KINETICS AND THERMODYNAMICS OF ALUMINIUM CORROSION INHIBITION BY *ANTHOCLEISTA DJALONENSIS* LEAF EXTRACT IN HYDROCHLORIC ACID SOLUTION

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ABSTRACT

Adsorption of *anthocleista djalonensis* leaf extract on aluminum in hydrochloric acid solution was studied at 30°C and 60°C using gravimetric technique. Increasing the concentration (v/v %) of *anthocleista djalonensis* leaf extract was observed to increase its corrosion inhibition efficiency. Temperature studies revealed an increase in inhibition efficiency with rise in temperature. Comparative analysis of kinetic and thermodynamic parameters revealed effective inhibition. This paper demonstrates the use of two statistical approaches – Analysis of variance (ANOVA) and Duncan multiple range test, in the determination of the performance of various linearised Langmuir equations.

Key words: Kinetics, Thermodynamics, ANOVA, Duncan multiple range test, Linearised langmuir equations, Corrosion inhibition.

INTRODUCTION

The use of inhibitors is one of the best options of protecting metals against corrosion[1]. Studies have shown that natural products derivable from agricultural by - products generally exhibit corrosion inhibition efficiencies[1-3]. These natural products have been shown to be environmentally friendly, easily available and economic as potential corrosion inhibitors[1,4]. The corrosion inhibition properties of these natural products have been demonstrated to be due to the presence of phytochemicals. These phytochemicals possess some physico-chemical properties-functional groups, aromaticity, steric effects and electron density of donor atoms, which confer on them their ability to adsorb on the metal surfaces, hence, their ability to reduce corrosion[5]. These physico-chemical properties are

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inherent in the phytochemicals of *anthocleista djalonensis* leaf extract because sitosterol, stigmasterol, ursolic acid, sweroside or djalonenoside, and 3-oxo-Δ-4,5-sitosterone are present[6].

Adsorption models have been employed to explain adsorption mechanisms, hence, have aided the determination of adsorption parameters. One of such common adsorption models is the Langmuir adsorption model[7]. The accuracy of the model, however, will depend on: whether the appropriate adsorption model was chosen; whether the experimental conditions were representative of environmental conditions; and whether an appropriate parameter estimation method was used[7].

One of the most commonly used models is the Langmuir isotherm. This commonly used Langmuir model is non-linear, therefore, fitting this model to measured data requires: a trial and error approach; special optimization programs[7]; the availability of these programmes and expertise needed in using these special programmes. It is therefore necessary that the linearsied versions of the non-linear Langmuir models are tried out. However, the use of these linear models have come under criticisms, on the basis that they introduce errors from the linearisations of the Langmuir adsorption model[7,8].

Analysis of variance (ANOVA) is one of the commonly used statistical methods to compare several groups[9]. It is appropriate for testing the significant difference among K-population means simultaneously and without altering the probability of making type one error[10]. When differences between groups exist, a post hoc test can be done to identify which group (s) that differ (s) from the others[9]. In this paper, Duncan multiple range test was used.

This paper aims to X-ray: the linearization results of seven linearised Langmuir equations; and identify the group (s) which gave statistically different mean (s).

To accommodate the purpose, the adsorption of *anthocleista djalonensis* leaf extract on aluminium in hydrochloric acid, was studied.

EXPERIMENTAL

Chemicals and apparatus

Pure aluminium metal of type AA 1090 obtained from Tower Aluminium Nigeria Limited, Ogba-Ikeja, Lagos Nigeria was used for the study. Each sheet was mechanically press cut into 4 cm x 5 cm coupons. The specimen were used as supplied without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and store in a

moisture free desiccator prior to use in corrosion studies. All chemicals used in this study were of BDH-Analar grade, however, deioinzed water was got from International Institute of Tropical Agriculture (IITA), Ibadan.

Methods preparation of plant extracts

Anthocleista djalonensis leaf was collected at Owo, Ondo State in Nigeria, air dried and ground to powder form. Forty grams of the powder was digested in 400 mL of 0.1 M HCl, kept for 24 hours, filtered and stored. Test solutions were prepared at concentrations 10, 20, 30 and 40 (v/v %) from the stock solution.

For the gravimetric measurements, clean weighed aluminium was immersed in 100 mL beaker containing the corrodent and inhibitor. The beakers were placed in a constant thermo-stated oven maintained at 30^oC and 60^oC. The coupons were retrieved at 24 hour interval progressively for 168 hours (7 days), scrubbed with bristle brush in de-ionized water at room temperature, dried in acetone and weighed[11]. The difference in weight of the coupons were taken as the weight loss, and used to compute the corrosion rate given by[12]:

$$\text{Corrosion rate } (\rho) = \frac{M_1 - M_2}{At} \qquad \qquad ...(1)$$

where M_1 and M_2 are the masses of the specimen before and after corrosion respectively, A is the total area of the specimen and t is the corrosion time.

The inhibition efficiency (% I) was calculated using[13]:

$$\% I = 100 \, \theta$$

$$= \frac{W_1 - W_0}{W_1} \times 100 \qquad \qquad ...(2)$$

where θ is the degree of surface coverage, W_0 and W_1 are the corrosion rates for aluminium in the presence and absence of inhibitor respectively in HCl solution at the same temperature.

Analysis of variance (ANOVA)

The ANOVA technique becomes appropriate in a situation where there are K groups (where $K > 2$)[10], to make for efficiency. Also, ANOVA maintains the type one error rate at the pre-established alpha level[14].

ANOVA test compares two variance estimations: variance within group (the un-

systematic variation or error in the data) and variance between groups (effects due to the experiment)[9].

In this paper, experimental or actual data and forecast or predicted results (Langmuir-I, Langmuir-II, Langmuir-III, Langmuir-IV, Langmuir-V, Langmuir-VI and Langmuir-VII), were compared by ANOVA. The experiment has variability values from linearisations. The estimated values from these techniques (linearisations) were compared with the actual (observed) data using ANOVA. The hypotheses were:

$$H_O: \mu_i \neq \mu_j \qquad i, j = 1,2,3,\ldots, I \neq j$$

$H_1: \mu_1 = \mu_2 = \mu_3 = \ldots = \mu_4$ where μ_1, μ_2, μ_3, μ_4, μ_5, μ_6, μ_7 and μ_8 were the mean estimations obtained from observed or actual data, Langmuir-I, Langmuir-II, Langmuir-III, Langmuir-IV, Langmuir-V, Langmuir-VI and Langmuir-VII, respectively.

The hypotheses were tested by using level of significance (α) assumed as 0.05. If F_{cal} is greater than the F_{crit}, then, the result between methods has significant difference (null hypothesis is rejected). Otherwise, it can be concluded that there is no significant difference between methods (null hypothesis is accepted)[9].

Duncan multiple range test

Duncan multiple range test is a post hoc test which can maintain a low overall type one error[15] and uses a studentised range statistic within a multiple stage test, referred to as a multiple range test[9]. A least significance error (LSR) is calculated and associated with an increasing number of sample subset means. The population mean is significantly different if the range of subset is greater than the least significant range (LSR)[9].

LSR was found from Duncan's table for the confidence level, $\alpha = 0.05$. LSR were computed as shown below[15]: mean sum of square error (MS) = 0.011, n = 5, and the standard error of each average

$$(S) = \sqrt{\frac{MS}{n}} = 0.047 \qquad \qquad \ldots(3)$$

There are eight groups, hence, the total number of ranges are seven. From the Duncan's table and $\alpha = 0.05$, the seven ranges were calculated as shown below:

$$r_2 = r_{0.05 \,(2,36)} = 2.868$$
$$r_3 = r_{0.05 \,(3,36)} = 3.015$$

$$r_4 = r_{0.05\ (4,36)} = 3.111$$

$$r_5 = r_{0.05\ (5,36)} = 3.180$$

$$r_6 = r_{0.05\ (6,36)} = 3.232$$

$$r_7 = r_{0.05\ (7,36)} = 3.274$$

$$r_8 = r_{0.05\ (8,36)} = 3.307$$

LSR can be calculated from the equation (9):

$$R_P = r_P \ X \ S \hspace{5cm} …(4)$$

By applying equation (4), LSR results obtained were: $R_2 = 0.135$, $R_3 = 0.142$, $R_4 = 0.146$, $R_5 -0.149$, $R_6 = 0.152$, $R_7 = 0.154$ and $R_8 = 0.155$.

RESULTS AND DISCUSSION

Inhibition efficiency and adsorption considerations

The values of inhibition efficiency obtained from gravimetric measurements for different inhibitor concentrations in 0.1 M hydrochloric acid at 30°C and 60°C are shown in Table 1.

Table 1: Variation of inhibition efficiency with inhibitor concentrations at 30°C and 60°C

Inhibitor concentration (v/v %)	Inhibition efficiency	
	30°C	**60°C**
10	57.35	57.68
20	67.65	73.59
30	76.47	80.32
40	80.88	81.40
50	82.35	83.29

The inhibitor efficiency increases with inhibitor concentration. This behavior may be attributed to the increase of the surface area covered by the adsorbed molecules of inhibitor as inhibitor concentration increases. The net adsorption of the extract organic matter on the metal surface creates a barrier to charge and metal transfer, thus, protecting the metal surface from corrodent attack[16].

Effect of temperature

Two types of interaction often describe adsorption of organic inhibitors on a corroding metal surface: chemical adsorption and physical adsorption. Suggestions[16] are that physisorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The more efficient inhibitors appear to protect anodic areas preferentially by chemisorptions[16].

The variation of inhibition efficiency with temperature is shown in Table 1. Experimental data reveal that inhibition efficiency values for the various studied inhibition efficiency concentrations at 60^oC are higher than those obtained at 30^oC. This observed trend suggests chemical adsorption mechanism[13].

Thermodynamics parameters

The apparent activation energy values (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation (5):

$$\log \frac{\rho_2}{\rho_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad ...(5)$$

where ρ_1 and ρ_2 are the corrosion rates at temperature T_1 and T_2 respectively. The values of activation energy are presented in Table 2. Estimates of the heats of adsorption (Q_{ads}) were obtained from the trend of surface coverage with temperature as follows[5]:

$$Q_{ads} = 2.303\, R \left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1 T_2}{T_2 - T_1} \qquad ...(6)$$

where θ_1 and θ_2 are the degrees of surface coverage at T_1 and T_2 and R is the gas constant. The calculated values of E_a and Q_{ads} are presented in Table 2.

Table 2: Calculated values for the thermodynamic parameters of system

System/concentration	E_a (KJ/mol.)	Q_{ads} (KJ/mol.)
Blank (0.1 M)	543.245	-
Inhibitor (v/v %)		
10	27.855	-8.337

System/concentration	E_a (KJ/mol.)	Q_{ads} (KJ/mol.)
20	22.389	- 20.560
30	23.082	- 32.998
40	27.296	- 40.360
50	26.551	- 43.160

From Table 2, energy of activation for blank was far higher than for the various inhibitor concentrations. The low energy of activation values for the various inhibitor concentrations suggest that adsorptions of inhibitor on aluminium in hydrochloric acid at 30°C and 60°C brought about corrosion inhibition. The values of heats of adsorption are negative and increases as inhibitor concentration increase. The negative values of heats of adsorption obtained, suggest spontaneous adsorption processes, in agreement with earlier works[13]. According to Bhajiwala and Vashi (2001) in Obot and co-workers' work[5], positive Q_{ads} value suggest increased efficiency of inhibitor at higher temperature. This is in contrast with our findings, as can see in Tables 1 and 2 that Q_{ads} values are negative and inhibition efficiency was increased at higher temperature.

Adsorption considerations

In order to elucidate the nature of adsorption of *anthocleista djalonensis* leaf extract, adsorption isotherm describing the adsorption process was determined.

The most frequently used isotherm is the Langmuir isotherm[7]:

$$\theta = \frac{KC}{1 + KC} \qquad \qquad ...(7)$$

where θ is the degree of surface coverage, K is the adsorption capacity and C is the inhibitor concentration.

Equation (7) is a non-linear equation that poses difficulty because of unavailability of (special) programmes needed to solve it. Therefore, we resorted to the linearised versions of the non-linear Langmuir isotherm. The various versions gave adsorption capacity values, Gibb's free energy values and correlation coefficient values as presented in Table 3. Various plots of the linearised equations helped to obtain the correlation coefficients using Microsoft Excel version 2003 and the adsorption capacity values also were obtained from either slopes or intercepts of these plots. The determination of standard free energy of adsorption (ΔG^o_{ads}), however, was obtained using this expression[5]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \qquad ...(8)$$

Table 3: Adsorption capacity (K_{ads}), standard free energy of adsorption (ΔG^o_{ads}) and correlation coefficient (R^2) values of various linearised Langmuir isotherm

Isotherm	Linear equation	Temp.	K_{ads}	ΔG^o_{ads} (KJ/mol)	R^2
Langmuir – I (Hanes-Woolf)	$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$	30°C	13.624	-16.697	0.9986
		60°C	16.639	-18.904	0.999
Langmuir – II (Line weaver-Burke)	$\frac{1}{\theta} = \frac{1}{K_{ads}} \cdot \frac{1}{C} + 1$	30°C	7.698	-15.259	0.8732
		60°C	8.361	-16.999	0.9998
Langmuir – III (Eadie-Hofstee)	$\theta = 1 - \frac{\theta}{K_{ads}} \cdot \frac{1}{C}$	30°C	15.038	-16.946	0.9454
		60°C	16.949	-18.955	0.7932
Langmuir – IV (Scatchard)	$\frac{\theta}{C} = K_{ads} - K_{ads}\theta$	30°C	1.041	-10.219	0.9031
		60°C	0.985	-11.078	0.8978
Langmuir – V (Nnaji-Okoye-Obiegbedi)	$C\theta = C - \frac{\theta}{K_{ads}}$	30°C	11.123	-16.186	0.999
		60°C	11.148	-17.795	0.9998
Langmuir –VI (Nnaji-Ani)	$\frac{1}{C} = \frac{K_{ads}}{\theta} - K_{ads}$	30°C	1.850	-11.668	0.8131
		60°C	1.850	-12.823	0.8131
Langmuir –VII (Nnaji-Ani-Nnabugwu)	$\log\left(\frac{C}{\theta}\right) = \log\frac{1}{K_{ads}} - \log(1-\theta)$	30°C	0.146	-5.270	0.9576
		60°C	0.172	-10.182	0.7636

Table 3 shows the adsorption capacity values (K_{ads}) obtained from equation (8) above. The K_{ads} values (as the name implies), denote the strength between adsorbate and adsorbent. The low K_{ads} values therefore clearly imply that the adsorption types were physisorption.

The standard free energy of adsorption, ΔG^o_{ads}, which can characterize the interaction of adsorption molecules on metal surface, was calculated by using equation (8). The negative values of ΔG^o_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface[5]. Generally, the values of ΔG^o_{ads} around -20 KJ/mol or lower are consistent with physisorption, and those around -40 KJ/mol or higher involve chemisorptions[11]. The values of ΔG^o_{ads} shown in Table 3, reveal spontaneous and stable adsorbed layers on aluminium surface. However, the ΔG^o_{ads} values at 30°C and 60°C are all below - 20 KJ/mol, indicating that the molecules of *anthocleista djalonensis* leaf

extract are physisorbed onto aluminium surface. Evidence is available, as can be seen in Table 1 and as previously explained from temperature studies, that molecules of *anthocleista djalonensis* leaf extract chemisorbed on aluminium surface and brought about corrosion inhibition. In contrast, our obtained thermodynamic parameters (K_{ads} and ΔG^{o}_{ads}), shown in Table 3, indicate physisorptoin. Equipped therefore with these, we suggest that both chemisorptoin and physisorption occurred. Earlier work[13] had reported adsorption mechanism where chemisorption and physisorption took place simultaneously.

Kinetic Studies

Earlier work[12] used a kinetic model to predict: (adsorption) reaction order and corrosion inhibition efficiency, for the adsorption of organic matter on metal surface in an aggressive medium (corrodent). In this work therefore, plots of log W_f versus time were made or done using the following equation (12):

$$\log W_f = Kt + C \qquad \qquad …(9)$$

where W_f is the final weight of aluminium coupon after treatment, K is the rate constant, t is the time and C is the intercept on y-axis. Linear plots were obtained indicating first order kinetics[12,17]. The values of the rate constant (K) obtained from the plots of log W_f versus time were, therefore, substituted into:

$$t_{1/2} = \frac{0.693}{K} \qquad \qquad …(10)$$

where $t_{1/2}$ is the half-life for first order reactions[17]. The values of half-life ($t_{1/2}$), shown in Table 4, reveal that the presence of *anthocleista djalonensis* leaf extract extended the duration of the corrosion of aluminium in 0.1 M HCl.

Table 4: Calculated values of half life for system

System	Half-life ($t_{1/2}$) 30°C	(days) 60°C
Blank (0.1M)	115.5	42.0
Inhibitor (v/v %)		
10	266.5	110.0
20	346.5	230.8
30	462.0	315.0
40	577.5	277.2
50	533.1	288.8

At studied temperatures, the presence of *anthocleista djalonensis* leaf extract in hydrochloric acid solution extended the duration of aluminium corrosion. As can be seen in Table 4, higher $t_{1/2}$ values were obtained for all inhibitor concentrations at studied temperatures. Leaf extract of *anthocleista djalonensis*, from our kinetics study, exhibited good corrosion inhibition of aluminium in HCl.

Analysis of variance (ANOVA)

From the ANOVA results shown in Table 5, it can be concluded that in $\alpha = 0.05$, the null hypothesis was rejected because: $F_{crit} = 2.21$ and $F_{cal} = 45.267$, where $F_{cal} > F_{crit.}$

Table 5: ANOVA results

Groups	Frequency	Sum	Mean	Variance
Experimental	5	3.648	$0.730 = \overline{X}_1$	0.093
Langmuir-I	5	3.829	$0.766 = \overline{X}_2$	0.106
Langmuir-II	5	3.288	$0.658 = \overline{X}_3$	0.128
Langmuir-III	5	3.949	$0.790 = \overline{X}_4$	0.099
Langmuir-IV	5	1.140	$0.228 = \overline{X}_5$	0.087
Langmuir-V	5	3.650	$0.730 = \overline{X}_6$	0.114
Langmuir-VI	5	1.689	$0.338 = \overline{X}_7$	0.115
Langmuir-VII	5	0.207	$0.041 = \overline{X}_8$	0.017

Source of variation	SS	df	MS	F_{cal}	F_{crit}	Inference
Between groups	4.067	8	0.508	45.267	2.21	S
Within groups	0.404	36	0.011			
Groups total	4.471	44				

The ANOVA tested whether any of the samples means differ from each other. A multiple comparison test, however, was conducted to check which sample(s) mean(s) differ from the others. The following section reports the application of Duncan's multiple range test.

Duncan multiple range test experiment

The means of linearisations in Table 5 for Langmuir-I, Langmuir-II, Langmuir-III…, Langmuir-VIII are respectively $\overline{X}_1, \overline{X}_3, ...\overline{X}_8$. Then, each group was compared as the following[9]:

Actual difference $\overline{X}_1 - \overline{X}_2 = 0.036 < R_2 = 0.135$

Actual difference $\overline{X}_1 - \overline{X}_3 = 0.072 < R_3 = 0.142$

Actual difference $\overline{X}_1 - \overline{X}_4 = 0.060 < R_4 = 0.146$

Actual difference $\overline{X}_1 - \overline{X}_5 = 0.501 > R_5 = 0.149$

Actual difference $\overline{X}_1 - \overline{X}_6 = 0.000 < R_6 = 0.152$

Actual difference $\overline{X}_1 - \overline{X}_7 = 0.392 > R_7 = 0.154$

Actual difference $\overline{X}_1 - \overline{X}_8 = 0.689 > R_8 = 0.155$

The following linearised Langmuir-IV, Langmuir-VI and Langmuir-VII equations, performed poorly in describing adsorption dataset compared to other linearisations. The actual differences as shown above were greater than the various LSR values. Also shown below, the mean differences of Langmuir-IV, Langmuir-VI and Langmuir-VII were greater than their various LSR values (9):

Actual difference $\overline{X}_2 - \overline{X}_5 = 0.538 > R_2 = 0.135$

Actual difference $\overline{X}_2 - \overline{X}_7 = 0.428 > R_7 = 0.154$

Actual difference $\overline{X}_2 - \overline{X}_8 = 0.725 > R_8 = 0.155$

This indicates that Langmuir-IV, Langmuir-VI, and Langmuir-VII are not appropriate linearisatoins to be fitted to the adsorption dataset. Other linearisations, in contrast, reveal small differences. The differences obtained for Langmuir-I, Langmuir-II, Langmuir-III and Langmuir-V were less than their various LSR values. These suggest that Langmuir-I, Langmuir-II, Langmuir-III and Langmuir-V can be used to fit the adsorption dataset.

The actual difference, however, for Langmuir-V $(\overline{X}_2 - \overline{X}_5) = 0$, reveal (not only) that it is less than its LSR value and also that its mean is the same for that obtained for experimental data. We may therefore state from the foregoing that the Duncan multiple range test also 'sorted' out Langmuir-V as the best linearization that fitted the adsorption dataset.

CONCLUSION

The following main conclusions can be drawn from the present study:

- *Anthocleista djalonensis* leaf extract was found to be a good inhibitor of aluminium corrosion in acidic medium.

- The inhibition efficiency increased with inhibitor concentration to attain a value of 83.29% (50 v/v %) at 60°C.

- Inhibition efficiency increased with an increase in inhibitor concentration but decreased with rise in temperature.

- The presence of inhibitor decreased the corrosion activation energy and the adsorption heats gave negative values.

- The free energy of adsorption indicates that the process was spontaneous.

- ANOVA and Duncan multiple range test statistics revealed that: linearisations of the non-linear Langmuir isotherm to various linear forms have variability values; Langmuir-IV, Langmuir-VI and Langmuir-VII could not be fitted well to adsorption data set; Langmuir-I, Langmuir-II, Langmuir-III and Langmuir-V fitted well to adsorption data set.

- Duncan multiple range test predicts that the best fit was obtained by fitting Langmuir-V equation to the adsorption dataset.

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