

Phytochemical profile, Adsorptive and Inhibitive behaviour of *Costus afer* extracts on aluminium corrosion in hydrochloric acid.

[†]Ekemini B. Ituen and Uwemedimo E. Udo

Corrosion and Electrochemical Laboratory, Department of Chemistry, Faculty of Science, University of Uyo, PMB 1017, Uyo, Nigeria.

ABSTRACT

Phytochemical screening and aluminium corrosion inhibitive property of aqueous stem and leaf extracts of *Costus afer* in hydrochloric acid was investigated using weight loss and hydrogen evolution techniques. Results indicate that the stem extract (SE) contains alkaloids, flavonoids, phenols, tannins, anthraquinones, glycosides, and terpenoids whereas saponins, flavonoids, tannins, glycosides and phlobatannins were detected in the leaf extract (LE). Values of corrosion inhibition efficiency obtained from hydrogen evolution method ranged from 58.93 % to 49.43 % and 65.43 % to 51.28 % at 303K to 333K for LE and SE respectively. From weight loss measurements, the values ranged from 56.21 % to 46.71 % and 61.14 % to 50.19 % for LE and SE respectively at 303K – 333K. The extracts of *C. afer* inhibited the corrosion process via physical adsorption mechanism and the adsorption process was best approximated by the Freundlich adsorption model. Arrhenius and transition state plot afforded kinetic and thermodynamic parameters like activation energy, enthalpy change, entropy change and change in free energy of adsorption. The higher corrosion inhibition efficiency of the stem is rationalised in terms of its many phytoconstituents which are rich sources of some heteroatoms like oxygen and nitrogen, usually implicated in corrosion inhibition.

Keywords: *Costus afer* extract, corrosion inhibitor, adsorption, inhibition efficiency.

INTRODUCTION

A corrosion inhibitor, when added in a minute quantity, slows down the rate of corrosion of a metal or a metal alloy in the aggressive medium so embedded. Owing to their industrial importance, most corrosion inhibitors have been synthesized from cheap raw materials or chosen from compounds containing heteroatoms in their aromatic or long carbon chain [1, 2]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. A brief review on the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment has been reported elsewhere [3].

The plant *Costus afer* Ker (Zingiberaceae) is among the 150 species of stout, perennial and rhizomatous herbs of the genus *Costus*. It can be found in the forest belt of Senegal, South Africa, Guinea, Niger, Sierra Leone and Nigeria [4, 5]. *C. afer* is commonly called bush cane or by other names in the Nigerian languages viz: Ireke omode (Yoruba), Opete (Igbo), Mbriem (Efik/Ibibio). *Costus afer* contains several bioactive metabolites [6], hence its extensive use in folkloric medicine as remedy for cough, rheumatic pains, sleepiness and cardiotoxic [7, 8]. Tea

from the dried aerial parts is used for hypertension while the leaves are used as poultry feed additives to increase both the size and number of eggs of treated birds.

Studies on different parts of *C. Afer* reveals *invitro* and *invivo* pharmacological activities [9], essential oil [10], topical anti-inflammatory activity [11], phytochemical composition and antioxidant activities [12], antimicrobial activity [13] and phytochemical, proximate and mineral element composition [14]. A few chemical studies have shown that *C. afer* contains oxalic acid, lanosterol, trigogenin, new diosgenin, stigmasterol, Sitosterol, costugenin [15], a new steroidal saponin aferoside A [16]. The corrosion inhibition potentials of *Costus afer* on mild steel in H₂SO₄ medium have also been reported [17]. There is however no report on the adsorptive and inhibitive behaviours of *Costus afer* (bush cane) on aluminium in hydrochloric acid. In the present study, phytochemical screening of the extract has been carried and the inhibitive/adsorptive behaviors of the aqueous extracts investigated on aluminium in HCl.

MATERIALS AND METHOD:

Pure aluminium metal (purity 98.5%) of the type AA 1060 obtained from System Metals Industries, Calabar, Nigeria, was used for the investigation. Each sheet was about 0.26 mm in thickness and was mechanically press cut into 4 cm x 4 cm coupons. These coupons were used without further polishing. However, for surface treatment, they were degreased in absolute ethanol, rinsed in acetone, air-dried at room temperature and stored in a desiccator devoid of moisture before use in corrosion studies. All reagents used for the study were analar grade and double distilled water was used for their preparation.

2.2 Sample collection and extraction:

Fresh samples of *Costus afer* (bush cane) were collected from Ikot Ebido village in Uyo Local Government Area of Akwa Ibom State, Southern Nigeria. The plant parts (stem and leaves) were identified at Department of Botany and Ecological studies of the University of Uyo, Nigeria, where a voucher specimen was also deposited. These plant parts (100 g in each case) were cut into pieces and air-dried for 6 days, grounded and soaked in distilled water for 72 h. After 72 h, the mixture was filtered. The filtrates were further subjected to evaporation at 373 K in order to leave the sample free of the solvent. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, and 0.5 g of the extract in 1 L of 0.5 M HCl respectively.

2.3 Phytochemical screening:

Phytochemical screening was performed on the extracts using standard procedures to identify chemical constituents as described elsewhere [18 – 20].

2.4 Gasometric method:

Gasometric methods were carried out at 303 to 333 K as described in literature [21, 22]. From the volume of hydrogen evolved per minute, inhibition efficiency (% I), and degree of surface coverage (θ) were calculated using equations 1 and 2 respectively.

$$I \% = \left(1 - \frac{V_{Ht}^1}{V_{Ht}^0}\right) \times 100 \quad (1)$$

$$\theta = 1 - \frac{V_{Ht}^1}{V_{Ht}^0} \quad (2)$$

Where V_{Ht}^1 is the volume of hydrogen evolved at time t for inhibited solution and V_{Ht}^0 is the volume of hydrogen evolved at time t for uninhibited solution. The volume of hydrogen gas evolved per minute was recorded until there was no evolution of the gas.

2.5 Gravimetric method:

In the weight loss experiment, the pre-cleaned aluminium coupons were dipped in 200 ml of the respective inhibitor/blank solutions maintained at 303 to 333 K in a thermostated bath. The weight loss was determined by retrieving the coupons at 2 h interval progressively for 10 hr. Prior to measurement, each coupon was washed in 20 % NaOH solution (containing 100 g/l of zinc dust), rinsed in deionized water and dried in acetone.

The difference in weight was taken as the weight loss of aluminium. From the weight loss, the inhibition efficiency (% I) of the extract and the corrosion rate (CR) of aluminium were calculated using equations 3 and 4 respectively. The corrosion rate was calculated from the weight loss data using the relationship:

$$CR = (m_1 - m_2)/AT \quad (3)$$

$$\% I = 100 (CR_b - CR_i)/CR_b \quad (4)$$

Where CR ($\text{mgcm}^{-2}\text{h}^{-1}$) is the corrosion rate, m_1 and m_2 (g) are the weights before and after immersion respectively in the test solutions, A (cm^2) is the surface area of the coupons, T (s) is the immersion time, CR_b and CR_i are the corrosion rates in the absence and presence of the inhibitor respectively.

RESULTS AND DISCUSSION

3.1 Phytochemical screening:

Table 1: Phytochemical constituents of aqueous stem and leaf extracts of *C. afer*.

Phytochemical	Stem	Leaf
Alkaloids	+	-
Flavonoids	+	+
Saponins	-	+
Phenols	+	-
Tannins	+	+
Anthraquinones	+	-
Cardiac glycosides	+	+
Terpenoids	+	-
Phlobatannins	-	+

KEY: + indicates presence and - absence respectively.

Table 2: Corrosion rates, inhibition efficiencies and degrees of surface coverage for corrosion of aluminium in 0.5 M HCl in the absence and presence of different concentrations of *C. afer* leaf extract from weight loss measurement.

C(g/L)	Corrosion rate ($\text{mgcm}^{-2}\text{h}^{-1}$)				Inhibition efficiency (%)				Surface coverage			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	5.12	10.98	13.11	16.02	-	-	-	-	0.451	0.429	0.397	0.355
0.1	2.81	6.27	7.90	10.34	45.13	42.86	39.72	35.45	0.492	0.452	0.417	0.391
0.2	2.60	6.01	7.65	9.75	49.15	45.24	41.65	39.14	0.562	0.540	0.491	0.467
0.5	2.24	5.04	6.67	8.54	56.21	54.03	49.12	46.71				

Table 3: Corrosion rates, inhibition efficiencies and degrees of surface coverage for corrosion of aluminium in 0.5 M HCl in the absence and presence of different concentrations of *C. afer* stem extract from weight loss measurement.

C(g/L)	Corrosion rate ($\text{mgcm}^{-2}\text{h}^{-1}$)				Inhibition efficiency (%)				Surface coverage			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	5.12	10.98	13.11	16.02	-	-	-	-	0.498	0.468	0.425	0.398
0.1	2.57	5.84	7.53	9.64	49.82	46.82	42.54	39.82	0.534	0.504	0.467	0.430
0.2	2.39	5.44	6.99	9.34	53.38	50.44	46.70	42.96	0.611	0.587	0.531	0.502
0.5	1.99	4.53	6.15	7.98	61.14	58.72	53.08	50.19				

Table 4: Corrosion rates, inhibition efficiencies and degrees of surface coverage for corrosion of aluminium in 0.5 M HCl in the absence and presence of different concentrations of *C. afer* leaf extracts from hydrogen evolution measurement.

C(g/L)	Corrosion rate ($\text{mgcm}^{-2}\text{h}^{-1}$)				Inhibition efficiency (%)				Surface coverage			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	5.11	10.96	13.13	16.08	-	-	-	-	0.474	0.435	0.411	0.384
0.1	2.69	6.21	7.72	9.87	47.42	43.46	41.11	38.42	0.514	0.473	0.427	0.400
0.2	2.49	5.79	7.51	9.61	51.37	47.25	42.73	40.01	0.589	0.561	0.526	0.494
0.5	2.10	4.83	6.21	8.10	58.93	56.05	52.61	49.43				

Table 5: Corrosion rates, inhibition efficiencies and degrees of surface coverage for corrosion of aluminium in 0.5 M HCl in the absence and presence of different concentrations of *C. afer* stem extracts from hydrogen evolution measurement.

C(g/L)	Corrosion rate (mgcm ⁻² h ⁻¹)				Inhibition efficiency (%)				Surface coverage			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	5.11	10.96	13.13	16.08	-	-	-	-	0.505	0.482	0.442	0.409
0.1	2.54	5.69	7.32	9.47	50.48	48.15	44.15	40.86	0.544	0.515	0.484	0.442
0.2	2.34	5.32	6.76	8.95	54.38	51.53	48.42	44.16	0.654	0.611	0.560	0.513
0.5	1.77	4.38	5.78	7.80	65.43	61.14	55.99	51.28				

Table 6: Adsorption parameters deduced from Freundlich adsorption isotherm for corrosion of aluminium in 0.5 M HCl in the presence of different concentrations of *C. afer* leaf and stem extracts.

Temp (K)	Weight loss				Hydrogen evolution			
	LE		SE		LE		SE	
	K _{ads}	ΔG _{ads}	K _{ads}	ΔG _{ads}	K _{ads}	ΔG _{ads}	K _{ads}	ΔG _{ads}
303	0.400	-17.77	0.445	-18.39	0.422	-18.08	0.436	-18.27
313	0.374	-17.96	0.412	-18.53	0.377	-18.01	0.426	-18.73
323	0.351	-18.15	0.379	-18.62	0.354	-18.20	0.398	-18.78
333	0.305	-17.85	0.351	-18.71	0.373	-19.09	0.362	-18.91

Table 7: Activation parameters deduced from Arrhenius and transition state plots for corrosion of aluminium in 0.5 M HCl in the presence of different concentrations of *C. afer* leaf and stem extracts.

System	Weight loss						Hydrogen evolution					
	LE			SE			LE			SE		
	E _a	ΔH	ΔS	E _a	ΔH	ΔS	E _a	ΔH	ΔS	E _a	ΔH	ΔS
Blank	2.93	2.70	-290.2	2.93	2.70	-290.2	2.94	2.70	-290.2	2.94	2.94	-290.2
0.1 g/L	3.37	3.16	-295.8	3.44	3.24	-296.5	3.37	3.14	-296.0	3.48	3.24	-296.7
0.2 g/L	3.48	3.27	-296.5	3.54	3.41	-297.3	3.71	3.41	-296.9	3.49	3.27	-297.4
0.5 g/L	3.52	2.29	-297.8	3.65	3.45	-298.4	3.56	3.45	-298.4	2.86	3.64	-299.9

3.2 Corrosion rate and inhibition efficiency:

The values of corrosion rate and percentage inhibition efficiency computed from both weight loss data and volume of hydrogen gas evolved for the different concentrations of the *C. afer* extracts at 303 – 333 K are presented in Tables 2-5, and the variation of inhibition efficiency with concentrations is displayed in Figure 1. Inspection of the data in the table reveals that the addition of *C. afer* decreased the corrosion rate of aluminium indicating the inhibitive effect of the added extract on aluminium corrosion in the acid medium.

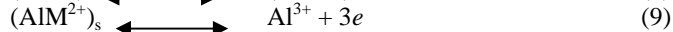
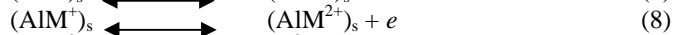
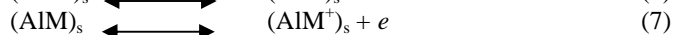
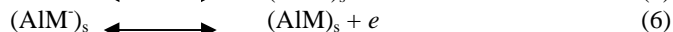
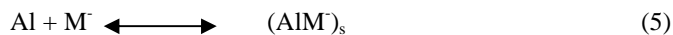
It is observable from Fig. 1 that the inhibition efficiency is dependent on the concentration of the added extract - increasing as the extract concentration increases. This observed inhibitive action of the *C. afer* extract could be attributed to the adsorption of its components on aluminium surface leading to the formation of a layer of adsorbed molecules with the potentiality of “blanketing” or isolating the metal surface from the aggressive acid solution and hence resulting in corrosion rate lowering. The corrosion rates and inhibition efficiencies obtained for the weight loss measurements were comparable with those obtained using hydrogen evolution method.

The chemical components of the extract of *C. afer* (table 1) are identified from our phytochemical screening to be made up of flavonoids, tannins, anthraquinones, and cardiac glycosides; the stem is exclusively rich in alkaloids, terpenoids and phenols which may be responsible for the higher inhibition efficiency of the stem extracts compared to the leaves extracts (solely rich in saponins and phlobatannins) which means that they contains more heteroatoms like oxygen and nitrogen in its molecules. Therefore the corrosion inhibition of aluminium may be attributed to adsorption of these components through these atoms, being potential centers of adsorption onto the metal surface. Assignment of inhibitive effect to a particular component is difficult at this stage because of the complex chemical composition of the extract although further investigation using surface analytical techniques will enable the characterization of the active materials in the adsorbed layer, thus assisting in identifying the most active ingredients in the adsorbed layer.

3.3 Mechanism of adsorption

Various mechanisms have been proposed for inhibition of metal corrosion in several aggressive acidic media. The mechanism reported earlier reported [23] is suitable for describing the adsorption of extracts of *C. afer* onto the surface of aluminium. Assuming a molecule or ion, M⁺, is adsorbed onto a solid metal surface, Al, the anodic

process results in the formation of a surface complex which subsequently desorbs from the same surface according to equations 5-9.



where 's' symbolizes a species at the surface. The inhibition of the aluminium corrosion in the aggressive medium is dependent on the relative stability of the adsorbed molecule or ion on the surface complex. Adsorption of components of *C. afer* extract or its phytochemicals therefore is assumed to result in the formation of a surface complex that blankets the surface of aluminium from the acid environment leading to inhibition of the corrosion process. In properly describing the mechanism of adsorption and nature of the surface complex formed, data obtained for degree of surface coverage (θ) were fitted into adsorption models proposed by Temkin, Langmuir, Freundlich, Florry-Huggins, Frumkin and El-Awady *et al*. All these isotherms can be represented as follows:

$$f(\theta, x) \exp(-2a\theta) = KC \quad (10)$$

where $f(\theta, x)$ represents the configuration factor which is dependent on the physical model and assumptions underlying the derivation of the isotherm, x is the size ration, ' a ' is the lateral molecular interaction parameter and K is the equilibrium constant of adsorption [24]. The correlation coefficients obtained ($0.930 \leq R^2 \leq 0.999$) indicate that the adsorption of extracts of *C. afer* onto the aluminium surface was best described by Freundlich adsorption isotherm (figures 2-5).

According to this model,

$$\theta = KC^n \quad (11)$$

$$\log \theta = n \log C + \ln K \quad (12)$$

where K is the adsorption-desorption equilibrium constant denoting the strength of interaction in the adsorbed layer and ' n ' is a constant such that $0 \leq n \leq 1$. Positive and large values of K obtained (table 6) suggest significantly strong interaction between the adsorbed components of the extracts and is independent of all factors except temperature. It is seen that K decreases with temperature, implying decrease in adsorption strength of these components with increase in temperature. The free energy change of adsorption (ΔG_{ads}) is directly related to K at a given temperature (T) as shown in equation 13 and was used to calculate ΔG_{ads} for *C. afer* extracts;

$$G_{\text{ads}} = -RT \ln(55.5K) \quad (13)$$

Negative values were obtained for ΔG_{ads} from both weight loss and hydrogen evolution measurements (table 6). It has been established that values of ΔG_{ads} of about -20 kJ/mol are characteristic of physical adsorption mechanism, while those more negative than -40 kJ/mol are consistent with chemical adsorption [25]. Physical adsorption (physisorption) is associated with intermolecular forces causing preferential binding of certain components of the extracts onto the adsorbent which is reversible on addition of heat while chemical adsorption involves chemical bond formation (coordinate covalent in nature) usually with release of large amount of heat [26]. Energetically, negative ΔG_{ads} obtained is consistent with the spontaneous nature of all adsorption processes. It is also observed that the strength of adsorption is larger for the stem extracts than leaf extracts. Consequently, adsorption of the phytochemicals of the stem extracts is more spontaneous than that of the leaf extracts and these observations are in good agreement for both the weight loss and hydrogen evolution measurements.

3.4 Kinetic/thermodynamic characterization:

The effect of temperature on the inhibition efficiency and adsorption behaviour of *C. afer* extracts was also investigated using weight loss and hydrogen evolution methods. The percentage inhibition efficiency decreased with increase in temperature for all the concentrations of the extracts studied. This trend signifies possible shift in adsorption-desorption equilibrium towards the desorption process as temperature increases [27], which is also in agreement with Le' Chatellier's principle which describes shifts in equilibrium position to annul the effects of changes in equilibrium conditions.

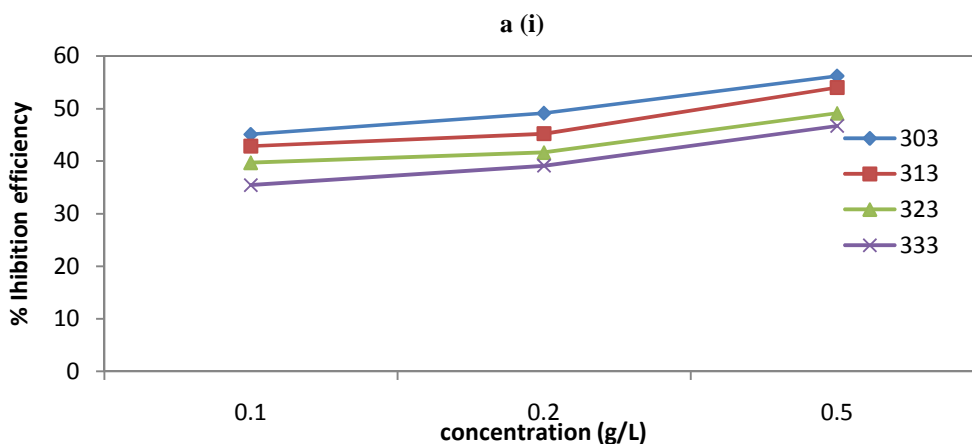
Arrhenius equation provides a relationship (equation 14) with which the experimental rate of corrosion of the aluminium in the acid medium (CR) was correlated with the respective system temperatures studied (T) from where activation energy (E_a), a quantity characteristic of the corrosion reaction with the dimensions of energy, was computed from a plot of $\log CR$ against $1/T$ both in the absence and presence of the *C. afer* extracts (figures 6-9).

In accordance with the concept of activation, the acid molecules must acquire sufficient energy in order to pass over an activation energy barrier to attack and dissolve the aluminium in the aqueous medium. The E_a values obtained for the inhibited solutions are larger than that of the free acid solution. This implies that the acid molecules must pass over a higher energy barrier in the presence of the *C. afer* extracts in order to corrode the metals. In other words, acid molecules unable to acquire these higher energies become deactivated and unable to collide with the metal surface (or the metal activity in the electrochemical reaction is retarded) and cause dissolution, hence inhibition (protection) of the metal surface with the extent of such protection being concentration dependent. Also, increase in E_a on addition of the inhibitor is usually correlated with electrostatic interactions which support the physical adsorption mechanism earlier proposed [25]. The E_a values obtained for weight loss and gasometric measurements were also in good agreement.

A classical thermodynamic model called the transition state equation (equation 14) was used to gain further insight on the enthalpy change (ΔH) and entropy change (ΔS) of activation (table 7) for the formation of the activation complex in the transition state;

$$CR = (RT/Nh) \exp (\Delta S/R) \exp (\Delta H/RT) \quad (14)$$

Where CR is the corrosion rate, h is Plank's constant, N is Avogadro's number, R is the universal gas constant and T is the absolute temperature. Straight lines as shown in figures 10-13, were obtained from plot of $\log CR$ against $1/T$ with slopes equal to $(\Delta H/2.303R)$ and intercept equal to $[\log(R/Nh) + (\Delta S/2.303R)]$. Inspection of the data reveals that ΔH values for the dissolution of aluminium are higher in the presence than in the absence of the extract, implying that the physical adsorption mechanism is involved. The positive values of ΔH indicate the endothermic nature of the process. Negative ΔS values indicate decrease in entropy and consequently increased orderliness in the system probably brought about by reduction of the number of molecules of the active constituents of the extracts in the bulk solution due to adsorption. The decrease in disorderliness is concentration dependent and in favour of higher inhibitor concentrations.



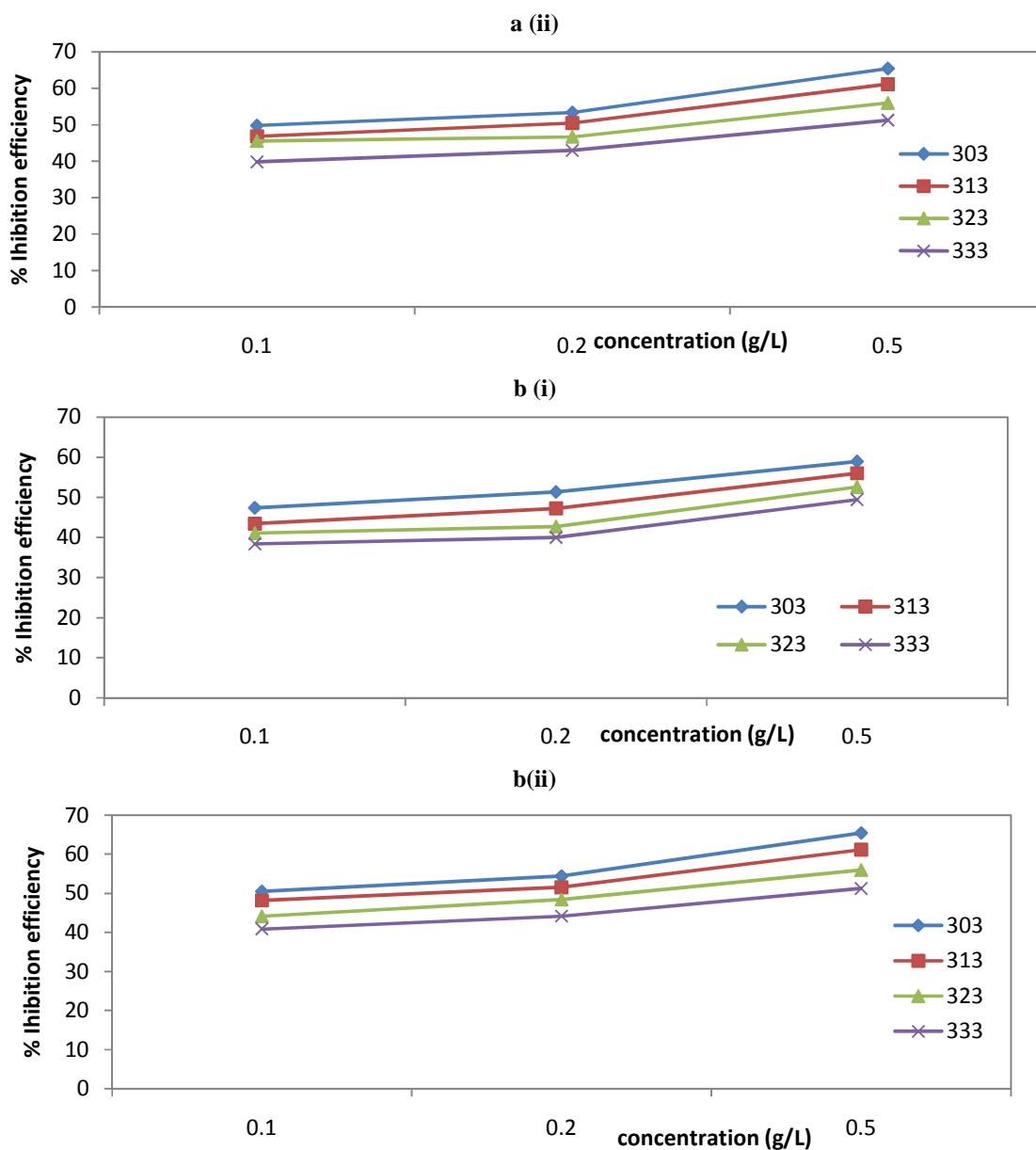


Figure 1: Plots of inhibition efficiency against concentration for (a) leaf extracts and (b) Stem extracts of *C. afer* using (i) weight loss and (ii) hydrogen evolution techniques at 303-333 K.

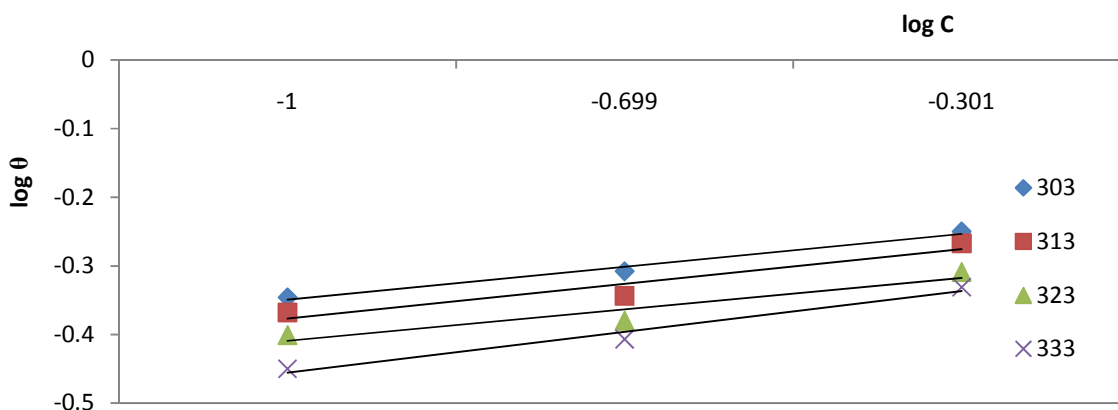


Fig. 2: Freundlich adsorption isotherm for the inhibition of aluminium corrosion in 0.5 M HCl by extract Leaf extracts of *C. afer* using weight loss technique.

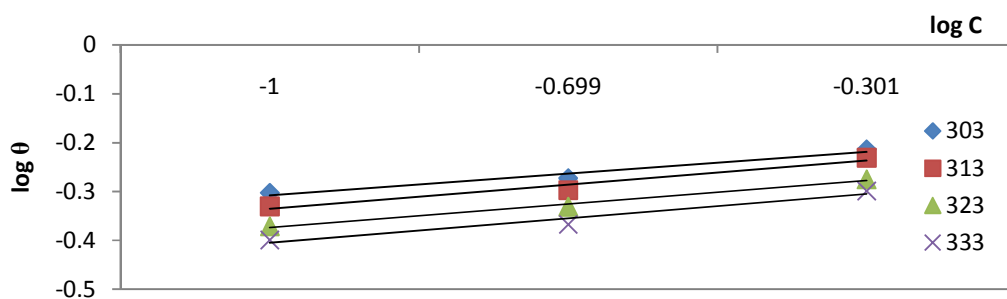


Fig. 3: Freundlich adsorption isotherm for the inhibition of aluminium corrosion in 0.5 M HCl by extract Stem extracts of *C. afer* using weight loss technique.

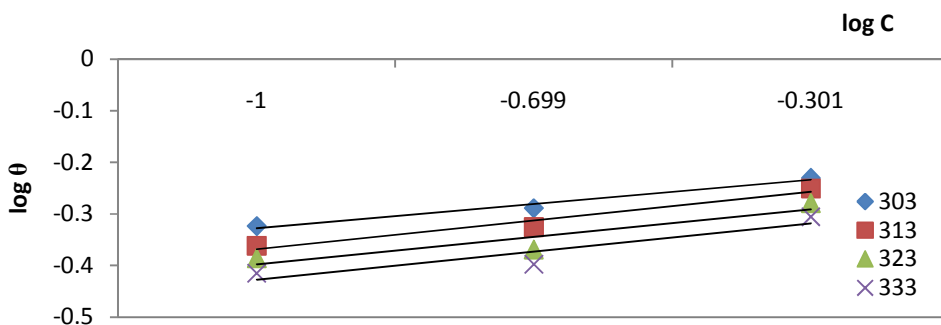


Fig. 4: Freundlich adsorption isotherm for the inhibition of aluminium corrosion in 0.5 M HCl by extract Leaf extracts of *C. afer* using hydrogen evolution technique.

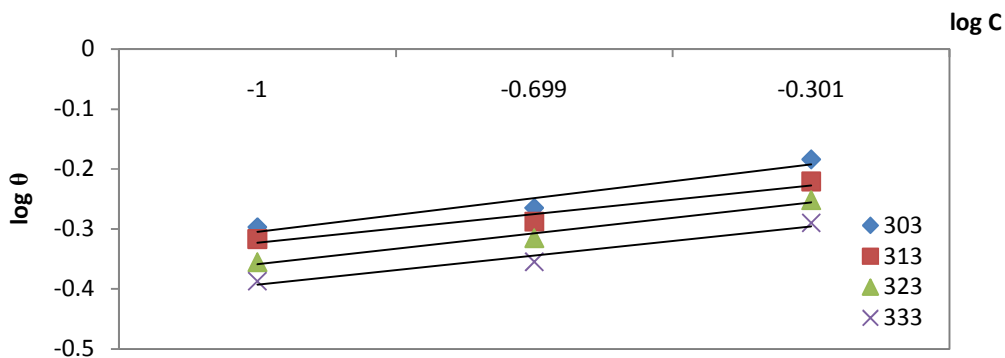


Fig. 5: Freundlich adsorption isotherm for the inhibition of aluminium corrosion in 0.5 M HCl by extract Stem extracts of *C. afer* using hydrogen evolution technique.

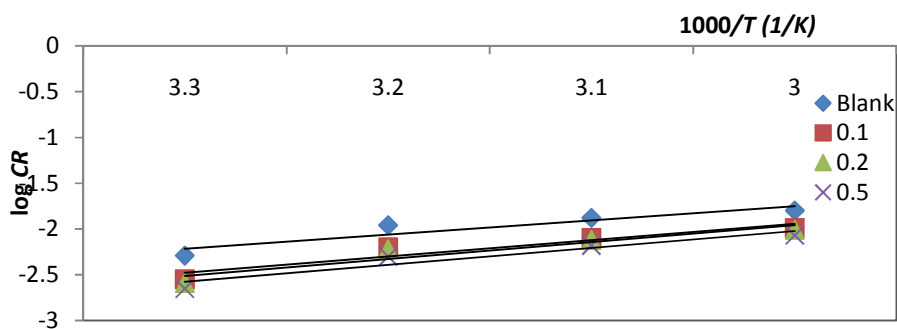


Fig. 6: Arrhenius plot for the inhibition of aluminium corrosion in 0.5 M HCl by leaf extract of *C. afer* using weight loss technique.

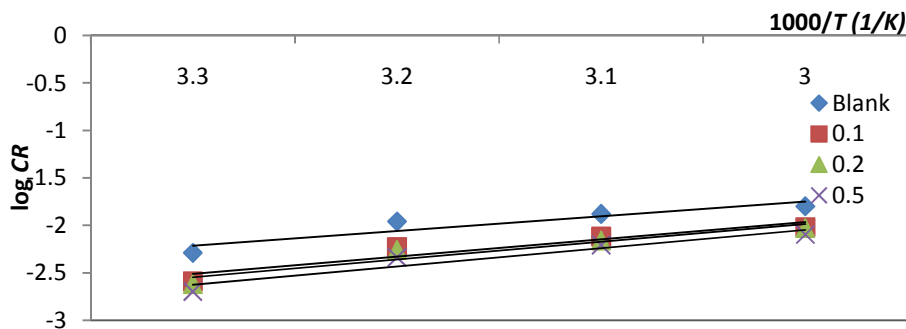


Fig. 7: Arrhenius plot for the inhibition of aluminium corrosion in 0.5 M HCl by stem extract of *C. afer* using weight loss technique.

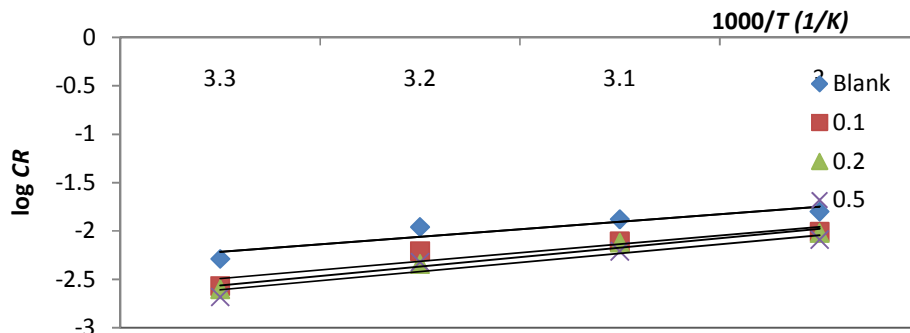


Fig. 8: Arrhenius plot for the inhibition of aluminium corrosion in 0.5 M HCl by leaf extract of *C. afer* using hydrogen evolution technique.

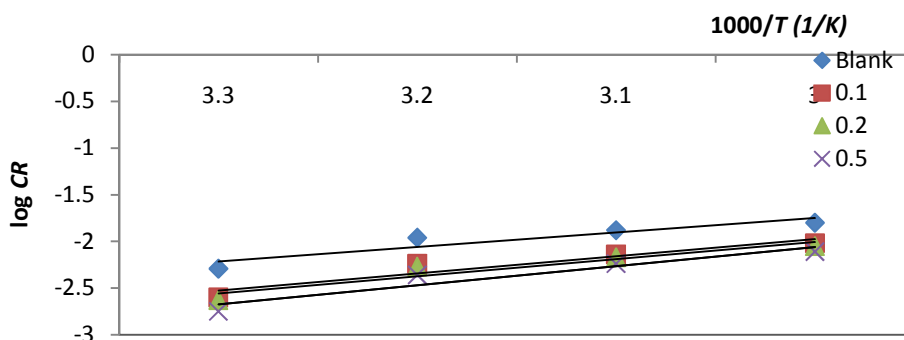


Fig. 9: Arrhenius plot for the inhibition of aluminium corrosion in 0.5 M HCl by stem extract of *C. afer* using hydrogen evolution technique.

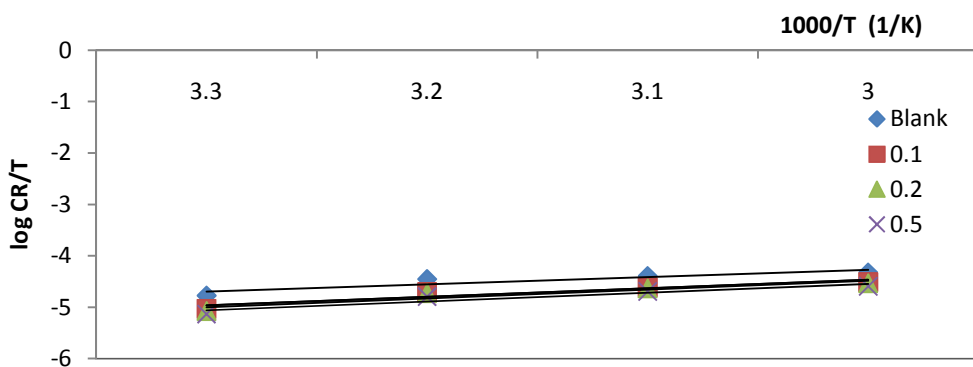


Fig. 10: Transition state plot for the inhibition of aluminium corrosion in 0.5 M HCl by leaf extract of *C. afer* using weight loss technique.

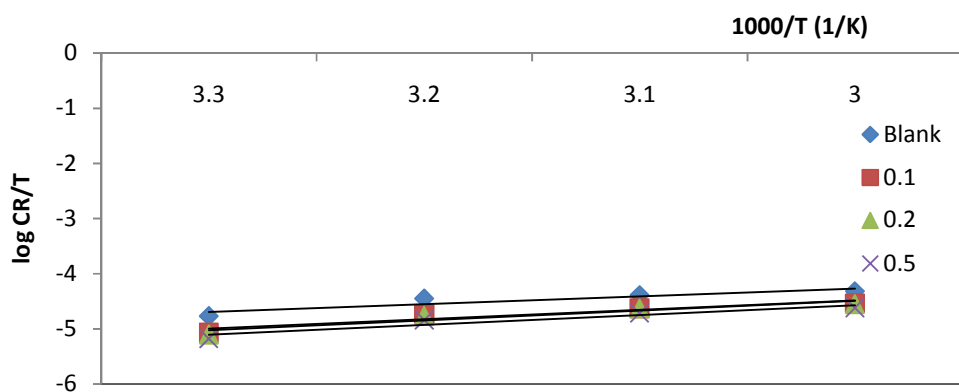


Fig. 11: Transition state plot for the inhibition of aluminium corrosion in 0.5 M HCl by stem extract of *C. afer* using weight loss technique.

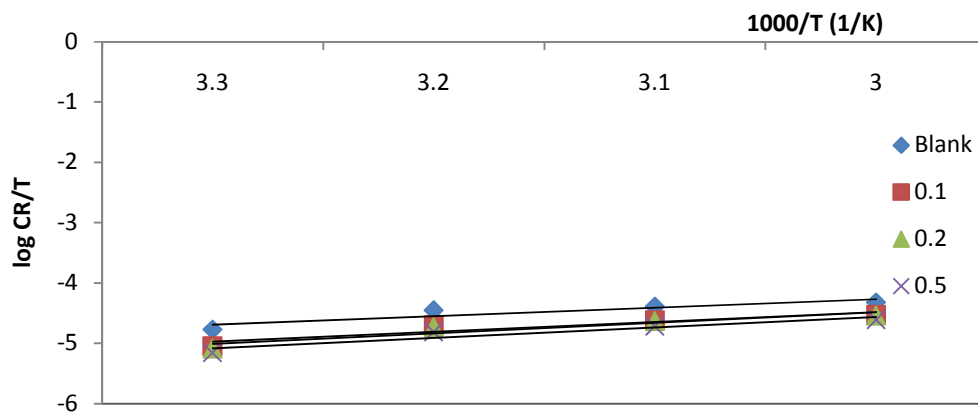


Fig. 12: Transition state plot for the inhibition of aluminium corrosion in 0.5 M HCl by leaf extract of *C. afer* using hydrogen evolution technique.

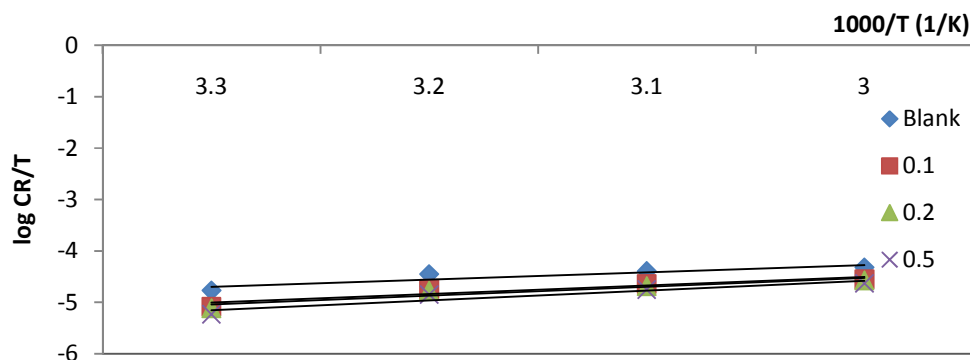


Fig.13: Transition state plot for the inhibition of aluminium corrosion in 0.5 M HCl by stem extract of *C. afer* using hydrogen evolution technique.

CONCLUSION

On the basis of this study, the following conclusions could be drawn.

1. The extracts of *C. afer* act as effective and efficient inhibitor against aluminium corrosion in the acid medium at all temperatures studied, with greatest efficiency at 303K.
2. The stem extract yielded better protection of the aluminium corrosion than the leaf extract due to large differences in their phytochemical composition.
3. Corrosion rate increases with increase in temperature both in the absence and presence of the extracts but significantly decreased further in the presence of the extracts.
4. The corrosion inhibition is probably due to the adsorption of the extracts on to the aluminium surface and thus blocking the corrosion active sites of the aluminium by the physical adsorption mechanism.
5. The inhibition of aluminium corrosion by *C. afer* extracts obeys Freundlich adsorption model at all the concentrations and temperatures studied.
6. There was orderliness in the system as adsorption progressed judged from the very low entropy values obtained.
7. The adsorption process is endothermic and spontaneous as inferred from positive values of enthalpy and negative values of free energy of adsorption.

REFERENCES

- [1] M. Abdallah. *Portugaliae Electrochimica. Acta*, **2004**, 22: 161-175.
- [2] E. H. El Ashry, A. El Nemir, S. A. Esawy, S. Ragab. *Electrochimica Acta*, **2006**, 51:3957 – 3968.
- [3] E. E. Ebenso, N. O. Eddy, A. O. Odiongenyi. *African Journal of pure and Applied Chemistry* **2008**, 2(11): 107-115.
- [4] H. M. Burkill. The useful plants of West Tropical Africa: Rev Dalziel's J.M. Royal Botanical Gardens Kew. 2nd ed. Families A-D., **1985**, 1:135-191.
- [5] H. O. Edeoga, B. E. Okoli. *Folia Geobotanica*, **2000**, 35: 315-318.
- [6] P. M. Stentoft. Flowering plants in West Africa. Cambridge University Press: London. **1988**. 130-131.
- [7] M. M. Iwu. *Planta Medica.*, **1981**, 44:413-415.
- [8] R. C. Agoha. Medicinal plants of Nigeria. Offsetdukkerij Facuteit der Wiskunde en Naturwetenschaapen Nijmegen. The Netherlands. **1974**. 53-54.
- [9] A. O. Anaga , C. J. Njoku , E. S. Ekejiuba , M. N. Esiaka , I. U. Asuzu . *Phytomedicine*, **2004**.11(2-3):242-8.
- [10] A. O. Taiwo, A. A. Bolanle. *Flavour and Fragrance Journal*, **2003**.18 (4), 309–311.
- [11] J. O. Moody, K. E. Okwabe. *Nigerian Journal of Natural Products Medicine*, **2003**, 7:46-48.
- [12] G. N. Anyasor, K. O. Ogunwenmo, O. A. Oyelana, B. E. Akpofunure. *African Journal of Biotechnology*, **2010**, 9 (31), 4880-4884.
- [13] M. M. Akpan, C. S. Odeomena, Nwachukwu, C. N., B. Danladi. *Asian journal of plant science and research*, **2012**, (2): 335-341.
- [14] U. D. Akpabio, U. E. Udo, A. E. Akpakpan. *Asian journal of plant science and research*, **2012**, 2 (5): 607-612.
- [15] R. Lin ,M. Lacaille-Dubois , B. Hanquet , M. Correia , B. Chauffert. *Journal of Natural Products*, **1997**, 60 (11):1165–1169.
- [16] L. Rui-Chao, B. Hanquet, M. Lacaille-Dubois. *Phytochemistry* , **1996**, 43(3): 665–668.

- [17] Eddy, N. O., Odoemelam, S. A., Ibiam. *Journal of surface science and technology*, **2009**, 25(3-4):1-14.
- [18] G. E. Trease, Evans, W. C. *pharmacognosy: a physician's guide to herbal medicine*, 13th edition. Bailliere Tindall London, **1989**, 176-180.
- [19] J. B. Harborne. *Phytochemical methods: a guide to modern techniques of plant analysis*. Chapman and Hill, London, **1973**, 182-201.
- [20] A. Sofowora. *Medicinal plants and traditional medicine in Africa*. Spectrum books Ltd. Ibadan, Nigerian, **1993**, 289.
- [21] E. E. Oguzie. *Pigment & Resin Technology*, **2006**, 35: 334-340.
- [22] S. A. Umoren, E. E. Ebenso, P. C. Okafor, U. J. Ekpe, O. Ogbobe. *Journal of Applied Polymer Science*, **2007**, 103: 2810-2816.
- [23] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, M. Saadawy. *Corrosion Science*, **2009**, 51(5):1038–1042.
- [24] N. O. Eddy, S. A. Odoemelam, A. O. Odiongenyi. *Green Chemistry Letters and Review*, **2009**, 2:111–119
- [25] E. E. Ebenso. *Material Chemistry & Physics*, **2003**, 79:58-70.
- [26] E. B. Uravov, D. R. Chapman, I. Alan. *Penguin dictionary of science*, Penguin books, **1971**, 25-87.
- [27] I.B. Obot and N.O. Obi-Egbedi, *Corrosion Science*, **2010**, **52**: 282.