SYNERGISTIC CORROSION INHIBITION EFFECT OF MILD STEEL IN SEA WATER BY 2-AMINO PYRIDINE - Zn^{2+} SYSTEM

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ABSTRACT: The corrosion inhibition efficiency of 2-Amino Pyridine (2AP) in controlling the corrosion of Mild steel immersed in Sea water for three days in the presence and absence of Zn^{2+} has been studied by weight loss method. The formulation consisting of 250 ppm of 2AP and 50 ppm Zn^{2+} offers 97% inhibition efficiency. The synergistic effect exists between 2AP and Zn^{2+} system. The influence of sodium lauryl sulphate (SLS)between 2AP and Zn^{2+} system control the microbial corrosion.Polarization study shows that the best formulation system controls anodic reaction predominantly. The AC impedance spectral studies reveal that the protective film formed on the metallic surface.The FTIR spectra study leads to the conclusion that the Fe^{2+}-2AP complex formed on anodic sites of the metal surface controlling the anodic reaction and $Zn(OH)_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction. The mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study and polarization study. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to investigate the nature of protective film formed on the Mild steel surface and for explaining the mechanistic aspects of the inhibition process.

Keywords: [2-Amino Pyridine, corrosion inhibition, Mild steel, weight loss study, polarization study, FT-IR and SEM.]

1. INTRODUCTION

Corrosion is the gradual destruction of material, usually metal, by chemical reaction with its Environment. Seawater is a complex natural electrolyte. Seawater contains many corrosive electrolytes such as sodium chloride, magnesium chloride, calcium chloride, etc.; hence, Mild steel immersed in seawater is corroded slowly because of chemical reactions between the metal and the electrolytes [1-3]. The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Seawater has been used as cooling fluid in various industries. Mild steel is widely used in infrastructure in marine environments [4].

It is one of the major constituents in structural steel applications including body of a ship, offshore platforms, foundation piling, sheet piling, and coastal facilities. It is also used in industry where the metal is exposed to acid corrosion. So, it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in seawater [5]. Inhibition of corrosion and scaling can be done by the application of inhibitors, which is one of the most practical and economic methods for protection against metallic corrosion [6,7]. Corrosion inhibitors disclose that most organic substances used as corrosion inhibitors can adsorb on the metal surface

employed through heteroatoms such as nitrogen, oxygen, sulphur, and phosphorus, multiple bonds or aromatic rings and block the active sites decreasing the corrosion rate [8-12].

2. MATERIALS AND METHODS
2.1. PREPARATION OF THE SPECIMEN

Mild steel (0.026%S, 0.06%P, 0.4%Mn, 0.1% C, and the rest Fe) specimen of dimension 1cm×4cm×0.2cm were used for weight loss study. Mild steel rod of the same composition, encapsulated in Teflon was polished to a mirror finish and degreased with trichloroethylene.

Sl.No.	SLS Solution		2-Amino pyridine(2AP)		ZnSO$_4$ solution		Total Volume made up with distilled water
	Ml	(ppm)	Ml	(ppm)	ml	Zn^{2+} (ppm)	ml
1.	1	100	0.5	50	1	10	100
2.	2	200	1	100	5	50	100
3.	3	300	2	200	10	100	100
4.	4	400	3	300	15	150	100
5.	5	500	4	400	20	200	-

Table 1- Preparation of Stock Solution

2.1.1. PREPARATION OF 2-AMINO PYRIDINE

1g of 2-amino pyridine(2AP) was dissolved in distilled water and made up to 100 ml.

2.2 WEIGHT LOSS METHOD

Two Mild steel specimens were immersed in 100 ml of test solution containing various concentrations of the inhibitors in the absence and presence of Zn^{2+}ions, for a period of three days. After exposure corrosion product were removed with Clarke's solution, and the weight of the specimens before and after immersion were determined using a metler balance.

2.2.1 CORROSION INHIBITION EFFICIENCY

Corrosion inhibition efficiency was calculated using the equation:

$$I.E = 100\left[1 - \frac{W_2}{W_1}\right]\%$$

where W$_1$= Corrosion rate in the absence of inhibitor, W$_2$= Corrosion rate in the presence of inhibitor.

2.3. SURFACE EXAMINATION

The Mild steel specimens were immersed in various test solutions for a period of three days, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic study.

2.4. FT-IR SPECTRA

FT-IR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

2.5. POTENTIODYANMIC POLARIZATION

Polarization studies were carried out in an H&CH electrochemical work station

impedanceanalyser model CHI660A. a three electrode cell assembly was used. The working electrode was Mild steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

2.6.   AC   IMPEDENCE MEASUREMENTS

The instrument used polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance, R_t and the double layer capacitance, C_{dl}were calculated.

3. RESULTS AND DISCUSSION

Inhibitor system: 2AP- Zn^{2+}

3.1 WEIGHT LOSS STUDY

The corrosion rates of Mild steel immersed in various test solution for a period of three days are presented in the following tables:

3.1.1 SYNERGISTIC EFFECT OF 2 AMINO PYRIDINE – Zn^{2+} SYSTEM

The calculated inhibition efficiencies of Mild steel immersed insea water, for a period of three days in the absence and presence of Zn^{2+} ion are given in table 3.1. The calculated value indicates the ability of 2AP to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Zn^{2+} ion. 2AP alone shows some IE. But the combination of 250 ppm 2AP and 50 ppm Zn^{2+} shows 95% IE. This suggests a synergistic effect exists between 2AP and Zn^{2+}.

Immersion period: 3 days

2AP	Zn^{2+}= 0 ppm		Zn^{2+} = 25 ppm		Zn^{2+} = 50 ppm	
ppm	IE%	CR(mmpy)	IE%	CR(mmpy)	IE%	CR(mmpy)
0	-	0.1211	12	0.1066	17	0.1005
50	13	0.1054	27	0.0884	34	0.0799
100	21	0.0957	39	0.0739	49	0.0618
150	33	0.0811	53	0.0569	67	0.0400
200	41	0.0714	75	0.0303	85	0.0182
250	49	0.0618	83	0.0206	95	0.0061

Table 2- Inhibition Efficiencies (IE%) and corrosion rates (CR) Obtained from 2AP- Zn^{2+} systems when Mild steel immersed in sea water.

3.1.2 INFLUENCE OF IMMERSION PERIOD ON IE OF 2AP-Zn^{2+} SYSTEM

The influence of immersion period on the IE of 2AP (250ppm) – Zn^{2+} (50ppm) system is given in table 3.2 is found that as the IP increases, the IE decreases. This due to the fact as the IP increases the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as chloride (16050ppm) present in

Sea water. There is a competition between two processes, namely, formation of $FeCl_2$ (and also $FeCl_2$) and Fe^{2+}-2AP complex on the anodic sites of the metal surface. It appears that the formation of iron chlorides is more favoured than the formation of Fe^{2+}-2AP complex film formed on the metal surface is converted into iron chlorides which go into solution and hence, the IE decreases as the IP increases.

System	Immersion period (days)			
	1	**3**	**5**	**7**
Sea water CR (mmpy)	0.1145	0.1211	0.1289	0.1317
Sea water+2AP(250ppm)+Zn^{2+}(50ppm); CR (mmpy)	0.0034	0.0061	0.0116	0.0184
IE %	97	95	91	86

Table 3- Influence of immersion period (IP) on IE of 2AP (250ppm) - Zn^{2+} (50ppm) system

3.1.3 INFLUENCE OF pHON IE OF 2AP-Zn^{2+} SYSTEM

The influence of PH OF IE of 2AP (250ppm) –Zn^{2+} (50ppm) system is given in table. It is found that at PH 8 the IE is 97%. When acid (dil. H_2SO_4) is added to attain pH 6, the IE decrease to 91%. When NaOH solution is added to boost the pH, (PH 10) IE decreases to 92%. When NaOH is added further (pH12) IE decreases to 89%. It is found that at pH 8 the IE was 95%, when acid was added (pH6), IE decreased. The protective film was brokened by H^+ ions of the acid. When NaOH was added further $Zn(OH)_2$ was solubilized as sodium zincate Na_2ZnO_2. Now 2APwas transported towards the metal surface. Hence IE increased [14-16].

Inhibitor system: 2AP-Zn^{2+} Immersion Period: 3 days

System	pH			
	6	8	10	12
Sea water CR (mmpy)	0.1388	0.1211	0.1062	0.0978
Seawater+2AP(250ppm)+Zn^{2+}(50ppm) CR (mmpy)	0.0125	0.0061	0.0085	0.0108
IE %	91	95	92	89

Table 4- Influence of pH on IE of 2AP (250ppm) - Zn^{2+} (50ppm) system

3.1.4 INFLUENCE OF SODIUM LAURYL SULPHATE (SLS) ON INHIBITION EFFICIENCY OF 2AP - Zn^{2+}SYSTEM

SLS is a cationic surfactant. It is a biocide. The IE and biocidal efficiency (BE) of 2AP-Zn^{2+}-SLS system is given here it is an observed from the results that 50 ppm of SLS in combination with 2AP-Zn^{2+} system has increased IE from 95% to 97%. However, anincrease in IE of 2AP-Zn^{2+} System is noticed when the SLS concentration increases from 100 ppm to 250 ppm. This is due to the formation of micelles at higher concentration of surfactant.

2AP ppm	Zn^{2+} ppm	SLS ppm	CR mmpy	IE%
0	0	0	0.1211	-
250	50	0	0.0061	95
250	50	50	0.0036	97
250	50	100	0.0022	98
250	50	150	0.0006	100
250	50	200	0.0005	100
250	50	250	0.0003	100

Table 5- Influence of SLS on inhibition efficiency (IE%) of Mild steel immersed in sea water

3.1.5 ANALYSIS OF POLARIZATION CURVES FOR 2AP-Zn²⁺ SYSTEM

The calculated corrosion parameters such as corrosion potential (E_{corr}), Tafel slopes (anodic slope b_a and cathodic slope b_c), linear polarization resistance (LPR) and corrosion current (I_{corr}) values are absence and presence of inhibitors are shown table 3.5. When Mild steel is immersed in sea water, its corrosion potential is -557mV vs saturated calomel electrode (SCE). The corrosion current is 12.89×10^{-6}A/cm². When 2AP (250 ppm) and Zn²⁺(50 ppm) are added to the above system the corrosion potential is shifted to the cathodic side (from -557mV). This suggests that the cathodic reaction is controlled predominantly. Moreover, in presence of the inhibitor system, the corrosion current decreases from 12.89×10^{-6}A/cm² to 1.51×10^{-6} A/cm². These observations indicate the formation of protective film on the metal surface [26-28].
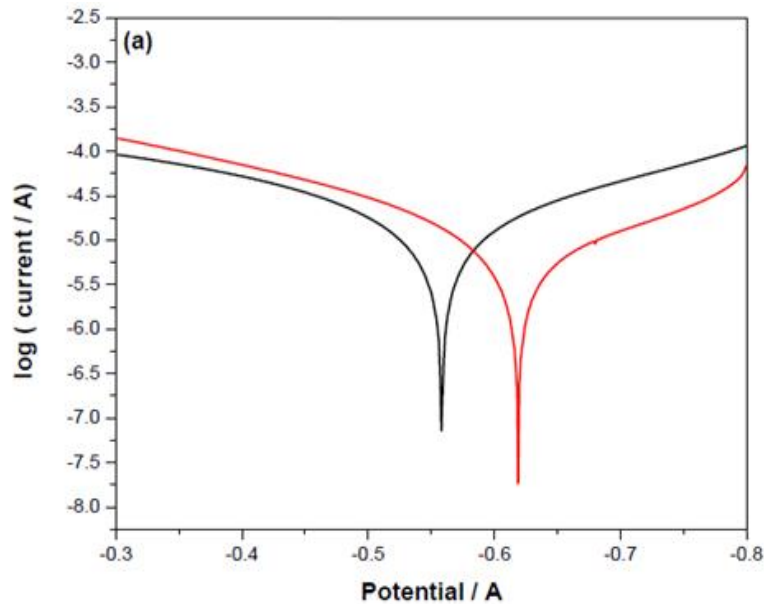

Figure1- Potentiodynamic polarization curves of Mild steel in various test solution
a) Sea Water b) Sea Water + 50 ppm Zn²⁺ + 250 ppm 2-AP

Description	E_{corr} mV/decade	b_a mV/decade	b_c mV/decade	I_{corr} A/cm²
Sea Water	-557	193	199	12.89×10^{-6}
Sea Water + 50 ppm Zn²⁺ + 250 ppm 2-AP	-618	138	187	1.51×10^{-6}

Table 6- Corrosion potential (E_{corr}), Tafel slopes (anodic slope b_a and cathodic slope b_c), linear polarization resistance (LPR) and corrosion current (I_{corr}) values are absence and presence of inhibitors

3.1.6 ANALYSIS OF AC IMPEDANCE SPECTRA FOR 2AP –Zn²⁺ SYSTEM

The AC impedance spectra of Mild steel immersed in sea water in the absence and presence of inhibitors are show in figure 3.2. The AC impedance parameters such as charge transfer resistance (R^1), double layer capacitance (C_{dl}) and impedance value [log (Z/ohm)] are given in the table 3.6. The R_t value is 219.75 ohm cm² and C_{dl} values 1.07×10^{-6} F/cm². When 2AP and Zn²⁺ are added to sea water, R_t value is 219.75 ohm cm² to 2608.20 ohm cm². The C_{dl} value decreases from 1.07×10^{-6} F/cm² to 4.04×10^{-8}. This confirms that the formation of protective film on the metal surface. This accounts for the very high IE of 2AP –Zn²⁺ system [26-28].
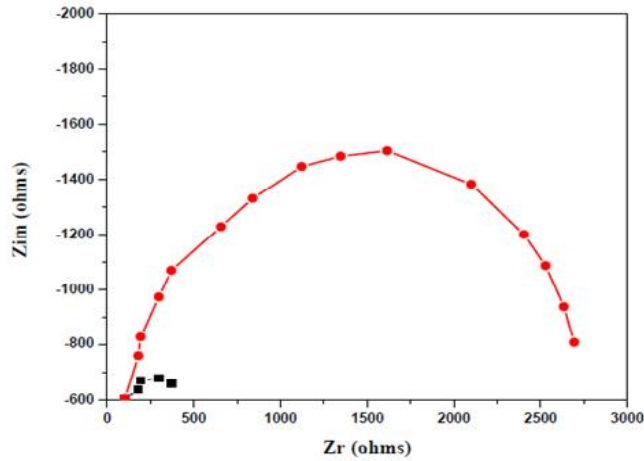
Figure 2- Impedance spectra curves of Mild steel in various test solution a). Sea Water b). Sea Water + 50 ppm Zn^{2+} + 250 ppm 2-AP

System	R_t (Ωcm^2)	C_{dl} (F/cm^2)
Sea Water	219.75	1.07×10^{-6}
Sea Water + 50 ppm Zn^{2+} + 250 ppm 2-AP	2608.20	4.04×10^{-8}

Table 7- Charge transfer resistance (R_t) and Double layer capacitance (C_{dl})

3.1.7 SRUCTURE OF 2-AMINO PYRIDINE
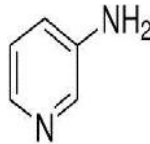
Figure 3

3.1.8 SURFACE ANALYSIS

The structure of 2-amino pyridine is shown in fig. 3.3. It contains C-N and N-H stretching vibrations.The protective film formed on the surface of the metal in the presence of 2-amino pyridine system and 2-amino pyridine–Zn^{2+} system in aqueous medium has been analysed by FT-IR spectroscopy
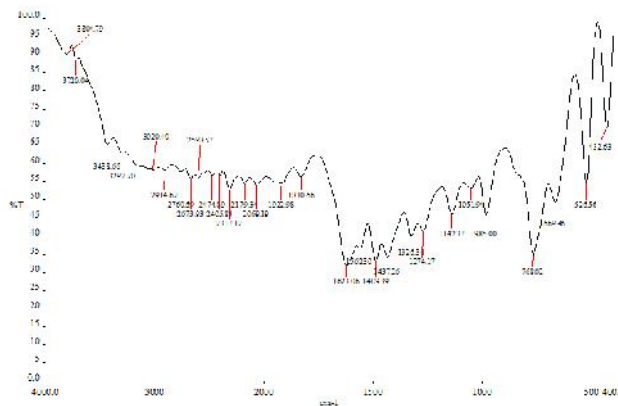
3.1.9. ANALYSIS OF FT-IR SPECTRA

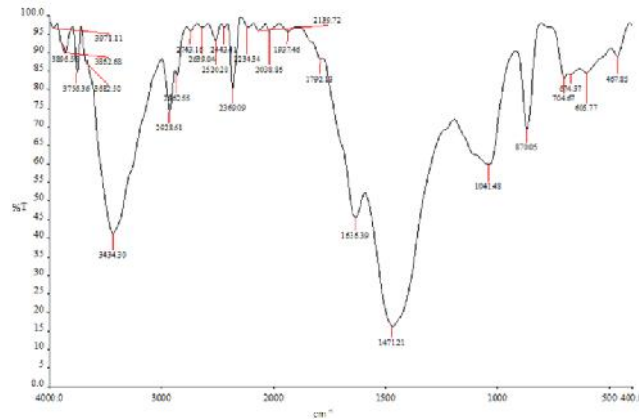**Figure 4- FT-IR Spectra of Pure 2-AP**

Figure 5- FT-IR Spectra of Sea Water+250ppm of 2AP+50ppm of Zn^{2+}

The FT-IR spectrum (KBr) of pure 2-amino pyridine is shown in the fig 3.4 C-N and N-H stretching frequency appears at 1142.37 cm^{-1} and 3438.66 cm^{-1}.The FTIR spectrum of pureSea Water+250ppm of 2AP+50ppm of Zn^{2+} is shown in the fig 3.5. These is a peak at 1623.06cm^{-1} due to N-Hbending.FT-IR spectrum (KBr) of the film formed on the surface of the metal after immersion of the solution containing 250 ppm of 2-amino pyridine and 50 ppm Zn^{2+} in aqueous medium is shown in figure 3.5. The C-N stretching frequency of 2-amino pyridine has decreased from 3438.66 cm^{-1} to 3434.30 cm^{-1}. The N-H stretching frequency of 2-amino pyridine has decreased from 1142.37 cm^{-1} to 1041.48 cm^{-1}. The band at 1471.21 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface.

3.2. SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron micrographs of Mild steel are shown in Fig 5. The SEM micrograph of polished Mild steel surface (control) is shown in Fig 5a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of Mild steel immersed in Seawater is shown in Fig 5b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Fig 5c shows that the presence of 250 ppm of 2AP and 50 ppm of Zn^{2+} in Seawater gives the formation of thick films on the Mild steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to block the active site present on the Mild steel surface [25-28]
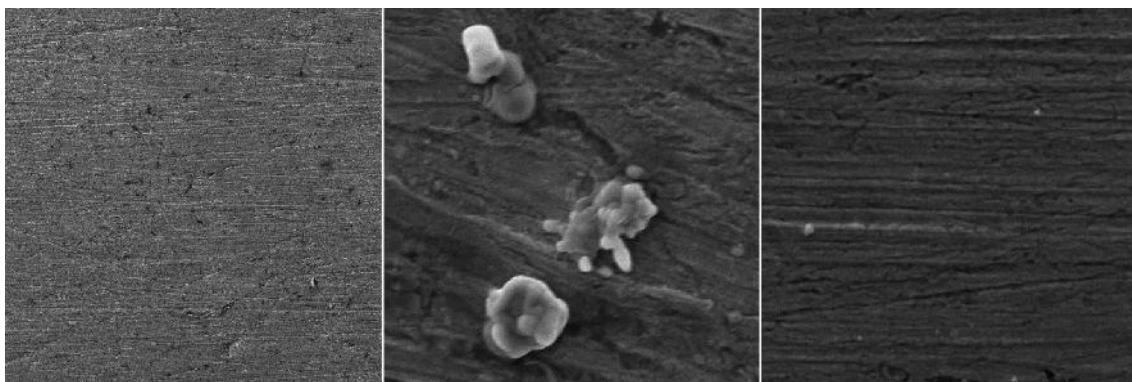

Figure 6- SEM images of Mild steel surface (a) Polished metal (b) Sea water (c) Sea water + 50 ppm of Zn^{2+} + 250 ppm 2AP

3.3 MECHANISM OF CORROSION INHIBITION

The results of weight loss study show that the formulation consists of 250 ppm 2AP and 50 ppm Zn^{2+} has 95% IE, in controlling corrosion of Mild steel in Sea water. A synergistic effect exists between 2AP and Zn^{2+}. Polarization study reveals that 2AP–Zn^{2+} system functions as anodic inhibitor controlling anodic reaction predominantly and controls anodic reaction to some extent. FTIR spectra reveal that the protective film consists of Fe^{2+}-2AP complex and $Zn(OH)_2$. SEM studies confirm the formation of protective film on the metal surface. The effective synergistic formulation consists of 250 ppm of 2AP, 50 ppm of Zn^{2+} and 50 ppm of SLS shows IE 98% BE. Also the effective synergistic formulation consists of 250 ppm of 2AP, 50 ppm of Zn^{2+} and 200 ppm of SLS shows IE 100% BE. The addition of 2AP reduces metal dissolution in an aqueous environment and this may be due to adsorption and complex formation at the metal surface with the combined application of 2AP and Zn^{2+}. Hence the corrosion process is inhibited. The mechanism can be generalized as follows. When the formulation consists of 2AP (250 ppm) and Zn^{2+} (50 ppm) is adde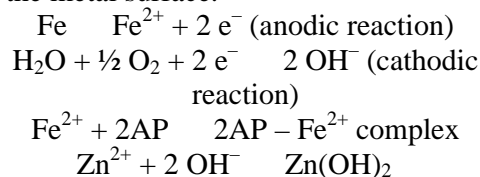d in Sea water there is a formation of 2AP – Zn^{2+} complex in solution. When Mild steel is immersed in this solution, 2AP – Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface. 2AP – Zn^{2+} complex is converted into 2AP – Fe^{2+} complex on the anodic sites of the metal surface with the release of Zn^{2+} ion.

$$2AP – Zn^{2+} + Fe^{2+} \quad 2AP – Fe^{2+} + Zn^{2+}$$

The released Zn^{2+} combined with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface.

$$Zn^{2+} + 2\,OH^- \quad Zn(OH)_2$$

Thus the protective film consists of 2AP – Fe^{2+} complex and $Zn(OH)_2$.

In near neutral aqueous solution, the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of 2AP – Fe^{2+} on the anodic sites of the metal surface. The cathodic reaction is the generation of OH^-. It is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

$$Fe \quad Fe^{2+} + 2\,e^- \text{ (anodic reaction)}$$
$$H_2O + \tfrac{1}{2}\,O_2 + 2\,e^- \quad 2\,OH^- \text{ (cathodic reaction)}$$
$$Fe^{2+} + 2AP \quad 2AP – Fe^{2+} \text{ complex}$$
$$Zn^{2+} + 2\,OH^- \quad Zn(OH)_2$$

This accounts for the synergistic effect of 2AP – Zn^{2+} system.

SUMMARY AND CONCLUSION

The Weight–loss study reveals that the formulation consisting of 50ppm of Zn^{2+} and 250ppm of 2-AP has 95% inhibition efficiency for three days' system and explains the Synergistic effect between 2-AP and Zn^{2+} complexes.

The protective film consists of Fe^{2+}-2-AP and $Zn(OH)_2$ is explained by FT-IR spectroscopy.

The results of polarization study show that the cathodic reaction is controlled predominantly indicating the reduction of resolution metal as more 2-AMINO PYRIDINE molecules are transported to the cathodic sites in the presence Zn^{2+} ions.

The AC impedance spectral studies reveal that the protective film obtained act as a barrier to the corrosion process that clearly explains the formation of the protective film on the metallic surface.

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