



# POLYAMIDES CONTAINING OXADIAZOLE RING MOIETY AS CORROSION INHIBITOR FOR ALUMINIUM IN ACID SOLUTION

\*Subha C<sup>1</sup>, Selvaraj A<sup>2</sup>, Thevi R<sup>2</sup> and Ravikumar L<sup>2</sup>

<sup>1</sup>Department of Chemistry, Nirmala College for Women, Coimbatore, Tamil Nadu- 641018, India

<sup>2</sup>Department of Chemistry, CBM College, Coimbatore, Tamil Nadu- 641042, India

## ABSTRACT

Corrosion control of metals is an important activity of technical, economic, environmental, and aesthetical importance. The use of inhibitors is one of the best options for protecting metals and alloys against corrosion. This study involves the investigation of new and effective polymeric material for the application of corrosion inhibition on aluminium in the acid medium using chemical and electrochemical methods. Results obtained from weight loss and potentiodynamic and impedance methods confirm that polyamides containing oxadiazole rings in their backbone can act as effective corrosion inhibitors. The adsorption behaviour of this polymer on aluminium in 1N HCl was found to obey Langmuir adsorption isotherm. SEM studies confirmed the protective film formed on aluminium by the adsorption of Polyamides.

**Keywords:** Corrosion, Polyamides, Oxadiazole, acid medium, Aluminium and Electrochemical

## 1. Introduction

A chemical reaction between the metal and gases in the surrounding environment causes corrosion. These unwanted reactions can be minimized by taking measures to control the environment. It can be as simple as reducing exposure to rain or seawater or more complex measures, such as controlling the amounts of sulfur, chlorine, or oxygen in the surrounding environment. An example would be treating the water in water boilers with softeners to adjust hardness, alkalinity, or oxygen content. Acid solutions are widely used in industries for picking, cleaning boilers, descaling, oil-well acidizing, etc. Corrosion inhibitors are employed to control the rate of undesirable base metal corrosion [1-4]. To minimize the percentage of metal loss during this process, various compounds, such as acetylenic alcohols, indoles, thiourea derivatives, dithiazones, etc. are widely used [5-10]. Among these, thiourea and its derivatives were found in commercial formulations, but because of their toxic nature, their use is unsafe. There is a great need to find a non-toxic replacement compatible with current industrial technologies. In the last two decades, there has been an increase in the use of

polymeric compounds as corrosion inhibitors [11]. One of the most critical applications of aluminium and its alloys is found in aluminium-air technology, first developed by Zaromb [12], which was of particular interest for its application to electric vehicle propulsion

[13,14]. Amongst various types of anode materials, aluminium exhibits a high theoretical energy density (8.10Wh/g) combined with a high negative standard potential (1.676 V vs SHE) [15]. Further arguments for its consideration are its low production cost and the existence of a large base for manufacture and distribution.

## 2. Material and Methods

### 2.1. Preparation of the specimens

Aluminium specimens of 99.98% of 6 cm<sup>2</sup> area with a hole drilled at the upper edge to hook it in the glass rod for immersion in the test solution were used for weight loss measurements. The aluminium specimens were polished to a mirror finish with emery papers of 1/0, 2/0, 3/0 and 4/0 grades, washed with double distilled water, degreased with acetone and used for the weight loss method and surface examination studies.

Polyamides containing oxadiazole ring is shown in figure 1 and it is used as corrosion inhibitors.

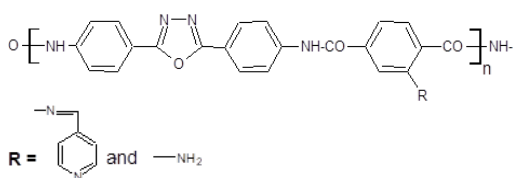


Fig. 1 Polyamides containing oxadiazole ring

\*Corresponding Author - E-mail: subha.moses@gmail.com

**2.2 Corrosion Inhibitor Studies**

The weight loss and temperature measurements were carried out as described elsewhere [16,17]. Inhibition efficiencies for different concentrations of P1 and P2 were calculated in the absence and presence of the inhibitor in 1N HCl solution at 30°C.

**2.2.1 Electrochemical Impedance Spectroscopy**

Electrochemical impedance measurements have been made to understand the mechanism of corrosion inhibition and the effectiveness of the oxadiazoles in the polymer ring. Impedance measurements were carried out at the open circuit potential using computer controlled potentiostat. After immersion of the specimen, before the impedance measurement, a stabilization period of 30min was observed for Eoc to attain a stable value. The ac frequency range extended from 10kHz to 0.01Hz with a signal amplitude of 10mV at the corrosion potential. Z-view software automatically controlled the measurements, and the impedance diagrams are given in the Nyquist representation (Zreal vs Zimaginary). From the Nyquist plots, electrochemical parameters such as Cdl and Rt were calculated.

**2.2.2 Polarisation measurements**

The Tafel polarization measurements were made after EIS studies in the same cell set-up for a potential range of -200mV to +200mV concerning open circuit potential at a scan rate of 1mV/sec. From the plot of E Vs log I, the potential corrosion Ecorr, corrosion current Icorr, Tafel slopes ba and bc were obtained in the absence and the presence of inhibitors at various concentrations.

**2.2.3 Surface Examination studies**

Aluminium specimens used for the weight loss method have been used for the entire Scanning Electron Microscopy study. Surface morphological characteristics of the inhibited and uninhibited samples were recorded after one-hour immersion in the aggressive medium at room temperature. The optimum concentration for recording SEM was chosen as 1000 ppm since the inhibitors exhibited the highest inhibition efficiencies at this concentration.

**3. Results and Discussion**

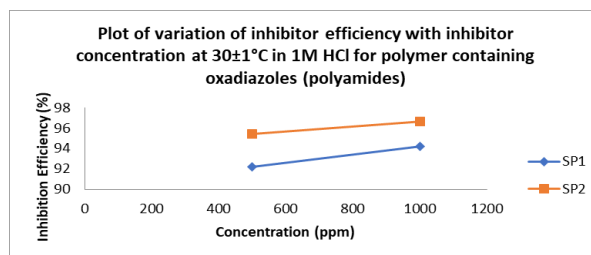
**3.1. Weight loss method**

Analysis of Weight loss data derived for the corrosion inhibition of aluminium surface in the absence and presence of various concentrations of polymeric inhibitors, viz, P1 and P2 in 1M HCl, reveals that the inhibition efficiency increases with the increase in the

concentration. Figure 2 shows the variation in inhibitor efficiency with change in concentration of inhibitor. The inhibitor efficiency is increased with increase in concentration of inhibitor from 450ppm to 1000ppm.

**Table 1 Inhibition Efficiency of Polymer on Aluminum in 1MHCl**

S. No	Name of the Inhibitor	Concentration (ppm)	Average Weight loss(g)	Corrosion Rate (mpy)	Degree of Surface Coverage	Inhibition Efficiency (%)
1	Blank	-	0.0807	0.4364	-	-
2	P1	500	0.0063	0.0341	0.9219	92.19
		1000	0.0047	0.0254	0.9418	94.18
3	P2	500	0.0037	0.0201	0.9542	95.42
		1000	0.0027	0.0146	0.9665	96.65



**Fig. 2 Variation of Inhibitor efficiency**

**3.2. Potentiodynamic polarization method**

Analysis of potentiodynamic polarization curves and data indicate that both the polymeric inhibitors exhibit excellent inhibition efficiency for aluminium corrosion in hydrochloric acid solution. For these polymer inhibitors, the inhibition efficiency increases with the increase in inhibitor concentration. Analysis of ba and bc values for the polymeric inhibitors P1 and P2 indicate that they behave as predominantly anodic inhibitors.

**Table 2 Inhibition Efficiency of the polymers in 1M HCl by polarization method at 30±1°C**

S. No	Name of the inhibitors	Inhibitor Concentration	ba mV/dec	bc mV/dec	-Ecorr (-mV)	Icorr (µA/cm²)	IE(%)
1.	Blank		0.365	0.291	0.1297	0.5589	
2.	P1	500	0.068	0.150	0.0559	0.1543	72.39
		1000	0.095	0.160	0.0429	0.1438	74.27
3.	P2	500	0.101	0.155	0.0489	0.1220	78.17
		1000	0.129	0.160	0.0232	0.1020	81.75

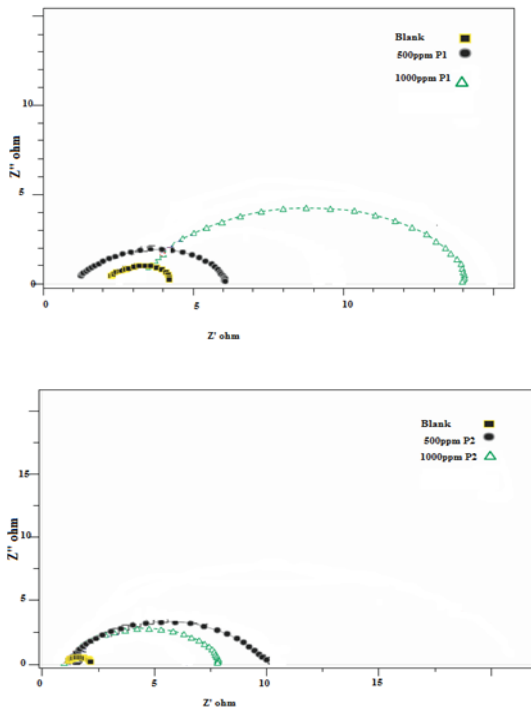


Fig. 3. Nyquist Plot

### 3.3. Electrochemical Impedance method

Figure 3 depicts the Nyquist plot for aluminium blank, film inhibitor with 500ppm and 1000ppm on aluminium. Analysis of the impedance data and the Nyquist plots reveals that polymeric inhibitors inhibit the corrosion of aluminium in 1M HCl solution with the inhibition efficiency varying from ~90% to ~96% for the change of inhibitor concentration from 500 ppm to 1000 ppm. The fact that the Cdl values for the inhibitors have decreased with the increase in inhibitor concentration indicates that inhibitor adsorption as the corroding surface has increased with increasing inhibitor concentration. Since the Nyquist plots are semicircular, the corrosion process is activation controlled in the presence of these inhibitors.

Table 3 Impedance parameters for corrosion of aluminium with polymers as inhibitors in 1M HCl

S.No	Name of the inhibitor	Concentration n (ppm)	R <sub>i</sub> (ohm/cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	IE (%)
1.	Blank	-	1.042	6.110	-
2.	P1	500	2.907	9.593	64.15
		1000	3.065	5.773	66.00
3.	P2	500	2.942	5.706	64.58
		1000	5.79	7.884	82.00

### 3.4. Adsorption Isotherm

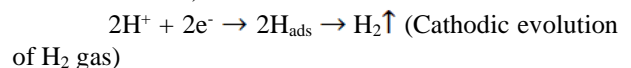
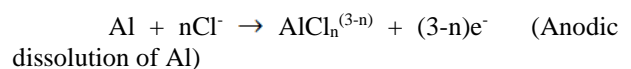
Analysis of adsorption data provides information regarding the interaction among the inhibitor molecules and their interaction with the metal surface. The adsorbed molecules may hinder the surface from adsorbing additional molecules at neighbouring sites. Hence, a monolayered or multilayered can be found from the analysis of  $\theta$  Vs  $\log C_{inh}$  plots. Analysis of these plots reveals that the adsorption is monolayered.

#### 3.4.1. Effect of Temperature on adsorption and inhibition efficiency

The data derived from temperature variation studies indicate that the surface coverage values and hence the % IE values decrease with the increase in temperature. It indicates that the adsorption is physical in nature (physisorption).

#### 3.4.2. mechanism of inhibition by oxadiazole polymers in the present investigation:

The most probable mechanism of corrosion of Al in HCl medium can be summarized as



Hence the prime step in the corrosion of Al in HCl medium is the attack of aluminium metal by Cl<sup>-</sup> ions of the aggressive acid medium.

Polymers contain nitrogen atoms in the polymeric chain, and the H<sup>+</sup> ions can protonate a sizeable proportion of them from the HCl medium. Then the binding of Cl<sup>-</sup> ions with polymeric inhibitor molecules may lead to forming a quaternary salt. These quaternary salt molecules with many cationic anchoring sites may adsorb on the anionic metal sites on the aluminium surface. Both the polymers are aromatic polymers; hence, aromatic rings are expected to participate in the adsorption process by the interaction of the  $\pi$ -electrons of the aromatic sextet with the vacant orbitals of the aluminium surface. In addition to the aromatic rings, the functional groups present in the polymer molecular such as -N=N-, C=N, will also be anchoring sites to facilitate the adsorption of polymer molecules. The unpaired electrons on the oxygen atom will also function as another anchoring site to help the adsorption process. The adoption of flat orientation of the entire molecule with respect to the metal surface assists the entire adsorption process.

### 3.4.3. Comparison of inhibition efficiency between P1 and P2

Although both P1 and P2 have inhibition efficiencies above 95%, P2 seems to be more efficient (~98%) than P1(~96%). This small difference in inhibition efficiency can be attributed to the steric factor arising from the presence of pendant units in the benzene ring of the dicarboxylic acid monomer. The absence of a pendant unit in P2 makes these molecules more readily adsorbed linearly on adjacent sites without steric hindrance. Further, the  $-NH_2$  groups adsorbed on neighbouring sites can interact due to the formation of hydrogen bonding as  $-N-----H-----N-$ . Consequently, P2 is a more efficient inhibitor as compared to P1.

### 3.4.4. SEM Studies

Figure 4a shows the Aluminium polished surface before immersion in 1M HCl solution, and figure 4b depicts the image of the aluminium sample after being immersed in 1M HCl solution. The electrolyte solution severely affects the uncoated aluminium due to corrosive species.

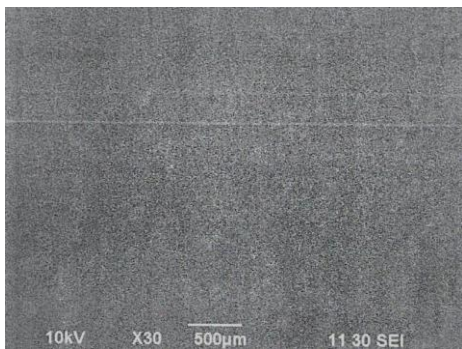


Fig 4a. Aluminium polished surface before immersion in 1M HCl Solution

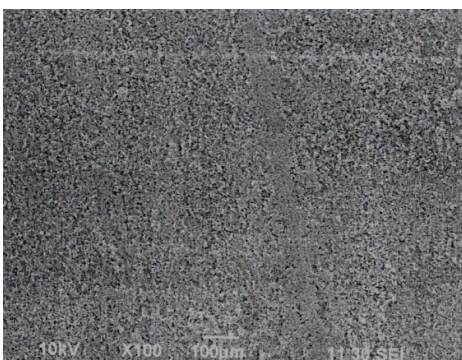


Fig. 4b SEM for aluminium after immersion in 1M HCl solution

Figure 5a shows the corroded image of aluminium coated with the P1 inhibitor, and figure 5b depicts the corroded image of the aluminium coated with the P2 inhibitor. As evidenced from SEM images, the resistance in corrosion has been higher in the P2 inhibitor when compared to the P1 inhibitor, as the P2-coated Al corroded image reveals less damage. Here, the P1 inhibitor-coated Al corroded image presents a severe corrosion attack.

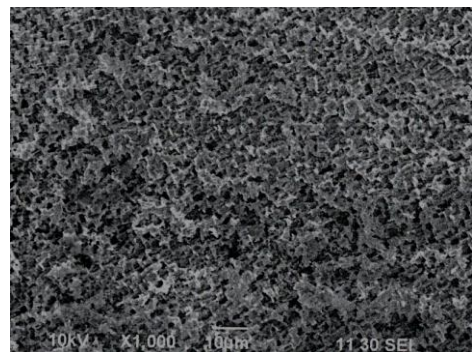


Fig 5a. SEM Image of Aluminium coated with P1 inhibitor

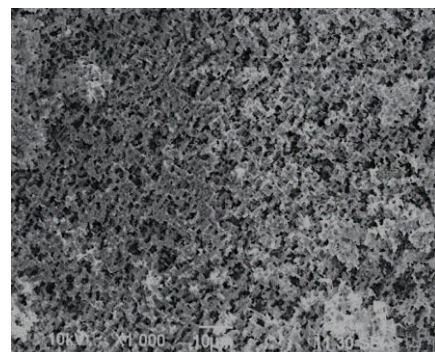


Fig 5b. SEM image of aluminium coated with P2 inhibitor

## 4. Conclusion

Polyamides containing oxadiazole ring perform well in 1N HCl solution and inhibits the corrosion of aluminium 1N HCl solution at a concentration of 1000 ppm. The adsorption of polyamides on the aluminium surface in 1N HCl solution obeys Langmuir adsorption isotherm. The SEM analysis confirmed the protective nature of the polyamide on the metal surface. Hence, newly synthesized polyamides containing oxadiazole ring may be considered a safe and effective inhibitor for decreasing the corrosion of Al in an acidic medium.

## References

1. Shukla S.K., Quraishi M.A. and Prakash R., A Self Doped Conducting Polymer Polyanthranilic Acid": An efficient corrosion inhibitor for mild steel in acidic solution, *Corros. Sci.*, 50, 2867-2872 (2008)
2. James A. O. and Akaranta O., Inhibition of Corrosion of Zinc in Hydrochloric Acid Solution by Red Onion Skin Acetone Extract, *Res.J.Chem.Sci.*, 1 (1), 31-37 (2011)
3. Manimaran N., Rajendran S., Manivannan M and John Mary S., Corrosion Inhibition of Carbon Steel by Polyacrylamide, *Res.J.Chem.Sci.*, 2 (3), 52-57 (2012)
4. Kumar Harish and Sunita, ADS, ALS, AHDS and ADDBS Surfactants as Corrosion Inhibitors for Carbon Steel in acidic Solution, *Res.J.Chem.Sci.*, 2 (7), 1-6 (2012)
5. Sribharathy V. and Susai Rajendran, Influence of Melonic acid on the Corrosion Inhibition of Sodium Metavanadate in Chloride Medium, *Res.J.Chem.Sci.*, 2 (6), 72-81 (2012)
6. Tripathi R., Chaturvedi A. and Upadhayay R.K. Corrosion Inhibitory Effects of Some Substituted Thiourea on Mild Steel in Acid Media, *Res.J.Chem.Sci.*, 2 (2), 18-27 (2012)
7. Moretti G., Quartarone G., Tassan A. and Zingales A., Some derivatives of indole as mild steel corrosion inhibitors in 0.5 M sulphuric acid, *British Corros. J.*, 31 (1), 49-54 (1996)
8. Stankovic Z.D. and Vukovic M., The Influence of thiourea on kinetic parameters on the cathodic and anodic reaction at different metals in H<sub>2</sub>SO<sub>4</sub> solution, *Electrochim. Acta*, 41, 2529-2535 (1996)
9. Sing A. and Chaudhary, R.S., Dithizone and Thiosemicarbazide as Inhibitors of Corrosion of Type 304 Stainless Steel in 1.0 M Sulfuric Acid Solution, *British Corros. J.*, 31(4), 300-304 (1996)
10. Sitaram S.P., Stoffe J.O. and Okeefe T.J., Application of conducting polymers in corrosion protection, *Journal of Coating Technology*, 69 (866), 65-69 (1997)
11. Subramania A., Sundaram N.T.K., Sathiya Priya R. and Muralidharan, V.S., Vasudevan T., Polymeric corrosion inhibitors -an overview, *Bull. Electrochem.*, 20 (2), 49 -58 (2004)
12. S. Zaromb, The use and behavior of aluminum anodes in alkaline primary batteries, *J. Electrochem. Soc.* 109 (1962) 1125.
13. K.F. Blurton, A.F. Sammells, Metal/air batteries: Their status and potential – a review, *J. Power Sour.* 4 (1969) 263.
14. D.D. Macdonald, C. English, Development of anodes for aluminium/air batteries – solution phase inhibition of corrosion, *J. Appl. Electrochem.* 20 (1990) 405.
15. A.J. Bard, R. Parsons, J. Jordan, in: *Standard Potentials in Aqueous Solution*, Marcel Dekker, Inc., New York, 1985, p. 566.
16. Subramania A., Sathiya Priya R., Saminathan K. and Muralidharan, V.S., Vasudevan, T., Aldimines-effective corrosion inhibitors for mild steel in hydrochloric acidsolution, *J. Applied Electrochem.*, 34 (7), 693-696 (2004)
17. Saithya Priya R., Muralidharan V.S. and Subramania A., Development of Novel Acidizing Inhibitors for Carbon Steel Corrosion in 15% Boiling Hydrochloric Acid, *Corrosion*, 64 (6), 541-552 (2008)