Deterioration resistance Behavior of Carbon Metal in Salt Water by Alanine- Zn^{2+} System

[1]S. Gowri, [2]J. Sathiyabama

[1]PG Department of Chemistry, St. Antonys's College of Arts and Sciences For Women, Thamaraipadi, Dindigul, Tamilnadu, India. gowrisri2411@gmail.com

[2]Research Dean, PG and Research Department of Chemistry, Corrosion Research Centre, GTN Arts College, Dindigul, TamilNadu, India.

Abstract - The inhibition effectiveness of Alanine - Zn^{2+} system in scheming deterioration of carbon steel in salt water has been evaluate by mass loss method. The formulation consisting of 250 ppm of Alanine and 25 ppm of Zn^{2+} has 87% IE. A synergistic effect exists among Alanine and Zn^{2+}. Polarization analysis reveals to facilitate the Alanine - Zn^{2+} system function as an anodic inhibitor and the formulation controls the anodic reaction mostly. The character of the shielding film on metal shell has been analyzed by AFM analysis.

Keywords: ***AFM, Amino acids, Alanine, Carbon Steel, Electro chemical techniques, Seawater.***

I. INTRODUCTION

Corrosion is a process through which metals in manufactured states return to their natural oxidation states. This process is a reduction-oxidation reaction in which the metal is being oxidized by its surroundings, often the oxygen in air. This reaction is both spontaneous and electrochemically favored. Corrosion is essentially the creation of voltaic, or galvanic, cells where the metal. [1-3]. Various techniques have been used to evaluate the corrosion inhibition efficiency of amino acids and to analyze the nature of protective film formed on the metal surface. Depending on the nature of metal and nature of corrosive environment amino acids obeys different types of isotherms and behaves as different type of inhibitor, namely, anodic, cathodic or mixed type.[4]

Amino acids have the ability to manage the deterioration of dissimilar metals.[5-8]

Normally amino acids contain two polar groups, namely, one amino group and one carboxyl group. It preserve harmonize with metals during the nitrogen atom and oxygen atom of the carboxyl group. A review of the existing literature reveals that the corrosion self-consciousness by amino acids (Glycine, alanine, glatamic acid and methionine) on copper, Carbon metal and Aluminium electrode in aqueous medium has been investigated.[6]

The present work is under taken;

1. To estimate the self-consciousness effectiveness of Alanine- Zn2+ system in controlling deterioration of carbon metal immerse in the absence and presence of Zn2+ by mass loss method.

2. To examine the mechanistic aspects of corrosion inhibition by means of electrochemical studies like polarization study.

3. To investigate the shielding film by AFM.

Experimental

Carbon metal specimens [0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron] of dimensions 1.0 cm x 4.0 cm x 0.2 cm were refined to a mirror finish and degreased with trichloroethylene.

Weight loss method

Carbon metal specimens were immerse in 100 mL of the salt water containing different concentrations of the inhibitor in the presence and absence of Zn2+ for one day. The mass of the specimens before and after immersion was resolute using a Shimadzu balance, model AY62. The deterioration products were cleansed with Clarke's solution17. The inhibition effectiveness (IE) was then intended using the equation:

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

Where W1 = corrosion rate in the absence of the inhibitor, W2 = corrosion rate in the presence of the inhibitor.

Potentiodynamic polarization

Polarization study was carry out in a CHI- electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrode cell assembly was used. The working electrode was carbon metal. A SCE was the reference electrode. Platinum was the counter electrode. From polarisation study, corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr), Tafel slopes anodic = ba and cathodic = bc

 DOI : 10.35291/2454-9150.2020.0277

and LPR value. The scan rate (V/S) was 0.01. Hold time at (Efcs) was zero and quiet time (s) was two.

Atomic Force Microscopy characterization (AFM)

The carbon metal specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. Atomic force microscopy (Veeco dinnova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 µm × 5 µm and the scan rate was 0.6 HZ /second.

II. RESULTS AND DISCUSSION

Analysis of Weight loss Study

Corrosion rate (CR) of carbon steel immersed in sea water in the absence and presence of inhibitors (Alanine and Zn^{2+} system):

The calculated corrosion inhibition efficiency (IE) and corrosion rates (CR) of Ala in controlling corrosion of carbon steel in sea water, for a period of one day in absence and presence of Zn^{2+} are given in Table 1.

It is observed from the Table 1, that the calculated value indicates the ability of Alanine to be a good inhibitor. The IE is found to be enhanced in the presence of Zn^{2+}. Ala alone shows some inhibition efficiencies. 50 ppm of Alanine shows 15% of IE, as the concentration of Alanine increases, the IE also increases. Similarly for a given concentration of Alanine the IE increases as the concentration of Zn^{2+} increases. A synergistic effect exists between Alanine and Zn^{2+}. For example, 25 ppm of Zn^{2+} has 64 % of IE; 250 ppm of L-Ala has 35 % IE. Interestingly their combination has high IE, namely, 87%.

Therefore the mixture of inhibitors shows better IE than individual inhibitors. In the presence of Zn^{2+}, more amount of Alanine is transported towards the metal surface. Fe^{2+} - L-Ala 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. This accounts for the synergistic effect existing between Zn^{2+} and Alanine. [1-6]

Table 1 Inhibition efficiencies (IE) and corrosion rates (CR) obtained from Alanine- Zn^{2+} systems, when the carbon steel immersed in sea water

Inhibitor system: Alanine- Zn^{2+} **Immersion period: 1 day**

Alanine (ppm)	Zn^{2+} (0 ppm)		Zn^{2+} (15 ppm)		Zn^{2+} (20 ppm)		Zn^{2+} (25 ppm)	
	IE %	CR mmpy	IE %	CR mmpy	IE%	CR mmpy	IE%	CR mmpy
0	-	0.1809	41	0.1067	41	0.1607	64	0.0651
50	15	0.1538	42	0.1049	43	0.1031	66	0.0615
100	17	0.1501	42	0.1049	48	0.0941	69	0.0561
150	25	0.1357	45	0.0995	52	0.0868	73	0.0488
200	31	0.1248	46	0.0967	57	0.0778	81	0.0344
250	35	0.1176	49	0.0923	62	0.0687	87	0.0235

Analysis of polarization curves of Alanine - Zn^{2+} system

Polarization analysis has been used to detect the formation of protective film on the metal surface during corrosion inhibition process. The calculated corrosion parameters such as corrosion potential (E_{corr}), tafel slopes (anodic slope b_a and cathodic slope b_c), Linear polarization resistances (LPR) and corrosion current (I_{corr}) values are given in the Table 2 The potentiodynamic polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitors are shown in Fig 1.

When the carbon steel is immersed in the sea water the corrosion potential is -784 mV vs SCE (saturated calomel electrode). The inhibitor system (Alanine (250 ppm) - Zn^{2+} (25 ppm)) shifts the corrosion potential to -774 mV vs SCE. This indicates that the anodic reaction is controlled predominantly.The corrosion current value and the LPR values for sea water are 7.042×10^{-6} A/cm^2 and 5.375×10^3 Ωcm^2 respectively. In the presence of inhibitors, the corrosion current value decreases to 6.202×10^{-6} A/cm^2 and the LPR value has increased to 6.124×10^3 Ωcm^2. This indicates that a protective film formed on the metal surface. [7].

 DOI : 10.35291/2454-9150.2020.0277

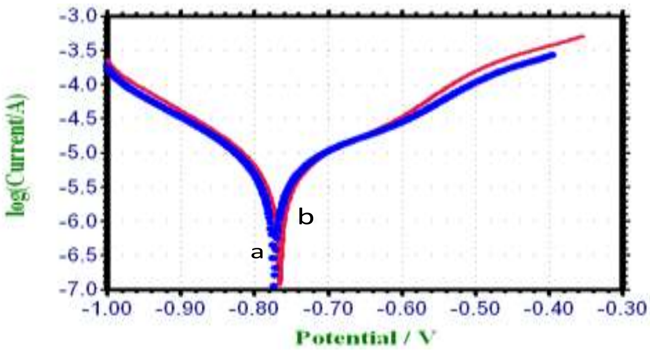


Fig 1. Polarization curves of carbon steel immersed in various test solutions
(a) Sea water (b) Sea water +250 ppm of Alanine + 25 ppm of Zn^{2+}

Table 2. Corrosion parameters of carbon steel immersed in sea water in the presence and absence of inhibitor obtained by polarization method

Alanine (ppm)	Zn^{2+} (ppm)	E_{corr} (mV vs SCE)	I_{corr} (Acm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	LPR (Ωcm^2)
0	0	-784	7.042×10^{-6}	232	139	5.375×10^{3}
250	25	-774	6.202×10^{-6}	215	147	6.124×10^{3}

Analysis of AC impedance Spectra for Alanine- Zn^{2+} system

AC impedance spectra have been used to detect the formation of protective film on the metal surface. Nyquist plot representation of carbon steel immersed in sea water in the absence and presences of inhibitors are shown in the Fig 2. The impedance parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values are given in the Table If a protective film formed on the metal surface, the charge transfer resistance (R_t) and double layer capacitance value decreases. It is clear from the plots that the impedance response of carbon steel significantly changed after addition of the inhibitors. The impedance diagram obtaines almost semicircular appearance. This indicates that the corrosion of carbon steel in aqueous solution is mainly controlled by a charge transfer process. The deviation from the perfect semicircle shape is due to the frequency dispersion of interfacial impedance. This anomalous behavior is generally due to the non- homogeneity of the metal surface arising from surface roughness or interfacial phenomena.

From the table the R_t value is 120.22 Ωcm^2 and C_{dl} value is 4.242×10^{-8} F/cm^2. When L-Ala (250 of ppm) and Zn^{2+} (25 of ppm) are added to sea water, R_t value increases from 120.22 Ωcm^2 to 129.46 Ωcm^2. The C_{dl} value decreases from 4.242×10^{-8} F/cm^2 to 3.939×10^{-8} F/cm^2. This confirms that the formation of protective film on the metal surface. This accounts for the very high IE of Alanine – Zn^{2+} system.[8]

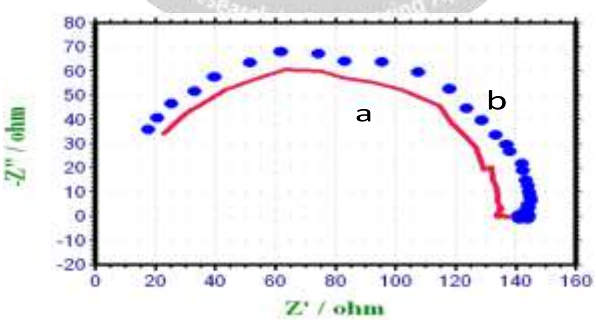


Fig 2 AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots)
(a) Sea water Sea water +L-Ala (250 ppm) + Zn^{2+} (25 ppm)

Table 3. Impedance parameters of carbon steel immersed in sea water in the absence and presences of inhibitors obtained by AC impedance spectra

L-Ala (ppm)	Zn^{2+} (ppm)	R_t (Ωcm^2)	C_{dl} (F/cm^2)
0	0	120.22	4.242×10^{-8}
250	25	129.46	3.939×10^{-8}

 DOI : 10.35291/2454-9150.2020.0277

Atomic Force Microscopy Characterization

Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. AFM is a powerful technique for the gathering of roughness statistics from a variety of surfaces. AFM becoming an accepted method of roughness investigation

The two dimensional (2D), three dimensional (3D) AFM morphologies and AFM cross- sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in sea water (blank sample) and the carbon steel surface immersed in sea water containing Alanine (250 ppm) – Zn^{2+} (25 ppm) are shown in Figs.3.1, 3.2 and 3.3 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). R_q is much more sensitive than R_a to Large and small height deviations from the mean.

The (R_q), (R_a), (P-V) value for carbon steel surface immersed in different environment are summarized in Table

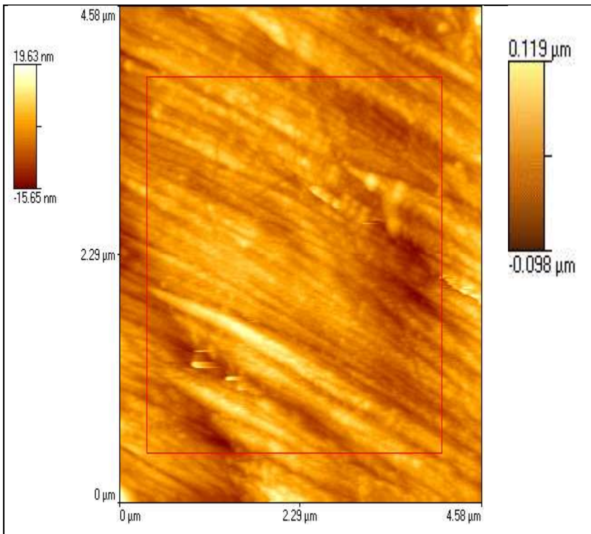
In Fig.3.1a. 3.2a, 3.3a the surface topography of uncorroded metal surface is shown. The values of R_q, R_a and P-V height for the polished carbon steel surface (reference sample) are 4.33 nm, 3.41 nm and 35.28 nm respectively. The data indicates a homogeneous surface. The slight roughness observed on the polished carbon steel surface is due to the atmospheric corrosion.

Figs.3.1b, 3.2b and 3.3b shows the pitted, corroded metal surface in the absence of the inhibitor immersed in sea water. The R_q, R_a and P-V height values for carbon steel surface are 40.2 nm, 31 nm and 191.9 nm respectively. These data suggest that carbon steel surface immersed in sea water has a far greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rough due to the corrosion of the carbon steel in sea water environment.

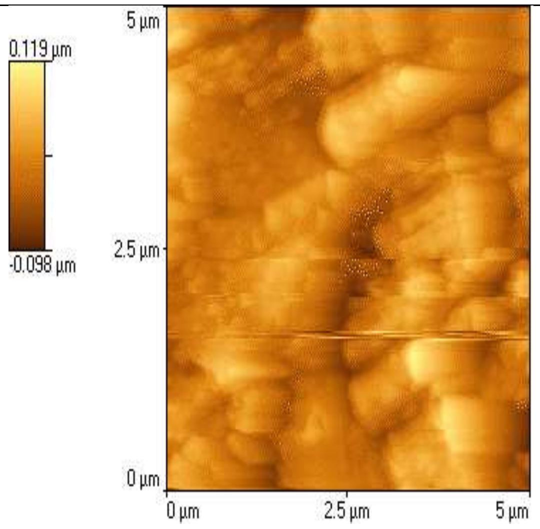
Figs.3.3c, 3.4c and 3.3c show the steel surface after immersion in sea water containingL-Ala (250 ppm) – Zn^{2+} (25 ppm). The R_q, R_a and P-V height values for carbon steel surface are 32.2 nm, 24.1 nm and 130.5 nm respectively. The R_q, R_a and P-V height values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+}-L-Ala complex and $Zn(OH)_2$ on the metal surface, thereby inhibiting the corrosion of carbon steel.

Also the increase in R_q, R_a and P-V values for carbon steel immersed in sea water in the presence of inhibitors, which are somewhat greater than the R_q, R_a and P-V height values of polished metal surface, confirms the presence of the film on the metal surface, which is protective in nature.[9]

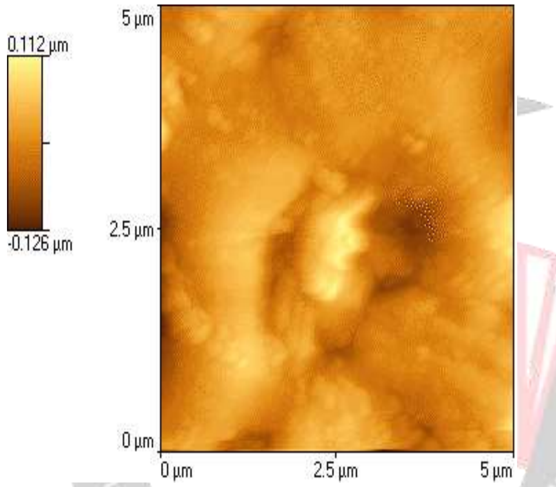
 DOI : 10.35291/2454-9150.2020.0277



(a)



(b)



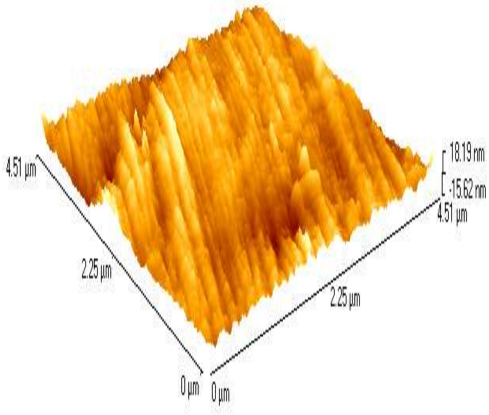
(c)

Fig. 3.1. Two dimensional AFM image of the surface

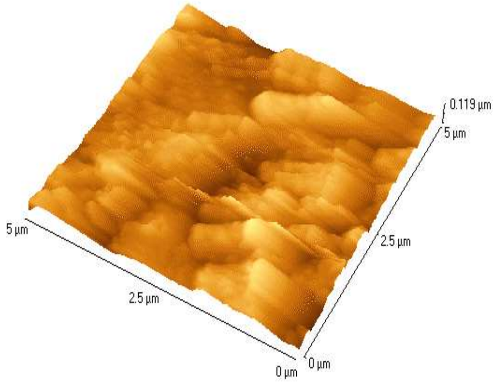
- **a) Polished carbon steel (control)**
- **b) Carbon steel immersed in sea water (blank)**
- **c) Carbon steel immersed in sea water containing Alanine (250 ppm) + Zn^{2+} (25 ppm)**

 DOI : 10.35291/2454-9150.2020.0277

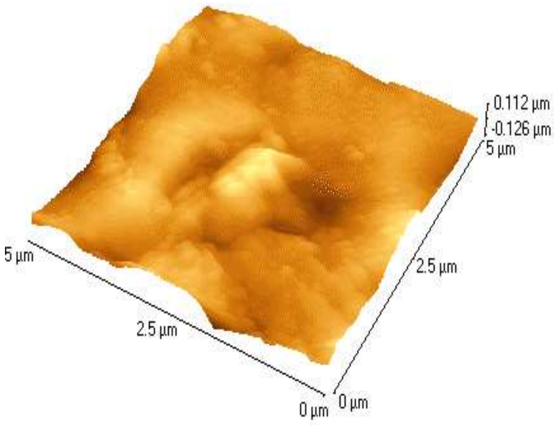
ISSN : 2454-9150 Vol-06, Issue-01, Apr 2020



(a)



(b)



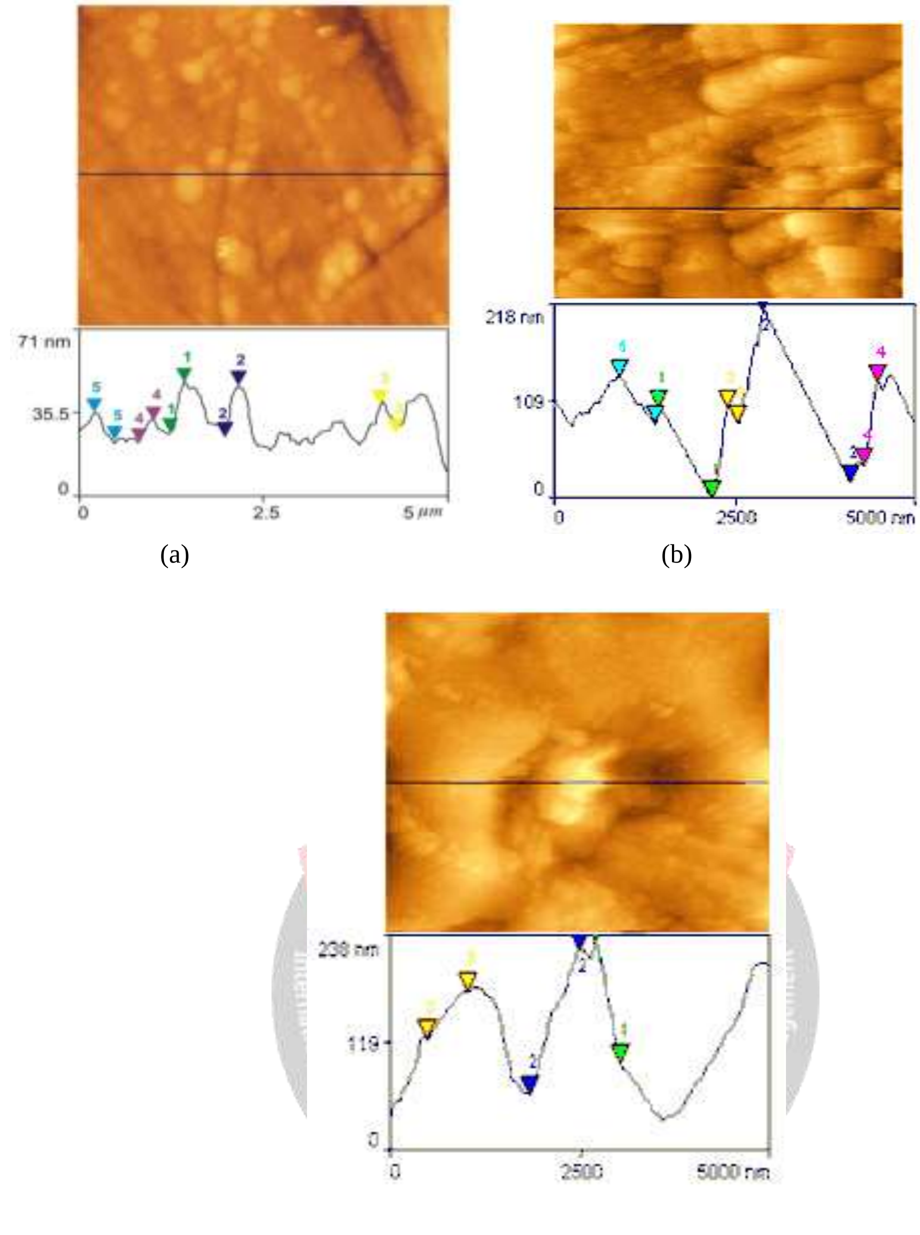
(c)

Fig3.2. Three dimensional AFM images of the surface of

a) **Polished carbon steel (control)**
b) **Carbon steel immersed in sea water (blank)**
c) **Carbon steel immersed in sea water Alanine (250 ppm) + Zn^{2+} (25 ppm)**

 DOI : 10.35291/2454-9150.2020.0277

ISSN : 2454-9150 Vol-06, Issue-01, Apr 2020



(c)

Fig.3.3 AFM cross sectional image of the surface of

a) Polished carbon steel (control)

b) Carbon steel immersed in sea water (blank)

c) Carbon steel immersed in sea water containing Alanine (250 ppm) + Zn^{2+} (25 ppm)

Table 4. AFM data for carbon steel surface immersed in inhibited and uninhibited environment

Sample	RMS(R_q) Roughness (nm)	Average(R_a) Roughness (nm)	Maximum Peak-to-valley height (nm)
1.Polished carbon steel	4.33	3.41	35.28
2.Carbon steel immersed in sea water (blank)	40.2	31.0	191.1
3.Carbon steel immersed in sea water + 250 ppm of Alanine+ 25 ppm Zn^{2+}	32.2	24.1	130.5

 DOI : 10.35291/2454-9150.2020.0277

ISSN : 2454-9150 Vol-06, Issue-01, Apr 2020

III. MECHANISM OF CORROSION INHIBITION

The results of weight loss study shows that the formulation consisting of 250 ppm of Alanine and 25 ppm of Zn^{2+} has 87% IE, in controlling corrosion of carbon steel in sea water. A synergistic effect exists between Alanine and Zn^{2+}. The polarization study reveals that the Alanine- Zn^{2+} system functions as anodic inhibitor controlling anodic reaction predominantly and controls cathodic reaction to some extent. AC impedance spectra and AFM analysis reveals that the formation of protective film on the metal surface.

When the solution containing sea water, 25 ppm Zn^{2+} and 250 ppm of Alanine is prepared, there is formulation of Zn^{2+}-Alanine complex in solution.

- When the carbon steel is immersed in this solution, the Zn^{2+}- Alanine complex diffuses from the bulk of the solution towards metal surface.
- Zn^{2+}- Alanine complex diffuses from the bulk of the solution to the surface of the metal and is converted into a Fe^{2+}-Alanine complex, which is more stable than Zn^{2+-} Alanine.
- On the metal surface Zn^{2+} - Alanine complex is converted in to Fe^{2+}-L-Ala on the anodic sites. Zn^{2+} is released.

  $$Zn^{2+}\text{- Alanine} + Fe^{2+} \text{-------}\rightarrow Fe^{2+}\text{- Alanine} + Zn^{2+}$$

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

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

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

IV. CONCLUSION

The inhibition effectiveness of Alanine - Zn^{2+} system in scheming deterioration of carbon metal in salt water has been evaluate by mass loss method. The formulation consisting of 250 ppm of Alanine and 25 ppm of Zn^{2+} has 87% IE. A synergistic effect exists among Alanine and Zn^{2+}. Polarization analysis reveals to facilitate the Alanine - Zn^{2+} system function as an anodic inhibitor and the formulation controls the anodic reaction mostly. The character of the shielding film on metal shell has been analyzed by AFM analysis

REFERENCE

[1] Landolt, Dieter. Corrosion and Surface Chemistry of Metals. EPFL Press, 2007.

[2] Perez, Nestor. Electrochemistry and Corrosion Science . Kluwer Academic Publishers, 2004.

[3] Petrucci, Ralph H., William S. Harwood, F G. Herring, and Jeffry D. Madura. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Pearson Education, Inc, 2007.

[4] S. Gowri, J. Sathiyabama, S. Rajendran, *Corrosion Inhibition By Amino Acids - An Over Review Eur. Chem. Bull.* 2012, *1(11)*, 470-476.

[5] Eddy N.O., *Journal of Advanced Research*, 2011, *2(1)*, 35-47.

[6] Gece G., Bilgiç S., *Corrosion Science*, 2010, *52(10)*, 3435-3443

[7] Khaled K.F, *Corrosion Science*, 2010, *52(10)*, 3225-3234.

[8] Tkalenko D.A., Venkatesvaran G., Vishevskaya Yu.P., Keny S.J., Byk M.V., Muthe K., *Protection of Metals and Physical Chemistry of Surfaces*, 2010, *46(5)*, 609-614.

[9] S.Gowri, Corrosion Inhibition of Carbon Steel in Sea Water by Glutamic Acid - Zn2+ System, *Chem Sci Trans.*, 2013, 2(1), 275-281 Chemical Science Transactions.

 DOI : 10.35291/2454-9150.2020.0277