

Protecting Aluminium Alloy of type AA8011 from Acid Corrosion Using Extract from *Allamanda cathartica* Leaves

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ABSTRACT: The extent to which *Allamanda cathartica* (AC) leaves extract would protect the corrosion of Aluminium in 1 M HCl have been studied using weight loss technique. The corrosion process was monitored at different temperatures; 303, 313 and 323K. The result showed that at the different temperatures studied, as the concentration of AC increased, the rate of corrosion of aluminium reduced. Corrosion rate was also found to decrease in the presence of inhibitor compared to the blank solution with free acid. The adsorption of the phytochemical constituents present in AC on the aluminum surface could be responsible for the inhibition. Physisorption mechanism is proposed for the inhibition behaviour of AC extracts on the aluminium surface. The adsorption of AC extract components onto the aluminium surface was found to be spontaneous and the experimental data fits perfectly into Freundlich adsorption isotherm.

KEYWORDS: *Allamanda cathartica*, Corrosion, Aluminium, Weight loss, Physisorption, Adsorption

I. INTRODUCTION

Corrosion is a serious challenge in chemical and petrochemical industries which has led to extensive investigations recently. It is responsible for the enormous loss of materials worth billions of dollars annually. Aluminium and its alloy is one of the most important metals used frequently in different industrial applications. It is a very reactive metal and will grab oxygen from any water it contacts. Though it forms a very thin adherent layer of aluminium oxide which usually protects the metal against further corrosion, in the presence of a lot of moisture and acid solutions, the vapour penetrates the film and corrosion continues. One of the most practical methods for preventing or minimizing aluminium corrosion is by the use of corrosion inhibitors, especially in acidic solutions. These inhibitors are substances when added to an aggressive environment in small amount effectively decreases the rate of corrosion of metals exposed to it [1]. Corrosion inhibitors reduce corrosion by adsorbing on the surface of the metal and blocking some of the reactions taking place at the metal/solution interface.

II. RELATED WORK

Recent research [2-5] has shown that inhibitors from natural products like plant extracts are more environmentally friendly than most synthesized organic and inorganic inhibitors. Many extracts from plant have been used as potential corrosion inhibitors for aluminium in acidic solution, such as: *Delonix regia* [6], *Opuntia* [7], *Chromolaena odorata* [8], *Euphorbia hirta* [9], *Sansevieria trifasciata* [10]. Besides aluminium, steel in acidic media [11 -13] and zinc in acidic media [14] were protected against corrosion by using plant extracts. The inhibitive performance of most plant extracts is normally due to phytochemical constituents like saponins, alkaloids, terpenes, tannins, carbohydrates, flavonoids etc present in their composition [15-17].

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In this study, we assess the inhibition effectiveness of *Allamanda cathartica* leaves extract on aluminium corrosion in 1 M HCl solutions using weight loss and gasometric techniques. The interaction mechanism between the inhibitor molecules and the aluminium surface was also explored.

III. EXPERIMENTAL

Materials

The aluminium sheets of type AA8011 used for this study were procured from First Aluminium PLC, Port-Harcourt, Nigeria. The weight percentage composition of the aluminium used is: Si-0.240%, Fe-0.241%, Cu-0.035%, Mn-0.102%, Ti-0.019%, Pb-0.014%, Zn-0.043% and the remainder Al. Each sheet of thickness 1.25 mm were mechanically pressed cut into coupons of dimension 20 mm × 40 mm. The coupons were prepared and cleaned as described elsewhere [18]. The blank corrodent was a solution of 1.0 M HCl prepared by diluting analytical grade HCl (37%) with distilled water. All experiments were carried out in unstirred solutions.

Extract Preparation

Allamanda cathartica leaves used in this study was collected and washed to remove impurities such as dust and then air dried at room temperature for 7 days. The air dried plant materials were reduced to a coarse powder using an electric blender. The powdered material was then subjected to Soxhlet extraction over 24 h using methanol. The extract was concentrated over a water bath at 60°C using a vacuum rotary evaporator. The extract was then stored in a desiccator and was reconstituted into a fresh aqueous solution prior to use. From the stock solution, inhibitor test solutions were prepared in concentration range of 0.1 g/L to 0.5 g/L.

Weight loss method

In the weight loss measurements, the prepared aluminium coupons were weighed using JA 1003A electronic weighing balance with the accuracy of ±0.005 before immersion in 250 mL beaker containing 200 mL of 1 M HCl solutions without and with various concentrations of the inhibitor. The setups were exposed for a period of 5 hours at 303 - 323K and each specimen was removed from the different test solutions after an interval of 1 hour. After immersion, each of the aluminium coupons were scrubbed with brush, rinsed with distilled water, dried with acetone and re-weighed. The weight loss was taken as the difference in weight of the specimens before and after immersion. Each experiment was run in triplicate and the mean value of the weight loss was reported.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Weight Loss and Corrosion Rate

The variation of weight loss with time for aluminium in 1 M HCl solution with and without various concentrations of AC leaves extract at different temperatures is given in Figure 1. It is observed, from Figure 1 that the weight loss of the aluminium in the acid was reduced in the presence of the inhibitor compared to the blank acid solution at the different temperatures studied. It suggests that the extract is a corrosion inhibitor for aluminium in 1M HCl solution. However, the weight loss increases as the time of exposure increases at the various inhibitor concentrations. This behaviour could be attributed to the loss of corrosion inhibition potency as the exposure time is increased.

From the weight loss values obtained, the corrosion rate (ρ) was determined from the equation below:

$$\rho = \frac{m_1 - m_2}{At} \quad (1)$$

Where m_1 and m_2 are the weights of the metal specimen (mg) before and after immersion in the test solutions, A is the area of the specimens (cm^2) and t is the exposure time (h).

The corrosion rate was studied for 5 hours of exposure of the aluminium alloy in 1 M HCl solution. Figure 2 reveals that corrosion rate of aluminium in the presence of the AC leaves extract decreases with increase in

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Vol. 7, Issue 10, October 2018

concentration, indicating that the protection ability of the extract as inhibitor was concentration dependent. Also, corrosion rate is seen to increase with temperature rise both in the absence and in the presence of the additives.

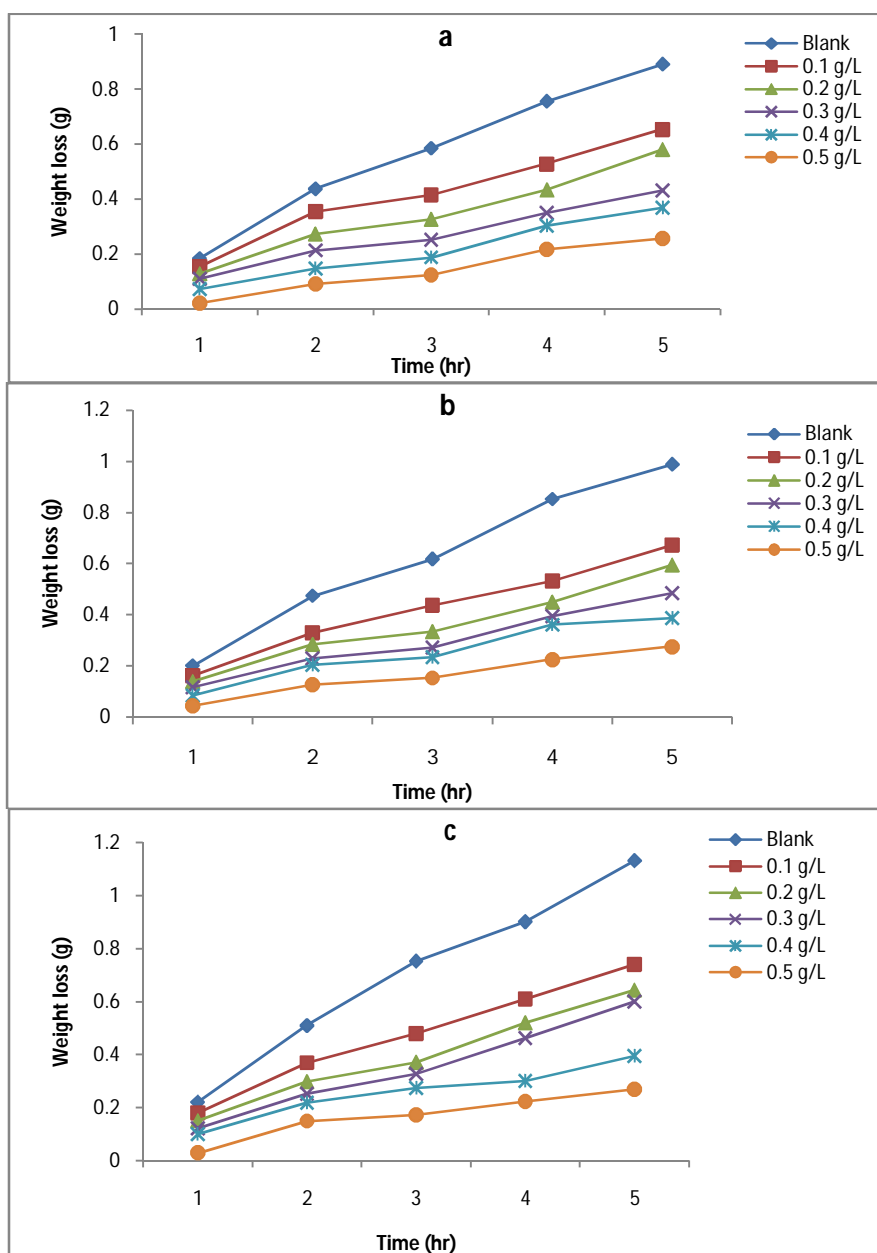


Fig. 1. Variation of weight loss with time for aluminium alloy in 1M HCl solution containing *Allamanda cathartica* leaves extract at (a) 303K (b) 313K (c) 323K

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 7, Issue 10, October 2018

The figure above shows the variation of weight loss with time for aluminium alloy in 1M HCl solution containing the inhibitor, *Allamanda cathartica* leaves extract at different temperatures; (a) is at 303K. (b) is at 313K and (c) is at 323K. . The weight loss decreases as the concentration of the extract increase at the different temperatures studied

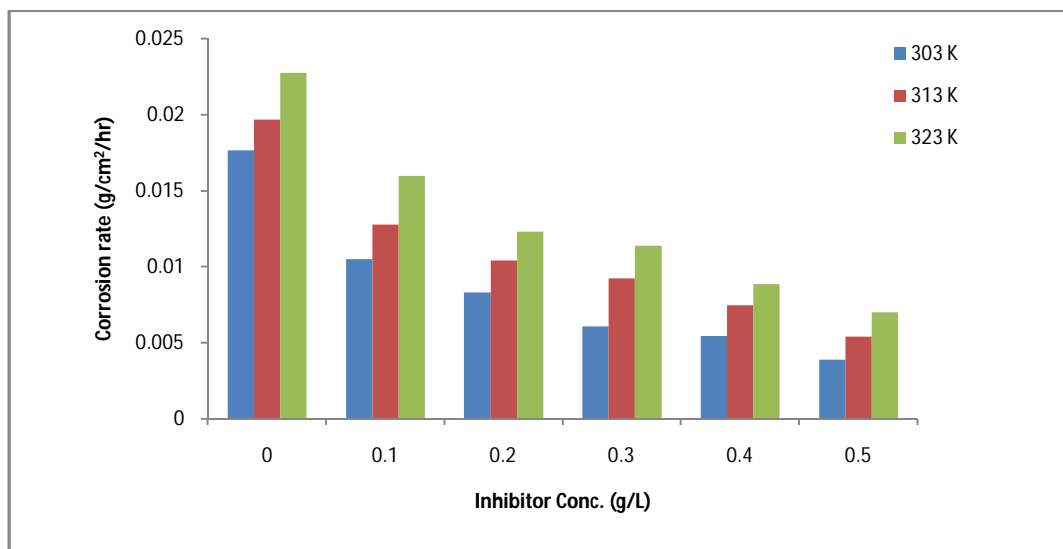


Fig. 2. Variation of corrosion rate for aluminium alloy with and without different concentrations of *Allamanda cathartica* leaves extract in 1 M HCl solution at different temperatures

The figure above shows the variation of corrosion rate for aluminium alloy with and without different concentrations of the inhibitor in 1 M HCl solution at 303, 313 and 323K. The corrosion rate of aluminium increases with increase in the concentration of the inhibitor. The corrosion rate also increases with temperature rise both in the absence and in the presence of the inhibitor.

Surface Coverage and Inhibition Efficiency

The surface coverage(θ) and inhibition efficiency ($\eta\%$) were calculated from the corrosion rate data according to equations 2 and 3, respectively:

$$\theta = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right) \quad (2)$$

$$\eta\% = \theta \times 100 \quad (3)$$

Where ρ_{blank} and ρ_{inh} are the corrosion rates in the absence and presence of the inhibitor respectively

From Figures 3, it is observed that inhibition efficiency increases with increase in the concentration of AC leaves extract but decreases with increase in temperature. The increase in inhibition efficiency with increase in the concentration of AC leaves extract is suggestive of the fact that some of the molecules of the inhibitor are adsorbed on the surface of the metal thereby protecting the aluminium alloy from further attack [19]. Increasing the concentration of the extract increases the degree of surface coverage, θ of the aluminium surface. A barrier to charge and mass transfer between the metal and the corrodent is constituted by the adsorbed molecules on the metal surface, thereby protecting the aluminium surface from corrodent attack. The larger the degree of surface coverage resulting from

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Vol. 7, Issue 10, October 2018

enhanced adsorption of molecules of the AC extract, the greater the protection to corrosion offered by the inhibitor [20].

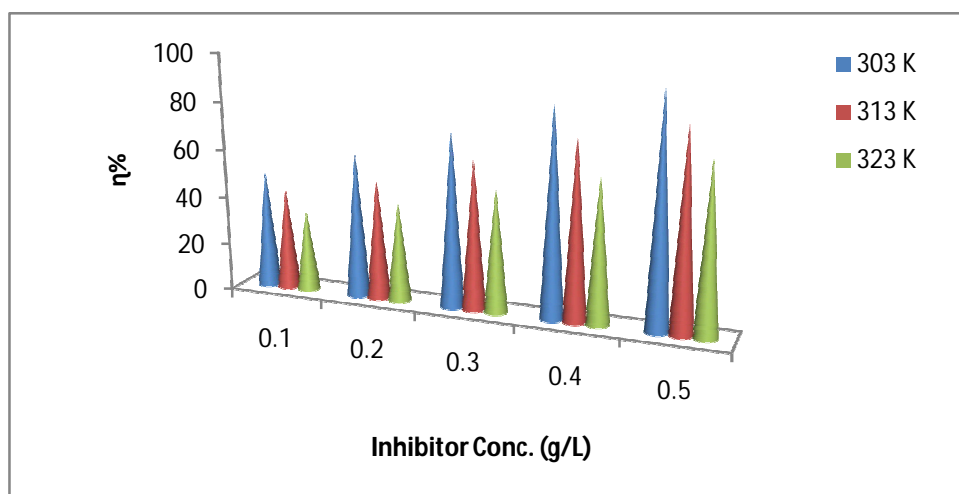


Fig. 3. Variation of inhibition efficiency (η%) with Inhibitor Concentration for aluminium in 1M HCl containing *Allamanda cathartica* at different temperatures

The figure above shows the variation of inhibition efficiency (η%) with Inhibitor Concentration for aluminium in 1M HCl containing the inhibitor at different temperatures. The inhibition efficiency increases with increase in the concentration of the inhibitor but decreases with increase in temperature.

Adsorption behaviour of *Allamanda cathartica*

In acid corrosion, it is assumed generally that inhibitors act through a process of adsorption on the metal surface. The knowledge of the adsorption behaviour of an inhibitor is important for the definition of its mechanism of action. The interaction between the adsorbed inhibitor molecules and the metal surface can be well understood from the adsorption isotherms. The adsorption process is influenced by the nature and surface charge of the metal, by the type of aggressive electrolytes, temperature and by the chemical structure of the inhibitors [21]. To examine the adsorption behaviour of AC extract in 1M HCl solution, several adsorption isotherm models were employed, such as Temkin, Langmuir, Frumkin, Freundlich and Flory-Huggins but the Freundlich adsorption isotherm was found to fit the experimental data well. Freundlich isotherm is given by the expression:

$$\ln \theta = \ln K_{ads} + n \ln C \quad (4)$$

Here, θ is the degree of surface coverage, K_{ads} is the adsorption equilibrium constant, n is the interaction parameter and C is the inhibitor concentration. The plot of $\ln \theta$ against $\ln C$ is shown in Fig. 4 to be linear for AC extract in 1 M HCl solution. Table 1 gives the adsorption parameters from the Freundlich adsorption isotherm plots. The values of the R^2 and K_{ads} suggest that the adsorption of AC extracts followed the Freundlich adsorption isotherm in 1 M HCl solution, showing that the extract constituents actually adsorbed themselves on the aluminium surface. The adsorption equilibrium constant, K_{ads} values (Table 1) indicate that the binding power of the inhibitor to the metal surface decreases with increase in temperature. This behaviour have been reported, that an increase in temperature results in desorption of some absorbed components of the extract on the metal surface which is consistent with the physisorption mechanism [22].

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 7, Issue 10, October 2018

From the values of K_{ads} , the standard free energy of adsorption (ΔG_{ads}), for AC at different temperatures was obtained as follows [23]:

$$\Delta G_{ads} = -2.303RT \log (55.5K_{ads}) \quad (5)$$

where R is the universal constant, T is the absolute temperature and 55.5 is the concentration of water molecules in solution. The calculated values of ΔG_{ads} are listed in Table 1. As shown in the table, ΔG_{ads} values for AC leaves extract in 1 M HCl is negative, indicating that the adsorption process was spontaneous and stable. The ΔG_{ads} values obtained in the present study are in the range -10.64 and -10.28 kJ/mol. These values are less negative than -40 kJ/mol and more negative than -20 kJ/mol. It has been reported in literature, that the value of ΔG_{ads} equal to -20 kJ/mol or less negative is taken to indicate physisorption involving electrostatic interaction between charged molecules whereas those in the order of -40 kJ/mol or more negative is interpreted as chemisorptions involving charge sharing or transfer from the inhibitors to the metal surface to form a kind of co-ordinate bond [23, 24]. From the values of ΔG_{ads} , it can be deduced that adsorption mechanism of AC extract on aluminium surface is physisorption.

Table 1. Calculated thermodynamic parameters from Langmuir adsorption isotherm

Temperature (K)	Intercept	Slope	R ²	K _{ads}	ΔG_{ads} (kJ/mol)
303	0.2061	0.4164	0.9810	1.2289	-10.64
313	0.0560	0.3947	0.9637	1.0576	-10.60
323	-0.1073	0.4505	0.9687	0.8983	-10.28

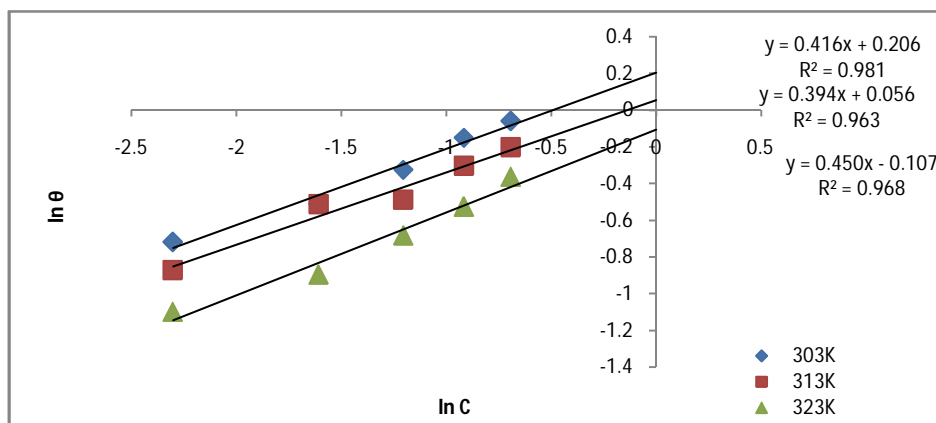


Fig. 4. Freundlich adsorption isotherm for AC extract on aluminium in 1 M HCl solution at different temperatures

Effect of Temperature

The effect of temperature on the rate of corrosion of aluminium in 1 M HCl containing different concentrations of AC was tested by weight loss techniques over a temperature range from 303 to 323K. The effect of increasing temperature on the corrosion rate (ρ) and inhibition efficiency ($\eta\%$) were obtained from weight loss measurements. Results obtained as depicted in Fig. 2 shows that corrosion rate increased with increase in temperature in the absence and presence of the inhibitors. It is observed from Fig.3 that inhibition efficiency increases with increase in the concentration of AC extract but decreases with increase in temperature. Decrease in inhibition efficiency with increase in temperature is often ascribed to physisorption of the inhibitor molecules on the metal surface.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

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Vol. 7, Issue 10, October 2018

The activation energy (E_a) of the corrosion process was calculated using the Arrhenius equation:

$$\ln \rho = \ln A - \frac{E_a}{RT} \quad (3)$$

where ρ is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, and A is pre-exponential factor. The Arrhenius plot of $\ln \rho$ against reciprocal of absolute temperature ($1/T$) shown in Fig. 5 gives a straight line with slope of $-E_a/R$ from which the activation energy was calculated and given in Table 2.

An estimate of heat of adsorption (Q_{ads}) was obtained from the trend of surface coverage with temperature as follows [25]:

$$Q_{ads} = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \quad (4)$$

Here θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 . The calculated values of Q_{ads} are listed in Table 2.

The data in Table 2 show that the values of E_a in the solution containing different concentrations of AC are higher than that of the blank solution. It has been reported [12] that higher E_a value in the presence of inhibitors relative to the blank is ascribed to physisorption while the reverse is interpreted to mean chemisorptions mechanism. It could be seen that with increasing concentration of AC extract the apparent activation energy increased, supporting the earlier proposed physisorption mechanism for AC extract. The increase in activation energy can be attributed to an appreciable decrease in the adsorption of the extract on aluminium surface with increase in temperature. Another thermodynamic parameter which further describes the adsorption mechanism operative in the corrosion inhibition process is the heat of adsorption, Q_{ads} . The negative Q_{ads} values indicate that the degree of surface coverage decreased with rise in temperature, also supporting the earlier proposed physisorption mechanism for AC extract.

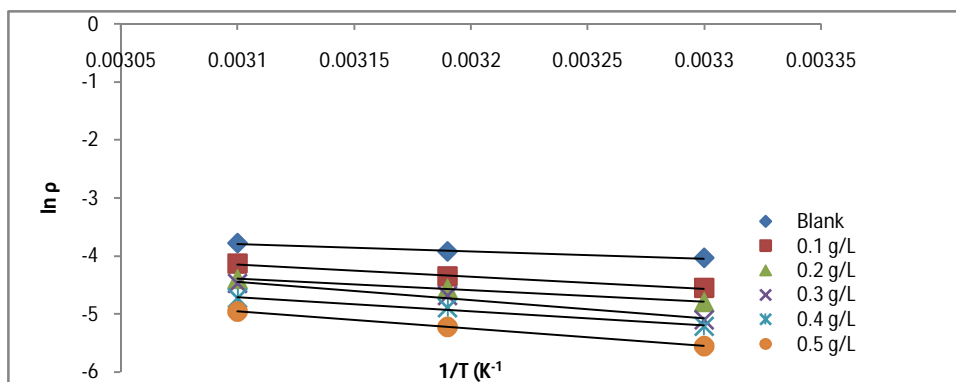


Fig. 3: Arrhenius plots for aluminium corrosion in 1 M HCl without and with different concentrations of AC extract

Table 2: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for aluminium corrosion in 1M HCl in the absence and presence of AC extract

Inhibitor concentration (g/L)	Activation Energy (KJ/mol)	Heat of adsorption (KJ/mol)
Blank	20.25	-
0.1	27.90	-11.98
0.2	30.19	-21.38
0.3	33.57	-20.54
0.4	33.85	-27.11
0.5	36.66	-29.53

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Vol. 7, Issue 10, October 2018

V. CONCLUSION

The investigation showed that AC leaves extract is a potent inhibitor for aluminium corrosion in 1 M HCl solution. Corrosion rate increases with increase in temperature both in the absence and presence of the inhibitor and decreases in the presence of the extracts. Corrosion inhibition performance is found to depend on the concentration of the inhibitors and temperature. Corrosion inhibition occurs by virtue of adsorption of the inhibitor molecules on the aluminium surface which was found to obey Freundlich adsorption isotherm from the fit of the experimental data at all the concentrations and temperatures studied. Phenomenon of physical adsorption is proposed from the thermodynamic parameters evaluated.

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