DOI: http://dx.doi.org/10.4314/gjpas.v19i1.4

GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 19, 2013: 23-31

 ISSN 1118-0579
www.globaljournalseries.com, Email: info@globaljournalseries.com

COMPARATIVE STUDY OF THE INHIBITION EFFECTS OF ALKALOID AND NON ALKALOID FRACTIONS OF THE ETHANOLIC EXTRACTS OF *COSTUS AFER* STEM ON THE CORROSION OF MILD STEEL IN 5 M HCl SOLUTION

I. E. UWAH, A. I. IKEUBA, B. U. UGI AND V. M. UDOWO

(Received 20 February 2013; Revision Accepted 25 March 2013)

ABSTRACT

The Alkaloid and Non- alkaloid fractions of the ethanolic extracts from Costus afer (AECA and NAECA) were comparatively studied for their inhibitive properties on the corrosion of mild steel in 5 M HCl solution using Gravimetric and Gasometric techniques. The results revealed that both extracts inhibited the corrosion of mild steel in HCl solution following the order: NAECA > AECA. The maximum inhibition efficiencies obtained were 49.2 % for AECA and 86.4% for NAECA at an inhibitor concentration of 5 g/L. Inhibition efficiency was found to increase with increase in concentration and increase in temperature. The adsorption of both extracts on the mild steel was found to be consistent with Langmuir adsorption isotherm.Physical adsorption mechanism was proposed for the adsorption of the components of the extracts on the mild steel surface.

KEYWORDS: Adsorption; Alkaloid; Corrosion inhibition; Non-alkaloid; Mild steel.

INTRODUCTION

Recent industrial history shows many failures due to the use of metallic mild steel structures which are in contact with aqueous media. This is a direct consequence of corrosion which causes great losses to the metallurgical industry. This however has serious safety and economic implications (El Etre , 2008). In the recent years, there has been an increasing awareness of the environment and green chemistry. Therefore, many works were conducted to use the environment friendly substances, as corrosion inhibitors in place of the harmful synthetic chemicals. Plant extracts are usually cheap, readily available and could be obtained by simple extraction process. (El Etre , 2008; Okafor *et al*., 2007). Phytochemicals in plant extracts have in recent times formed a major part of scientific research aimed at minimizing the problem of corrosion as widely reported by several authors (Okafor *et al*. 2008; 2010; 2011 and Uwah *et al* .2010) .

Costus afer is a member of the family Costaceae and a specie of the genus Costus. It is known by the common name Bush cane or Ginger lily. The plant is mostly found in swampy areas. The succulent part of the stem is edible while leaves are used to feed animals. *Costus afer* stem has been remedies of many diseases. This present work is aimed at investigating the effect of different concentrations of alkaloid extracts and non-alkaloid fractions of ethanolic extracts of *Costus afer* stem on the corrosion of mild steel in HCl solution using gravimetric and gasometric techniques. Alkaloids are a group of naturally occurring chemical compounds with basic nitrogen atoms. They are weak bases but some are amphoteric (Acamovic, et al., 2012)

Preparation of Alkaloid And Non-Alkaloid Plant Extracts

The stem of *Costus afer* used was obtained from a bush in Calabar. These were cut into smaller pieces and dried in an oven at 50° C. The dried chips were ground into powdery form. 100 g of the powder was extracted with 250 cm^3 of absolute ethanol in a Soxhlet extactor for 24 hours and the ethanol evaporated using a water bath.

10 g of the ethanol extract was partitioned between 100 cm^3 of chloroform and 100 cm^3 of 0.1 M HCl solution using a separating funnel. The tailing fraction was used as the non-alkaloid extract. The float fraction from the separating funnel was further basified using 100 cm^3 of ammonia and partitioned using 100 cm^3 of chloroform. The float was taken as the alkaloid extract. 5 g of the alkaloid and non-alkaloid extracts were soaked in 0.5 L of 5.0 M HCl solution and kept for 24 hours. The solutions thus obtained were filtered and stored. From the stock solutions of 10 g/L concentration, inhibitor test solutions of concentration: 0.5, 1.0, 2.0, 3.0 and 5.0 g/L were prepared. The prepared solutions were

I. E. Uwah, Corrosion and Electrochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, P. M. B. 1115, Calabar, Nigeria.
A. I. Ikeuba, Corrosion and Electrochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, P. M. B. 1115, Calabar, Nigeria.
B. U. Ugi, Corrosion and Electrochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, P. M. B. 1115, Calabar, Nigeria.
V. M. Udowo, Corrosion and Electrochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, P. M. B. 1115, Calabar, Nigeria.

then used to study the corrosion inhibition abilities of the extracts. This procedure is as described by Ikeuba *et al.,* 2012.

Treatment of Mild Steel Coupons

The sheet of mild steel used for this work was obtained from a mechanical workshop in Calabar. The gravimetric and volumetric analyses were conducted with mild steel coupons of dimension 5.00 x .0.08 x 4.00 cm and 1.2 x 0.08 x 4 cm respectively.

The coupons were polished using emery paper up to 600 grits, degreased with absolute ethanol, dried using acetone and then weighed and introduced into the corrodent.

EXPERIMENTAL TECHNIQUES

Gravimetric

The pretreated metal coupons were immersed into each of the beakers containing the blank and inhibitor test solutions with the help of rods and hooks at room temperature. The mild steel coupons were completely immersed in 100 cm^3 of test solutions and retrieved after 1 hour. The retrieved coupons were washed , scrubbed with a bristle brush, under fast flowing water, rinsed in absolute ethanol, dried using acetone, reweighed and re-immersed in the corrodent. The weight loss of mild steel coupon was evaluated in grams as the difference in the initial and final weights of the coupon. This experimental treatment was carried out for the alkaloid extract and the non-alkaloid extract using concentrations of 0.5, 1.0, 2.0, 3.0 and 5.0 g/L at ambient temperature.

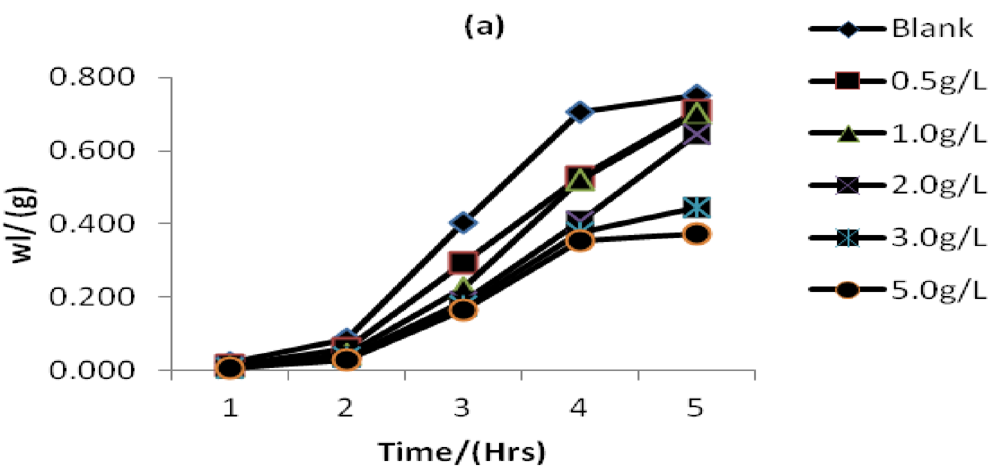
Hydrogen Evolution

Hydrogen evolution measurements were carried out at 30, 40 and 50^o C using a gasometric assembly.100 cm^3 of corrodent solution was introduced into the reaction chamber connected to the assembly and the initial volume of air in the burette was noted. Then the mild steel coupon was dropped into the corrodent and the reaction vessel quickly closed to prevent leakage of hydrogen gas.Variation in the volume of hydrogen evolved with time was recorded every minute by noting the decrease in paraffin oil level in the chamber for an hour interval. Each experiment was conducted on a fresh specimen of mild steel. The experiment was performed for inhibitor concentration of 0.5, 1.0, 2.0, 3.0 and 5.0 g/L and 5 M HCl solution at 50, 40 and 30^o C for AECA and NAECA.

RESULTS/ DISCUSSION

Weight loss result

The results obtained for the variation of weight loss with exposure time for the mild steel test specimen immersed in the two extracts of *Costus afer* (AECA and NAECA) are presented in Fig 1. From Fig 1 it can be observed that there is a remarkable drop in the gradient of the plot in the presence of the inhibitors when compared to that of the free solution. Also a further decrese in gradient is observed as the inhibitor concentration increases for both AECA and NAECA. This implies that more of the metal is preserved at higher inhibitor concentrations. However this fall in gradient is more pronounced in NAECA suggesting a better inhibitive property (Okafor *et al.,* 2007)



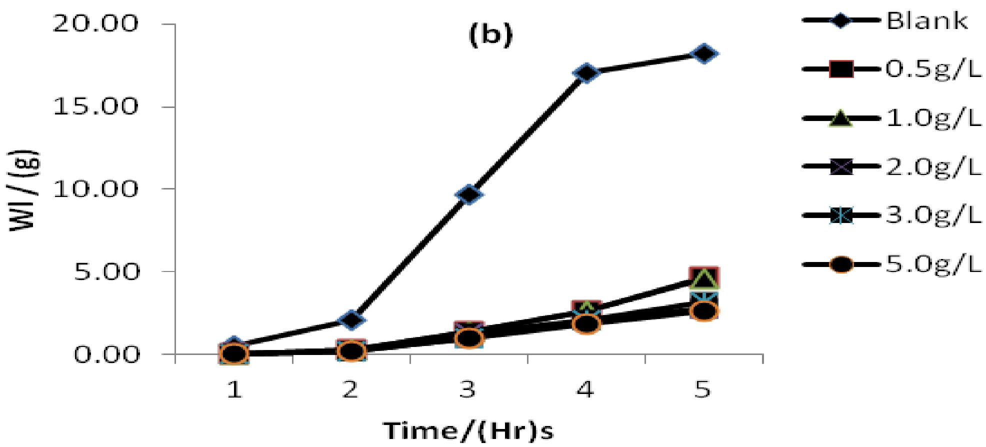


Fig. 1: Variation of weight loss with time for mild steel in 5.0 M HCl solution in the presence and absence of (a) AECA and (b) NAECA

The values for the corrosion rates, surface coverage and inhibition efficiency for mild steel coupons in 5.0 M HCl in the absence (blank) and presence of AECA and NAECA at 30^o C are presented in Table 1.

The corrosion rate *(CR)*, surface coverage (θ) and inhibition efficiency (IE), were calculated using equations 1-3. (Ebenso *et al.,* 1996)

$$CR - \frac{WL * 1000}{A * t} \quad 1$$

$$\theta = 1 - \frac{CR_{Inh}}{CR_{blank}} \quad 2$$

$$IE = \theta X 100 \quad 3$$

From the results obtained in Table 1 it can be seen that the corrosion rates decreased with increase in concentration of the AECA (from 5.024 to 2.550 mg/cm^2/hr) and NAECA (5.024 to 0.685 mg/cm^2/hr) at 30^o C. The corrosion rate followed the order AECA > NAECA. This suggests an unexposed heterocyclic nitrogen atom in the alkaloid structure. The efficacy of NAECA may be attributed to other active phytochemicals present in the extract such as tannins, saponins and anthraqiunoes (Bentiss *et al*., 2000). The surface coverage of the extracts was found to increase with increase in concentration of the inhibitor at low concentration (0.5 g/L) and high concentration (5.0 g/L) of the extracts. This implies that a larger fraction of the surface is covered with increase in the inhibitor concentration at high concentrations. Similar trends are observed for the IE which follows a reverse order as that of the corrosion rate. The maximum values were obtained at the highest inhibitor concentration of 5.0 g/L for AECA and NAECA (49.2% and 86.4% respectively). There is a remarkable increase in the value of the half life of the coupons from 845.1 to 2235.5 hours for AECA and 4951.0 to 6932.0 hours for NAECA which gives a measure of its life time for all the extracts studied. The drop in the rate constants gives a measure of the extent of retardation of the reaction for the extracts of *Costus afer*.

TABLE 1

Corrosion rates, surface coverage and inhibition efficiency for mild steel coupons in 5.0 M HCl in the absence (blank) and presence of AECA, NAECA and EECA at 30^{o}C.

System	CR (mg/cm^2/hr)	Coverage (Θ)	IE (%)	(t1/2) (Hrs)	k/ (Hrs x 10^{-3})
5 M HCl (Blank)	5.024	-	-	387.2	17.9
5 M HCl + 0.5 g/L AECA	4.500	0.104	10.4	845.1	8.2
5 M HCl + 1.0 g/L AECA	4.490	0.106	10.6	1004.3	6.9
5 M HCl + 2.0 g/L AECA	3.964	0.211	21.1	1283.3	5.7
5 M HCl + 3.0 g/L AECA	2.931	0.417	41.7	1925.0	3.6
5 M HCl + 5.0 g/L AECA	2.550	0.492	49.2	2235.5	3.1
5 M HCl + 0.5 g/L NAECA	1.153	0.771	77.1	4951.0	1.4
5 M HCl + 1.0 g/L NAECA	1.139	0.773	77.3	5775.0	1.2
5 M HCl + 2.0 g/L NAECA	0.828	0.835	83.5	5775.0	1.2
5 M HCl + 3.0 g/L NAECA	0.731	0.855	85.5	6300.0	1.1
5 M HCl + 5.0 g/L NAECA	0.685	0.864	86.4	6932.0	1.0

Adsorption Considerations

Adsorption Isotherms were tested to see the fitness of the experimental data. Langmuir adsorption isotherm was found suitable for the experimental findings for all the temperatures studied. The Langmuir adsorption isotherm is expressed in equation 4. (Okafor *et al.,* 2007)

$$\frac{c}{\theta} = \frac{1}{k} + c \quad (4)$$

Where k is given by equation 5

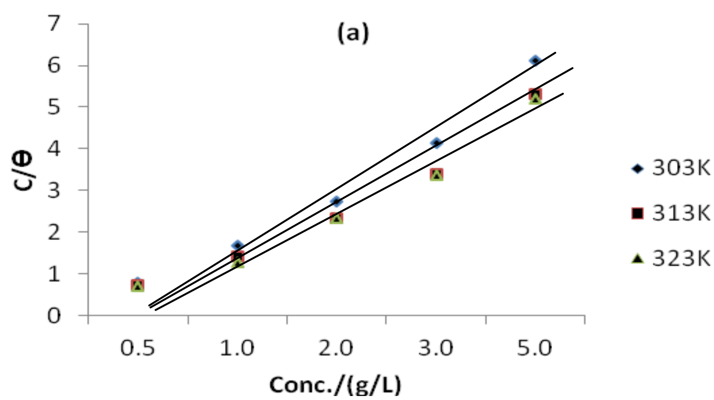
$$k = \frac{1}{55.5}\exp\frac{-\Delta G_{ads}}{RT} \quad (5)$$

A plot of c/ɗ against c gave straight lines as shown in Fig 2 with correlation factors presented in Table 2 (Anand *et al*., 2011). From the values of the correlation factors obtained from the Langmuir plot it can be seen that they are close to unity. This however indicates strict adherence to the assumptions underlying the derivation of Langmuir Isotherm. This implies that the molecules of the inhibitors are adsorbed on the surface of the metal with no interaction between the adsorbates. The values for the equilibrium constant and adsorption free energy for the extracts are also presented in Table 2. The adsorption free energies obtained were negative and below -40.0 kJ/mol. This indicates that the adsorption of the phytochemicals present in the extracts of the plant is spontaneous and stability of the adsorption layer. This also evidently confirms that the extracts from *Costus afer* exerts its inhibitive effects on the surface of mild steel by being spontaneously adsorbed on the surface of the metal. The maximum values obtained for the adsorption rate constant obtained for the extracts of *Costus afer* shows that K_{eq} for NAECA were generally higher than that of AECA indicating that the adsorption of NAECA is more thermodynamically favored when compared to AECA.

Evaluation of the Corrosion Inhibitive Properties

The extracts of *Costus afer* has been reported to contain terpenoids, flavonoids, phenols, alkaloids, glycosides, anthraquinones and tannins (Acamovic *et al.*, 2004) . Alkaloids have been elucidated to be good corrosion inhibitors for mild steel in 5 M H_2SO_4 solution (Ikeuba *et al.*, 2012). Because of the diversity of the structure of alkaloids, there is bound to be variations in their basic properties as a result of some chemical effects which includes inductive and electronic effects. The relatively low efficiency of AECA may be attributed to any or a combination of the following; (Ikeuba *et al.,* 2012)

- A relatively low concentration of alkaloid active principle in the ethanolic extracts of *Costus afer.*
- A relatively high basic strength of the Alkaloids in the extracts of *Costus afer* which makes the lone pair of electons on the heterocyclic nitrogen to be easily protonated in the presence of acids. This consequently will cause the unavailability of these electron pair through which the active principles are believed to adsorb on the metal surface (Lebrini et al., 2010; Ikeuba *et al,* 2012)
- A greater affinity of other phytochemicals such as tannins in the extracts toward adsorption which have been elucidated to be very good corrosion inhibitors in acid medium (Rahim *et al.,*2007, 2008)



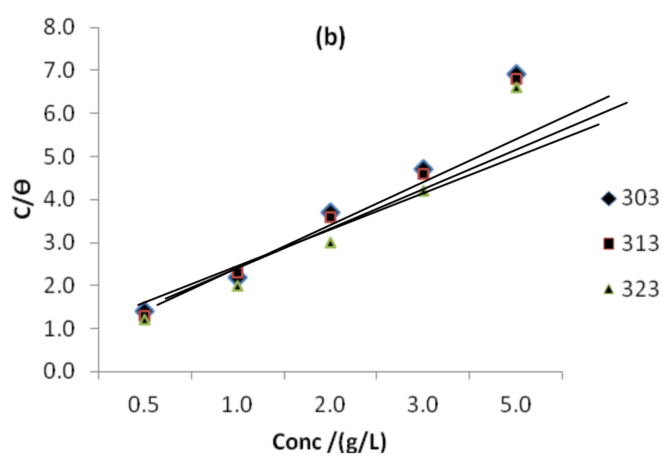


Fig. 2: Langmuir adsorption isotherm for mild steel in 5 M HCl containing (a) AECA and (b) NAECA at different temperatures.

TABLE 2
Equilibrium constant (K_{eq}), Adsorption free energy (φG_{ads}) and Correlation factors (R^2) for the adsorption of the inhibitors on the mild steel surface.

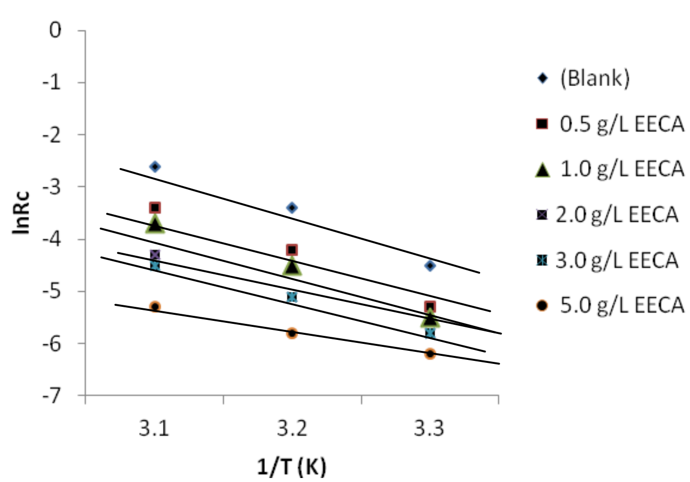
Inhibitor	AECA			NAECA		
T/(°K)	K_{eq} (L/g)	ΔG_{ads} (KJ/Mol)	R^2	K_{eq} (L/g)	ΔG_{ads} (KJ/Mol)	R^2
303	11.9	-16.36	0.973	37	-19.2	0.972
313	13.7	-17.26	0.964	37	-19.9	0.974
323	14.5	-17.97	0.959	20	-18.8	0.947

Thermodynamic Considerations
The temperature of the system was varied from 303 to 323 K to deduct some thermodynamic parameters for the corrosion of mild steel in the presence of the inhibitors. The Arrhenius equation and the Eyring transition state equations were used to deduce the thermodynamic parameters as given in equation 6 and 7 respectively (Ekpe *et al.*, 1995). E_a was calculated from the plot of ln R_c against the inverse of temperature (Fig. 3) and is presented in Table 3. ΔH^* was calculated from the slope of plot of ln (R_c/T) against the inverse of temperature (Fig 4) and it is presented in Table 3.

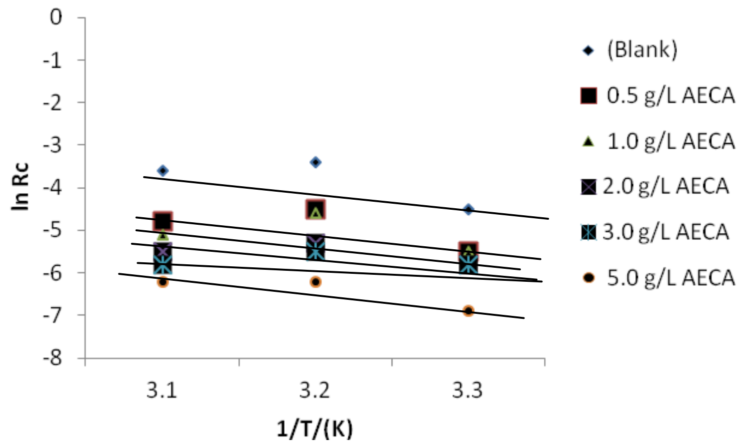
$$\ln R_c = \ln A - \frac{E_{ai}}{RT} \quad 6$$

$$R_c = \frac{kT}{h}\exp\left(\frac{\Delta S^*_i}{R}\right)\exp\left(\frac{-\Delta H^*_i}{RT}\right) \quad 7$$

Where R_c is corrosion rate, A is Arrhenius pre exponential factor , E_a is activation energy, R is universal gas constant, T is temperature, ΔS^*_i is entropy, ΔH^* is enthalpy, h is planks constant and *k* is Boltzmann constant. From Table 3 a remarkable increase is observed in E_a in the presence of AECA and NAECA in 5 M HCl when compared with that of the free solution (9.6 kJ/mol). The obtained results suggest that the extracts inhibit the corrosion reaction by increasing its activation energy. This could be done by adsorption on the steel surface making a barrier for mass and charge transfer. However, such types of inhibitors perform a good inhibition at ordinary temperature with considerable loss in inhibition efficiency at elevated temperatures (El-Etre, 2008 and Abiola, 2006). Moreover, the relatively low value of activation energy which were below 80 kJ/mol in presence of the extract suggests a physical adsorption process. This implies that a multilayer of inhibitors is formed on the surface of the metal. Comparing with the results obtained from the Langmuir isotherm (Table 2), the adsorption of the extracts on the metal surface is predominantly but not purely a physical process. This implies that a greater amount of energy is required for the corrosion to occur in the presence of the extracts. The values of Ea obtained for NAECA were generally higher than that obtained for AECA this implies that the extracts NAECA functioned as a better corrosion inhibitor when compared to AECA. The values for the Enthalpy of activation were positive for AECA and NAECA indicating the endothermic nature of the corrosion process (Ebenso and Ekpe, 1996).

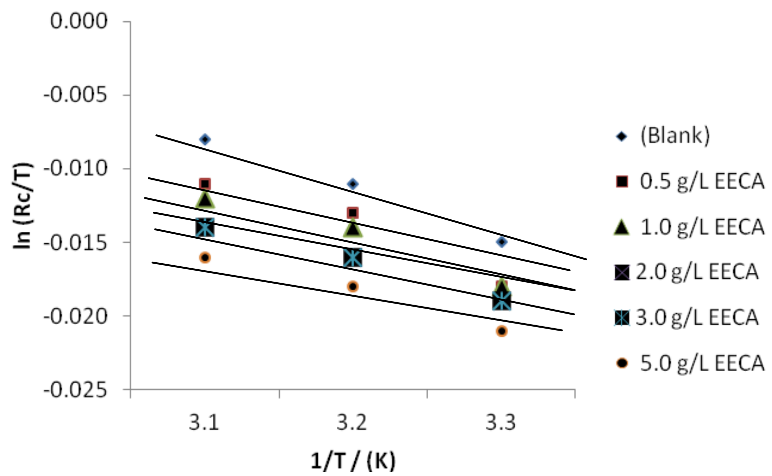


(a)

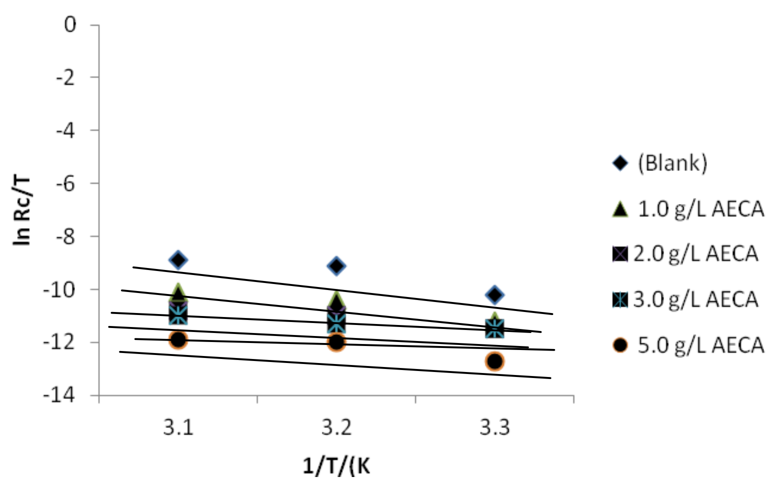


(b)

Fig. 3: Arrhenius plots for mild steel in 5 M HCl solution in the presence and absence of (a) NAECA and (b) AECA



(a)



(b)

Fig. 4: Eyring transition state plots for mild steel in 5 M HCl solution in the presence and absence of (a) NAECA and (b) AECA

TABLE 3

Activation energy (Ea) and Enthalpy of activation (φH*) for the corrosion of mild steel in the presence and absence of AECA and NAECA.

	AECA		NAECA	
System	**Ea (KJ/Mol)**	**ΔH * (KJ/Mol)**	**Ea (KJ/Mol)**	**ΔH * (KJ/Mol)**
5 M HCl (Blank)	**9.6**	**54.0**	**9.6**	**54.0**
5 M HCl + 0.5 g/L	**13.2**	**49.9**	**66.5**	**74.8**
5 M HCl + 1.0 g/L	**18.0**	**45.7**	**70.7**	**74.8**
5 M HCl + 2.0 g/L	**24.1**	**29.1**	**74.8**	**62.4**
5 M HCl + 3.0 g/L	**41.9**	**20.8**	**79.0**	**66.5**
5 M HCl + 5.0 g/L	**78.5**	**16.6**	**79.0**	**59.1**

CONCLUSION

The following conclusions have been drawn from the results of experiments

i. The Alkaloid and Non alkaloid fractions of the ethanolic extracts (AECA and NAECA) of *Costus afer* functioned as corrosion inhibitors for mild steel in HCl solution.
ii. The Non alkaloid component of the ethanolic extracts of *Costus afer* is a better corrosion inhibitor when compared with the alkaloid ethanolic extracts of *Costus afer*. The order of their inhibition efficiencies is given as NAECA > AECA.
iii. The inhibition efficiency of NAECA and AECA increases with increase in extract concentration.
iv. The compounds (NAECA and AECA) exert their inhibitive properties by being adsorbed spontaneously on the surface of mild steel. The adsorption characteristics of the compound have been found to obey physical adsorption mechanism and are consistent with Langmuir adsorption isotherm.

REFERENCES

Abiola, O. K., 2006. ñThe inhibition of mild steel corrosion in an acidic medium by fruit juice of *citrus paradisi*,ò Journal of Corrosion Science and Engineering, 5, (10): 112 ï 119.

El-Etre, A. Y., 2008. Inhibition of C-steel corrosion in acidic solution using the aqueous extract of zallouh root. Materials Chemistry and Physics 108, (2008): 278ï 282.

Acamovic, T., Stewart, C. S and Pennycott, T. W., 2004. Poisonous Plants and Related Toxins. Wallingford: CAB International. 67-71.

Anand, B and Balasubramanian, V., 2011. ñCorrosion behaviour of mild steel in acidic medium in presence of aqueous extract of *Allamanda blanchetii*,ò E-Journal of Chemistry, 8, (1): 226ï 230.

Bentiss, F., Traisnen, M and Langrenee, M., 2000. The substituted 1, 3, 4-ozadiazoles: a new class of corrosion inhibitors of mild steel in acidic media, Corrosion Science, (42): 127 ï 46.

Ebenso, E. E and Ekpe, U. J., 1996. Kinetic study of corrosion and corrosion inhibition of mild steel in H_2SO_4 using *carica papaya* leaves extract, West African Journal of Biology and Applied Chemistry, (41): 21-27.

Ekpe, U. J., Ibok, U. J., Ita, B. I., Offiong, O. E and Ebenso, E. E., 1995. Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in hydrochloric acid. Materials Chemistry and Physics, 40, (2): 87ï 93.

Ikeuba, A. I., Okafor, P. C and Ekpe, U. J., 2012. Alkaloidal and Non-alkaloidal extracts from *Garcinia kola* as green corrosion inhibitors of mild steel in H_2SO_4 solutions. Proceedings of the 35th Annual International conference, Workshop and Exhibition of the Chemical Society of Nigeria. (2): 240 -246

Lebrini, M., Robert, F and Bros, C., 2011. Alkaloids extract from *Policourea guinesis* as corrosive inhibitor for C38 steel in 1 M hydrochloric acid medium. International Journal of Electrochemical Science, (6): 847-859.

Okafor, P. C and Ebenso, E. E., 2007. Inhibitory action of *Carica papaya* extracts on the corrosion of mild steel in acidic media and their adsorption characteristics. Pigment and Resin Technology, 36, (3): 134 - 140.

Okafor, P. C., Ikpi, M. E., Uwah, I. E., Ebenso, E. E., Ekpe, U. J and Umoren, A. S., 2008. Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. *Corrosion Science, 50*(8): 2310ï 2317

Okafor, P. C., Ebenso, E. E and Ekpe, U. J., 2010. ñ*Azadirachta indica* extracts as corrosion inhibitor for mild steel in acidic mediaò International Journal of Electrochemical Science, 5, (7): 978-993.

Rahim, A. A., Rocca, E., Steinmetz, J and Kassim, M. J.,

2008. Inhibitive action of mangrove tannins and phosphoric acid on pre rusted steel via electrochemical methods. Corrosion Science, (50): 1546-1550.

Rahim, A. A., Rocca, E., Steinmetz, J., Kassim, M. J., Adnan, R and Ibrahim, M. S., 2007. Mangrove tannis and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium. Corrosion science (49): 402-417.

Uwah, I. E., Okafor, P. C and Ebiekpe, V. E., 2010. ñInhibitive action of ethanol extracts from *Nauclea latifolia* on the corrosion of mild steel in H_2SO_4 solutions and their adsorption characteristicsò Arabian Journal of Chemistry. Doi:1016/J.arabic.2010