



# ECO-FRIENDLY INHIBITOR GLYCINE-Zn<sup>2+</sup> SYSTEM CONTROLLING CORROSION OF CARBON STEEL IN WELL WATER

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The environmental friendly inhibitor system glycine-Zn<sup>2+</sup>, has been investigated by weight loss method. A synergistic effect exists between glycine and Zn<sup>2+</sup> system. The formulation consisting of 250 ppm of glycine and 50 ppm of Zn<sup>2+</sup> offers good inhibition efficiency of 82%. Polarization study reveals that this formulation functions as an anodic inhibitor. The FTIR spectra study leads to the conclusion that the Fe<sup>2+</sup>-Gly 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. The surface morphology and the roughness of the metal surface have been analyzed with atomic force microscopy. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study and surface analysis technique. The eco-friendly inhibitor glycine-Zn<sup>2+</sup> system may find application in cooling water system.

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The principles and practices of corrosion inhibition in recent years have begun taking into account the health and safety considerations. The use of hazardous chemicals has been restricted to no contact with the environment. Hence, there is a search for non-toxic, eco-friendly corrosion inhibitors. The use of inhibitors is one of the most practical methods to protect metals from corrosion. Corrosion inhibitor is a chemical substance which when added to the corrosive environment at an optimum concentration, there is a decrease in the corrosion rate of metals (or) alloys significantly. Unfortunately, many common corrosion inhibitors are highly toxic and health-hazardable, such as chromates,<sup>1</sup> nitrite<sup>2</sup> and aromatic heterocyclic compounds<sup>3</sup> etc. Therefore, it is better to look for environmentally safe inhibitors.<sup>4-6</sup> Some researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion.<sup>6-13</sup> This is due to 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, glycine, is chosen as the corrosion inhibitor for this present work. The literature presents some studies involving amino acids having the ability to prevent the corrosion of iron,<sup>14</sup> steel,<sup>15-17</sup> aluminium,<sup>18,19</sup> nickel<sup>20</sup> and copper.<sup>21-25</sup> The electrochemical studies such as polarization and AC impedance spectra<sup>26-30</sup> and cyclic voltammetry have been studied by using amino acids. The adsorption of amino acids on carbon steel in acidic environment has been investigated by Akiyama et al.<sup>31</sup>

The aim of the present study is

1. To evaluate the inhibition efficiency of glycine in controlling the corrosion of carbon steel in the absence and presence of Zn<sup>2+</sup>.
2. To analyze the protective film on carbon steel by FTIR spectrophotometry.
3. To study the mechanistic aspects by potentiodynamic polarization study.
4. To analyse the surface morphology by AFM
5. To propose a suitable mechanism for corrosion inhibition based on the results from the above study.

## 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 glycine in the presence and absence of Zn<sup>2+</sup> (as ZnSO<sub>4</sub>·7H<sub>2</sub>O) for a period of seven days. The corrosion products were cleaned with Clarke's solution.<sup>32</sup> The weight of the specimens before and after immersion was determined using Shimadzu balance AY62.

The corrosion inhibition efficiency was calculated with equation (1)

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

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.

From the weight loss, the corrosion rate (CR) was calculated

$$CR = \frac{\Delta m}{S t_{imm}} \frac{0.365}{\rho} \quad (2)$$

where

CR is the corrosion rate, (mmpy)

$\Delta m$  is the loss in weight (mg)

S is the surface area of the specimen (dm<sup>2</sup>)

$t_{imm}$  is the period of immersion (day)

$\rho$  is the density of the metal in g cm<sup>-3</sup> (7.86)

### 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  $E_f$ (s) was zero and quit time(s) was 2.

### FTIR spectra

The structure of glycine is shown in Fig.1. The carbon steel specimens immersed in various test solutions for seven days 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.

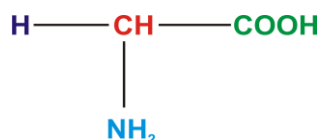


Figure 1. Structure of glycine

### Atomic force microscopy

Atomic force microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before.<sup>33-35</sup> The

microscope used for the present study was VECCO, Lab incorporation. Polished specimens prior to the initiation of all corrosion experiments were examined through an optical microscope to find out any surface defects such as pits or noticeable irregularities like cracks, etc., only those specimens, which had a smooth pit free surface, were subjected for AFM examination. The protective films formed on the carbon steel specimens after immersion in the inhibitor systems for different time durations were examined for a scanned area of 05 x 05  $\mu\text{m}$  at a scan rate of 6.68  $\mu\text{m}/\text{second}$ . the two dimensional and three-dimensional topography of surface film gave various roughness parameters of the film.

## Results and Discussion

### Weight loss method

The inhibition efficiency of glycine -Zn<sup>2+</sup> system in controlling corrosion of carbon steel in well water (Table 1) has been evaluated by weight loss method.

Table 1. Physico –chemical parameters of well water.

Parameter	Well water
pH	8.0
Conductivity	3110 $\mu\text{mhos cm}^{-1}$
Total dissolved solids	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

### Analysis of results of the weight loss method

Inhibition efficiencies (IE%) of Gly-Zn<sup>2+</sup> systems in controlling corrosion of carbon steel in well water (immersion period = 7 days) are given in Table 2 to 4. It is observed that Gly alone has poor inhibition efficiency. In the presence of various concentration of Zn<sup>2+</sup> (25 and 50 ppm), the IE of Gly increases. A synergistic effect exists between Gly and Zn<sup>2+</sup>. For example, 50 ppm of Gly has only 28% IE; 50 ppm of Zn<sup>2+</sup> has 20% IE. However, their combination has 82% IE. This suggests a synergistic effect existing between Gly and Zn<sup>2+</sup>. The corrosion rates of Gly-Zn<sup>2+</sup> systems are shown in Fig.2.

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.

Glycine, ppm	Zn <sup>2+</sup> ppm	CR, mmpy	IE, %
0	0	0.0874	--
50	0	0.0629	28
100	0	0.0673	23
150	0	0.0787	10
200	0	0.0804	8
250	0	0.0865	1

Inhibitor system: glycine - Zn<sup>2+</sup> (0 ppm), immersion period: 7 days, pH = 8.

**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.

Glycine, ppm	Zn <sup>2+</sup> , ppm	CR, mmpy	IE, %
0	0	0.0874	--
0	25	0.0742	15
50	25	0.0603	31
100	25	0.0550	37
150	25	0.0524	40
200	25	0.0507	42
250	25	0.0472	46

Inhibitor system: glycine-Zn<sup>2+</sup> (25 ppm), immersion period: 7 days, pH = 8

**Table 4 :** 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.

Gly ppm	Zn <sup>2+</sup> ppm	CR mmpy	IE %
0	0	0.0874	--
0	50	0.0699	20
50	50	0.0350	60
100	50	0.0280	68
150	50	0.0219	75
200	50	0.0192	78
250	50	0.0157	82

Inhibitor system: glycine - Zn<sup>2+</sup> (50 ppm), Immersion period: 7 days, pH = 8

Synergism parameter ( $S_I$ ) have been used to know the synergistic effect existing between two inhibitors.<sup>36-41</sup> Synergism parameter ( $S_I$ ) can be calculated using the following relationship.

$$S_I = \frac{1 - \theta_1 + 2}{1 - \theta_1 + 2} \quad (3)$$

where

$\theta_1$  = surface coverage

$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$

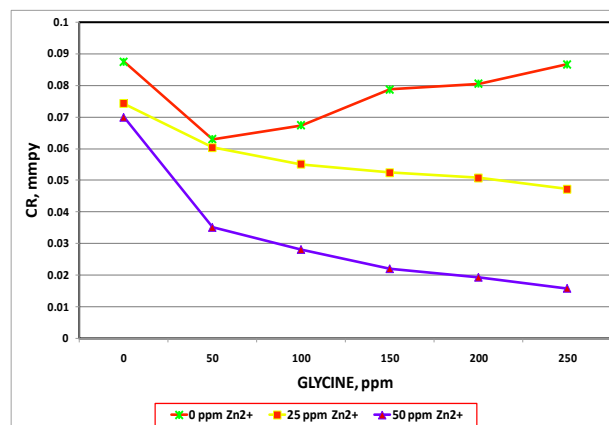
$\theta_1$  = surface coverage by glycine

$\theta_2$  = surface coverage by Zn<sup>2+</sup>

$\theta_{1+2}$  = surface coverage by both glycine and Zn<sup>2+</sup>

and where

$$\theta = \frac{IE(\%)}{100}$$



The synergism parameters of Glycine-Zn<sup>2+</sup> system are given in Table 5. For different concentrations of inhibitors,  $S_I$  approaches 1 when no interaction between the inhibitor compounds exists. When  $S_I > 1$ , it points to synergistic effects. In the case of  $S_I < 1$ , it is an indication that the synergistic effect is not significant. From Tables 5 and 6, 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 exists between glycine and Zn<sup>2+</sup>.<sup>38,39,41</sup> Thus, the enhancement of the inhibition efficiency caused by the addition of Zn<sup>2+</sup> ions to glycine is due to the synergistic effect.

**Figure 2.** Corrosion rates (CR) of carbon steel immersed in various test solutions

#### Analysis of potentiodynamic polarization study (pH=8)

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process.<sup>42-47</sup> If a protective film is formed on the metal surface, the linear polarization resistance value (LPR) increases and 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.3. The corrosion parameters are given in Table 6. When carbon steel was immersed in well water the corrosion potential was -668 mV vs SCE. When glycine (250 ppm) and Zn<sup>2+</sup> (50 ppm) were added to the above system the corrosion potential shifted to the noble side (-652 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<sup>2+</sup>-Gly complex on the anodic sites of the metal surface. The formation of protective film on the metal surface is further supported by the fact that the anodic Tafel slope ( $b_a$ ) increases from 104 to 132mV.

Further, the LPR value increases from  $5.630 \times 10^4$  ohm cm<sup>2</sup> to  $10.62 \times 10^5$  ohm cm<sup>2</sup>; the corrosion current decreases from  $5.775 \times 10^{-7}$  A/cm<sup>2</sup> to  $3.461 \times 10^{-7}$  A/cm<sup>2</sup>. Thus, polarization study confirms the formation of a protective film on the metal surface.

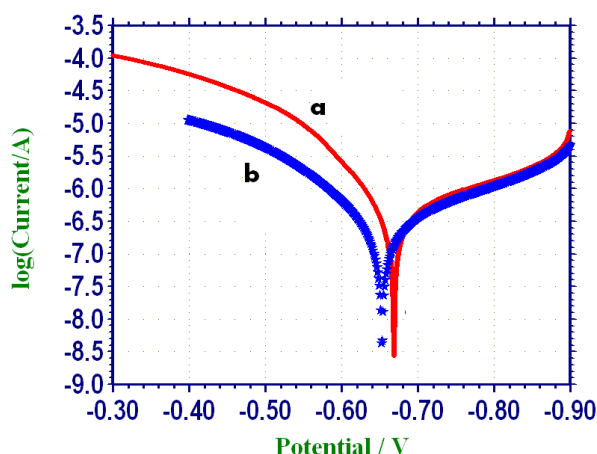
**Table 5 :** Inhibition efficiencies and synergism parameters for various concentrations of Gly- $\text{Zn}^{2+}$  (50 ppm) systems, when carbon steel is immersed in well water

Glycine, ppm	Inhibition efficiency, IE (%)	Surface coverage, $\theta_1$	$\text{Zn}^{2+}$ , ppm	Inhibition efficiency, IE (%)	Surface coverage, $\theta_2$	Combined IE %, $I'_{1+2}$	Combined surface coverage, $\theta'_{1+2}$	Synergism parameter, $S_i$
50	28	0.28	50	20	0.20	60	0.60	1.440
100	23	0.23	50	20	0.20	68	0.68	1.925
150	10	0.10	50	20	0.20	75	0.75	2.880
200	8	0.08	50	20	0.20	78	0.78	3.345
250	1	0.01	50	20	0.20	82	0.82	5.410

Immersion period: 7 days, pH = 8

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

System	$E_{\text{corr}}$ , mV vs SCE	$b_c$ , mV/decade	$b_a$ , V/decade	$I_{\text{corr}}$ , $\text{Acm}^{-2}$	LPR, $\text{ohm cm}^2$
Well water	-668	268	104	$5.775 \times 10^{-7}$	$5.630 \times 10^4$
Well water+Gly(250ppm)+ $\text{Zn}^{2+}$ (50ppm)	-652	235	132	$3.461 \times 10^{-7}$	$10.62 \times 10^5$

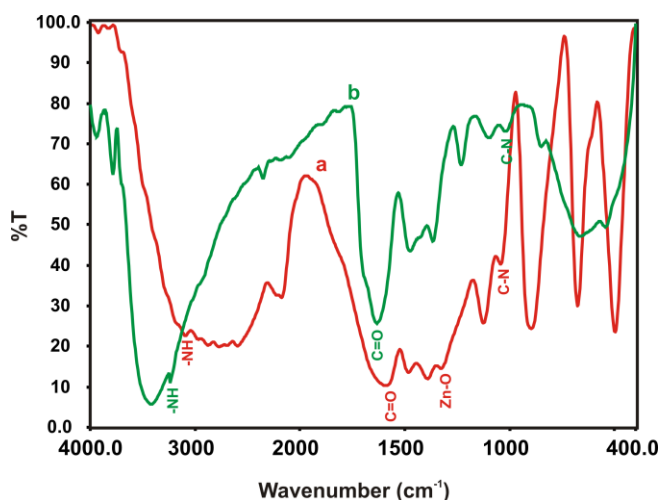
**Figure 3.** Polarization curves of mild steel immersed in various test solutions. a) well water (blank); b) well water + glycine (250 ppm) +  $\text{Zn}^{2+}$  (50 ppm)

#### Analysis of FTIR spectra

FTIR spectra have been used to analysis the protective film formed on the metal surface.<sup>44,48-55</sup> The FTIR spectrum (KBr) of pure glycine is shown in Fig.4(a). The C=O stretching frequency of carboxyl group appears at  $1598 \text{ cm}^{-1}$ . The CN stretching frequency appear at  $1126 \text{ cm}^{-1}$ . The NH stretching frequency of the amine group appears at  $3105 \text{ cm}^{-1}$ .<sup>50-52</sup>

The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of glycine and 50 ppm  $\text{Zn}^{2+}$  is shown in Fig.4(b). The C=O stretching frequency has shifted from  $1598$  to  $1609 \text{ cm}^{-1}$ . The CN stretching frequency has shifted from  $1126$  to  $1039 \text{ cm}^{-1}$ . The NH stretching frequency has shifted from  $3105$  to  $3209 \text{ cm}^{-1}$ . This observation suggest that glycine has coordinated with  $\text{Fe}^{2+}$  through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of

$\text{Fe}^{2+}$ -glycine complex on the anodic sites of the metal surface. The peak at  $1331 \text{ cm}^{-1}$  corresponds to Zn-O stretching. The peak at  $3422 \text{ cm}^{-1}$  is due to  $\text{OH}^-$  stretching. This confirms that  $\text{Zn}(\text{OH})_2$  is formed on the cathodic sites of metal surface.<sup>48,53-55</sup> Thus the FTIR spectral study leads to the conclusion that the protective film consist of  $\text{Fe}^{2+}$ -gly complex and  $\text{Zn}(\text{OH})_2$ .

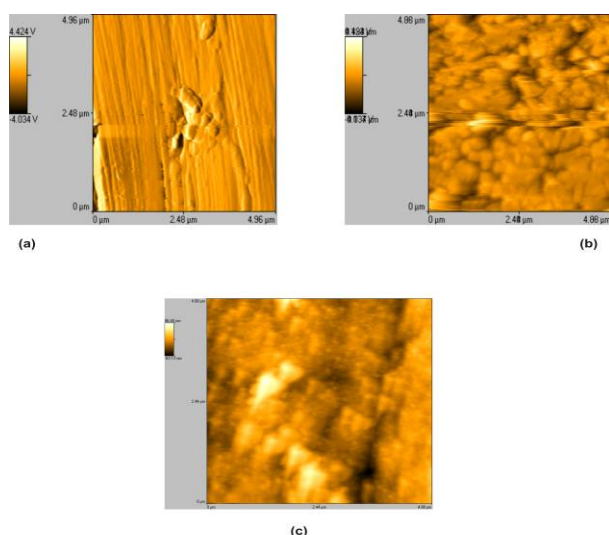
**Figure 4.** FTIR spectra of a) pure glycine; b) film formed on the metal surface after immersion in well water + Gly (250 ppm) +  $\text{Zn}^{2+}$  (50 ppm)

#### Atomic Force Microscopy Characterization

Atomic force microscopy is a powerful technique for gathering of roughness statistics from a variety of surfaces.<sup>56</sup> AFM is becoming an accepted method of roughness investigation.<sup>57-63</sup>

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  $05 \mu\text{m} \times 05 \mu\text{m}$  areas at a scan rate of  $6.68 \mu\text{m}/\text{second}$ .





**Figure 5.** 2D AFM images of the surface of a) polished carbon steel (control); b) carbon steel immersed in well water (blank); c) carbon steel immersed in well water containing glycine (250 ppm) +  $\text{Zn}^{2+}$  (50 ppm)

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 Gly 250 ppm and 50 ppm of  $\text{Zn}^{2+}$  are shown as Fig.5(a,d,g), (b,e,h), (e,f,i) 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 deviations 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).<sup>62</sup>  $R_q$  is much more sensitive than  $R_a$  to large and small height deviations from the mean.<sup>63</sup>

Table 7 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 31 nm, 10 nm and 63 nm respectively, which shows a more homogeneous surface, with some places in which the height is lower than the average depth.<sup>56</sup> Fig.5(a,d,g) 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 68 nm, 18 nm and 131 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

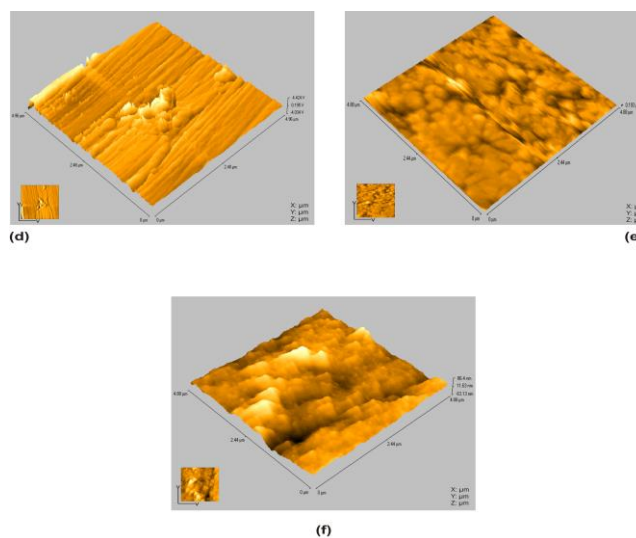
well water. Fig.5(b,e,h) displays the corroded metal surface with few pits.

The presence of 250 ppm of Gly and 50 ppm of  $\text{Zn}^{2+}$  in well water reduces the  $R_q$  by a factor of 32 nm from 68 nm and the average roughness is significantly reduced to 11 nm when compared with 18 nm of carbon steel surface immersed in well water. The maximum peak-to-valley height also was reduced to 60 nm from 131 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  $\text{Fe}^{2+}$ - Gly complex and  $\text{Zn}(\text{OH})_2$  on the metal surface thereby inhibiting the corrosion of carbon steel.

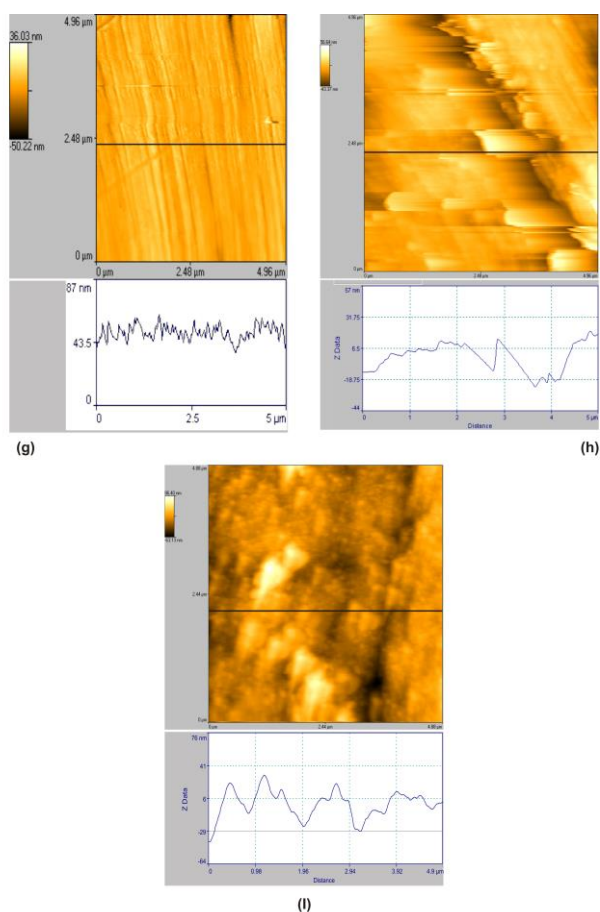
Also the above parameters observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.

**Table 7.** AFM data for carbon steel surface immersed in inhibited and uninhibited environments

Samples	Roughness, nm		Maximum peak-to-valley height (nm)
	RMS ( $R_q$ )	Average ( $R_a$ )	
Polished carbon steel (control)	31	10	63
Carbon steel immersed in well water	68	18	131
Carbon steel immersed in well water Gly (250 ppm) + $\text{Zn}^{2+}$ (50 ppm)	32	11	60



**Figure 5.** 3D AFM images of the surface of d) polished carbon steel (control); e) carbon steel immersed in well water (blank); f) carbon steel immersed in well water containing Glycine (250 ppm) +  $\text{Zn}^{2+}$  (50 ppm)



**Figure 5.** The cross sectional profile which are corresponding to as shown broken lines in AFM images of the surface of g) polished carbon steel (Control); h) carbon steel immersed in well water (blank); i) carbon steel immersed in well water containing Glycine 250 ppm + Zn<sup>2+</sup> 50 ppm

### Mechanism of Corrosion inhibition

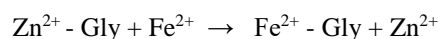
The results of the weight-loss study show that the formulation consisting of 250 ppm Gly and 50 ppm of Zn<sup>2+</sup> has 82% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn<sup>2+</sup> and Gly. Polarization study reveals that this formulation functions as anodic inhibitor. FTIR spectra reveal that the protective film consists of Fe<sup>2+</sup>-Gly complex and Zn(OH)<sub>2</sub>. (In order to explain these facts the following mechanism of corrosion inhibition is proposed.<sup>64-70</sup>

When the solution containing well water, 50 ppm Zn<sup>2+</sup> and 250 ppm of Gly is prepared, there is formation of Zn<sup>2+</sup>-Gly complex in solution.

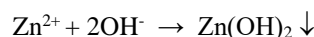
When carbon steel is immersed in this solution, the Zn<sup>2+</sup>-Gly complex diffuses from the bulk of the solution towards metal surface.

Zn<sup>2+</sup>-Gly complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe<sup>2+</sup>-Gly complex, which is more stable than Zn<sup>2+</sup>-Gly.<sup>49</sup>

On the metal surface Zn<sup>2+</sup> - Gly complex is converted in to Fe<sup>2+</sup> - Gly on the anodic sites. Zn<sup>2+</sup> is released.



The released Zn<sup>2+</sup> combines with OH<sup>-</sup> to form Zn(OH)<sub>2</sub> on the cathodic sites.<sup>49</sup>



Thus the protective film consists of Fe<sup>2+</sup>-Gly complex and Zn(OH)<sub>2</sub>.<sup>71,72</sup> The AFM images confirm the formation of protective layer on the metal surface.

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