ISSN: 2348-8948
Vol: 2; Issue: 7

RESEARCH ARTICLE

Spectroscopic methods used for analyzing protective film formed by L-Histidine on carbon steel

S.Sivakumar[1] , A.Sahaya Raja[1*], J.Sathiyabama[1],V.Prathipa[2]

1. PG and Research Department of Chemistry, GTN Arts College, Dindigul – 624005, Tamil Nadu, India
2. Department of Chemistry, P.S.N.A. College of Engineering &Technology, Dindigul, Tamil Nadu, India

Date Received:	Date of Accepted:	Date Published:
22-Jul-2014	27-Jul-2014	31-Jul-2014

Abstract:
The corrosion inhibition of carbon steel (CS) using the "green" inhibitor, L-Histidine (L-His) was investigated. This study was conducted at pH 7.8. The effect caused by Zn^{2+} additive also was investigated. The study was done over a range of concentrations. Gravimetric method and electrochemical methods were applied. It was found that the L-Histidine acts as a good inhibitor at pH 7.8. The inhibition efficiency increases with increasing L-His concentration. The addition of Zn^{2+} to L-Histidine significantly increased the inhibition efficiency. Tafel results indicated that decrease the corrosion current (I_{corr}) value. The influence of biocide SDS on the inhibition efficiency of L-Histidine – Zn^{2+} system has been investigated. Also it is evident that at minimum concentration of biocides added to the inhibitor system, 100 % biocidal efficiency is noticed. The protective film formed on the metal surface has been analyzed by FT-IR, SEM and EDAX spectra. It is found that the protective film consists of Fe^{2+} - L-Histidine complex and $Zn(OH)_2$.

Keywords: L-Histidine, Synergistic effect, FTIR, SEM,EDAX

Introduction

Carbon Steel is widely used as the constructional material in most of the major industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. The use of inhibitors is one of the most practical methods to prevent the corrosion or to reduce the corrosion rate. Organic inhibitors[1-3] containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus etc shows better corrosion inhibition by forming protective film on the metal surface. Corrosion inhibitor is a chemical substance which, when added to the corrosive environment at an optimum concentration, significantly decreases the corrosion rate of metals (or) alloys.

Metals are usually extracted from ores through the application of a considerable amount of energy. Corrosion is simply the strong tendency of an elemental metal to revert back to its natural state [4]. Hence, corrosion is the primary means by which metals deteriorate. These substances, which are sometimes referred to as retarding catalyst, are generally called inhibitors [5]. The use of inhibitors is one of the best methods for protecting metals against corrosion. Corrosion is a chemical or electrochemical process in nature with four components are: an anode, a cathode, an electrolyte and some direct electrical connection between the anode and cathode, the adsorbed inhibitor then acts to slow corrosion process by either:

1.Increasing the anodic or cathodic polarization behaviour; 2.Reducing the movement or diffusion of ions to the metallic surface. It is better to look for environmentally safe inhibitors [6-8]. Some researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion [8-15]. This is due to the fact that amino acids are non-toxic, biodegradable, relatively cheap, and completely soluble in aqueous media and produced with high purity at low cost. The environmental friendly L-Histidine (Fig.1) is chosen as the corrosion inhibitor for this present work. The literature presents some studies involving L-Histidine having the ability to prevent the corrosion of carbon steel. The aim of this research is to investigate the inhibitive effect of L-Histidine. For this purpose the electrochemical studies such as potentiodynamic polarization impedance spectroscopy have been used in the present studied by using L-Histidine.

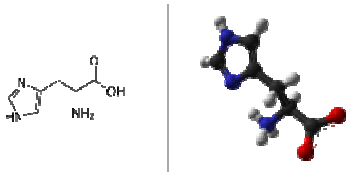


Figure.1 Structure of L-Histidine

2. Experimental Procedure

2.1 Preparation of the carbon steel specimens

The carbon steel specimens were chosen from the same sheet of the following composition. Carbon – 0.1 percent, Sulphur-0.026 percent, phosphate- 0.06 percent, Manganese- 0.4 percent and the balance iron. Carbon steel specimen of the dimension 1.0× 4.0×0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for weight-loss and surface examination studies. Carbon steel rod encapsulated in Teflon with an exposed cross section of 1 cm^2 area was used as the working electrode in potentiodynamic polarization studies. The surface of the electrode was polished to mirror finish and degreased with trichloroethylene.

2.2 Weight-Loss method

2.2.1 Determination of surface area of the specimens

The length, breath and the thickness of carbon steel specimens and the radius of the holes were determine with the help of venire callipers of high precision and the surface areas of the specimens were calculated.

2.2.2: Weighing the specimens before and after Corrosion

All the weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance – AY62.

2.2.3: Determination of corrosion rate:

The weight specimen in triplicate were suspended by means of glass hooks in 100 ml various test solutions and after 24 hour of immersion, the specimens were taken out, Washed in running water, dried and weighed. From the change in weight of the specimen, corrosion rates were calculated using the following relationship.

$$\text{Corrosion rate(mm/y)} = \frac{\text{Loss in weight (mg) x1000}}{\text{Surface area of the specimen (dm}^2\text{) X Period of immersion (days)}} \times \frac{0.0365}{\rho}$$

Corrosion inhibition efficiency (IE) was then calculated using the equation.

$$IE = 100[1-(W2 / W1)] \%$$

Where,

W_1= Corrosion rate (mm/yr) in absence of Inhibitor.

W_2 = Corrosion rate (mm/yr)in presence of Inhibitor.

IE = Inhibition efficiency.

2.3 Surface Examination Study:

The carbon steel specimens were immersed in various test solution for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimen was analyzed.

2.4 Potentiodynamic Polarization Study:

Potentiodynamic polarization studies were carried out using CHI electro chemical impedance analyzer, model 660A. Three electrode cell assemblies were used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode exposed. A saturated calomel electrode (SCE) was used as a reference electrode and a rectangular platinum foil was used as the counter electrode.

The working electrode and platinum electrode were immersed in well water in the absence and presence of inhibition saturated calomel electrode was connected with the test solution through a salt bridge. Potential (E) vs log current (I) plots were then recorded. Corrosion potential (Ecorr) and Tafel slopes b_a and $b_c$were determined from E vs log current (I) plots.

2.5 AC impedance measurements:

A CHI electrochemical impedance analyzer (Model 660A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system.TheR_t (charge transfer resistance) and C_{dl}(double layer capacitance) values were calculated.

2.6 Synergism parameters:

Synergism parameters are indication of synergistic

effect existing between two inhibitors (1, 2)
Synergism Parameters were calculated using the relation
$S_I = [1-\theta_{1+2}/1-\theta'_{1+2}]$
Where,
$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2)$
Where,
θ_1 = inhibition efficiency of substance 1
θ_2 = inhibition efficiency of substance 2
θ'_{1+2}= combined inhibition efficiency of substance 1&2
θ = surface coverage = IE% / 100

2.7 Analysis of Variance (F-test):

F-test was carried out to investigate whether the synergistic effect existing between L-Histidine and Zn^{2+} system statistically significant or not.

2.8 UV-Visible Spectra:

UV- visible absorption spectra of solutions were recorded in a UV spectra S-100 Analytic Jena spectrophotometer.

2.9 FTIR Spectra:

These spectra were recorded with the Perkin-Elmer 1600 spectrophotometer. The FTIR spectrum of the protective film was recorded by; carefully removing the film mixed it with KBr and making the pellet.

2.10 SEM Study:

The Surface morphology measurements of the carbon steel were examined by using JEOL JSM 6390 model. All SEM micrographs of carbon steel are taken at a magnification of X=1000.

3. Result and Discussion

3.1 Analysis of the weight loss method

Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor (L-Histidine) are given in tables 1-2. The inhibition efficiencies (IE) are also given these tables. It is observed from table 1, that L-Histidine shows some inhibition efficiencies. 50 ppm of L-Histidine has 35% percent IE, as the concentration of L-Histidine increases, IE increases.

Table 1: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method.

Inhibition system : L-Histidine - Zn^{2+} (0 ppm)

Immersion period : 1 day
pH = 7.8

3.2 Influence of Zn^{2+} on the inhibition efficiencies of L-Histidine

The influence of Zn^{2+} on the inhibition efficiencies of L-Histidine is given in table 2. It is observed that as the concentration of L-Histidine increases the IE increases. Similarly for a given concentration of L-Histidine the IE increases as the concentration of Zn^{2+} increases. It is also observed that a synergistic effect exists between L-Histidine and Zn^{2+}. For example, 5 ppm of Zn^{2+} has 12% percent IE;250 ppmof L-Histidine has 55% percent IE.Interestingly their combination has a high IE, namely, 98% percent.

L-His (ppm)	Zn^{2+}ppm	Corrosion Rate	Inhibition Efficiency
0	0	0.1569	----
50	0	0.0994	35
100	0	0.0887	42
150	0	0.0841	45
200	0	0.0795	48
250	0	0.0688	55

In presence of Zn^{2+} more amount of L-Histidine is transported towards the metal surface. On the metal surface Fe- L-Histidine complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH-, which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn^{2+} and L-Histidine.

$Fe \text{------} > Fe^{2+} + 2e^-$ (Anodic reaction)
$Fe^{2+} + Zn^{2+}$ - L-Histidine complex------> Fe^{2+}- L-Histidine complex + Zn^{2+}
$O_2 + 2H_2O + 4e^- \text{-----} > 4OH^-$ (Cathodic reaction)
$Zn^{2+} + 2OH^- \text{-------} > Zn(OH)_2 \downarrow$

Table 2: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method.

Inhibition system : L-Histidine - Zn^{2+} (5ppm)
Immersion period : 1 day
pH = 7.8

L-His (ppm)	Zn^{2+} Ppm	Corrosion Rate	Inhibition Efficiency
0	0	0.1569	----
0	5	0.1346	12%
50	5	0.0260	83%
100	5	0.0168	89%
150	5	0.0122	92%
200	5	0.0076	95%
250	5	0.0031	98%

3.3 Synergism Parameter (S1)

Synergism parameter (S_I) have been used to know the synergistic effect existing between two inhibition (16-21). Synergism parameter (S_I).Can be

calculated using the following relationship.

$$\text{Synergism parameter } (S_i) = 1 \quad \frac{1-\Theta_{1-2}}{1-\Theta'_{1+2}}$$

Where,

$\Theta_{1+2} = (\Theta_1 + \Theta_2) - (\Theta_1 \Theta_2)$

Θ_1 = surface coverage by L-Histidine

Θ_2 = surface coverage by Zn^{2+}

Θ'_{1+2} = surface coverage by L-Histidine and Zn^{2+}

Where Θ = surface coverage = IE% / 100

The synergism parameters of L-Histidine –Zn^{2+} system are given in table 4 and 5. For different concentration of inhibitor compounds exists. When S_i>1, it points to synergistic effects[20]. In the case of S_i<1, it is an indication that the synergistic effect is not significant. From tables 4 and 5 it is observed that value of synergism parameters (S_i) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exist between L-Histidine and Zn^{2+}(18,19,21). Thus the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} ions to L-Histidine is due to the synergistic effect.

Table3; Inhibition efficiencies synergism parameters for various concentrations of L-Histidine - Zn^{2+} (5 ppm) system.When carbon steel is immersed in well water.
Immersion period : 1 day
pH= 7.8

L-Histidine	Inhibition efficiency IE%	Surface coverage Θ_1	Zn^{2+} ppm	Inhibition efficiency IE%	Surface coverage Θ_2	Combined IE% I_{1-2}	Combined Surface coverage Θ_{1-2}	Synergism parameters S_I
50	35	0.35	5	12	0.12	83	0.83	3.36
100	42	0.42	5	12	0.12	89	0.89	4.64
150	45	0.45	5	12	0.12	92	0.92	6.05
200	48	0.48	5	12	0.12	95	0.95	9.15
250	55	0.55	5	12	0.12	98	0.98	19.8

3.4 "F" test

To know whether the synergistic effect existing between L-Histidine and Zn^{2+} is statistically significant or not , F-test was used [22]. The results are given in table4.It is observed that the calculated F-value 119.2 is greater than the table value 5.32 for 8 degrees of freedom at 0.05 level of significance.Hence it is concluded that the synergistic effect existing between L-Histidine and Zn^{2+} (5 ppm) is statistically significant.

Polarization study has been used to confirm the formation of protective flim formed on the metal surface during corrosion inhibition process [23-28]. If a protective film is formed on the metal surface, the corrosion current value (I_{corr}) decreases.

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in fig 2, the corrosion parameters are given table 5. When carbon steel was immersed in well water the corrosion potential was -619.27 mV vs SCE. When L-Histidine (250 ppm) and Zn^{2+} (5 ppm) wre added to the above system the corrosion potential shifted to the noble side-564.812 mV vs SCE. This indicates that a film is formed on the anodic sites of the metal surface. This film controls the anodic reaction of metal dissolution by forming Fe^{2+} L-His complex on the anodic sites of the metal surface.

The corrosion current decreases from 1.95418×10^{-7} A/cm^2to1.86383×10^{-7} A/cm^2. Thus polarization study confirms the formation of a protective film on the metal surface.

3.6 Analysis of AC Impedance spectra

ACimpedance spectra (electrochemical impedance spectra) have been used to confirm the formation of protective film on the metal surface[29-31]. if a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L-Histidine-Zn^{2+}) are shown in (Nyquist plot). The AC impedance parameters namely charge transfer resistance (Rt) and double layer capacitance (Cdl) derived from Nyquist plots are given in table 6.

It is observed that when the inhibitors (L-His (250 ppm) +Zn^{2+} (5 ppm)) are added the charge transfer resistance (R_t) increases from 950 Ω cm2 to 1470 Ω cm^2. The C_{dl} value decreases from 4.8939×10^{-9} F/cm^2 to 3.162732×10^{-9} F/cm2.

3.7 Analysis of UV Visible spectra

The UV-Visible absorption spectrum of an aqueous solution of L-Histidine and Fe^{2+} (Freshly prepared $FeSO_4$solution) is shown in Fig.4.(a) A peak appears at 242nm. This is due to Fe^{2+} -L-Histidine complex formed in solution.

surface. To understand the nature of the surface film in

The UV-Visible absorption spectrum of the film formed on the metal surface after immersion in the solution containing well water 250 ppm of L-Histidine and 5ppm of $Zn^{2+}$is shown in Fig.4(b) Peak appears at 250nm. This matches the Fe^{2+}- L- Histidine complex in solution. Hence it is confirmed that the protective film consist of Fe^{2+}- L-Histidine complex. [32,33]

3.8 FTIR Test

FTIR spectra have been used to analysis the protective film formed on the metal surface[34-41]. The FTIR spectrum of pure L-Histidine is shown in Fig.5(a). The C=O stretching frequency of carboxyl group appears at1462cm^{-1}. TheCN stretching frequency appear at 1064 cm^{-1}. The NH stretching frequency of the amine group appears at 3008cm^{-1}[36-38]. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of L-Histidine and 5 ppm Zn^{2+} is shown in Fig.5(b)The C=O stretching frequency has shifted from 1462 to 1401 cm^{-1}. The CN stretching frequency has shifted from 1064 to 1026 cm^{-1}. The NH stretching frequency has shifted from 3008 to 2925 cm^{-1}. This observation suggest that L-Histidine has coordinated with Fe^{2+} through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe^{2+} -L-Histidine complex on the anodic sites of the metal surface. The peak at 761 cm^{-1} corresponds to Zn-O stretching. The peak at 3425 cm^{-1} is due to OH-stretching. This confirms that $Zn(OH)_2$ is formed on the cathodic sites of metal surface[34,39,41]. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+}-L-Histidine complex and $Zn(OH)_2$.

3.9 Influence of Sodium Dodecyl sulphate (SDS) on the corrosion inhibition efficiency of the L-His -Zn^{2+} system (pH = 7.8)

SDS is a anionic surfactant. It is a biocide, the corrosion IE and biocidal efficiency of the L-His-Zn^{2+} SDS system are given in the table.7. when carbon steel was immersed in well water (in the absence of inhibitor), the number of colony formingunits perml is 9×10^3. Various concentration of SDS (50, 100, 150, 200, 250) ppm were added to the L-Histidine (250 ppm) –Zn^{2+} (5 ppm) system. The corrosion IE and the biocidal efficiency were calculated. The formulation consisting, of 250 ppm of L-Histidine and 5 ppm Zn^{2+} has 98% corrosion IE and 11% biocidal efficiency. When 50 ppm of SDS is added to the L-Histidine -Zn^{2+} system, the IE increases from 98% to 99% the biocidal efficiency increases from 11% to 83%. It is observed that the formulation consisting of 250 ppm L-Histidine; 5 ppm of Zn^{2+} and 100 ppm of SDS has 99% corrosion IE and 100% biocidal efficiency.

3.10 SEM Analysis of Metal Surface

SEM provides a pictorial representation of th the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined[20,43,44].

The SEM image of magnification (X 1000) of carbon steel specimen immersed in well water for 1 day in the absence and presence of inhibitor system are shown in Fig 6 (a,b,c).The SEM micrographs of polished carbon steel surface (control) in Fig 6(a) shows the smooth surface of the metal. This shows the absence of any corrosion products (or) inhibitor complex formed on the metal surface.The SEM micrographs of carbon steel surface immersed in well water Fig6(b) shows the roughness of the metal surface which indicates the highly corroded area of carbon steel in well water. However Fig (c) indicates that in the presence of inhibitor L-His (250 ppm) +Zn^{2+} (5 ppm) the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The metal surface almost free from corrosion due to the formation of insoluble complex on the surface of the metal [20]. In the presence of L- His and Zn^{2+} the surface is covered by a thin layer of inhibitors which effectively controls the dissolution of Carbon steel.

3.11. Energy Dispersive Analysis of X-Rays (EDAX)

The EDAX survey spectra were used to determine the elements present on the metal surface before and after exposure to the inhibitors solution[42-45]. The goal of this section was to confirm the results obtained from chemical and electrochemical measurements that a protective surface film of inhibitor is formed on the metal surface. To achieve this goal EDAX examinations of the metal surface were performed in the absence and presence of inhibitors system.

The EDAX spectrum of carbon steel immersed in well water is shown in Fig 7(a). they show the characteristic peaks of some of the elements constituting the carbon steel sample. The EDAX spectrum of carbon steel immersed in well water containing 250 ppm of L-His and 5 ppm of Zn^{2+} is shown in Fig7(b). In addition, the intensity of C and O signals are enhanced. The enhancement in C and O signal is due to the presence of inhibitor. These data show that metal surface is covered the N, O, C atoms.This layer is undoubtedly due to the inhibitor system. The high contribution of O and C is not present on the metal surface exposed in well water. Fig 7(b) shows that the Fe peaks observed in the presence of inhibitor are considerably suppressed relative to these observed in well water (blank solution). The suppression of the Fe peaks occurs because of the overlying inhibitor film. This observation indicates the existence of an adsorbed layer of inhibitor that protects steel against corrosion. These results suggest that N, O and C atoms of L-Histidine has coordinated with Fe^{2+}, resulting in the

Table 4

Distribution of F value Between the Inhibition Efiiciencies of L - His and Zn^{2+} System

Source of variance	Sum of squares	Degrees of freedom	Mean Square	F	Level of significance
Between the sample	1058	1	1058	119.2	>0.05
Within the sample	71	8	8.875		

Table 5: corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study.

System	E mV vs SCE	B_c mV/ decade	B_c mV/ decade	I_{corr} A/cm^2
Well water	-619.27	73.445	52.61	1.95418×10^{-7}
Well water + L-His (250 ppm) +Zn^{2+} (50 ppm)	-564.812	53.853	53.537	1.86383×10^{-7}

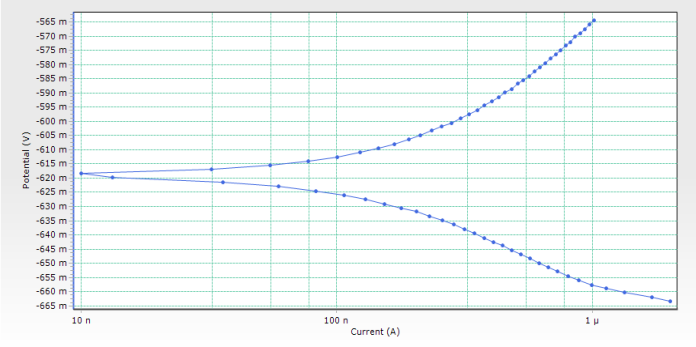


Figure.2 Polarization curves of Carbon steel immersed in test solution
(a) Wellwater(Blank)

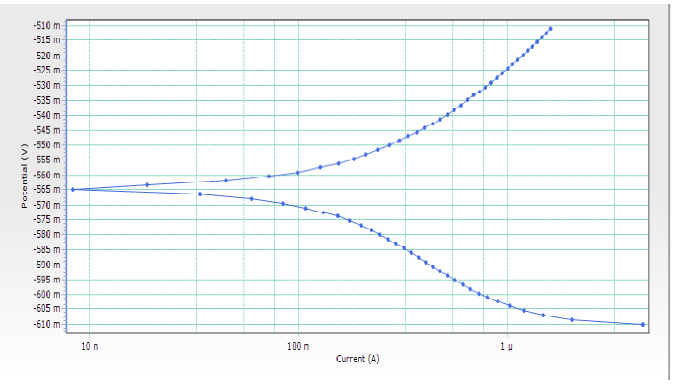


Figure.2 Polarization curves of Carbon steel immersed in test solution

b) well water +L - Histidine (250 ppm) + Zn^{2+} (5 ppm)

Table 6 : corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system

obtained from AC impedance spectra (pH=7.8)

System	Nyquist plot	
	R_t ohm cm^2	**C_{dl} F/cm^2**
Well water	950	4.8939×10^{-9}
Well water + L - His (250 ppm) + Zn^{2+} (5 ppm)	1470	3.162732×10^{-9}

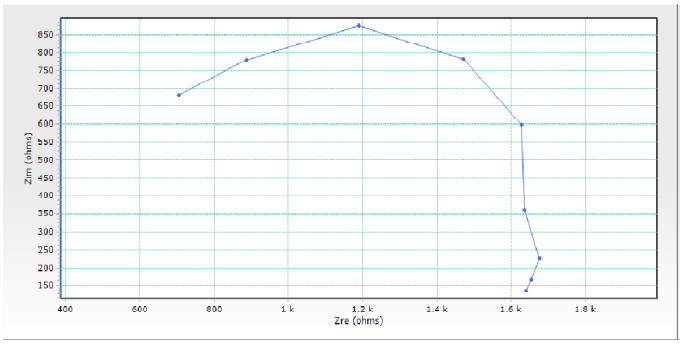


Figure.3 AC impedance spectra of carbon steel immersed in test solution
(a) Well water (Blank)

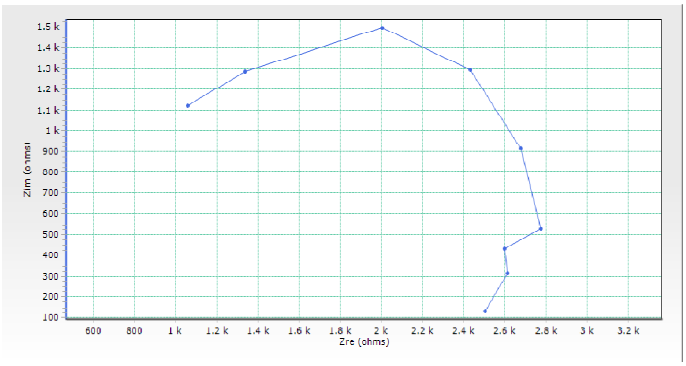


Figure.3 (b) Well water + L-Histidine (250 ppm)+Zn^{2+}(5ppm)

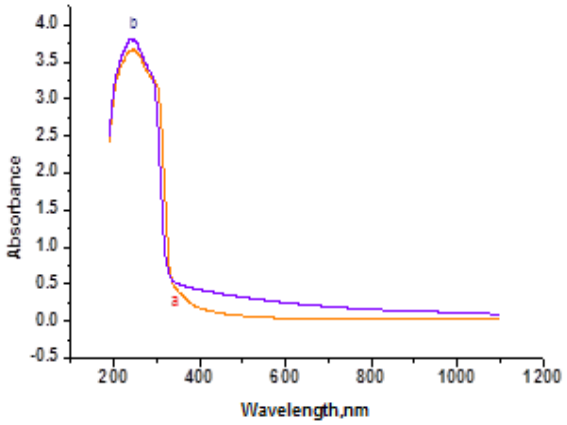


Figure.4UV-absorption spectra of solution containing
a) L-Histidine + Fe^{2+} complex in solution
b) Protective film formed on the surface of Carbon steel immersion in the solution containing 250 ppm of L-Histidine + 5

ppm of Zn^{2+}

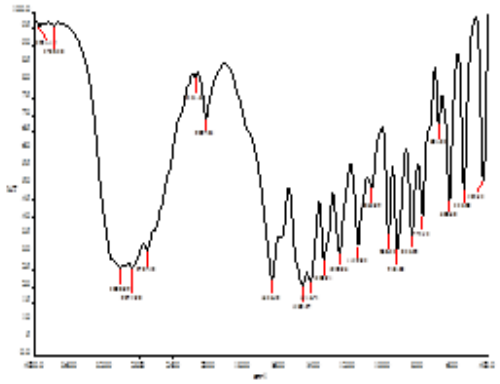


Figure.5 FTIR spectra

a) Pure L – Histidine

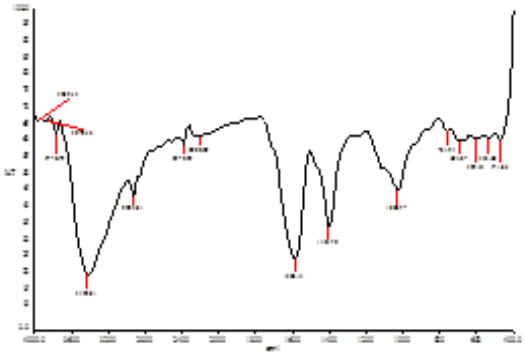
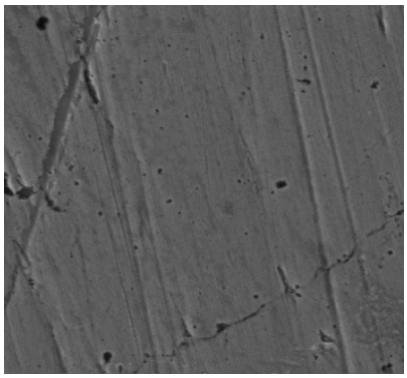


Figure.5 FTIR spectra

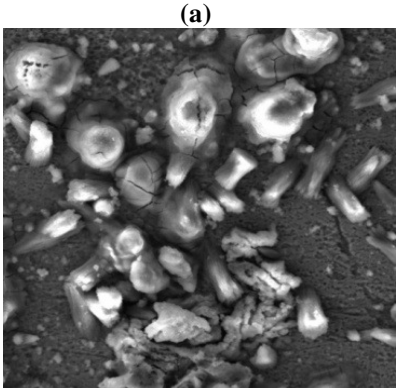
(b). Film formed on metal surface after immersion in test solution containing 250ppm L-Histidine +5ppm Zn^{2+}

Table 7: Influence of SDS on the corrosion inhibition efficiency of the L-Histidine (250ppm)+ Zn^{2+} (5ppm) system (pH= 7.8)

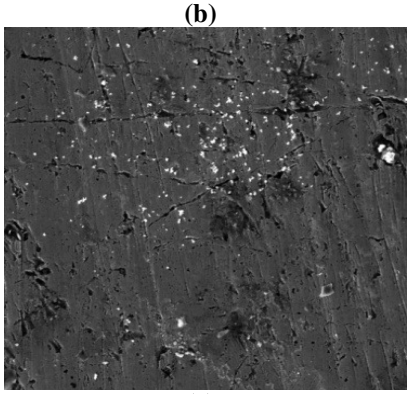
L-His (ppm)	Zn^{2+} (ppm)	SDS (ppm)	CR mm/y	IE %	Colony forming units/mL	BiocidalEfficiency (BE) %
0	0	0	0.1569	-	$9x10^3$	-
250	5	0	0.0031	98	$8x10^3$	11
250	5	50	0.0015	99	$1.5x10^3$	83
250	5	100	0.0015	99	Nil	100
250	5	150	0.0015	99	Nil	100
250	5	200	0.0015	99	Nil	100



(a)



(b)



(c)

Figure.6 a, b, c. SEM analysis carbon steel

a) Carbon steel
b) Carbon steel immersed in well water
c) Carbon steel immersed in well water +L-Histidine (250 ppm) + Zn^{2+} (5 ppm)

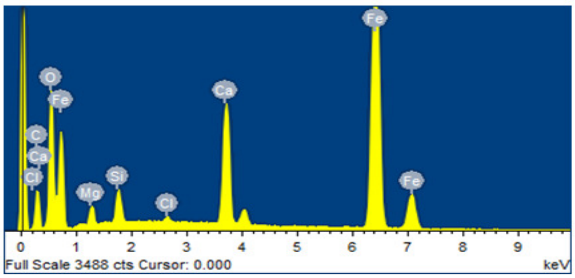


Figure.7(a)

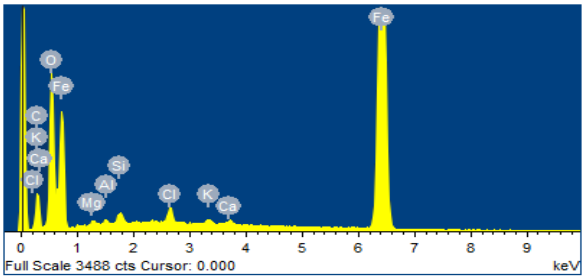


Figure.7(b)

Figure.7 EDAX spectra of
7(a) Carbon steel sample after immersion in well water (blank)
7(b) Carbon steel sample after immersion in solution containing well water + 250 ppm of L-His + 5 ppm of Zn^{2+}

formation of Fe^{2+}-L-His complex on the anodic sites of metal surface.

3.12.Mechanismof Corrosion Inhibition

Results of the weight-loss study show that the formulation consisting of 250 ppm L-His and 5 ppm Zn^{2+} has 98% IE controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and L-His. Polarization study reveals that this formulation functionasanodicinhibitor.AC impedance spectra reveals that protective film is formed on the metal surface. In order to explain these facts the following mechanism of corrosion inhibition is proposed [46-52].

- When the solution containing well water 250 ppm L-His and 5 ppm Zn^{2+} is prepared, there is formulation of Zn^{2+}-L-His complex in solution.
- When carbon steel is immersed in this solution the Zn^{2+} - L-His complex diffuses from the bulk of the solution towards metal surface.
- Zn^{2+}-L-His complex diffuses from the bulk solution to the surface of the metal and is converted into Fe^{2+} -L-His complex. Which is more stable than Zn^{2+} - L-His.
- Onthe metal surface Zn^{2+}-L-His complex is converted into Fe^{2+} - L-His on the anodic sites Zn^{2+} is released.
  Zn^{2+}- L-His + Fe^{2+}—--> Fe^{2+}-L-His + Zn^{2+}
- The released Zn^{2+} combines with OH^- to from Zn $(OH)_2$ on the cathodic sites.
  Zn^{2+} + 2OH ------> Zn $(OH)_2$
- Thus the protective film consists of Fe^{2+} -L- His complex and Zn $(OH)_2$.
- The EDAX analysis SEM micrographs image confirm the formation of protective layer in the metal surface.

Conclusion

Present study leads to the following conclusions.

1.The formulation consisting of 250 ppm of L-Histidine and 5 ppm of Zn^{2+}offers good inhibition efficiency of 98%.

2. Polarizationstudy reveals that this formulation functions as a anodicinhibitor.

3. AC impedance spectra reveal that a protective filmis formed on the metal surface.

4. The FTIR spectral study leads to the conclusion that the Fe^{2+} - L-Histidine formed on anodic sites of the metal surface controls the anodic reaction.

5. $Zn(OH)_2$ formed on the cathodic sites of the metal surface controls the cathodic reaction

6. SEM and EDAX confirm the presence of a protective film on the metal surface.

Acknowledgement

We are grateful to the department of chemistry, GTN Arts College, Dindigul for providing necessary facilities for the research work.

References

1. Elkadi L.,Mernari B., Traisnel M., Bentiss F and LagreneeM.,The inhibition action of 3,6-bis(2-methoxyphenyl)-1,2-dihydro-1,2,4,5-tetrazine on the corrosion of mild steel in acidic media, Corros sci,42(4),703-719(2000).
2. Khaled KF and Abdel-Rehims.s., Electro chemical investigation of corrosion and corrosion inhibition of iron in hydrochloric acid solutions, Arab.J.Chem, 4,397-40 (2011).
3. Acvi G., Inhibitor effect of N,N'-Methylenediacrylamide on corrosion behaviour of mild steel in 0.5 M HCl, *Mater.Chem.Phys*., 112, 234-238 (2008).
4. K.R.Threthewey, J.Chamberlain, corrosion for science and engineering, Addison Wesley, Longman, London (1995).
5. L.E. Umoru, I.A. Fawehinmi, A.Y. Fasasi, J. Appl.Sci. Res. 2, 4, (2006)
6. A.Y. El-Etre, *Corros. Sci.* 45 (2003) 2485-2495.
7. A.Y. El-Etre, *Corros. Sci.* 40(1998) 1845-1850.
8. H. Ashassi-Sorkhabi, M.R. Majidi and K. Seyyedi, *Appl. Surf. Sci.* 225(2004) 176-185.
9. Z. Ghasemi, A. Tizpar, *Appl. Surf. Sci.* 252(2006)

3667-3672.
10. D.Q. Zhang, L.X. Gao, G.D. Zhou, *J. Appl. Electrochem.* 35(2005) 1081-1085.
11. O. Olivares, N.V. Likhanova, B. Gomez, J. Navarrete, M.E. Llanos-Serrano, E. Arce, J.M.Hallen, *Appl. Surf. Sci.* 252 (2006) 2894-2909.
12. W.A. Badawy, K.M. Ismail, A.M. Fathi, *Electrochim. Acta*51 (2006) 4182-4189.
13. K.M. Ismail, *Electrochim. Acta*52(2007) 7811-7819.
14. H. Ashassi-Sorkhabi, Z. Ghasemi, D. Seifzadeh, *Appl. Surf. Sci.* 249(2005) 408-418.
15. E.E.Oguzie, Y.Li,F.H.Wang, J. Colloid Interf Sci.S310(2007).90-98.
16. G.K. Gomma, Mater.Chem.Phys.55 (1998) 241.
17. K. Aramaki and N. Hackermann J. Electrochem. Soc. 116 (1969) 568.
18. M.A.Quraishi, J. Rawat and M.Ajmal, Corrosion. 55 (1999) 919.
19. S.AgnesiaKanimozhi and S.Rajendran Int. Journal of Electrochemical Society, 4 (2009) 353.
20. D.Gopi, S.Manimozhi, K.M.Govindaraju, P.Manisankarand S.Rajeswari, J.Appl.Electrochem, 37 (2007) 439-449.
21. S.Rajendran, A.J.Amal Raj, M.J.Joice, N.Anthony, D.C.Trivedi, M.Sundaravadivelu, Corros. Rev. 22 (2004) 233
22. S.Rajendran, A.Rosaly andS.Thangasamy, Journal of Materials Education 28 (2006) 315.
23. Jacinto Morales Roque, T.Padiyan, J.Cryz. E.Garcia-Ochoa, Corrosion science, 50(2008) 614
24. O.Benali, L.Larabi, M.Traisnel, L.Gengembre, Y.Harek, Applied Surface Science, 253 (2007) 6130
25. H.Amar, T.Braisaz, D.Villemin, B.Moreau, Materials Chemistry and Physics 110 (2008), P 1-6.
26. J.ArockiaSelvi, SusaiRajendran, V.GangaSri, JohnAmalraj, B.Narayanasamy, Portugaliae Electrochimica Acta, 27(1)(2009) 1.
27. S.Rajendran, J.Paulraj, P.Rangan, J.Jeyasundari and M.Manivannan, "Corrosion behavior of metals in artificial saliva in presence of spirulina powder", Journal of Dentistry and Oral Hygiene, 1 (2009) 001-008.
28. E.Kalman, I.Felhosi, F.H. Karman, et al., Corrosion and Environnmental Degradation, M.Schutze, Ed., Weinheim :Wiky-VCH, 1 (2000) 471.
29. Shengtao Zhang, Zhihua Tao, Weihua Li, BaorongHou, Applied surface Science, 255(200906757.
30. F. El-TaibHeakal, A.S Fouda, M.S.Radwan, Materials Chemistry and Physics, 125(2011)26.
31. S.Rajendran, M.Kalpana Devi, A.PeterPaxcal Regis, A.JohnAmalraj, J.Jeyasundari and M.Manivannan, ZastitaMaterijala, 50(2009) 13.
32. SusaiRajendran, R.MariaJoany, S.V.Apparao and N.Palaniswamy, Indin Journal of Chemical Technology, 9 (2002)197-200.
33. SusaiRajendran, B.R. Earnest John Peter, A.Peter Pascal RTegis, A.JohnAmalraj and M.Sundaravadivelu, Transactions of the SAEST, 38(1)(2003)11-15.
34. R.kalavani, B.Narayanaswamy, J.a. Selvi, A>J.Amalraj, J.Jeyasundari and S.Rajendran, PortugaliaeElectrochimicaActa, 27(2009) 177.
35. J,Sathiyabama, SusaiRajendran, J.ArockiaSelvi and J.Jeyasundari. The open Corrosion Journal, 2(2009)76.
36. R.M.Silverstein, G.C.Bassler, T,Moril, "Spectrometric Identification of Organioc Compound" John Wiley and Sons, New York (1981) 95.
37. A.D.Cross, "Intreduction Scientific Publication, London (1990)73
38. KzauoNakamoto, Infrared and Raman Spectra of inorganic Coordination compound, Wiley Interscience, New York (1986)
39. S.Rajendran, B.V.Apparao and N.Palanniswamy, Bulletin of Electrochemistry, 12()199615
40. I.Sekine and V.Hirakawa, Corrosion 42(1986)276
41. S.Rajendran, B.V.Apparao and N.Palanniswamy Proc. 8thEurop.Symp. Corros.Inhibitors, Ferrara, Italy 1(1995)465.
42. S.Sayed Abdel RehimA.OmarHazzazi, A.Mohammed Amin, F.Kaled Corrosion Science, 50(2008)2258-2271.
43. A.Mohammed Amin, S.Sasyed Abdel Rehim, E.E.F.Eisherbini, Rady, S.Bayoumi, Electrochemical Acta (52) 2007, 3588-3600
44. A.Mohammed Amin, S.Sasyed Abdel Rehim, HeshamT.M.Abdel-Fatah, Corrosion Science, 51 (2009)882-894
45. M.A.Migahed, E.M.S. AzzamAnd S.M.I. Morsy, Corrosion Science 51(2009), 1636-1644.
46. Gopi,.D, N.Bhuvaneswaran, S.Rajeswari,Bulletein of Electrochemistry,18(2002)29.
47. Gopi,.D, S.rajeswari, J.Solid State Electrochemistry, 6 (2002)194.
48. D.Gopi,S.Rajeswari,Proc.International Conference on Advances in Surface Scienceand Enineering (INSURE), Chennai,India.21-23 Feb.(2001) 210.
49. D.Gopi,S.Rajeswari, Proc. NACE International Conf., Corossion its Mitigation and Preventive Maintenance,Mumbai,India,20-23 Nov.1(2000)435.
50. D.Gopi.S.Rajeswari, Proc. Tenth National Congress on Corrosion Control, Conf., Madurai, India, 6-8 Sep.(2000) 353.
51. A.Veres, G.Reinhard, E.Kalman, Br.Corros.J., 27(1992)147.
52. E.Kalman, Corrosion Inhibitors, Published for EFC No.11,Institute of Materials London(1994).