



Original Article

Study of corrosion inhibition of Aluminum in nitric acid solution using Anisaldehyde (4-methoxy benzaldehyde) as inhibitor

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ABSTRACT

The inhibitive action of Anisaldehyde (4-methoxy benzaldehyde) on corrosion of Aluminum in nitric acid solution was studied through weight loss method. Fourier Transform Infrared Spectroscopic Analysis (FTIR) was used to characterize the inhibitor and the corrosion product. The effect of different inhibitor concentrations was studied at 308, 313 and 318 K. The present study showed that the percentage of inhibition efficiency (% I.E.) is enhanced with increase of inhibitor concentration and decrease with rising in temperature. Maximum I.E. of Anisaldehyde was found 86.32 % at 308 K and 0.1M inhibitor concentration in 1.4M HNO₃ solution. The inhibitive action of the inhibitor is discussed in view of adsorption of Anisaldehyde molecule on the metal surface. It was found that the adsorption of the inhibitor on the metal surface follows Langmuir adsorption isotherm. Activation parameters governing the adsorption process were evaluated and discussed in detail.

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1. Introduction

Corrosion is the damage to metal as a result of reaction with its environment; damage is specified on purpose to exclude processes, like anodizing of Aluminum, chemical milling and bluing of steel, which modify the metal intentionally. Rusting is a type of corrosion but it is the corrosion of ferrous metals (irons and steels) only, producing that familiar brownish-red corrosion product called rust [1]. Corrosion is a natural process for metals that causes them to react with their environment to become more stable compounds [2]. Aluminum is

among the most commonly used metal in the world. Its lightness coupled with its strength, conductivity, barrier properties and its excellent corrosion resistance has all been its most important advantages and the main reasons for the continual growth in the usage of Aluminum [3]. Impure Aluminum has very good corrosion resistance in most environments. This is normally because Aluminum forms a thin, but effective oxide layer that prevents further oxidation. However, the oxide layer dissolve at a pH less than 4 or greater than 9,

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thus leading to the rapid corrosion of Aluminum [4]. Mineral acids and strong alkaline solutions are thus very corrosive for Aluminum. Acidic solutions are used for pickling, chemical and electrochemical etching of Aluminum [5]. Therefore, prevention of Aluminum corrosion in acidic media has great importance. One of the most common methods to prevent metals against acid corrosion is the use of organic compounds containing functional groups, heteroatoms such as (P, S, N and O), and pi electrons in their structure, as corrosion inhibitors [6]. Corrosion inhibitor is a chemical added to the corrosive environment in small quantity, so that they can adsorb on the metal surface to block the active sites on the surface, thus reduce the corrosion rate. Certain inhibitors interfere with the anode reaction, some with the cathode reaction, and some with both [7]. They are normally used to prevent general corrosion but majority are not effective in preventing localized attack, like pitting corrosion, crevice, or stress cracking corrosion. Inhibitors usually interact with the metal surface in some way to form a protective film of adsorbed inhibitor [8,9]. These inhibitors are commonly used in acids solution, although a few functions in neutral or alkaline solutions. Several organic compounds have been evaluated as corrosion inhibitors for Aluminum in acidic media, so, this work aims to study the inhibiting effect of Anisaldehyde for the corrosion of Aluminum in 1.4M HNO_3 by using weight loss method. However, the inhibitor and the corrosion product were characterized by FTIR analysis.

2. Materials and Methods

2.1. Specimen Preparation

Pure Aluminum metal (purity 99.5%) obtained from Metal Focus Fabrication Technology Incubation Centre Kano State, Nigeria, was used for the study. Each sheet was about 0.1 cm thickness and was mechanically press cut into 2 cm x 3 cm coupons. These coupons were with different grade emery paper. They were also degreased in absolute ethanol, rinsed in acetone, air-dried at room temperature and stored in a desiccator devoid of moisture before use in corrosion studies.

2.2. Preparation of Solutions

Nitric acid with percentage purity (68%) and density (1.51 g/L) was used as corrosive solution. The stock solution was used to prepare 1.4M concentration by diluting analytical grade of HNO_3 using double distilled water. Anisaldehyde (4-methoxy benzaldehyde) with percentage purity (98%) and density (1.11 g/cm³), thus, concentrations of the inhibitor used for the study were 0.02, 0.04, 0.06, 0.08 and 0.1M. Each of these concentrations was diluted in the prepared desired concentrations of acids for use as test solutions in weight loss.

2.3. Weight loss measurement

For weight loss experiment, the prepared Aluminum coupons were each suspended completely in 1.4M HNO_3 solutions without and with different concentrations of Anisaldehyde with the help of glass hooks at 308 K for 3h. The volume of solution kept 100 cm³, the coupons are retrieved after 3h, washed by distilled water, dried well and reweighed. From the weight loss data, corrosion rate in mg/cm² was calculated.

2.4. Temperature effect

To study the effect of temperature on corrosion rate, the prepared Aluminum coupons were completely immersed in 100 cm³ of 1.4M HNO_3 solution without and with different concentrations of Anisaldehyde at 308, 313 and 318 K for 3h.

2.5. Fourier Transform Infrared Spectroscopic Analysis

FTIR analysis of the fresh inhibitor and that of the corrosion product obtained from the reaction of Aluminum immersed in 1.4M HNO_3 for 3h immersion time in the presence of 0.1 M inhibitor at 308 K were carried out using Agilent Technology, FTIR (Cary 630) Fourier Transform Infrared Spectrophotometer. 650 – 4000 cm⁻¹ wave number was used to scan the sample during the analysis.

3. Results and discussion

3.1. Weight loss experiments

The weight loss and corrosion rate of Aluminum in 1.4 M of HNO_3 solution without and with 0.02, 0.04, 0.06, 0.08 and 0.10M concentration of Anisaldehyde for an exposure period of 3h was calculated from the weight loss data using following equation:

$$\Delta W = W_1 - W_2 \quad (1)$$

Where W_1 and W_2 are the weight of coupons before and after immersion

$$C_R \text{ (mg/cm}^2\text{h}^{-1}\text{)} = \frac{\text{Weight loss (g)}}{\text{Metal surface area (cm}^2\text{)} \times \text{Time (hrs)}} \quad (2)$$

The degree of surface coverage (Θ) and inhibition efficiency (I.E.) for different concentrations of the inhibitor in acidic media have been evaluated from weight loss experiments using the equations below:

$$\Theta = \frac{W_0 - W}{W_0} \quad (3)$$

$$\text{I.E. (\%)} = \frac{W_0 - W}{W_0} \times 100 \quad (4)$$

Where W_0 and W are the weight of the coupon in the absence and presence of inhibitor.

3.2. Effect of inhibitor on corrosion rate and inhibition efficiency

Results from this study as presented in Figure 1 for the plot of corrosion rate against inhibitor concentration for Aluminum corrosion in 1.4M HNO_3 at different temperatures reveals that the corrosion rate of the metal decreases with increase in inhibitor concentrations at all studied temperature. Inspection of the result further indicates that the protection ability of the inhibitor

was concentration dependent. The corrosion rates in the presence of inhibitors were reduced indicating the inhibiting action of the compounds as inhibitors. This suggests that as the concentration of inhibitors increases, there was an increase in surface coverage of the adsorbed molecules on the Aluminum surface which provided a barrier (film) and reduced further corrosion as reported by Olasehinde *et al* [10].

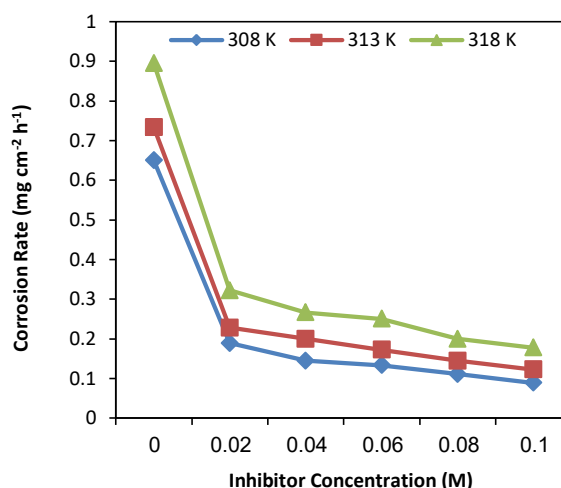


Fig 1. Variation of Corrosion Rate with Inhibitor Concentration for Al Corrosion in 1.4 M HNO_3

The surface coverage (Θ) and inhibition efficiency (% I E) were found to increase with increasing inhibitor concentration. The variation of inhibition efficiency against inhibitor concentration is shown in Figures 2. The highest inhibition efficiency was observed at the highest inhibitor concentration (0.1 M) at 308 K.

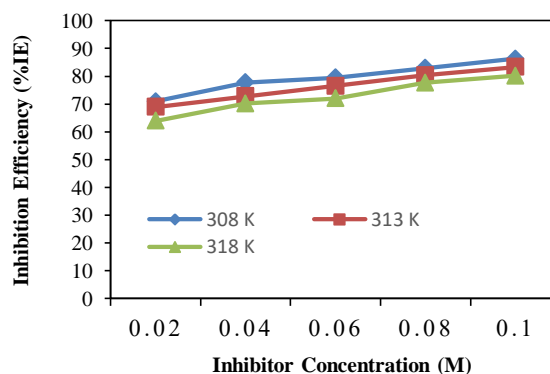


Fig 2. Variation of Inhibition Efficiency with Inhibitor

Concentration for Al Corrosion in 1.4M HNO₃.

This trend was observed due to increase in surface coverage (Θ) of adsorbed specie on surface of the metal as a result of increase in inhibitor concentration. This shows that more inhibitor molecule is adsorbed on the metal surface, thus lead to increase in inhibition efficiency. A similar result was reported by Nnanna *et al* [11].

3.3. Effect of Temperature on Corrosion Rate and Inhibition Efficiency

The result of the effect of temperature on the corrosion rate of Aluminum for inhibited and uninhibited solution is presented on Figure 3 at 308, 313 and 318K. From the result, it can be seen that the rate of inhibited and uninhibited solution increases with increase in temperature. It can be observed from the results that the highest corrosion rate of Aluminum was observed at the highest temperature (318 K). This observation is due to the fact that chemical reaction rates generally increase with rising temperature. Increase in temperature leads to increase in the kinetic energy possessed by the reacting molecules thereby making the molecules to overcome the energy barrier faster [12,13]. Similar work was reported by Fouda *et al* [14].

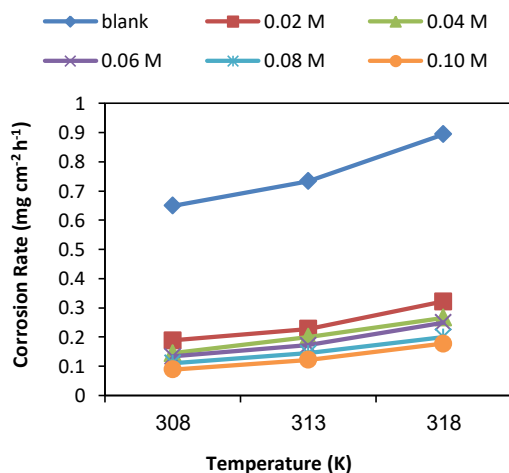


Fig 3. Variation of Corrosion Rate with Temperature for Al Corrosion in 1.4M HNO₃

The result of the effect of temperature on the inhibition efficiency of Aluminium at 308, 313 and

318 K is presented in Figure 4. It can be seen that from the result inhibition efficiency decreases with increase in temperature. Increase in temperature cause the desorption and destabilization of the inhibitor molecule absorbed on the metal surface and thus results in decrease of inhibition efficiency. Such behaviour suggests that investigated inhibitor was physically adsorbed on the Aluminum surface. Similar result was reported by Mohamed *et al* [15].

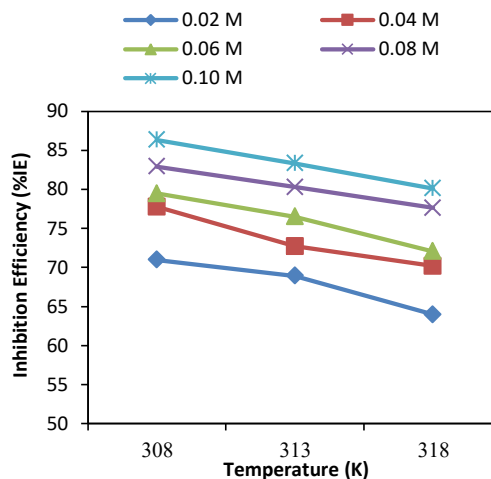


Fig 4. Variation of Inhibition Efficiency with Temperature for Al Corrosion in 1.4 M HNO₃

3.4. Thermodynamic Study

3.4.1. Determination of Activation Energy (E_a)

In order to elucidate the inhibitive properties of the inhibitor and the dependence of the temperature on the corrosion rates, the activation energy (E_a) for the corrosion process in the absence and presence of the studied inhibitor was calculated from Arrhenius-type plot according to the equation given below:

$$\ln(C_R) = B - \frac{E_a}{RT} \quad (5)$$

Where E_a is the apparent activation corrosion energy, R is the universal gas constant, T is the absolute temperature and B is a constant. Values of apparent activation energy for the corrosion of Aluminum in 1.4M HNO₃ without and with various

concentrations of inhibitor are shown in Table 1. These values were determined from the slope of in C_R versus $1/T$ plots presented in Figure 5. The results of activation energy from Table 1 showed that the value of E_a for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of Aluminum is slow in the presence of the inhibitors. It is known from Arrhenius equation that the higher E_a values lead to the lower corrosion rate, this is due to the formation of a film on the

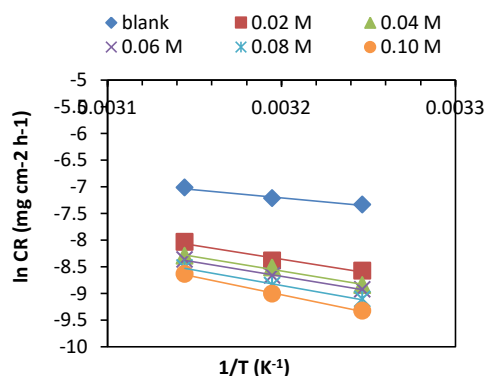


Fig 5. Arrhenius plot for Aluminum in 1.4 M HNO_3 in the blank and presence of the inhibitor

Aluminum surface serving as an energy barrier for Aluminum corrosion. Similar work was reported by Vashi and Prajapati [16] in their study for corrosion inhibition of Aluminum in hydrochloric acid using Bacopa monnieri leaves extract as green inhibitor. And the result of activation energy in uninhibited solution was 18.21 kJ/mol which increased to 58.26 kJ/mol in the presence of 0.6 g/L inhibitor concentration.

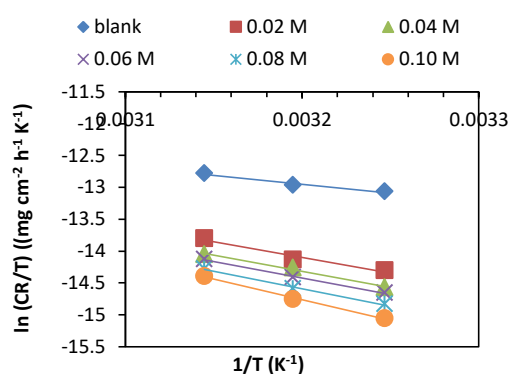


Fig 6. Transition State plot Aluminum in 1.4 M HNO_3 in the blank and presence of the inhibitor

Table 1: Activation Parameters for the Corrosion of Aluminum in 1.4 M HNO_3 .

Inhibitor Conc. (M)	E_a (kJ mol ⁻¹)	ΔH (kJmol ⁻¹)	$-\Delta S$ (JK ⁻¹ mol ⁻¹)
Blank	25.95	23.35	230.48
0.02	43.45	40.84	184.07
0.04	44.73	42.12	181.77
0.06	45.55	42.95	197.98
0.08	47.84	45.23	174.09
0.10	56.46	53.85	147.96

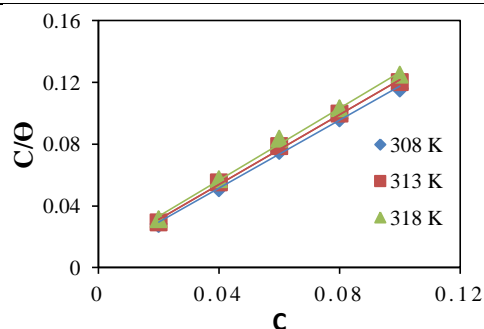


Fig 7. Langmuir adsorption isotherm plot for Aluminum Corrosion in 1.4M HNO_3 with different inhibitor concentration at different temperature

3.4.2. Enthalpy change (ΔH) and Entropy change (ΔS)

An alternative formulation of Arrhenius equation is the transition state equation. Enthalpy change (ΔH) and entropy change (ΔS) of activation process were evaluated from the transition state equation.

$$\ln \left(\frac{C_R}{T} \right) = \ln \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S_a}{R} \right) - \left(\frac{\Delta H_a}{RT} \right) \quad (6)$$

Where h is the Planck's constant, N is Avogadro number, ΔS_a is the entropy change of activation and ΔH_a is the enthalpy change of activation. Figure 6 shows a plot of $\ln (C_R/T)$ against $(1/T)$, straight line is obtained with a slope of $(-\Delta H/R)$ and intercept of

($\ln R/Nh + \Delta S/R$) from which the value of ΔH_a & ΔS_a are calculated and presented in Table 1. It can be seen from Table 1 all the values of enthalpies (ΔH_a) are positive and the positive signs of the enthalpies (ΔH_a) reflect the endothermic nature of Aluminum dissolution process. The entropy of activation in presence and absence of the inhibitor was large and negative. This implies that the activated complex in the rate determining step represents association rather than dissociation, indicating that a decrease in disorder takes place, going from reactant to the activated complex. Similar work was reported by Udom *et al.* [17] during the study of the effect of *Acanthus montanus* leaves extract on corrosion of Aluminum in hydrochloric acid medium and the result of enthalpy was positive ranging from 17.41 to 24.42 kJmol⁻¹ in 1×10^{-6} to 5×10^{-2} M inhibitor concentration while that of entropy was large and negative.

3.5. Adsorption Isotherm

Deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system is one of the most convenient ways of expressing adsorption quantitatively. Adsorption isotherm provide the basic information on the interaction between the inhibitor and the metal surface. The values of the degree of surface coverage (θ) were evaluated at different concentrations of the inhibitors in 1.4 M HNO₃ solution. Various adsorption isotherms were applied to fit θ values, but the best fit was found to obey Langmuir adsorption isotherm which are represented in Figure 7 at 308, 313 and 318K. Langmuir adsorption isotherm may be expressed by equation 7 [18].

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (7)$$

Where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage, and K_{ads} is the adsorption equilibrium constant. A plot of C/θ gave a straight line with slope equals to K_{ads} . The correlation coefficient (R^2) values obtained are presented in Table 2.

3.6. Free Energy of Adsorption (ΔG_{ads})

Figure 7 shows relationship between C/θ and C where K (equilibrium constant) is obtained from the intercept of the straight line and it is known that free energy adsorption (ΔG_{ads}) is related to equilibrium constant by the equation given below

$$\Delta G_{ads} = -RT \ln (55.5 \times K_{ads}) \quad (8)$$

The values of free energy of adsorption calculated by using Equa.7 are all negative as presented in Table 2. The negative values of ΔG_{ads} indicate the spontaneous adsorption of the inhibitor molecules on the Aluminum surface. Generally, values of ΔG_{ads} around -20 kJ mol⁻¹ or lower are consistent with physical adsorption, while those around -40 kJ mol⁻¹ or higher involves chemical adsorption as reported by Toliwal *et al* [19]. In the present study, the values of free energy obtained are all around -20 kJ mol⁻¹ which is consistent with physical adsorption mechanism. Similar work was reported by Babatunde *et al* [20].

Table 2: Adsorption parameters deduced from Langmuir adsorption isotherm for corrosion of Aluminum.

Temp. (K)	R^2	K_{ads}	ΔG (kJ mol ⁻¹)
308	0.9981	135.13	22.84
313	0.9974	119.04	22.88
318	0.9966	101.01	22.82

3.7. Infrared Spectroscopy Analysis Results

The result presented in Figures 8 and 9 shows the FTIR analysis of the inhibitor (Anisaldehyde) and the corrosion product of Aluminum in 1.4 M HNO₃ with 0.1 M inhibitor concentration. The analysis of the inhibitor in figure 8 shows C-H aromatic stretching frequency, C-H aldehyde stretching frequency, C=O carbonyl stretching frequency and OCH₃ bending frequency. The analysis of the corrosion product presented in Figure 9 shows the appearance of C-H aromatic stretching frequency,

C-H aldehyde stretching frequency, C=O carbonyl stretching frequency and OCH₃ bending frequency and this con-firmed that the adsorption of the inhibitor on the metal surface took place.

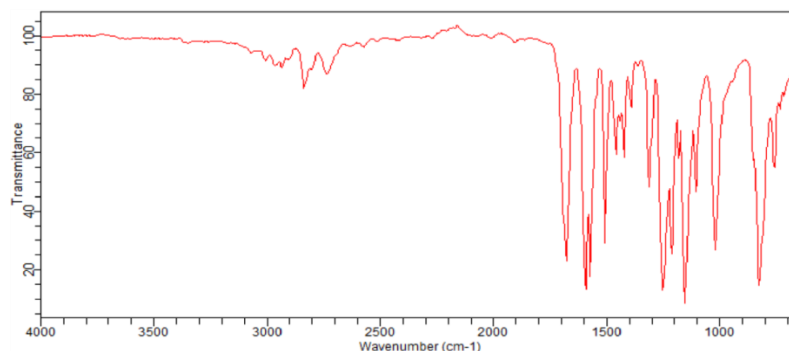


Fig 8. FT-IR Spectra of Anisaldehyde

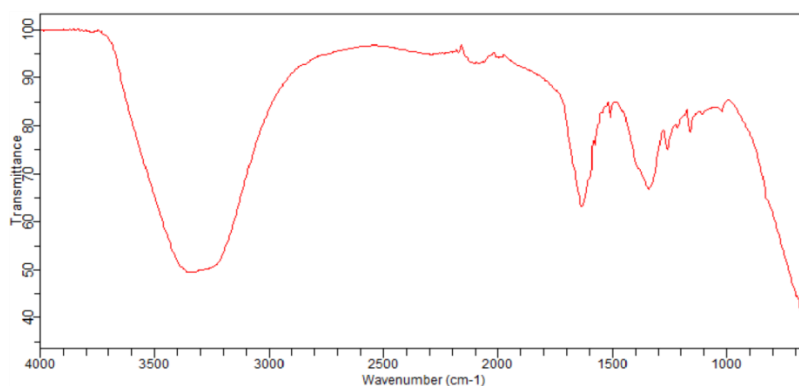


Fig 9. FT-IR Spectra of Aluminum in 1.4M HNO₃ with 0.1M Anisaldehyde.

4. Conclusion

The present study shows that Anisaldehyde (4-methoxy benzaldehyde) was found to be a good inhibitor for the corrosion protection of Aluminum in nitric acid solution. Corrosion rate decreases with increasing inhibitor concentration and increases with rising temperature. The inhibition efficiency was increased with increase in concentration of the

inhibitor and decreases with rises temperature. The maximum I.E., was found 86.32 % at 308K and 0.1M inhibitor concentration in 1.4 M HNO₃ solution. The adsorption of the inhibitor on the surface of Aluminum follows Langmuir adsorption isotherm and undergoes physical adsorption mechanism.

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