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Corrosion Inhibition by Self Assembling Nanofilms of Glutaric Acid

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Abstract: **The inhibition efficiency of glutaric acid in controlling corrosion of Aluminium in an aqueous solution at pH 10, in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm of glutaric acid and 50 ppm of Zn^{2+} has 90% corrosion inhibition efficiency. A synergistic effect exits between glutaric acid and Zn^{2+}. The mechanistic aspects of corrosion inhibition have been evaluated by polarization study. In the presence of inhibitor, linear polarization resistance increases and corrosion current decreases; The protective film has been analyzed by FTIR spectroscopy. The protective film consists of Aluminium-glutaric acid complex and zinc-glutaric acid complex. The surface morphology of the film has been investigated by AFM. The protective film is in the order of nano range. The protective film consists of self assembled monolayers of glutaric acid which is confirmed by FTIR spectroscopy and AFM study.**

Keywords: **Corrosion inhibition, Aluminium at pH 10, glutaric acid, FTIR, AFM, self assembling nanofilms.**

1. INTRODUCTION

Many researches are going on in the field on nano technology,because nanoparticles have special properties (optical, electrical etc) and special application in many fields. Aluminium is 100% recyclable without any loss of its natural qualities. In Europe aluminium experiences high rates of recycling, ranging from 42% of beverage cans, 85% of construction materials and 95% of transport vehicles [1]. Corrosion resistance can be excellent due to a thin surface layer of aluminium oxide that forms when the metal is exposed to air, effectively preventing furtheroxidation. The strongest aluminium alloys are less corrosion resistant due togalvanic reactions with alloyed copper [12]. This corrosion resistance is also often greatly reduced when many aqueous salts are present, particularly in the presence of dissimilar metals.

The present work is undertaken:

*To evaluate the inhibition efficiency of glutaric acid in controlling corrosion of aluminium immersed in an aqueous solution at pH 10, in the absence and presence of Zn^{2+} using the weight loss method

*To study the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and AC impedance spectra

* To analyze the protective film by FTIR and AFM spectra.

2. METHODS AND MATERIALS

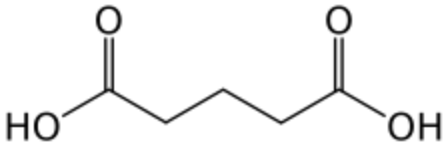
2. 1 Preparation of specimens:

Commercial aluminium specimens of dimensions 1. 0 x 4. 0 x 0. 2cm, containing 95% pure aluminium were polished to mirror finish, degreased with trichloroethylene, and used for the mass-loss method.

2. 2 Inhibitor solution:

1g glutaric acid was dissolved in double distilled water and NaoH solution and the solution was made up to 100ml. The pH of the solution is 10 and this solution was used as a inhibitor solution

The structure of glutaric cacid is shown in scheme 1.



Scheme 1 –glutaricacid

2. 3. Weight loss method:

Three aluminium specimens were immersed in 100ml of the solution at pH 10 and various concentrations of the inhibitor in the absence and presence of Zn^{2+} for a period of 1 day. The weight of the specimen before and after immersion was determined using Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship.

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

Where W1 and W2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

2. 4. Potentiodynamic polarization study:

Polarization study was carried out in a CHI electrochemical work station impedance analyzer model 660A. A three electrode cell assembly was used. The working electrode was Aluminium, A saturated calomel electrode (SCE) was the reference electrode and platinium was the counter electrode. The corrosion parameters such as linear polarization Resistance. (LPR), corrosion potential, E_{corr}, corrosion current, I_{corr}, and Tafel slopes (b_a and b_c) were measured.

2. 5. Alternating current impedance spectra:

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance **(**C_{dl}) values were calculated.

2. 6. Atomic Force of microscopy:

Atomic force microscopy is a powerful technique for gathering statistics from a variety of surfaces. Atomic force microscopy (Veeco diInnova model)was used to observe the samples surface in tapping model, using cantilever with linear tips. The scanning image in the image was 5µm x 5µm and the scan rate was 0. 6Hz /seconds

2. 7 FTlR Spectra:

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

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3. RESULTS AND DISCUSSION

3. 1. Analysis of the weight loss method:

The corrosion rate of aluminium in an aqueous solution at pH 10 in the absence and presence of inhibitor obtained by weight loss method are given in Table 1. The inhibition efficiency are also given in Table-1. It is observed from Table -1 that glutaric acid (GA) has good inhibition efficiency (IE). As the concentration of inhibitor increases, the inhibition efficiency (IE) also increased. As the concentration inhibitor increases, more inhibitor molecules are adsorbed on the metal surface and hence, corrosion protection increases. Corrosive ions are not able to attack the metal surface.

Table -1 Corrosion rates of Aluminium in an aqueous solution at pH 10,in the absence and presence of inhibitor system and the inhibition efficiencies (IE) obtained from weight loss method.

Inhibitor system : glutaric acid (GA)and Zn^{2+}

glutaric acid ppm	Zn^{2+} system ppm	Corrosion rate mdd	Inhibition efficiency %
0	0	23. 48	--
50	0	5. 40	77
100	0	4. 93	79
150	0	4. 69	80
200	0	4. 22	82
250	0	3. 52	85

Table -2 Corrosion rates of Aluminium in an aqueous solution at pH 10, in the absence and presence of inhibitor system and the inhibition efficiencies (IE) obtained from weight loss method.

Inhibitor system : glutaric acid (GA) and Zn^{2+}

glutaric acid ppm	Zn^{2+}system ppm	Corrosion rate mdd	Inhibition efficiency %
0	0	23. 48	--
0	50	19. 25	18
50	50	3. 28	86
100	50	2. 58	89
150	50	2. 34	90
200	50	1. 64	93
250	50	1. 17	95

3. 2. Influence of Zn^{2+} on the inhibition efficiency of glutaric acid (GA):

The influence of Zn^{2+} on the IE of GA is given in Table 1 and 2. In the presence of Zn^{2+} (50 ppm) excellent inhibitive property is shown by GA. A synergistic effect exists between GA and Zn^{2+} For example, 250 ppm of GA has 86% IE, 50 ppm of Zn^{2+} has 13 or 18% IE. But their combination has 95% inhibition efficiency. This suggest that a synergistic effect exist between GA and Zn^{2+}

3. 3. Analysis of polarization curves:

Polarization study has been used to confirm the formation of protective film formed on the metal surface during co rrosion inhibition process[3-15] The potentiodynamic polarization curves of aluminium immersed in various solutions at pH 10 are shown in Figure1. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_a, b_c) and linear polarization (LPR) are given in Table 3.

When aluminium is immersed in an aqueous solution at pH 10, the corrosion potential is -583 mV vs SCE. When the inhibitors are added, (250ppm of GA and 50ppm of Zn^{2+}) the corrosion potential shifted to anodic side (-434mV vs SCE). A shift of corrosion potential in the noble side is an indication of formation of protective film on the metal surface. Further LPR value increases from 50260 to 99482 Ohm cm^2 and corrosion current decreases from 5. 226 x 10^{-7} A/cm^2 to 2. 895x 10^{-7} A/cm^2. These results suggest that a protective film is formed on the metal surface.

Table -3 Corrosion parameters of Aluminium immersed in an aqueous solution at pH 10,in the absence and presence of inhibitor system obtained from polarization study

Inhibitor system : glutaric acid (GA)and Zn^{2+}

GA ppm	**Zn^{2+} ppm**	**E_{corr} mV vs SCE**	**bc mV**	**ba mV**	**LPR Ohm cm^2**	**I corr A/cm^2**
0	0	-583	293	284	50260	5. 226x10^{-7}
250	50	-434	178	105	99482	2. 895x10^{-7}

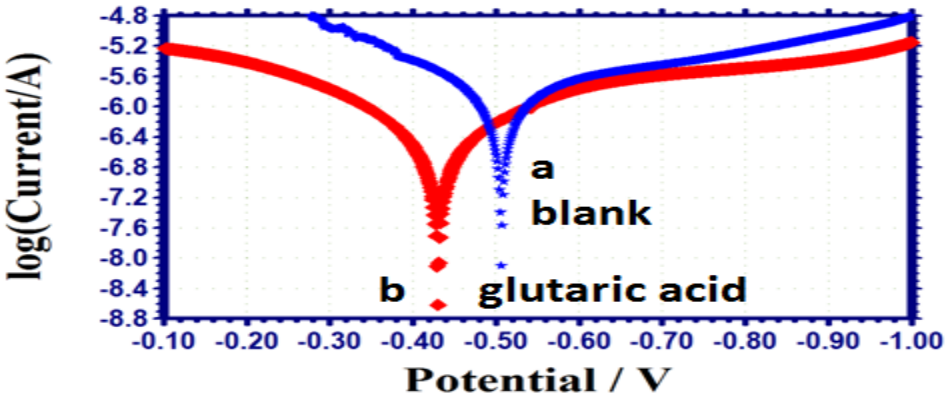


Fig 1:Polarization curves of aluminium immersed in various test solution.

a)Aqueous solution at pH 10. b)In presence of 250 ppm GA + 50 ppm Zn^{2+}.

3. 4. Analysis of AC impedance spectra:

AC impedance spectra (electrochemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases and double layer capacitance value (C_{dl}) decreases. The AC impedence spectra of aluminium immersed in various solution are shown in Figure. The Nyquist plots are shown in Fig 2(a) and 2(b). The Bode plots are shown in Fig 3(a) and 3(b). The corrosion parameters such as charge transfer resistance (Rt), double layer capacitance value (C_{dl}) derived from Nyquist and Bode plots are given in Table 4.

When aluminium is immersed in an aqueous solution at pH 10, the charge transfer resistance R_t is 1. 955 Ohm cm^2, the double layer capacitance $\mathbf{C_{dl}}$ is 5. 950 x 10^{-8} F/cm^2. When the formulation consisting of AA and Zn^{2+} is added, the R_t, value increases and C_{dl} value decreases. This confirms that a protective film is formed on the metal surface. This decreases the corrosion rate of aluminium and increases the inhibition efficiency.

Table -4 Corrosion parameters of Aluminium immersed in an aqueous solution at pH 10,in the absence and presence of inhibitor system obtained from AC impedance spectra

Inhibiton system: glutaric acid (GA) and Zn^{2+}

GA ppm	Zn^{2+} ppm	Rt Ohm cm^2	Cdl F/ cm^2	Bode plot Impedance log(z/ohm)
0	0	85. 71	5. 950x10^{-8}	1. 955
250	50	2937	1. 702x10^{-9}	3. 629

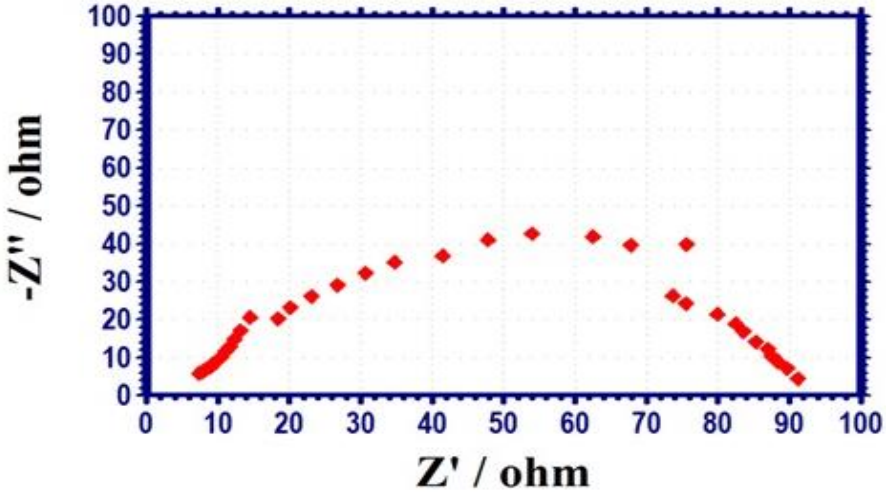


Fig 2(a) : AC impedance spectra of aluminium immersed in an aqueous solution at pH 10Nyquist plot)

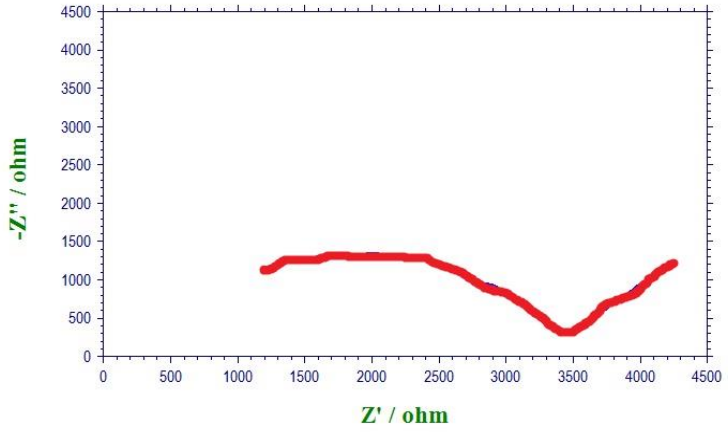


Fig 2 (b) : AC impedance spectra of aluminium immersed in an aqueous solution GA 250ppm + Zn^{2+} 50ppm at pH 10(Nyquist plot)

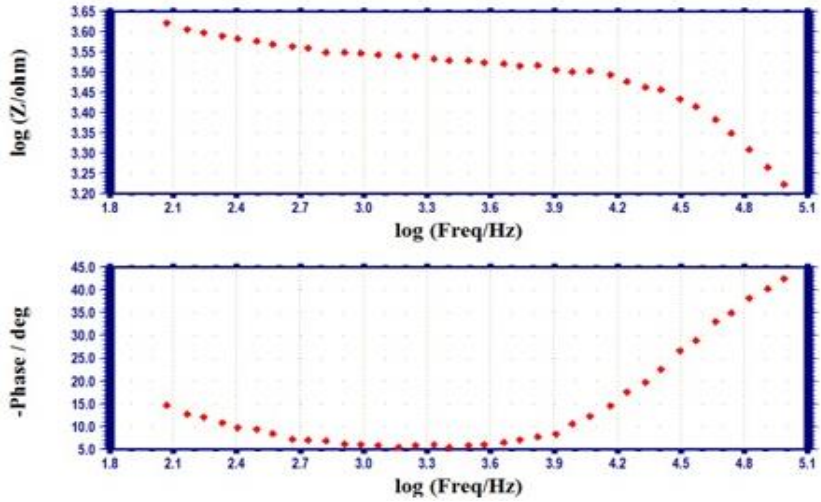


Fig 3(a) :AC impedance spectra of aluminium immersed in an aqueous solution at pH 10 (Bode plot)

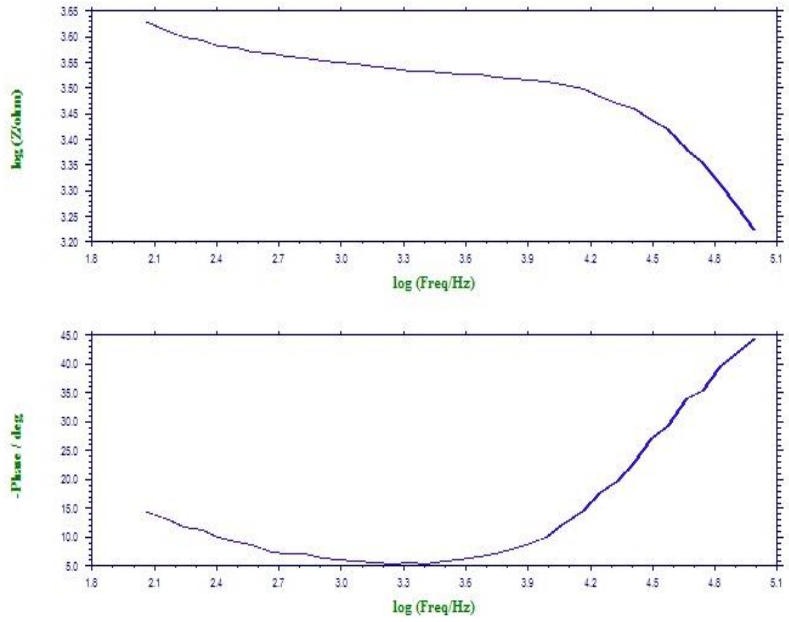


Fig 3(b) :AC impedance spectra of aluminium immersed in an aqueous solution in presence of GA 250ppm+ Zn^{2+} 50ppm pH 10 (Bode plot)

3. 7 Analysis of FTIR spectra:

FTIR spectra have been used to confirm the presence of protective film formed on metal surface [16]. FTIR spectra of pure adipic acid (kBr) is shown in Figure 4 (a). The peak appears at 1629. 3cm^{-1} is due to the CO stretching frequency of the carbonyl groups. The OH stretching frequency of the carboxyl groups appears at 3431. 9 cm^{-1}. The aliphatic CH stretching frequency appears at 2855. 2 cm^{-1}h. Thus adipic acid is confirmed by FTIR spectra. The FTIR spectra (kBr) of the protective film formed on the metal surface after immersion in the solution containing 250ppm of glutaricacid and 50ppm of Zn^{2+} is shown in Figure7 (b). Its observed that CO stretching frequency has shifted from 1629. 3cm^{-1} to1641. 4cm^{-1}. The OH stretching frequency has shifted from 3431. 9 cm^{-1}to 3450. 8 cm^{-1}. This suggest that adipic acid has coordinate with Al^{3+} on the metal surface through carbonyl oxygen atom of carboxyl groups. The peak at 673. 9 is due to a Metal –Oxygen bond[M-O]. The peak at 3450. 8 cm^{-1} is due to OH groups. This indicates that there is possibility of zinc hydroxide and /or aluminum hydroxide on metal surface. Thus if analysis of FTIR spectra leads to the conclusion that the protective film consist of Al^{3+} /Al complex and zinc hydroxide. There is also possibility of formation of aluminium hydroxide on the metal surface.

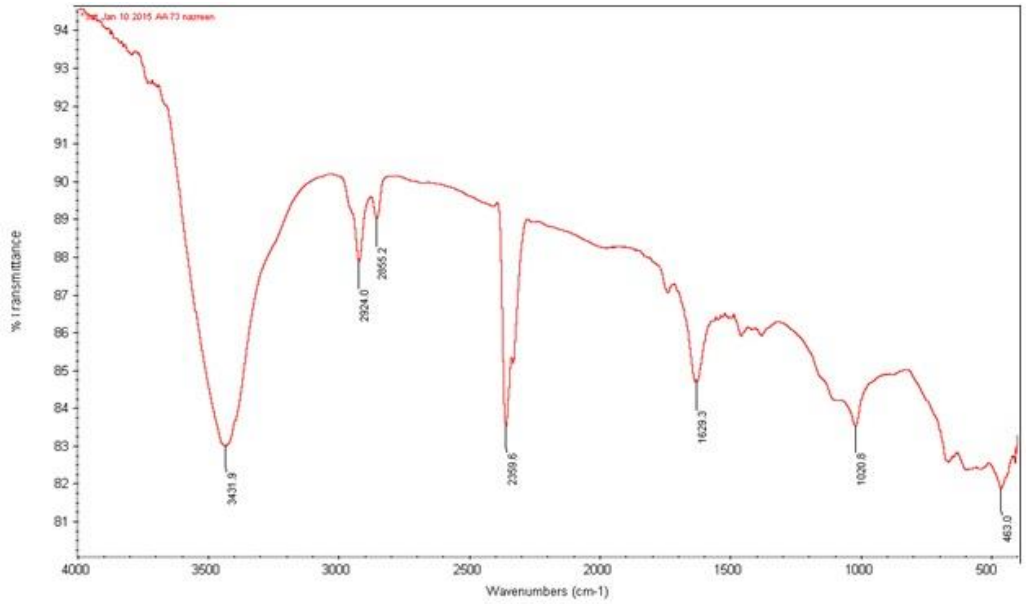


Fig -4a) FTIR spectrum of glutaric acid

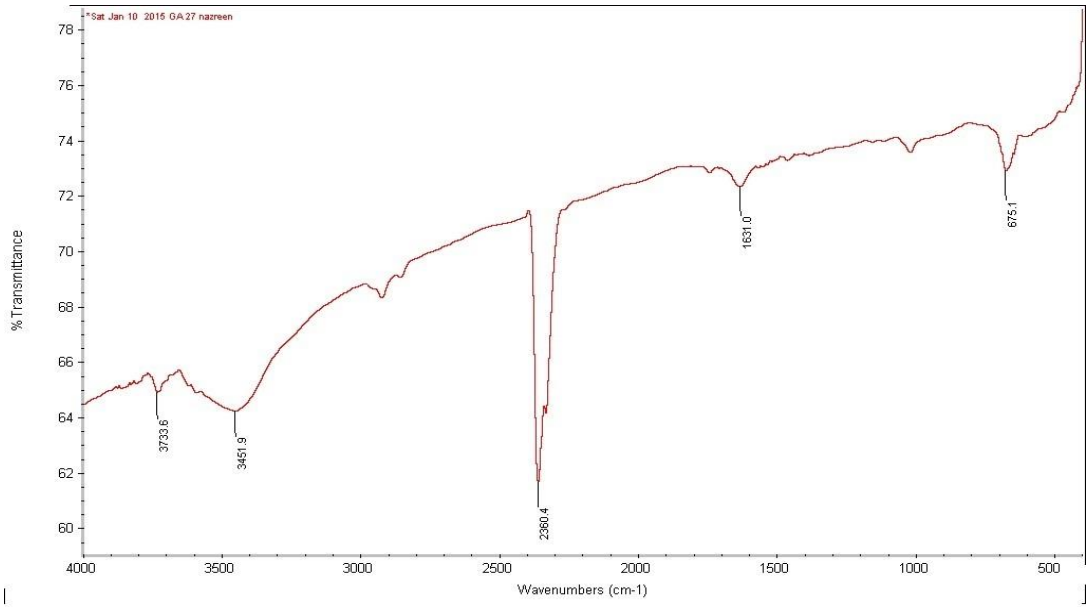


Fig -4 b) FTIR spectrum of film formed on metal surface after immersion in solution containing GA 250ppm+ Zn^{2+} 50ppm

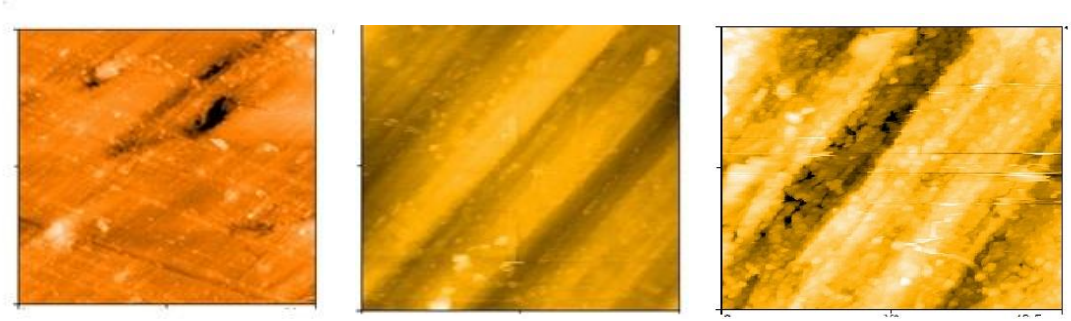
3. 9 Analysis of Atomic Force Microscopy:

Atomic Force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces [17]. AFM is becoming an accepted method of roughness investigation [18,19,20]. The AFM images of polished metal, surface immersed in corrosive medium (an aqueous solution pH 10) and that of film formed on metal surface after immersion in the inhibitor solution containing 250 ppm of GA and 50 ppm of Zn^{2+} are shown in Figure 10. The RMS roughness ($_{Rq}$), average roughness ($_{Ra}$) and peak valley (P-V) height are given in Table. 8. For polished metal surface, the RMS roughness (Rq) is 27. 95nm. When the metal is immersed in the corrosive medium, corrosion products are produced and hence the RMS roughness is very high (612. 8nm). Interestingly, in the inhibitor system, the roughness is less (78. 7nm) than that for corrosive medium; but higher than that for the polished metal. This indicates that a protective film is formed on the metal surface whose thickness is of the order of 78. 7nm. This is due to the formation of self assembling monolayers of adipic acid on the metal surface on the anodic sites of the metal surface.

Table -5 AFM data for glutaric acid and Zn^{2+} surface immersed in inhibited and uninhibited environment

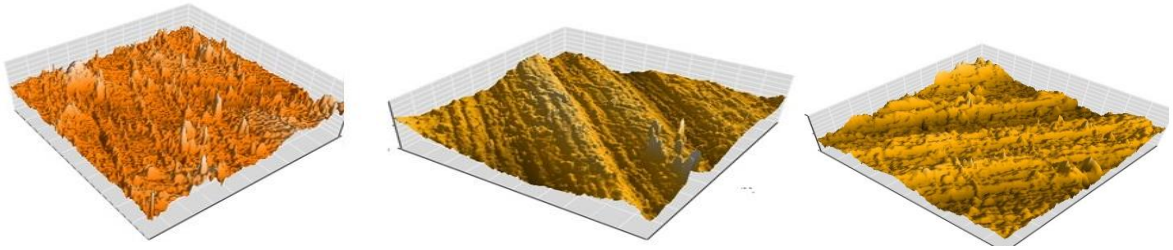
Samples	**RMS roughness $(_{Rq})_{nm}$**	**Average roughness $(_{Ra})_{nm}$**	**Peak - Valley (P-V) height $_{nm}$**
Polished metal	27. 95	34. 91	238. 92
Metal in corrosive medium	168. 8	189. 08	332. 95
Metal in presence of inhibitors	66. 07	79. 61	225. 11

(Rq is RMS roughness, Ra is Average roughness,P-V is maximum Peak –to –valley Height)



(a) polished metal **(b) Metal in corrosive medium** **(c) Metal in presence of inhibitors**

Fig 5: 2D AFM images of the surface of Aluminum metal



(c) polished metal **(d) Metal in corrosive medium** **(c) Metal in presence of inhibitors**

Fig 6: 3D EDX images of the surface of Aluminium metal

4. CONCLUSION

* The present study leads to the following conclusion

* The Formulation consisting of 250ppm of glutaric acid and 50ppm of Zn^{2+} offers 95% inhibition efficiency of aluminum immersed in an aqueous solution at pH 10;

* Polarization study reveals that the composition of 250 ppm GA and 50 ppm Zn^{2+} function as the anodic inhibitor;

* AC impedance spectra reveals that a protective film formed on the metal surface;

* FTIR spectra reveal that the protective film consists of Al^{3+} /Al complex and $Zn(OH)_2$

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