the protective film by X ray diffraction (XRD) and FTIR and (iv) to propose a suitable mechanism of corrosion inhibition based on the results of weight loss study, polarization study, XRD and FTIR.

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 x 4 x 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 0.5 cm 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 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn²⁺, 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 products were cleaned with Clarke's solution [7]. The percent 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 analyzer, 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 1000 μ V/ second.

Surface examination study

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

X ray diffraction technique

The XRD patterns of the dry 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. The scan rate was 0.05-20⁰ per step and the measuring time was 1 second per step.

FTIR spectra

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

RESULTS AND DISCUSSION

Weight loss study

The results of the weight loss study are given in Table I. It is observed that the formulation consisting of 50 ppm HEDP and 50 ppm Zn²⁺ has 98% inhibition efficiency (IE). When the concentration of Zn²⁺ is reduced to 10 ppm, the IE decreases, in general. It is observed that the formulation consisting of 10 ppm Zn²⁺ and 300 ppm HEDP has only 40% IE, whereas in the presence of 50 ppm Zn²⁺, 300 ppm HEDP showed 99% IE.

Influence of carboxymethyl cellulose on HEDP-Zn²⁺ system

Various concentrations of carboxymethyl cellulose (CMC) are added to the HEDP (300 ppm)-Zn²⁺ (10 ppm) system. It is observed that addition of 10 ppm CMC improves the IE from 40% to 50%; addition of 50 ppm CMC improves the IE to 80%.

Further addition of CMC (≥ 100 ppm) lowers the IE. This may be explained by the fact that when the concentration of CMC is ≥ 100 ppm, the resistance to the rate of diffusion of the inhibitors from the bulk of the solution towards the metal surface increases.

Polarization study

The potentiostatic polarization curves of mild steel immersed in various environments are given in Fig. 1. It is observed that CMC alone and also HEDP alone shift the corrosion potential towards anodic side (positive region), whereas their combination shifts the corrosion potential towards the cathodic side (negative region). Zn²⁺ controls the cathodic reaction predominantly. The formulation consisting of 300 ppm HEDP, 10 ppm Zn²⁺ and 50 ppm CMC shifts the corrosion potential to a potential which is in between that

TABLE I: Corrosion rates of mild steel in neutral aqueous environment ($\text{Cl}^- = 60$ ppm) in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method
Inhibitor system: HEDP + Zn²⁺ + CMC

HEDP (ppm)	Zn ²⁺ (ppm)	CMC (ppm)	Corrosion rate(mdd)	Inhibition efficiency(%)
0	0	0	15.54	—
10	50	0	13.52	13
50	50	0	0.37	98
100	50	0	0.31	98
150	50	0	0.31	98
200	50	0	0.31	98
300	50	0	0.16	99
300	0	0	10.10	35
300	0	50	9.32	40
0	50	0	19.11	-23
0	10	0	13.99	10
0	0	50	15.52	0
0	10	50	14.92	4
10	10	0	13.99	10
50	10	0	12.12	22
100	10	0	10.88	30
150	10	0	10.10	35
200	10	0	9.63	38
300	10	0	9.32	40
300	10	10	6.84	56
300	10	50	3.10	80
300	10	100	8.50	45
300	10	200	8.40	46

of Zn²⁺ alone and HEDP alone and also CMC alone. These results suggest that the HEDP-Zn²⁺-CMC system functions as a mixed inhibitor, controlling the anodic reaction of dissolution of metal and cathodic reaction of generation of OH⁻.

X ray diffraction

The X ray diffraction (XRD) patterns of mild steel surface immersed in various environments are given in Fig. 2. The surface of the polished metal not immersed in any environment shows peaks at $2\theta = 44.8^\circ$, 65.10° , 88.40° and 99.00° . The XRD pattern of pure CMC shows peaks at $2\theta = 7.60^\circ$ and 20.30° . The XRD pattern of the metal specimen immersed in the environment consisting of 60 ppm Cl⁻, 300 ppm HEDP and 50 ppm CMC shows iron peaks at $2\theta = 44.30^\circ$ and 64.70° . The peaks due to CMC appear at $2\theta = 8.00^\circ$ and 20.20° . This suggests the presence of CMC on the metal surface, probably as iron-CMC complex.

The XRD pattern of the metal specimen immersed in the environment consisting of 60 ppm Cl⁻, 300 ppm HEDP, 50 ppm CMC and 10 ppm Zn²⁺ shows iron peaks at $2\theta = 44.30^\circ$ and 64.70° . The peaks at $2\theta = 8.00^\circ$ and 20.20° suggest the

presence of CMC on the metal surface probably as iron-CMC complex.

FTIR spectra

The FTIR spectrum of pure CMC reveals that the C = O stretching frequency of the carboxyl group appears at 1611.6 cm^{-1} . The FTIR spectrum of pure HEDP reveals that the P-O stretching frequency appears at 1119 cm^{-1} .

The FTIR spectrum (multiple internal reflection) of the film formed on the surface of the metal immersed in the environment consisting of 60 ppm Cl⁻, 300 ppm HEDP, 50 ppm CMC reveals that the P-O stretching frequency of HEDP decreases from 1119 cm^{-1} to 1018.7 cm^{-1} . It is suggested that the oxygen atom of the phosphonic acid is coordinated to Fe²⁺ resulting in the formation of Fe²⁺-HEDP complex on the metal surface.

It is also inferred that the C = O stretching frequency of carboxyl group of CMC decreases from 1611.6 cm^{-1} to 1573.7 cm^{-1} . It is suggested that the carboxyl group of CMC is coordinated to Fe²⁺, resulting in the formation of Fe²⁺-CMC complex on the metal surface.

The FTIR spectrum (Multiple internal reflection) of the film formed on the surface of the metal immersed in the environment consisting of

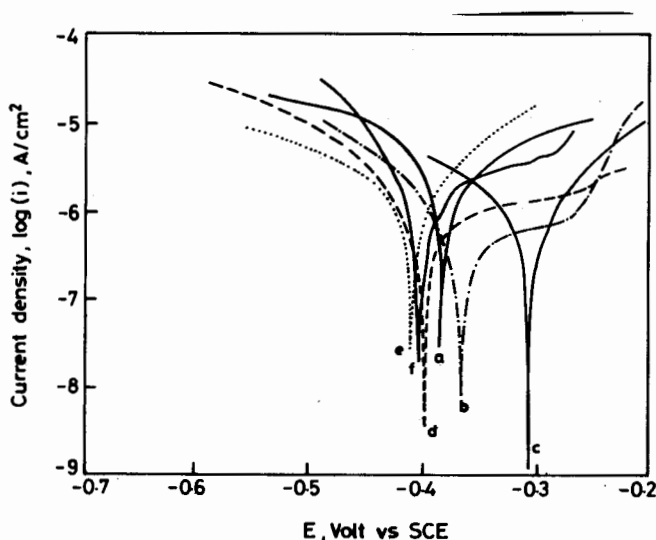


Fig. 1: Polarisation curves of mild steel immersed in various environments

- (a) Cl⁻ 60 ppm (b) Cl⁻ 60 ppm + HEDP 300 ppm
 (c) Cl⁻ 60 ppm + CMC 50 ppm
 (d) Cl⁻ 60 ppm + HEDP 300 ppm + CMC 50 ppm
 (e) Cl⁻ 60 ppm + Zn²⁺ 10 ppm
 (f) Cl⁻ 60 ppm+HEDP 300 ppm+CMC 50 ppm+Zn²⁺ 10 ppm

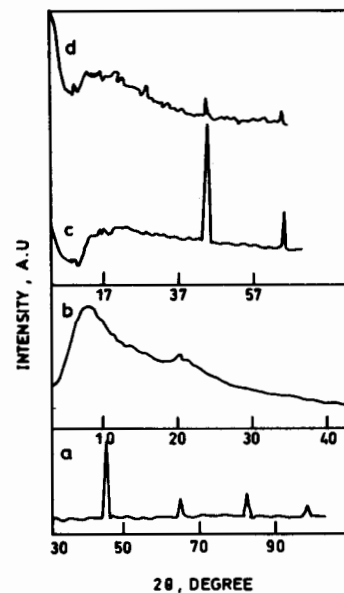


Fig. 2: X ray diffraction patterns of pure CMC (b) and mild steel surface immersed in various environments
 (a) polished metal (b) CMC
 (c) Cl⁻ 60 ppm + HEDP 300 ppm + CMC 50 ppm
 (d) Cl⁻ 60 ppm+HEDP 300 ppm+CMC 50 ppm+Zn²⁺ 10 ppm

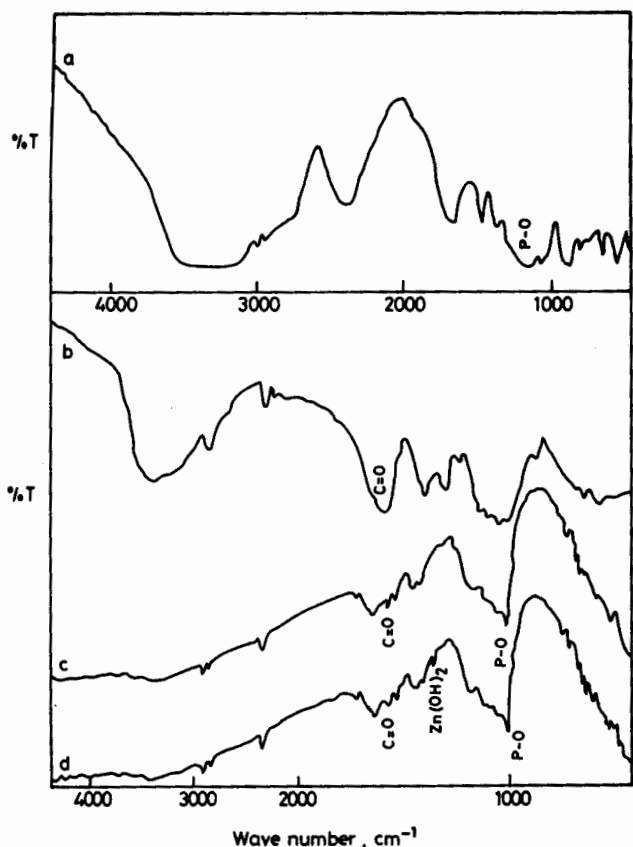


Fig. 3: FTIR spectra of HEDP (a), CMC (b) and of mild steel surface immersed in various environments

(a) HEDP (b) CMC

(c) Cl⁻ 60 ppm + HEDP 300 ppm + CMC 50 ppm

(d) Cl⁻ 60 ppm+HEDP 300 ppm+CMC 50 ppm+Zn²⁺ 10 ppm

60 ppm Cl⁻, 300 ppm HEDP, 50 ppm CMC and 10 ppm Zn²⁺ reveals that the P-O stretching frequency of HEDP decreases from 1119 cm⁻¹ to 1018.6 cm⁻¹. This is due to the formation of Fe²⁺-HEDP complex on the metal surface. The peak at 1352.5 cm⁻¹ corresponds to Zn(OH)₂ formed on the metal surface. The C = O stretching frequency of carboxyl group of CMC decreases from 1611.6 cm⁻¹ to 1565.6 cm⁻¹. This is due to the formation of Fe²⁺-CMC complex on the metal surface [8-9].

Mechanism of corrosion inhibition

The following mechanism of inhibition of corrosion is proposed.

- ✧ When the environment consisting of Cl⁻, HEDP, CMC and Zn²⁺ is prepared, there is formation of Zn²⁺-HEDP complex and Zn²⁺-CMC complex in solution.
- ✧ When the metal specimen is immersed in this environment, Zn²⁺-HEDP complex and Zn²⁺-CMC complex diffuse from the bulk of the solution towards the metal surface.
- ✧ On the metal surface Zn²⁺-HEDP complex and Zn²⁺-CMC are converted into Fe²⁺-HEDP complex and Fe²⁺-CMC complex respectively, on the anodic sites.
- ✧ The released Zn²⁺ combines with OH⁻ to form Zn(OH)₂ on the cathodic sites.
- ✧ Thus the protective film consists of Fe²⁺-HEDP complex, Fe²⁺-CMC complex and Zn(OH)₂.

Acknowledgement: S Rajendran is thankful to Dr Terry Savage of UK and Dr Jay Bryson Good Year Tire and Rubber Company, USA, Mr Ranjit Soundararajan, the Correspondent, Mr N Muralidharan, VPT, Professor L George Joseph, the Secretary and Prof G Subramanian, the Principal of GTN Arts College, Dindigul, Rtn PHF, G Sundararajan for their help and encouragement and he also thanks UGC, New Delhi, India for financial assistance.

REFERENCES

1. Y Gonzalez, M C Lafont and N Pebere, *J Appl Electrochem*, **26** (1996) 1259
2. T Korvath, E Kalman, G Kutsan and A Rauscher, *Brit Corros J*, **29** (1994) 215
3. E Kalman, F H Karman, J Telegdi, B Varhegyi, J Balla and T Kiss, *Corros Sci*, **35** (1993) 1477
4. S Rajendran, B V Apparao and N Palaniswamy, *Bull Electrochem*, **13** (1997) 441
5. S Rajendran B V Apparao and N Palaniswamy, *Anti Corrosion Methods and Materials*, **47** (2000) 308
6. S Rajendran, B V Apparao and N Palaniswamy, *Electrochim Acta*, **44** (1998) 533
7. G Wranglen, *Introduction to Corrosion and Protection of Metals*, Chapman and Hall, London (1985) 236
8. K Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York (1986) 168
9. R M Silverstein, G C Bassler and T C Morrill, *Spectrometric identification of Organic Compounds*, John Wiley Sons, New York (1981) 166