



Inhibition of corrosion of aluminium in alkaline medium by succinic acid in conjunction with zinc sulphate and diethylene triamine penta (Methylene phosphonic acid)

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ABSTRACT

The inhibition efficiency (IE) of succinic acid (SA) in conjunction with Zn^{2+} and diethylene triamine penta (methylene phosphonic acid) [DTPMP] on the corrosion of aluminium in 0.01M NaOH was investigated by weight loss and electrochemical techniques. The ternary system SA (240 ppm) – Zn^{2+} (20 ppm) - DTPMP (20ppm) has 98% IE. IE values calculated from electrochemical polarization studies were in good agreement with those calculated from weight loss studies. ΔG Values were calculated from surface coverage values. Effect of temperature on the IE was also studied from which E_a and ΔH were computed. Surface morphology studies were done using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The inhibitors act as mixed inhibitors and obey Langmuir adsorption isotherm.

Key words: *Aluminium corrosion, Mixed type inhibitors, Succinic acid, adsorption isotherm, surface morphology.*

INTRODUCTION

Corrosion of aluminium and its alloys have been a subject of numerous studies due to their high technological value and wide range of industrial and house hold applications. Aluminium and its alloys are very good corrosion resistant materials in neutral aqueous solution, due to the formation of passive film. It is well known that pitting corrosion occurs on metals covered with passive films. The Cl^- ions cause the passive film to break down at certain weak spots on the metal surface. During pitting corrosion large parts of the metal surface are covered with a protective film and are in the passive state, while other small parts of the surface are in the active state. Corrosion behaviour of aluminium in various media has been studied. Several inhibitors have been used to control the corrosion of aluminium. To prevent the corrosion of aluminium in acid medium, inhibitors such as imidazoline derivatives [1], Capparis decidua [2] polyethylene glycol and polyvinyl alcohol [3], delonix regia extract [4] and Sansevieria trifasciata extract [5], have been used. In alkaline medium, adipic acid-DTPMP[6], polyvinyl alcohol [7], gongronema latifolium extract [8], bismark brown dye [9], methyl orange [10], [3 – (4 – hydroxy – 3 methoxy – phenyl) – 1 – phenyl – propenone] [11], 1 – (2,4 – dihydroxy phenyl) – 3 - (2 – hydroxyl phenyl) – propenone [12], adathoda vasica leaves extract [13] and onion and onion extract, [14] have been used as corrosion inhibitors to prevent corrosion of aluminium. Corrosion inhibition of aluminium using super hydrophobic films [15], structure and stability of adhesion promoting aminopropyl phosphonate layers at polymer / aluminium oxide interfaces [16], microbially influenced corrosion of aluminium [17], corrosion inhibition of aluminium by rare earth chlorides [18], effects of inhibitors on corrosion behaviour of dissimilar aluminium alloy corrosion using fluorometric methods [19], surface modification for aluminium pigment inhibition [20] and filiform on 6000 series aluminium [21], have been investigated. Because of the voice raised by environmental scientists, several corrosion researchers have started using environmental friendly natural products as corrosion inhibitors [22-26]. Water extracts from leaves of date palm, phoenix dactylifera, henna, Lawsonia inermis, corn and Zea mays, were tested as corrosion inhibitors for

steel, aluminium, copper and brass in acid chloride and sodium hydroxide solutions, using weight loss, solution analysis and potential measurements [27]. Priya *et al.* have studied the corrosion behaviour of aluminium in rain water containing garlic extract [28]. Jain *et al.* have investigated the electrochemical behaviour of aluminium in acidic media [29]. Several investigators have reported the corrosion inhibition behaviour of carbon steel, mild steel and copper in acidic medium[30-33].

This paper reports the corrosion behaviour of commercial aluminium metal in 0.01 M NaOH solution and the inhibition of corrosion of aluminium by succinic acid, Zn²⁺ and DTPMP at 30^o, 40^o and 50^oC. Weight loss method and electrochemical techniques were used to calculate the IE Values.

Free energy change, activation energy and enthalpy values were computed and discussed. Surface morphology of the metal surface was studied using SEM and AFM. Langmuir adsorption isotherm was drawn and analysed.

EXPERIMENTAL SECTION

Commercial aluminium specimens, of dimensions 1.0x 4.0 x 0.14 cm, containing 99% pure aluminium were polished to a mirror finish, degreased with trichloro ethylene, and used for the weight loss method and for surface examination studies. All the weighings of the aluminium specimens before and after corrosion were carried out using a Denver Electronic balance (TP214) with readability of and 0.1 mg in 200g range. This balance has reproducibility (standard deviation) of 0.1 mg. AR grade ZnSO₄, succinic acid and DTPMP were used to prepare inhibitor combinations in double distilled water.

Determination of inhibition efficiency (IE)

The weighed specimens in triplicate were suspended by means of glass hooks in 150ml beakers containing 100 ml of various test solutions in 0.01M NaOH medium. After one hour of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weight of the specimens, the corrosion inhibition efficiency (IE) was calculated using the equation:

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

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

Corrosion Rate (C_R) is calculated by using the following relationship, in mmpy unit.

$$C_R = \frac{\text{Weight loss (mg)} \times 87.6}{\text{Immersion Time (h)} \times \text{density of the metal (g/cm}^3\text{)} \times \text{area of specimen (cm}^2\text{)}}$$

$$\text{Surface coverage } (\theta) = \frac{(W_1 - W_2)}{W_1}$$

Where W₁ = Corrosion rate in the absence of the inhibitor (blank) and W₂ = Corrosion rate in the presence of the inhibitor.

The effect of temperature on the IE was studied at three different temperatures, namely, 30^oC, 40^oC and 50^oC. Ea values were calculated using Arrhenius equation and ΔH values were calculated using the equation : ΔH = Ea – RT.

The free energy of adsorption, ΔG⁰_{ads}, is calculated using the equation :

$$\Delta G_{ads}^0 = - RT \ln (55.5 \times K_{ads})$$

Where 55.5 is the molar concentration of water in solution and K_{ads} = θ / C (1-θ).

Electrochemical Polarization measurements

A conventional three electrode cell consisting of Aluminium as working electrode, Platinum as counter electrode and a saturated calomel electrode as reference electrode was

used for potentiodynamic polarization studies. Cyclic potentiodynamic polarization studies were carried out in VSP electrochemical analyzer and the data were analyzed by EC – Lab for windows V 9.43(software), Internet serve V 9.40 (firmware) and command interpreter V 9.42 (firmware) % I.E. was calculated by using the formula.

$$\text{IE \%} = \frac{(I_0 - I_{\text{inh}})}{I_0} \times 100$$

Where I_0 = Corrosion current in the absence of inhibitor and I_{inh} = Corrosion current in the presence of inhibitor.

AC impedance spectroscopic studies were also carried out, using the same electrochemical analyser.

Surface Morphology studies

Scanning Electron microscopy (SEM) and Atomic Force Microscopy (AFM) were used for surface morphology studies.

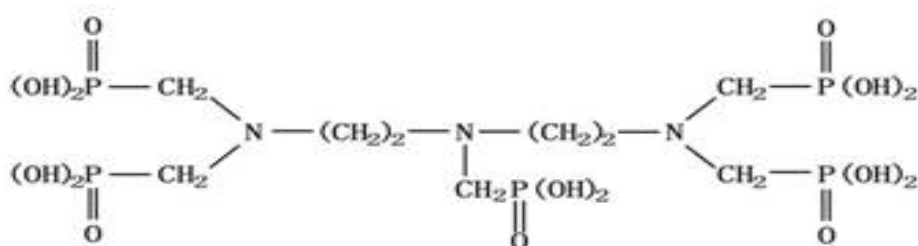
SEM images of polished Aluminium metal, Corroded Metal and Corrosion inhibited metal surfaces are recorded with VEGA 3 TESCAN microscope and compared.

Atomic force microscopy (also known as scanning force microscopy) is a powerful technique for the gathering of roughness statistics from a variety of surfaces [34]. AFM is becoming a well accepted method of roughness investigation [35-40].

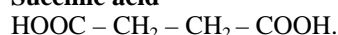
All AFM images were obtained on a pico SPM 2100 AFM instrument operating in contact mode in air.

Structure of inhibitors

DTPMP



Succinic acid



RESULTS AND DISCUSSION

Weight loss study

The percentage inhibition efficiencies (IE%) of Zn^{2+} ions, DTPMP and SA separately and in combination, have been evaluated in 0.01 NaOH medium, by weight loss technique at 30°C and the results are summarized in Table 1 (a) to 1 (c).

Table 1(a) illustrates the effect of concentration of SA on the IE at 30°C. It is observed that 280 ppm of SA has maximum IE 69.3%.

Table 1(b) depicts the influence of Zn^{2+} and SA on the IE, which increases from 49% to 85.7% during increase of SA from 40ppm to 280 ppm.

Table 1(c) explains the combined effect of DTPMP, Zn^{2+} and SA on the IE. At an optimum constant concentration of 20ppm of DTPMP, an increasing trend of IE is demonstrated during the increase of concentration of SA, which reaches nearly 98% at a concentration of 240ppm SA.

Electrochemical Studies

The results of the potentiodynamic polarization studies for the blank and various environments containing the inhibitor systems are summarized in Table 2(a). IE values calculated from the polarization data are in good agreement with those obtained from weight loss data. The Tafel curves in figures 1(a) to 1(d) illustrate that the

nature of the curves remains almost the same, even after the addition of inhibitors. However, on increasing the concentrations of the inhibitors, the curves are gradually shifted towards lower current Density.

Table 1(a)

Zn ²⁺ = NIL, DTPMP = NIL Temp 30°C			
Concentration of SA (ppm)	Corrosion Rate C _R (mmpy)	IE%	Surface Coverage θ ₁
0(Blank)	29.43	—	—
40	25.83	12.3	0.123
80	18.02	38.8	0.388
120	14.42	51.0	0.510
160	12.61	57.0	0.570
200	11.41	61.2	0.612
240	9.61	67.4	0.678
280	9.01	69.3	0.693

Table 1 (b)

Zn ²⁺ = 20 ppm, DTPMP- NIL Temp. 30°C			
Concentration of SA (ppm)	Corrosion Rate C _R (mmpy)	IE %	Surface Coverage θ ₂
0 (Blank)	29.43	-	-
40	15.02	49.0	0.490
80	9.61	67.0	0.670
120	8.41	71.4	0.714
160	6.61	77.5	0.775
200	5.41	81.6	0.816
240	4.81	83.7	0.837
280	4.20	85.7	0.857

Table 1 (c)

Zn ²⁺ = 20 ppm Temp. 30°C				
Concentration (ppm)		Corrosion Rate C _R (mmpy)	IE %	Surface Coverage θ ₃
DTPMP	SA			
20	40	12.26	58.9	0.589
20	80	6.66	77.4	0.774
20	120	5.61	81.0	0.810
20	160	2.45	89.3	0.893
20	200	3.15	91.7	0.917
20	240	0.71	97.6	0.976
20	280	0.72	97.5	0.975

The corrosion potential values also are shifted towards negative direction, indicating the decrease in the rate of the cathodic reaction. Further, the decrease in the anodic and cathodic Tafel slopes β_a and β_c are related to the decrease in both the cathodic and anodic currents. The inhibitors act as mixed inhibitors.

Table 2 (a) - Potentiodynamic Polarization Data

Zn ²⁺ 20ppm; DTPMP 20 ppm				Respective Figure
SA (ppm)	-E _{corr} (V)	I _{corr} (mA)	IE %	
0 (Blank)	1.58	7.556	-	1(a)
80	1.671	1.8	76.2	1(b)
160	1.623	1.0	86.7	1(c)
240	1.605	0.35	95.4	1(d)

Table 2 (b) – Impedance Data

Zn ²⁺ 20 ppm; DTPMP – 20 ppm			Respective Figure
SA (ppm)	R _{ct} (Ω cm ²)	C _{dl} (μF/cm ²)	
0 (Blank)	0.876	56.3	2(a)
240	1.80	0.1928	2(b)

The impedance Nyquist graphs are given fig 2(a) and 2(b). The R_{ct} and C_{dl} values tabulated in Table 3 (b) confirm the adsorption of the inhibitor system and formation of the layer of the inhibitor on the metal surface.

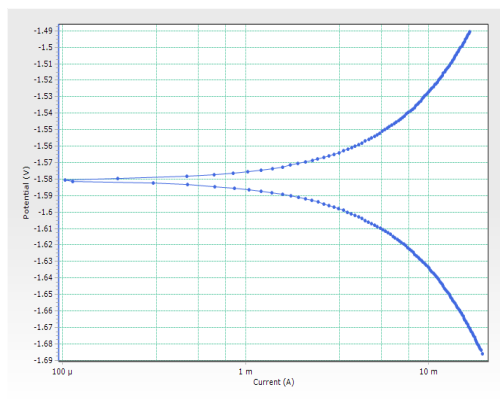


Figure 1(a) Polarization graph (Tafel)

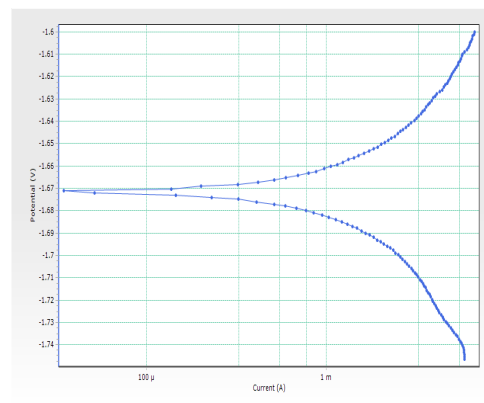


Figure 1 (b) Polarization graph (Tafel)

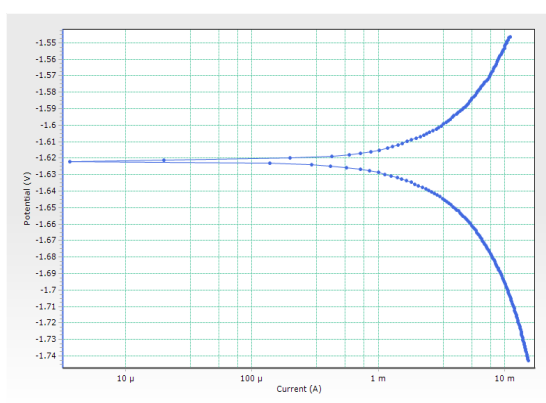


Figure 1(c) Polarization graph (Tafel)

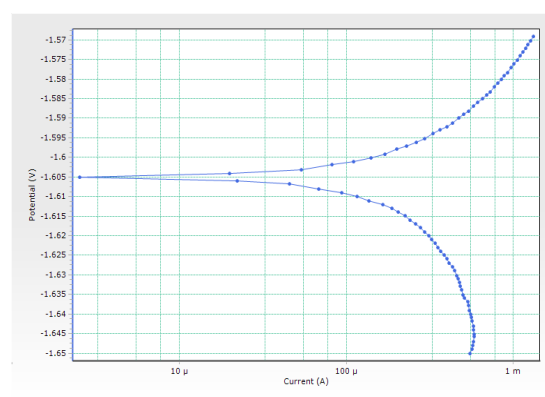


Figure 1 (d) Polarization graph (Tafel)

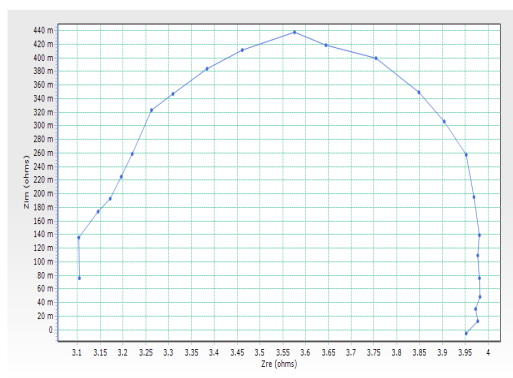


Figure 2 (a) Impedance graph (Nyquist)

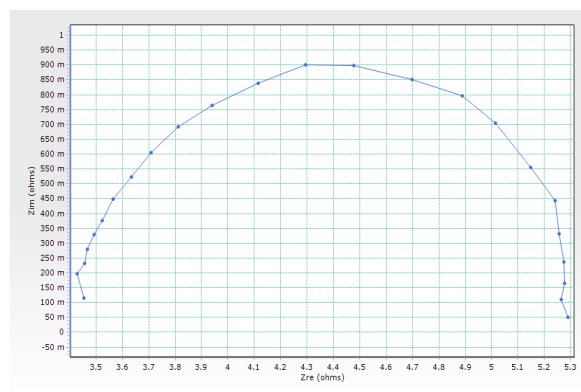


Figure 2 (b) Impedance graph (Nyquist)

Table 3 (a). Effect of temperature on IE

Concentration of SA (ppm)	Zn ²⁺ = DTPMP = 20 ppm		
	IE % at 30 ^o C	IE % at 40 ^o C	IE % at 50 ^o C
40	58.9%	55.9%	29.6%
80	77.4%	65.8%	40.8%
120	81%	76.6%	53.1%
160	89.3%	80.6%	64.6%
200	91.7%	81.7%	73.9%
240	97.6%	92.1%	76.9%

Table 3 (b) Activation Energy and Enthalpy Changes

Process	Average Ea (KJ/mol)	ΔH (KJ / mol)
Corrosion in the absence of Inhibitors	17.6	15.0
Corrosion in the Presence of inhibitors (SA =240ppm)	109.5	106.9

Effect of temperature on inhibition efficiency

The effects of the inhibitor systems containing 20ppm DTPMP, 20ppm Zn^{2+} and various concentrations of SA were studied through weight loss measurement at the elevated temperatures of 40^oC and 50^oC also and the results are presented in Table 3(a). The IE values decrease with the rise of temperature.

Activation energy (Ea) values and Enthalpy change (ΔH) values for the corrosion process are calculated and given in Table 3(b).

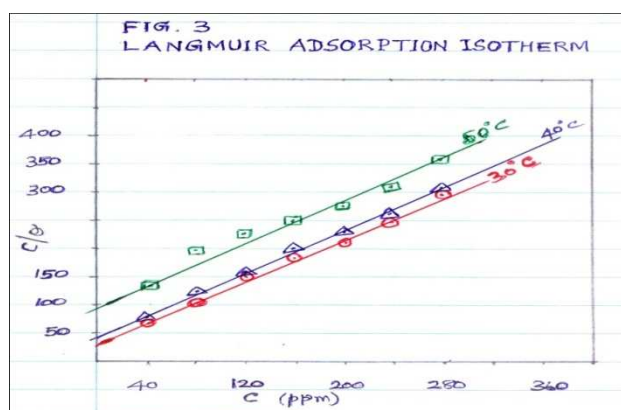
More positive the values of Ea and ΔH , less spontaneous is the corrosion process i.e. corrosion is decreased in the presence of inhibitors.

Adsorption Isotherms

The surface coverage values (θ) calculated from weight loss measurements were fitted into the Langmuir adsorption isotherm.

The Langmuir adsorption isotherm model has the form $C/\theta = 1/K_{ads} + C$.

Where C is the concentration, K_{ads} is the equilibrium Constant of adsorption process. A plot of C/θ Vs C is linear (Fig 3). The slope deviates from unity indicating that there is attraction or repulsion in the adsorbed layer of inhibitor on the aluminium surface [41-42]



From the K_{ads} values, calculated using the θ values for various concentrations of inhibitors at different temperatures, ΔG_{ads}^0 values were also calculated and tabulated in table 4.

Table : 4.Free energy of adsorption (ΔG_{ads}^0) values (KJ / mol⁻¹)

SA (ppm)	Additives added to SA				
	DTPMP = Nil; Zn ²⁺ = Nil	DTPMP = Nil; Zn ²⁺ = 20 (ppm)	DTPMP = 20 ppm ; Zn ²⁺ = 20 ppm.		
	at 30 ^o C	at 30 ^o C	at 30 ^o C	at 40 ^o C	at 50 ^o C
40	- 25.3	- 30.15	- 31.16	- 30.85	- 28.07
80	- 27.38	- 29.63	- 31.61	- 30.15	- 27.57
120	- 27.58	- 29.79	- 31.14	- 30.39	- 27.80
160	- 27.48	- 29.89	- 31.11	- 30.35	- 28.20
200	- 26.82	- 29.95	- 32.25	- 29.97	- 28.82
240	- 27.57	- 29.97	- 35.07	- 31.92	- 27.86

The values of ΔG_{ads}^0 are negative and range from - 31.11 to - 35.29 KJ mol⁻¹. The negative values indicate that the adsorption of the inhibitors on the aluminium surface is spontaneous.

The ΔG_{ads}^0 values decrease with the increase of temperature suggesting that there is a decrease in adsorption of the inhibitors as the temperature increase from 30 to 50^oC.

In general, the values of ΔG_{ads}^0 around -20 KJ mol^{-1} correspond to physisorption while those above -40 KJ mol^{-1} correspond to chemisorption. [43,44].

Analysis of SEM images

The SEM images of polished metal, the same immersed in 0.01M NaOH solution and in the combined inhibitor system are given in Fig 4(a), 4(b) and 4(c), respectively.

A comparative examination of these images, clearly suggest that the surface of Aluminium specimen is smoothed to a very large extent in the presence of the combined inhibitor system. This smoothing might be due to the adsorption of the inhibitor molecules on it and thus the surface is fully covered.

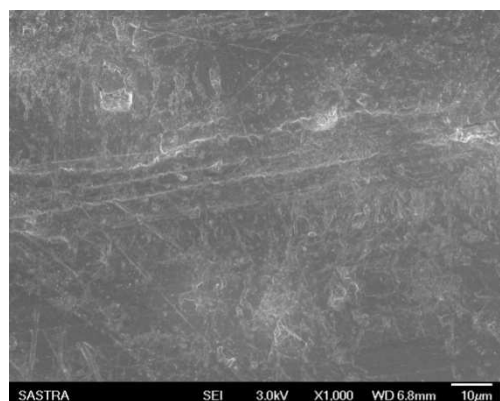


Figure 4 (a) SEM

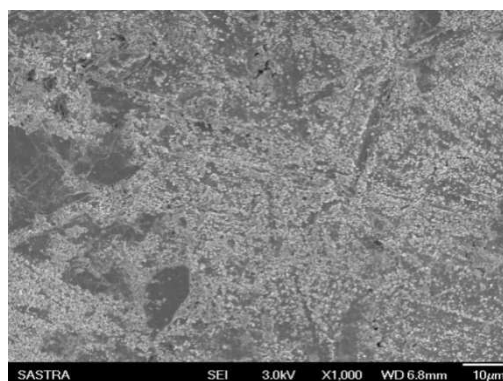


Figure 4(b) SEM

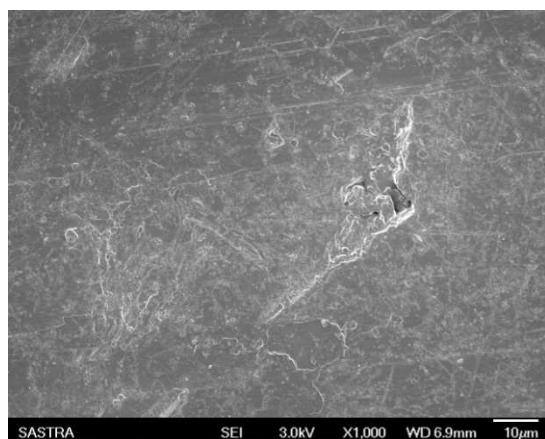


Figure 4 (C) SEM

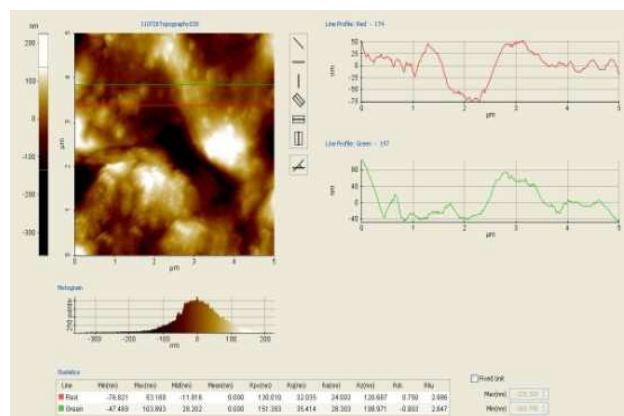


Figure 5(a) AFM

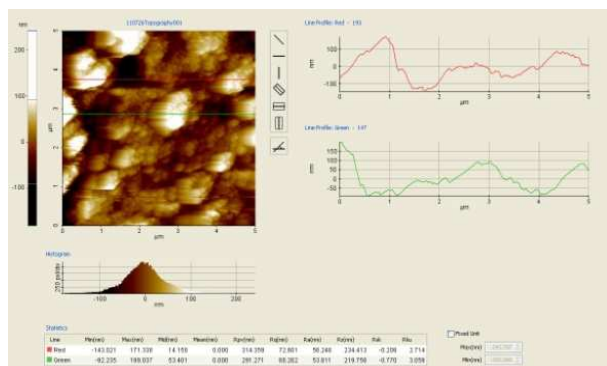


Figure 5 (b) AFM

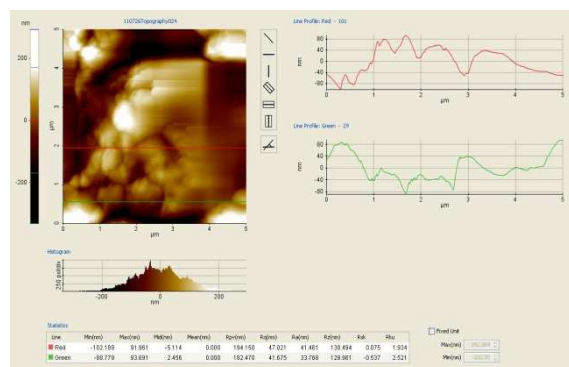


Figure 5 (c) AFM

Analysis of AFM images

Fig 5(a), 5(b) and 5(c) show the AFM images of polished metal, corroded surface in the absence of inhibitors and the smoothed surface in the presence of inhibitors, respectively. Table 5 gives the corresponding roughness and peak-to-valley height values.

Table-5 - AFM roughness data

Sample	RMS(Rq) Roughness (nm)	Average roughness(Ra) (nm)	Maximum peak-to-valley height (P-V) (nm)	Respective Figure
Polished Al metal	32	24	130	5 (a)
Al immersed in 0.01M NaOH solution	72.6	56.2	314	5 (b)
Al immersed in combined inhibitor system	41	33	182	5 (c)

A comparative view of the above roughness table clearly demonstrates that the surface of the metal is smoothed due to the adsorption layer formed.

CONCLUSION

- i. SA has a maximum of 69% IE at 30°C for aluminium in 0.01M NaOH medium. In the presence of 20ppm Zn²⁺ ions, the IE of SA shifts to a maximum of 85.7% at 280 ppm concentration. The ternary system consisting of 20ppm DTPMP, 20ppm Zn²⁺ and 240ppm SA has a remarkably high IE, 97.5%.
- ii. The IE% decreases with increase of temperature to 40°C and 50°C.
- iii. The IE Values calculated from electrochemical polarization studies are in good agreement with those of weight loss studies. Electrochemical polarization studies show that the inhibitor system acts as a mixed inhibitor.
- iv. Observations made from SEM, AFM and Langmuir adsorption isotherm suggest that the corrosion inhibition occurs through the adsorption of inhibitors on the surface of aluminium.
- v. The negative values of ΔG indicate that the adsorption of the inhibitors on the aluminium surface is spontaneous. E_a and ΔH values of the corrosion process also support this observation.

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