

## Inhibition of corrosion of carbon steel in well water by L-Lysine – Zn<sup>2+</sup> system

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**ABSTRACT:** The environmental friendly inhibitor system L-Lysine-Zn<sup>2+</sup>, has been investigated by weight loss method. A synergistic effect exists between L-Lysine and Zn<sup>2+</sup> system. The formulation consisting of 250 ppm of L-Lysine and 50 ppm of Zn<sup>2+</sup> offers good inhibition efficiency of 98%. Polarization study reveals that this formulation functions as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. The FTIR spectra study leads to the conclusion that the Fe<sup>2+</sup>-L-Lysine complex formed on anodic sites of the metal surface controlled the anodic reaction and Zn(OH)<sub>2</sub> formed on the cathodic sites of the metal surface controlling the cathodic reaction. UV and Fluorescence spectrum study reveals the metal film formed on the solution containing 250 ppm of L-Cysteine and 50 ppm of Zn<sup>2+</sup>. The morphology of the metal is studied by AFM images. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study and surface analysis technique. Synergism parameters have been calculated. They are found to be greater than 1 suggesting that a synergistic effect exists between L-Lysine and Zn<sup>2+</sup>.

**Keywords:** L-Lysine corrosion inhibitor, synergistic effect, carbon steel, well water, zinc ion, aminoacids.

### I. INTRODUCTION

Awareness has been created about the health hazards of corrosion inhibition and suitable remedies have also been suggested with the view to maintaining health and safety. Hazardous chemicals have been checked thereby preventing their contact with environment in order to ensure non-toxic, eco-friendly corrosion inhibitors. Metals by and large can be protected from corrosion by the Pragmatic methods of using inhibitors. Corrosion rate of metals or alloys can be decreased by the application of corrosion inhibitor on the corrodible surface to a great extent. Nevertheless, the use of inhibitors like chromates [1], nitrite [2] and aromatic heterocyclic compounds [3] to the optimum level, may pose health hazards and hence environmentally safe inhibitors [4-6] are much sought after. Researches have shown that the use of eco-friendly inhibitors like aminoacids [6-13] on metal corrosion. These aminoacids have brought excellent results as they are found to be Bio-degradable, non-toxic, cost-effective and soluble in aqueous media. L-Lysine, is selected as the environment-friendly corrosion inhibitor for this present research. The research presents some studies about the capability of amino acids to prevent corrosion in iron [14], steel [15-17], aluminium [18, 19], nickel [20] and copper [21-25]. Polarization and AC impedance spectra [26-30] and cyclic voltametry [19] have been studied by using amino acids. The adsorption of amino acids on carbon steel in an acidic environment has been researched by Adiyama et al. [31]. The Objective of the Present Study is

1. To determine the inhibition effectiveness of L-Lysine in regulating the corrosion of carbon steel in the absence and presence of Zn<sup>2+</sup>
2. To analyse the protective film on carbon steel by FTIR spectrophotometry.
3. To study the mechanistic aspects by AC impedance and potentiodynamic polarization studies.
4. To evaluate the protective film on carbon steel by UV and Fluorescence Spectrum studies.
5. To study the surface morphology by AFM.
6. To propose a suitable mechanism for corrosion inhibition based on the results from the above study

### II. EXPERIMENTAL PROCEDURE

#### Preparation of specimens

Carbon steel specimens (0.0267% S, 0.067% P, 0.4% Mn, 0.1% C and the rest iron) of the dimensions

1.0cm x 4.0cm x 0.2cm were polished to mirror finish and degreased with trichloroethylene and used for weight loss method and surface examination studies.

### Weight loss method

Relevant data on the well water used in this study are given in Table 1. Carbon steel specimens, in triplicate were immersed in 100 ml of well water and various concentrations of L-Lysine in the presence and absence of  $Zn^{2+}$  (as  $ZnSO_4 \cdot 7H_2O$ ) for a period of seven days. The corrosion products were cleaned with Clarke's solution [32]. The weight of the specimens before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency was calculated with equation (1)

$$IE = 100 [ 1 - ( W_2/W_1 ) ] \% \text{-----} (1)$$

Where  $W_1$  is the corrosion rate in the absence of the inhibitor and  $W_2$  is the corrosion rate in the presence of inhibitor.

### Potentiodynamic polarization study

Potentiostatic polarization studies were carried out using a CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm<sup>2</sup> area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded using IR compensation. The results, such as Tafel slopes, and  $I_{corr}$ ,  $E_{corr}$  and LPR values were calculated. During the polarization study, the scan rate (v/s) was 0.01; hold time at Ef(s) was zero and quit time(s) was 2.

### 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 to attain its open circuit potential. The real part  $Z'$  and imaginary part  $Z''$  of the cell impedance were measured in ohms at various frequencies. The values of the charge transfer resistance  $R_t$ , double layer capacitance  $C_{dl}$  and impedance value were calculated.

$$R_t = (R_s + R_t) - R_s \text{-----} (3)$$

where  $R_s$  = solution resistance

$$C_{dl} = \frac{1}{2} \pi R_t f_{max} \text{-----} (4)$$

Where  $f_{max}$  = maximum frequency

AC impedance spectra were recorded with initial  $E(v) = 0$ ; high frequency (Hz) = 1; amplitude (v) = 0.05; and quiet time(s) = 2.

### FTIR spectra

The structure of L-Lysine is shown in Fig. 1. The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer.

### Ultraviolet and visible spectroscopy

While interaction with infrared light causes molecules to undergo vibrational transitions, the shorter wavelength, higher energy radiation in the UV (200-400nm) and visible (400-700nm) range of the electromagnetic spectrum causes many organic molecules to undergo electronic transitions. What this means is that when the energy from UV or visible light is absorbed by a molecule, one of its electrons jumps from a lower energy to a higher energy molecular orbital.

### Fluorescence spectroscopy

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation. The most striking example of fluorescence occurs when the absorbed radiation is in the ultraviolet region of the spectrum, and thus invisible to the human eye, while the emitted light is in the visible region, which gives the fluorescent substance a distinct color that can only be seen when exposed to UV light. However, unlike phosphorescence, where the substance would continue to glow and emit light for some time after the radiation source has been turned off, fluorescent materials would cease to glow immediately upon removal of the excitation source. Hence, it is not a persistent phenomenon.

Fig.1 Structure of L-Lysine



**III. RESULTS AND DISCUSSION**

**Analysis of Results of The Weight Loss Method**

Inhibition efficiencies (IE%) of L-Lysine-Zn<sup>2+</sup> systems in controlling corrosion of carbon steel immersed in well water in the presence and absence of inhibitor system (Immersion period = 7 days) are given in the tables 1 to 3 and scheme 1 to 3.

**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.

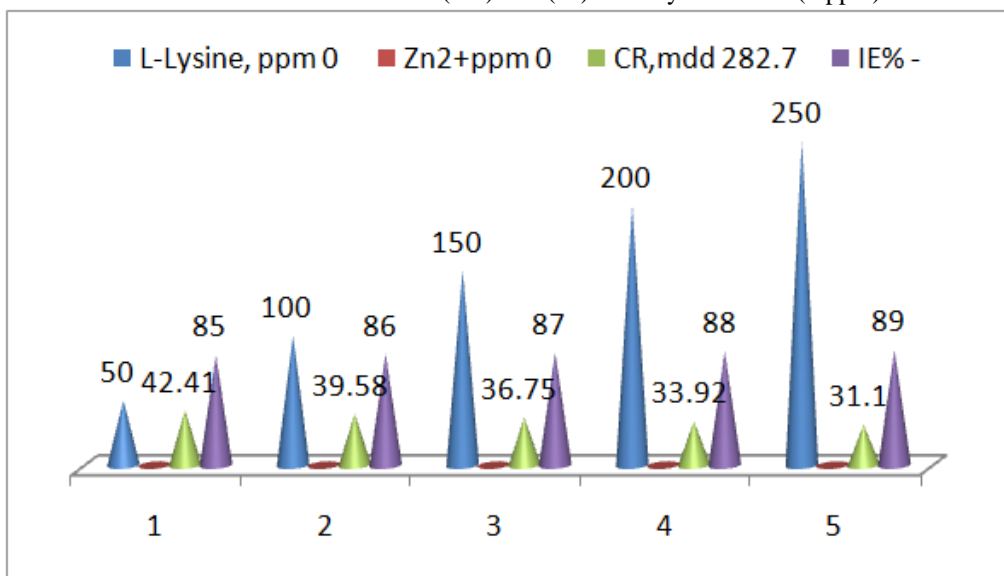
Inhibitor system : L-Lysine-Zn<sup>2+</sup> (0 ppm)

Immersion period: 7 days

pH : 3

L-Lysine, ppm	Zn <sup>2+</sup> ppm	CR, m d d	IE %
0	0	282.70	-
5	0	42.41	85
1	0	39.58	86
1	5	36.75	87
2	0	33.92	88
2	5	31.10	89

**Scheme : 1** Corrosion rates (CR) and (IE) of L-Lysine-Zn<sup>2+</sup> (0 ppm)



**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.

Inhibitor system : L-Lysine-Zn<sup>2+</sup> (10 ppm)

Immersion period: 7 days

pH : 3

L-Lysine, ppm	Zn <sup>2+</sup> ppm	CR, mdd	IE %
0	0	282.70	-
0	1	254.43	1
5	0	33.92	88
1	0	28.27	90
1	5	25.44	91
2	0	22.62	92
2	5	19.79	93

Scheme : 2 Corrosion rates (CR) and (IE) of L-Lysine - Zn<sup>2+</sup> (10 ppm)

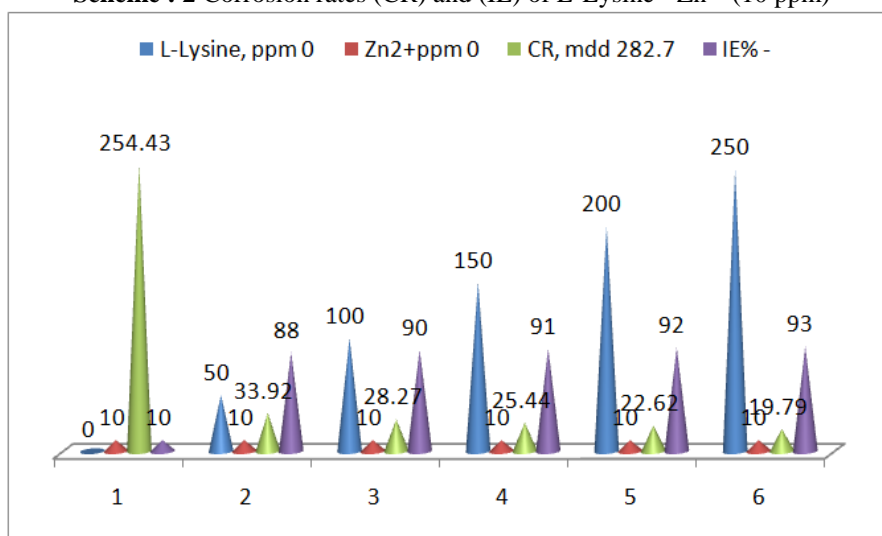
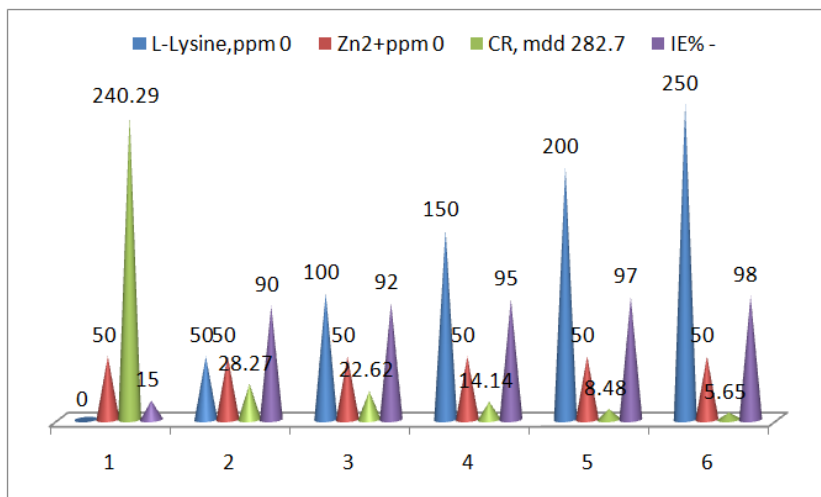


Table 3: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method.  
 Inhibitor system : L-Lysine-Zn<sup>2+</sup> (50 ppm)  
 Immersion period: 7 days  
 pH : 3

L-Lysine, ppm	Zn <sup>2+</sup> ppm	CR, mdd	IE %
0	0	282.70	-
0	5	240.29	1
5	0	28.27	90
1	0	22.62	92
1	5	14.14	95
2	0	8.48	97
2	5	5.65	98

Scheme : 3 Corrosion rates (CR) and (IE) of L-Lysine - Zn<sup>2+</sup> (50 ppm)



It is observed that L-Lysine alone has poor inhibition efficiency. In the presence of various concentration of Zn<sup>2+</sup> (10 and 50 ppm) the IE of L-Lysine increases. A synergistic effect exists between L-Lysine and Zn<sup>2+</sup>.

For example 50 ppm of L-Lysine has only 78% IE; 50 ppm of Zn<sup>2+</sup> has 15% IE. However their combination has 98% IE. This suggests a synergistic effect existing between L-Lysine and Zn<sup>2+</sup>.

**Synergism parameter (S<sub>I</sub>)**

Synergism parameter (S<sub>I</sub>) have been used to know the synergistic effect existing between two inhibitors [9 -14]. Synergism parameter (S<sub>I</sub>) can be calculated using the following relationship.

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

Where

- θ = surface coverage
- θ<sub>1+2</sub> = (θ<sub>1</sub>+θ<sub>2</sub>)-( θ<sub>1</sub>θ<sub>2</sub>)
- θ<sub>1</sub> = surface coverage by L-Lysine
- θ<sub>2</sub> = surface coverage by Zn<sup>2+</sup>
- θ' <sub>1+2</sub> = surface coverage by both L-Lysine and Zn<sup>2+</sup>
- and where θ =  $\frac{IE\%}{100}$

**Table-4:**Inhibition efficiencies and synergism parameters for various concentrations of L-Lysine-Zn<sup>2+</sup> (10ppm) system.

L-Lysine, ppm	Inhibition Efficiency, IE %	Surface Coverage, θ <sub>1</sub>	Zn <sup>2+</sup> , ppm	IE%	Surface coverage θ <sub>2</sub>	combined IE% θ' <sub>1+2</sub>	Combined surface coverage, θ <sub>1+2</sub>	Synergism parameter S <sub>I</sub>													
5	0	8	5	0	8	5	1	0	10	0	1	0	8	8	0	8	8	1	1	3	
1	0	0	8	6	0	8	6	1	0	10	0	1	0	9	0	0	9	0	1	2	6
1	5	0	8	7	0	8	7	1	0	10	0	1	0	9	1	0	9	1	1	3	0
2	0	0	8	8	0	8	8	1	0	10	0	1	0	9	2	0	9	2	1	3	5
2	5	0	8	9	0	8	9	1	0	10	0	1	0	9	3	0	9	3	1	4	1

The synergism parameters of L-Lysine -Zn<sup>2+</sup> system are given in table 4. For different concentrations of inhibitors, S<sub>I</sub> approaches 1 when no interaction between the inhibitor, compounds exists. When S<sub>I</sub>>1, it points to synergistic effects. In the case of S<sub>I</sub><1, it is an indication that the synergistic effect is not significant. From table 4, it is observed that value of synergism parameters (S<sub>I</sub>) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between L-Lysine and Zn<sup>2+</sup>[11,12,14]. Thus the enhancement of the inhibition efficiency caused by the addition of Zn<sup>2+</sup> ions to L-Lysine is due to the synergistic effect.

**Table-5:**Inhibition efficiencies and synergism parameters for various concentrations of L-Lysine-Zn<sup>2+</sup> (50ppm) system.

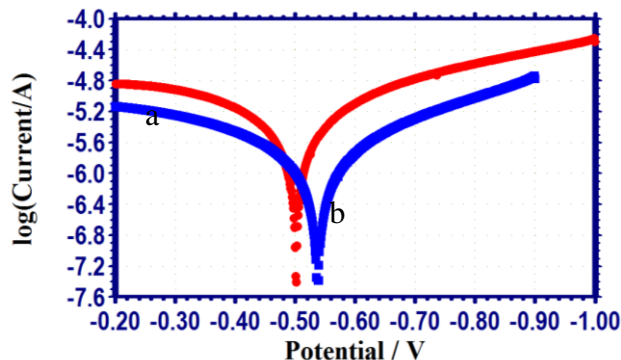
L-Lysine, ppm	Inhibition Efficiency, IE %	Surface Coverage, θ <sub>1</sub>	Zn <sup>2+</sup> , ppm	IE%	Surface coverage θ <sub>2</sub>	combined IE% θ' <sub>1+2</sub>	Combined surface coverage, θ <sub>1+2</sub>	Synergism parameter S <sub>I</sub>													
5	0	8	5	0	8	5	5	0	15	0	1	5	9	0	0	9	0	1	2	8	
1	0	0	8	6	0	8	6	5	0	15	0	1	5	9	2	0	9	2	1	4	9

1	5	0	8	7	0	8	7	5	0	15	0	1	5	9	5	0	9	5	2	2	1
2	0	0	8	8	0	8	8	5	0	15	0	1	5	9	7	0	9	7	3	4	0
2	5	0	8	9	0	8	9	5	0	15	0	1	5	9	8	0	9	8	4	6	8

**Analysis of potentiodynamic polarization study (pH = 3)**

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [39–44]. If a protective film is formed on the metal surface, the linear polarization resistance value (LPR) increases and corrosion current value ( $I_{corr}$ ) decreases. The potentiodynamic polarization curves of carbon steel immersed in well water in the presence and absence of inhibitors are shown in Fig. 2. The corrosion parameters are given in Table 5. When carbon steel was immersed in well water the corrosion potential was -502 mV vs SCE. When L-Lysine (250 ppm) and  $Zn^{2+}$  (50ppm) were added to the above system the corrosion potential shifted to the cathodic side (-538 mV vs SCE). This indicates that the inhibitor system controls the cathodic reaction (formation of  $OH^-$ ) predominantly. In the presence of inhibitor system, the corrosion potential is shifted from -502 to -538 mV vs SCE. This shift is with 50 mV/decade. Hence, it is concluded that the inhibitor system functions as mixed type inhibitor system.

The anodic reaction ( $Fe \rightarrow Fe^{2+} + 2e^-$ ) is controlled by formation of  $Fe^{2+}$  - inhibitor complex on the anodic sites of the metal surface. The cathodic reaction ( $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ) is controlled by formation of zinc hydroxide ( $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$ ) on the cathodic sites of the metal surface. Thus both anodic reaction of generation of  $Fe^{2+}$  and cathodic reaction of formation of  $OH^-$  are effectively controlled by the inhibitor system. This accounts for the mixed type of inhibitor system and the synergistic effect existing between L-Lysine and  $Zn^{2+}$  system. Further, the LPR value increase from 12948.8 ohm  $cm^2$  to 35923.9 ohm  $cm^2$ ; the corrosion current decreases from  $3.521 \times 10^{-6}$  A/ $cm^2$  to  $1.224 \times 10^{-6}$  A/ $cm^2$ . Thus, polarization study confirms the formation of a protective film on the metal surface.



**Fig. 2 :** Polarization curves of carbon steel immersed in various test solutions.

- a) Well Water.
- b) Well water + L-Lysine (250 ppm) +  $Zn^{2+}$  (50 ppm)

**Table 6:** Corrosion parameters of carbon steel immersed in well water in the absence of inhibitor system obtained from potentiodynamic polarization study.

S y s t e m	E <sub>corr</sub> mV vs SCE	b <sub>c</sub> , mV/decade	b <sub>a</sub> , mV/decade	I <sub>corr</sub> , A/cm <sup>2</sup>	L P R , ohm cm <sup>2</sup>
Well water	- 5 0 2	1 9 4 . 3	2 2 7 . 6	$3.521 \times 10^{-6}$	12948.8
Well water + L-Lysine (250 ppm) + $Zn^{2+}$ (50 ppm)	- 5 3 8	1 8 9 . 3	2 1 7 . 1	$1.224 \times 10^{-6}$	35923.9

**Analysis of AC impedance spectra**

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface [45-47]. If a protective film is formed on the metal surface, charge transfer resistance ( $R_t$ ) increases; double layer capacitance value ( $C_{dl}$ ) decreases and impedance  $\log(z/ohm)$  value increases. The phase angle also increases. The AC impedance spectra of carbon steel immersed in well water in presence and absence of inhibitors (L-Lysine -  $Zn^{2+}$ ) are shown in Figs. 3 (a, b) (Nyquist plots) Figs.4 (a,b) Figs.5 (a,b) (Bode plots). The AC impedance parameters namely charge transfer resistance ( $R_t$ ) and double layer capacitance ( $C_{dl}$ ) derived from Nyquist plots are given in Table 6. The impedance  $\log(z/ohm)$  values derived from Bode plots are also given in Table 6. It is observed that when the inhibitors [L-Lysine (250ppm) +  $Zn^{2+}$  (50 ppm) ] are added, the charge transfer resistance ( $R_t$ ) increase from 4737 ohm  $cm^2$  to 7304 ohm  $cm^2$ . The  $C_{dl}$  value decreases from  $1.056 \times 10^{-9}$  F/ $cm^2$  to  $0.6845 \times 10^{-9}$  F/ $cm^2$ . The impedance value [ $\log$

(z/ohm)] increases from 3.8862 to 4.040. The phase angle increases from 34.00° to 39.00°. These results lead to the conclusion that a protective film is formed on the metal surface.

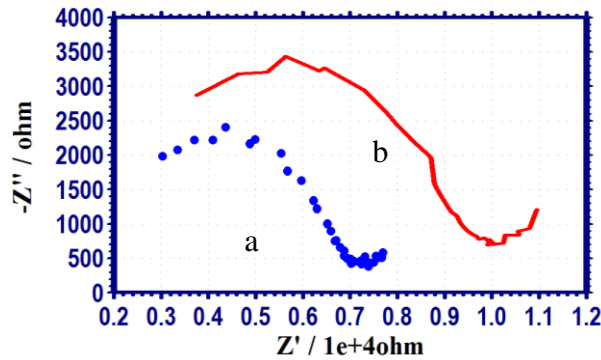


Fig. 3 : AC impedance spectra of Carbon Steel immersed in various test solutions.

(Nyquist Plot) pH = 3.

- a) Well Water.
- b) Well water + L-Lysine (250 ppm) + Zn<sup>2+</sup> (50 ppm)

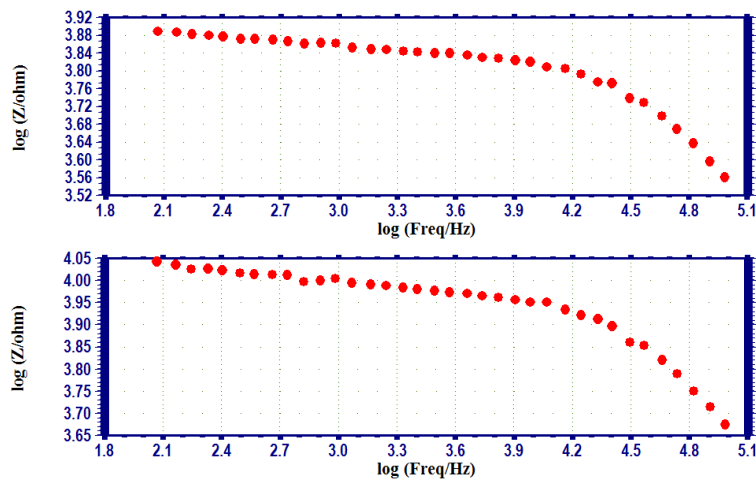


Fig. 4 : AC impedance spectra of Carbon Steel immersed in various test solutions.

(Impedance – Bode Plot) pH = 3.

- a) Well Water.
- b) Well water + L-Lysine (250 ppm) + Zn<sup>2+</sup> (50 ppm)

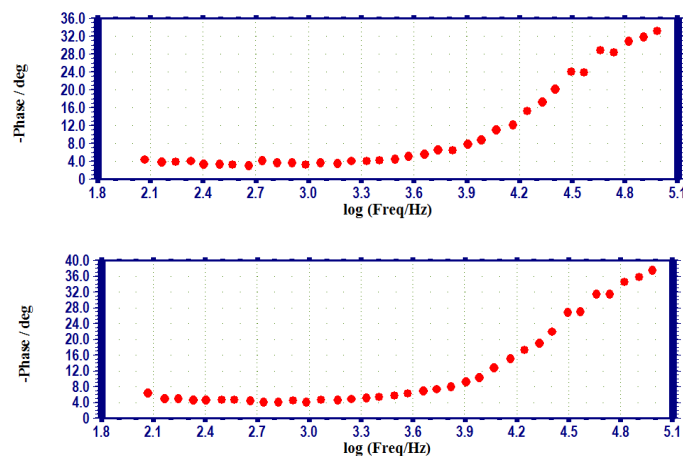


Fig. 5 : AC impedance spectra of Carbon Steel immersed in various test solutions.

(Phase – Bode Plot) pH = 3.

- a) Well Water.
- b) Well water + L-Lysine (250 ppm) + Zn<sup>2+</sup> (50 ppm)

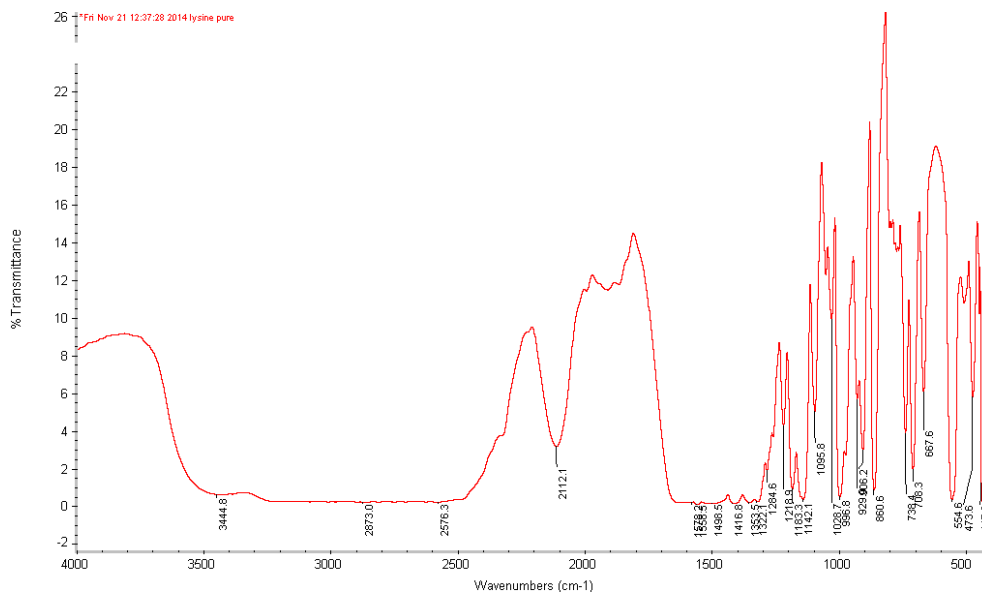
**Table 7:** Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra (pH = 3).

System	Nyquist plot		Bode plot
	R <sub>t</sub> ohm cm <sup>2</sup>	C <sub>d</sub> F/cm <sup>2</sup>	Impedance value Log(z/ohm)
Well water	4737	1.056×10 <sup>-9</sup>	3.886
Well water + L-Lysine (250 p	7304	0.6845×10 <sup>-9</sup>	4.040

**Analysis of FTIR spectra**

FTIR spectra have been used to analysis the protective film formed on the metal surface, [48-56]. The FTIR spectrum (KBr) of pure L-Lysine is shown in Fig. 6(a) The -C=O stretching frequency of carboxyl group appears at 1670cm<sup>-1</sup>. The -CN stretching frequency appears at 1142.1cm<sup>-1</sup>. The -NH stretching frequency of the amine group appears at 2873.0 cm<sup>-1</sup> [51-53].

The FTIR spectrum of the film formed on the metal surface after immersion in the well water, 250 ppm of L-Lysine and 50 ppm Zn<sup>2+</sup> is shown in Fig.6(b). The -C=O stretching frequency has shifted from 1670 to 1620 cm<sup>-1</sup>. The -CN stretching frequency has shifted from 1142.1 to 1010 cm<sup>-1</sup>. The -NH stretching frequency has shifted from 2873.0 to 2360.8 cm<sup>-1</sup>. This observation suggests that L-Lysine has coordinated with Fe<sup>2+</sup> through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe<sup>2+</sup> - L-Lysine complex on the anodic sites of the metal surface. The peak at 473.6cm<sup>-1</sup> corresponds to Zn-O stretching. The peak at 3610.0cm<sup>-1</sup> is due to -OH stretching. This confirms that Zn(OH)<sub>2</sub> is formed on the cathodic sites of metal surface, [45,54-56]. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe<sup>2+</sup> -L-Lysine complex and Zn(OH)<sub>2</sub>.



**Fig. 6**

(a) FTIR Spectrum of pure L-Lysine



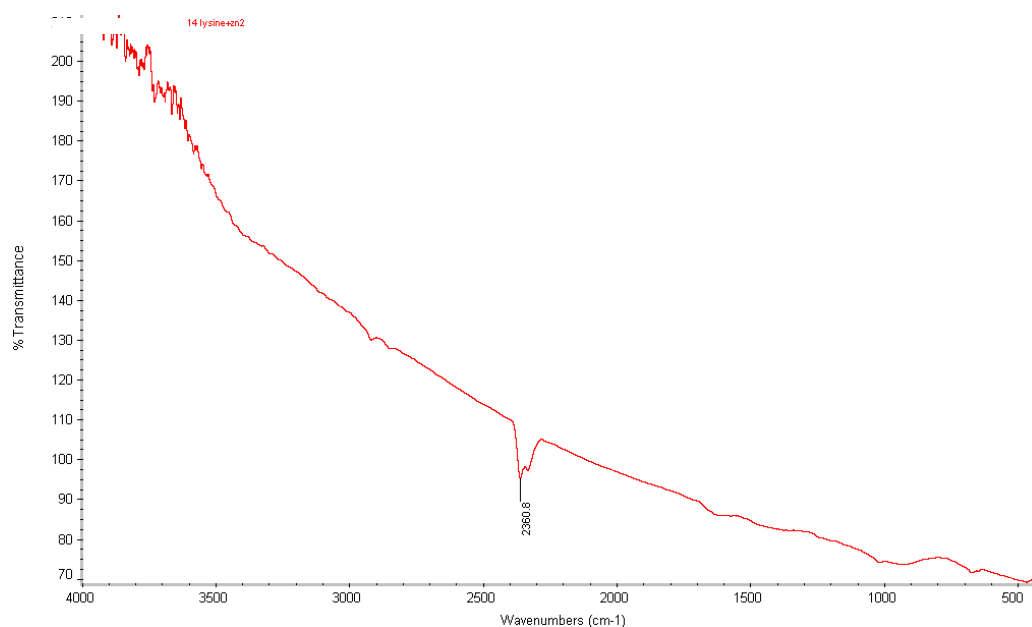


Fig. 6

(b) FTIR Spectrum of film formed on metal surface of the immersion in solution containing L-Lysine – Zn<sup>2+</sup>.

#### UV- Visible Absorption Spectroscopy

UV-visible absorption spectrum of an aqueous solution containing L-Lysine and Fe<sup>2+</sup> (freshly) prepared FeSO<sub>4</sub>·7H<sub>2</sub>O is shown in Fig. 7.

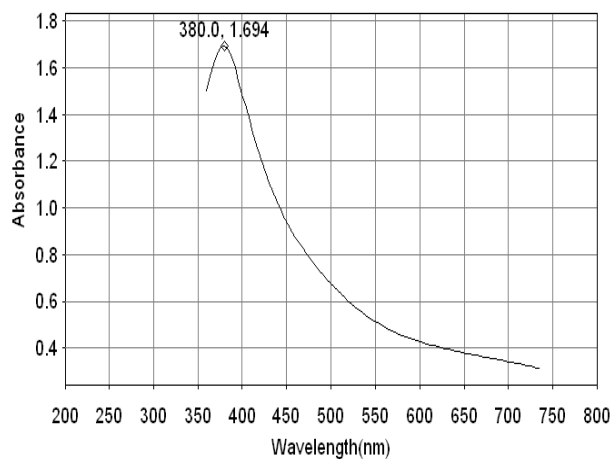


Fig. 7. UV – Visible absorption Spectrum

A peak appears at 380.0 nm. This peak is due to the formation of Fe<sup>2+</sup>- L- Lysine complex formed in solution.

#### Fluorescence Spectrum

The fluorescence spectrum ( $\lambda_{ex}$ =380.0nm) of an aqueous solution containing L-Lysine and Fe<sup>2+</sup> (Freshly prepared FeSO<sub>4</sub>·7H<sub>2</sub>O) is shown in Fig. 8(a).

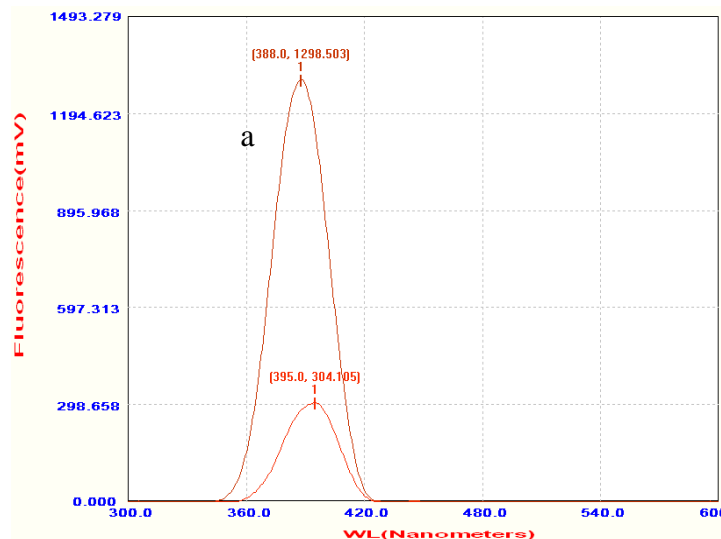


Fig. 8. Fluorescence Spectrum

- (a) Solution containing L-Lysine +  $\text{Fe}^{2+}$ .  
 (b) Solution containing 50 ppm of  $\text{Zn}^{2+}$  + 250 ppm of L-Lysine.

Peak appears at 388.0 nm. This spectrum is due to  $\text{Fe}^{2+}$ - L-Lysine complex formed in solution.

The fluorescence spectrum of ( $\lambda_{\text{ex}} = 380.0$  nm) film formed on metal surface after immersion in the solution containing 50 ppm of  $\text{Zn}^{2+}$  and 250 ppm of L-Lysine is shown in Fig. 8(b).

Peak appears at 395.0 nm. This peak match with the fluorescence spectrum of  $\text{Fe}^{2+}$  - L-Lysine complex. Hence it is confirmed that the protected film formed on the metal surface consists of  $\text{Fe}^{2+}$  - L-Lysine complex [57-62].

Fluorescence spectra have been used to confirm the formation of protective film on the metal surface.

#### Atomic force Microscopy Characterization

Atomic force microscopy is a powerful technique for gathering of roughness statistics from a variety of surfaces [63]. AFM is becoming an accepted method of roughness investigation.[64-70]All atomic force microscopy images were obtained in a VECCO lab incorporation AFM instrument operating in contact mode in air. The scan size of all the AFM images are 05 m x 05 m areas at a scan rate of 6.68 m/second.The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in well water (blank sample) and carbon steel surface immersed in well water containing the formulation of Lys 250 ppm and 50 ppm of  $\text{Zn}^{2+}$  are shown as Fig. 9. (a, b, c) Fig. 10. (a, b, c) Fig. 11. (a, b, c) respectively.

#### Root – mean-square roughness, average roughness and peak-to-valley value

AFM image analysis was performed to obtain the average roughness,  $R_a$  (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness,  $R_q$  (the average of the measured height deviation taken within the evaluation length and measured from the mean line) and the maximum peak-to- valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights).[69]  $R_q$  is much more sensitive than  $R_a$  to large and small height deviations from the mean.[70] Table. 8. is the summary of the average roughness ( $R_a$ ), rms roughness ( $R_q$ ) maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments.

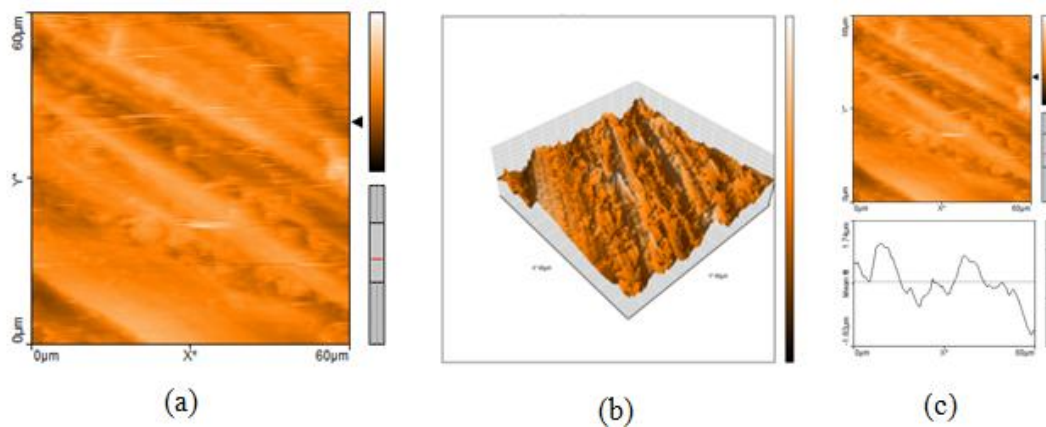
The value of  $R_{\text{RMS}}$ ,  $R_a$  and P-V height for the polished carbon steel surface (reference sample) are 60.751 nm, 51.444 nm and 151.04 nm respectively, which shows a more homogeneous surface, with some places in which the height is lower than the average depth.[63] Fig. 9. (a, b, c) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The rms roughness, average roughness and P-V height values for the carbon steel surface immersed in well water are 751.72 nm, 581.77 nm and 1088.3 nm respectively. These data suggest that carbon steel surface immersed in well water has a greater surface roughness than the polished metal surface. This shows that the unprotected carbon steel surface is rougher and is due to the corrosion of the carbon steel in well water . Fig. 10. (a, b, c) displays the corroded metal surface with few pits.

The presence of 250 ppm of Lys and 50 ppm of  $\text{Zn}^{2+}$  in well water reduces the  $R_q$  by a factor of 60.751 nm from 751.72 nm and the average roughness is significantly reduced to 51.444 nm when compared with 581.77 nm of carbon steel surface immersed in well water. The maximum peak-to-valley height also was

reduced to 151.04 nm from 1088.3 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe<sup>2+</sup>- Lys complex and Zn (OH)<sub>2</sub> on the metal surface thereby inhibiting the corrosion of carbon steel. Also the above parameters observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.

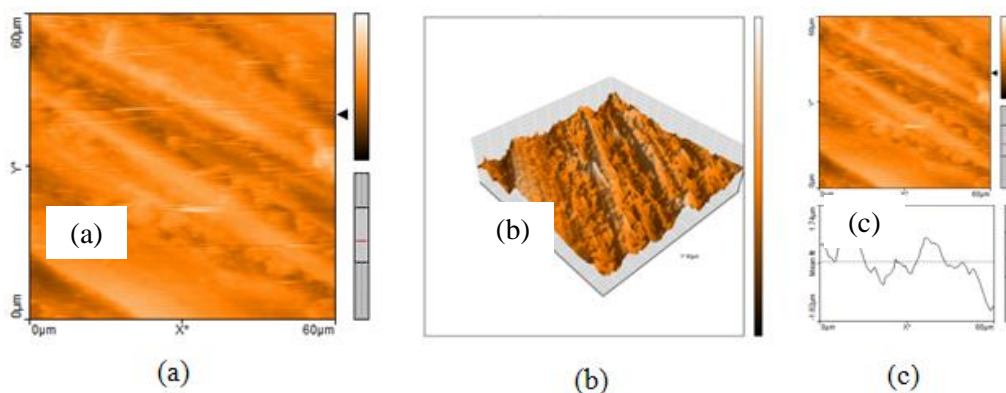
**Table 8.** AFM data for carbon steel surface immersed in inhibited and uninhibited environments

S a m p l e s	R o u g h n e s s , n m		Maximum peak-to-valley height (nm)
	R M S ( R <sub>q</sub> )	A v e r a g e ( R <sub>a</sub> )	
Polished carbon steel (control)	5 0 . 1 4 9	4 1 . 5 4 5	1 0 0 . 7 3
Carbon steel immersed in well water.	7 5 1 . 7 2	5 8 1 . 7 7	1 0 8 8 . 3
Carbon steel immersed in well water, Lys (20 ppm) + Zn <sup>2+</sup> (50 ppm)	6 0 . 7 5 1	5 1 . 4 4 4	1 5 1 . 0 4



**Fig. 9.** Polished Carbon Steel surface (reference sample)

- (a) 2D AFM images of the surface
- (b) 3D AFM images of the surface
- (c) The cross-sectional profile which are corresponding to as shown broken lines in AFM images of the surface.



**Fig. 10.** Carbon Steel immersed in well water (blank sample)

- (a) 2D AFM images of the surface
- (b) 3D AFM images of the surface
- (c) The cross-sectional profile which are corresponding to as shown broken lines in AFM images of the surface.

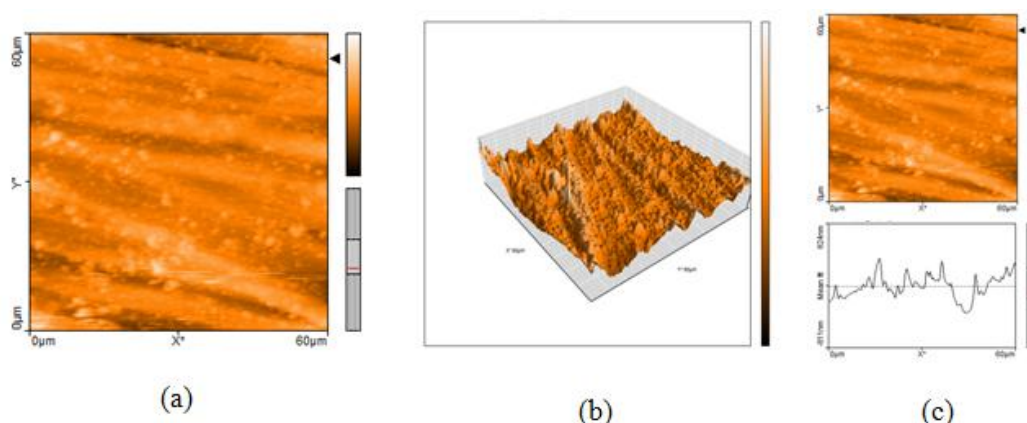


Fig. 11. Carbon Steel immersed in well water containing 250 ppm of Lys and 50 ppm of  $Zn^{2+}$

- (a) 2D AFM images of the surface  
 (b) 3D AFM images of the surface  
 (c) The cross-sectional profile which are corresponding to as shown broken lines in AFM images of the surface.

#### Mechanism of corrosion inhibition

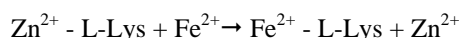
The results of the weight-loss study show that the formulation consisting of 250ppm L-Lys and 50 ppm of  $Zn^{2+}$  has 99% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between  $Zn^{2+}$  and L-Lys. Polarization study reveals that this formulation functions as mixed type of inhibitor. AC impedance spectra reveals that a protective film is formed on the metal surface. FTIR spectra reveals that the protective film consists of  $Fe^{2+}$  - L-Lys complex and  $Zn(OH)_2$ . In order to explain these facts the following mechanism of corrosion inhibition is proposed [71-82].

When the solution containing well water, 50 ppm  $Zn^{2+}$  and 250 ppm of L-Lys is prepared, there is formation of  $Zn^{2+}$  L-Lys complex in solution.

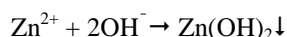
When carbon steel is immersed in this solution, the  $Zn^{2+}$  - L-Lys complex diffuses from the bulk of the solution towards metal surface.

$Zn^{2+}$  - L-Lys complex diffuses from the bulk solution to the surface of the metal and is converted into a  $Fe^{2+}$  - L-Lys complex, which is more stable than  $Zn^{2+}$  - L-Lys [50].

On the metal surface  $Zn^{2+}$  - L-Lys complex is converted in to  $Fe^{2+}$  - L-Lys on the anodic sites.  $Zn^{2+}$  is released.



The released  $Zn^{2+}$  combines with  $OH^-$  to form  $Zn(OH)_2$  on the cathodic sites [50].



Thus the protective film consists of  $Fe^{2+}$  - L-Lys complex and  $Zn(OH)_2$  [83,84].

#### IV. CONCLUSION

1. Polarization study reveals that this formulation functions as a mixed type of inhibitor system.
2. AC impedance spectra reveal that a protective film is formed on the metal surface.
3. The FTIR spectra study leads to the conclusion that the  $Fe^{2+}$  - L-Lys 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.
4. The protective film on carbon steel is studied by UV and Fluorescence spectrum studies.
5. The morphology of the metal is studied by AFM images.

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