

INHIBITIVE ACTION OF ALKALOIDS AND NON ALKALOID FRACTIONS OF THE ETHANOLIC EXTRACTS OF *PHYLLANTHUS AMARUS* ON THE CORROSION OF MILD STEEL IN HCl SOLUTION

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ABSTRACT

The corrosion inhibition of mild steel in 2.0 M HCl solution by non-alkaloidal and alkaloidal fractions of the extracts of *Phyllanthus amarus* (NAEPA and AEPA respectively) was studied using gravimetric and gasometric techniques at 303 and 323 K. The results revealed that the extracts functioned as good corrosion inhibitors. Inhibition efficiency was found to increase with the concentration of the extracts. The inhibition efficiency was found to increase with temperature for NAEPA and increase with decrease in temperature for AEPA. A mechanism of chemical and Physical adsorption is proposed for NAEPA and AEPA respectively. The adsorption of the inhibitors followed the Langmuir adsorption isotherm.

KEYWORDS: *Phyllanthus amarus*, mild steel, alkaloid, corrosion inhibition.

INTRODUCTION

Corrosion of metallic materials in acidic solution causes considerable costs. In order to reduce the corrosion of metals, the application of inhibitors is one of the best methods of preventing metals against corrosion (Odiongenyi *et al.*, 2008). It has been found that most corrosion inhibitors are organic compounds containing polar fractions with nitrogen, sulphur or oxygen in the conjugated system that severely inhibit the corrosion of mild steel in acidic and alkaline environments (Ameer and Khamis, 2000; Ekpe *et al.*, 1994 ; Ebenso and Ibok, 1998). However the toxicity of most corrosion inhibitors has greatly affected the environment and the living organism (Odiongenyi *et al.*, 2008). Due to the toxicity of some corrosion inhibitors there have been a new search for green corrosion inhibitors (Sehaibani, 2000). Inhibitors in this class are those that are environmentally friendly and are obtained from natural product such as plant extracts and several studies have been carried out on the inhibition of corrosion of metals by plant extracts. In most of these and other studies, nothing has been reported on the use of alkaloid and non-alkaloidal

fraction of *Phyllanthus amarus* for the inhibition of the corrosion of mild steel in HCl. The present study aimed at broadening the application of plant extracts for metallic corrosion inhibition by investigating the inhibitory action of alkaloid and non alkaloid ethanolic extracts of the *Phyllanthus amarus* on the corrosion of mild steel in HCl. *Phyllanthus amarus* is an erect annual herb of not more than one and half feet tall and has small leaves and yellow flowers. The plant is widely distributed in tropical and subtropical countries as earlier reported by Okafor *et al.*, 2006; 2007. It was first identified in central and southern Indian in the 18th century but is now found in many countries including Cuba, Philippines and Nigeria (Okafor *et al.*, 2006; 2007). The extracts of *Phyllanthus amarus* is used to treat diabetes, gonorrhoea, irregular menstruation etc. In Nigeria the plant grows as weeds and large quantities of the plants are weeded and wasted every year.

EXPERIMENTAL

The mild steel sheets used in this work were obtained from Ejison Resources (Nigeria) and has the composition given in Table 1.

Table 1: Chemical composition of the mild steel

Element	Mn	P	C	S	Fe
Wt %	0.6	0.36	0.15	0.07	98.79

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The mild steel sheet was mechanically press-cut to two different couponsizes. The gasometric experiments were conducted on mild steel coupons of dimension 4.00 × 1.20 × 0.08 cm (Surfacearea10.10cm²). Gravimetric experiments on the coupons of dimension 5.00 × 4.00 × 0.08 cm (Surface area41.0cm²). Each coupon was degreased by washing with ethanol. The washed sample was dipped in acetone, removed and allowed to dry. All reagents used for the study were analar grade.

Extraction of plant extracts

Samples of *Phyllanthus amarus*leaves were obtained within the premesis of the Department of Pure and Applied ChemistryUniversity of Calabar; Nigeria. They were dried in a memmert oven at 323 K, ground to powder form and extracted in soxhlet extractor using ethanol. The resultant solution was filtered and stored.

Isolation of crude non-alkaloid component of extract of *Phyllanthus amarus*(NAEPA)

20 grams of the ethanol extract was partitioned between 100ml of chloroform and 100 mL of 0.1 M HCl solution using a separating funnel. The tailing fraction was used as the non-alkaloid extract.

Isolation of crude alkaloid component of extract of *Phyllanthus amarus*(AEPA)

20 grams of the ethanol extract was partitioned between 100ml of chloroform and 100 mL of 0.1 M of ammonia. The float from the separating funnel above was further basified with 100 mL of ammonia and partitioned with 100mL of chloroform to obtain the alkaloid extract (Ikeuba *et al.*, 2013)

2 g of the alkaloid and non-alkaloid extracts (AEPA and NAEPA) were soaked in 0.5 litre of 5 M H₂SO₄ solution and kept for 24 hours. The resultant solutions were filtered and stored. From the stock solutions (10 g/L) inhibitor test solutions of concentration; 0.1, 0.5, 1.0, 2.0, and 4.0 g/L were prepared. These solutions were then used for the corrosion test.

Gravimetric measurement

In the gravimetric experiment a previously weighed metal (mild steel) coupon was completely immersed in 250 mLof the test solution ie in presence and absence of the inhibitor in an open beaker. Then inserted into a water bath maintained at a temperature of 303 K and after every 1 hour, each sample was withdrawn from the test solution, washed in distilled water for several time, degreased by washing with ethanol and finally dried with acetone before re-weighing. From the weight loss data the corrosion rates (CR) were calculated from equation 1.

$$CR = \frac{WL}{At} \times 1000 \text{ (mg cm}^{-2} \text{ hr}^{-1}) \dots\dots 1$$

where WL is weight loss in mg, A is the specimen surface area and t the immersion period in hours (5 hrs).From the corrosion rate, the surface coverage (θ) and inhibition efficiencies (I %) were determined using equation 2 and 3 respectively.

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \dots\dots 2$$

$$I \% = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \dots\dots 3$$

where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of NAEPA and AEPA respectively.

Gasometric measurement

Hydrogen evolution measurements were carried out at 303 and 333 K. From the value of hydrogen gas evolved, the rate of evolution of the gas (R_{VH}), degree of surface coverage (θ) and inhibition efficiency (I %) were calculated using equations 4, 5 and 6 respectively.

$$R_{VH} = \frac{\Delta V}{\Delta t} \dots\dots\dots 4$$

$$\theta = \frac{R_{VHblank} - R_{VHinh}}{R_{VHblank}} \dots\dots\dots 5$$

$$I\% = \frac{R_{VHblank} - R_{VHinh}}{R_{VHblank}} \times 100 \dots\dots\dots 6$$

Where R_{VHblank} and R_{VHinh} are the rate of hydrogen evolution in the absence and presence of the inhibitors respectively.

RESULT AND DISCUSSION

Gravimetric measurements

The gravimetric measurements for the mild steel in 2.0 M HCl at 303 K containing different concentrations of the plant extracts as a function of time (in hour) are presented in Fig. 1a-1b. The results show that the weight loss values increase with an increase in the period of contact but decrease with an increase in the concentrations of non-alkaloid and alkaloidal fraction of *Phyllanthus amarus*. The decrease is due to the inhibitive effects of the plant extracts(Obot *et al.*, 2011; Obot and Obi-Egbedi, 2009; Okafor and Ebenso, 2007; Oguzie, 2008).

The corrosion rates for the test medium without the plant extracts addition were higher when compared to the rest of the solutions containing the extracts as shown in Table. 2. Table 2 also shows that the corrosion rates of the mild steel decreased with increase in the plant extract concentration indicating that the extracts inhibit the corrosion of mild steel in 2.0 M HCl solution (Martinez and Sterm, 2001;Nnanna *et al.*, 2010). As expected, HCl acid is a very strong acid and it has pronounced corrosion effect on unprotected mild steel (Umoren *et al.*, 2006; Solmaz *et al.*, 2008; Ekpe *et al.*, 1994).With the addition of the various concentrations of the alkaloid and non alkaloid extracts, the corrosion rate became significantly reduced. Fig .1 shows decrease in weight loss with increase with inhibitor concentration. The corrosion rate for all concentrations studied followed the trend NAEPA>AEPA. The values of inhibition efficiency of different fractions of plant extracts are also given in Table 2. The plant extracts show a significant inhibitive effect on the mild steel in HCl solution that was up to 90.2 % and 87.0% for the alkaloid (AEPA) and non alkaloid (NAEPA) fractions of the extracts respectively at the highest concentration of 4.0 g/L. This could be due to increased viscosity of solution as a result of dissolved corrosion products thereby diluting the effect of the acid (Oguzie, 2007;2008: Okafor *et al.*, 2008; 2010: Patel *et al.*, 2009). This could also be due to the formation of large film on the surface of the metal due to the large size of the inhibiting molecule in the extract according to Aywin and Igho (2001), Oguzie (2005) and Okafor *et al.*, (2005). Fig. 2 shows the variation of Inhibition efficiency

with extract concentration for mild steel in 2.0 M HCl solutions containing different fractions of the plant extracts and affirmed that the inhibition efficiencies increased with increase in the Plant extract concentration. The efficiencies followed the trend AEPA > NAEPA.

A Plot of the $\ln(W_f/W_o)$ of the measured weight in grams of the mild steel after and before post treatment against time helped to explain the kinetics of the corrosion of mild steel in the acidic media in the absence and presence of NAEPA and AEPA (El-Ashry *et al.*, 2006; Okafor *et al.*, 2007). Linear plots were obtained as shown in Fig. 3 which is consistent with first order kinetics and which can also be obtained mathematically from equation 7 (Atkins and Depaula, 2010; Shama and Shama, 2004; Engel and Reid, 2006).

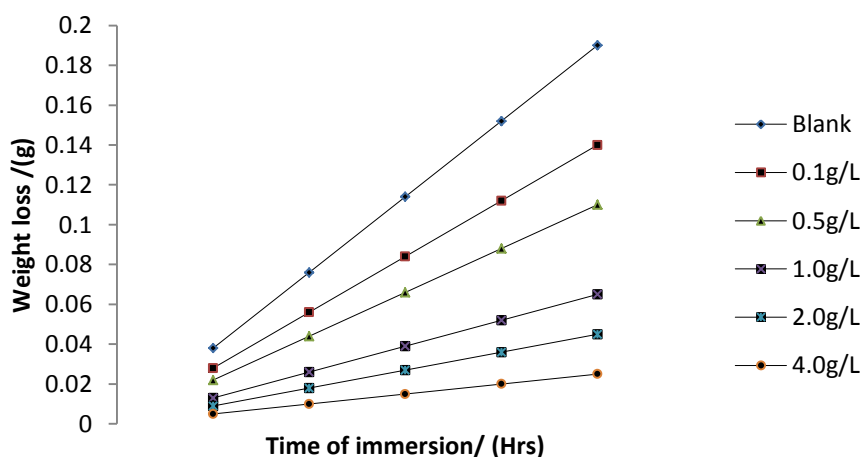
$\ln(W_f/W_o) = -kt$ 7
 where k is the rate constant. The values of the rate constants k obtained from the slope of the plot in Fig.3

are presented in Table 2. The results obtained indicate that the rate constants decrease with increase in the extracts concentrations (Okafor *et al.*, 2007). If the rate constant doubles, so will the rate of the reaction. But in this case the result showed a decrease in rate constant with increase in concentration which informs a good inhibitor and a slower corrosion reaction rate. From the rate constant values, the half life values were calculated using Equation 8 and the deduced data also presented in Table 2. The half life values were observed to increase with increase in concentration of the plant extracts. Increasing $t_{1/2}$ also support the assertion that the compounds are corrosion inhibitors for mild steel in HCl solution according to Oguzie *et al* (2007) and Umoren and Ebenso (2008), since the greater the extract concentration, the more time it takes for the mild steel to corrode to half the original size..

$t_{1/2} = \frac{0.693}{k}$ 8

Table 2: Calculated values of corrosion rate, inhibition efficiency, rate constant and half life for mild steel coupons in 2 M HCl solution containing non-alkaloid and alkaloid fractions of *Phyllanthus amarus*

System	Conc. g/L	Corrosion rate (mg cm ⁻² hr ⁻¹)	I %	Rateconstant (hr ⁻¹)x10 ⁻³	Half life (hours)
NAEPA	Blank	0.556	-	3.88	178.61
	0.1	0.409	26.4	2.82	245.75
	0.5	0.321	42.1	2.20	351.00
	1.0	0.190	70.7	1.33	521.05
	2.0	0.131	76.7	0.90	770.00
	4.0	0.073	87.0	0.50	1386.00
AEPA	Blank	0.585	-	3.99	173.68
	0.1	0.321	45.1	2.20	351.00
	0.5	0.146	75.0	1.42	488.03
	1.0	0.131	77.9	1.28	541.40
	2.0	0.087	85.1	0.60	1155.00
	4.0	0.058	90.2	0.40	1732.50



(a)

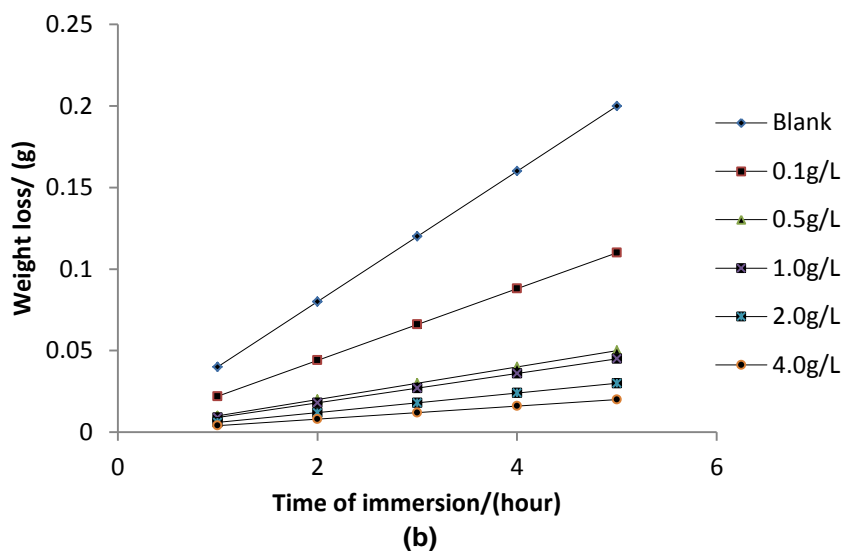


Figure 1: Variation of weight loss with time for the corrosion of mild steel in 2.0 M HCl containing various concentrations of (a) non alkaloid (b) alkaloid Extracts of *Phyllanthus amarus* at 303 K .

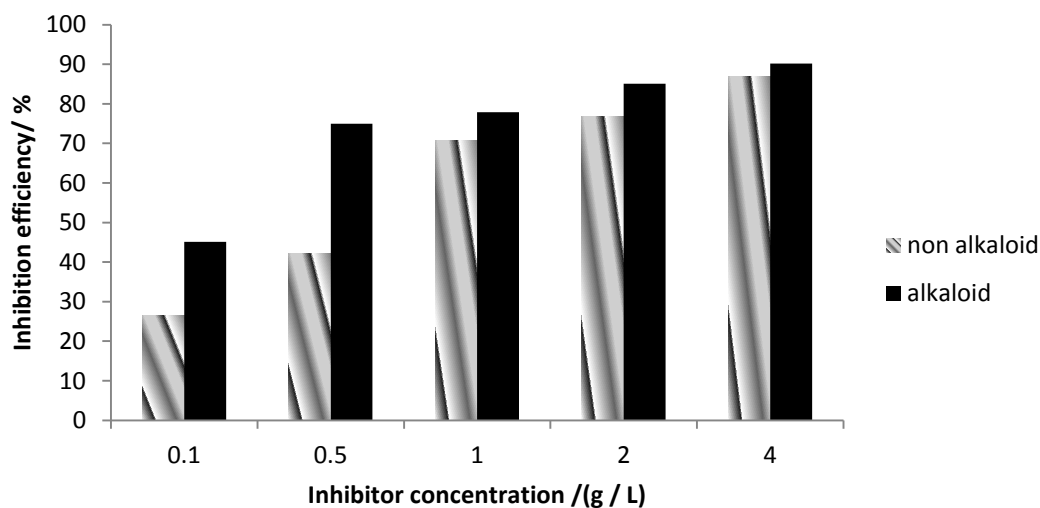
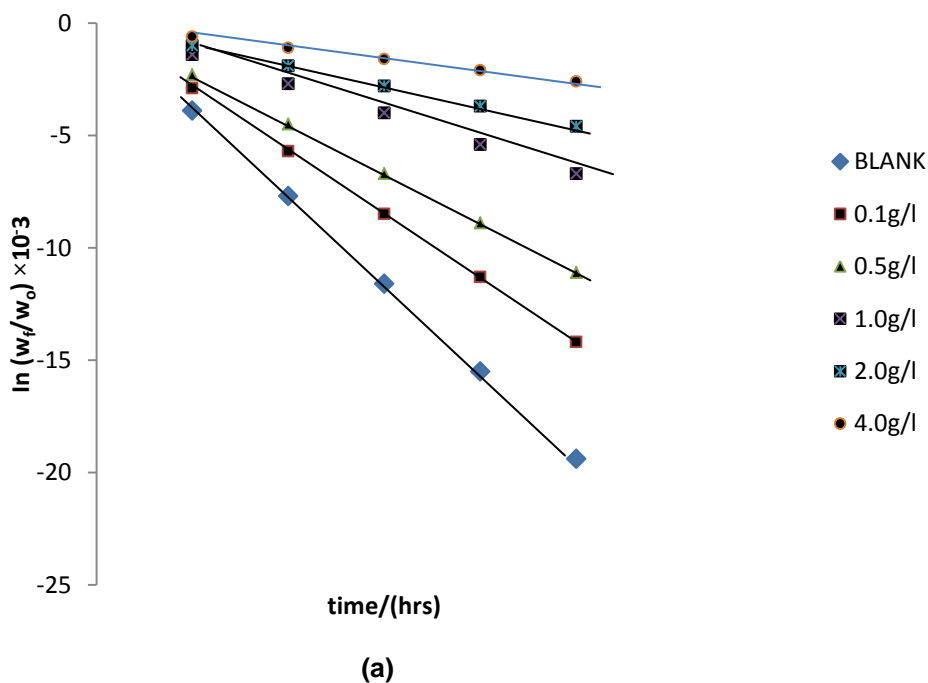


Fig. 2: Maximum inhibition efficiency for mild steel coupons in 2 M HCl for different concentration of plant extracts of *Phyllanthus amarus*



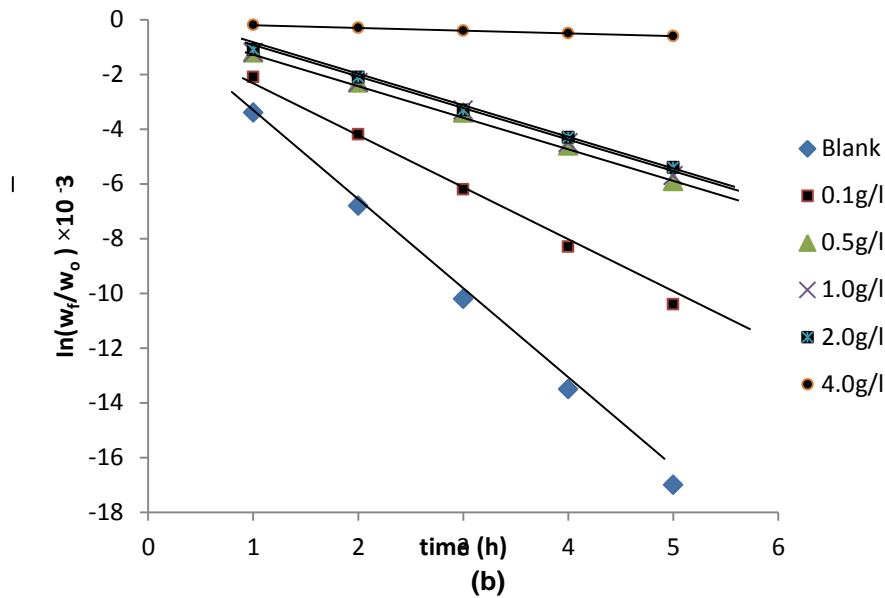


Fig.3: Variation of $\ln(w_t/w_0) \times 10^{-3}$ with time for the corrosion of mild steel in 2 M HCl solution containing various concentration of (a) NAEPA and (b) AEPA.

Gasometric results

The corrosion of mild steel is characterized by evolution of hydrogen gas and the rate of corrosion is proportional to the amount of hydrogen gas evolved (Joseph and Raj, 2010; Okafor and Ebenso, 2007). The volume of hydrogen evolved V_H during the corrosion of mild steel in 2 M HCl solution in the absence and presence of the plant extracts at 303 K and 333 K were measured as a function of time. The results obtained showed that in the presence of non-alkaloid and alkaloidal fractions of the extract the volume of hydrogen evolved during the corrosion reaction decreased. The corrosion rate was determined from equation 9 (Ekanem et al., 2010).

$$CR_H = \frac{V_t - V_i}{t_t - t_i} \dots\dots\dots 9$$

where V_t and V_i are the volume of hydrogen evolved at time t_t and t_i respectively. Calculated values of corrosion rate, inhibition efficiency, activation energy, heat of adsorption and enthalpy for mild steel coupons in acid media containing fractions of extracts from *Phyllanthus amarus* using gasometric method are presented in Fig 6-7 and Table 3. The results showed that the corrosion rate decreased with increase in the NAEPA and AEPA concentrations, but increase with temperature for NAEPA and decreased in temperature for AEPA. From the corrosion rates the inhibition efficiency was determined using equation 6.

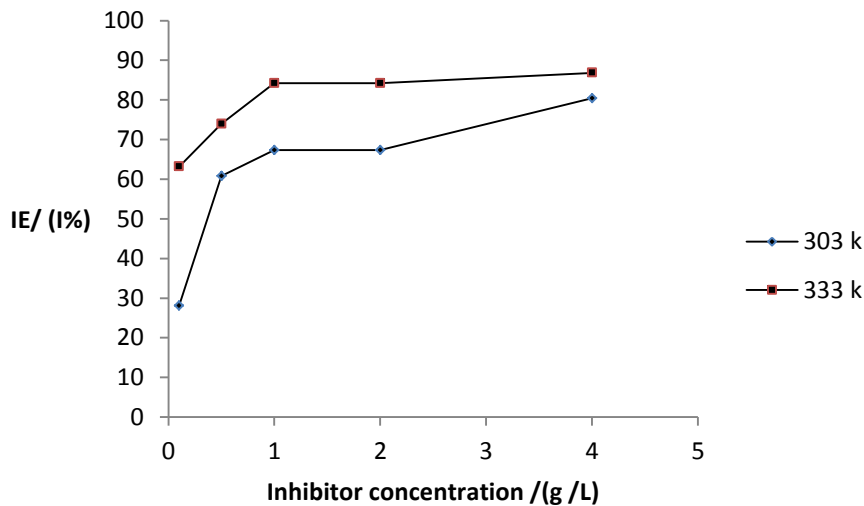


Fig..6: Variation of inhibition efficiency (I %) with concentration of NAEPA in 2 M HCl at 303 and 333K.

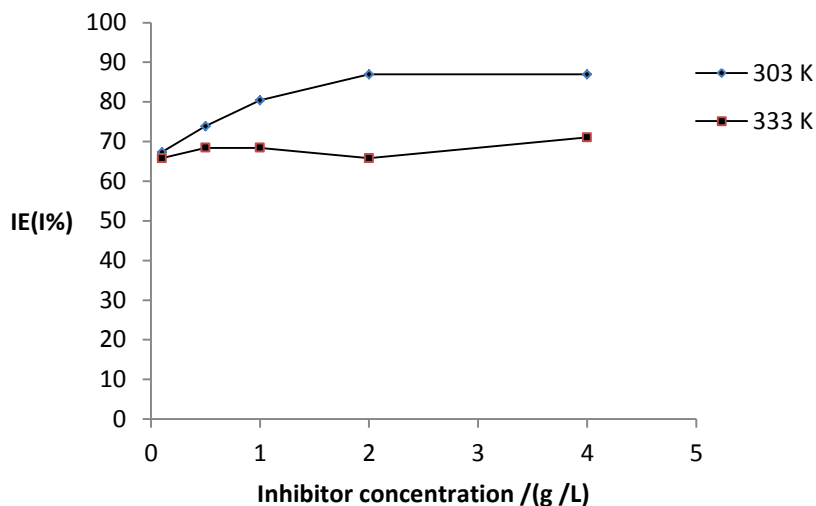


Fig. 7: Variation of inhibition efficiency (I %) with concentration of AEPA in 2 M HCl at 303 and 333 K.

Table 3: Calculated values of corrosion rate, inhibition efficiency, activation energy, heat of adsorption and enthalpy for mild steel coupons in acid media containing fraction of extracts from *Phyllanthus amarus* using gasometric method.

System	Inhibitors (g/L)	RV _H (cm/min)		I%		E _a (KJ/mol)	Q _{ads} (KJ/mol)	ΔH _{ads} (KJ/mol)
		303 K	333 K	303 K	333 K			
NAEPA	Blank	0.015	0.038	-	-	27.32	-	27.26
	0.1	0.011	0.014	28.1	63.1	5.26	73.7	5.28
	0.5	0.006	0.008	60.7	78.9	7.36	44	7.44
	1.0	0.005	0.006	67.3	84.2	5.84	47.4	5.09
	2.0	0.005	0.006	67.3	84.2	4.38	47.4	4.30
	4.0	0.003	0.005	80.3	86.8	11.08	23.7	11.25
AEPA	Blank	0.015	0.038	-	27.3	27.32	-	27.26
	0.1	0.005	0.013	67.3	65.7	34.73	-3.4	34.75
	0.5	0.004	0.012	73.8	68.4	35.67	-13.5	35.73
	1.0	0.003	0.012	80.3	68.4	45.34	-31.8	36.91
	2.0	0.002	0.013	86.9	65.7	52.52	-61.8	40.69
	4.0	0.002	0.011	86.9	65.7	53.67	-49.7	33.85

It is observed that inhibition efficiency increases with increase in extract concentration as well as an increase in temperature for NAEPA and decrease in temperature for AEPA. This suggests that fractions of *Phyllanthus amarus* are adsorbed on the metal surface thereby protecting metal from the action of corrodent according to Okafor *et al.* (2010), Popoova *et al.* (2003) and Obot *et al.* (2011). The trend in temperature suggests chemical and physical adsorption all together (Ekpe *et al.*, 1994). Comparing the inhibition efficiencies of the plant extracts in Figs. 6a and 6b shows that efficiencies follow the trend AEPA > NAEPA. This trend proves the efficacy of the alkaloid phytochemicals in corrosion protection. These phytochemicals are believed to be adsorbed on to the metal surface via its basic nitrogen present in the heterocyclic ring (Ikeuba *et al.*, 2013). Similar trend was observed in 2 M HCl for weight loss results. From the calculated values of Q_{ads} (Table 3), it can be deduced that the adsorption of the inhibitor on mild steel surface is exothermic (negative value) for AEPA and endothermic (positive value) for NAEPA (Oguzie, 2005). The transition state equation was applied graphically (Figs. 11 – 12) to determine the standard enthalpy of activation. The negative values from the result indicate that the degree of surface coverage decreased with rise in temperature and the positive

values entail that surface coverage increased with rise in temperature (El-Ashry *et al.*, 2006; Vracar and Drazic, 2002), supporting the earlier proposed physisorption and chemical adsorption mechanisms. The positive values of ΔH° (5.28 to 11.25 kJ/mol for NAEPA and 34.75 to 40.69 kJ/mol) indicate that the dissolution of the metal is an endothermic reaction (Okafor *et al.*, 2007). This also suggests that mild steel dissolution requires less energy in 2 M HCl in the presence of the extract (Okafor *et al.*, 2010).

Adsorption considerations

The possible adsorption mode is investigated by testing the experimental data obtained with several adsorption isotherms. Such investigations will greatly throw more light to understanding of the corrosion inhibition mechanism. It is suspected that the inhibition of metal corrosion occurred as a result of the adsorption of the active principles of the extracts onto the metal surface (Okafor and Ebenso, 2007). Adsorption on corroding surface never reaches the real equilibrium but tends to be an adsorption steady state (Ekanem *et al.*, 2010). However, when the corrosion rate is sufficiently small, the adsorption steady state has a tendency to become quasi equilibrium state. The experimental data fitted the Langmuir adsorption isotherm model (Sehaibani, 2000;

Odiongenyi, *et al.*, 2008; Solmaz *et al.*, 2008). The Langmuir adsorption isotherm is given by the expression $\frac{C}{\theta} = \frac{1}{K_{ads}} + C$ where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process. The plot of C/θ against C is shown in Figs. 8 - 9. Linear plots were obtained across the temperatures studied with very good correlation coefficients which suggest that adsorption of the extracts followed Langmuir since they were very close to unity. Slight deviations were observed for the slope to the curves. These may be due to interactions between adsorbates. The Langmuir adsorption parameters in the presence of the extracts

are presented in Table 4. It is clearly seen from Table 4 that K_{ads} values of NAEPA are almost the same with K_{ads} values of AEPA which implies more efficient adsorption thus better inhibition efficiency (Obot and Obi-Egbedi, 2009). The observed deviation of the slope from unity explained the basis of the interaction among the adsorbed species on the surface of the metal (Okafor *et al.*, 2008; Oguzie, 2008). The negative values of ΔG_{ads}° (Table 4) indicate spontaneous nature of adsorption of inhibitors on mild steel surface. Values from -12.77 to -19.55 kJ suggest a strong interaction of the inhibitor molecules.

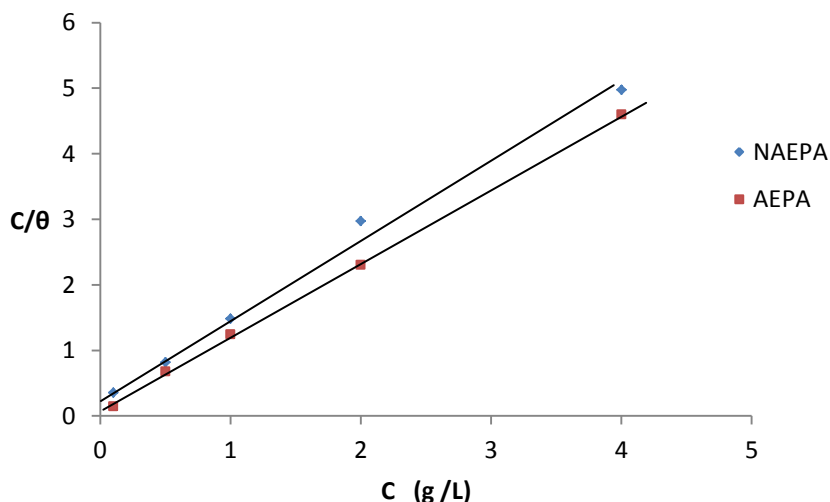


Figure 8: Langmuir isotherm for the adsorption of NAEPA and AEPA on the surface of mild steel. at 303 K

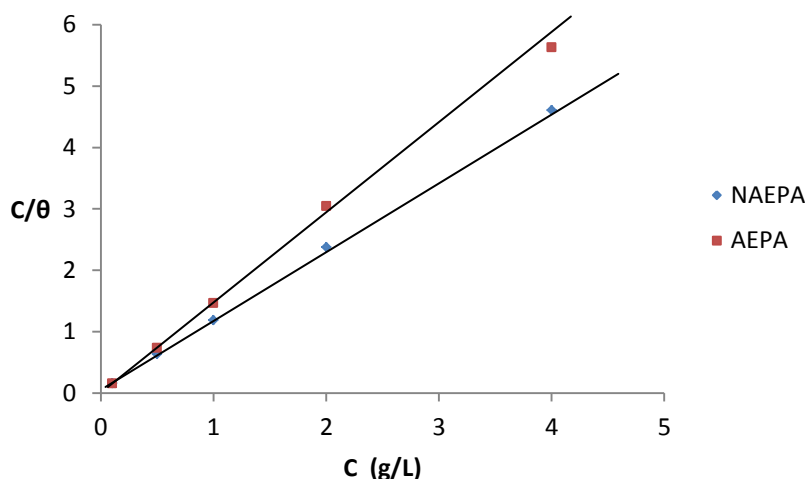


Fig. 9: Langmuir isotherm for the adsorption of NAEPA and AEPA on the surface of mild steel.at 333 K

Table 4: Langmuir adsorption parameters for mild steel in the presence of NAEPA and AEPA at 303 and 333 K

System		Slope	R ²	K _{ads}	ΔG _{ads} (KJ/mol)
NAEPA	303	1.19	0.99	3.35	-12.77
	333	1.14	0.99	17.24	-19.00
AEPA	303	1.12	0.99	12.98	-16.57
	333	1.41	0.99	17.54	-19.05

Effects of Temperature

The corrosion rate was found to increase exponentially with rise in temperature following the influence of temperature on the corrosion of mild steel in 2 M HCl in the absence and presence of NAEPA and AEPA of varying concentrations. The Arrhenius equation was used to determine the activation energies (E_a) according to Okafor *et al.* (2010), Patel *et al.* (2009) and Aywin and Igho, (2001).

$$\log CR = \log A - \frac{E_a}{2.303RT} \dots\dots\dots 11$$

where CR is the corrosion rate at various absolute temperatures, A is exponential factor and R the molar gas constant. The variation of logarithm of corrosion with the reciprocal of absolute temperature is shown in Fig. 10 for mild steel corrosion in 2 M HCl containing NAEPA and AEPA respectively. The calculated values of E_a are given in Table 3. Increase in activation energy (E_a) in inhibited solutions of AEPA compared to the blank suggest that inhibitor is physically adsorbed on the corroding metal surface while decreased in activation energy (E_a) in the presence of NAEPA suggests it is chemically adsorbed on the metal surface (Umoren and Ebenso, 2008).The heat of adsorption was obtained from the trend of surface coverage with temperature.

$$Q_{ads} = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1} \right) \text{KJmol}^{-1} 12$$

where θ_1 and θ_2 are the degree of the surface coverage at temperatures T_1 and T_2 . The calculated values of

heat of adsorption (Q_{ads}) are presented in Table 3. The positive Q_{ads} values indicate that the degree of the surface coverage increased with rise in temperature, supporting earlier proposed chemisorptions mechanism for NAEPA and the negative Q_{ads} values indicate that the degree of surface coverage decreases with rise in temperature in the presence of AEPA supporting physisorption mechanism (Popoova et al, 2003).The difference in the mechanism of adsorption may be accounted for on the basis of the phytochemical composition of the extracts. AEPA contains predominantly alkaloids which are heterocyclic compounds with basic nitrogen atoms. NAEPA contains a mixture of different phyto chemicals such as tannins, saponin, flavonoids, cardiac glycosides etc (Ikeuba et al., 2013). The increase in inhibition efficiency for NAEPA suggests that the molecules of the NAEPA are relatively small hence increasing its tendencies for chemical bonding. The decrease in inhibition efficiency with temperature for AEPA suggests that the molecules are relatively large hence occupying a large surface area thus reducing its tendency towards chemical bonding and increasing its tendency towards other intermolecular forces such as vander waals force of attraction.

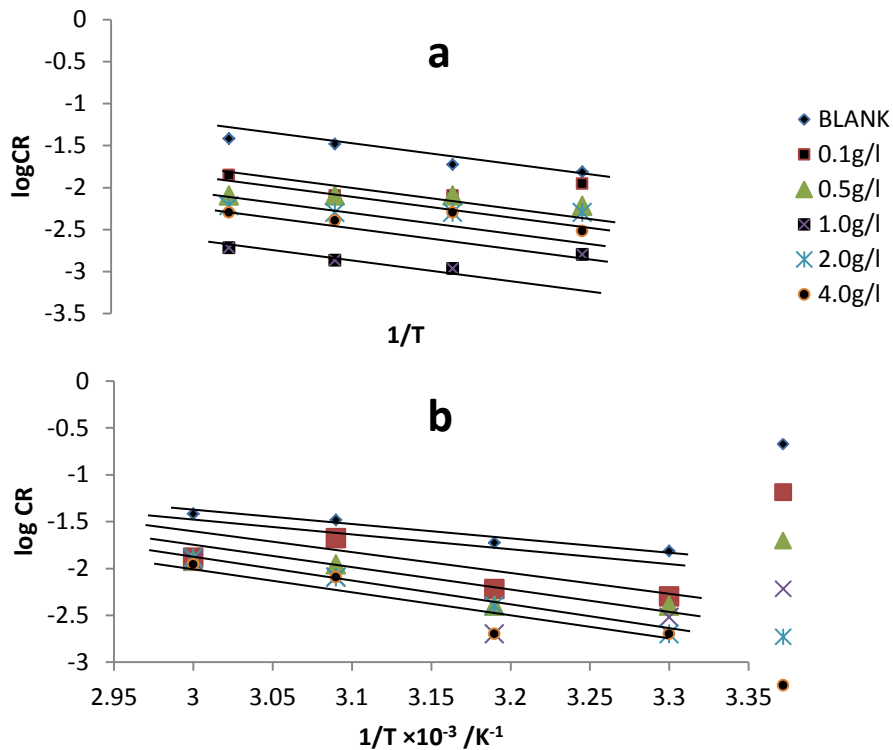


Fig 10: Arrhenius plot for the corrosion of mild steel in the presence and absence of (a) NAEPA and (b) AEPA

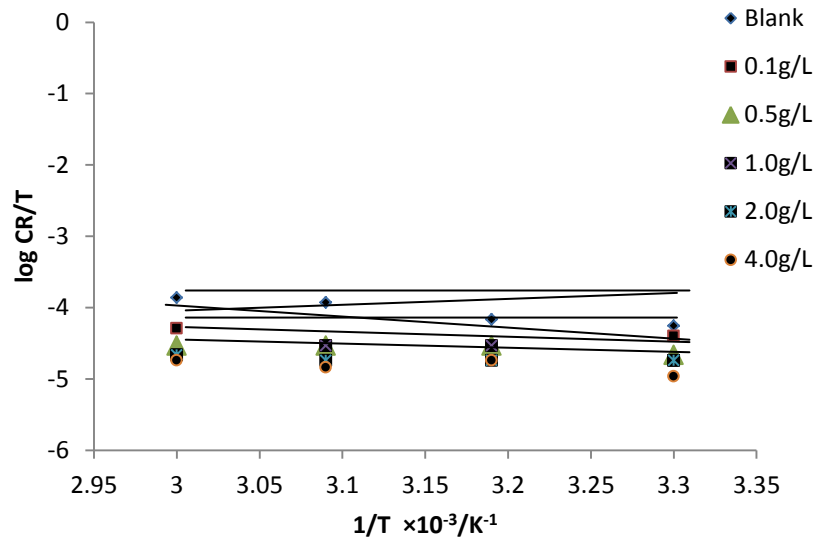


Fig. 11: Transition state plot for the corrosion of mild steel in the presence of non- alkaloid extract of *Phyllanthus amarus*.

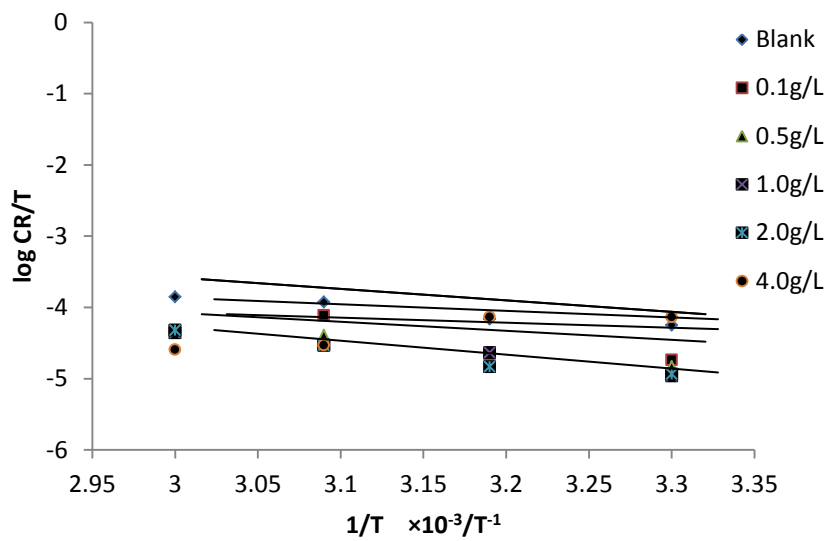


Fig. 12: Transition state plot for the corrosion of mild steel in the presence of alkaloid extract of *Phyllanthus amarus*.

CONCLUSION

Non-alkaloid and alkaloid extracts of *Phyllanthus amarus* was found to be good corrosion inhibitors for mild steel in HCl. Inhibition efficiency (%) of the extracts increased with an increase in concentration of extracts. The experimental data obtained from adsorption of NAEPA and AEPA can be approximated by the Langmuir adsorption isotherm. The non-alkaloid extract of *Phyllanthus amarus* are chemically adsorbed on the mild steel surface hence defining its suitability for high temperature systems. The alkaloid fractions *Phyllanthus amarus* are physically adsorbed on the metal surface. The difference in adsorption mechanism is attributed predominantly to the difference in the phytochemical constituents of the fractions. This study provides new information on the inhibiting characteristics of *Phyllanthus amarus* extract which could find application in metal surface coating industries.

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