The inhibitive effect of *Irvingia gabonensis* extract on the corrosion of aluminium in 1M HCl solution

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ABSTRACT

The inhibitive effect of leaf extract of Irvingia gabonensis on the corrosion of aluminum in 1M HCl solution was investigated using chemical method at 30, 35 and 40 ^{o}C respectively. The inhibition efficiency for the extract increased with increasing concentration of the extract and decreased with increase in temperature. The adsorption of the inhibitor molecules on aluminium surface was found to obey Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed based on the thermodynamic parameters that govern the inhibition process.

Keywords: Aluminium; *Irvingia gabonensis*; acid corrosion, inhibitor.

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INTRODUCTION

The use of synthetic compounds as corrosion inhibitors are desirable due to their metal protecting properties, however, the problem of toxicity, non-degradability and environmental pollution posed by these compounds have been of serious concern .[1] Continuous usage of these materials would in no small measure compound the present environmental problems. The need, therefore, for alternative means of corrosion inhibition with resultant minimal environmental impasse cannot be overstressed and a good number of inexpensive environmentally friendly natural products have proved successful as corrosion inhibitors [2, 3].

Extracts of the following plants amongst others have been reported to have inhibitive effect on the rate of corrosion of metals in acidic media; *Veronica amygdalina* [4], *Cocos nucifera* [5], *Mimosa tannin* [6], *Occimum viridis* [7] and *Allium sativum* [8]. Surfactant molecules have also been used as inhibitors [9-11]

Irvingia gabonensis contains several organic compounds of high molecular weight with heteroatoms such as tannins, saponins, alkaloids, anthraquinones and phenols which are capable of physicochemical adsorption on metal surfaces. Presently, to the best of our knowledge there is no reported work on the effects of *Irvingia gabonensis* on the acid corrosion of aluminium in acid solution using chemical method.

In furtherance of our interest on the development of green inhibitors, we report in this paper the inhibitive effects of the extract of leaf of *Irvingia gabonensis* on the corrosion of aluminium in 1 M HCl solution using weight loss method (chemical method).

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MATERIALS AND METHODS

The sheet of aluminium was mechanically press-cut into 3 X 2cm coupons of 0.38mm thickness. Each coupon was perforated with a hole of about 0.02 cm in diameter at one end to allow passage of polythene string. The coupons were used as supplied without further polishing. However they were degreased in absolute ethanol, rinsed with bidistilled water and dried with acetone. The blank corrodent was 1 M HCl. Plant extracts were obtained by soaking weighed amount of dried and ground plant materials in distilled water for 24 hours after which the mixture was filtered and concentrated with minimal heat. Inhibitor test solutions were prepared in the concentration range of 0.3 – 1.2 (g/L) using 1 M acid as solvent at 30, 35 and 60°C using water bath.

Weight loss experiment
The clean coupons were weighed before experiment using JB 1603-L-C Mettler Toledo electronic weighing balance with the accuracy of ±0.001. Pre-weighed coupons were each immersed in test solution for 30 mins after which the coupons were withdrawn and rinsed severally under running tap. The coupons were then rinsed in absolute acetone, air dried and then reweighed. The weight loss was calculated in grams as the difference between the initial weight prior to immersion, and weight after removal of the corrosion product. Duplicate experiments were conducted in each case and the mean values reported. Percentage inhibition efficiency was calculated using equation (1).

$$\% \, Inhibition \quad = \quad \frac{W_c - W_{in}}{W_c} \; x \; \frac{100}{1} \tag{1}$$

Where W_c and W_{in} are the uninhibited and inhibited weight losses, respectively. The values of corrosion rate were determined for 30 min immersion period using equation 2:

$$Corrosion \, rate \quad = \quad [\Delta w/At] \tag{2}$$

where Δw is weight loss of Al(g), A is the area of Al coupon (cm^2) and t is the immersion time (h).

RESULTS AND DISCUSSION

Results from this study as presented in Figures 1 for the plot of corrosion rate against inhibitor concentration for aluminium corrosion in 1M HCl at different temperatures reveal that the rate of corrosion of the metal decreases with increase in inhibitor concentrations at all temperatures studied.
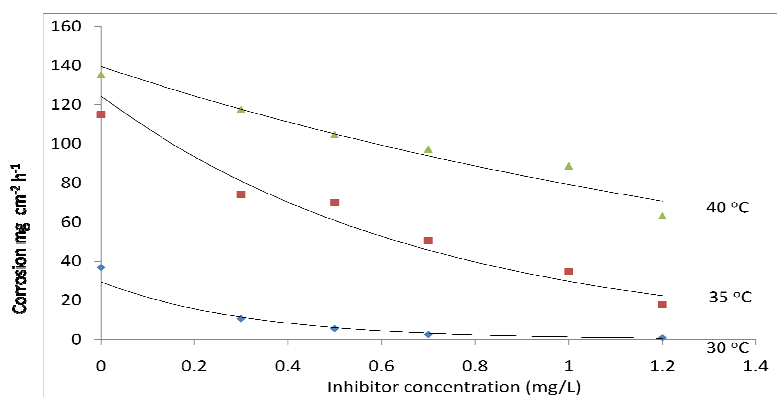

Figure 1: Plot of corrosion rate against inhibitor concentration (mg/L) for aluminium in 1M HCl at different temperatures

The variation of inhibition efficiency with inhibitor concentration for the extract at different temperatures is presented in Table1. Previous screening of *Irvinga gabonensis* revealed some of the plant's important chemical constituents to be saponins, tannis, alkaloids, flavones and essential oil, and these are capable of physicochemical interaction with metal surface thereby preventing close approach of corrodent on metal surface. It is, therefore, difficult to assign the inhibitive effect to any particular constituent of the extract. The results from this study show

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that the efficiency of the extract decreases with increasing temperature. This can be attributed to increase in corrosion rate due to desorption of inhibitor molecules from Al surface at elevated temperatures. Similar results were reported by Ebenso et. Al [12], who rationalized the trend on the basis of increased solubility of the protective films and reaction products precipitated on the surface of the metal that may otherwise inhibit metal corrosion.

Table1: Variation of inhibition efficiency (%I.E) with different concentrations of leaf extract of Irvinga gabonensis at temperatures, 30^0 C, 35^0 C and 40^0 C.

Inhibitor Concentration (g/L)	% 1.E At 30^{0}C	% 1.E At 35°C	% 1. E At 40^{0}C
0.3	78.78	46.61	14.35
0.5	85.15	54.57	21.59
0.7	87.27	57.20	23.76
1.0	96.46	82.70	35.12
1.2	97.76	90.87	37.21

Adsorption Isotherm

The adsorption characteristics of inhibitors can be predicted by fitting the dependence of surface coverage, θ (θ = IE/100), on inhibitor concentration into adsorption models. The Langmuir model developed to account for monolayer coverage on uniform surfaces [13] can be expressed in the form given in equation (3).

$$\frac{c}{\theta} = \frac{1}{K} + C \qquad (3)$$

Where C is the inhibitor concentration and K is the adsorptive equilibrium constant, representing the degree of adsorption. Langmuir parameters were obtained by fitting the experimental data into the adsorption model (Figure 2) and the results are summarized in Table 2. It can be inferred, from the linear plots and high values of correlation coefficient that the adsorption of the chemical constituents of the extract on Al surface obey Langmuir adsorption isotherm.
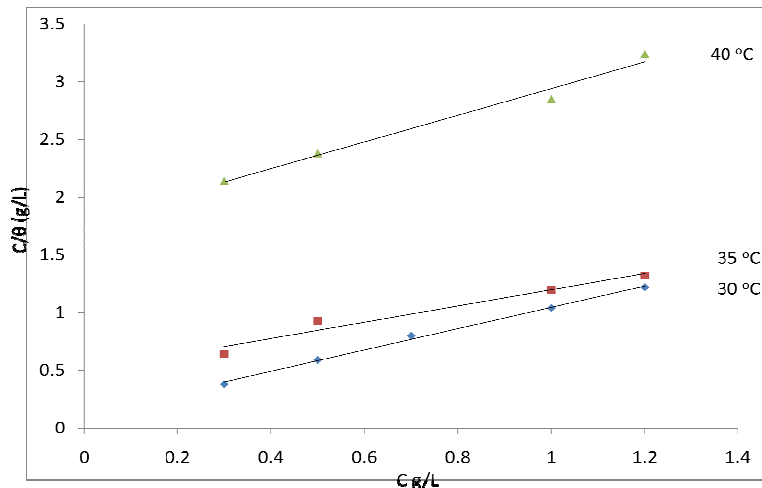
Figure 2. Langmuir isotherm for *Irvingia gabonensis* adsorption on aluminium in 1 M HCl.

Table 2. Values of Langmuir parameter for the inhibited corrosion of aluminium in 1 M HCl.

Temperature/ K	R^2	Intercept	K
303	0.996	0.123	8.13
308	0.957	0.704	1.42
313	0.981	1.178	0.84

The value of adsorptive equilibrium constant, K, decreases with increase in temperature signifying a decrease in the degree of adsorption of molecules on metal surface at elevated temperatures for the reasons earlier stated.

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Thermodynamic Studies

The mode of adsorption of inhibitors which can either be physio or chemisorption may be predicted from the knowledge of thermodynamic parameters that govern the adsorption process. The apparent activation energies (Ea) for corrosion process in the absence and presence of leaf extract of *Irvingia gabonensis* were calculated using a form of Arrehnius equation (4)

$$\ln W \quad = \quad lnA \quad + \quad -\frac{Ea}{RT} \qquad (4)$$

where W is corrosion rate in mg/cm^{-2} h, A, the frequency factor and R is gas constant. The plots of corrosion rate versus reciprocal of temperature are presented in Figure 3 and the values of activation energy in Table 3.
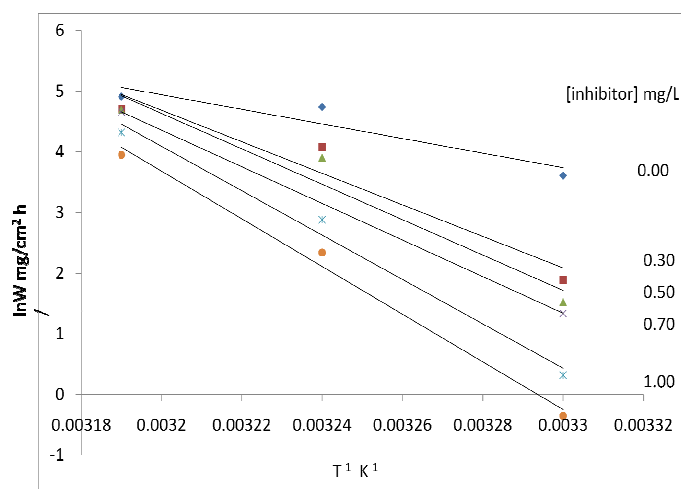

Figure 3. Plot of lnW versus 1/T for corrosion of aluminium without and with inhibitor in 1 M HCl at 30, 35, and 40 ºC.

Table 3. Activation energy values for the corrosion of aluminium without and with inhibitor in 1 M HCl.

[inhibitor] g/L	R^2	Ea/ kJ mol^{-1}
0.00	0.882	**100.00**
0.30	0.935	**216.12**
0.50	0.948	**242.57**
0.70	1.000	**250.09**
1.00	0.988	**304.05**
1.20	0.991	**326.57**

The apparent activation energy of the metal corrosion increases with inhibitor concentration which is indicative of modification of corrosion process attributable to the interaction of extract chemical constituents with metal surface or corrodent. Similar results in literature [14,15] have been attributed to physiosorption in which inhibition efficiency at normal temperatures is high but diminishes at elevated temperatures [16].

In order to have more insight into the mechanism of inhibition of corrosion process, other thermodynamic parameters were calculated using Erying's equation.

$$\ln\left(\frac{W}{T}\right) \quad = \quad ln(k_B /h) \quad + \quad \frac{\Delta S^*}{R} \quad - \quad \frac{\Delta H^*}{RT} \qquad (5)$$

W is corrosion rate, k_B is Boltzman's constant, h, the Plank's constant, ΔS^* and ΔH^* are changes in entropy and enthalpy of activation.

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The plots of ln(W/T) versus reciprocal of temperature are presented in Figure 4 and the values of enthalpy change and entropy change of activation in Table 4.
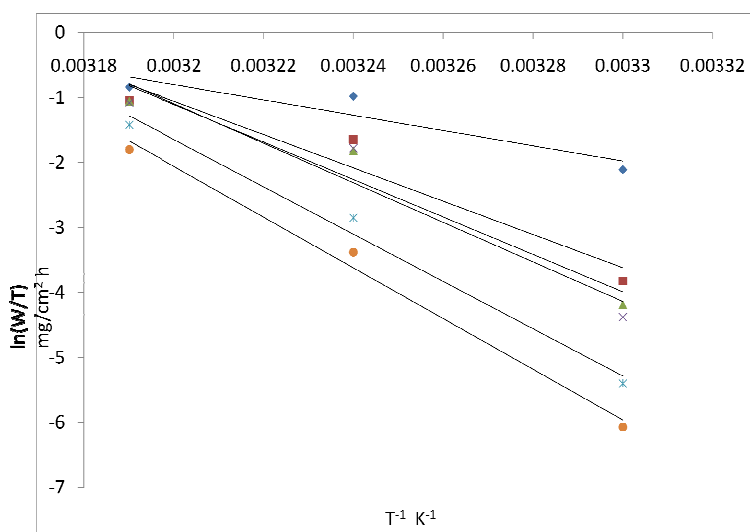

Figure 4. Plot of lnW versus 1/T for corrosion of aluminium without and with inhibitor in 1 M HCl at 30, 35, and 40 °C.

Table 4. Values of changes in Enthalpy and Entropy of activation for the corrosion of aluminium without and with inhibitor extract in 1 M HCl.

[Extract]/g/L	R^2	Intercept	ΔH^* J/mol	ΔS^* J/mol
0.00	0.791	35.18	93.47	95.01
0.30	0.867	78.25	205.93	453.04
0.50	0.889	88.34	232.24	536.88
0.70	0.867	93.02	244.40	575.86
1.00	0.955	112.93	297.43	741.36
1.20	0.960	120.94	319.95	807.75

The values of entropy change of activation are positive for corrosion of Al in blank solution and in the presence of inhibitor. This is indicative of disorder at the transition state of corrosion process. Similar result [17] has been attributed to the increased degree of randomness at the solid-solution interface during the adsorption process due to the structural changes in the solid caused by the intercalation of metal ions, the release of hydrated water during the metal ions' transition and the distribution of rotational and translational energies among the solute molecules in the adsorbed state. The enthalpy change of activation is positive indicating endothermic process and this observation in some corrosion processes is attributed to chemisorption but in this study we attribute the inhibition by *Irvingia gabonensis* to physiosorption due to other factors that lend more weight to the latter.

Meaningful conclusions can be drawn about the feasibility of reactions based on the value of the Gibb's Free Energy change. In this context, the standard free energy of adsorption, Δ G°, for the corrosion process was calculated using equation (6) and the values presented in Table 5.

$$K \quad = \quad \frac{1}{5.55} e^{-\frac{\Delta Go}{RT}} \qquad\qquad (6)$$

The standard ΔG° values ranged -11.49 to 20.44 kJ /mol at the three temperature studied. The negative value for ΔG° is indicative of spontaneous adsorption of inhibitor molecules on Al metal surface. It is generally accepted [18,19] that the values of ΔG° $\leq$ -20kJ/mol are consistent with physicsorption, while those around -40kJ/mol or higher involve chemisorptions. The result from the present study shows that the inhibition of corrosion by the extract of *Irvingia gabonensis* is spontaneous.

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Table 5. Values of Free energy change for the corrosion of aluminium without and with inhibitor extract in 1 M HCl.

Temperature/K	ΔG^o /kJ mol^{-1}
303	-9.58
308	-5.28
313	-3.99

CONCLUSION

The results from present study have shown that leaf extract of *Ivingia gabonensis* inhibit the corrosion of Al in 1 M HCl solution and the inhibition efficiency decrease with rise in temperature. The corrosion activation energy in the presence of inhibitor is higher than that in its absence. These observations are indicative of physiosorption mode of adsorption in the inhibition process.

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