ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Green corrosion inhibitors control the disaster of carbon steel surface

J. Wilson Sahayaraj[1*], A. John Amalraj[2], Susai Rajendran[3]
[1]Department of Chemistry, Jeppiaar Engineering College, Chennai- 600119, Tamil Nadu, India.
Corresponding author email: wils.sarc@gmail.com
[2]PG and Research Department of Chemistry, Periyar E.V.R College, Trichy - 620023, Tamil Nadu, India.
[3]Corrosion Research Center, Department of Chemistry, RVS School of Engineering and Technology, Dindigul – 624005, Tamil Nadu, India.
***Corresponding author: E-Mail: wils.sarc@gmail.com**

ABSTRACT

The accidents due to corrosion can be greatly exaggerated in many industries. The impact of environmental safe inhibitor valine controls the natural damage on the surface of steel immersed in rain water by mass-loss method. The mixture of 50 ppm valine - 50 ppm zinc sulphate system has 74% inhibition efficiency. This is due to the synergistic effect exist between valine and zinc ion. That is, the combined inhibitors show excellent inhibition percentage than individual. The addition of additive increases the inhibition efficiency and prevents the corrosion on metal surface. The polarization study reveals the types of inhibitor. The formation of protective film on the steel specimens confirms by AC-impedance and scanning electron microscopy. The FTIR spectra concluded that the iron - Val complex existed to control the anodic reaction and $Zn(OH)_2$ produced on the cathode region to control the cathodic reaction. The EDS study determines the elements of Val - Zn^{2+} system in the carbon steel specimens. The formulation consisting of 50 ppm Val-50 ppm Zn^{2+}-100 ppm of CTAB system has 100% biocidal efficiency.

KEY WORDS: Corrosion inhibition, carbon steel, Valine, Biocidal efficiency.

1. INTRODUCTION

The corrosion is disaster of the material, usually metal or alloys by chemical or electrochemical attack on their surroundings. Increased industrialization and urbanization lead to the atmospheric pollution in acid rain. However, the rain water nature is mostly alkaline in southern India. The rain water use for corrosion inhibition studies (Ebenso, 2009) due to most availability. Hence, carbon steel suspended in rain water medium undergoes corrosion. Most organic inhibitors practiced as corrosion inhibitor (Telegdi, 2000; Okafor, 2009). The plant extracts of stem, seed, flower etc used as corrosion inhibitors by many researchers to control the corrosion rate (Khaled KF, 2010). The many amino acids control the corrosion without damaging environment. The L-valine attested as environmental safe corrosion inhibitor by FTIR specra and electrochemical studies (Wilson Sahayaraj, 2010; Ingrid Milošev, 2013; Ghasemi Z, 2006).

The present paper objectives are:

1. To examine the inhibition percentage of Valine –zinc sulphate system on steel surface suspended into the rainwater.
2. To know the adsorbed substance produced on sites of steel by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).
3. The role of biocide CTAB on inhibition efficiency (IE) of Valine –zinc sulphate system has been studied.
4. To control the microbial activity on steel by the addition of CTAB on 50 ppm Val-50 ppm of Zn^{2+} system has been studied.
5. To frame the possible corrosion prevention mechanism are given by results obtained in this study.

2. MATERIALS AND METHODS

Preparation of the specimen: The composition of carbon steel specimen are 0.06%P, 0.1% C, 0.026%S, 0.4%Mn, and the rest Fe and their dimension (1cmx4cmx0.2cm) used for mass-loss study. The steel specimens polished to mirror finish with help of emery paper of different grade and cleansed with the solvent trichloroethylene.

Weight loss method: The steel specimens suspended in 100 ml of water in rain water (Table 1) with the presence and absence of inhibitors for three days. The metal weights were measured using Shimadzu balance, AY62 model. The corrosion products were removed with Clarke's solution. The corrosion rates (CR) were calculated by the given relationship:

Where

$$CR = \frac{\Delta m}{A * t}$$

CR - corrosion rate; Δm - loss in weight (mg); A - surface area of the specimen (dm^2)
t - Period of immersion (days)

The corrosion inhibition efficiency (IE) was calculated by using the equation

$$IE = 100\left(1 - \frac{W_2}{W_1}\right)$$

Where, W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

Table.1.Parameters of Rain water

Parameters	Value
pH	8.15
Conductivity	390 µmhos/cm
TDS	273 ppm
Chloride	72 ppm
Sulphate	14 ppm
Total Hardness	8 ppm

Surface analysis: The steel samples immersed in the inhibitor systems for three days. After the periods, the specimens were removed from the beaker, washed with pure water and dried. The film formed on the metal surface can be used for surface examination studies.

SEM / EDS study: The Surface structure of the steel samples examined by using JEOL JSM 6390 model. All steel samples SEM micrographs are taken at a magnification of X=500.

Biocidal study: The L-valine – zinc sulphate formulation which offered the best inhibition percentage was selected. The biocidal percentage of N-cetyl-N,N,Ntrimethylammonium bromide (CTAB) and inhibition percentage of on the best formulated system were determined. Zobell-medium prepared by mixing of 1g yeast extract, 5g peptone, 0.1g potassium dihydrogen phosphate and 15g agar-agar in one litre water. This medium sterilised by 15 pounds psi for ¼ hour in an autoclave. The different concentrations of biocide CTAB added to best formulated system. Polished and degreased steel samples immersed in these environments for 3 days. After the periods, one ml each of test solutions was pipetted out into sterile petri dishes each containing about 20ml of the sterilized Zobell-medium. The petri dishes were kept in a sterilised condition that is inside the laminar flow system fabricated and supplied by CEERI-Pilani, for 1 day. The total viable heterotropic bacterial colonies were counted using a bacterial colony counter. The inhibition percentage of the best formulated system in the presence of various concentrations of CTAB was also determined.

3. RESULT & DISCUSSION

Weight - loss method: The inhibition percentage of steel samples in 3 days immersion in rain water environment by the weight - loss method is given in the Table 2 and 3. The weight - loss method reveals that valine itself (SSA) alone shows very poor percentage of IE. But the addition of zinc sulphate offers good IE. For example 50ppm valine alone is 2% inhibition percentage; 50ppm zinc sulphate alone is 15% IE**.** But it is interestingly noted that the combination of 50ppm of val and 50ppm Zn^{2+} system shows 74% inhibition percentage. This is due to the fact that there is synergistic effect existing between val and zinc ion system (Florence, 2005). This means that the mixed inhibitors work better than individuals.

Table.2.Inhibition efficiency (IE) of steel in the presence and absence of inhibitor by weight loss method (Inhibitor system: Val alone; Immersion Period: three days)

Val (ppm)	IE (%)
0	--
25	4
50	2
75	0
100	-4
125	-11
150	-12

Table.3.The Inhibition efficiency (IE) of steel immerse in the presence and absence of inhibitors by weight loss method. (Inhibitor system: Val and Zinc sulphate system; Immersion Period: three days)

Val (ppm)	Zn^{2+}(ppm)	IE (%)
0	0	--
0	50	15
25	50	74
50	50	74
75	50	67
100	50	67
125	50	67

Analysis of SEM: The steel samples immersed in rain water for 3 days in absence and presences of inhibitor are shown in figure 1. The SEM micrograph, of polished steel (control) in figure 1a shows the smooth surface of the metal. This shows that there is no damage on the steel surface. The SEM micrograph of steel sample is given figure. 1b shows the roughness of the metal surface which indicates the corrosion of steel. Figure.3c indicates that in the

presence of 50ppm val-50ppm Zn^{2+} mixture in water, protective layer covered by forming the insoluble complex on the metal surface covered by a thin layer of inhibition which effectively controls the dissolution of the carbon steel.

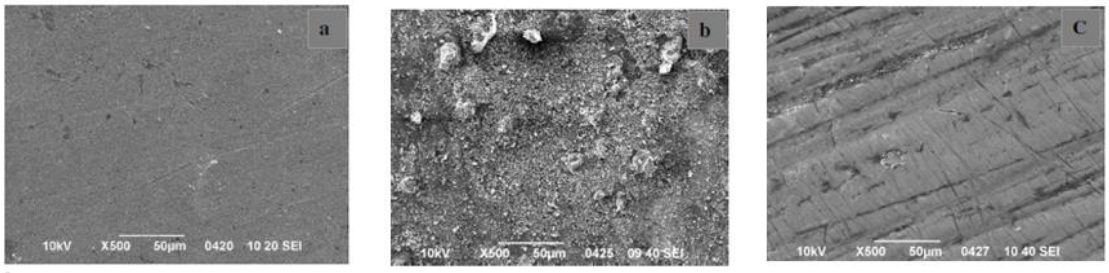

Figure.1.SEM images of carbon steel
a. Carbon steel (Blank); b. Carbon steel immersed in rain water
c. Film formed on steel after immersion in rain water containing 50ppm val and 50ppm Zn^{2+}

Analysis of EDS: The energy dispersive spectroscopy (EDS) of steel sample immersed in rain water is shown in figure 2a. This indicates the presence of Carbon(C), sulphur(S), phosphorous(P), anganese(Mn) and iron(Fe) along with C 50 ppm of val and 50ppm Zn^{2+} showsthe presence of Zn and oxygen along with Carbon(C), sulphur(S), phosphorous(P), manganese(Mn) and iron(Fe) is shown in figure 2b. This indicates that oxygen atom of carboxyl group of LV has coordinated with Fe^{2+}, resulting in the formation of Fe^{2+}-val complex on the anodic sites of metal surface and $Zn(OH)_2$ formed on the cathodic sites of metal surface.

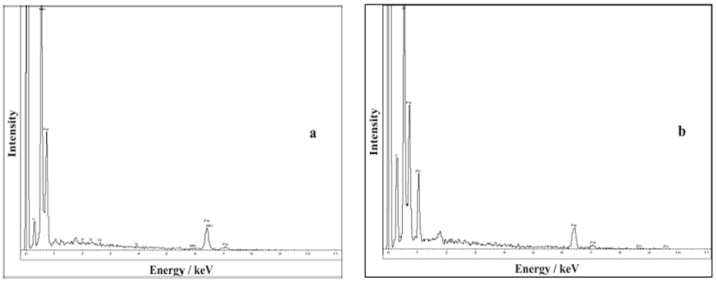

Figure.2.EDS spectra of carbon steel
a. Rain Water;
b. Film formed on carbon steel after immersion in rain water containing 50ppm val and 50ppm Zn^{2+}

Influence of CTAB on the corrosion inhibition efficiency of the Val – Zn^{2+} system: The influence of CTAB on the inhibition percentage of LV – Zn^{2+} is given in Table 4. The corrosion rates are shown in Figure 3. It is seen from Table 4 that when the concentration of CTAB increases, IE is also increases. Thus it is seen from Table 4 that the formulation consisting of 50ppm Zn^{2+}, 50ppm val and 250ppm CTAB has 52%.

Influence of the Val – Zn^{2+} system on the biocidal efficiency of CTAB: The influence of the Val – Zn^{2+} system on the biocidal percentage of CTAB is given in Table 5. The number of colony forming units as a function of the concentration of CTAB, in the presence Val – Zn^{2+} system is shown in Figure 4. The formulation consisting of 50ppm val and 50ppm Zn^{2+} system shows 358 CFU/ml. When the 50 ppm of CTAB is added to the above formulation, the number of colony forming units/ml is 46. This is objectionable. When 100 ppm of CTAB is added, nil colony forming units/ml is obtained. The biocidal efficiency is 100%. Hence, the optimum concentration of CTAB is 100 ppm. Thus, it is seen from Table 5 that the combination of 50ppm Zn^{2+}, 50ppm val and 100ppm CTAB has 100% biocidal efficiency.

Table.4.Influence of CTAB on the corrosion inhibition efficiency of the val – Zn^{2+} system
Inhibitor system: val + Zn^{2+} + CTAB

Val (ppm)	Zn^{2+} (ppm)	CTAB (ppm)	CR (mdd)	IE (%)
0	0	0	16.60	--
50	50	0	7.02	74
50	50	50	21.87	19
50	50	100	17.01	37
50	50	150	15.12	44
50	50	200	14.04	48
50	50	250	12.96	52

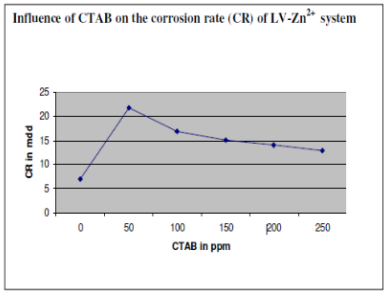

Figure.4.The biocidal efficiency of CTAB on the Val – Zn^{2+} system

Mechanism of Corrosion inhibition: The environmental friendly (Zucchi, 1985; Huang, 2013) mixture of 50 ppm valine and 50ppm Zn^{2+} shows good inhibition efficiency of 74%. The SEM study confirms the protective film formed on the metal surface. EDS study determine the elements of Val - Zn^{2+} system on the metal surface. When the mixture of 50ppm valine and 50ppm Zn^{2+} is prepared, there is a formation of Zn^{2+}- Val complex in solution. When the steel sample is dipped in this solution, Zn^{2+}- Val complex diffuses from the bulk of solution to the metal surface. On the sites of steel surface, the Zn^{2+}- Val complex is converted in to Fe^{2+}- Val complex on the local anodic sites.

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

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

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

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

4. CONCLUSION

- ✓The weight – loss study showed that the combination of 50ppm Zn^{2+}-50ppm valine has 74% IE. Synergistic effect appears between the environmental safe inhibitor.
- ✓The corrosion due to microorganism controlled by addition biocide CTAB. The addition of CTAB on valine and zinc sulphate system offers 100% biocidal efficiency.
- ✓The results of SEM and EDS suggest that the stable film consists of iron - Val and $Zn(OH)_2$.
- ✓The amino acid valine inhibitor control the disaster of carbon steel surface as well as microbial corrosion.

ACKNOWLEDGEMENT

The authors are very much grateful to their respective managements for their support and back-up.

REFERENCES

Ebenso EE, Eddy NO, Odiongenyi AO, Corrosion inhibition and adsorption properties of Methocarbamol and mild steel in acidic medium, Portugaliae Electrochimica Acta, 27(1), 2009, 13–22.

Florence GRH. Antony AN, Sahayaraj JW, Amalraj AJ, Rajendran S, Corrosion inhibition of carbon steel by adipic acid-Zn^{2+} system, Indian Journal of Chemical Technology, 12, 2005, 472-478.

Ghasemi Z, Tizpar A, The inhibition effect of some amino acids towards Pb-Sb-Se-As alloy corrosion in sulfuric acid solution, Applied Surface Science, 252(10), 2006, 3667–3672.

Huang J, Cang H, Liu Q, and Shao J, Environment friendly inhibitor for mild steel by Artemisia halodendron, International Journal of Electrochemical Science, 8(6), 2013, 8592–8602.

Ingrid Milošev, Jasminka Pavlinac, Milan Hodošček, Antonija Lesar, Amino acids as corrosion inhibitors for copper in acidic medium: Experimental and theoretical study, Journal of serbian chemical society, 78(12), 2013, 2069–2086.

Khaled KF, Corrosion control of copper in nitric acid solutions using some amino acids—a combined experimental and theoretical study, Corrosion Science, 52(10), 2010, 3225–3234.

Okafor PC, Zheng Y, Synergistic inhibition behaviour of methylbenzyl quaternary imidazoline derivative and iodide ions on mild steel in H_2SO_4 solutions, Corrosion Science, 51(4), 2009, 850–859.

Telegdi J, Shaban A, Kálmán E, EQCM study of copper and iron corrosion inhibition in presence of organic inhibitors and biocides, Electrochimica Acta, 45(22), 2000, 3639–36470.

Wilson Sahayaraj J, Susai Rajendran, Muthu Megala TS, John Amalraj A, Eco-Friendly inhibitor L-Valine – Zn^{2+} system controlling corrosion of carbon steel in rain water, Zaštita Materijala, 51, 2010, 232-236.

Zucchi F, Omar IH, Plant extracts as corrosion inhibitors of mild steel in HCl solutions, Surface Technology, 24(4), 1985, 391–399.