



Study of Synergistic effect of diethylene triamine penta (methylene phosphonic acid) and adipic acid on the inhibition of corrosion of alkaline aluminium

S. Rajendran*, C. Thangavelu and T. Venkatesh

PG and Research Dept of Chemistry, Periyar EVR College (Autonomous), Trichirapalli – 620023, TamilNadu, India.

ABSTRACT

The inhibition efficiency (IE) of diethylene triamine penta (methylene phosphonic acid) [DETAPMP] in controlling the corrosion of Aluminium metal in a medium containing 0.01M NaOH and Zn^{2+} ions was studied by using weight loss measurements and electrochemical polarization studies. Similar investigations were carried out by adding the second inhibitor viz adipic acid (AA) also. The combined IE of the above two inhibitors was found to be more than 90%. All the synergism factor values (Sf) calculated were greater than unity, confirming the synergistic effect of the two inhibitors. The protective film formed on the metal surface consists of $Zn(OH)_2$ and complexes of Al^{3+} and Zn^{2+} with DETAPMP and AA. This is confirmed by UV – Visible spectra, FTIR Spectra and Atomic Force Microscopy (AFM). Surface morphology studies were done using scanning electron microscopy (SEM) and AFM. Both inhibitors act as mixed inhibitors and obey Langmuir adsorption isotherm.

Keywords : Alkaline Aluminum Corrosion, mixed type inhibitors, Synergism factor, Langmuir adsorption isotherm, surface morphology.

INTRODUCTION

Aluminium and aluminium alloys represent an important category of materials due to their high technological value and wide range of industrial applications especially in aerospace and household industries. The use of these materials in light weight installation is widespread. 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 mediums 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, aegle marmelos leaves extract [6], polyvinyl alcohol [7], gongronema latifolium extract [8], bismark brown dye [9], methyl orange [10] and onion extract [11] have been used as corrosion inhibitors to prevent corrosion of aluminium. Corrosion inhibition of aluminium using super hydrophobic films [12], structure and stability of adhesion promoting aminopropyl phosphonate layers at polymer / aluminium oxide interfaces [13], microbially influenced corrosion of aluminium [14], corrosion inhibition of aluminium by rare earth chlorides [15], effects of inhibitors on corrosion behaviour of dissimilar aluminium alloy corrosion using fluorometric methods [16], surface modification for aluminium pigment inhibition [17] and filiform on 6000 series aluminium [18], have been investigated. Because of the voice raised by environmental scientists, several corrosion researchers have started using environmental friendly natural products as corrosion inhibitors [19-23]. 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 [24]. Priya et al. have studied the corrosion behaviour of aluminium in rain water containing garlic extract [25]. Jain et al. have investigated the electrochemical behaviour of aluminium in acidic media [26]. Several investigators have reported the corrosion inhibition behaviour of carbon steel, mild steel and copper in acidic medium. [27-31]

The Objectives of the present study are :

1. To study the inhibition of corrosion of aluminium metal in 0.01M NaOH solution, by Zn^{2+} ions and DETAPMP using weight loss method.
2. To study the inhibition of corrosion of aluminium in 0.01M NaOH solution, by Zn^{2+} and adipic acid (AA) using weight loss method.
3. To investigate the combined synergistic inhibition of corrosion of aluminium in 0.01M NaOH solution, by Zn^{2+} , DETAPMP and AA. The synergism factor is to be calculated from the surface coverage data. IE Values are to be calculated from electrochemical polarization data also.
4. To Confirm the possibility of formation of complexes of the inhibitors with aluminium and with zinc, using UV - Visible Spectroscopy.
5. To analyse the nature of the protective film formed on the metal surface using FTIR, AC impedance, SEM and AFM techniques.
6. To examine the inhibition mechanism by drawing Langmuir adsorption isotherms.

MATERIALS AND METHODS

Commercial aluminium specimens, of dimensions 1.0x 4.0 x 0.2 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.

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 W_1 = Corrosion rate in the absence of inhibitor, and

W_2 = Corrosion rate in the presence of inhibitor.

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

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

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.

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

Where, I_0 = Corrosion current in the absence of inhibitor.

I_{inh} = Corrosion current in the presence of inhibitor.

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

Synergism Factor (Sf)

The Synergistic effect the two inhibitors was studied by calculating the Synergism factor (Sf), by using the following formula.

$$Sf = \frac{1 - \theta_{1+2}}{1 - \theta_c}$$

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

θ_1 = Surface coverage when inhibitor 1 is used.

θ_2 = Surface coverage when inhibitor 2 used.

θ_c = Surface coverage when the combined inhibitor system is used.

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

Where W_1 = Corrosion rate in the absence of the inhibitor (blank)

W_2 = Corrosion rate in the presence of the inhibitor.

The UV – Visible absorption spectra of solutions

The Possibility of formation of complexes of Zn^{2+} and Al^{3+} with DETAPMP and AA in solution was examined by mixing the respective solutions and recording their UV – Visible absorption spectra using Lambda 35 Spectrophotometer.

SURFACE EXAMINATION STUDY**FTIR Spectra**

After the immersion period in various environments, the specimens were taken out of the test solutions and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout. FTIR spectra of the scrapings (KBr pellet) were recorded using Perkin – Elmer 1600 spectrophotometer with a resolving power of 4 cm^{-1} .

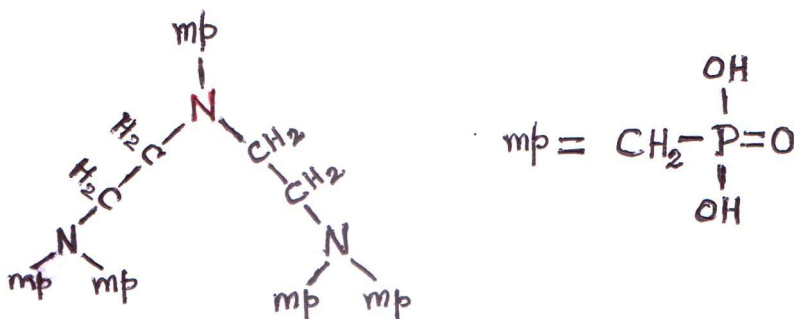
Surface Morphology

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 [32]. AFM is becoming a well accepted method of roughness investigation [33-38].

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

Structure of inhibitors.**DETAPMP**

Adipic acid HOOC – CH₂ – CH₂ – CH₂ – CH₂ – COOH.

RESULTS AND DISCUSSION

Weight loss study :

The percentage inhibition efficiencies (IE%) of Zn^{2+} ions, DETAPMP and AA 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 I_(a) to I_(d).

Table I_(a) illustrates the effect of concentration of DETAPMP on the IE. It is observed that 50 ppm of DETAPMP has maximum IE 74.2%. which gradually decreases during the increase of its concentration. This may be due the steric hindrance experienced by the bigger molecules of DETAPMP in travelling through the bulk of the solution towards the metal surface and desorption of adsorbed molecules at higher concentrations.

Table I_(b), depicts the influence of concentration of AA on the IE, which increases from 18% to 44% during increase of AA from 40ppm to 240 ppm.

Table I_(c) explains the combined effect of DETAPMP and AA on the IE. At an optimum constant concentration of 200ppm of DETAPMP, an unequivocal increasing trend of IE is demonstrated during the increase of concentration of AA, which reaches nearly 90% at a concentration of 320ppm adipic acid.

Table I_(d) also shows the combined effect of the two inhibitors, but with a constant amount of AA, along with varying concentrations of DETAPMP. Here also, a maximum IE (98.9%) is observed at 50 ppm DETAPMP, which decreases to 79.8% at 300 ppm concentration.

Table I(a)

Zn²⁺ = 20 ppm, Adipic acid – NIL			
Concentration of DETAPMP ppm	Corrosion Rate CR (mmpy)	IE%	Surface Coverage θ_1
0(Blank)	28.29	-	-
10	18.10	38.2	0.382
25	8.88	69.6	0.696
50	7.57	74.2	0.742
100	17.44	40.5	0.405
150	23.37	20.2	0.202
200	23.70	19.1	0.191
250	23.70	19.1	0.191
300	23.37	20.2	0.202

Table I (b)

Zn²⁺ = 20 ppm, DETAPMP- NIL			
Concentration of A.A ppm	Corrosion Rate C _R (mmpy)	IE %	Surface Coverage θ_2
0 (Blank)	28.29	-	-
40	24.02	18	0.180
80	22.71	22.5	0.225
120	21.06	28.0	0.280
160	18.76	36.0	0.360
200	16.13	44.9	0.449
240	14.81	49.4	0.494
280	14.81	49.4	0.494
320	15.13	48.3	0.483

Table I(c)

Zn²⁺ = 20 ppm				
Concentration (ppm)		Corrosion Rate C _R (mmpy)	IE %	Surface Coverage θ_c
DETAPMP	AA			
200	0	23.37	20.2	0.202
200	80	8.23	71.9	0.712
200	120	6.58	77.5	0.775
200	160	5.60	80.9	0.809
200	200	4.61	84.9	0.849
200	240	3.61	87.7	0.877
200	280	3.29	88.8	0.888
200	320	2.96	89.9	0.899

Table I (d)

$Zn^{2+} = 20$ ppm		Corrosion Rate C_R (mmpy)	IE%	Surface Coverage θ_c
AA	DETAPMP			
200	0	16.13	44.9	0.449
200	50	0.33	98.9	0.989
200	100	1.32	95.9	0.955
200	150	4.61	84.3	0.843
200	200	4.94	83.2	0.832
200	250	5.6	80.9	0.809
200	300	5.92	79.8	0.798

UV - Visible spectral analysis:

The increase in absorbance values in the UV – Visible spectra of pure inhibitor compounds and their mixtures with Al^{3+} and Zn^{2+} suggest the possibility of formation of complexes of inhibitors with Al^{3+} and Zn^{2+} [Fig 1(a), 1(b), 1(c) and 1(d)].

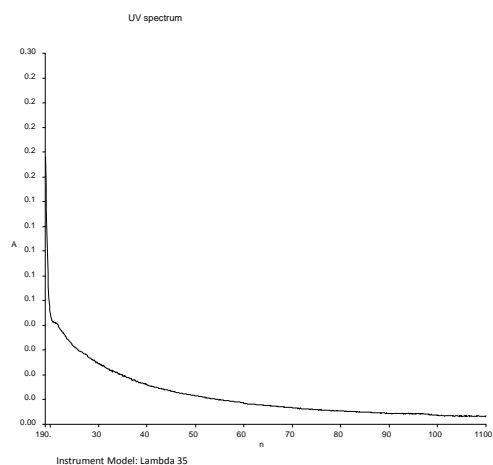


Figure 1(a) Pure Adipic Acid (AA)

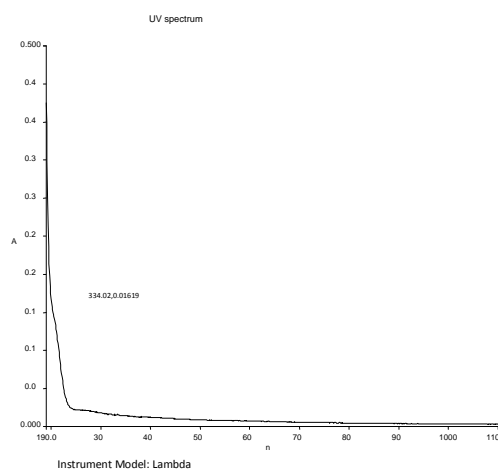
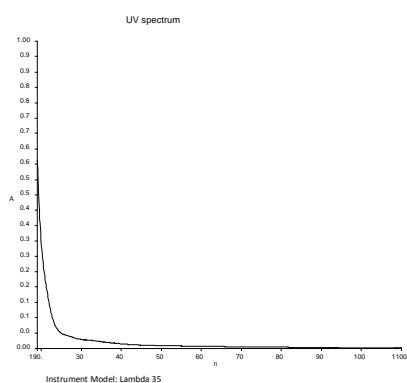
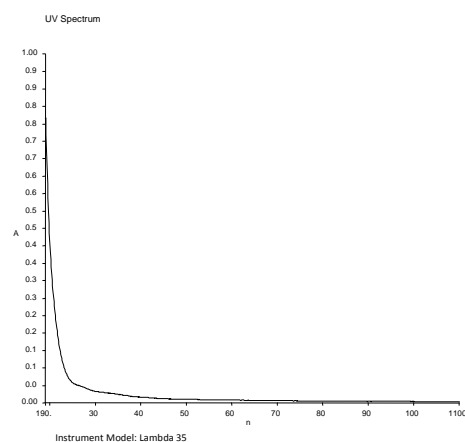


Figure 1(b) Pure DETAPMP

Figure 1(c) DETAPMP+ Zn^{2+} + Al^{3+} Figure 1(d) DETAPMP+ Zn^{2+} + Al^{3+} +Adipic Acid(AA)

FTIR Spectral analysis

The FTIR Spectra of pure Adipic acid and pure DETAPMP are given in Fig 2(a) and 2(b) respectively. The characteristic absorption peaks of these two compounds are very well seen in the spectra.

FTIR Spectrum of the scrapings of adipic acid – Zn²⁺ inhibitor layer formed on Aluminium specimen is given in Fig 2(c) and that of the scrapings of the inhibitor system (Zn²⁺ and DETAPMP) is given in Fig 2(d).

The shifts in the frequencies of the absorption peaks, clearly indicate the formation of complexes of the inhibitors with Al³⁺, and Zn²⁺ which are adhered on the surface of the Aluminium specimen during immersion.

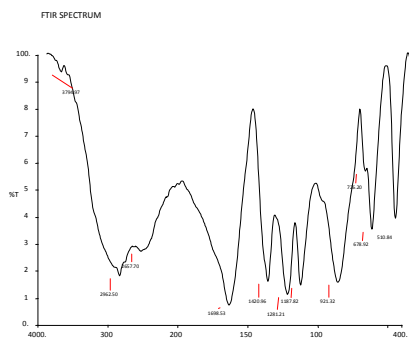


Fig: 2 (a) Pure Adipic Acid (AA)

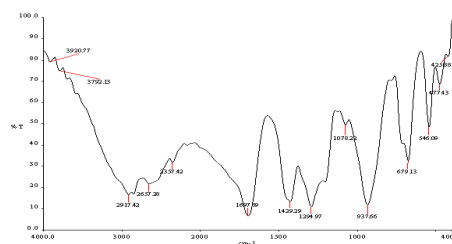
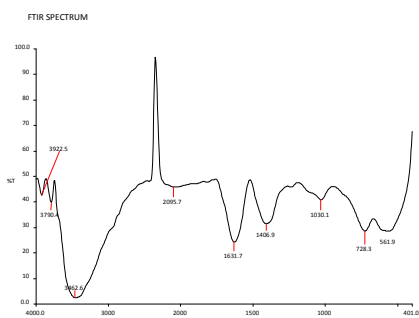
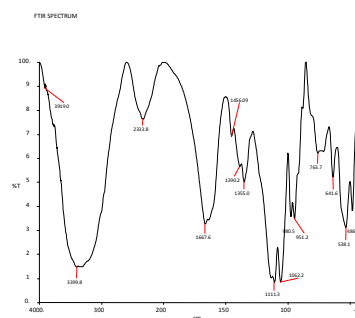
Fig : 2 (c) Adipic Acid + Zn²⁺ Al³⁺

Fig: 2(b): Pure DETAPMP

Fig: 2(d): DETAPMP+Zn²⁺+Al³⁺**Table II (a) - Potentiodynamic Polarization Data**

AA ppm	Zn ²⁺ 20ppm; DETAPMP 200 ppm			Respective Figure	
	-	E _{corr} (V)	I _{corr} (mA)		IE %
0	-	1.58	7.556	-	3(a)
80	-	1.641	2.333	69.2	3(b)
160	-	1.663	1.20	84.1	3(c)
240	-	1.658	0.78	89.7	3(d)
320	-	1.605	0.48	93.6	3(e)

Electrochemical Studies

The results of the potentiodynamic polarization studies for the blank and various environments containing the inhibitor systems are summarized in Table II(a). IE values calculated from the polarization data are in good agreement with those obtained from weight loss data. The curves in figures 3(a) to 3(e) 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. 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. Both the inhibitors act as mixed inhibitors.

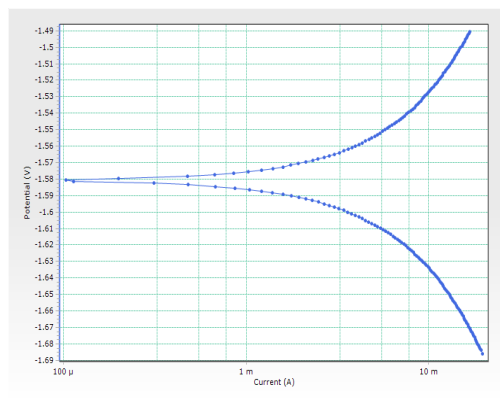


Figure 3(a)

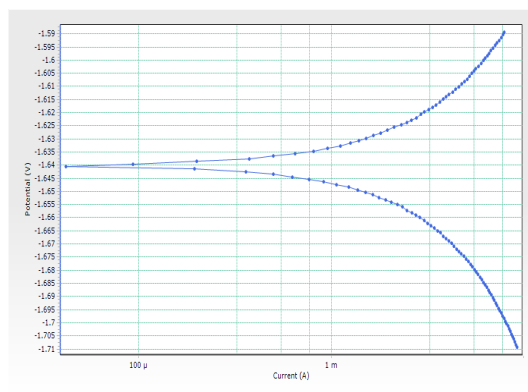


Figure 3 (b)

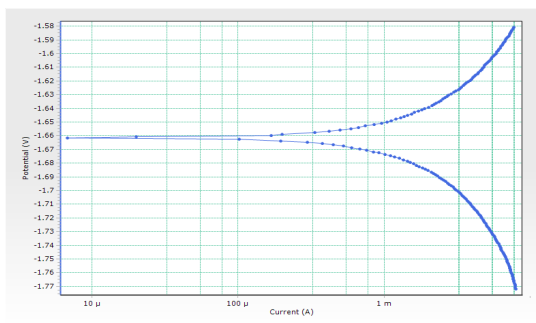


Figure 3(c)

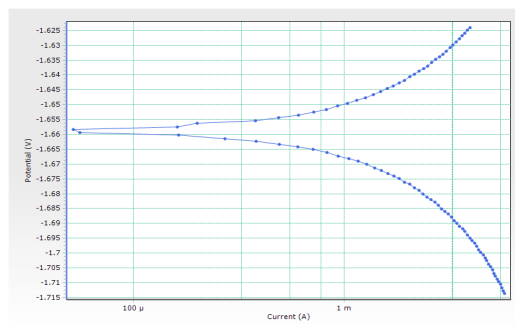


Figure 3 (d)

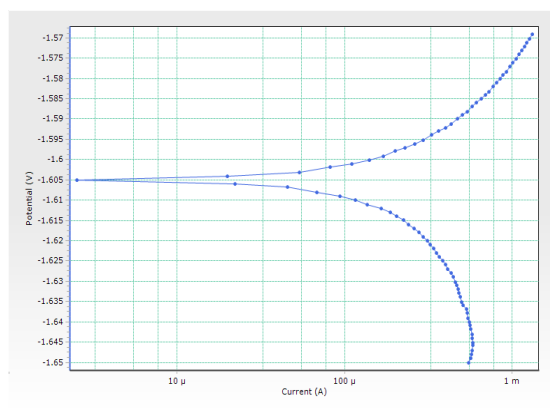


Figure 3(e)

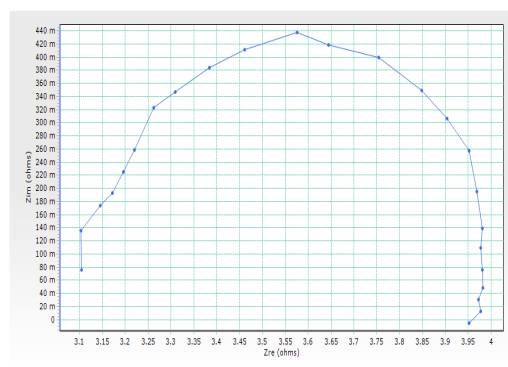


Figure 4 (a)

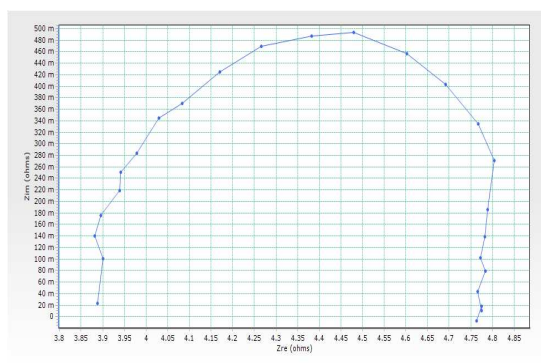


Figure 4 (b)

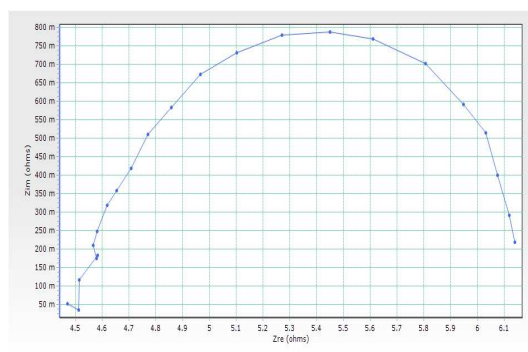


Figure 4 (c)

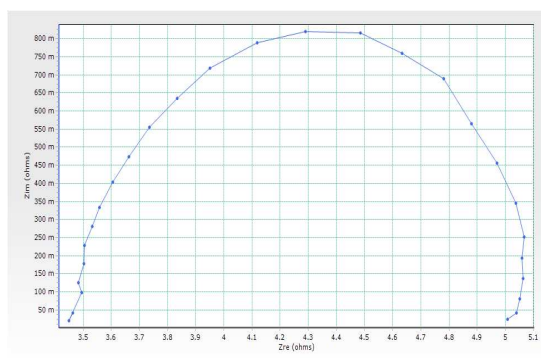


Figure 4 (d)

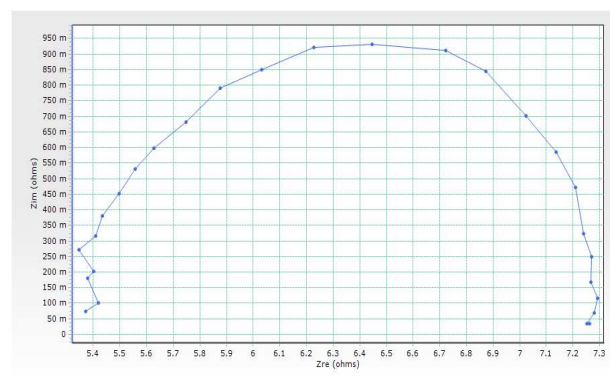


Figure 4 (e)

The impedance spectral graphs are given fig 4(a) to 4(e). The impedance values (Zimagi) tabulated in Table II(b) confirm the adsorption of the inhibitor system and formation of the layer of the inhibitor complexes on the metal surface.

Table II (b) – Impedance Data.

Zn ²⁺ 20 ppm; DETAPMP – 200 ppm		Respective Figure
AA ppm	Zimaginary (m ohms).	
0	438	4 (a)
80	492	4(b)
160	790	4(c)
240	825	4(d)
320	925	4(e)

Synergism Factors (S_f)

The synergism factor (S_f) values are calculated and presented in tables III(a) and III(b). It is interesting to note that all the S_f values are greater than unity, proving the high degree of synergistic effect of the two inhibitors used. Maximum Synergistic effect is seen with the inhibitor system containing 20ppm Zn²⁺, 50 ppm DETAPMP and 200 ppm AA (S_f = 13.9) .

Table III(a) SYNERGISM

Concentration (ppm)		S _f
DETAPMP	AA	
200	80	2.2
200	120	2.6
200	160	2.7
200	200	2.8
200	240	3.4
200	280	3.7
200	320	4.1

Table III(b) SYNERGISM

Concentration (ppm)		S _r
AA	DETAPMP	
200	50	13.9
200	100	8.2
200	150	2.8
200	200	2.7
200	250	2.4
200	300	2.2

Adsorption Isotherms

The mechanism of corrosion inhibition proceeds through adsorption process. The complexes formed by the inhibitors get adsorbed on the metal and a thin layer is formed on its surface. The surface area covered by the inhibitors is directly proportional to retardation in corrosion rate and the adsorption process must obey Langmuir adsorption isotherm.

$$\text{Log} \frac{\theta}{1 - \theta} = \text{log A} + \text{log C} - \frac{Q}{2.303 \text{ RT}}$$

The validity of Langmuir isotherm is confirmed by the linearity of the $\text{log}[\theta/(1-\theta)]$ Vs log C plots

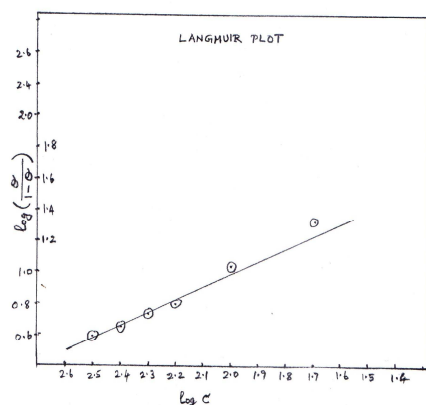


Fig. 5 (a) 200 ppm AA + Various amounts of DETAPMP.

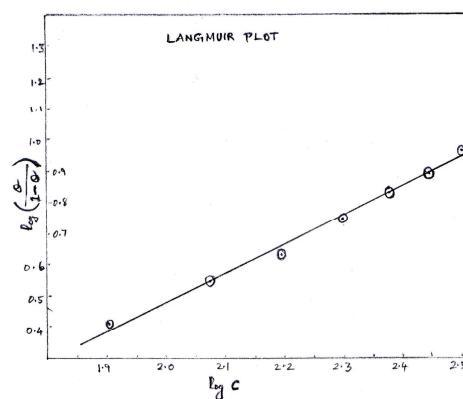


Fig. 5 (b) 200 ppm DETAPMP + Various amounts of AA.

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 6(a), 6(b) and 6(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 – metal complex molecules on it and thus the surface is fully covered.

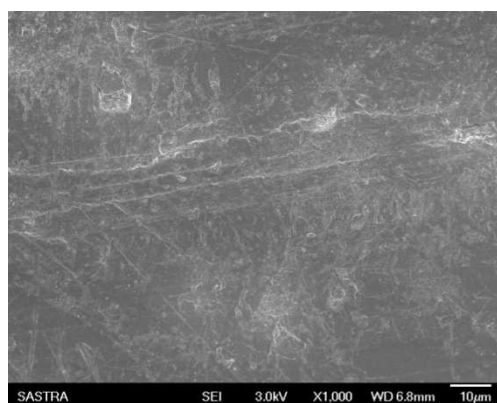


Figure 6 (a)

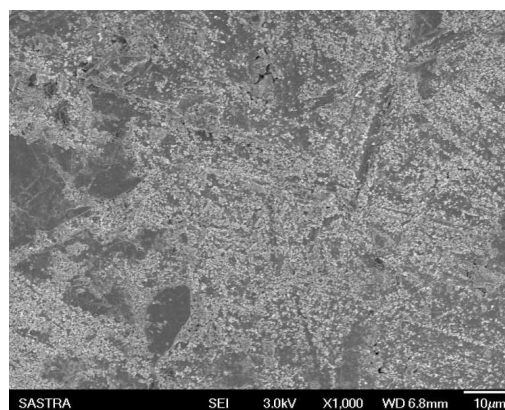


Figure 6(b)

Figure 6 (c)

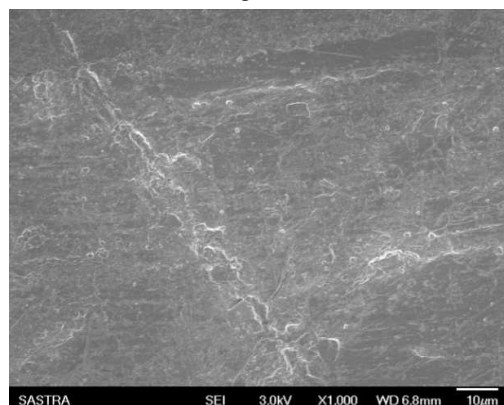


Figure 6 (d)

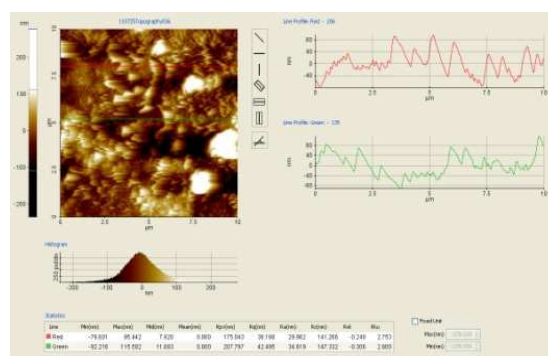
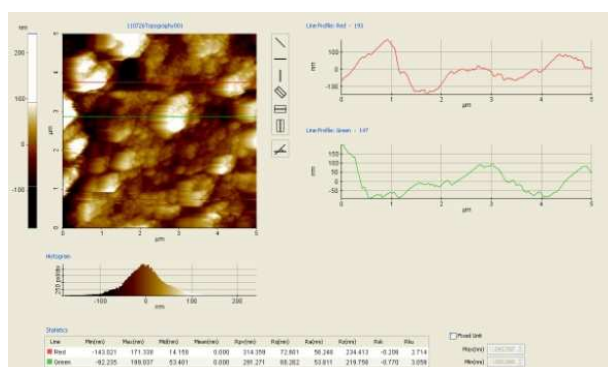
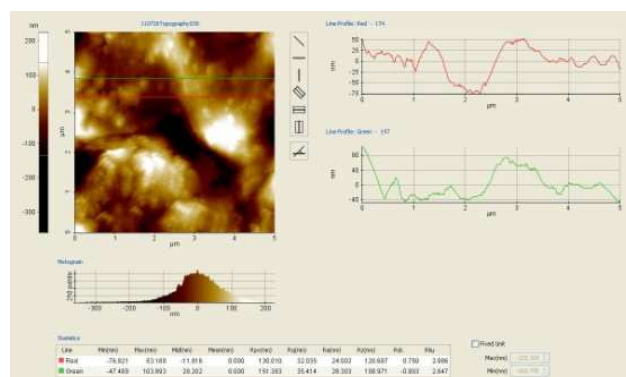


Figure 7 (b)

Figure 7 (c)

Analysis of AFM images

Fig 7(a),7(b) and 7(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 IV gives the corresponding roughness and peak-to-valley height values.

Table-IV - 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	7 (a)
Al immersed in 0.01M NaOH solution	72.6	56.2	314	7 (b)
Al immersed in combined inhibitor system	38	29	175	7 (c)

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

CONCLUSION

- DETAPMP has reasonably high corrosion inhibition upto 74% in the presence of Zn^{2+} ions for aluminium in 0.01M NaOH solution. But beyond 50ppm, increase of concentration of DETAPMP decreases the IE.
- AA also acts as a fairly good inhibitor for aluminum in 0.01M NaOH Solution, in the presence of Zn^{2+} ions. IE increases with the concentration of AA and it is maximum, 49%, at 240 ppm of AA.
- When both DETAPMP and AA are used together, the combined IE increases remarkably upto 98%. IE values calculated from polarization studies also are in good agreement with those of weight loss studies.
- Synergism factor (Sf) values are certainly greater than unity, confirming the high degree of synergistic effect of DETAPMP and AA.
- Electrochemical polarization studies show that the inhibitors act as mixed inhibitors.
- Observations made from FTIR, SEM, AFM and Langmuir adsorption isotherm suggest that the corrosion inhibition occurs through the adsorption of inhibitors on the surface of aluminum.

REFERENCES

- [1] Quraishi M.A., Rafique M.Z.A, Khan S, Saxna N, *Appl J, Electrochem.* 37 **2007** 1153.
- [2] Arora P, Kuma S, Sharma M K , Muthur S P, *E – J. Chem.* 4 **2007** 450.
- [3] Umoren S A, Ogbobe O, Okafor P C, Ebenso E E, *J.Polym. Sci.* 105 **2007** 3363.
- [4] Abiola O K , Oforka N C, Ebenso E E, .Nwinuka N M, *Anti – Corrosion Methods Mater*, 54 **2007** 219.
- [5] Oquzie E E, *Corros. Sci* 49 **2007** 1579.
- [6] Lakshmi Praba K , Shameela Rajam, and Venkatraman B R, *Der chemica sinica*, **2012**, 3 (1), 114.
- [7] Umoren S A, Ebenso E E, Okafor P C, Ekpe U J, Ogbobe O, *AppL J, Sci.* 103 **2007** 2810.
- [8] Oguzie E E, Onuoha G N, Ejike E N, *Pigment and Resin Technol.* 30 **2007** 44.
- [9] Oguzie E E, Okolue B N, Ogukwe C E, Unaegbu C, *Mater Let.* 60 **2006** 3376.
- [10] Rajendran S, Manivannan M, Sahayaraj J.E, Selvi J A, *SAEST41 J* **2006** 63.
- [11] Rajendran S, Muthulakshmi S, Rajeswari R, Vijitha A, *Electrochem J, Soc., India* 54 **2005** 50.
- [12] Barkhudarov P M , Shah P B, Watkis E B, Doshi D A, Brinker C J, Majewski J, *Corros Sci – 50* **2008** 897.
- [13] Wapner K, Stratmann M, Grundmaier G, Int, *Adhesion Adhesives J*, 28 **2008** 59.
- [14] Juzeliunas E, Ramanauskas R, Lugauskas A, Leinartas K, Samuleviciene M, Sudavicius A, Juskenas R, *Corros. Sci.*49 **2007** 4098
- [15] Mishra A.K, Balasubramaniam R, *Mater. Chem Phys.* 103 **2007** 4098.
- [16] Srinivasan P B, Dietzel W, Zettler R, dos Santos J F, Sivan V, *Corros. Eng. Sci. Techn.* 42 **2007** 161.
- [17] Chambers B. D, Taylor S R, *Corros. Sci.* 49 **2007** 1597.
- [18] Karisson P, Palmquist A E C, Holmberg Adv K. *Colloid Interf. Sci* 128 – 130 **2007** 121.
- [19] Coleman A J, McMurray H N, Williams G., Afseth A, Seamans G, *Sci. Forum* 519 – 521 (PART 1) **2006** 629.
- [20] Rajendran S, Ganga Sri V, Arockia Selvi J and John Amalraj A, *Bulletin of Electrochemistry* 21(8) **2005** 367 – 377.
- [21] Rajendran S, Shanmugapriya S, Rajalakshmi T, Amalraj A J, *Corrosion* 61 **2005** 685.
- [22] Anthony N, Malarivizhi M, Maheswari P, Rajendran S, Palaniswamy N, *Ind. Chem J, Tech.* 11 **2004** 346.
- [23] Rajendran S , Amalraj A J, Joice M J , Anthony N, D.C. Trivedi, Sundaravadivelu M. *Corros Rev.* 22 **2004** 233.
- [24] Rehan H H, *Materialwissenschaft and Werkstofftechnik* 34 **2003** 232.
- [25] Priya L, Chitra A. Rajendran S, Anuradha, Surf K, Eng. 21 **2005** 229.
- [26] Jain T, Chowdhary R, Mathur S P, *Mater, Corros.* 57 **2006** 422
- [27] Hany Abd Et Lateef M, Aliyeva L I. Abbasov V M, Ismoyilov T I, *Advances in Applied science Research.* **2012**, 3(2), 1185.
- [28] Rosaline Vimala J, Leema Rose A, Raja S, *Der Chemica sinica* **2012**, 3(3), 582.
- [29] Shaker N O, Badr e e and Kandeel E.M. , *Der Chemica Sinica* **2011**, 2(4), 26.
- [30] El. Maghraby A.A, Sonor T.Y, *Advances in Applied science research*, **2012** 1(2), 155.
- [31] Jamal Abdul Nasser A, Rethinagini V, *Der Chemica Sinica* **2012**,3(5), 1239.
- [32] Rajendran S, Apparao V, and Palaniwamy N, Proc. 2nd Arabian Corrsion conference, Kuwait, **1996** 483.
- [33] Vera R, Schrebler R, Cury P, Del Rio R, and Rometro H, *J Appl Electronchem*, 37 **2007** 519 – 525.
- [34] Dumas PH, Butffakherddine B, Am O.Vatel C, Ands E, Galindo R, and Salvan F, *Europhys. Lett.* 22 **1993** 717 – 722.
- [35] Bennett J M , J.Jahannir, Podlesny J C, Batier T L, and Hobbs D T, *Appl. Opt.*, 43 **1995** 213 – 230.
- [36] Duparre A, Kasier N, Truckenbrodi H, Berger M, and Kohler A, Microtopography investigations of optical surfaces and thin film by light scattering, optical profilometry, and atomic force microscopy, Int. Symp. on optics, Imaging and instrumentation, 1 1-16 July 1993. San Diego, CA, Proc. SPIE. 1995 SPIE. 1995 **1993** 181 – 192.
- [37] Duparre A, Kasier N, and Jokobs S, Morphology investigation by Atomic Force Microscopy of thin films and substances for excimer laser mirros, Annual Symp. on Optical Materials for High Power Lasers. 27-29 October 1993, Boulder, CO, Proc. SPIE, 2114 **1993** 394.
- [38] Thomas T, “Rough Surfaces:”, Longman, New York, **1982**.