Original Research Paper

Adsorption and Inhibition Effect of *Eremomastax polysperma* Leaf Extract on Aluminium Corrosion in Acidic Medium

ABSTRACT

The inhibitory effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in hydrochloric acid solution was investigated using weight loss and thermometric methods. Analyses of the experimental data show that the inhibition efficiency increased with increase in *Eremomastax polysperma* leaf extract concentration and decrease in temperature. The highest inhibition efficiency of 81.78% occurred at 4.0 g/L extract concentration at 30℃ by weight loss measurements. The adsorption of the leaf extract on aluminium surface is proposed to occur via physisorption mode. The experimental data fit the modified Langmuir isotherm. The negative values of $\Delta G°_{ads}$ obtained reveal the spontaneity of the adsorption process while the positive values of $\Delta H°_{ads}$ indicate that the adsorption of *Eremomastax polysperma* leaf extract on aluminium surface was an endothermic process.

Keywords: Eremomastax polysperma, aluminium, Langmuir isotherm, physisorption, weight loss, thermometric, corrosion.

1. INTRODUCTION

Aluminium has a wide variety of uses domestically and industrially. One of the consequences of corrosion of a metal is the weakening of its mechanical strength [1]. The breakdown of equipment due to the corrosion of its metallic components is a regular occurrence in industry. In the petroleum industry, for instance, the shutdown of refineries for turn-around maintenance due to corrosion of vital components is a common industrial practice. Efforts geared at reducing the corrosion of metals in contact with aggressive environments led to the discovery of some inorganic and synthesised organic compounds as corrosion inhibitors. Although many of these compounds inhibit the corrosion of metals excellently in various media, their usage is being discouraged in recent time because of their toxicity [2] and non-environmentally friendly characteristics [3]. In the pickling of aluminium, there is the need to add inhibitor to the pickle liquor in order to minimise the loss of the metal in the acid solution used. The quest for efficient eco-friendly corrosion inhibitors as replacement for the traditional inhibitors is now focused on natural products. Some leaves extracts have been reported as good inhibitors of aluminium corrosion in acidic media [4 – 9]. The search for more efficient eco-friendly inhibitors of aluminium corrosion in acidic medium is ongoing since among the known inhibitors, there is none that offers a 100% inhibition efficiency on aluminium corrosion in acidic medium.

Eremomastax polysperma (Efik/Ibibio name: Edem ididuot) is a medicinal plant belonging to the family Acanthaceae. Its use in traditional medicine by the people of Nigeria has been documented [10 - 11]. The phytochemical analysis of *Eremomastax polysperma* leaf extract showed the presence of phenol, flavonoids, saponins, sterol tannins and alkaloids [12]. Previous studies [13] revealed that *Eremomastax polysperma* leaf extract is a good inhibitor of mild steel corrosion in acidic medium. The aim of this work was to assess the inhibitory effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in acidic medium.

2. MATERIALS AND METHODS

2.1Test materials

The chemical composition (weight %) of the aluminium sheet used for this work was: Al (99.60),Si (0.13), Fe (0.09), Mn (0.05), Mg (0.10) and Cu (0.03). The sheet was mechanically press - cut into 4 cm x 5 cm coupons. Different grades of silicon carbide papers were used to polish the coupons until mirror finish. Before use for the corrosion tests, the coupons were degreased in absolute ethanol, dried in acetone and stored in a moisture – free desiccator.

2.2 Preparation of *Eremomastax polysperma* Leaf Extract

Eremomastax polysperma leaves used for this work were obtained from a farm in Nung Oku Ibesikpo, Akwa Ibom State, Nigeria. The leaves were plucked and washed before air – drying at 30℃ for seven days. *Eremomastax polysperma* leaf extract was obtained following a procedure reported previously [4, 8]. For the weight loss studies, *Eremomastax polysperma* extract concentrations of 1.0 g/L - 4.0 g/L in 0.5 M HCl solution were used at 30℃, 40℃, 50℃ and 60℃ while similar extract concentrations were used in 2 M HCl solution for the thermometric tests.

2.3 Weight Loss Method

Previously weighed aluminium coupons were suspended with the aid of glass hooks and rods and immersed in 100 mL of 0.5 M HCl solution (blank) and in 0.5 M HCl solution containing 1.0 g/L – 4.0 g/L *Eremomastax polysperma* leaf extract (inhibitor) in open beakers. In each experiment, one aluminium coupon per beaker was used. The beakers were then placed in a thermostatic water bath maintained at 30℃, 40℃, 50℃, and 60℃, respectively. The aluminium coupons were retrieved from the test solutions after four (4) hours and scrubbed with bristle brush under running water. They were dipped in acetone and air - dried before reweighing.
The corrosion rate was calculated using the equation [4]:

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

where A is the total surface area (cm^2), t is the exposure time (hours) while W is the weight loss (mg).

The inhibition efficiency of *Eremomastax polysperma* leaf extract was calculated using the formula [14]:

$$\mathrm{I}(\%) = \left(\frac{\mathrm{W}_0 - \mathrm{W}_1}{\mathrm{W}_0}\right) \times 100 \qquad (2)$$

where W_0 is the weight loss of aluminium coupon in HCl solution without inhibitor (blank) while W_1 is the weight loss of aluminium coupon in the presence of inhibitor.

2.4 Thermometric method

The instrumentation and method for the thermometric method used for this work have been described by other workers [15 – 16]. A 50 mL of 2 M HCl solution was transferred into the reaction vessel. The initial temperature of the solution was maintained at 30.0℃. The variation of temperature with time was recorded every 60 seconds for 120 minutes to the nearest ± 0.1℃ with a very sensitive thermometer.

The reaction number (RN) was calculated through the equation [16]:

$$RN\ (°C\ min^{-1}) = \frac{T_m - T_i}{t} \qquad (3)$$

where T_m is the maximum temperature, T_i is the initial temperature while 't' is the time (min) taken to reach the maximum temperature.

The inhibition efficiency, I(%) by the thermometric method was calculated using the formula [16]:

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

where RN_0 is the reaction number in the absence of inhibitor while RN_1 is the reaction number in the presence of inhibitor.

3. RESULTS AND DISCUSSION

3.1 Effect of *Eremomastax polysperma* Leaf Extract Concentration on Inhibition Efficiency

Fig. 1 illustrates the effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in 0.5 M HCl. The inhibition efficiency at a particular temperature increased with increase in extract concentration. The highest inhibition efficiency of 81.78% was obtained at 30℃ at 4.0 g/L *Eremomastax polysperma* leaf extract concentration. Fig. 2 depicts the thermometric results for aluminium corrosion in 2 M HCl solution in the absence (blank) and in the presence of *Eremomastax polysperma* leaf extract. It is seen that the extract concentration varied directly with the time taken to reach the maximum temperature and inversely with the maximum temperature. An increase in extract concentration resulted in an increase in the time needed to reach the maximum temperature and a decrease in the maximum temperature attained. The resultant effect was an increase in the inhibition efficiency with increase in *Eremomastax polysperma* leaf extract concentration (Table 1).This shows that an increase in the extract concentration led to an increase in the energy barrier of the reaction. At a particular temperature, the more effective the extract is, the higher the energy barrier; the higher the energy barrier, the slower (or more inhibited) the reaction. The weight loss and thermometric methods gave similar trend of inhibition efficiency.

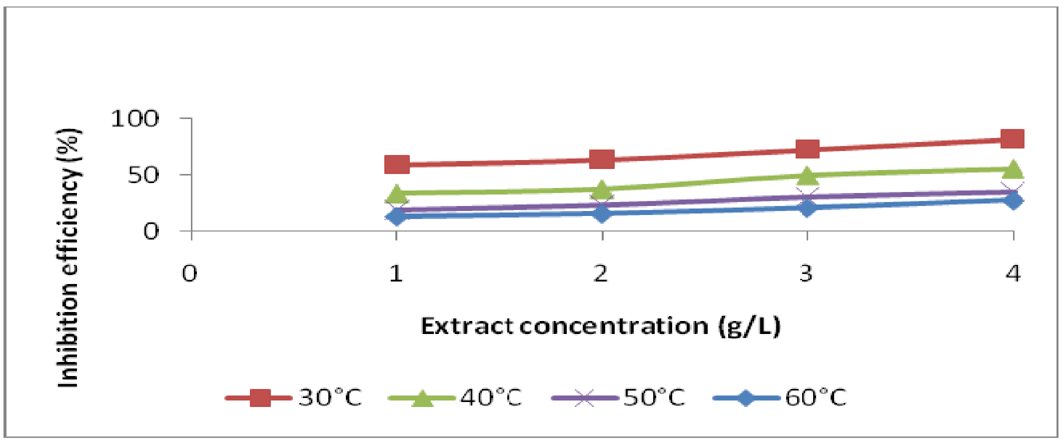

Fig.1. Variation of inhibition efficiency (%) with *Eremomastax polysperma* leaf extract (g/L) for aluminium corrosion in 0.5 M HCl

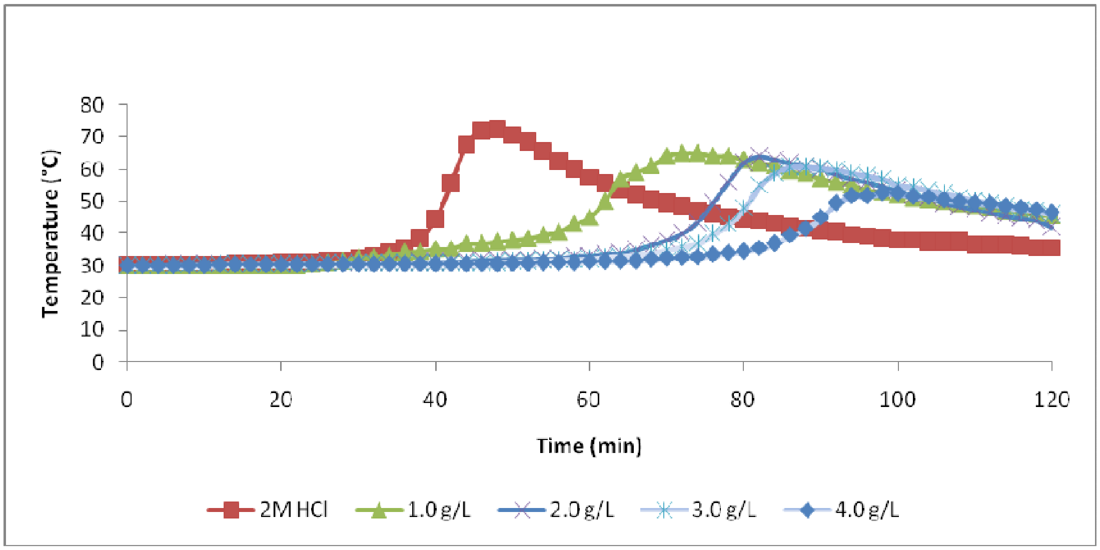

Fig. 2. Variation of temperature (°C) with time (min) for aluminium corrosion in 2 M HCl in absence and presence of *Eremomastax polysperma* leaf extract

Table 1. Thermometric measurements for aluminium corrosion in 2 M HCl solution in absence and presence of *Eremomastax polysperma* leaf extract

Extract concentration C (g L^{-1})	Initial temperature T_i (°C)	Maximum temperature T_m (°C)	Time taken to reach maximum temp. t (min)	Reaction number RN (°C min^{-1})	Inhibition efficiency I (%)
Blank	30.0	72.5	48	0.8854	-
1.0	30.0	65.0	72	0.4861	45.09
2.0	30.0	64.2	82	0.4171	52.89
3.0	30.0	61.0	88	0.3523	60.21
4.0	30.0	52.7	98	0.2316	73.84

3.3 Effect of temperature on inhibition efficiency

The effect of temperature on the inhibition effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in 0.5 M HCl solution is shown in Table 2. It is observed that an increase in temperature led to a decrease in the inhibition efficiency of the extract. This occurred because as the temperature increased, the reactant molecules acquired more energy and overcame the energy barrier more easily than at lower temperatures. Consequently, the reaction rate increased with increase in temperature, thereby giving lower inhibition efficiencies. A decrease in inhibition efficiency with increase in temperature indicates that *Eremomastax polysperma* leaf extract was more effective in inhibiting aluminium corrosion at lower temperatures than at higher temperatures. Furthermore, a decrease in inhibition efficiency with increase in temperature indicates a physical adsorption (physisorption) mechanism.

The values of the activation energy (E_a) for aluminium corrosion in 0.5 M HCl solution in the presence and absence of *Eremomastax polysperma* leaf extract, respectively, were obtained using the alternative formulation of Arrhenius equation [17]:

$$\ln \mathrm{CR} = \frac{-\mathrm{E_a}}{\mathrm{RT}} + \ln \mathrm{A} \quad (5)$$

where R is the universal gas constant, CR is the corrosion rate, T is the temperature in Kelvin while A is the pre-exponential factor.

Table 2. Weight loss data for aluminium corrosion in 0.5 M HCl solution in absence and presence of *Eremomastax polysperma* leaf extract at 30℃ – 60℃

Extract Conc.	Weight Loss (g)				Corrosion Rate (mg cm^{-2} hr^{-1})				Inhibition Efficiency (%)			
	30℃	40℃	50℃	60℃	30℃	40℃	50℃	60℃	30℃	40℃	50℃	60℃
Blank	0.0225	0.0442	0.0946	0.2428	0.1406	0.2763	0.5913	1.5175	-	-	-	-
1.0 g/L	0.0092	0.0294	0.0766	0.2103	0.0575	0.1838	0.4788	1.3144	59.11	33.48	19.03	13.39
2.0 g/L	0.0082	0.0277	0.0725	0.2043	0.0513	0.1731	0.4531	1.2769	63.56	37.33	23.36	15.86
3.0 g/L	0.0062	0.0222	0.0657	0.1922	0.0388	0.1388	0.4106	1.2013	72.44	49.77	30.55	20.84
4.0 g/L	0.0041	0.0196	0.0615	0.1760	0.0256	0.1225	0.3844	1.1000	81.78	55.66	34.99	27.51

The activation energies (E_a) of aluminium corrosion in 0.5 M HCl solution, with and without inhibitors, were obtained from the gradients of ln CR vs. 1/T plots (Figure 3) and the results presented in Table 3. Table 3 shows that the E_a values in the presence of the leaf extract were higher than the E_a value of the blank (65.65 kJ mol^{-1}). This indicates an increase in the energy barrier of the reaction in the presence of *Eremomastax polysperma* leaf extract compared to the blank. The corrosion of aluminium in HCl solution containing the leaf extract will therefore be slower than in its absence. When the E_a values in the extract - HCl medium is greater than the E_a value in the HCl solution, physical adsorption is implied. On the contrary, chemical adsorption is signified when the E_a value in the extract – HCl medium is less than that in HCl solution [18]. It can therefore be proposed that *Eremomastax polysperma* leaf extract physically adsorbed onto aluminium surface.

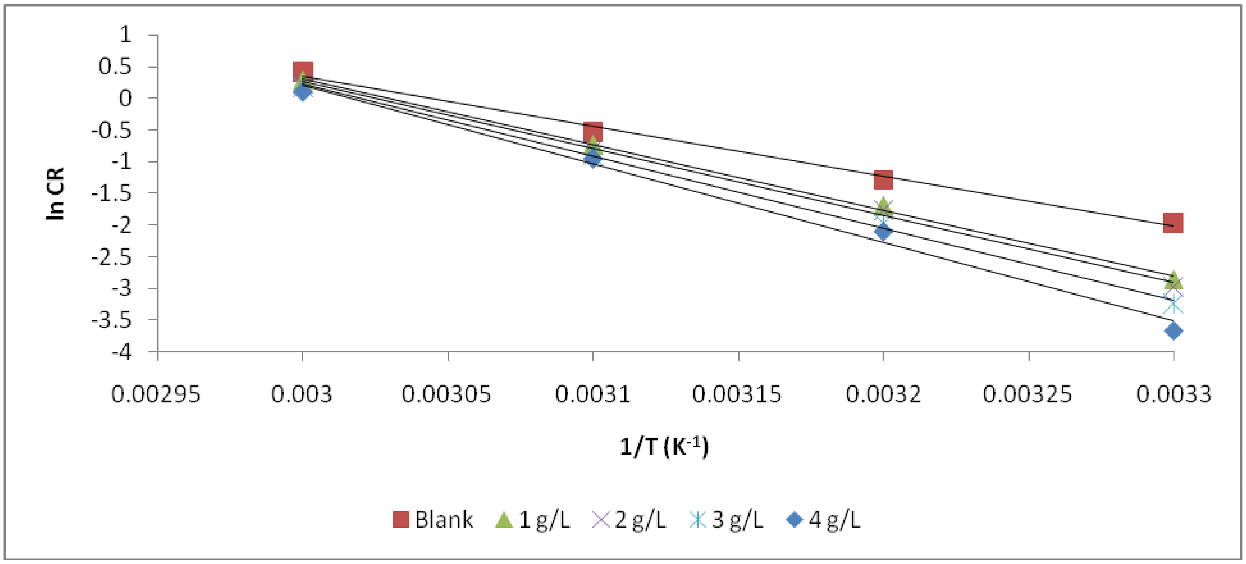

Fig. 3. Arrhenius plot for aluminium corrosion in 0.5 M HCl in the absence and presence of *Eremomastax polysperma* leaf extract

The values of enthalpy of activation (ΔH°_{ads}) and entropy of activation (ΔS°_{ads}) were obtained from an alternative formulation of the transition state equation [15]:

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\circ_{ads}}{R}\right] - \frac{\Delta H^\circ_{ads}}{RT} \qquad (6)$$

where T is the temperature in Kelvin, CR is the corrosion rate, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is the Planck's constant while N is the Avogadro's number.

The values of ΔH°_{ads} and ΔS°_{ads}, which were evaluated from the gradients and intercepts of ln (CR/T) against 1/T plots (Figure 4), respectively, are contained in Table 3. The positive values of ΔH°_{ads} both in the blank and in the presence of extracts indicate the endothermic nature of the aluminium corrosion process. Since in an endothermic reaction the molecules absorb heat from the surrounding, increasing the number of molecules (by increasing the extract concentration) led to an increase in the amount of heat absorbed. Hence, the observed increase in the value of ΔH°_{ads} with increase in extract concentration. The positive values of ΔS°_{ads} in the presence of the leaf extract indicate an increase in the disorderliness of the extract on aluminium surface. This accounts for the spread (adsorption) of the extract all over the metal surface. The increase in the value of ΔS°_{ads} with increase in extract concentration indicates an increase in the spread of adsorbate on aluminium surface, as extract concentration increased.

Table 3. Thermodynamic parameters for aluminium corrosion in 0.5 M HCl solution in the absence and presence of *Eremomastax polysperma* leaf extract

Extract concentration	E_a (kJ mol^{-1})	$\Delta H°_{ads}$ (kJ mol^{-1})	$\Delta S°_{ads}$ (J K^{-1} mol^{-1})
0.5 M HCl (Blank)	65.65	63.04	- 53.84
1.0 g/L	86.02	83.40	6.84
2.0 g/L	88.20	85.58	13.20
3.0 g/L	94.67	92.05	32.21
4.0 g/L	103.28	100.66	57.87

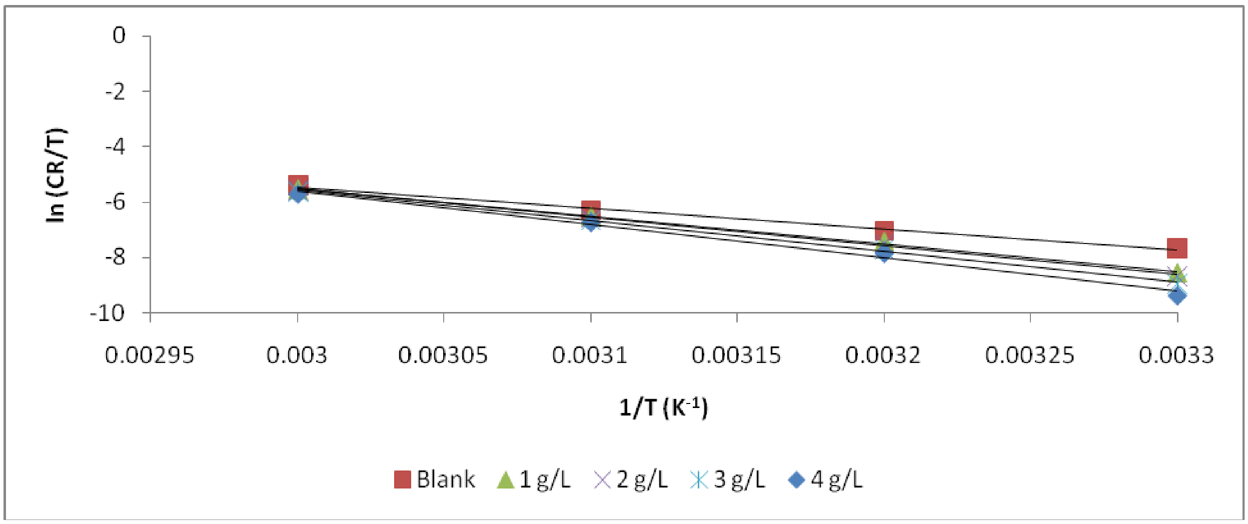

Fig. 4. Transition state plot for aluminium corrosion in 0.5 M HCl solution in the absence and presence of *Eremomastax polysperma* leaf extract

3.4 Adsorption Isotherm

After testing several adsorption isotherms, the best fit of the experimental data obtained for the adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface was found to obey the Langmuir adsorption isotherm [19]:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \qquad (7)$$

where θ is the degree of surface coverage, C is the inhibitor concentration while K_{ads} is the equilibrium constant of the adsorption process. Fig. 5 reveals linear plots of C/θ. vs. C, with gradients of 'n' and intercepts of $1/K_{ads}$. The linear plots have 'n' values (gradients) greater than 1, indicating that the extract occupied more than one adsorption site on the metal surface [17]. Furthermore, values of 'n' greater than 1 implies multi-layer coverage of the metal's surface by the extract. The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 4. The decrease in the values of K_{ads} with increase in temperature indicates that *Eremomastax polysperma* leaf extract became loosely adsorbed onto aluminium surface as the temperature was increased. This assertion is supported by an increase in the entropy of the system as temperature increased (Table 3).

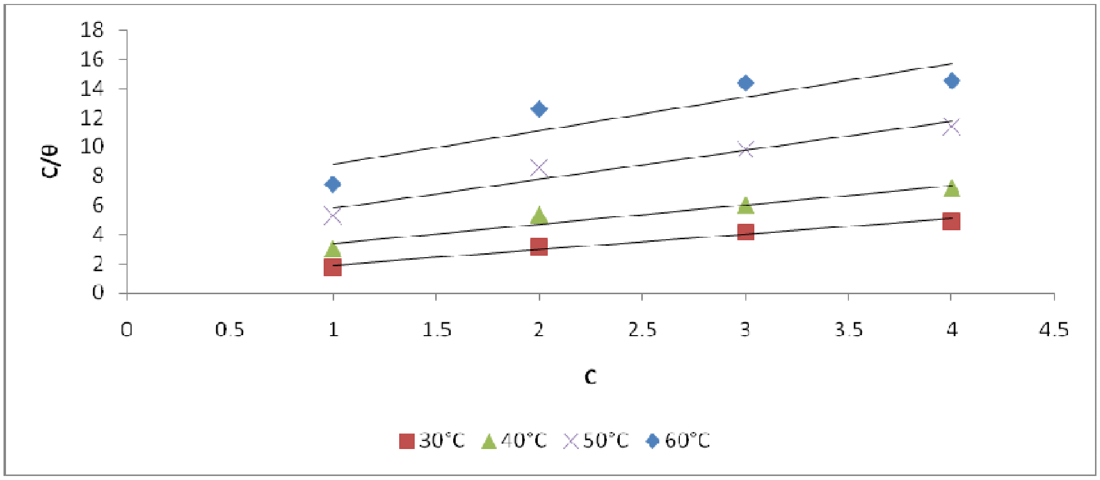

Fig. 5. Langmuir isotherm plot for aluminium corrosion in 0.5 M HCl solution containing *Eremomastax polysperma* leaf extract

The standard free energy of adsorption (ΔG°_{ads}) was calculated using the equation [20]:

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

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

The values of ΔG°_{ads}, which are negative (Table 4), reveal that the aluminium corrosion inhibition process by *Eremomastax polysperma* leaf extract occurred spontaneously. Generally, values of ΔG°_{ads} less negative than -20 kJ mol^{-1} are attributed to physical adsorption while values of ΔG°_{ads} more negative than -40 kJ mol^{-1} have been interpreted to signify chemical adsorption of inhibitor onto metal surface [21 – 22]. Physical adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface has been proposed since the values of ΔG°_{ads} obtained in this study are less negative than -20 kJ mol^{-1} in addition to a decrease in the inhibition efficiency with increase in temperature.

Table 4. Langmuir adsorption parameters for aluminium corrosion in 0.5 M HCl solution containing *Eremomastax polysperma* leaf extract at 303K – 333K

Temperature	R^2	n	$1/K_{ads}$ (g L^{-1})	K_{ads} (g^{-1}L)	$\Delta G°_{ads}$ (kJ mol^{-1})
303K	0.9779	1.06	0.82	1.22	- 10.62
313K	0.9355	1.33	2.07	0.48	- 8.54
323K	0.9511	1.98	3.82	0.26	- 7.17
333K	0.8054	2.30	6.50	0.15	- 5.87

4. CONCLUSION

Based on the results of this work, *Eremomastax polysperma* leaf extract could be a relatively good inhibitor of aluminium corrosion in HCl solution. The inhibition efficiency increased with increase in extract concentration and decrease in temperature. Physical adsorption process has been proposed for the adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface due to a decrease in the inhibition efficiency with increase in temperature, higher values of E_a in the extract-HCl medium relative to the blank in addition to $\Delta G°_{ads}$ values for the adsorption process which are less negative than -20 kJ mol^{-1}.The spontaneous nature of the adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface was revealed by the negative values of $\Delta G°_{ads}$ obtained. The positive values of $\Delta H°_{ads}$ indicates that the adsorption process was endothermic. The adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface fit the modified Langmuir isotherm.

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