Synthesis and Characterization of Corrosion Inhibitor Of 2-Amino 5-Oleyl-1, 3, 4-Thiadiazol in 1M HCL solution for Mild Steel

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ABSTRACT:

Novel corrosion inhibitor as a green chemical product namely derivative, 2-amino 5-oleyl-1,3,4-thiadiazol (AOT) was synthesized by cyclization of oleic acid. AOT was evaluated as corrosion inhibitor for Mild Steel in 1M of Hydrochloric acid solution using Potentiodynamic and Electrochemical Impedance Spectroscopy (EIS) technique. Results obtained show that AOT acts as a good corrosion inhibitor for mild steel in 1M HCl solution.

Keywords: Corrosion Inhibitor; Oleic acid phosphorousoxychloride; thiosemicarbazide; aminooleylthiadiazole,EIS,Potentiodynamic,Mild Steel.

1. INTRODUCTION

Mild Steel is used as a structural material for vessels reactor, pipelines, tank etc. which are known to corrode invariably in contact with various solvents. From the view point of nation's economy and financial implications of corrosion hazard, it is necessary to adopt appropriate means and ways to reduce the losses due to corrosion and. In acidic/alkaline aqueous environments, its corrosion and prevention are well studied, however in non-aqueous solvents limited reports are available [1-4]. Thiadiazole compounds with wide applications in medicinal chemistry as antibacterial, antimicrobial, antidepressant, anti-inflammatory, antiviral, and human antifungal agents, and in agricultural science as potent fungicides, herbicides and insecticides [5-12]. Thiadiazole compounds have emerged as a new and potential class of corrosion inhibitors. The corrosion inhibiting behavior of thiadiazoles on Mild Steel in acidic media were reported by authors [13–16] A survey of the literature reveals that despite the high ability of thiadiazole compounds to strongly interact with metal surfaces, little attention has been made on the use of these compounds as corrosion inhibitors in hot acids.The research area is primarily concerned to synthesize the corrosion inhibitor molecule by combination of natural products with synthetic chemical that environmentally friendly and ecologically acceptable. The work is focused on the synthesis of amino oleyl thiadiazole which used oleic acid as raw material. Performance evaluation of the product and correlation between the molecular structure of the product and its inhibition efficiency, electrochemical studies such as potentiodynamic polarization and electrochemistry impedance spectroscopy were conducted.

2. EXPERIMENTAL

Chemical composition
(Ideal analysis to meet the majority of grades listed above)

Carbon	0.16-0.18%
Silicon	0.40% max
Manganese	0.70-0.90%
Sulphur	0.040% Max
Phosphorus	0.040% Max

Mechanical properties in cold drawn condition

Max Stress	400-560 n/mm^2
Yield Stress	300-440 n/mm^2 Min
0.2% Proof Stress	280-420 n/mm^2 Min
Elongation	10-14% Min

2.1. Synthesis of 2-amino 5-oleyl-1, 3, 4-thiadiazol

The inhibitor 2-amino 5-oleyl-1,3,4-thiadiazol (AOT) was synthesized by the cyclization reaction of oleic acid and thiosemicarbazide. Briefly, a mixture of phosphorylchloride (20 ml) was added to the oleic acid (0.05 mol) and the mixture was stirred for one hour at room temperature. Thiosemicarbazide (4.56 g, 0.05mol) was added and the mixture was heated under reflux for 24 hours. On cooling, the mixture was poured on to ice. After 4 hours, the mixture was stirred for 15 minutes, to decompose the excess phosphorusoxychloride, and then heated under reflux for 30 minutes; cool the mixture was neutralized by 5 % potassium hydroxide. The precipitated was filtered, washed with water, dried and re-crystallized from ethanol.

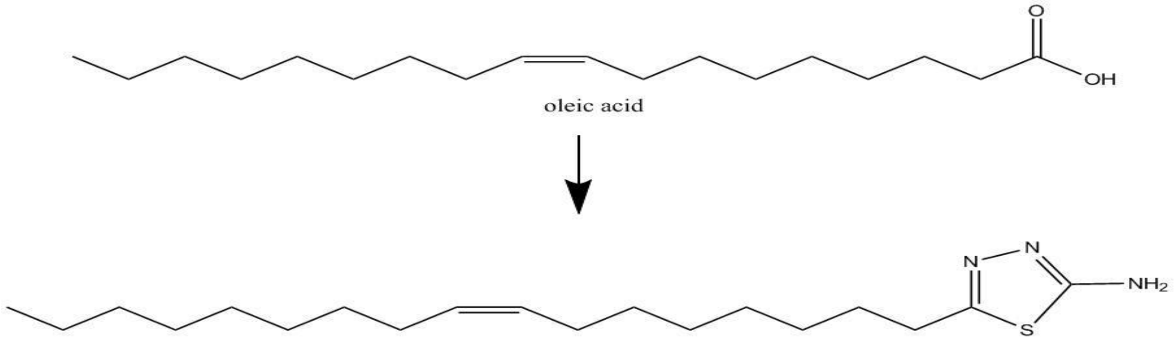

Figure 1. Amino Oleyl Thiadiazole reaction formation

2.2. Inhibition Performance Test

Electrochemical measurements were conducted in a standard three-electrode cell. The counter electrode was a mesh of platinum of high purity (99.9%) and the reference electrode consisted of a saturated calomel electrode (SCE). The third electrode was the working electrode which was prepared from a round bar of carbon steel fixed in a cylindrical rod made out of Teflon. The cross-section area in contact with the solution was 1 cm^2. All of the tests were conducted in atmospheric at 30±1°C. Electrochemical testing was conducted using CH-Instrument(USA). Before measurements, the surface of working electrode was mechanically abraded using different grades of abrasive papers, which ended with the 2000 grade. The disc was cleaned by washing with bidistilled water, thoroughly degreased with acetone, washed once more with bidistilled water and finally dried with a filter paper. For each test, a newly abraded electrode was used. The freshly polished electrode was pretreated further before each experiment by holding the potential at –1 V vs. a saturated calomel electrode for 1 min to reduce the oxide surface layer, and then open circuit potential (E-$_{ocp}$) was allowed to stabilize for 10 minutes.

The corrosion tests were conducted in 1.0 M HCl solution in the absence and presence of various AOT concentrations of which molecular structures are given in Fig. 1. HCl solutions (1.0 M) were prepared from concentrated HCl solution and diluted by distilled water. The concentrations of the inhibitors employed were varied from 10.0 to 50 ppm. All of the test solutions were prepared from analytical-grade chemical reagents in distilled water without further purification. For each experiment, a freshly prepared solution was used. The test solutions were opened to the atmosphere without stirring and the temperature was controlled thermostatically at 30^{o}C.

2.3 Electrochemical Impedance Spectroscopy (EIS)

The EIS method is very useful in characterising electrode behaviour. The electrode characterisation includes the determination of the polarisation resistance (Rp), corrosion rate and the electrochemical mechanism. The usefulness of these data permits the analysis of the alternating current (AC) impedance data, which are based on modelling a corrosion process by an electrical circuit. The EIS technique is based on the response of an equivalent circuit for an electrode/solution interface. The response can be analysed by transfer functions due to an applied small-amplitude potential excitation at varying signals and sweep rates. In turn, a sine-wave perturbation of small amplitude is employed on a corroding system being is modelled as an equivalent circuit for determining the corrosion mechanism and polarisation resistance.12Table 5 lists the impedance parameters of the Nyquist plots of the ethyl acetate extract of gambir in different concentrations. From this experiment, the Nyquist plot shows that, at a concentration of 150 ppm, the percentages of inhibition efficiency are highest when the charge transfer potential, Rct, is also in good agreement (Fig. 4). In these spectra, the variation of impedance responses of mildsteel after the addition of the ethyl acetate extract of gambir to the pH 5 aqueous solution is remarkable. The Randles CPE circuit was known as the equivalent circuit in our study.

2.4 Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

Figure 6 shows the SEM micrographs of different slides of mild steelafter immersion in the aqueous solution with the absence and presence of the inhibitor. Here, the micrograph exhibited a cocoon-like structure for solution with the absence of the inhibitor. This explains the fact that the surface was already undergoing a localised attack, which resulted in a cocoon-like structure, whereas there was an improvement in the surface morphology of mild steel that was treated with the inhibitor. From the EDX evaluation, it is clear that the upraising value of O is due to the formation of the ferrous hydroxide, whereas, for C, it is due to the presence of catechin that acts as the active inhibitor and complexes with the mild steel surface (Table 6 and Fig. 7).

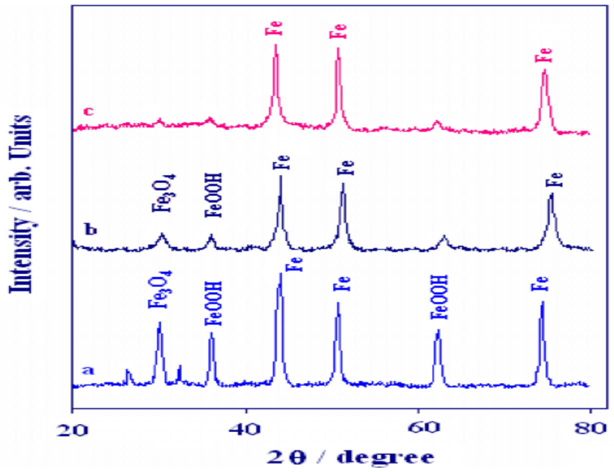

Fig.2 XRD of Mild steel with and without inhibitor

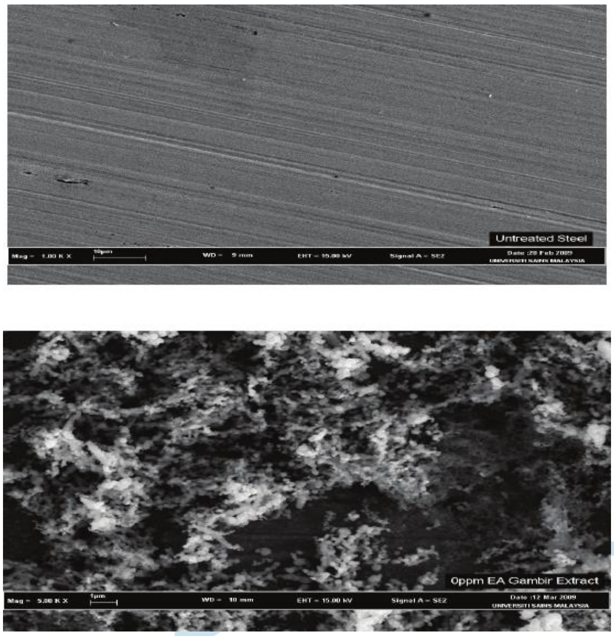

Figure 3: SEM micrographs of mild steel with and without inhibitor

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic and Electrochemical Impedance Spectroscopy Measurement

The anodic and cathodic polarization curve recorded on Al 7075 in 1M of HCl at 30^{O}C in absence and presence of various concentration of AOT is shown in Fig 2. The cathodic current densities (I-corr) were determined by extrapolation of the cathodic Tafel lines to the corrosion potential (E-corr). In acid solution the anodic process of corrosion is the passage of metal ion from metal surface in to the solution and the principle cathodic process is the discharge of hydrogen ion to produce hydrogen gas or oxygen reduction.

The effect of the concentration of AOT was shown in Figure 2 which presents the anodic and cathodic Tafel curves of mild steel in 1 M of HCl. The inhibition efficiency (IE%) was calculated from polarization with AOT concentration for mild steel electrode in 1M of HCl solutions using equation 1 below:

$$IE\,(\%) = \left[\frac{io_{Corr.} - i_{Corr.}}{io_{Corr.}} \right] \times 100\% \qquad (1)$$

The result indicates that the I_{corr} decreased proportionally with increase inhibitor concentrations, that mean the metal dissolve in to the solution was decreased. The anodic and cathodic Tafel lines of Al 7075 in presence of AOT to be found was linear by increasing inhibitor concentrations. Values of anodic βa and cathodic βc Tafel constant and corrosion current density are listed in Table 1. This value was calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at E_{corr}. The inhibition efficiencies are calculated without and with AOT in 1.0 M HCl solution.

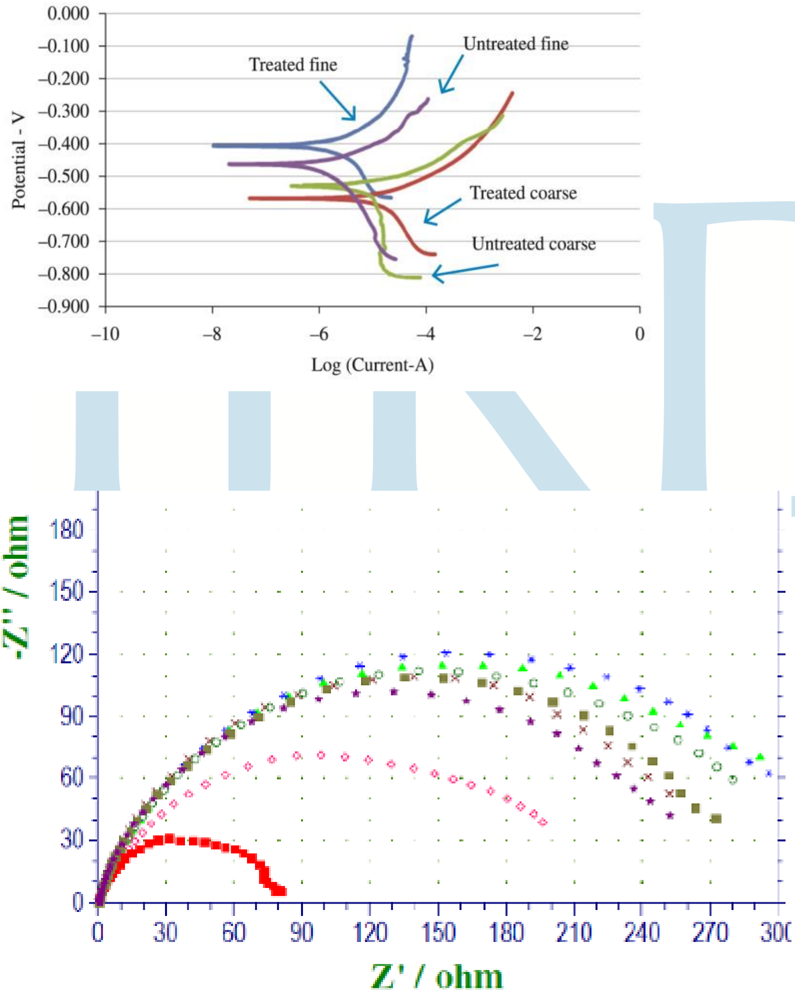

Figure 4. Potentiodynamic polarization curve & AC Impedence(EIS) of Mild Steel recorded in 1M HCl containing different concentration of AOT

4. CONCLUSION

2-amino 5-oleyl-1,-3,-4-thiadiazol (AOT) was synthesized and The corrosion inhibition property was evaluated by potentiodynamic and electrochemical impedance spectroscopy methods. It has been proved that AOT has good protection effect. The active site of the molecule is located on Nitrogen atom in the heterocyclic ring (thia-diazole) and leads to the transfer of *chelation* center.

The electrochemical studies proved that AOT displays inhibitor properties that work best at a concentration of 150 ppm and at a pH of 5. The polarisation measurement demonstrates that the extract under investigation acts as a mixed-type inhibitor, and the electrochemical impedance spectra shows inhibition when the sample was fitted with the Randles CPE circuit. SEM-EDX analysis shows that there was some improvement in the surface morphology of inhibited mild steel compared with uninhibited mild steel.

Acknowledgments

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