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Research Article

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Adsorption and inhibition effect of *Maesobatrya barteri* leaf extract on aluminium corrosion in hydrochloric acid solution

Okon U Abakedi*, Idorenyin E Moses, James E Asuquo

Department of Chemistry, University of Uyo, P.M.B. 1017, Uyo, Nigeria.

Abstract The inhibition of aluminium corrosion in hydrochloric acid solution by ethanolic extract of *Maesobatrya barteri* leaf was studied using weight loss and thermometric methods. The results obtained show that *Maesobatrya barteri* leaf extract significantly inhibited the corrosion of aluminium in HCl solution. Inhibition efficiency was found to decrease with increase in extract concentration and temperature. The adsorption of the extract obeyed Freundlich adsorption isotherm. Physical adsorption has been proposed for the adsorption of *Maesobatrya barteri* leaf extract on aluminium surface. The calculated thermodynamic parameters reveal that the corrosion inhibition process was both endothermic and spontaneous.

Keywords Corrosion inhibition, Freundlich isotherm, *Maesobatrya barteri,* Physical adsorption

Introduction

The use of traditional inhibitors of metal corrosion is limited in this era of global environmental safety concerns, due to their toxicity and non-environmentally friendly properties. The need for the development and/or discovery of cheap, renewable and eco-friendly inhibitors has led to the use of naturally occurring substances, especially of plant origin. Plant extracts contain organic nitrogen, oxygen and/or sulphur in the combined form. The corrosion inhibitory action of these extracts is attributed to their adsorption on the metal surface.

Several plant extracts have been reported as good inhibitors of aluminium corrosion in acidic media [1-7]. Presently, no extract or inhibitor that offers a total protection for aluminium in acidic medium has been reported. *Maesobatrya barteri* (English name: Bush cherry; Efik/Ibibio name: Nyanyatet; Igbo name: Uvune) is a broad - leafed medicinal plant belonging to the family Euphorbiaceae. The plant is highly treasured by the people of south eastern Nigeria, not only for its succulent edible berries but also for its acclaimed therapeutic effect on some ailments. Ailments treated traditionally with parts of the plant have been reported by researchers [8 - 9].

Previous studies [10**]** revealed that *Maesobatrya barteri* leaves contain tannins, saponins, cardiac glycoside, deoxy sugar and terpenes. The presence of these organic N, S and O atoms in *Maesobatrya barteri* leaf extract qualifies it as a potential corrosion inhibitor.

As part of our effort in the global search for efficient eco-friendly inhibitors of aluminium corrosion in acidic media, this work aims at assessing the inhibitory properties of *Maesobatrya barteri* leaf extract on the corrosion of aluminium in hydrochloric acid solution.

Materials and Methods

Materials

Aluminium sheet (purity 98.5%) of the type AA1060 used for this work was obtained from System Metal Industries Limited, Calabar, Nigeria. Each sheet was 0.4 mm in thickness and was mechanically press cut into 4 cm x 5 cm coupons (for weight loss measurements) and 2 cm x 5 cm (for thermometric tests). These coupons were used without further polishing. The surface treatment of the coupons involved degreasing in absolute ethanol, drying in acetone and storing in a moisture-free desiccator prior to use in corrosion studies.

Preparation of *Maesobatrya barteri* leaf extract

Fresh leaves of *Maesobatrya barteri* were collected from the Main Campus of University of Uyo, Uyo, Nigeria. They were plucked, washed and air – dried at 30°C for seven days. They were then ground to powder. The dried ground samples of *Maesobatrya barteri* leaf were macerated with 90% ethanol for seven days at room temperature in a large glass trough with cover. The mixture was then filtered. The filtrate was evaporated at 40°C in a water bath to constant weight, leaving a dark green extract in the beaker. Extract concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L, 2.0 g/L, and 4.0 g/L respectively in 0.5M HCl solution were used for the weight loss studies at 30°C – 60°C. The same extract concentrations were used in 2M HCl solution for the thermometric tests.

Weight loss method

The apparatus and procedure followed for the weight loss measurements were as previously reported [11]. The corrodent concentration was 0.5M HCl and the volume of the test solution used was 100 mL. All tests were made in aerated solutions. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to compute the corrosion rate given by [12]:

$$CR\ (mg\ cm^{-2}hr^{-1}) = \left(\frac{W}{A\ t}\right) \qquad (1)$$

where W is the weight loss (mg), A is the area of the specimen (cm^2) while is t the exposure time (hr).

The inhibition efficiency (I%) of *Maesobotrya barteri* leaf extract acting as inhibitor in 0.5M HCl was calculated using the formula [13]:

$$\%I = 100\ X \left(\frac{W_0 - W_1}{W_0}\right) \qquad (2)$$

where W_0 and W_1 are the weight losses of the aluminium coupons in the absence and presence of inhibitors, respectively, in HCl at the same temperature.

Thermometric method

The reaction vessel and procedure for determining the corrosion behaviour by this method has been described by other authors [14]. In the thermometric technique the corrodent concentration was kept at 2M HCl. The volume of test solution used was 50 mL. The initial temperature in all experiments was kept at 30.0°C. The progress of corrosion reaction was monitored by determining the changes in temperature with time using a calibrated thermometer (0 -100°C) to the nearest ± 0.1°C. This method enabled the computation of the reaction number (RN) defined as [15]:

$$RN\ (°C/min) = \frac{T_m - T_i}{t} \qquad (3)$$

where T_m and T_i are the maximum and initial temperatures, respectively, while 't' is the time (min) taken to reach the maximum temperature. The inhibition efficiency (%I) was evaluated from percentage reduction in the reaction number, via the equation:

$$\%I = \left(\frac{RN_0 - RN_1}{RN_0}\right) \times 100 \qquad (4)$$

where RN_0 is the reaction number in the absence of inhibitors (blank) and RN_1 is the reaction number of 2M HCl containing studied inhibitor.

Results and Discussion

Effect of extract concentration on inhibition efficiency

The variation of inhibition efficiency with concentration of *Maesobatrya barteri* leaf extract in 0.5M HCl solution by weight loss measurements is depicted in Fig. 1. It is observed that *Maesobatrya barteri* leaf extract was more effective in inhibiting the corrosion of aluminium in HCl solution at lower concentrations than at higher concentrations. Furthermore, at a particular temperature, the inhibition efficiency decreased with increase in the concentration of the leaf extract. A decrease in inhibition efficiency with increase in inhibitor concentration indicates a weak interaction between the metal surface and the inhibitor.

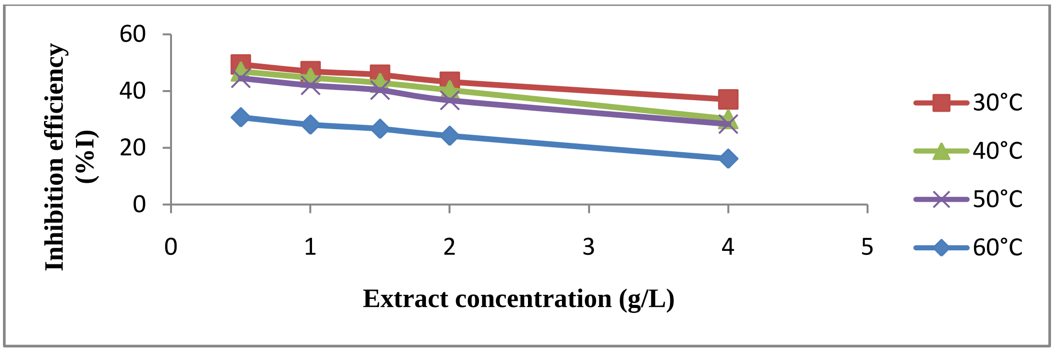

Figure 1: A plot of inhibition efficiency against various concentrations of Maesobatrya barteri leaf extract at 30-60°C

Thermometric measurements

The thermometric tests for aluminium corrosion in 2M HCl solution containing *Maesobatrya barteri* leaf extract are illustrated in Fig. 2. Inspection of Fig. 2 shows that as the concentration of the leaf extract increases, the time (t) required to reach the maximum temperature decreases while the maximum temperature (T_m) increases. The calculated values of reaction number (RN) and inhibition efficiency (%I) for aluminium corrosion in 2M HCl containing *Maesobatrya barteri* leaf extract are contained in Table I. Table I reveals that the inhibition efficiency by the thermometric method decreased with increase in the leaf extract concentration. The inhibition efficiency by the thermometric method followed the same trend as that obtained by the weight loss measurements.

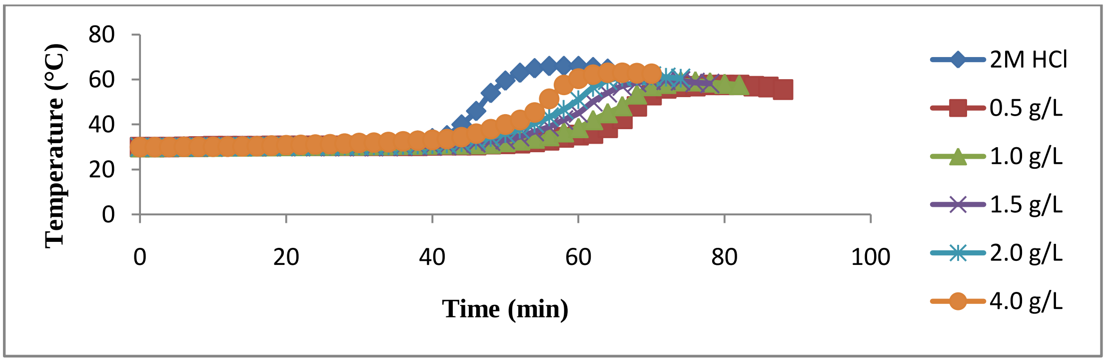

Figure 2: Temperature – time curves for aluminium corrosion in 2M HCl obtained in absence and presence of Maesobatrya barteri leaf extract

Table 1: Effect of *Maesobatrya barteri* leaf extract on inhibition efficiency of aluminium corrosion in 2M HCl solution (Thermometric measurements)

Extract Concentration	**Initial Temperature T_i (°C)**	**Maximum Temperature T_m (°C)**	**Time taken to Reach Maximum temp t (min)**	**Reaction Number RN (°C)**	**Inhibition Efficiency (%I)**
2M HCl (Blank)	30.0	66.0	56	0.6429	-
0.5 g/L	30.0	57.5	78	0.3526	45.15
1.0 g/L	30.0	59.2	74	0.3946	38.62
1.5 g/L	30.0	59.5	70	0.4214	34.45
2.0 g/L	30.0	61.5	68	0.4632	27.95
4.0 g/L	30.0	63.0	64	0.5156	19.80

Effect of temperature on inhibition efficiency

An increase in temperature led to a decrease in the inhibition efficiency of *Maesobatrya barteri* leaf extract (Table 2). This indicates a weakening of adsorption bonds between metal and inhibitor as well as a physical adsorption mechanism.

The activation energy (E_a) of the corrosion process in the absence and presence of the leaf extract was evaluated using the Arrhenius equation:

$$CR = Ae^{\frac{-E_a}{RT}} \quad (5)$$

where CR is the corrosion rate, E_a is the activation energy, R is the universal gas constant, T is the absolute temperature and A is the pre – exponential factor. Hence, a plot of ln CR vs. 1/T should be linear, with a gradient of $-E_a/R$ and an intercept of ln A, if the Arrhenius equation is obeyed. Fig. 3 depicts an Arrhenius plot of ln CR vs. 1/T for aluminium corrosion in 0.5M HCl solution in the absence and presence of various concentrations of the leaf extract.

Table 2: Calculated values of weight loss, corrosion rate and inhibition efficiency for aluminium corrosion in 0.5M HCl solution containing *Maesobatrya barteri* leaf extract at 30°C – 60°C

Extract	Weight loss (g)				Corrosion rate (mg cm^{-2} hr^{-1})				Inhibition efficiency (%I)			
Conc	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
0.5M HCl	0.0081	0.0275	0.0360	0.1210	0.0500	0.1788	0.2375	0.7813	-	-	-	-
0.5 g/L	0.0041	0.0146	0.0200	0.0838	0.0256	0.0913	0.1250	0.5238	49.30	46.90	44.44	30.75
1.0 g/L	0.0043	0.0152	0.0209	0.0869	0.0269	0.0950	0.1306	0.5431	46.91	44.73	41.94	28.18
1.5 g/L	0.0044	0.0157	0.0215	0.0887	0.0275	0.0981	0.1344	0.5544	45.68	42.91	40.28	26.69
2.0 g/L	0.0046	0.0164	0.0228	0.0917	0.0288	0.1025	0.1425	0.5731	43.21	40.36	36.67	24.21
4.0 g/L	0.0051	0.0192	0.0258	0.1015	0.0319	0.1200	0.1613	0.6345	37.04	30.18	28.33	16.12

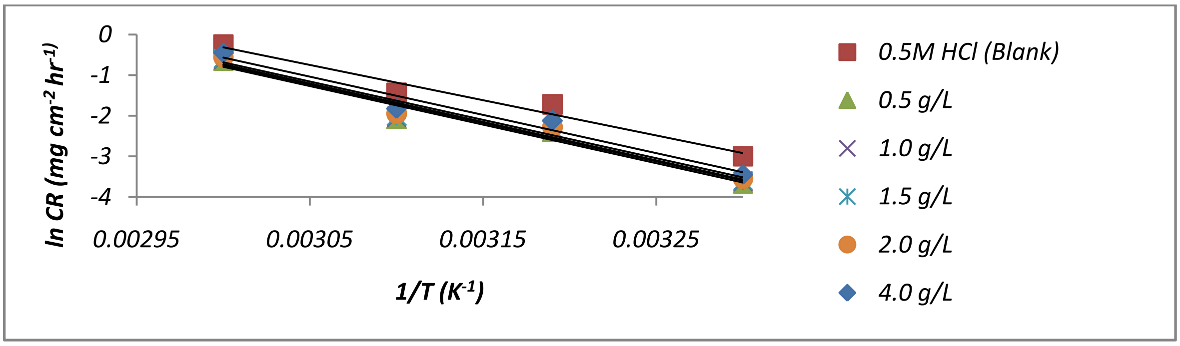

Figure 3: Plot of ln CR vs. 1/T (Arrhenius plot) for aluminium corrosion in 0.5M HCl in the absence and presence of Maesobatrya barteri leaf extract

The E_a values were calculated from the slopes of the linear plots and are presented in Table 3. It is clear that E_a values in the presence of various concentrations of leaf extract are higher than in their absence. An increase in the E_a values in the presence of the extract compared to the blank denotes physical adsorption while the reverse is usually attributed to chemical adsorption [16]. The increase in the E_a values in the presence of *Maesobatrya barteri* leaf extract compared to the blank coupled with a decrease in inhibition efficiency as temperature increases indicates physical adsorption.

The values of enthalpy of activation (ΔH^0_{ads}) and entropy of activation (ΔS^0_{ads}) were obtained from the transition state equation:

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S^0_{ads}}{R}\right)\exp\left(\frac{-\Delta H^0_{ads}}{RT}\right) \quad (6)$$

where CR is the corrosion rate, h is the Planck's constant, N is the Avogadro's number, T is the absolute temperature and R is the universal gas constant. Linear plots of ln (CR/T) vs. 1/T (Fig. 4) were obtained with gradients of $(-\Delta H^0_{ads}/R)$ and intercepts of [ln (R/Nh) + $\Delta S^0_{ads}/R$] from which the values of ΔH^0_{ads} and ΔS^0_{ads}

were calculated and listed in Table3. The positive values of ΔH^0_{ads} both in the absence and presence of the leaf extract reflect the endothermic nature of the aluminium corrosion process while the negative ΔS^0_{ads} values indicate an ordered arrangement of inhibitor on aluminium surface due to a decrease in the disorderliness of the system.

Table 3: Calculated values of thermodynamic parameters for aluminium corrosion in 0.5M HCl solution containing *Maesobatrya barteri* leaf extract

Extract concentration	E_a (kJ mol^{-1})	ΔH^0_{ads} (kJ mol^{-1})	ΔS^0_{ads} (J K^{-1} mol^{-1})
0.5M HCl (Blank)	72.0549	69.4186	- 40.2472
0.5 g/L	79.0362	76.3940	- 23.2534
1.0 g/L	78.7236	76.0864	- 23.8687
1.5 g/L	78.6696	76.0299	- 23.8271
2.0 g/L	78.4600	75.8204	- 24.1093
4.0 g/L	78.2231	75.5842	- 23.8437

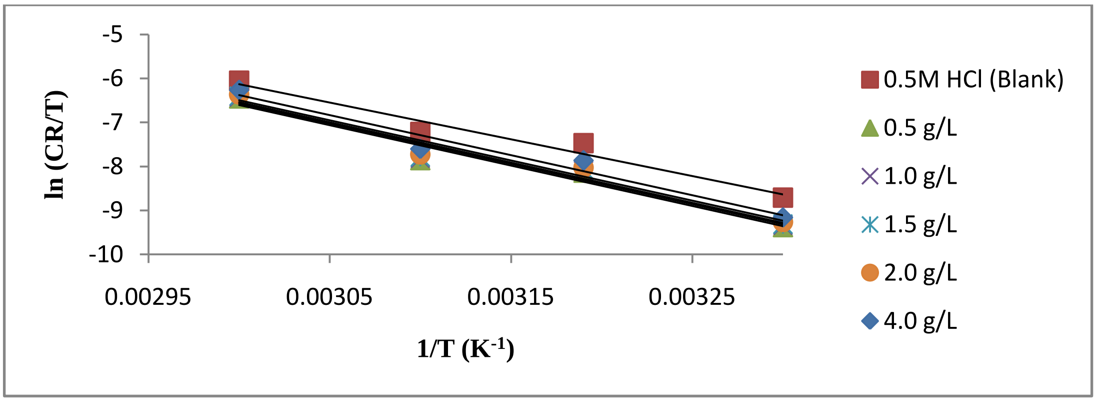

Figure 4: Plot of ln (CR/T) vs 1/T (Transition state plot) for aluminium corrosion in 0.5M HCl solution in the absence and presence of Maesobatrya barteri leaf extract

Adsorption isotherm

Several adsorption isotherms were assessed. The best fit for the adsorption of *Maesobatrya barteri* leaf extract on aluminium surface was obtained with Freundlich adsorption isotherm defined as [17]:

$$\log\theta = n\log C + \log K \quad (7)$$

where C is the inhibitor concentration, θ is the degree of surface, n is the interaction parameter while K_{ads} is the equilibrium constant of the adsorption process. Plot of log θ vs. log C gives straight lines (Fig. 5). The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 4. K_{ads} is related to the standard free energy of adsorption (ΔG^0_{ads}) by the formula [12, 18]:

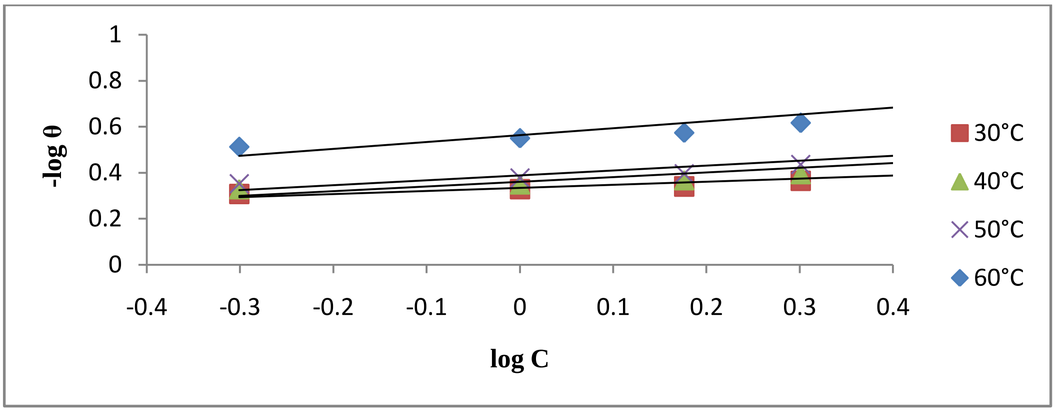

Figure 5: Plot of log θ vs log C (Freundlich isotherm) for aluminium corrosion in 0.5M HCl solution containing Maesobatrya barteri leaf extract

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \quad (8)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant white T is the absolute temperature.

Table 4: Some parameters of the linear regression of Freundlich adsorption isotherm for aluminium corrosion in 0.5M HCl solution containing *Maesobatrya barteri* leaf extract

Temperature	R^2	n	K_{ads} (g^{-1}L)	ΔG^0_{ads} (kJ mol^{-1})
30°C	0.9029	- 0.13	4.641 x 10^{-1}	- 8.1840
40°C	0.8255	- 0.20	4.363 x 10^{-1}	- 8.2934
50°C	0.8681	- 0.21	4.088 x 10^{-1}	- 8.3835
60°C	0.8479	- 0.30	2.740 x 10^{-1}	- 7.5353

The thermodynamic parameters for the adsorption of *Maesobatrya barteri* leaf extract on aluminium surface are shown in Table 4. The negative values of ΔG^0_{ads} indicate the spontaneity of the adsorption process. Generally, values of ΔG^0_{ads} less negative than -20kJ mol^{-1} indicate physical adsorption while those more negative than -40kJ mol^{-1} indicate chemical adsorption [19 -20]. Consequently, the values of ΔG^0_{ads} obtained in this work being less negative than -20kJ mol^{-1} coupled with a decrease in the inhibition efficiency with increase in temperature indicates a physical adsorption process.

Conclusion

The following conclusions could be drawn based on this work**.**

1 *Maesobatrya barteri* leaf extract acts as inhibitor for aluminium corrosion in acidic medium.

2. Inhibition efficiency of *Maesobatrya barteri* leaf extract decreases with increase in concentration of the extract and temperature.

3. The values of ΔG^0_{ads} are negative indicating that the adsorption of the inhibitor on aluminium surface was a spontaneous process. The values obtained support the physical adsorption mechanism.

4. The fit of experimental data show that *Maesobatrya barteri* leaf extract conform to the Freundlich adsorption isotherm.

5. The E_a values in the presence of the extract being higher than in the blank coupled with a decrease in the inhibition efficiency with increase in temperature indicates a physical adsorption process.

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