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SYNERGISTIC EFFECT OF Zn^{2+} IONS AND 2-CARBOXYETHYL PHOSPHONIC ACID ON THE CORROSION INHIBITION OF MILD STEEL IN NEUTRAL ENVIRONMENT

GURUSWAMY GUNASEKHARAN[A,B], N PALANISWAMY[A] AND B V APPARAO[B]

[A] Central Electrochemical Research Institute, Karaikudi 630 006. Tamil Nadu. INDIA

[B] Chemistry Department, Gandhigram Rural Institute, Gandhigram 624 302. Tamil Nadu. INDIA

Synergistic effect of Zn^{2+} ion and 2-Carboxyethylphosphonic acid (2-CEPA) on the corrosion inhibition of mild steel in water containing low concentration (60 ppm) of chloride ion has been evaluated by weight loss and potentiostatic polarisation methods. The results show that 96% inhibition efficiency is achieved with binary system consisting of 100 ppm Zn^{2+} and 100 ppm 2-CEPA. The mechanistic aspects of corrosion inhibition and the nature of the film formed on the metal surface have been analysed with the help of x-ray diffraction (XRD) technique, UV-Vis-NIR spectra and Luminescence spectra.

Keywords: Corrosion inhibitors, synergistic effect and phosphonic acid

INTRODUCTION

Phosphonic acids have been widely used as water treatment agents because of their low toxicity, high stability towards hydrolysis, high scale-resistance and high degree of corrosion inhibition in neutral aqueous media. Several studies on the use of phosphonic acids as corrosion inhibitors in cooling water systems have been reported in the literature [1-7]. But there is no report on the use of 2-carboxy ethyl phosphonic acid (2-CEPA) as corrosion inhibitor in cooling water systems.

In this study attempts have been made to clarify the action mechanism of 2-CEPA, zinc sulphate and combination of 2-CEPA and zinc sulphate on corrosion of mild steel in sodium chloride investigated through measurement of weight loss and polarisation. The adsorption state of 2-CEPA on the mild steel surface was analysed by XRD for the specimen after the immersion for two days in the test solution. The complex formation of 2-CEPA was clarified by ultraviolet analysis and ultraviolet fluorescence analysis with the test solution and the mild steel specimen after immersion in the test solution.

EXPERIMENTAL

Materials

An aqueous solution of 60 ppm Cl^- (NaCl) was used as a blank solution. The concentrations of 2-CEPA used were in the range from 20 ppm to 150 ppm. Zn^{2+} ions were added to 2-CEPA in the form of zinc sulphate ($ZnSO_4$ $7H_2O$). All the test solutions were adjusted to *p*H 7.00 ± 0.1. The composition of mild steel used for this study is 0.02-0.03% S, 0.3-0.8% P, 0.4-0.5% Mn, 0.1-0.2% C and rest is Fe.

Weight loss measurement

Before use, the specimens 1x4x0.2 cm were polished on 60 emery wheel and successively washed with distilled water and degreased with trichloro ethylene. The specimens were immersed in inhibitor solutions for a period of seven days. The corrosion inhibition efficiency is calculated from the change in weight loss.

Polarisation Measurement

A mild steel rod of 0.1963 cm^2 cross section embedded in Teflon was used as a working electrode. The counter electrode was a platinum wire and the potential was measured with reference to calomel electrode. Polarisation

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study was carried out in a three electrode cell assembly connected to Bioanalytical system (BAS - 100A) electrochemical analyser. The cross section of the test electrode was abraded with emery papers 1/0, 2/0, 3/0, 4/0 and successively washed with water and degreased with trichloro ethylene. The electrodes were first immersed in aqueous NaCl solution (60 ppm) in the absence and presence of inhibitor. After 15 minutes IR compensation was done and polarisation studies were carried out, keeping the solution under constant stirring condition at a sweep rate of 1000 micro volts/sec. E vs log I plots were recorded.

Surface Examination Studies

The polished mild steel specimens were immersed in solution with and without inhibitors for two days. After two days the specimens were taken out and washed with distilled water and dried. The dried specimens were used for surface examination studies.

X-ray Diffraction

XRD spectra were obtained by using a computer controlled X-ray powder diffractometer, JEOL JDX 8030 with CuK_α (Ni filtered) radiation at a rating of 40 kV, 20 mA. The scan rate was 0.05-20° per step and the measuring time was 1S per step. The full width at half maximum (f whm) of the most intense peak of the patterns were measured using the existing peak search software.

UV-Visible NIR Diffused Reflectance Spectra

UV-visible NIR diffused reflectance spectra of the film present on the metal surface were recorded using Hitachi U-3400 spectro photometer.

Luminescence Spectra

Luminescence spectra of the film formed on the metal surface were recorded using Hitachi 650-10S fluorescence spectrophotometer equipped with a 150 W xenon lamp and a Hemamatsu R 928 F photomultiplier tube. The emission spectra were corrected for the spectral response of the photomultiplier tube used. The 404 nm wavelength is used for excitation of test solutions and metal surfaces.

RESULTS AND DISCUSSION

Weight Loss Measurement

Fig. 1 shows the results of corrosion rate measured through weight loss for various combinations of 2-CEPA and Zn^{2+} at room temperature in 60 ppm Cl^- solution. The 2-CEPA solution above shows high rate of corrosion. The inhibition efficiency of phosphonic acids are improved by addition of Zn^{2+} ion [1]. Various concentrations of Zn^{2+} were added to 2-CEPA for improving the corrosion efficiency. Maximum 10% efficiency is achieved at low ppm of 2-CEPA (20 ppm) and high ppm of Zn^{2+} (80 ppm). However increasing concentration of 2-CEPA as well as Zn^{2+}, maximum inhibition is achieved. When 2-CEPA is 50 ppm and Zn^{2+} is 120 ppm, the efficiency is 91%. When the concentration of 2-CEPA is increased to 100 ppm and the concentration of Zn^{2+} decreased to 100 ppm the efficiency is increased from 91% to 96%. The maximum corrosion inhibition efficiency is achieved by the following system; 50 ppm 2-CEPA and 120 ppm Zn^{2+} (91%) and 150 ppm 2-CEPA and 100 ppm Zn^{2+} (95%).

The combinations showing excellent inhibition were investigated to determine whether it obeyed the Langmuir isotherm. Assuming that the inhibitor forms a monomolecular layer on the steel surface at the maximum inhibition of corrosion, the surface coverage (θ) of the inhibitor is unity. The θ value can be calculated from the following

$$\theta = \frac{(W_0 - W)}{(W_0 - W_m)}$$

where W_o and W are the weight losses of the uninhibited and inhibited mild steel specimens respectively and W_m is the weight loss given the maximum inhibition.

A correlation between θ and the concentration [C] of inhibitor in the electrolyte can be represented by the Langmuir adsorption isotherm [8].

$$\frac{C}{\theta} = \frac{1}{k} + C$$

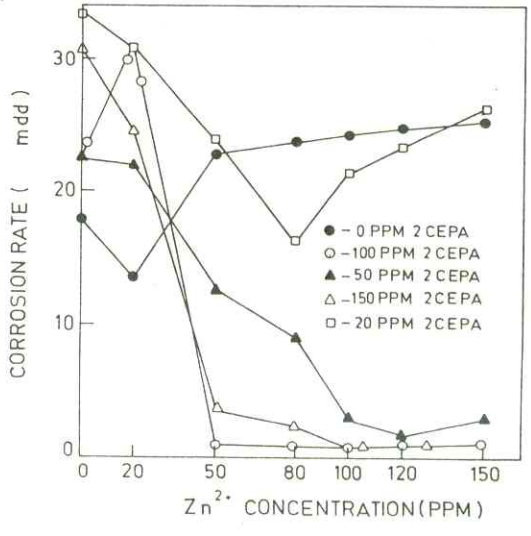

Fig. 1: Corrosion rate vs the concentration of Zn^{2+} in 60 ppm Cl^- solution at various concentrations of 2CEPA

where k is the constant of adsorption. The relation between C/ and C at 50 ppm, 100 ppm and 150 ppm of 2-CEPA with addition of Zn^{2+} is shown in Fig. 2. The plots at each 2-CEPA concentration were found to yield a straight line and their slopes were nearly one. This shows the combinations of Zn^{2+} and 2-CEPA obeys Langmuir adsorption isotherm.

Polarisation Study

The polarisation curves for the systems 100 ppm Zn^{2+}, 100 ppm 2CEPA and a combination of 100 ppm Zn^{2+} and 100 ppm 2CEPA are shown in Fig. 3. The E_{corr} value for blank (60 ppm Cl^-) is -360 mV. 2CEPA acts as an anodic inhibitor. Zinc ion acts as a cathodic inhibitor. 2CEPA and zinc ion mix solution acts as a mixed inhibitor.

Fig. 4 shows the plot between corrosion current (I_{corr}) and various concentrations of Zn^{2+} in presence of 2CEPA. The maximum inhibition efficiency is achieved for the combinations of 50 ppm 2CEPA and 100 ppm Zn^{2+} and 100 ppm 2CEPA and 50 ppm Zn^{2+}. This has excellent agreement with weight loss method. But in the case of 20 ppm 2CEPA and 150 ppm 2CEPA, the maximum inhibition efficiency is achieved by adding 20 ppm Zn^{2+}. This tendency is not consistent with that of the weight loss. This shows polarisation measurements give instantaneous corrosion rate whereas weight loss data are being measured over a period of 7 days.

X-Ray Diffraction

The XRD spectra are presented in Fig. 5. The diffraction patterns were recorded for the mild steel specimens after 2 days in presence of 60 ppm Cl^- (blank) (5a); 100 ppm Zn^{2+}

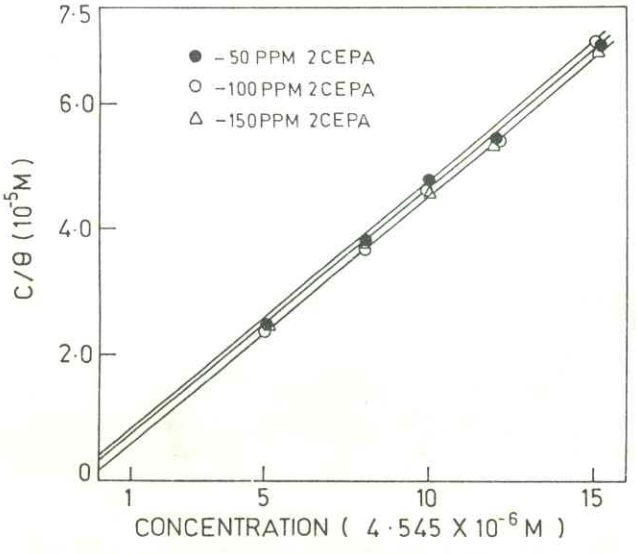

Fig. 2: Langmuir adsorption isotherm of Zn^{2+} on mild steel in 60 ppm Cl^- solutioin at various concentrations of 2CEPA

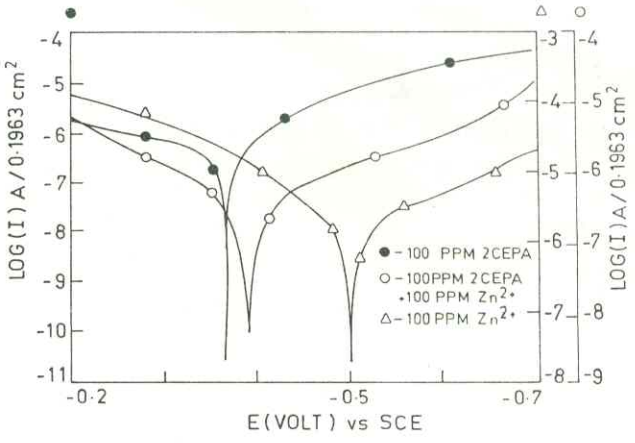

Fig. 3: Influence of 2CEPA and the Zn^{2+} on the polarisation curves

(5b); 100 ppm 2CEPA (5c) and a mixture of 100 ppm 2CEPA and 100 ppm Zn^{2+} (5d). XRD was also recorded for Zn-2CEPA powder complex (5e). The mild steel specimen immersed in 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture (5d) shows mostly metallic iron peaks. But in case of mild steel specimen immersed in blank solution (5a), 100 ppm Zn^{2+} solution (5b) and 100 ppm 2CEPA solution (5c), presence of Fe_3O_4 and a-FeOOH [9] were also detected. This shows the excellent inhibition nature of 100 ppm 2CEPA [9] were also detected. This shows the excellent inhibition nature of 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture.

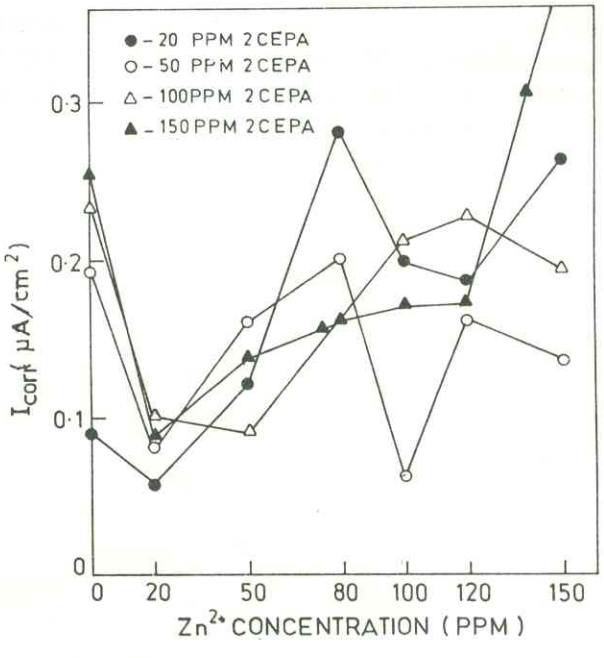

Fig. 4: I_{corr} vs the concentration of Zn^{2+} in 60 ppm of Cl^- at various concentrations of 2CEPA

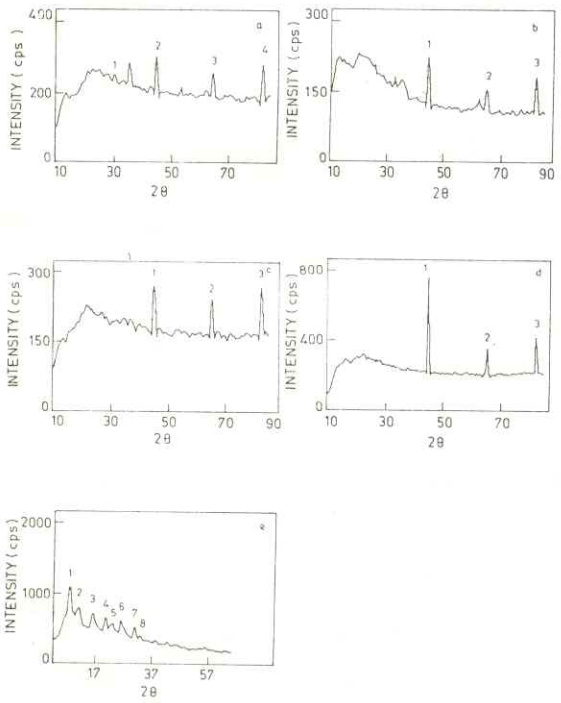

Fig. 5: XRD spectra of mild steel immersed in (a) blank solution; (b) 100 ppm Zn^{2+}; (c) 100 ppm 2CEPA and (d) 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture; (e) XRD spectra of Zn-2CEPA powder complex

UV-Visible NIR Diffused Reflectance Spectra

The UV-visible diffused reflectance spectra were recorded using the surface of the mild steel specimens immersed in blank solution (6a), 100 ppm Zn^{2+} (6b) 100 ppm 2CEPA (7b) and mixture of 100 ppm 2CEPA and 100 ppm Zn^{2+} (7a). A band at 550 nm for the systems blank (6a), 100 ppm Zn^{2+} (6b) and 100 ppm 2CEPA (7b) shows that the nature of the layer on the surface is semiconducting. This is due to the presence of iron oxides on the surface of blank (6a), 100 ppm Zn^{2+} (6b) and 100 ppm 2CEPA (7b) systems. But in case of 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture (7a) there is no such baseline decrease at 550 nm. This also proves that blank (6a), 100 ppm Zn^{2+} (6b) and 100 ppm 2CEPA (7b) systems are corrosive.

A fairly large peak at 290 nm was observed in 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture system. These peaks are due to the formation of iron-2CEPA complex on the surface of the metal specimen. Because the adsorption spectra change with a chelate formation in the UV region [10].

UV-Luminescence

There are very few reports in the literature on the luminescence of iron-organic ligand complex [11]. Luminescence spectra were recorded for the metals immersed in 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture (8a); 100 ppm Zn^{2+} (8c) and 100 ppm 2CEPA (8d). A peak at 445 nm for the system 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture shows the presence of iron-2CEPA complex. This is confirmed by preparing Fe^{3+}-2CEPA complex also gave a peak at 445 nm. This confirms the presence of iron-2CEPA complex on the specimen immersed in 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture.

The following solutions were subjected to luminescence spectra to confirm the formation of iron-2CEPA in solution 100 ppm 2CEPA (9a); 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture (9b); the solution of 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture after two days of metal immersion (9c) and the

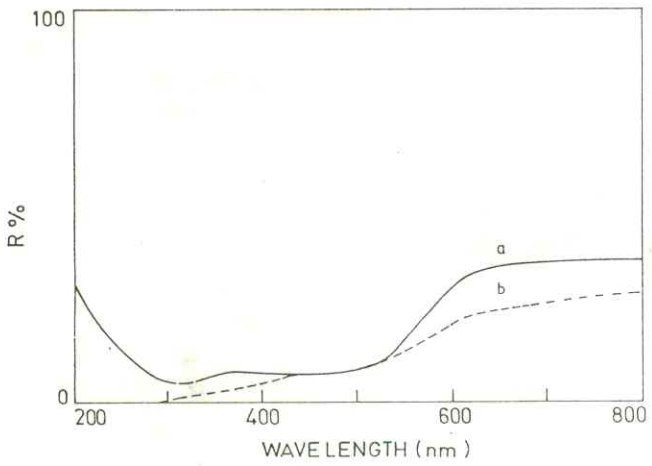

FIg. 6: UV-visible diffused reflectance spectra of mild steel specimens immersed in (a) blank solution and (b) 100 ppm Zn^{2+}

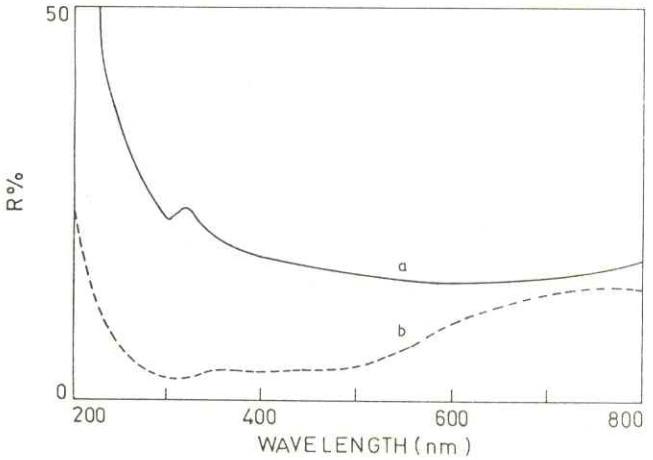

Fig. 7: UV-visible diffused reflectance spectra of mild steel specimens immersed in (a) 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture and (b) 100 ppm 2CEPA

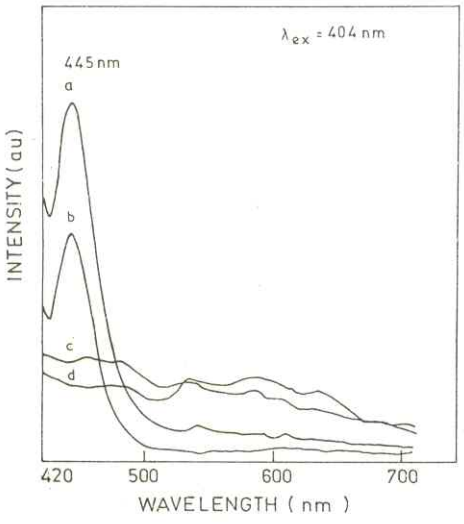

Fig. 8: Luminescence spectra of mild steel immersed in (a) 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture; (c) 100 ppm Zn^{2+} and (d) 100 ppm 2CEPA; (b) Luminescence spectra of Fe^{3+} 2CEPA complex

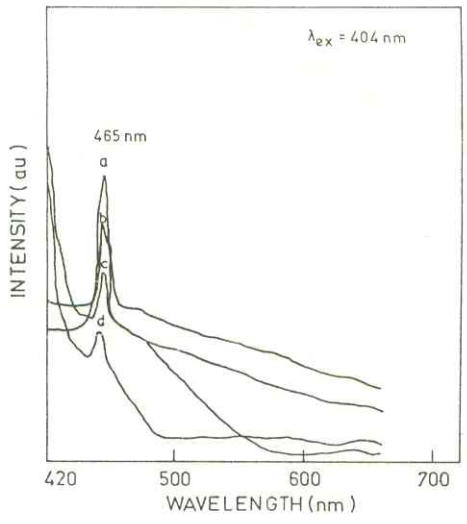

FIg. 9: Luminescence spectra of (a) 100 ppm 2CEPA; (b) 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture (c) The solution of 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture after two days of metal immersion and (d) The solution of 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture after seven days of metal immersion

solution of 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture after 7 days of metal immersion (9d). In all these cases a peak at 465 nm is observed. This peak is due to the presence of 2CEPA. The peak intensity of the solution of 100 ppm 2CEPA and 100 ppm Zn^{2+} mixture after 7 days of metal immersion is less than the solution of 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture after two days of metal immersion. This is because part of 2CEPA was consumed for forming iron-2CEPA complex. The above results show iron-2CEPA complex is not forming in the solution but forming on the surface of the metal.

CONCLUSION

1. Maximum corrosion inhibition efficiency is achieved for the mild steel immersed in 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture.
2. Various combinations of Zn^{2+} and 2CEPA obeys Langmuir adsorption isotherm.
3. 100 ppm Zn^{2+} and 100 ppm 2CEPA mixture acts as a mixed inhibitor.
4. Iron-2CEPA complex is only forming on the surface of the metal.

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