

## **Acid Extract of *Aloe vera* as Corrosion Inhibitor for the Corrosion of Mild Steel in Acidic Media.**

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### **ABSTRACT**

The corrosion inhibition of mild steel in *Aloe vera* extract (AVE) medium at 30 – 60°C , 0.1 - 0.5M acids (HCl and HNO<sub>3</sub>) and 0.01-0.03g/l AVE were investigated by standard weight loss method. The corrosion rate was calculated in the absence and presence of the inhibitor. The inhibition efficiencies of AVE in both acid media increase with increase in concentration and decrease with increase in temperature and period of immersion. The corrosion inhibitory effect of AVE was very insignificantly greater in HCl phase than in HNO<sub>3</sub> phase for identical conditions. The results showed that acid of AVE is adsorption inhibitor and inhibition efficiency of up to 77.32% could be obtained. Values of the activation energy obtained for the extract based media are greater than that of the blank. Thermodynamics results indicate that corrosion adsorption of AVE on mild steel surface was spontaneous, physically controlled and occurred according to Langmuir adsorption isotherm ..

**Keywords:** Corrosion, Inhibition, Mild steel, *Aloe vera*, HCl, HNO<sub>3</sub>.

### **INTRODUCTION**

Metal consumption of many countries increases with technological and economic development. However, destruction of metals by environmental factors is the main problem for industrial companies. Metals and alloys that come into contact with water are susceptible to corrosion, because of their thermodynamics instability in the cooling system [1]. The common approach for corrosion protection is to use only durable materials. However, this approach involves huge cost and investment. The use of local inhibitors is one of the best methods of protecting metals against corrosion at a relatively

low cost [2]. An inhibitor can be chosen from compounds that have heteroatom in their aromatic ring system or synthesized from cheap raw materials [3]. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors [4]. Most of the natural products are non-toxic, cheap, biodegradable and readily available in abundance [5].

The protective efficiency is based on the adsorption ability of their molecules, where the resulting adsorbed film acts as a barrier separating the metal from the corroding medium. According to Oguzie [2], the inhibitor acts as the interphase created by corrosion product between the metal and aqueous corroding solution. Thus, the nature of inhibitor interaction with the metal and efficiency may be dependent on the chemical, mechanical and structural characteristics of this adsorbed film layer [2]. The extent of inhibition depends [6- 8] on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor and the type of corrosion media.

The inhibitor under investigation is the acid extract of *Aloe vera* (AV). *Aloe vera* is from plant kingdom, a member of Asphodelaceae family and order of Asparagales [9]. AV is a specie of succulent plant that probably originated from Northern Africa, the Canary Islands and Cape Verde. *Aloe vera* grows in arid climates and is widely distributed in Africa, India and other arid areas. The species are frequently cited as being used in herbal medicine. Many scientific studies on the use of *Aloe vera* have been undertaken, some of them conflicting. Despite these limitations, there is some preliminary evidence that AV extracts may be useful in the treatment of wound and burnt healing, diabetes, elevated blood lipids in humans and corrosion inhibition for materials.

The aim of the present work is to investigate a naturally occurring, cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel in acidic media.

### *Sample preparation*

Mild steel sheet ( <0.25% carbon and dimensions: 5cm x 3cm x 0.01cm) with elemental analysis shown in table 1, was mechanically press-cut to different coupons to reduce the cold working effect of the sheared edges. Subsequently, each of the coupons was polished, drilled at one end and numbered by punching. The samples were polished with 400 grade emery papers and degreased in ethanol. The washed samples were dipped in acetone, removed and allowed to dry in air before use [10]. All reagents used for the study were analar grade and distilled water was used for their preparation

**Table 1:** Analysis of the experimental mild steel with ARL 3460 metal analyser

Parameter	Symbols	Composition (wt %)
Iron	Fe	90.42
Lead	Pb	0.73
Zinc	Zn	Nil
Copper	Cu	2.08
Manganese	Mn	0.02
Phosphorus	Pb	1.31
Sulphur	S	2.5
Fixed Carbon	C	0.94

## ***Extraction of Aloe vera extract(AVE)***

10g, 20g and 30g samples of Aloe vera leaves were weighed, grounded and soaked into various 500ml of HCl and HNO<sub>3</sub> at 0.1, 0.3 and 0.5M concentrations. The mixture was left for 48hours and resultant filtrate made up to 500ml using the various corresponding acid concentrations.

## ***Phytochemical Analysis***

Phytochemical analysis of the extract was carried out according to the method reported by standard methods[8-10,19].

## **Corrosion weight loss measurment**

Weighed samples of mild steel were immersed completely in 100ml of the test media for 5days. The mild steel specimens were taken out of the solution every 24hours. After the test, any corrosion product(s) on the coupon were removed by cleaning in water, washing in liquor and drying in acetone. The mild steel samples were reweighed and the weight lost taken as the difference between the initial and final weights. The rate of corrosion ( $\text{gcm}^{-2}\text{hr}^{-1}$ ), surface coverage and inhibition efficiency(%) were calculated using equations1, 2, and 3, respectively expressed below:

$$\text{CR} = \frac{W_1 - W_2}{AT} \quad (1)$$

$$\theta = 1 - \frac{W_s}{W_b} \quad (2)$$

$$\text{IE}\% = 1 - \frac{W_s}{W_b} \times 100 \quad (3)$$

where

$W_1$  = initial weight (g),  $W_2$  = final weight (g),  $A$ = Area of the coupon ( $\text{cm}^2$ ),  $T$  = exposure time (hours),  $W_s$  is coupon weight loss in solution with inhibitor.  $W_b$  is the

coupon weight loss in solution without inhibitor,  $\theta$  = surface coverage, IE(%) = inhibition efficiency, CR = corrosion rate ( $\text{gcm}^{-2}\text{hr}^{-1}$ ).

The variable parameters used for the present study are given below:

Acid Concentrations: 0.1, 0.3 and 0.5M

Inhibitor Concentrations: 0.01, 0.02 and 0.03g/l

Temperatures: 303, 313 and 333K

Times: 24, 48, 72, 96 and 120hours

## RESULTS AND DISCUSSIONS

### *Phytochemical Analysis of Aloe vera extract*

This analysis shown in table 2 was carried out to determine the quantitative values of the phytochemicals present in the AVE. The composition indicates that AVE contains condensed tannins, alkaloids, anthocyanins, flavonoids and steroids. All these constituents combined to form the inhibitory properties of the sample. It could be attributed that the inhibition efficiency of the extract is due to the presence of some or all of the above listed phytochemical constituents. Eddy and Ebenso [3] also stated that saponins, tannins and alkaloids are active constituents of most green inhibitors.

**Table 2:** Phytochemical characteristics of *Aleo vera* extract in gram percent.

S/No	Phytochemical	gram %
1	Alkaloids	0.18
2	Anthocyanins	1.2
3	Flavonoids	1
4	Condensed Tannins	0.19
5	Steroids	0.06

### *Temporal effects of inhibitor / acid concentrations and temperature on CR and IE.*

Figures 1 and 2 show representative weight loss with time for the uninhibited corrosion of mild steel in 0.1, 0.3 and 0.5M concentrations of HCl and HNO<sub>3</sub> at 333K. From the

figures, it can be seen that weight loss of mild steel increased linearly with time. The figures revealed that weight loss increased as time and concentrations of acid increased, indicating that the rate of corrosion of mild steel increased with concentration of acid and period of immersion. Values of weight loss were also found to vary with concentration of HCl and HNO<sub>3</sub> in such a way that the trend of increase in weight loss with time was  $0.5 > 0.3 > 0.1\text{M}$  for both HCl and HNO<sub>3</sub>. Similar trends of plot (not shown) were obtained for 303 and 313K.

Figure 3 shows representative graphs of weight loss with time for the corrosion of mild steel in 0.5M of HCl and HNO<sub>3</sub> containing various AVE concentrations at 333K. The figure revealed that weight loss increased as time increased but decreases as the concentration of the acid extract of *Aloe vera* increased, indicating that the AVE inhibited the corrosion of mild steel in both media. Similar results (not shown) were obtained for 0.1 and 0.3M. The inhibitory effects of AVE are very apparent considering the wide margin in magnitude of weight loss between inhibited and uninhibited phases.

Figures 4 and 5 show the variation of weight loss with time for the corrosion of mild steel in 0.5M of HCl and HNO<sub>3</sub>, respectively at different temperatures. The figures revealed that increase in temperature increased the rate of corrosion in both acids. It should be noted that generally, the rate of reaction increases with increase in temperature, following induced higher collision of reacting species as temperature is elevated. It can be inferred from figures 1-5 that rate of corrosion of mild steel in acidic medium is affected by concentration of acid, concentration of inhibitor, period of immersion and temperature.

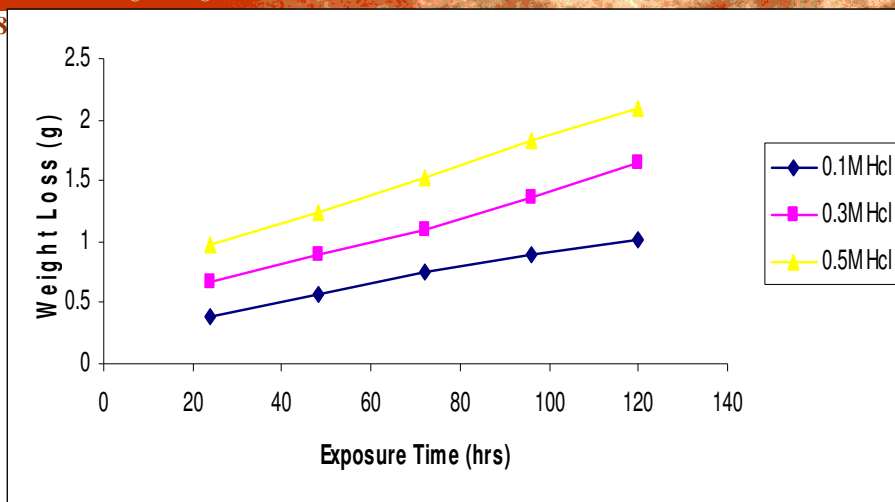


Fig. 1: Uninhibited weight loss as a function of time at 333K and varying HCl concentrations

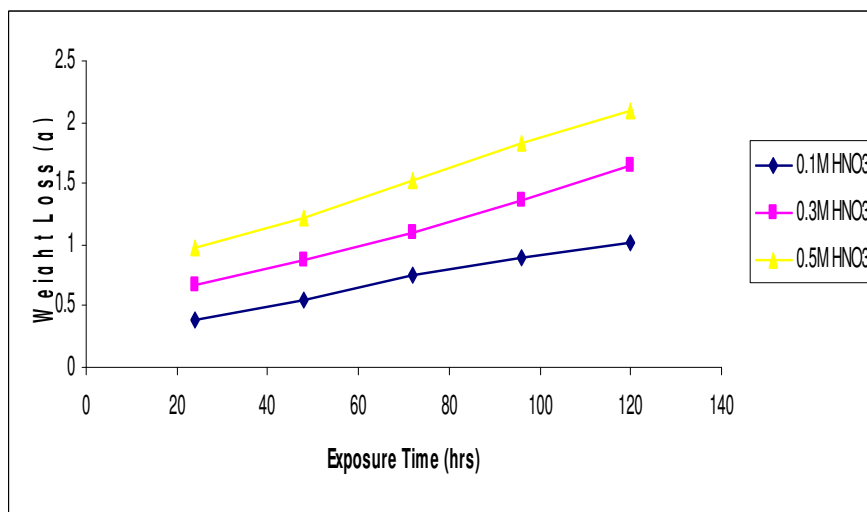


Fig.2: Uninhibited weight loss as a function of time at 333K and varying HNO<sub>3</sub> concentrations .

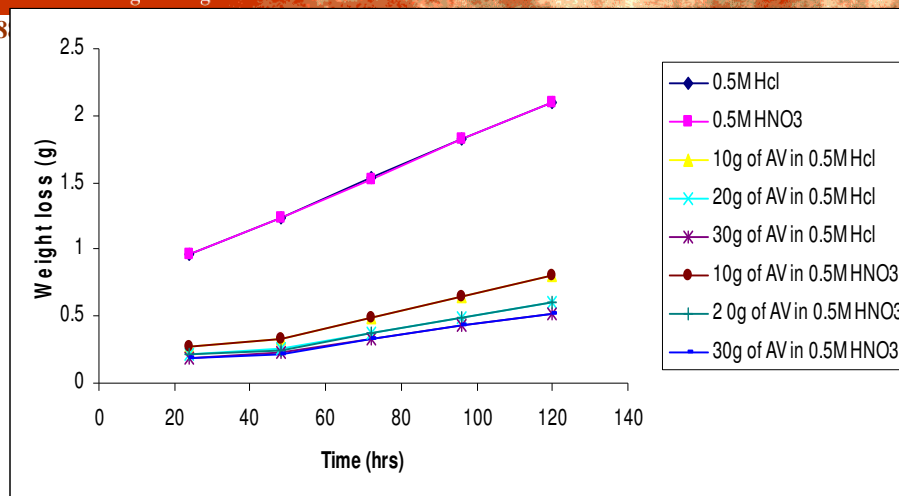


Fig.3: Inhibited weight loss as a function of time at 333K for varying acid concentrations.

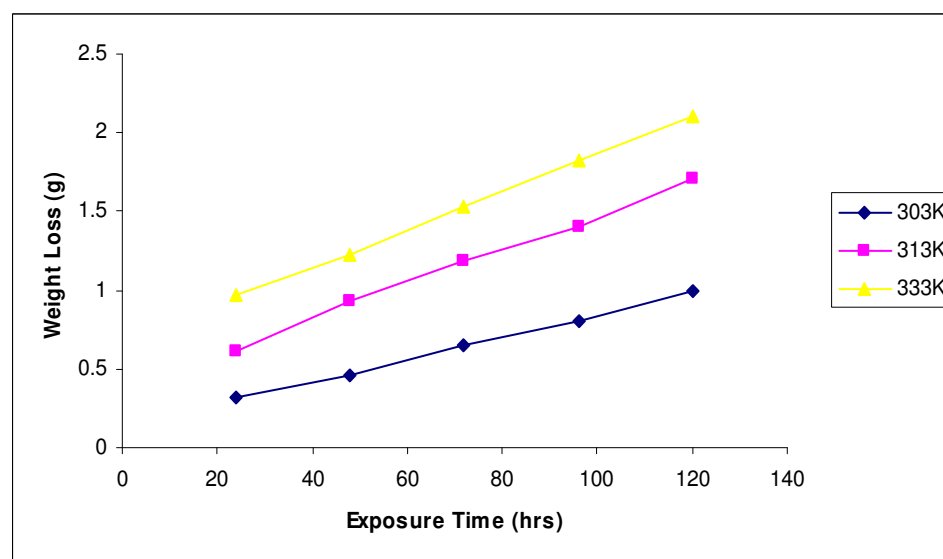


Fig.4: Weight loss as a function of time for 0.5M HCl at different temperatures



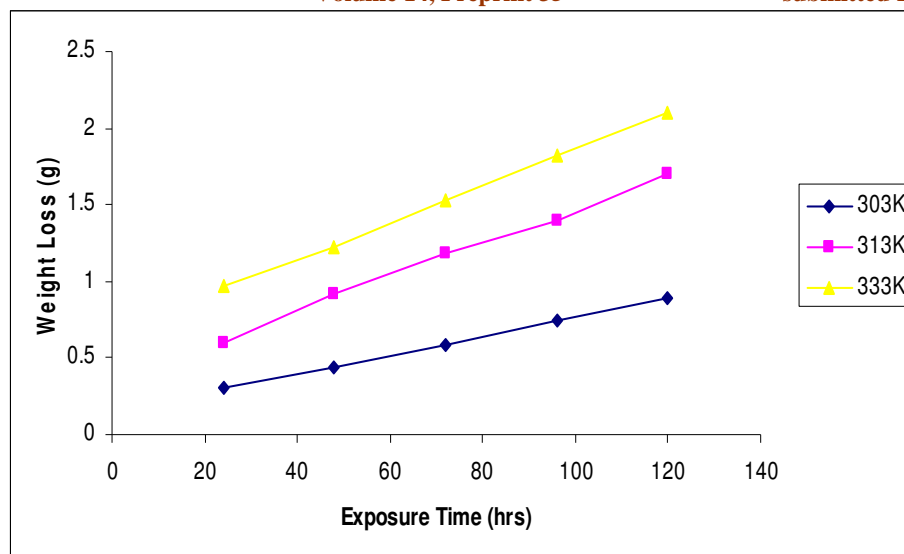


Fig.5: Weight loss as a function of time for 0.5M HNO<sub>3</sub> at different temperatures

Tables 3 and 4 show representative results of corrosion rate (CR) and the Inhibition Efficiency (IE %) of AVE on mild steel in 0.5M HCl and HNO<sub>3</sub> at 303, 313 and 333K for 120 hours immersion time. Results show that corrosion rate, obtained from equation 1 decreased as the concentration of AVE increased but increased with an increase in temperature. The values of corrosion rate in blank were higher than that of inhibited medium. This revealed that the AVE retarded the corrosion of mild steel in both media [5]. As temperature increases the rate of corrosion also increases indicating that the rate of chemical reaction increases with an increase in temperature. Comparing values of corrosion rate of mild steel in HCl and HNO<sub>3</sub>, it can be seen that there exists insignificant difference in the values recorded. This could be because both HNO<sub>3</sub> and HCl are known to be strong acids. It could be argued that the minute CR recorded by HNO<sub>3</sub> above HCl at the conditions of this study is due to the formation of less corrosive adsorptive phytochemical- hydrochloro complex.

The representative results of IE(%) , obtained from equation 3 is displayed in tables 3 and 4. It could be observed that inhibition efficiency of AVE for the corrosion of mild steel in the acidic media increased with an increase in the concentration of the inhibitor but decreased with increase in temperature, suggesting that the extract is physical adsorption inhibitor [5]. For a physical adsorption mechanism, efficiency of an inhibitor decreases with temperature but for a chemical adsorption mechanism, the efficiency is expected to increase with temperature. Values of inhibition efficiency (%IE) obtained at 333K were lower than the

**Table 3:** CR and IE w.r.t. AVE on mild steel in 0.5M HNO<sub>3</sub> at different temperatures.

Conc. (g/l)	Inhibition Efficiency (%IE)			Corrosion Rate (g/cm <sup>2</sup> hrs) x 10 <sup>-5</sup>		
	303K	313K	333K	303K	313K	333K
Blank 0.5M HCl	-	-	-	57.50	86.01	101.10
0.01	69.85	64.83	62.88	8.25	9.23	11.23
0.02	71.90	69.91	67.90	7.01	8.60	10.00
0.03	75.31	73.30	70.32	6.36	7.01	8.75

**Table 4** CR and IE w.r.t. AVE on mild steel in 0.5M HCl at different temperature.

Conc. (g/l)	Inhibition Efficiency (%IE)			Corrosion Rate (g/cm <sup>2</sup> hrs) x 10 <sup>-5</sup>		
	303K	313K	333K	303K	313K	333K
Blank 0.5M HNO <sub>3</sub>	-	-	-	57.40	85.07	99.99
0.01	69.89	64.84	62.89	8.23	9.20	11.20
0.02	71.94	69.93	67.93	6.93	8.55	9.75
0.03	77.32	73.35	70.34	6.34	7.00	8.64

### Corrosion adsorption

The adsorption characteristic of the inhibitor was also studied by fitting data obtained for degree of surface coverage into different adsorption isotherms. The tests revealed that the adsorption of acid extract of AV on the surface of mild steel is best described by langmuir adsorption isotherm. Hence, no further consideration of other models was attempted. The Langmuir adsorption isotherm can be expressed as equation 4 [11]:

$$K_L C = \frac{\theta}{1 - \theta} \quad (4)$$

where C is the concentration of the inhibitor, K<sub>L</sub> is the Langmuir adsorption constant.

The langumir adsorption isotherm can be rearranged to obtain equation 5:

Taking logarithm of both sides of equation 5, yields:

$$\text{Log } (C/\theta) = \log C - \log K_L \quad (6)$$

By plotting values of  $\text{Log } (C/\theta)$  versus  $\log C$ , linear plots were generated (figures 6 and 7), for the evaluation of  $\log K_L$  from the intercepts. Values of adsorption parameters obtained from the isotherms are presented in table 5. The values of  $R^2$  obtained from figures 6 and 7 indicate a good fit, though it can be viewed that Langmuir isotherm is best applicable at 303K. The implication of these results is the absence of interaction between the adsorbed species and that the adsorption behaviour of the inhibitor was strongly influence by temperature.

There exist facts that apart from temperature, inhibition efficiency depends on several factors, such as the number of adsorption sites and their charge density, pH of the corrodent, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation of metallic complexes [12]. Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion. This is the case with the inhibition of mild steel by AVE. Adsorption provides the information about the interaction around the adsorbed molecules themselves as well as their interaction with the mild steel surface.

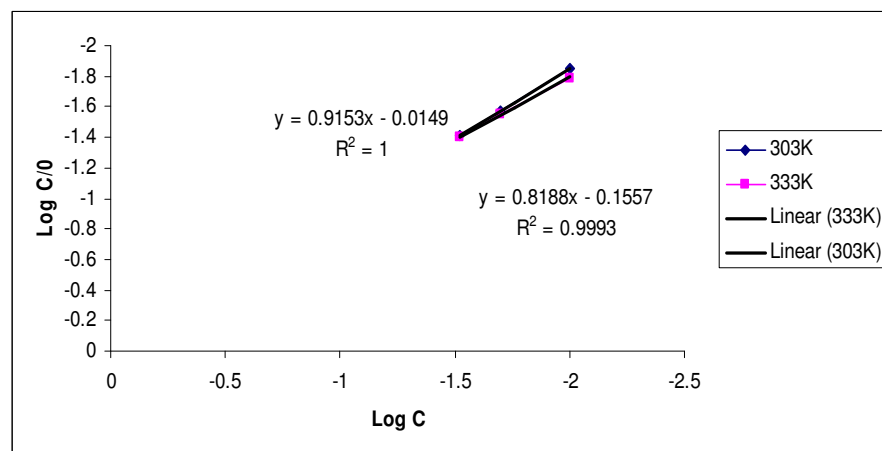


Fig. 6: Langmuir adsorption isotherm for AVE at 0.5M HCl.

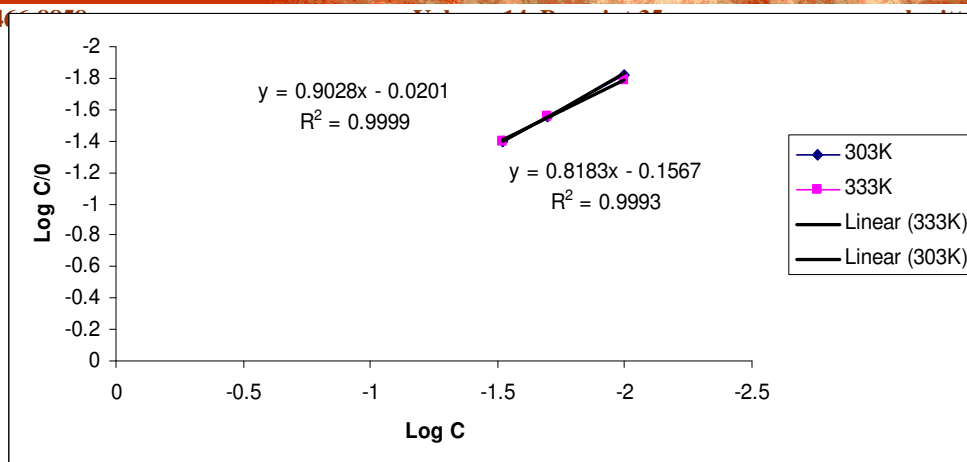


Fig. 7: Langmuir adsorption isotherm for the AVE at 0.5M HNO<sub>3</sub>.

**Table 5: Langmuir adsorption parameters w.r.t. AVE on mild steel surface**

parameters	HCL		HNO <sub>3</sub>	
	medium		medium	
	(303K)	(333K)	(303K)	(303K)
Log K <sub>L</sub>	0.0148	0.1557	0.0201	0.1567
K <sub>L</sub> (g/l)	1.0346	1.4311	1.0473	1.4344
Slope	0.9153	0.8188	0.9028	0.8183
R <sup>2</sup>	1.000	0.9993	0.9999	0.9993

### *Corrosion thermodynamics*

The activation energy, E<sub>a</sub> for both inhibited and uninhibited corrosion of the steel was evaluated using Arrhenius equation 7, linerised into equation 8 and simultaneously solved for T<sub>1</sub> and T<sub>2</sub> as equation 8 [13].

$$CR = A \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

$$\text{Log } \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9)$$

R is the gas constant,  $CR_1$  and  $CR_2$  are the corrosion rates at temperatures  $T_1(303K)$  and  $T_2(333K)$ , respectively. Values of  $E_a$  calculated from equation 9 are recorded in table 6. These values are found to range from 27.81 to 23.05kJ/mol in  $HNO_3$  and 28.05 to 23.14kJ/mol in HCl. The observed results indicated that the adsorption of these extracts is consistent with the mechanism of physical adsorption. For physical adsorption mechanism, the activation energy should be less than 80kJ/mol, as observed for the values in table 6 [14]. Also the values of  $E_a$  obtained in the presence of acid extract of AV were higher than the values obtained for blank, indicating that the extract retarded the corrosion of mild steel in HCl and  $HNO_3$ [15].

The heat of adsorption of acid extract of *Aloe vera* on the surface of mild steel was calculated using equation 10 [14]. Values of  $Q_{ads}$  calculated are recorded in table 6. The values are negative and relatively low, an index of exothermic process.

$$Q_{ads} = 2.303R \left( \log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right) \times \frac{T_1 T_2}{T_2 - T_1} \quad (10)$$

**Table 6:** Activation energies and adsorption heat w.r.t. AVE on steel surface.

Concentration (g/l)	$E_a$ (kJ/mol)		$Q_{ads}$ (kJ/mol)	
	$HNO_3$	HCl	$HNO_3$	HCl
Blank 0.5M	4.785	10.112	-	-
0.01	27.81	28.048	-10.233	-6.125
0.02	24.278	24.431	-4.372	-5.81
0.03	23.048	23.137	-2.59	-2.112

The thermodynamic parameter,  $\Delta G$  for corrosion adsorption was calculated from equation 12 on transforming equations 11 into 12 [11, 16]:

$$\Delta G_{ads} = -2.303RT \log (55.5K) \quad (12)$$

where  $C_{solvent}$  represents the molar concentration of the solvent (55.5 mol/dm<sup>3</sup> in the case of water), Results posted in table 7 are negative, indicating spontaneous adsorption of the inhibitor on the surface of mild steel. The  $\Delta G_{ads}$  values are negatively lower than the threshold value of -40kJ/mol required for chemical adsorption [17]; hence the adsorption of acid extract of the inhibitor on the surface of mild steel is spontaneous and favours the mechanism of physical adsorption. Generally, the more negative the value of  $\Delta G_{ads}$  the stronger the strength of adsorption.

**Table 7:** Adsorption free energy w.r.t. AVE and 0.5M acids on steel surface.

Conc. (g/l)	$-\Delta G_{ads}$ (kJ/mol)			
	303K		333K	
	HCl	HNO <sub>3</sub>	HCl	HNO <sub>3</sub>
0.01	27.918	27.979	25.208	25.209
0.02	26.993	27.011	24.489	24.499
0.03	27.054	27.076	23.899	23.906

#### D. Corrosion Kinetics

Data obtained from weight loss measurement were fitted into equation 13 to test for the order of corrosion reaction in the presence of AVE.

$$\ln (\text{weight loss})=k_1t \quad (13)$$

where  $k_1$  is the first order reaction constant and  $t$  is time.

. The tests revealed that the plots (not shown) of  $\ln (\text{weight loss})$  versus time (in days) were linear with  $R^2$  close to unity. This indicates that a first order kinetic is applicable to the corrosion of mild steel in the presence of acid extracts of the inhibitor [18]. Therefore, the corrosion of mild steel in the acid extracts of the inhibitors can be significantly represented by equation 13.

In addition, the half lives ( $t_{1/2}$ ) of the corrosion of mild steel in the various media were calculated using equation 14.

Values of rate constant ( $k_1$ ) obtained from the slope of the plots of equation 13 and the half life calculated from equation 14 are presented in Tables 8 and 9. From the results obtained, it is significant to note that half life increases with increase in concentration of acid extracts of AV. This suggests that half life of steel in the acids increases with increasing concentration of the inhibitors. Also from Tables 8 and 9, it can be shown that the half life of the acid extracts of the inhibitors at 333K is lower than that at 303K. This indicates that inhibition efficiency is inversely related to temperature. Similar results had been reported elsewhere [19].

**Table 8: Kinetic parameters w.r.t HNO<sub>3</sub> /AV extract on steel surface**

C(g/l)	k <sub>1</sub> (1/hour)		t <sub>1/2</sub> (hour)		R <sup>2</sup>
	(303K)	(333K)	(303K)	(333K)	
Blank	0.268	0.289	2.68	2.40	0.959
0.01	0.247	0.278	2.91	2.51	0.987
0.02	0.199	0.273	3.67	2.61	0.985
0.03	0.191	0.269	3.81	2.64	0.979

**Table 9: Kinetic parameters w.r.t HCL/AV on steel surface**

C(g/l)	k <sub>1</sub> (1/hour)		t <sub>1/2</sub> (hour)		R <sup>2</sup>
	(303K)	(333K)	(303K)	(333K)	
Blank	0.261	0.286	2.79	2.44	0.956
0.01	0.240	0.274	2.99	2.52	0.987
0.02	0.196	0.267	3.69	2.62	0.985
0.03	0.184	0.263	3.92	2.69	0.976

## Conclusion

At the conditions of the experiment, acid extract of *Aloe vera* is a good adsorption inhibitor for the corrosion of mild steel in HCl and HNO<sub>3</sub>. The inhibition of the corrosion of mild steel is due to the photochemical constituents of the extract. These photochemical



constituents enhanced the adsorption behaviour of the inhibitors. Inhibition efficiency increased with increase in concentration of the acid extract of *Aloe vera* but decreased with increase in temperature. Activation energies were higher in the presence of the inhibitor suggesting physisorption mechanism. The adsorption of the inhibitors on the surface of mild steel is spontaneous, physically control and in line with langmuir isotherm. At the conditions of this study, there is negligible difference in the inhibitory effects of AVE on both HCl and HNO<sub>3</sub> phases.

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