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ECO –FRIENDLY INHIBITOR SYSTEM FOR CORROSION INHIBITION OF CARBON STEEL IN HIGH CHLORIDE MEDIA

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ABSTRACT

The corrosion Inhibition Efficiencies (I.E), and Corrosion Rates (C.R) of carbon steel in neutral aqueous environment containing 100 ppm chloride in the presence and absence of ATMP - Zn^{2+} inhibitor system at various concentrations are obtained by weight-loss method . From the results, it is clear that ATMP by itself is a poor inhibitor , but when it combines with zinc ions (ATMP 150 ppm +Zn ions 50 ppm) , it offers 98% I.E. So there is a synergistic effect of ATMP and Zinc ions .The nature of film formed on the surface of carbon steel has been studied by FTIR and UV-luminescence spectral methods and electrochemical method

Key words : Phosphonates, Inhibitor, Carbon steel

INTRODUCTION

Corrosion is the cancer of metals due to thermodynamic instability[1].The term corrosion includes the reactions of metals ,glasses ,ionic solids, polymeric solids and composites with the environments of liquid metals, gases ,non-aqueous electrolytes and other non –aqueous electrolytes and other non –aqueous solutions[2].Carbon steel is used under different conditions in chemical and allied industries for handling alkaline acid and salt solutions. Chloride ,sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. Corrosion products are formed when a metal give its electrons to the oxidising substances. This can be delayed by painting the metal , or other way of protecting these metal , or other way of protecting these metal from corrosion is to use corrosion inhibitors. The need to develop formulations free from environment hazardous chromates, nitrates and inorganic phosphorous compounds has stimulated research work on phosphonates as eco-friendly inhibitors have been widely used as corrosion inhibitors due to their hydrolytic stability, ability to form complex with metal ions and scale inhibiting property[3-16].Generally ,phosphontes as such are not promising inhibitors. When blended with other compounds or metal ions like zinc ions phosphonates give excellent inhibition efficiencies.

The aim of the present study to investigate the phenomenon of synergism and also mechanistic aspects of corrosion inhibition of carbon steel in the presence of one synergist ,namely zinc ions (binary system).

EXPERIMENTAL

Preparation of carbon steel specimens

The carbon steel specimens were selected from the same sheet of the following composition. Sulphur - 0.026 percent ,phosphorous - 0.06 percent , manganese - 0.4 percent, carbon - 0.1 percent and the rest iron.

The carbon steel specimens of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish and then degreased with trichloroethylene .They were used in the weight–loss method and surface examination studies.

Carbon steel rod encapsulated in Teflon with an exposed cross section of 1 cm^2 diameter was used as the working electrode in potentiostatic polarisation studies. The surface of the electrode was polished to mirror finish. Trichloroethylene was used to degrease the electrode.

Preparation of the environments

The details regarding the preparation of various environments used for weight loss method in the present study are explained in table 1 for one set of solution.

Weight loss method

Determination of surface area of the specimens were determined with specimens and the radius of the hole were determined with the help of of vernier calliper of high precision and the surface areas of the specimens were calculated.

Weighing the specimens before and after corrosion

All the weighings of the carbon steel specimens before and after corrosion were carried out using a Mettler analytical balance –AE 240 dual range balance with readability of 0.01 mg in 40g range and 0.1 mg in 200g was supplied by Mettler instrument. AG, CH-8606 Greifensee, Switzerland.

Table 1 :Preparation of the environment for weight - loss method

Sl.No	NaCl Solution		Sodium Phosphonate Solution		ZnSO4 Solution		Total volume made up with triple distilled water
	Ml	Cl^- (ppm)	Ml	ppm	ml	Zn^{2+} ppm	ml
1	1	100	-	-	-	-	100
2	1	100	1	10	-	-	100
3	1	100	1	10	1	10	100
4	1	100	1	10	5	50	100
5	1	100	1	10	10	100	100
6	1	100	1	10	15	150	100
7	1	100	1	10	20	200	100
8	1	100	1	10	30	300	100

Detrmination of corrosion rate

The weighed specimens in triplicate ,were suspended by means of glass hooks in 100 ml of various test solutions. After seven days of immersion , the specimens were taken out , washed in running water , dried and weighed .From the change in weight of the specimens , corrosion rates were calculated with the help of the following relationship.

Corrosion rate = [Loss in weight (mg) / Surface area of x Period of immersion (days) the specimen]

Corrosion inhibition efficiency (I.E) was the calculated using the equation

$$I.E = 100\,[1-W2 / W1]\ \%$$

Where, W1= Corrosion rate in the absence of inhibitor and; W2 = Corrosion rate in the presence of inhibitor

Potentiostatic polarisation study

The measurement were carried out using corrosion measurements system (EG & G electrochemical Impedence Analayzer Model 6310). A three electrode cell assembly was used .The

working electrode used was rectangular specimens of carbon steel ,with one face of the electrode of 1 cm^2 area exposed and the rest being shielded with red lacquer . A rectangular platinum foil was used as the counter electrode . The area of the counter electrode was much larger compared to the area of the working electrode. This can exert a uniform potential field on the working and minimize the polarization effect on the counter.

The reference electrode used was saturated calomel electrode (SEC).The reference electrode was placed close to the working electrode to minimize IR contribution. A time interval of about 5 to 10 min was given for the working electrode to attain a steady state open circuit potential. The results such as inhibition efficiency ,Tafel slope, E_{corr} and I_{corr} values are presented.

Surface analysis by FTIR spectroscopy

After the immersion period of two days in various environments, the specimens were taken out the test solutions and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so was to make it uniform throughout. FTIR spectrum of the powder (KBr pellet) was recorded using perkin –Elmer 1600 FTIR spectrophotometer with resolving power of 4 cm^{-1}.

Surface analysis by UV – luminescence spectroscopy

Luminescence spectra of the film formed on the metal surface were recorded using Hitachi 650-610S fluorescence spectrometer.

RESULTS AND DISCUSSION

Analysis of the result of weight – loss measurements

The corrosion inhibition efficiencies (IE) of carbon steel in neutral aqueous environment containing 100 ppm chloride in the presence and absence of inhibitor at various concentrations obtained by weight – loss method are given in table 2 . The corrosion rates are also given in the Table 2.

It is clear from these results that ATMP by itself is a poor corrosion inhibitor and zinc ions are found to be corrosive .However, it is interesting that ATMP zinc ions combinations offers good corrosion inhibition at 150 ppm ATMP and 50 pm Zinc ions .This clearly indicates the synergistic effect of ATMP and zinc ion combination. It is observed that the formulation of 150 ppm ATMP and 50 ppm zinc ions offers 98% IE . this is the maximum IE offerd by this system..A thin interface multicoloured film is on the inhibited metal during the weight loss experiment

Analysis of the results of potentiostatic polarisation study

The potentiostatic polarisation curves of carbon steel surface immersed in the various environments are given in Fig1.The corrosion parameters are given in the Table 3

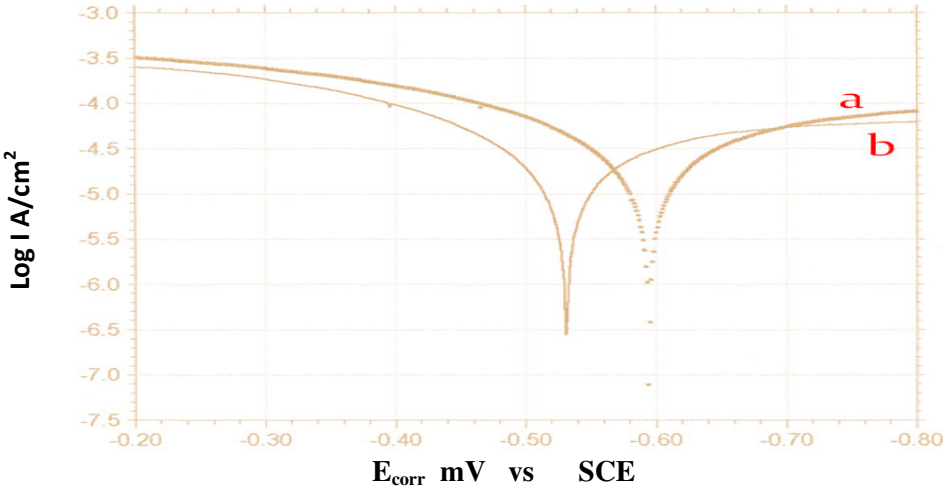

Fig.-1: Potentistatic polarization curves of carbon steel surface immersed in the various environments; (a) Cl^-100 ppm; (b) Cl^-100 ppm + Zn^{+2} 50 ppm + ATMP 150 ppm

Table-2: Corrosion inhibition efficiency of carbon steel in chloride aqueous environment (chloride =100 ppm), in the presence and absence of inhibitor and the corrosion rates obtained by the weight loss method.
Inhibitor system : ATMP +Zinc ions; pH=7

S.No.	Concn of ATMP ppm	Concn of Zinc ions Ppm	Corrosion Rate Mdd	Inhibition efficiency %
1	0	0	25.63	-
2	25	50	27.94	-9
3	50	50	9.48	-13
4	75	50	5.13	-14
5	100	50	5.13	-15
6	25	50	1.79	93
7	150	50	0.51	98
8	0	50	-36.14	-41
9	150	0	29.98	-17

Table -3; Corrosion parameters of carbon steel in neutral aqueous environment (chloride =100 ppm), in the presence and absence of inhibitor and the corrosion rates obtained by the polarisation method
Inhibitor system : ATMP + Zinc ions

S.No	Concen. Of ATMP ppm	Concen. Of Zinc ions ppm	E_{corr} mV vs SCE	b_a mV	b_c mV	I_{corr} A/cm2	R_p ohm
1	0	0	-594	335	220	3.9×10^{-5}	1.5×10^{3}
2	150	50	-531	380	210	3.3×10^{-5}	1.6×10^{3}

When carbon steel is immersed in aqueous environment containing 100 ppm Cl^-, E_{corr} is 594 mV vs SCE and the corrosion current is 3.9×10^{-5} A /cm^2. When 150 ppm ATMP and zinc ions are added E_{corr} shifts to the anodic region (-594 mv vs SCE to -531 mV vs SCE). I corr also decreases to 3.3×10^{-5} A/cm2. The shift to anodic region is due to control of dissolution of iron.

The FTIR spectrum of the film carefully scratched from the surface of the metal immersed in the environment consisting of 100 ppm cl^{-1} and 100 ppm and 150 ppm ATMP is shown in the fig 2. It is observed that the C-N stretching frequency of ATMP has shifted from 1145 cm^{-1} to 1070 cm^{-1}.And the P-O stretching frequency has shifted from 1002 cm^{-1} to 974 cm^{-1}.These shifts would have been caused by the decrease of electron cloud density of C-N bond and the P-O bond. Due to the shift of electron cloud density , N and O atoms of ATMP are coordinated to Fe^{2+} resulting in the formation of Fe^{2+} - ATMP complex on the metal surface. The band at 1374 cm^{-1} is due to $Zn(OH)_2$ [10-20].

The luminescence emission spectra (λ_{ex}=300 nm) are given in fig 3 ,the spectra for the surface of the metal immersed in the ATMP 150 ppm alone (a) and for the surface immersed in 100 ppm Cl^{-1} and 150 ppm ATMP (b) are nearly same..While the spectrum of the surface immersed in 100 ppm Cl^{-1} 150 ppm ATMP and 50 ppm Zn^{2+} combination (c) is different from other two. This indicates that the luminescence emission is due to Fe^{2+} - ATMP complex embedded in oxides of iron in the former two case while it is due to Fe^{2+} - ATMP complex alone in the later.

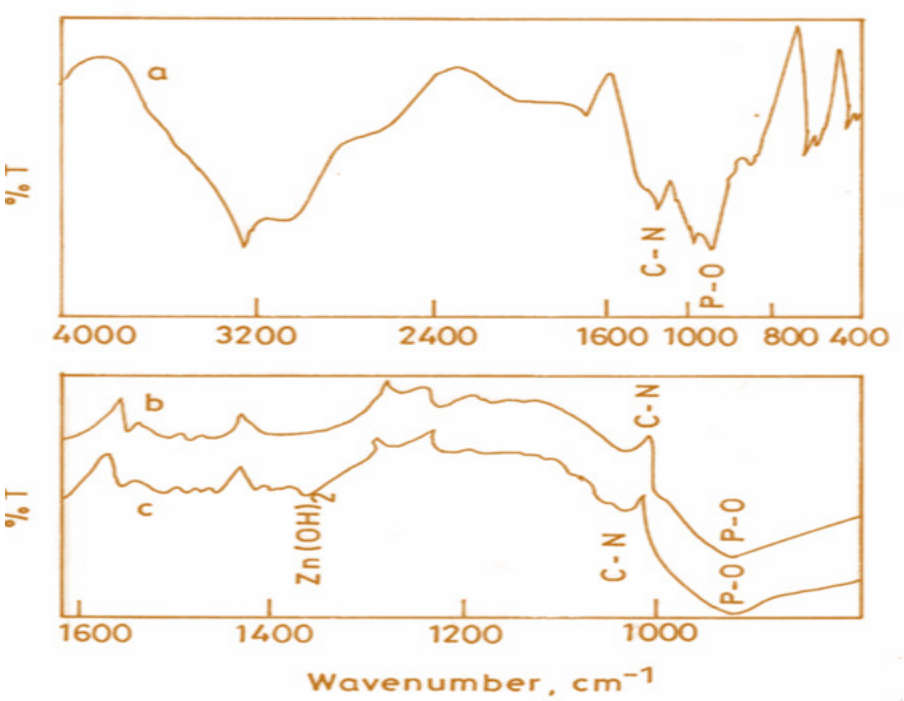

Fig.-2: Analysis of the FTIR Spectra, (a) pure ATMP; (b) Cl^- 100 ppm + ATMP 150 ppm; (c) Cl^- 100 ppm +ATMP 150 ppm + 50 ppm Zn^{2+}

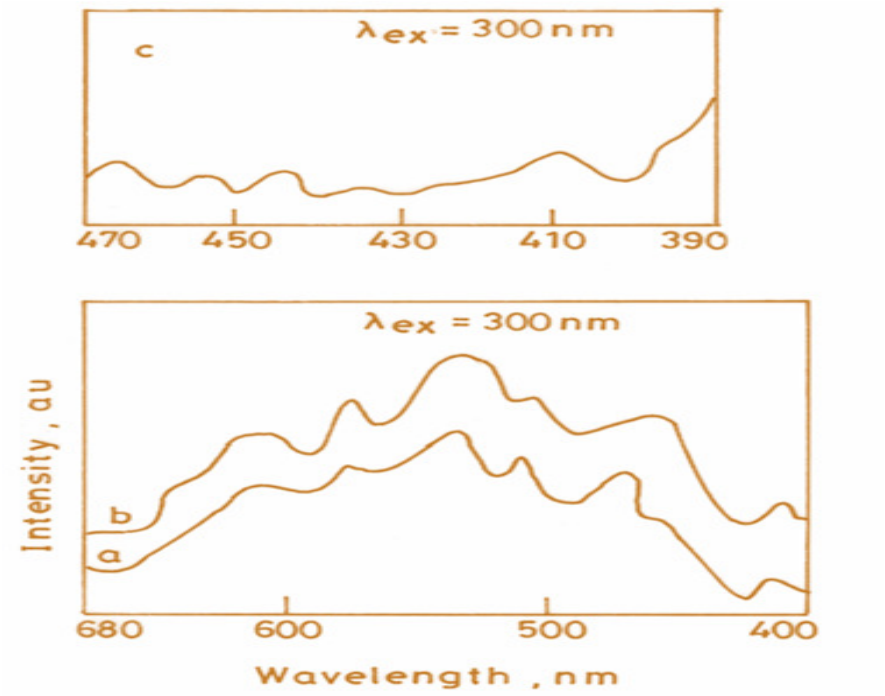

Fig.-3: Analysis of UV- luminescence spectra

CONCLUSION

The synergistic effect of ATMP and Zn^{2+} ions in controlling corrosion of carbon steel immersed in an aqueous solution containing 100 ppm of Cl^- has been evaluated in the present study. In order to

investigate the nature of the protective film ,corrosion inhibition ,FTIR spectroscopy, UV luminescence spectroscopy and electron chemical method like potentiostatic polarisation have been used.
The maximum corrosion inhibition efficiency offered by ATMP-Zn^{2+} ions and the system is 98% with the formulation consisting of 150 ppm of ATMP and 50 ppm Zn^{2+} ions. The protective film consisting of Fe^{2+}- ATMP complex $Zn(OH)_2$ and iron oxides. This protective film is found to be luminescent. The ATMP – Zn^{2+} ion system function as cathodic inhibitor.

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