



Evaluation of Inhibitory Effect of Different Extracts of *Vernonia Amygdalina* on Corrosion of Aluminium in Hydrochloric Acid

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Abstract: Corrosion inhibition of aluminium using different extracts of *vernonia amygdalina* was studied using gravimetric method. The result of the study revealed that different concentrations of extracts of *vernonia amygdalina* inhibit aluminium corrosion. The inhibition efficiency of extracts increases as concentration of extracts increases. This study revealed that inhibition efficiency decreases as temperature increases. The apparent activation energy, E_a , of the inhibited corrosion reaction of aluminium was greater than the values obtained for the blank. The ΔG_{ads} values obtained at 303k and 333k were negative indicating spontaneous adsorption of inhibitor on the surface of aluminium. The experimental data were corroborated with Langmuir as well as Flory – Huggins adsorption isotherms. The inhibition efficiency of extracts was in order: $C_2H_5OH > \text{distilled } H_2O > \text{IM HCl at 303k and } C_2H_5OH > \text{IM HCl} > \text{distilled } H_2O \text{ at 333k.}$

Keywords: Corrosion, inhibitors, *Vernonia amygdalina*, adsorption.

INTRODUCTION

The study of aluminium corrosion in different acidic and alkaline environments has attracted considerable attention in view of important application of the metal. Aluminium is a hard, strong, white metal. It is highly electropositive and resistant to corrosion because of hard, tough film of oxide it forms on the surface¹. This surface film is amphoteric; hence the metal could dissolve readily in both strong acid and alkaline media. Hydrochloric acid solutions are normally used for pickling of aluminium and for its

chemical and electrochemical etching processes that normally lead to substantial loss of metal to corrosion.

Corrosion behaviour of aluminium has been studied in acid media². It has been reported that addition of halide salt to sulphuric acid solution containing organic inhibitor, effectively inhibits iron corrosion³. Halides have been reported to inhibit corrosion of some metals in strong acids and this effect depends on ionic size and charge, the electrostatic field set up by the negative charge of anion on adsorption sites and the nature and concentration of halide ions^{2, 3}.

It has been reported that aluminium surface film dissolution have been protected from aggressive acid and alkaline media by the application of sulphur, oxygen or nitrogen containing organic compounds as corrosion inhibitors to hinder the corrosion reaction and thus reduce corrosion rate⁴⁻⁷. These organic compounds function by forming a protective adsorption layer on the metal surface which isolates the corroding metal from the action of the corrodent.

The use of chemical inhibitors for prevention of corrosion of metals have been giving researchers a lot of concern in view of its toxicity and poisoning of living organisms in the environment. In view of this harmful effect of chemical inhibitor, the use of plant extracts as an inhibitor of corrosion is being considered. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The use of plant extracts to prevent corrosion has become important because they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors.

Vernonia amygdalina (bitter leaf) is widely distributed in tropical Africa especially, Nigeria. It belongs to Asteraceae family and its genus is vernonia. The Igbos of the Eastern Nigeria call it Olugbo, while the Yorubas of Western Nigeria call it Ewekoro. It is a small shrub and hairy herb having height of 30-120 cm. It is planted through the root system in the first quarter of the year and can be harvested after one year when it is fully grown and matured⁸. It has multiple health benefits and has also found application for the treatment of emesis and diabetes⁹.

MATERIALS AND METHOD

Material Preparation: Aluminium sheets of the type AA 1060 and purity 98.98% were obtained from Material and Metallurgical Engineering Workshop, Federal University of Technology, Owerri, Nigeria. Each sheet which was 0.1 cm in thickness was mechanically press-cut into coupons of dimension 3 cm x 3 cm. The coupons were descaled using wire brush in acetone, weighed and stored in a moisture-free desiccator prior to use. The solvents used for the extraction of *vernonia amygdalina* leaf were ethanol, IM HCl and distilled water, respectively. All the solvents used in this study were of analytical reagent grade.

Extraction of Plant: Sample leaves of *vernonia amygdalina* were obtained from a farm near Nekede River, Owerri, Nigeria. The leaf samples were washed and dried under the sun and ground to fine powder. The ground samples of leaf were extracted with soxhlet extractor for 3 h using IM HCl, ethanol and distilled water, respectively. After extraction the samples were cooled and filtered. The filtrate obtained was used to prepare inhibitor concentrations in the range between 200mg/l and 1000mg/l in HCl corrodents.

GRAVIMETRIC METHOD

In the weight loss experiment, a hole with diameter 0.5 cm was drilled in each aluminium coupon so that it could hang freely in solution. The aluminium coupons were suspended in beakers containing 200 ml of

test solution maintained at 303K-333K with glass hooks and rod in a thermostated water bath. The weight loss was determined by retrieving the coupons from test solutions at 3 h intervals. The coupons after retrieving from test solutions were scrubbed with bristle brush under running water, dried in acetone and weighed⁶. The difference in weight was taken as the weight loss of aluminium. From the weight loss, the inhibition efficiency (% I.E) of the extract and the corrosion rate (CR) of aluminium were calculated using Eq. 1 and 2, respectively.

$$\% \text{ I. E} = \left[1 - \frac{\text{CR}_{\text{inh}}}{\text{CR}_{\text{BL}}} \right] \times 100 \quad \dots 1$$

$$\text{CR} (= \text{gh}^{-1} \text{ cm}^{-2}) = \Delta W / AT \quad \dots 2$$

Where CR_{inh} and CR_{BL} are corrosion rate of aluminium in presence and absence of the inhibitor, respectively. A is area of coupon in cm^2 , T is the period of immersion in hours and $\Delta W = W_1 - W_2$. Where W_1 is the initial weight of aluminium and W_2 is the final weight of aluminium. The degree of surface coverage was calculated using:

$$\theta = 1 - \left(\frac{\text{CR}_{\text{inh}}}{\text{CR}_{\text{BL}}} \right) \quad \dots (3)$$

Where θ is surface coverage, CR_{inh} is corrosion rate for aluminium in presence of inhibitor, CR_{BL} is corrosion rate for aluminium in absence of inhibitor.

RESULTS AND DISCUSSION

Weight loss consideration: Figs 1 and 2 represented data of weight loss against concentration for aluminium corrosion in IM HCl in absence and presence of different concentrations of used inhibitor, *vernonia amygdalina* (V.A) at 303K and 333K, respectively. **Figs 1** and **Figs.2** show that as concentration of inhibitor increases the weight loss of aluminium samples decreases. The result indicates that weight loss of Al samples increases as temperature increases as shown in Fig.2. The decrease in weight loss as inhibitor concentration increases indicates that components of inhibitor retards corrosion of Al samples. This may probably due to adsorption of inhibitor onto the surface of aluminium and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of anodic and cathodic processes. The result indicates that weight loss of Al sample in different extracts of inhibitor were in order: IM HCl > distilled H_2O > $\text{C}_2\text{H}_5\text{OH}$ at 30°C and Distilled H_2O > IM HCl > $\text{C}_2\text{H}_5\text{OH}$ at 60°C. The highest weight loss observed with distilled H_2O extract of inhibitor at 60°C may be attributed to desorption of inhibitor components from aluminium surface as temperature increases.

Inhibition Efficiency and Surface Coverage: The percentage of Inhibition efficiency (% I.E) was calculated and represented as shown in tables 1 and 2 at 303K and 333K, respectively. The result shows that different extracts of inhibitor inhibits corrosion of Al sample in hydrochloric acid solution. The result revealed that % I.E increases as concentration of inhibitor increases. A parameter θ , which represents the part of metal surface covered by inhibitor molecules was calculated for different inhibitor concentrations and represented in **Table-1** and **Table-2**.

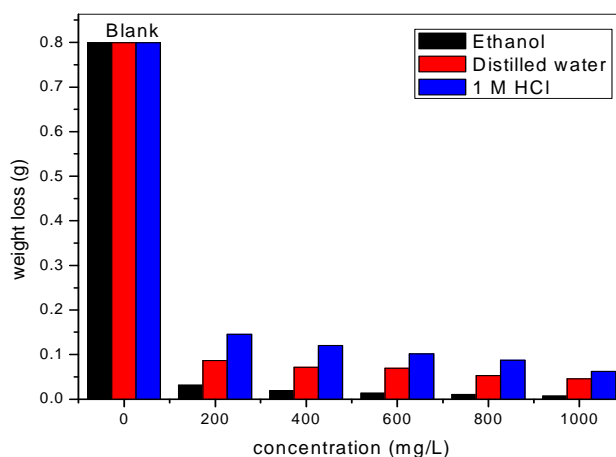


Fig. 1: Variation of weight loss of aluminium in HCl at various concentrations of 1 M HCl, ethanol and distilled water extracts of *Vernonia amygdalina* at 303K.

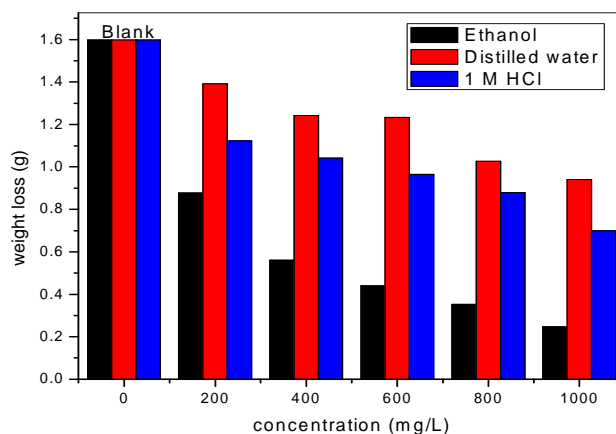


Fig. 2: Variation of weight loss of aluminium in HCl at various concentrations of 1 M HCl, ethanol and distilled water extracts of *Vernonia amygdalina* at 333K.

Table- 1: Effect of various inhibitor Extracts on % I.E and θ for Al corrosion in IM HCl at 303k

Concentration Mg/L	IM HCl extract of <i>Vernonia amygdalina</i>		Distilled water extract of <i>Vernonia amygdalina</i>		Ethanol extract of <i>Vernonia amygdalina</i>	
	% I.E.	θ	% I.E.	θ	% I.E.	θ
200.00	81.80	0.8176	89.20	0.8916	96.10	0.9606
400.00	84.90	0.8492	91.10	0.9105	97.60	0.9764
600.00	87.30	0.8731	91.30	0.9130	98.30	0.9830
800.00	89.00	0.8901	93.40	0.9388	98.70	0.9869
1000.00	92.00	0.9225	94.30	0.9431	99.10	0.9911

Table- 2: Effect of various Inhibitor Extracts on %I.E and θ for Al corrosion in IM HCl at 333K

Concentration Mg/L	IM HCl extract of <i>Vernonia amygdaliam</i>		Distilled water extract of <i>Vernonia amygdalina</i>		Ethanol extract of <i>Vernonia amygdalina</i>	
	% I.E.	θ	% I.E.	θ	% I.E.	θ
200.00	29.70	0.2974	13.00	0.1301	45.10	0.4514
400.00	34.90	0.3486	22.30	0.2233	64.90	0.6490
600.00	39.60	0.3963	22.90	0.2290	72.50	0.7247
800.00	45.00	0.4500	35.80	0.3577	78.00	0.7796
1000.00	56.70	0.5666	41.20	0.4115	84.60	0.8455

The result indicates that θ increases as inhibitor concentrations increases. The increase in inhibition efficiency and surface coverage as concentration of extracts increases may be attributed to complex chemical composition of extracts. The increase in inhibition efficiency with increase in inhibition concentration suggests that inhibitor species were adsorbed on the aluminium sample/solution interface where the adsorbed species mechanically screen the coated part of aluminium surface from the action of corrosion medium.

The result indicates that ethanolic extract shows higher inhibition efficiency and surface coverage when compared to values obtained for distilled water and IM HCl extracts, respectively. The higher inhibition efficiency and surface coverage of ethanolic extract may be attributed to more complex chemical composition of ethanolic extract when compared to IM HCl and distilled H₂O extracts, respectively.

¹⁰Alinnor reported that ethanolic extract of *vernonia amygdalina* leaf contains alkaloid, saponins, flavonoids, tannins etc. The adsorption of these compounds from the extracts onto the aluminium surface reduces the surface area available for corrosion, thereby increasing inhibition efficiency and surface coverage, respectively.

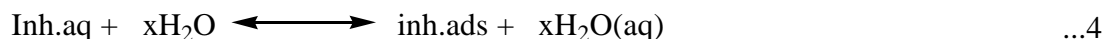
Table-2 shows inhibition efficiency and surface coverage for Al corrosion at 333k. The result indicates that inhibition efficiency and surface coverage increases as concentration of the extracts increases. The %I.E and θ were lower when compared to values obtained at 303k in table 1. The decrease in % I.E and θ at higher temperature of 333k when compared to 303k may be attributed to increase in average kinetic energy of components of extracts, thus making adsorption between the components of extracts and Al surface insufficient to retain the species at binding site. This could result in desorption of species off the surface of aluminium surface, instead of colliding and combining with it. The result indicates that increase in temperature may be attributed to decrease in stability of extract components – aluminium surface complex. It has been reported that¹¹ working on corrosion of mild steel in H₂SO₄ using ethanolic extract of *Piper Guinensis* reported decrease in inhibition efficiency at higher temperature. It has also been reported¹² working on corrosion of mild steel in H₂SO₄ using *Telferia occidentalis* observed decrease in inhibition efficiency at higher temperature. ¹³Noor working on corrosion inhibition of mild steel in acidic solutions with aqueous extract of Fenugreek leaves reported decrease in inhibition efficiency at higher temperature. ¹⁴James et al. working on corrosion of aluminium in HCl with aqueous extract of Aloe vera leaf reported decrease in inhibition efficiency at higher temperature.

Figs.3 and Fig.4 shows the plot of inhibition efficiency against different concentrations of inhibitor at 303k and 333k, respectively. Fig. 3 shows that inhibition efficiency was high when compared to values obtained in Fig.4 at higher temperature. The inhibition efficiency of different extracts of inhibitor at 303k were in order C₂H₅OH>distilled H₂O>IM HCl whereas at 333k the order is as follows C₂H₅OH >IM HCl>

distilled H₂O. The observed trend indicates that at higher temperature there were desorption of distilled H₂O components of extract from the aluminium surface, thereby decrease in inhibition efficiency.

ADSORPTION CONSIDERATION

The adsorption of an inhibitor species, Inh, on the aluminium surface in aqueous solution should be considered as exchange reaction:



Where x is size ratio that is number of water molecules displaced by one molecule of organic inhibitor. When equilibrium is reached as shown in Eq. (4) it is possible to obtain different forms of adsorption isotherm. Langmuir adsorption isotherm was found to be suitable for these experimental findings and has been used to describe the adsorption characteristic of the inhibitor used. Langmuir adsorption isotherm is expressed in Eq. (5)¹⁵.

$$C_{\text{inh}}/\theta = 1/K + C_{\text{inh}} \quad \dots (5)$$

Where C_{inh} is inhibitor concentration, K is equilibrium constant of adsorption, θ is degree of surface coverage. **Figs. 5 and Figs. 6** shows the plot of C_{inh}/θ versus C_{inh} at 303K and 333k, respectively for ethanol, 1M HCl and distilled H₂O extracts of inhibitor studied. **Figs. 5 and Figs. 6** were linear showing that adsorption of inhibitor is consistent with assumption of Langmuir adsorption isotherm meaning there is no interaction between the adsorbed species.

The adsorption of inhibitor extracts on aluminium surface follows Flory – Huggins isotherm in Eq. (6)¹²

$$\text{Log} \left[\frac{\theta}{C_{\text{inh}}} \right] = \log k + x \log (1-\theta) \quad \dots 6$$

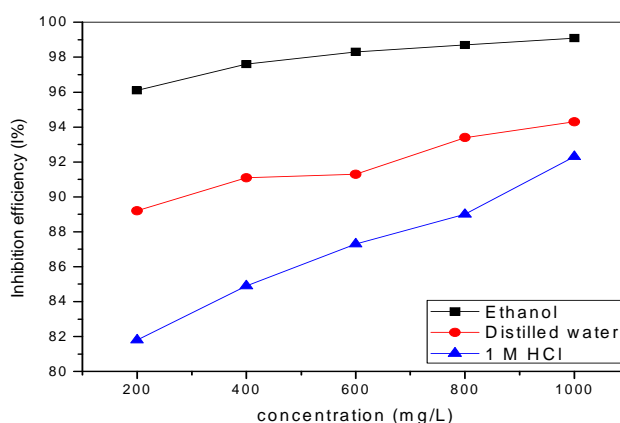


Fig. 3: Variation of inhibition efficiency with concentration of 1M HCl, ethanol and Distilled water extracts of *Vernonia amygdalina* at 303K

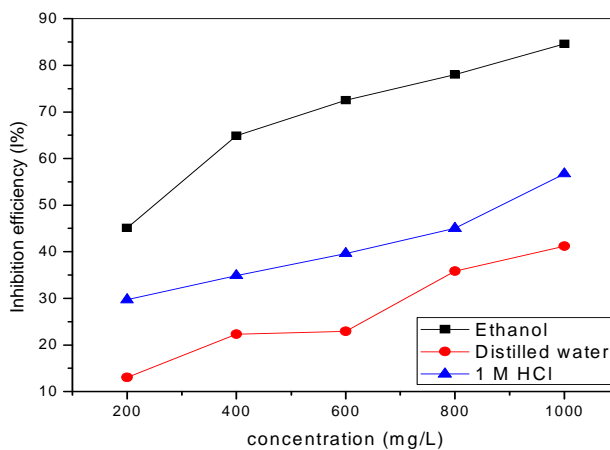


Fig. 4: Variation of inhibition efficiency with concentration of 1M HCl, ethanol and distilled water extracts of *Vernonia amygdalina* at 333K.

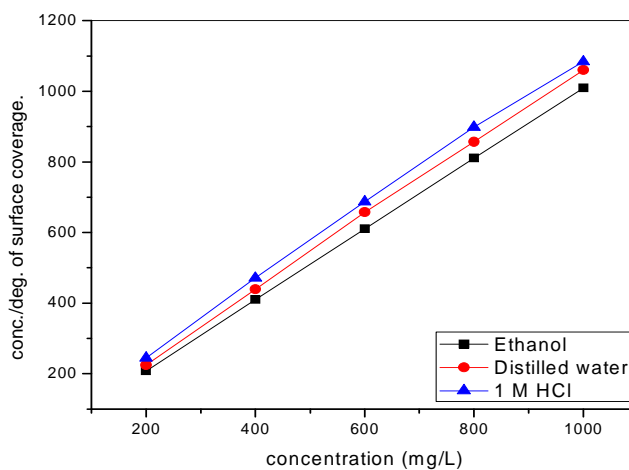


Fig. 5: Langmuir adsorption isotherm at 303K for 1M HCl, ethanol and distilled water extracts of *Vernonia amygdalina*.

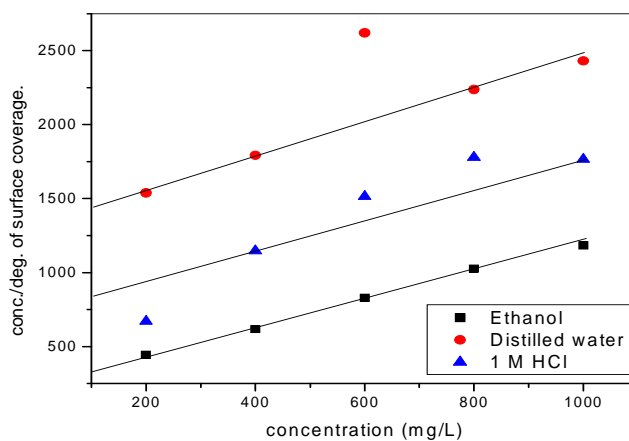


Fig. 6: Langmuir adsorption isotherm at 333K for 1M HCl, ethanol and distilled water extracts of *Vernonia amygdalina*.

Where θ is degree of surface coverage, C_{inh} is inhibitor concentration, x is number of water molecules replaced by one inhibitor molecule and k is equilibrium constant for adsorption process. **Figs.7, Figs.8** and **Figs.9** shows Flory – Huggins adsorption isotherm for different extracts of inhibitor with IM HCl, ethanol and distilled water at 303k and 333k, respectively. The values of x and k calculated for IM HCl extract of the inhibitor were 1.05 and 0.001 for 303k, and 0.95 and 0.32 for 333k, respectively.

The values of x and k obtained using ethanol extract of inhibitor were 1.43 and 0.001 for 303k, and 0.80 and 0.13 for 333k, respectively. The values of x and k using distilled water extract of inhibitor were 1.93 and 0.001 for 303k, and 1.17 and 0.39 for 333k, respectively. The result indicates that values for x were more than unity at 303k, indicating that each molecule of inhibitor is attached to one active site on aluminium surface.

Values of free energy of adsorption, ΔG_{ads} of IM HCl, ethanol and distilled water extracts of inhibitor on aluminium surface were calculated using Eq. (7)¹⁶.

$$\Delta G_{ads} = -2.303RT \log (55.5k) \quad \dots (7)$$

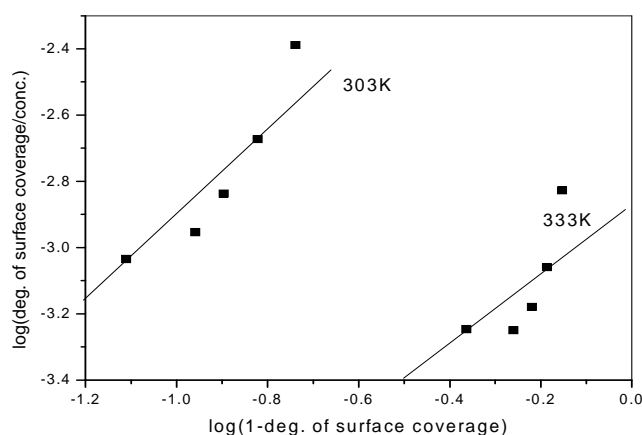


Fig. 7: Flory-Huggins adsorption isotherm at 303K and 333K for 1M HCl extract of *Vernonia amygdalina*.

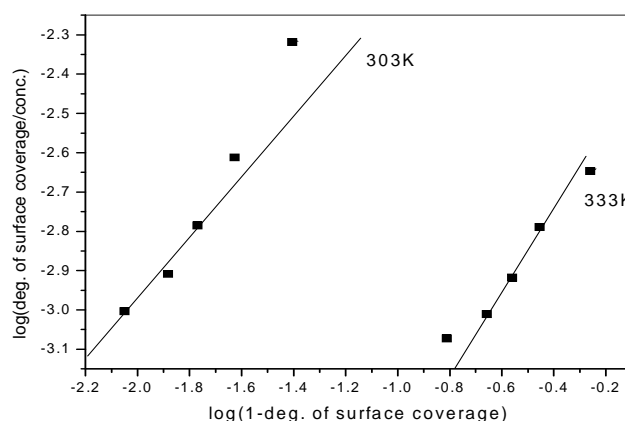


Fig. 8: Flory-Huggins adsorption isotherm at 303K and 333K for ethanol extract of *Vernonia amygdalina*

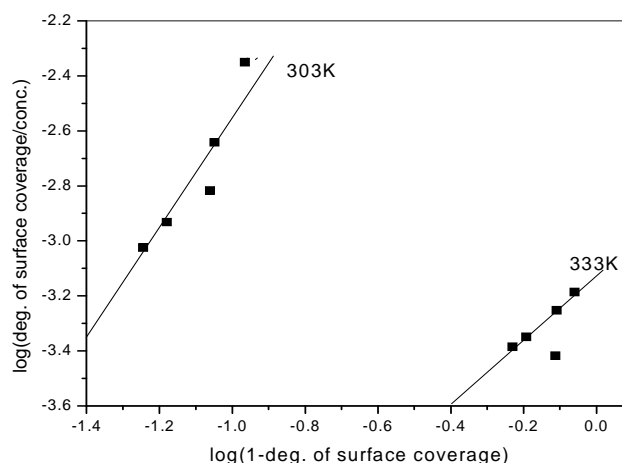


Fig. 9: Flory-Huggins adsorption isotherm at 303K and 333K for distilled water extract of *Vernonia amygdalina*.

Where R is gas constant, T is temperature and k is equilibrium constant of adsorption, given as

$$k = \frac{\theta}{1 - \theta}$$

and 55.5 is the concentration of water in the solution. The values of ΔG_{ads} calculated from Eq. (7) of different inhibitor extracts were recorded in **Tables 3, 4 and 5**, respectively. These values of ΔG_{ads} were negative in both 303k and 333k indicating spontaneous adsorption of inhibitor on surface of aluminium¹⁷, and propose mechanism is by physical adsorption ($\Delta G_{\text{ads}} < 40 \text{ kJ/mol}$)^{18, 19}.

Table- 3: Values of thermodynamic parameters for adsorption of Ethanol Extract of *Vernonia amygdalina* on the surface of aluminium in IM HCl.

Concentration of <i>Vernonia amygdalina</i> (mg/L)	Activation energy, E_a (kJ/mol)	Heat of adsorption Q_{ads} (kJ/mol)	Free energy change, ΔG_{ads} (kJ/mol) of adsorption at 303k	Free energy Change, ΔG_{ads} (kJ/mol) of adsorption at 333k
Blank	19.39	-	-	-
200.00	93.04	-94.78	-18.17	-10.58
400.00	94.83	-86.92	-19.50	-12.82
600.00	97.24	-86.41	-20.34	-13.80
800.00	98.26	-85.54	-21.01	-14.62
1000.00	99.27	-84.27	-21.99	-15.83

Table-4: Values of thermodynamic Parameters for Adsorption of Distilled water Extract of *Vernonia amygdalina* on the surface of aluminium in IM HCl

Concentration of <i>Vernonia amygdalina</i> (mg/L)	Activation energy, E_a (kJ/mol)	Heat of adsorption Q_{ads} (kJ/mol)	Free energy change ΔG_{ads} (kJ/mol) of adsorption at 303k	Free energy change, ΔG_{ads} (kJ/mol) of adsorption at 333k
Blank	19.39	-	-	-
200.00	77.65	-112.07	-15.43	-5.86
400.00	79.84	-99.74	-15.96	-7.67
600.00	80.43	-99.70	-16.04	-7.76
800.00	82.95	-90.39	-16.79	-9.50
1000.00	84.72	-88.54	-17.19	-10.13

Table-5: Values of thermodynamic Parameters for Adsorption of IM HCl Extract of *Vernonia amygdalina* on the surface of aluminium in IM HCl

Concentration of <i>vernonia amygdalina</i> (mg/L)	Activation energy, E_a (kJ/mol)	Heat of adsorption Q_{ads} (kJ/mol)	Free energy ΔG_{ads} (kJ/mol) of adsorption at 303k	Free energy Change, ΔG_{ads} (kJ/mol) at adsorption at 333k
Blank	19.39	-	-	-
200.00	57.10	-66.00	-13.90	-8.74
400.00	60.32	-65.82	-14.47	-9.39
600.00	63.02	-65.71	-14.98	-9.96
800.00	64.44	-64.11	-15.39	-10.78
1000.00	67.55	-67.55	-16.36	-11.86

Effect of Temperature: The effect of temperature on corrosion reaction of aluminium in absence and presence of different concentrations of inhibitor has been shown in Figs. 1 and 2. The increase in temperature decreases inhibition efficiency and degree of surface coverage. The reason for this observation has been explained earlier in this study.

The apparent activation energy, E_a , for corrosion reaction of Al in absence and presence of various concentrations of inhibitor were investigated using Arrhenius equation (8)^{20, 21}.

$$\text{Log} [C_{R2}/C_{R1}] = E_a / 2.303R [1/T_1 - 1/T_2] \quad \dots (8)$$

Where C_{R1} and C_{R2} are corrosion rates at temperatures T_1 and T_2 , respectively, and R is gas constant. The values of activation energy as shown in tables 3, 4 and 5 in presence of inhibitor ranges from 93.04 to 99.27 kJ/mol for ethanolic extract, 77.67 to 84.72 kJ/mol for distilled water extract and 57.10 to 67.55 kJ/mol for IM HCl extract, respectively suggesting that inhibitor must have first been adsorbed on surface of aluminium according to physical adsorption mechanism followed by chemical adsorption.²² Ebenso, reported that E_a greater than 80kJ/mol is consistent with mechanism of chemical adsorption indicating that the range for E_a values obtained in this study especially for ethanolic extract fall between two types of adsorption, physical and chemical adsorption, respectively. It has been reported earlier in this study that inhibition efficiency decreases as temperature increases, however, it will not be conclusive to attribute chemical adsorption phenomenon to adsorption of *vernonia amygdalina* on surface of aluminium, and since²³ reported that inhibition efficiency of chemically adsorbed specie increases as temperature

increases. The result revealed that apparent activation energy obtained for blank was lower than values obtained for different extracts of inhibitor, indicating that these extracts retards corrosion reaction of aluminium²⁴. Since corrosion primarily occurs at surface sites free of adsorbed inhibitor, the higher E_a values in inhibited solution imply that extracts mechanically screen the active sites of Al surface thereby decreasing the surface area available for corrosion. The order of apparent activation energy, E_a of different extracts are $C_2H_5OH > \text{distilled } H_2O > \text{IM HCl}$.

The heat of adsorption (Q_{ads}) of inhibitor on surface of Al was evaluated using Eq. (9)²⁵

$$Q_{ads} = 2.303R [\log (\theta_2/1-\theta_2) - \log (\theta_1/1-\theta_1)] \times T_1T_2/T_2-T_1 \quad \dots (9)$$

Where θ_1 and θ_2 are the degree of surface coverage at temperature T_1 and T_2 . The calculated values of heat of adsorption, Q_{ads} of different inhibitor extracts are shown in Tables 3, 4 and 5, respectively. The values of Q_{ads} ranged from – 84.27 to – 94.78 kJ/mol for ethanolic extract, whereas distilled water extract has values from - 88.54 to –112.07kJ/mol and IM HCl extract ranges from – 64.11 to - 67.55 kJ/mol, respectively. The negative Q_{ads} values indicates that adsorption of inhibitor extract on aluminium surface is exothermic²⁶.

CONCLUSION

This study shows that *vernonia amygdalina* extract effectively inhibit aluminium corrosion in presence of IM HCl. The corrosion process is inhibited by adsorption of the extract on the aluminium surface and inhibition efficiency increases as inhibitor concentration increases. Also inhibition efficiency and surface coverage decreases as temperature increases. Activation energy of different extracts increases as concentration of inhibitor increases. The negative values of ΔG_{ads} shows that the adsorption of inhibitor extract on the surface of Al is spontaneous. Also the negative values of Q_{ads} indicates that adsorption of inhibitor extract on aluminium is exothermic. The trend of inhibition efficiency of different extracts of inhibitor was in the order: $C_2H_5OH > \text{distilled } H_2O > \text{IM HCl}$ at 303K and $C_2H_5OH > \text{IM HCl} > \text{distilled } H_2O$ at 333K.

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