

The Inhibition Chemistry of 2-Amino, 5-Phenyl 1, 3, 4-Triazole for Aluminium in Hydrochloric Acid Solution

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Abstract: The inhibitor 2-amino, 5-phenyl 1,3,4-triazole have been synthesized in alcohol medium. Corrosion of aluminium in 2N hydrochloric acid and the effect of the inhibitors in combating the corrosion have been investigated. The conventional weight loss method and electrochemical potentiodynamic polarization method have been employed for aluminium plates. From the above analysis, the inhibiting efficiencies increases with increasing inhibitor concentration then decreases. Polarization and impedance values shows that triazole inhibitor is marginally anodic controlled and activation controlled. SEM micrographs indicate that the metal surface is fully covered with inhibitor molecules thereby providing high degree of protection.

Key Words: Corrosion, Inhibitor, Potentiodynamic polarization, Triazole, Weight loss method.

I. Introduction

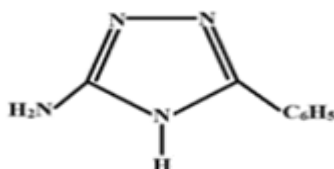
Corrosion is defined as degradation or deterioration of materials due to chemical or electrochemical activity on the surroundings^{[1],[2]}. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Replacing or repairing components of corroded systems are expensive, but proper maintenance can reduce much of the cost. Corrosion inhibitors are often added to paints, coolants, fuels, hydraulic fluids, boiler water, engine oil and many other fluids used in industry. A common mechanism for inhibiting corrosion involves formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal. Corrosion inhibitors used to protect fuel pipelines, storage tanks and pumping equipments.

II. Experimental Methods

All the reagents used are of analar grade.

2.1 Preparation of Inhibitor:

The synthesis of triazole involves the synthesis of 1,3,4-oxadiazole and their conversion into triazole. The synthesis generally involves three stages. In the first stage semicarbazone was prepared from semicarbazide hydrochloride and sodium acetate crystals. 1-oxa-3,4-diazoles have been synthesized in the second stage by following the available literature^[3]. 2-amino, 5-phenyl 1,3,4-triazoles were synthesized by refluxing oxadiazoles(from stage 2) in alcohol with ammonia for 1-2 hrs in the third stage. The reaction mixture was cooled in ice to get the 2-amino, 5-phenyl 1,3,4-triazole. The structure of the inhibitor is



2.2 Material Used

The aluminium specimens have been used for this studies. Aluminium is used excessively in the modern world and the uses of the metal are extremely diverse due to its many unusual combinations of properties in the transports, constructions, packaging and electrical sectors. It is often observed that may suffer corrosion damage from ingress of chlorides and other extraneous anions as a result of inadequate provision for corrosion mitigation such as faulty design features and nonintroduction of suitable corrosion inhibitors into the system. The use of organic inhibitors is the most economical and practical method of protecting metals against aqueous corrosion^[4-6]. These inhibitors contain hetero atoms such as sulphur, oxygen and nitrogen in their structures in addition to multiple bonds and may contain cyclic hydrocarbons as well^[7-9].

The aluminium specimen contains 99.9% aluminium. The hydrochloric acid used is of A.R grade for the preparation of 2N HCl solution using double distilled water. Standard inhibitor solutions were prepared by dissolving in ethyl alcohol diluted to suitable volumes and standardized using standard acid solutions.

2.3 Techniques Used For The Study

2.3.1 Weight Loss Measurement

This method is the most reliable method. Aluminium panel of 1cm x 2.5 cm has been used. It was polished using 100, 200, 300, 400, 500 and 600 emery papers and finally degreased with the organic solvent acetone. The specimens were immersed in 1N hydrochloric acid with and without inhibitor. After 1 hour, the specimens were washed with distilled water, dried and again weighed. The weight loss was noted. From this weight loss value, corrosion rate and inhibitor efficiency were determined.

2.3.2 Corrosion Rate

Corrosion rate has been determined from the following relationship,

$$\text{" Corrosion rate (mpy) = } \frac{\text{Weight loss x 87.6}}{\text{Area x Time x Density}} \text{ " -----(1)}$$

Where, W = Weight loss in mg

D = density in g/cc.

A = area of exposure in cm² and

T = time in hours

2.3.3 Inhibitor Efficiency

Inhibitor efficiency has been determined by using the following relationship

$$\text{"I.E(\%) = } \frac{W_o - W_i}{W_o} \times 100 \text{ " -----(2)}$$

Where W_o is the weight loss without inhibitor and W_i is the weight loss with inhibitor.

2.3.4 Temperature Studies

The inhibitor efficiencies at room temperature 35°, 45° and 50°C have been determined for optimum inhibitor concentration by using weight loss experiments.

2.3.5 Measurement Of Surface Coverage (θ)

The surface coverage (θ) is calculated using the formula

$$\text{"Surface coverage(\theta) = } \frac{W_b - W_i}{W_b} \text{ " -----(3)}$$

Where W_b and W_i are the weight losses per unit area per unit time without and with inhibitor respectively.

2.3.6 Potentiodynamic Polarization Technique (Tafel Polarization Method)

The potentiodynamic polarization studies were made using the BAS Electrochemical work station.

2.3.6.1 Experiment

100ml of 1N HCl solution was taken in the standard polarization test cell. A polished aluminium electrode of 0.19635cm² area was mounted through Teflon gasket assemble as the working electrode. A platinum gauze electrode was introduced as the auxiliary electrode. The calomel electrode was introduced into cell by means of a Luggin capillary and the working electrode was allowed to attain steady state for about 20 minutes. The whole cell assembly was maintained at 30 ± 0.1°C.

Potentiodynamic polarization curves was recorded at a scan rate of 20mV/min using an X-Y recorder. The polarization curve was recorded by starting at -200mV cathodic to the open circuit potential and continued through E_{corr}, in the anodic direction upto +200mV. Similar polarization curves were recorded by employing various concentrations of the inhibitors.

2.3.6.2 Electrochemical Impedance Studies

The electrochemical impedance spectroscopic studies were carried out using the same experimental set-up before recording the polarization curves. The impedance measurements curve taken at the open circuit potentials using an a.c. signal amplitude of 10mV and by varying the ac frequency from 10 KHz to 0.01 Hz.

2.3.7. Scanning Electron Microscope (SEM)

Surface examination of aluminum specimens were made using scanning electron microscopy.

III. Results And Discussion

3.1 Weight Loss Analysis

The kinetic parameters derived from the weight loss measurements on the corrosion and inhibition by 2-amino, 5-phenyl 1,3,4-triazole have been summarized and present in Table-1. It is evident from these data that the inhibition efficiency increased with the increase in inhibitor concentration and then decreases. The weight loss data at higher temperatures are given in Table-2.

3.2 Impedance Spectroscopic Analysis

Corrosion inhibition behavior of aluminium in 1M HCl with different concentrations of the additives selected for the current study has been investigated by employing AC impedance measurements. The impedance data have been presented in Table-3. Fig.1 contain the Nyquist plots for aluminium in 1M HCl without and with various concentrations of inhibitor 2-amino, 5-phenyl 1,3,4-triazole. The quantitative results of impedance measurements show that the inhibiting efficiencies increases with increasing inhibitor concentration then decreases.

3.3 Potentiodynamic Polarization Analysis

Fig.2 show the anodic and cathodic polarization curves for aluminium in HCl without and with the inhibitor 2-amino, 5-phenyl 1,3,4-triazole. Electrochemical parameters obtained from the Tafel extrapolation method of the polarization curves are given in Table-4. The trend in the variation of inhibition efficiency with concentration from polarization studies is same as that observed from other techniques discussed above.

3.3.1 Polarization Behavior And Impedence Characteristics Of Inhibitor 2-Amino, 5-Phenyl 1,3,4-Triazole

Analysis of the curves presented in Fig.1 and the corrosion kinetic parameters available in Table-3 shows that for both cathodic and anodic curves, a lower current density (I_{corr}) value has been observed in the presence of 2-amino, 5-phenyl 1,3,4-triazole. Further, the addition of these compounds has caused the shifting of E_{corr} value slightly and resulted in the variation of both the Tafel slopes. However, b_a has been shifted to a slightly greater extent than b_c , suggesting that the inhibition of aluminium by the inhibitor 2-amino, 5-phenyl 1,3,4-triazole is marginally anodic controlled.

A perusal of Nyquist plots(Fig.1) reveals that all these plots are semicircular nature both in the presence and absence of inhibitor. This indicates that the corrosion reaction and its inhibition by triazoles are activation controlled.

Analysis of the impedance data in Table-3 shows that C_{dl} value has increased first and then decreased progressively with the increase in inhibitor concentration, suggesting that these inhibitor molecules function by adsorption mechanism at metal solution interface forming a protective layer.

3.4 SEM Analysis

In Fig.3 and Fig.4 the scanning electron micrographs of aluminium exposed to 1M HCl containing 5mM concentrations of the inhibitor have been presented. Fig.3 for blank indicates uniform corrosion. Further, flakes are noticed in this micrographs suggesting the formation of corrosion products such as metal hydroxides and oxides. Fig.4 recorded for inhibited solutions indicate that the metal surface is fully covered with inhibitor molecules thereby providing high degree of protection.

Table – 1 Inhibition Efficiencies Of Various Concentrations Of Inhibitors For The Corrosion Of Aluminium In 1N HCl By Weight Loss Method At 30±1°C.

Name Of The Inhibitor	Inhibitors Concentratio (mM)	Weight Loss In gm	IE(%)	Corrosion Rate (mpy)	Surface Coverage (θ)
Blank	-	0.2422	-	1.3097	-
2-amino, 5-phenyl 1,3,4-triazole	1	0.0265	89.06	0.1433	0.8906
	2	0.0238	90.17	0.1287	0.9017
	3	0.0272	88.77	1.1471	0.8877
	4	0.0319	86.83	0.1725	0.8683
	5	0.0358	85.22	0.1936	0.8522

Table – 2 Inhibition Efficiencies At 1mM Concentrations Of Inhibitors For The Corrosion Of Aluminium In 1N HCl By Weight Loss Method At Higher Temperature.

Name Of The Inhibitor	Temperature (°C)	Weight Loss In (gm)	IE(%)	Corrosion Rate (mpy)	Surface Coverage (θ)
Blank	35	0.2729	-	1.4757	-
	45	0.2603	-	1.4075	-
	50	0.2846	-	1.5389	-
2-amino, 5-phenyl 1,3,4-triazole	35	0.1430	47.60	0.7733	0.4760
	45	0.1503	42.26	0.8127	0.4226
	50	0.1631	42.69	0.8819	0.4269

Table – 3 Impedance Parameters For Aluminium For Different Concentration Of The Inhibitors In 1N HCl.

Name Of The Inhibitors	Inhibitors Concentration (mM)	R _t Ohm cm ²	C _{dl} µf/cm ²	IE (%)
2-amino, 5-phenyl 1,3,4-triazole	Blank	1.979	56.03	-
	1	1.414	95.93	55.17
	2	6.302	57.73	68.60
	3	6.382	57.06	68.99
	4	9.753	78.84	79.71
	5	1.150	92.01	72.09

Table – 4 Corrosion Parameters For Aluminium With Various Concentrations Of The Inhibitors In 1N HCl By Potentiodynamic Polarization Method.

Name Of The Inhibitor	Inhibitors Concentration (mM)	Tafel Slopes		E _{corr} (-)mv	I _{corr} µa/cm ²	Corrosion Rate	IE (%)
		b _a	b _c				
2-amino, 5-phenyl 1,3,4-triazole	Blank	0.115	0.187	0.0536	0.003258	10.66	-
	1	0.068	0.150	0.0559	0.001543	5.048	52.64
	2	0.095	0.160	0.0429	0.001438	4.706	55.86
	3	0.101	0.155	0.0489	0.001220	3.993	62.55
	4	0.129	0.160	0.0232	0.001320	4.321	59.48
	5	0.140	0.167	0.0252	0.001333	4.361	59.09

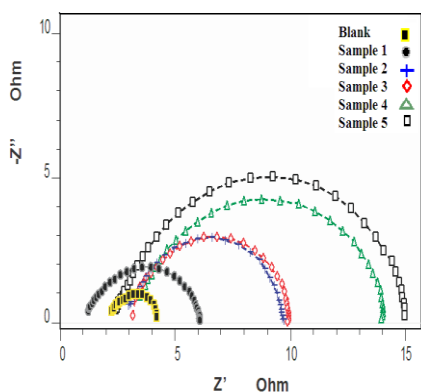


Fig.1. Nyquist diagram for aluminium in 1N HCl for different concentrations of Inhibitor.

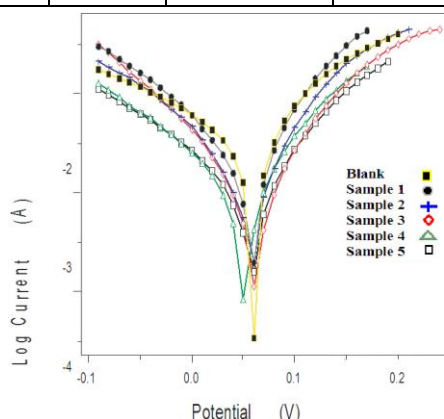


Fig.2 Polarization curves for aluminium recorded in 1N HCl for different concentrations of inhibitor.

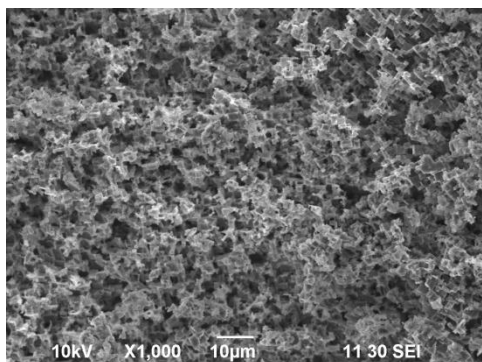


Fig.3. SEM image of aluminium in 1N HCl in absence of inhibitors

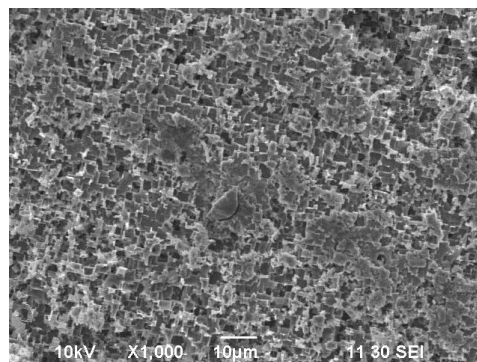


Fig.4. SEM image of aluminium in 1N HCl in presence of 2-amino, 5-phenyl, 1,3,4 –triazole

IV. Conclusion

The triazole was used as corrosion inhibitors for aluminium in HCl acid. The inhibition efficiency generally increased with the increase in inhibitor concentration. Increase of temperature leads to a decrease in inhibition efficiency. The potentiodynamic polarization analysis, indicates that the inhibitors are predominantly anodic. The impedance spectroscopic analysis indicates that the corrosion reaction and its inhibition by substituted triazoles are activation controlled. The inhibitor providing high degree of protection by the metal surface is fully covered with inhibitor molecules is suggested by SEM analysis.

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