Int. J. Electrochem. Sci., 8 **(2013)** 7455 - 7467

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Alkaloid and Non-Alkaloid Ethanolic Extracts from Seeds of *Garcinia Kola* as Green Corrosion Inhibitors of Mild Steel in H_2SO_4 Solution

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Received: 2 March 2013 / *Accepted:* 9 April 2013 / *Published:* 1 May 2013

The inhibitive effects of the extracts of *Garcinia kola* seeds: ethanolic (EEGK), alkaloid ethanolic (AEGK) and non alkaloid ethanolic (NEGK) on the corrosion of mild steel in sulphuric acid medium was investigated using the hydrogen evolution (via gasometric assembly) and the weight loss methods at 307- 373 K. The extracts were found to inhibit mild steel corrosion to different extents in the following order AEGK > EEGK > NEGK. The inhibition efficiency increased with increase in the concentration of the inhibitors and decrease in temperature. A phenomenon of physical adsorption is proposed for the inhibition from the trend of inhibition efficiency with temperature, E_a and ΔG_{ads} values, and the process followed the Langmuir adsorption isotherm.

Keywords: Alkaloids, Non- alkaloids, Ethanolic, Mild steel, Corrosion Inhibitors, Plant extract, Acid corrosion

1. INTRODUCTION

The study of mild steel corrosion is of theoretical and practical importance. Mild steel is used in the industries for the fabrication of engineering materials, reaction tanks, vessels, and pipes etc. which get easily corroded in the presence of acids. Acids come in contact with these materials during the process of cleaning, pickling or descaling. Inhibitors which are mostly synthetic and toxic are usually introduced into the system to deter or inhibit the corrosion process. The search for eco friendly inhibitor is the major pivot for the use of natural products as environmentally friendly inhibitors. The inhibition of corrosion of mild steel by plant extracts has been investigated in recent times. Plant extracts have been found to generally exhibit good inhibition efficiencies [1-3]. From the results it was found that the extent of inhibition generally increases with increase in plant extract concentration.

The natural products like tannins, lignin and alkaloids have been evaluated as very effective acid corrosion inhibitors in standard as well as in stringent conditions [4]. The inhibitive action of ethanol extracts from *Garcinia kola* for the corrosion of mild steel in H_2SO_4 solutions has been investigated by Okafor *et al.* [5] using hydrogen evolution technique. Results obtained indicate that the extract inhibits corrosion of mild steel in acidic medium and that the inhibition efficiency increases with increase in the concentration of the extracts and decreasing temperature. However, the associated alkaloids and non-alkaloids have not been investigated to clearly assign the inhibitive property to a given active agent in the plant. In the present work the effects of the ethanol extracts from *Garcinia kola* seeds (EEGK) and its associated alkaloid (AEGK) and non alkaloid (NEGK) components of the ethanol extracts in 5 M H_2SO_4 solutions were studied at 307, 323, 333 and 343K using gravimetric and volumetric techniques.

2. EXPERIMENTAL

2.1. Materials Preparation

The mild steel sheets used in this work were obtained from Ejison Resources (Nigeria) Ltd, Calabar. This has the composition as previously described by Okafor *et al.* [5]. The mild steel coupons were mechanically polished with series of Emery paper of variable grades starting with the most coarse and proceeding in steps to the finest (600) grade. These polished coupons were degreased with ethanol, dried with acetone and weighed. The weighed coupons were then used for analysis. The weight loss and hydrogen evolution analyses were conducted with mild steel coupons of dimensions 4.0 x 0.08 x 5.0 cm and 4.0 x 0.08 x 1.2 cm respectively. All the experimental solutions were prepared with distilled water. All the chemicals used were Analar grade and all weighing were done with AE ADAM PGW 253e digital analytical balance.

2.2. Preparation of the plant seed extracts

The seeds of *Garcinia kola* were bought from a local market in Calabar, Nigeria. These were cut into small chips and dried in an N53C – Genlab laboratory oven at 50^{o}C. The dried chips were ground into powder form. 100 g of the powder was extracted continually with 250 cm^3 of absolute ethanol in a Soxhlet extractor for 24 hours. The extract was heated in a water bath at 60^{o}C until almost all of the ethanol evaporated.

20 g of the ethanol extract was dissolved in 2 L of 5.0 M H_2SO_4 solution, agitated vigorously and kept overnight (24 hours). The resultant solution was filtered and stored. This stock solution (10 g/L) was used as the ethanol extract (EEGK) for weight loss measurements. The test solutions for the

inhibitor were prepared by serial dilution of the stock solution to concentrations of 0.5, 1.0, 2.0, 3.0, 5.0 and 7.5 g/L.

20 g of the ethanol extract was partitioned between 100 mL 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 (NEGK).

The float from the separating funnel above was further basified with 100 mL of ammonia and partitioned with 100 mL of chloroform to obtain the alkaloid extract (AEGK). 5 g of the alkaloid and non alkaloid extracts (AEGK and NEGK) were soaked in 0.5 litre of 5.0 M H_2SO_4 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; 0.5, 1.0, 2.0, 3.0, 5.0 and 7.5 g/L were prepared. These solutions were then used for the corrosion test.

2.3. Weight loss technique

Weighed mild steel coupons were suspended in a beaker containing 100 mL of the test solution with the aid of glass rods and hooks at room temperature. The mild steel coupons were completely immersed in the test solutions and retrieved every hour for 5 hours for the 4.0 x 0.08 x 5.0 cm coupons and at the end of the hydrogen evolution measurements for the 4.0 x 0.08 x 1.2 cm coupons. The retrieved coupons were washed, scrubbed with a bristle brush, under fast flowing water, rinsed in absolute ethanol, dried using acetone, re-weighed 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 weight of the coupon. The same experimental treatment was carried out for the EEGK, NEGK and AEGK using concentrations of 0.5, 1.0, 2.0, 3.0, 5.0 and 10 g/L at ambient temperature. The elevated temperature weight loss measurements were carried out with coupons of dimensions given above in reaction chamber maintained at a steady temperature for 303, 323, 333 and 343 ± 2K. The rates were obtained from the slope of the trend line of the graph of weight loss against time and the inhibition efficiency was calculated using equation 1

$$IE = \frac{R_b - R_i}{R_b} x 100 \qquad 1$$

where R_b and R_t are corrosion rates of the mild steel without and with inhibitors respectively [6].

2.4. Hydrogen evolution technique

In the gasometric measurements the volume of hydrogen evolved was determined following procedures previously described [3-5, 7-11]. 100 mL of the corrodent was introduced into the reaction chamber, connected to a burette through a delivery tube. Two weighed mild steel coupons were dropped into the solution in the chamber and the reaction vessel was quickly closed to avoid any escape of hydrogen gas. The volume of the hydrogen gas evolved from the reaction was monitored by the depression (in mL) in the level of paraffin oil. This depression in the paraffin oil level was recorded every minute for 40 minutes at ambient temperature. The same experiment was repeated in the presence of the inhibitor with concentrations of 0.5, 1.0, 2.0, 3.0, 5.0, 7.5 and 10.0g/L for the different extracts from *Garcinia kola* (EEGK, AEGK and EEGK). The same procedure was repeated at elevated temperatures of 323, 333 and 343 ± 2 K. The weight loss of the mild steel coupons after retrieval from the hydrogen evolution chamber was also calculated and used for gravimetric analysis. The inhibition efficiency was calculated using equation 1.

The rate for the hydrogen evolution was obtained from the slope of the trend line of the graph of volume of hydrogen evolved against time. The rate for the weight loss measurements were obtained using equation 2

3. RESULTS AND DISCUSION

Experiments were performed with different concentrations of the inhibitors. The corrosion rate, surface coverage and inhibition efficiency for mild steel in 5 M H_2SO_4 solution at 307, 323, 333 and 343 K in the absence and presence of EEGK, AEGK and NEGK from hydrogen evolution data are given in the Table 1.

Table 1. Rate of hydrogen evolution, surface coverage and inhibition efficiency of mild steel in 5 M H_2SO_4 with and without different concentrations EEGK, AEGK and NEGK using the gasometric method. IE for weight loss in bracket.

Extract	Conc. (g/L)	Rate of hydrogen evolution (cm/min)				Surface Coverage, θ				Inhibition efficiency, IE (%)			
		307 K	323 K	333 K	343 K	307 K	323 K	333 K	343 K	307 K	323 K	333 K	343 K
EEGK	Blank	0.034	0.153	0.339	0.592	-	-	-	-	-	-	-	-
	0.5	0.02	0.109	0.245	0.472	0.411	0.287	0.277	0.202	41.1 (30.3)	28.7 (27.6)	27.7 (27.3)	20.2 (24.8)
	1.0	0.017	0.072	0.2	0.422	0.5	0.529	0.411	0.287	50 (46.5)	52.9 (46.3)	41.1 (44.0)	28.7 (26.2)
	2.0	0.012	0.06	0.135	0.24	0.647	0.604	0.601	0.594	64.7 (53.5)	60.4 (54.1)	60.1 (53.6)	59.4 (42.0)
	3.0	0.012	0.045	0.117	0.233	0.647	0.705	0.654	0.606	64.7 (59.7)	70.5 (55.6)	65.4 (56.1)	60.6 (46.3)
	5.0	0.009	0.043	0.103	0.228	0.735	0.719	0.696	0.614	73.5 (59.7)	71.9 (62.7)	69.6 (57.9)	61.4 (49.1)
	7.5	0.009	0.036	0.097	0.213	0.735	0.764	0.713	0.639	73.5 (65.7)	76.4 (55.6)	71.3 (53.6)	63.9 (50.3)
	10.0	0.007	0.027	0.076	0.169	0.794	0.823	0.775	0.714	79.4 (67.5)	82.3 (70.0)	77.5 (62.5)	71.4 (53.2)
NEGK	0.5	0.014	0.085	0.183	0.482	0.603	0.444	0.46	0.186	60.3 (28.7)	44.4 (26.9)	46 (26.9)	18.6 (21.5)
	1.0	0.013	0.074	0.167	0.477	0.618	0.516	0.507	0.194	61.8 (51.2)	51.6 (36.7)	50.7 (29.2)	19.4 (22.6)
	2.0	0.012	0.082	0.152	0.371	0.647	0.464	0.552	0.373	64.7 (52.3)	46.4 (34.6)	55.2 (30.6)	37.3 (38.5)

	3.0	0.011	0.062	0.12	0.281	0.677	0.595	0.646	0.525	67.7 (53.5)	59.5 (52.7)	64.6 (46.8)	52.5 (38.5)
	5.0	0.011	0.072	0.114	0.224	0.677	0.529	0.664	0.622	67.7 (58.2)	52.9 (54.5)	66.4 (43.7)	62.2 (44.9)
	7.5	0.009	0.048	0.108	0.178	0.735	0.686	0.681	0.699	73.5 (57.0)	68.6 (51.4)	68.1 (47.9)	69.9 (46.1)
	10.0	0.008	0.047	0.082	0.168	0.762	0.693	0.758	0.716	76.2 (64.7)	69.3 (64.2)	75.8 (62.8)	71.6 (52.8)
AEGK	0.5	0.008	0.031	0.172	0.237	0.765	0.797	0.493	0.6	76.5 (78.5)	79.7 (58.8)	49.3 (73.0)	60 (50.2)
	1.0	0.005	0.021	0.15	0.15	0.853	0.863	0.558	0.747	85.3 (88.1)	86.3 (90.7)	55.8 (82.9)	74.7 (58.9)
	2.0	0.002	0.015	0.029	0.06	0.941	0.902	0.915	0.899	94.1 (88.6)	90.2 (96.1)	91.5 (97.2)	89.9 (67.5)
	3.0	0.001	0.013	0.026	0.02	0.975	0.915	0.923	0.966	97.5 (94.4)	91.5 (94.6)	92.3 (93.4)	96.6 (70.8)
	5.0	0.001	0.009	0.012	0.017	0.977	0.941	0.965	0.971	97.7 (98.6)	94.1 (89.1)	96.5 (94.4)	97.1 (97.6)
	7.5	0.001	0.008	0.006	0.011	0.991	0.948	0.982	0.981	99.1 (98.8)	94.8 (98.5)	98.2 (95.9)	98.1 (97.7)
	10.0	0.001	0.007	0.005	0.011	0.994	0.954	0.985	0.982	99.4 (98.8)	95.4 (98.0)	98.5 (97.2)	98.2 (97.3)

From the results obtained from Table 1 it can be seen that as the concentration of the extracts increases, the rate of corrosion decreases, surface coverage increases and inhibition efficiency increases. The highest inhibition efficiencies for EEGK, AEGK and NEGK obtained at 10 g/L are 70.0%, 98.8% and 64.7%, respectively at an inhibitor concentration of 10g/L for the weight loss method. Similar trend was observed for the hydrogen evolution technique as shown in Table 2 with the highest inhibition efficiencies for EEGK, AEGK and NEGK obtained at 10 g/L are 82.3%, 99.4% and 76.2% respectively. The order for the corrosion rate in the presence of the inhibitor for the extracts is AEGK<EEGK<NEGK. The order for the surface coverage and inhibition efficiency followed the opposite trend AEGK>EEGK>NEGK as shown in Table 1. The values of the inhibition efficiency obtained indicate that AEGK is a good corrosion inhibitor for mild steel while EEGK and NEGK are relatively good. The results obtained suggest that the alkaloid component of *Garcinia kola* is predominantly responsible for the inhibitive properties of the plant extracts. The decrease in inhibition efficiency with temperature for the inhibitors suggests a physical interaction between the inhibitor and the metal surface. The higher value for I E of AEGK suggests an antagonistic kind of relationship between the natural products in G. *kola.* The lower inhibition efficiencies for the EEGK and NEGK may be attributed to intermolecular interactions such as weak vanderwaal force of attraction, hydrogen bonding, and dipole - dipole attractions between the active principles present in the extract. Such interactions may involve consumption of electron pairs on the molecular active sites. This in turn leads to the unavailability of electron pair on the hetero atom for bonding to the metal surface. The higher inhibition efficiency of EEGK over NEGK indicates that nitrogenous heterocyclic compounds are predominantly responsible for in the inhibitive action of G. *kola.*

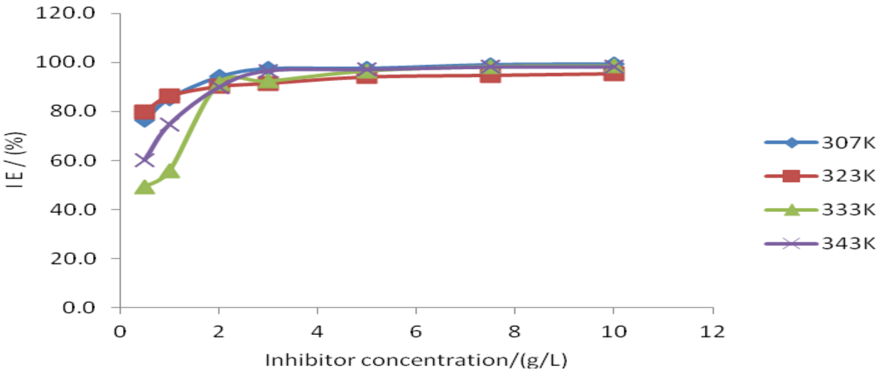

Figure 1. Variation of inhibition efficiency of different concentrations AEGK for mild steel in 5 M H_2SO_4 at different temperatures.

Fig 1 shows the variation of inhibition efficiency with temperature for AEGK at different extract concentration. A leveling off is observed at high inhibitor concentration indicating greater coverage of the metal surface. Similar plots (not shown) were obtained for EEGK and NEGK for both hydrogen evolution and weight loss methods.

3.1. Kinetics of the Process

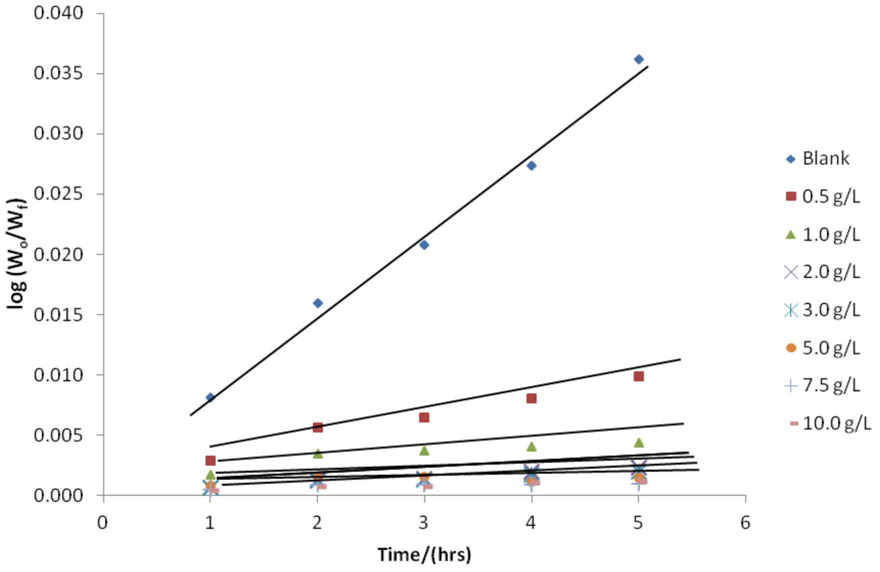

Figure 2. Plot of Log (W_o/W_f) against time for mild steel in 5 M H_2SO_4 solution in the absence and presence of AEGK at 307 K

A plot of the logarithm of measured weight mild steel after post treatment against time as depicted in Fig .2 helps to explain the kinetics of the corrosion of mild steel in the presence and absence of the inhibitors. Fig. 2 shows that a linear variation is observed from the plot both in the presence and absence of the plant extracts. The first order integrated rate law was tested to determine if it fits experimental data. The experimental data fitted well into the equation 3.

$$\log\left(\frac{W_o}{W_f}\right) = kt \qquad 3$$

where W_f and W_o are weight in grams after post treatment of coupons and initial weight before immersion respectively, k is the rate constant and t is the time in hours [5].

The values of the rate constants obtained from the slope in Fig. 2 are presented in Table 2. The half life for the dissolution of mild steel in the acid solution in the presence and absence of the inhibitors were calculated using equation 4:

$$T = \frac{\ln 2}{K} \qquad 4$$

From Table 2 it can be seen that there is a tremendous increase in the value of the half life for the reaction for the alkaloid extracts from *Garcinia kola* confirming the efficacy of alkaloid active principles in the phytochemicals present in the extract. The increase in the half life of the mild steel corrosion in the presence of the alkaloids extracts to a value of 6930 hours compared with the maximum values of the half life in the presence of EEGK and NEGK (693 and 231 hours respectively) indicates that AEGK is a more efficient corrosion inhibitor in H_2SO_4 solution.

Table 2. Corrosion rate, R_c (in mg/cm^2/hr), rate constant, k (in hr^{-1}) and half life $t_{1/2}$ (in hrs) for mild steel in 5 M H_2SO_4 in the absence (blank) and presence of different concentrations of Extracts of *Garcina kola* at 307 K (EEGK, AEGK and NEGK)

Inhibitor Conc. (g/L)	EEGK				AEGK			NEGK		
	c	I $*10^{-3}$	K 1/2	t c	I $*10^{-3}$	K 1/2	t c	l $*10^{-3}$	K 1/2	t
Blank	.730	3 .0	7 9.0	9 .558	3 .0	7 9.0	9 .730	3 .0	7 9.0	9
0.5	.736	2 .0	5 38.6	1 .875	0 .0	1 93.0	6 .615	3 .0	6 15.5	1
1.0	.278	2 .0	4 73.3	1 .308	0 .5	0 386.0	1 .511	3 .0	6 15.5	1
2.0	.916	1 .0	3 31.0	2 .217	0 .4	0 732.5	1 .185	3 .0	5 38.6	1
3.0	.850	1 .0	4 73.3	1 .167	0 .3	0 310.0	2 .799	2 .0	5 38.6	1
5.0	.136	1 .0	5 93.0	6 .058	0 .1	0 930.0	6 .557	2 .0	4 73.3	1
7.5	.387	1 .0	2 46.5	3 .054	0 .1	0 930.0	6 .046	2 .0	3 31.0	2
10.0	.332	1 .0	3 31.0	2 .010	0 .1	0 930.0	6 .853	1 .0	3 31.0	2

From the graph of half life against the inhibitor concentration as shown in Fig 3 the following linear equations (5, 6 and 7) were obtained from the trend line of the plots.

$$t_{\frac{1}{2}} = 776.0\, c_a + 563 \qquad (5)$$

$$t_{\frac{1}{2}} = 22.5\, c_e + 178 \qquad (6)$$

$$t_{\frac{1}{2}} = 14.1.0\, c_n + 104 \qquad (7)$$

where $t_{1/2}$ is the half life for the corrosion of mild steel in 5 M H_2SO_4 , c_a , c_e , and c_n are the concentrations of AEGK, EEGK and NEGK, respectively. Equations 5, 6 and 7 can be used to estimate the half life for the corrosion of mild steel in different concentrations of the inhibitors.

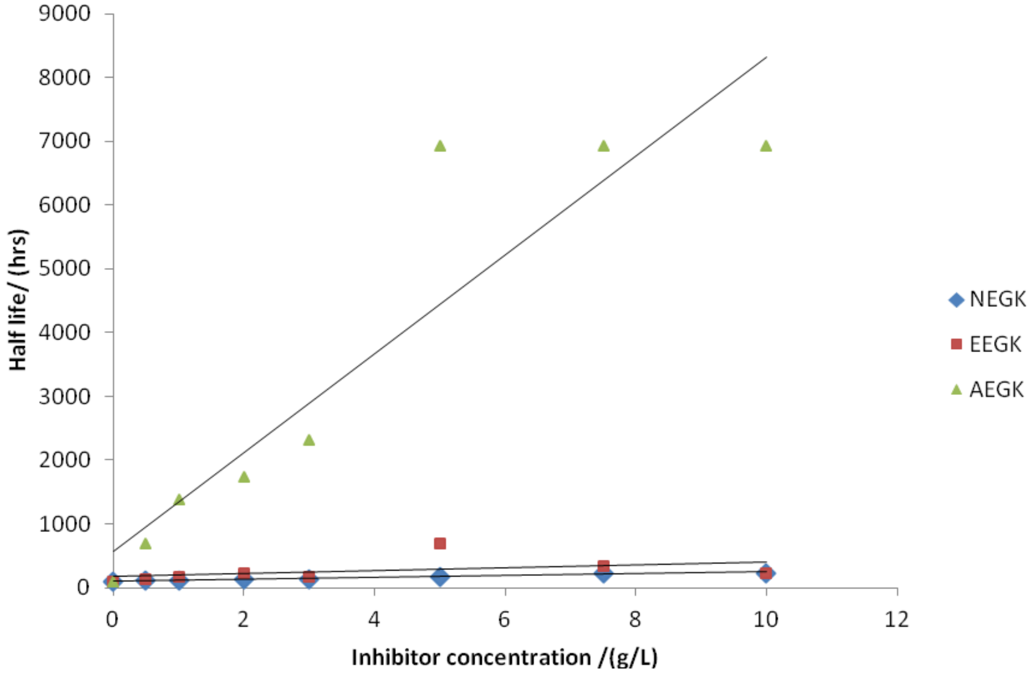

Figure 3. Plot of half life versus inhibitor concentration for the corrosion of mild steel coupons in 5 M H_2SO_4 in the absence and presence of different concentrations of EEGK, NEGK and AEGK at 307K

The coefficients of c_a , c_e , and c_n is the rate of increase in half life with concentration for the mild steel which is a measure of inhibition efficiency. The minimum inhibitor concentration (MIC) value which is the minimum amount of inhibitor that must be present for inhibition to occur in $1 cm^2$ surface at a given temperature were calculated using equations 5, 6 and 7 by substituting the value for the blank (99 hrs) into the equations and solving for the c values. Negative values where obtained for c_a , c_e , and c_n (-0.59, -3.55, and -0.3769, respectively). Negative values when compared to the expected ideal value of 0 for the MIC indicates that there were no inhibitor molecules on the surface of the metal in the blank analysis, it also indicates that a very minute amount of the inhibitor would probably cause an obvious increase in the half life of the mild steel in the acid solution. This also indicates that the extracts are good corrosion inhibitors for mild steel. MIC values greater than zero implies that little amount of the inhibitor does not cause any significant increase in half life, hence an indication of a relatively bad inhibitor.

3.2. Thermodynamic considerations

The activation energies (E_a) for the corrosion of mild steel in the absence and presence of different concentrations of the plant extracts were calculated using Arrhenius-type equation.

$$\ln R_c = \ln A - \frac{E_{ai}}{RT} \qquad 8$$

where E_a is the activation energy, R is universal gas constant, A is the Arrhenius pre-exponential factor, T is absolute temperature and R_c is corrosion rate.

Table 3. Thermodynamic parameters for the corrosion of mild steel in 5 M H_2SO_4 solution in the absence and presence of different concentration of the inhibitors.

Inhibitor	Conc (g/L)	Thermodynamic parameters					
		Ea (kJ/mol)	ΔS* (J/K/mol)	ΔH* (kJ/mol)	Ea- ΔH* (kJ/mol)	Ea(ads) (kJ/mol)	ln A
EEGK	Blank	70.38	169.01	67.68	2.69	-	24.25
	0.5	77.43	187.71	74.74	2.69	7.05	26.50
	1.0	78.98	190.62	76.29	2.69	8.61	26.85
	2.0	73.72	171.42	71.03	2.69	3.34	24.54
	3.0	73.01	168.26	70.32	2.69	2.63	24.16
	5.0	78.73	184.80	76.04	2.69	8.36	26.15
	7.5	77.58	180.56	74.88	2.69	7.20	25.65
	10.0	78.12	180.15	75.42	2.69	7.74	25.59
NEGK	0.5	85.96	211.91	83.26	2.69	15.58	29.41
	1.0	87.23	212.74	83.71	3.53	16.85	29.50
	2.0	82.23	199.27	79.53	2.69	11.85	29.51
	3.0	77.89	184.14	75.21	2.69	7.52	27.89
	5.0	72.44	167.09	69.75	2.69	2.06	24.03
	7.5	73.84	169.59	71.15	2.69	3.46	24.32
	10.0	73.03	166.18	70.34	2.69	2.65	23.91
AEGK	0.5	87.90	213.15	85.21	2.69	17.53	29.56
	1.0	90.66	218.56	87.97	2.69	20.29	30.21
	2.0	82.43	185.38	79.74	2.69	12.06	26.22
	3.0	81.42	177.73	78.73	2.69	11.04	25.30
	5.0	74.43	153.37	71.73	2.69	4.05	22.38
	7.5	84.50	179.65	81.80	2.70	14.13	25.54
	10.0	92.82	203.67	90.12	2.69	22.44	28.42

Calculated from gasometric data

The values of E_a were evaluated from the slope of the plots of R_c versus 1/T (not shown) and it is given in Table 3. The enthalpy of activation (ΔH*) and the entropy of activation (ΔS*) for the corrosion of mild steel in H_2SO_4 was estimated using the transition state equation.

$$R_c = \frac{KT}{h}\exp\left(\frac{\Delta S^*_i}{R}\right)\exp\left(\frac{-\Delta H^*_i}{RT}\right) \qquad 9$$

where *K* is the Boltzmann constant, *h* is the Planck constant, *A* is Arrhenius pre-exponential factor, *T* is the absolute temperature and R_c is corrosion rate. The values of ΔH^* and ΔS^* obtained are given in Table 3.

The activation energies of adsorption E_{ads} for EEGK, NEGK and AEGK calculated from equation 9 [11] are listed in Table 3

$$E_{a(ads)} = E_{a(system)} - E_{a(blank)}. \qquad 10$$

$E_{a(blank)}$ is the apparent activation energy in the absence of the inhibitor, $E_{a(system)}$ is the apparent activation energy in the presence of the inhibitor and $E_{a(ads)}$ is the apparent activation energy of adsorption.

The data in Table 3 indicates that the addition of EEGK leads to increase in E_a and ΔH^* to values greater than that of the free solution. The average difference value of $(E_a\text{-}\Delta H^*)$ is 2.69 KJ/mol which is approximately equal to the value of RT (i.e. 8.314 x 326.5 = 2.71 KJ/mol) at the average temperature studied. This result agrees that the corrosion process is uni-molecular reaction defined by the perfect gas equation given by equation 11:

$$E_a - \Delta H^* = RT \qquad 11$$

Positive values of enthalpies ΔH^* reflect endothermic nature of mild steel dissolution. The presence of inhibitors increases ΔH^* and the reaction become more endothermic when compared to blank. Large and positive values of entropies show that the activated complex in the rate determining step represents a dissociation step meaning that an increase in disordering takes place on going from reactants to the activated complex. Positive values for ΔS also indicate spontaneity of the adsorption process.

3.3. Adsorption isotherm behaviour

The inhibition process is generally related to adsorption of inhibitor species unto the metallic surface. In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of the inhibitors. The Langmuir theory allows the most basic presentation of adsorption on an ideal surface. The Langmuir adsorption isotherm may be written in the form:

$$\frac{c}{\theta} = \frac{1}{k} + c \qquad 12$$

where *c* is the concentration of the inhibitor, *k* is adsorption equilibrium constant and θ is surface coverage [6]..

The relationship between *c*/θ and *c* gives a linear behaviour at all temperatures studied for EEGK, NEGK, and AEGK as shown in the Figure 4 (for AEGK and EEGK).

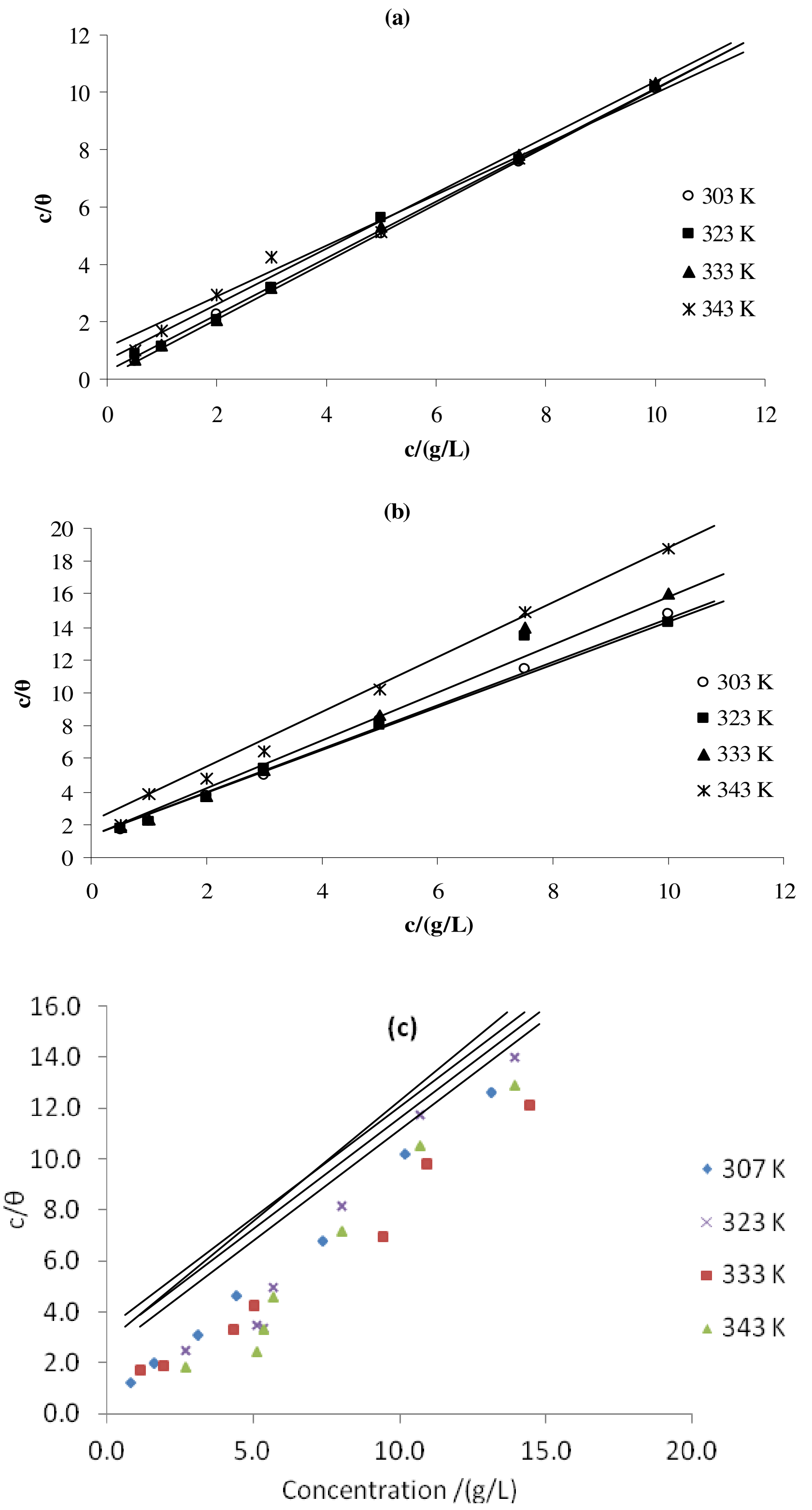

Figure 4. Langmuir adsorption isotherm for mild steel in 5 M H_2SO_4 containing (a) AEGK , (b) EEGK and (c) NEGK at different temperature

The values of the adsorption rate constant *k* from the isotherm and the correlation factors *R* were also estimated from the plot are presented in Table 4.

Table 4. Langmuir adsorption constant, Gibbs free energy and correlation factors for the corrosion of mild steel in 5M H_2SO_4 inhibitors at different temperatures

Temperature (K)	EEGK			NEGK			AEGK		
	k (L/g)	ΔG (kJ/mol)	R^2	*k* (L/g)	ΔG (kJ/mol)	R^2	*k* (L/g)	ΔG (kJ/mol)	R^2
303	1.08	-11.67	0.998	1.15	-11.85	0.991	5.74	-16.44	0.999
323	0.98	-11.4	0.973	0.6	-10.01	0.966	4.43	-15.69	0.997
333	1.25	-12.1	0.998	0.42	-9.03	0.939	6.66	-16.86	0.999
343	0.68	-10.37	0.996	0.46	-9.26	0.989	-	-	1

The correlation factors *R* for the temperature range studied ranged from 0.973 to 0.999. This suggests a deviation from Langmuir theory of adsorption. From the *k* values, the standard adsorption free energy ΔG_{ads} values (shown in Table 4) were obtained using the equation:

$$k = \frac{1}{55.5}\exp\frac{-\Delta G_{ads}}{RT} \qquad 13$$

The *k* values of the rate constants obtained and that of the standard free energy of adsorption ΔG_{ads} (Table 3) followed the same trend as the inhibitor efficiency AEGK > EEGK > NEGK. This suggests that the thermodynamically favored inhibitor is the AEGK. Negative values of ΔG_{ads} indicate spontaneity and stability of the adsorption layer. The values of the free energy obtained which were below -40kJ/mol also suggests a physical adsorption mechanism for adsorption of the inhibitor on the mild steel surface in H_2SO_4 solution.

4.CONCLUSIONS

The following conclusions have been drawn from the results of the study: .

1. Ethanolic extracts of *Garcinia kola* seeds (EEGK) and its associated alkaloid (AEGK) and non alkaloid (NEGK) ethanolic components are good corrosion inhibitors for mild steel in H_2SO_4 solution.
2. The inhibition efficiency of EEGK, NEGK and AEGK increases with increase in extract concentration and decrease in temperature and is in the order AEGK > EEGK > NEGK
3. The extracts (EEGK, NEGK and AEGK) 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 follows Langmuir adsorption isotherm which deters the endothermic monoatomic dissolution of mild steel in H_2SO_4 solution.

4. The inhibition properties of *Garcinia kola* seeds may be attributed predominantly to the alkaloid active principles present in the extract which adsorb on the metal surface via its basic nitrogen.
5. There is a probable intermolecular interaction between active principles present in the extracts of *Garcinia kola* which deters the rate of adsorption of the alkaloids on the mild steel surface.
6. Trace amounts of the inhibitors in the system would cause a significant increase in half life of mild steel in H_2SO_4 solution as is evident from the MIC values for these inhibitors.

ACKNOWLEDGEMENTS
Bertha O. Nkwocha is acknowledged for assistance in taking some measurements and Prof, F. N. I. Morah is acknowledged for fruitful discussion on the extraction and chemistry of alkaloids.

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