J. WILSON SAHAYARAJ[1], SUSAI RAJENDRAN[2],*
T.S. MUTHU MEGALA[2], A. JOHN AMALRAJ[3]

Eco-Friendly Inhibitor L-Valine – Zn^{2+} System Controlling Corrosion of Carbon Steel in Rain Water

The environmental friendly inhibitor system L-valine –Zn^{2+}, has been investigated by weight loss method. A synergistic effect exists between L-valine and Zn^{2+} system. The formulation consisting of 50 ppm of L-valine and 50 ppm of Zn^{2+} offers good inhibition efficiency of 74%. Polarization study reveals that this formulation functions as a mixed inhibitor. AC impedance spectra reveal the presence of a protective film on the metal surface The FTIR spectra study lead to the conclusion that the Fe^{2+} - LV complex formed on anodic sites of the metal surface controlled the anodic reaction and $Zn(OH)_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction. The ecofriendly inhibitor L-valine – Zn^{2+} system may find application in cooling water system.

Key words : *L-valine, corrosion inhibitor, synergistic effect, carbon steel, rain water;*

INTRODUCTION

Corrosion in a broad sense signifies the whole range of reactions between metals and their environments. Corrosion inhibitor is defined as a chemical substance which when added to the corrosive environment at an optimum concentration, decreases the corrosion rate of metals or alloys significantly. The toxic inhibitors like chromate based inhibitors were used to control corrosion process but it creates the environmental hazards. The use of chromates at high concentration has declined in recent years because of health and safety considerations.

Amino acids form a class of non-toxic organic compounds which are completely soluble in aqueous media and produced with high purity at low cost. These properties would justify their use as corrosion inhibitors. The Environmental friendly inhibitor chosen in the present study is L-valine. The Literature presents some studies involving amino acids on the corrosion prevention of iron [1], steeel [2-4], aluminium [5,6], nickel [7] and copper [8-12]. The electrochemical behaviour of cysteine has been studied by cyclic voltametry using solid electrode [13,14]. The adsorption of amino acid on carbon steel in acidic environment have been investigated by Akiyama et.al.,[15]. A detailed study on L-valine as corrosion inhibitor has not been carried out. In the present work:

1. The synergistic effect existing between L-valine and Zn^{2+} has been evaluated by weight loss method.

2. The influence of immersion period on the inhibition efficiency (IE) of L-valine – Zn^{2+} system has been evaluated. The environment

3. chosen is rain water because in most of the industries water treated thro' demineralising unit is used in cooling water and it consists of very low concentration of chloride. All the experiments are carried at room temperature.

4. The Electrochemical studies such as polarization study and AC impedance spectra were analyzed.

5. The protective film has been analyzed by FTIR spectroscopy.

MATERIALS AND METHODS

Preparation of the carbon steel specimens

The carbon steel specimens were chosen from the same sheet of the following composition: sulphur – 0.026 percent, phosphorus – 0.06 percent, manganese – 0.4 percent, carbon – 0.1 percent and the rest iron.

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

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

Weight-loss method

The rain water collected from roof top and stored in concrete tank. The chemicals present in the roof top and concrete tank account for the presence of nitrate, chloride etc. The weighed specimens in triplicate, were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions in rain water (Table1). After three 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:

Authors adresses : [1]Department of Chemistry, Jeppiaar Engineering College, Rajiv Gandhi salai, Chennai – 600 119, [2]Corrosion Research Centre, Department of Chemistry, GTN Arts College, Dindigul – 624 005, Tamil Nadu, India, [3]Department of Chemistry, Peiryar E.V.R. College, Trichy, Tamil Nadu, India.

Corrosion rate = Loss in weight (mg) / [Surface area of the specimen (dm^2) x Period of immersion (days)]

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

I.E. = 100 [1- (W_2 / W_1)] % ,

Where W_1 = Corrosion rate in the absence of inhibitor, and W_2 = Corrosion rate in the presence of inhibitor.

Table 1 - Parameters of Rain water

Parameters	Value
pH	8.15 ppm
Total Dissolved Solid	273 ppm
Electrical Conductivity	390 micromhos/cm
Nitrate	9 ppm
Chloride	72 ppm
Sulphate	14 ppm
Fluoride	0.2 ppm
Total Hardness as CaCO3	88 ppm

Potentiostatic polarisation study

The measurements were carried using corrosion measurements system (CHI660 Electrochemical Workstation). A three electrode cell assembly was used. The working electrode used was a rectangular specimen of carbon steel, with one face of the electrode of constant 1 cm^2 area exposed and the rest being shielded with red 1acquer. 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 electrode and minimize the polarisation effect on the counter. The reference electrode used was saturated calomel electrode (SCE). The results such as inhibition efficiency, Tafel slopes, E_{corr} and i_{corr} values are presented.

A.C. Impedance Measurements

CHI660 Electrochemical Workstation has introduced a very effective approach to A.C. impedance measurements. The cell set up was the same as that used for polarisation measurements. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_t and C_{dl} values were calculated.

Surface analysis by FTIR spectroscopic study

After the immersion period of three days in various environments, the specimens were taken out of 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.

RESULT AND DISCUSSION

Analysis of the results of weight-loss method

Corrosion rates of carbon steel immersed in rain water in the absence and presence of inhibitor at various concentrations obtained by the weight–loss method are given in Tables 2 to 6. The corrosion inhibition efficiencies (IE) of the system, L-valine (LV) – Zn^{2+} are also given in these Tables.

Table 2 - Corrosion rates of carbon steel in rain water environment in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method.

Inhibitor System: LV + Zn^{2+}　　　　　　*pH = 7*

LV ppm	Zn2+ ppm	CR mdd	IE %
0	0	27.00	---
25	0	25.72	4
50	0	26.46	2
75	0	27.00	0
100	0	28.08	-4
125	0	29.97	-11

Table 3 - Corrosion rates of carbon steel in rain water environment in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method.

Inhibitor System: LV + Zn^{2+}　　　　　　*pH = 7*

LV ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	27.00	---
0	10	25.65	5
25	10	18.90	30
50	10	21.87	19
75	10	28.08	-4
100	10	28.89	-7
125	10	34.83	-29

Table 4: Corrosion rates of carbon steel in rain water environment in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method.

Inhibitor System: LV + Zn^{2+}　　　　　　*pH = 7*

LV ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	27.00	---
0	25	24.84	8
25	25	8.10	70
50	25	8.91	67
75	25	9.99	63
100	25	11.88	56
125	25	17.01	37

Table 5 - Corrosion rates of carbon steel in rain water environment in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method.

Inhibitor System: LV + Zn^{2+} 　　　　 *pH = 7*

LV ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	27.00	---
0	50	22.95	15
25	50	7.02	74
50	50	7.02	74
75	50	8.91	67
100	50	8.91	67
125	50	8.91	67

Table 6 - The influence of immersion period on corrosion rates of carbon steel in rain water environment.

Inhibitor System: LV + Zn^{2+} 　　　　 *pH = 7*

Day ppm	LV ppm	Zn^{2+} ppm	CR mdd	IE %
1	50	50	4.18	78
3	50	50	7.02	74
5	50	50	24.48	32
7	50	50	40.85	5

It is evident from the Table 2. that LV by itself is a poor corrosion inhibitor. In the presence of Zn^{2+}, better inhibition efficiencies are obtained. As the concentration of Zn^{2+} increases, IE also increases (Tables 3 to 5). For example 50 ppm of L-valine has 2% IE and 50 ppm of Zn^{2+} has 22% IE. However, interestingly the formulation consisting of 50 ppm of L-valine and 50 ppm of Zn^{2+} has 74% IE. This is due to synergistic effect existing between LV - Zn^{2+} system. This is found to be the maximum inhibition efficiency offered by this system. A thin interference film is observed on the surface of the inhibited metal during the weight loss experiment.

Influence of immersion period on the inhibition efficiency of the LV - Zn^{2+} system

The influence of immersion period on the inhibition efficiency of the LV - Zn^{2+} system is given in Table 6. It is found that as the immersion period increases, the inhibition efficiency decreases. This is due to the fact that as the immersion period increases, the protective film is broken by the aggressive of chloride ion present in the rain water.

Analysis of potentiostatic polarization curves

The potentiostatic polarization curves of carbon steel immersed in various solutions are shown in Figure 1. The corrosion parameters are given in Table 7. When carbon steel is immersed in rain water, the corrosion potential is –536mV vs saturated calomel electrode (SCE). The formulation consisting of 50 ppm of LV and 50 ppm of Zn^{2+}shifts the corrosion potential to -519mV vs SCE. This suggests that the anodic reaction is controlled predominantly. The formulation consisting of LV and Zn^{2+} shifts the anodic slopes and cathodic slopes almost equally (103 mV/decade and 106mV/decade respectively). This suggests that the LV - Zn^{2+} formulation functions as a mixed inhibitor controlling the anodic reaction of formation Fe^{2+} and cathodic reaction of formation of OH⁻

$$Fe \rightarrow Fe^{2+} + 2e^{-} \text{ (Anodic reaction)}$$

$$2H_2O + O_2 + 4e^{-} \rightarrow 4OH \text{ (Cathodic reaction)}$$
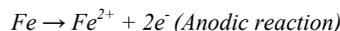
The corrosion current for sea water is 2.239×10^{-5} A/cm². The corrosion current for formulation consisting of LV (50 ppm) – Zn^{2+}(50 ppm) has decreased to 1.585×10^{-5} A/cm².
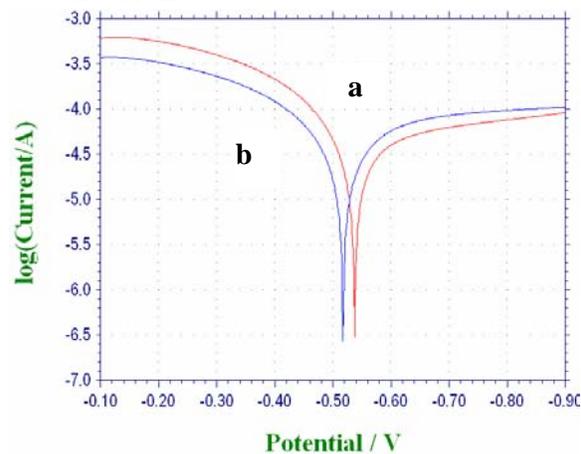

Figure 1 - Polarization study of carbon steel immersed in various environment: a) Rain water, b) Rain water + 50 ppm of L-valine + 50 ppm Zn^{2+}

Table 7 - Corrosion parameters of carbon steel in rain water environment in the presence and absence of inhibitor obtained by the polarization method

Inhibitor system: LV + Zn^{2+}

LVp pm	Zn^{2+} ppm	E_{corr} mV vs SCE	b_a mV/ decade	b_c mV/decade	I_{corr} A/cm²
0	0	-536	115	205	2.239×10^{-5}
50	50	-517	103	106	1.585×10^{-5}

Analysis of AC impedance spectra

The impedance measurements are widely used in the study of metal corrosion inhibition. Besides, anodic behavior of metals under active passive conditions can also be studied. The uniqueness of this techniques lies in its measurements in highly resistance media. The behavior of several metals has been studied in various aqueous media such as acidic, basic and neutral. The

Nyquist plots for the corrosion behavior of carbon steel immersed in various solutions are shown in Figure 2. The AC impedance parameters, namely, charge transfer resistance(R_t) and double layer capacitance(C_{dl}) are given in Table 8. Rain water has R_t value of 374 Ω cm^2 and C_{dl} value of 1.363 x10^{-8} Fcm^{-2}. When LV and Zn^{2+} are added to rain water, R_t value increases tremendously from 374 Ω cm^2 to 526 Ω cm^2. The C_{dl} decreases from 1.363x10^{-8} Fcm^{-2} to 0.9651x10^{-8} Fcm^{-2}. This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of LV - Zn^{2+} system.
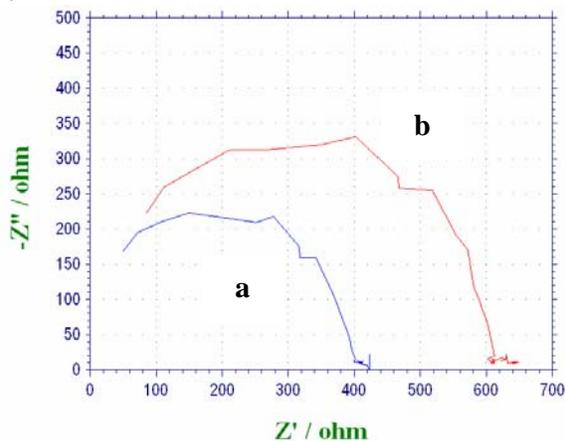

Figure 2 - AC impedance spectra of carbon steel immersed in various environment: a) Rain water, b) Rain water + 50 ppm of L-valine + 50 ppm Zn^{2+}

Table 8 - Corrosion parameters of carbon steel in rain water environment in the presence and absence of inhibitor obtained by A.C. Impedance method

Inhibitor system: LV + Zn^{2+}

LV ppm	Zn^{2+} ppm	R_t (ohm)	C_{dl} (F cm^{-2})
0	0	374	1.363 x 10^{-8}
50	50	528	0.9651 x 10^{-8}

Analysis of FTIR spectra

The FTIR spectrum of pure L-valine is shown in Figure 3a. The C=O stretching frequency of carboxyl group appears at 1647 cm^{-1}. The C-N and N-H stretching frequency appears at 1177 cm^{-1} and 3132 cm^{-1} respectively. The formulation consisting of 50 ppm of L-valine and 50 ppm of Zn^{2+} system has 74% IE. The FTIR spectrum (KBr pellet) steel surface after immersion in the rain water containing 50 ppm of L-valine and 50 ppm of Zn^{2+} system is shown in Figure 3b. The C=O stretching frequency has decreased from 1627 cm^{-1} to 1598 cm^{-1}. The C-N stretching frequency has decreased from 1180 cm^{-1} to 1177 cm^{-1}. The N-H stretching frequency has shifted from 3132 cm^{-1} to 3366 cm^{-1}. This indicates that these groups of L-valine has

coordinated with Fe^{2+} on the anodic sites of the metal surface, resulting in the formation of Fe^{2+} - LV complex. The peak at 1387 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface. Thus FTIR spectra study leads to the conclusion that the Fe^{2+} - LV complex formed on anodic sites of the metal surface controlled the anodic reaction and $Zn(OH)_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction[16 - 17].
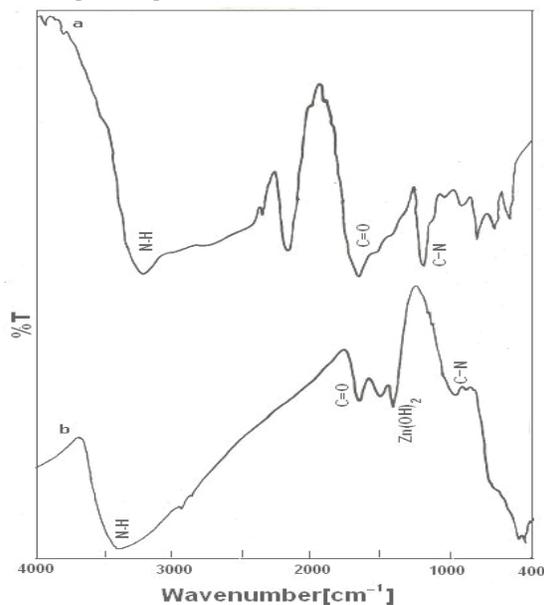

Figure 3 - FTIR Spectra: a) Pure L-valine (KBr), b) Film formed on carbon steel after immersion in rain water containing 50 ppm of L-valine and 50 ppm of Zn^{2+}

Mechanism of Corrosion inhibition

The formulation consisting of 50 ppm of L-valine and 50 ppm of Zn^{2+} offers good inhibition efficiency of 74%. Polarization study reveals that this formulation functions as a mixed inhibitor. AC impedance spectra reveal the presence of a protective film on the metal surface. FTIR spectra reveal that the protective film consist of Fe^{2+} - LV complex $Zn(OH)_2$. In order to explain these observations in a holistic way, the following mechanism of corrosion inhibition is proposed.

➢ When the formulation consisting of 50 ppm of L-valine and 50 ppm of Zn^{2+} is prepared, there is a formation of Zn^{2+}- LV complex in solution.

➢ When the carbon steel is immersed in this solution, Zn^{2+}- LV complex diffuses from the bulk of solution to the metal surface.

➢ On the metal surface, the Zn^{2+}- LV complex is converted in to Fe^{2+}- LV complex on the local anodic sites as later is more stable than former.

$$Zn^{2+} - LV + Fe^{2+} \rightarrow Fe^{2+}- LV + Zn^{2+}$$

➢ The released Zn^{2+} ions combine with OH$^-$ ions forming $Zn(OH)_2$ precipitate in the local cathodic sites

$$Zn^{2+} + OH \rightarrow Zn(OH)_2 \downarrow$$
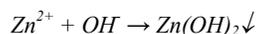
- Thus the protective film consist of Fe^{2+} - LV complex and $Zn(OH)_2$.

CONCLUSIONS

- ✓ The formulation consisting of 50 ppm of L-valine and 50 ppm of Zn^{2+} offers good inhibition efficiency of 74%.
- ✓ Polarization study reveals that this formulation functions as a mixed inhibitor.
- ✓ AC impedance spectra reveal the presence of a protective film on the metal surface
- ✓ The FTIR spectra study lead to the conclusion that the Fe^{2+} - LV complex formed on anodic sites of the metal surface controlled the anodic reaction and $Zn(OH)_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction.
- ✓ The Ecofriendly inhibitor L-valine – Zn^{2+} system may find in cooling water system. If further investigation is made under dynamic condition at high temperature.

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