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Research Article

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Inhibition of aluminium corrosion in hydrochloric acid solution by *Stachytarpheta indica* leaf extract

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Abstract The inhibition and adsorption characteristics of *Stachytarpheta indica* (STA) leaf extract for the corrosion of aluminium in hydrochloric acid solution have been studied using weight loss and thermometric methods. The results obtained reveal that various concentrations of STA leaf extract inhibited the corrosion of aluminium in HCl solution at both 30°C and 60°C. The inhibition efficiency was found to decrease with increase in extract concentration but increased with increase in temperature. Thermodynamic parameters indicate that the extract chemically adsorbed onto aluminium surface. The adsorption of STA leaf extract on aluminium surface conformed to the Temkin adsorption isotherm.

Keywords Corrosion inhibition, *Stachytarpheta indica*, aluminium, acidic medium, chemisorption

Introduction

The natural resistance of aluminium to corrosion due to the thin oxide layer on its surface gets weakened when aluminium comes in contact with strongly acidic and alkaline solutions, leading to the dissolution of aluminium in these media. The pickling of aluminium, for instance, apart from removing the oxide layer on the metal, also corrodes it. It is therefore necessary to add inhibitor to the pickling liquor in order to minimise the loss of the metal during the pickling process.

The traditional inhibitors of metal corrosion have many disadvantages. Some of these include biotoxicity, environmentally unfriendly properties, high cost and non-availability on demand. This has necessitated the need for a new class of inhibitors to overcome the above – mentioned challenges. Plant extracts readily come as a viable alternative because they are cheap, non-toxic, readily available and environmentally friendly. Several leaf extracts have been reported as good inhibitors of aluminium corrosion in acid medium [1-10]. The need for efficient eco-friendly inhibitors of aluminium corrosion in acidic medium cannot be over-emphasised.

Stachytarpheta indica (English name: Aeron's rod or Brazilian tea; Efik/Ibibio name: Aran umon) belongs to the family Verbenaceae. It is a highly treasured plant used in traditional medicine by the people of south eastern Nigeria for the treatment of malaria. The phytochemical screening of *Stachytarpheta indica* leaf extract by some workers [11] showed it to contain phlobotanin, saponin, tannins, proteins, carbohydrates and alkaloids. Previous work [12] revealed that *Stachytarpheta indica* leaf extract is a good inhibitor of mild steel corrosion in acid medium. The aim of this work is to inhibit the corrosion of aluminium in hydrochloric acid solution using *Stachytarpheta indica* leaf extract.

Materials and Methods

Test materials

Aluminium sheet (purity 98.5%) of the type AA1060 used for this work was obtained from System Metal Industries Limited, Calabar, Nigeria. It was mechanically press-cut into 4 cm x 5 cm coupons. These coupons were used without further polishing. However, the surface treatment of the coupons involved degreasing in absolute ethanol, drying in air after dipping in acetone before storing in a moisture-free desiccator prior to use in corrosion studies.

Preparation of *Stachytarpheta indica* leaf extract

Fresh leaves of *Stachytarpheta indica* (STA) were collected from a farm in Calabar, Nigeria. They were plucked, washed and air– dried under shade at 30°C for seven days. They were then ground to powder. The dried ground samples of *Stachytarpheta indica* leaves 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 thermostatic 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 and 2.0 g/L, respectively, in 0.5M HCl solution were used for the weight loss studies at 30°C and 60°C. The same extract concentrations were used in 2M HCl solution for the thermometric tests.

Weight loss measurements

The apparatus and procedure followed for the weight loss measurements were as previously reported [1]. The corrodent concentration was kept at 0.5M HCl and the volume of the test solution used was 100 mL. 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:

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

where W is the weight loss (mg), A is the surface area of the specimen (cm^2) while t is the exposure time (hr). The inhibition efficiency (I %) of *Stachytarpheta indica* leaf extract acting as inhibitor in 0.5M HCl was calculated using the formula [13]:

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

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 measurements

The reaction vessel and procedure for determining the corrosion behaviour by this method has been described elsewhere by other authors [14]. In the thermometric technique, the corrodent (HCl) concentration was kept at 2M. 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]:

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

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:

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

where RN_0 is the reaction number in the absence of inhibitors (blank) and RN_1 is the reaction number in the presence of studied inhibitor.

Results and Discussion

Effect of extract concentration on inhibition efficiency

Fig. 1 reveals that an increase in *Stachytarpheta indica* (STA) leaf extract led to a decrease in the inhibition efficiency of aluminium in HCl solution, at both 30°C and 60°C, by the weight loss method. At a given temperature, a decrease in inhibition efficiency with increase in extract concentration indicates that the inhibitor was more effective at lower concentrations than at higher concentrations. A decrease in the inhibition efficiency with increase in inhibitor concentration indicates a weak interaction between the metal surface and the inhibitor [7].

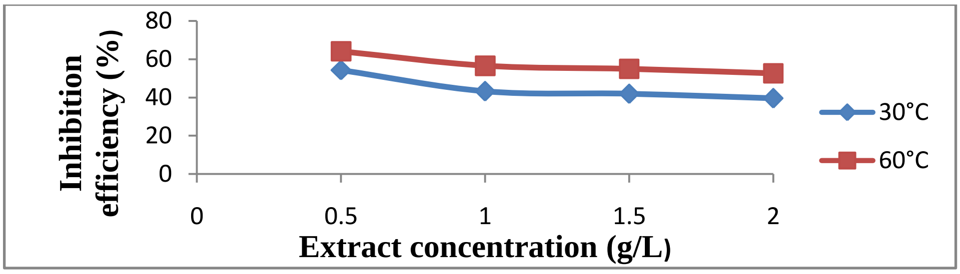

Figure 1: A plot of inhibition efficiency against Stachytarpheta indica (STA) leaf extract concentrations at 30°C and 60°C

Thermometric studies

Fig. 2 illustrates the thermometric measurements for aluminium corrosion in 2M HCl solution containing *Stachytarpheta indica* leaf extract. Fig. 2 reveals that as the concentration of STA leaf extract increases, the time required to reach the maximum temperature decreases while the maximum temperature increases. Additionally, Fig. 2 also reveals that at the onset of the reaction, there was no significant increase in temperature with time. This horizontal (flat) portion of the graph indicates the time (duration) aluminium could remain passive in 2M HCl solution. The calculated values of reaction number and inhibition efficiency as presented in Table 1 show that the inhibition efficiency of STA leaf extract decreased with increase in extract concentration. The inhibition efficiency by both the weight loss and thermometric methods followed a similar trend.

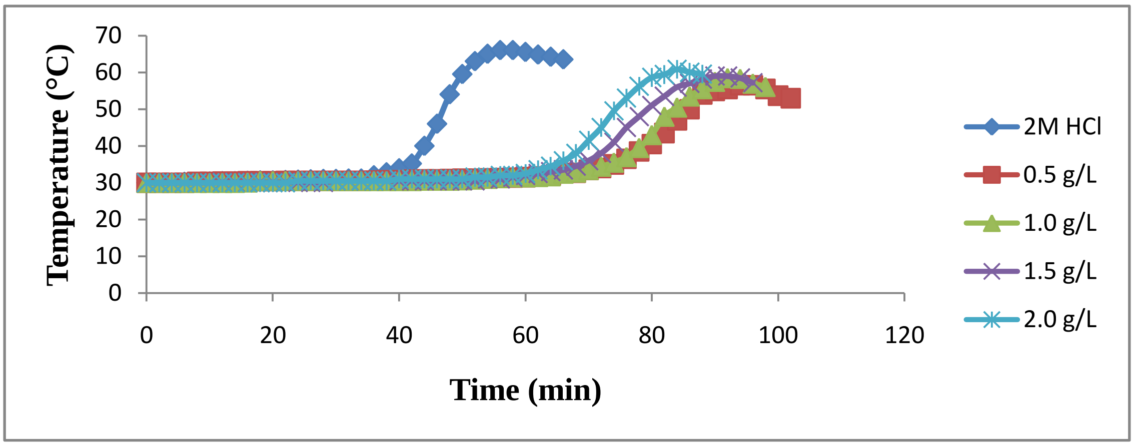

Figure 2: Temperature – time curves for aluminium corrosion in 2M HCl obtained in absence and presence of Stachytarpheta indica leaf extract

Table 1: Effect of *Stachytarpheta indica* 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/min)**	**Inhibition efficiency (%)**
2M HCl	30.0	66.0	56	0.6429	-
0.5 g/L	30.0	56.5	94	0.2819	56.15
1.0 g/L	30.0	58.5	92	0.3098	51.81
1.5 g/L	30.0	59.0	90	0.3222	49.88
2.0 g/L	30.0	60.8	84	0.3667	42.96

Effect of temperature on inhibition efficiency

Inhibition efficiency increased with increase in temperature at all concentrations of STA leaf extract studied (Table 1). An increase in inhibition efficiency with increase in temperature indicates a strong interaction between the metal surface and inhibitor as well as chemical adsorption mechanism. Consequently, STA chemically adsorbed on the aluminium surface.

Table 2: Calculated values of corrosion rate and inhibition efficiency for aluminium corrosion in 0.5M HCl solution containing *Stachytarpheta indica* (STA) leaf extract (Weight loss measurements)

Extract concentration	**Corrosion rate (mg cm^{-2} hr^{-1})**		**Inhibition efficiency (%)**	
	30°C	**60°C**	**30°C**	**60°C**
0.5M HCl	0.0506	2.3831	-	-
0.5 g/L STA	0.0231	0.8531	54.32	64.20
1.0 g/L STA	0.0288	1.0350	43.21	56.57
1.5 g/L STA	0.0294	1.0731	41.98	54.97
2.0 g/L STA	0.0306	1.1294	39.51	52.61

The values of heat of adsorption (Q_{ads}) presented in Table 3 were calculated using the equation [16]:

$$Q_{ads} = 2.303R\left[log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1T_2}{T_2-T_1}\right] \quad (5)$$

where θ_1 and θ_2 are the degrees of surface coverage at T_1 and T_2, respectively, and R is the universal gas constant.

The activation energy (E_a) of the corrosion process in the absence and presence of the leaf extract was evaluated using the Arrhenius equation [17]:

$$log\left(\frac{CR_2}{CR_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (6)$$

where CR_1 and CR_2 are corrosion rates at T_1 (303K) and T_2(333K),respectively, and R is the universal gas constant (8.314 JK^{-1} mol^{-1}).

The calculated values of activation energy (E_a) from equation (6) are presented in Table 3. It is observed that the E_a value for the blank (107.737 kJ mol^{-1}) is higher than the E_a for STA – H_2SO_4 medium. A decrease in the E_a value in an inhibited solution compared to the blank indicates chemical adsorption mechanism while the reverse indicates physical adsorption [18]. The values of Q_{ads} obtained in this work were positive and ranged from 11.495 kJ mol^{-1} to 15.037 kJ mol^{-1}. Positive values of Q_{ads} indicate that the adsorption of STA leaf extract onto aluminium surface and hence the inhibition efficiency increased with increase in temperature [19 - 20].

Table 3: Calculated values of activation energy and heat of adsorption for aluminium corrosion in 0.5M HCl solution containing *Stachytarpheta indica* (STA) leaf extract

Extract concentration	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})
0.5M HCl (Blank)	107.737	-
0.5 g/L STA	100.936	11.495
1.0 g/L STA	100.174	15.037
1.5 g/L STA	100.608	14.625
2.0 g/L STA	100.919	14.837

Adsorption isotherm

Several adsorption isotherms were assessed to fit the experimental data. The best fit for the adsorption of STA leaf extract on aluminium surface was obtained with the Temkin adsorption isotherm defined as [21]**:**

$$\theta = \frac{1}{f}\ln K_{ads} C \quad (7)$$

where θ is the degree of surface coverage, C is the inhibitor concentration, f is the heterogeneous factor of the metal surface while K_{ads} is the adsorption equilibrium constant. Linear plot of θ vs. ln C (Fig. 3) indicate that the obtained data fit the Temkin adsorption isotherm. The values of the linear regression of Temkin isotherm for aluminium corrosion in 0.5M HCl solution containing STA leaf extract are presented in Table 4. The constant 'f' depends on the intermolecular interaction in the adsorption layer and on the heterogeneity of the surface. If 'f' is positive, mutual attraction of molecules occurs; if 'f' is negative, repulsion occurs [22]. The negative values of 'f' obtained in this work indicate a repulsion between the molecules. The adsorption equilibrium constant, K_{ads}, is related to the standard free energy of adsorption (ΔG^0_{ads}) by the formula [23]:

$$\Delta G^0_{ads} = -RT\ ln(55.5K_{ads}) \quad (8)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant while T is the absolute temperature. The negative values of ΔG^0_{ads} obtained reveal that the adsorption of *Stachytarpheta indica* leaf extract on aluminium surface occurred spontaneously.

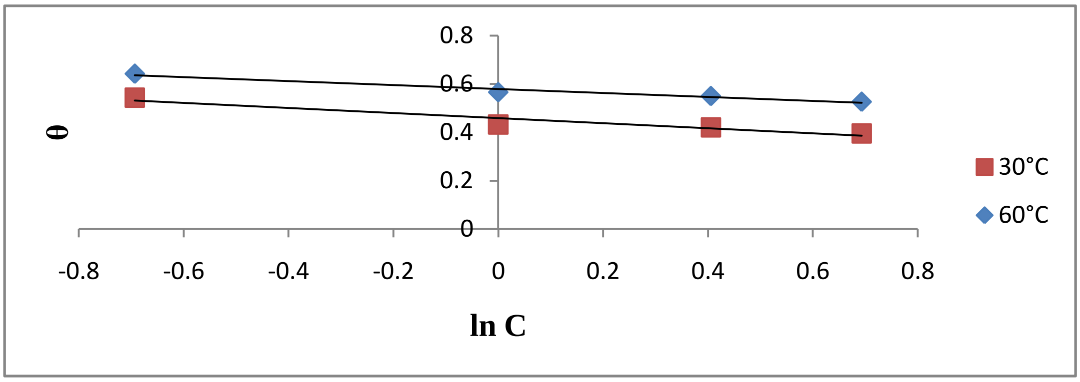

Figure 3: Plot of θ vs. ln C (Temkin isotherm) for aluminium corrosion in 0.5M HCl containing Stachytarpheta indica leaf extract

Table 4: Some parameters of the linear regression of Temkin adsorption isotherm for aluminium corrosion in 0.5M HCl solution containing *Stachytarpheta indica* leaf extract

Temperature	R^2	f	ln K_{ads}	K_{ads}	ΔG^0_{ads} (kJ mol^{-1})
30°C	0.9270	-9.51	0.4582	1.5812	-11.2721
60°C	0.9674	-12.20	0.5792	1.7846	-12.7231

Conclusion

The following conclusions could be drawn based on this research.

1. *Stachytarpheta indica* leaf extract inhibited the corrosion of aluminium in hydrochloric acid solution.
2. Inhibition efficiency of *Stachytarpheta indica* leaf extract decreased with increase in extract concentration but increased with increase in temperature.
3. The negative values of $\Delta G°_{ads}$ obtained show the spontaneity of the adsorption process.
4. The adsorption of *Stachytarpheta indica* leaf extract on aluminium surface obeyed the Temkin adsorption isotherm.
5. The E_a values in the presence of the extract being lower than in the blank coupled with an increase in the inhibition efficiency with increase in temperature indicates a chemical adsorption process.

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