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Adsorption behavior and corrosion inhibition potential of extract of *Baissea axillaries* on hydrochloric acid- aluminium interface

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ABSTRACT

The adsorption and inhibition of Aluminium corrosion in 1.0 M HCl using different concentrations of extracts of *Baissea axillaris* was investigated at 303 and 323K using weight loss technique. Weight loss and corrosion rate increased with increase in temperature both for the free acid and inhibited solutions, with marked reluctance to increase in both observable in for the presence of the extracts, varying with the extract concentration. Inhibition efficiency increased with increase in the concentration of the extract. The maximum inhibition efficiency of 86.3% was obtained for 10 µg/L extract but decreased to 68.4 % on increasing the temperature from 303 K to 323 K. The adsorption was best described by the Temkin and Langmuir adsorption isotherm from where negative Gibbs free energy change was obtained indicating spontaneous adsorption while negative heat of adsorption was obtained indicating exothermicity. Activation Energy was deduced from the Arrhenius equation while thermodynamic approach yielded the heat of adsorption.

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Introduction

Baissea axillaris is a familiar creeping climber found on fences and trees in Nigeria and usually grows to a very long length. It is popular with herbalists who mix it with other ingredients and administer as a concoction for people living with HIV/AIDS especially in Nigeria [1]. It is also administered for infertility in women, anti-ulcer and an antihypertensive [2]. In Philippines Island, it is used as tea by diabetic natives, serving as successful substitute for unavailable insulin [3]. Extracts of *B. axillaris* has been reported to have antimicrobial activity; the methanolic extract is rich in saponins, phenolic compounds, eugenol oil, glycosides and tannins [4] while alkaloids and cyanogenetic glycosides were also found in the aqueous extracts [1]. The presence of these organic compounds as reported motivated the authors to investigate the anti-corrosive effect of the extract since the constituent compounds contain potential active adsorption sites for interaction with the metal surface [5].

Experimental

Materials

The aluminium sheets of type AA1060 and purity 98.8 % supplied by Sky Aluminium Limited, Uyo, Nigeria with uniform thickness of 0.14cm were mechanically press-cut into coupons of dimensions 4 cm x 4 cm. Without polishing, the coupons were degreased in absolute ethanol, washed with ethanol-water (80-20) mixture, rinsed in acetone, air-dried and stored in moisture-free desiccators prior to use. All reagents used were BDH analytical grade.

Preparation of *B. axillaries* extracts

Fresh samples of *B. axillaris* consisting of the leaves and stem were collected locally from Ikot Ambon in Ibesikpo-asutan Local Government Area of Akwa Ibom State, Southern Nigeria. The samples were identified at Department of Botany and Ecological studies of the University of Uyo, Nigeria. The samples were cut into pieces and air-dried for 7 days, grounded and soaked in a solution of ethanol for 48 hours for extraction, cooled and filtered. The filtrates were further subjected to evaporation at 353 K (80 °C) so as to free the extracts of the

ethanolic solvent. The dry extracts so obtained were prepared into different mass concentrations by dissolving appropriate mass of the extracts in freshly prepared 0.5 M HCl respectively.

Weight loss technique

Pre-weighed aluminium coupons were totally immersed in about 200 ml of the hydrochloric solution in the absence and presence of different concentrations of the extracts. The metal specimens were retrieved at 2 hours interval and re-weighed using FA2014A digital balance of sensitivity ± 0.0001 g and the weight loss was recorded progressively for 10 hours. The corrosion rate, *R*, and inhibition efficiency, % *I* were computed using equations (1) and (2) respectively:

$$R = (W_o - W_t)/AT \quad - \quad - \quad - \quad (1)$$

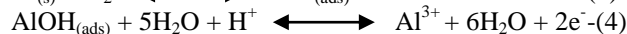
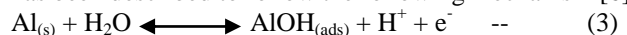
$$\%I = 100(R_b - R_i)/R_b \quad -- \quad - \quad - \quad (2)$$

Where *R_b* and *R_i* is the corrosion rate in the presence and absence of the inhibitor respectively, *A* is the area of the coupon, *T* is the immersion time and % *I* is the inhibition efficiency.

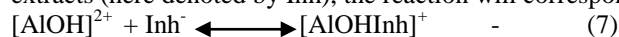
Results and Discussion

Gravimetric corrosion parameters

The weight loss data was used to calculate the basic gravimetric parameters viz corrosion rate, inhibition efficiency and degree of surface coverage. The dissolution of aluminium has been described to follow the following mechanism [6]



The complexation reaction between the hydrated cation and the anion in Equation 5 controls the dissolution of the metal in the medium. In the presence of the active components of the extracts (here denoted by *Inh*⁻), the reaction will correspond to:



Therefore, the rate of dissolution of the metal will thus be expected to be influenced by the concentration of the *Inh*⁻ ions present. Table 1 shows the corrosion rate (*R*), inhibition efficiency (% *I*) and the degree of surface (Θ) obtained at the studied temperatures. The variation of Inhibition efficiency and

corrosion rate in the absence and presence of different concentrations of the extracts respectively are shown in figures 1 (a) and (b). It can be seen that the addition of *B. axillaris* extracts reduces the corrosion rate of aluminium compared to that of the free acid solution. However, for both the free acid and the inhibited solutions, the corrosion rate increases with increase in temperature but decreases with increase in the concentration of the extracts. The inhibition efficiency increases as *B. axillaris* extracts concentration increases-the addition of even a very small amount (20 µg/L) of *B. axillaris* extracts to the acid solution retarded the corrosion rate of the aluminium, the extent of retardation being both concentration and temperature dependent.

Table 1: calculated values of corrosion rate, inhibition efficiency and surface coverage in the presence of *B. axillaris* extracts alone

Conc (µg/L)	<i>R</i> (mgcm ⁻¹ h ⁻¹)		<i>I</i> (%)		Θ	
	303 K	323 K	303 K	323 K	303 K	323 K
Blank	7.32	31.53	-	-	-	-
20.0	2.89	20.59	60.5	34.7	0.605	0.347
40.0	2.53	17.37	65.4	44.9	0.654	0.449
60.0	2.06	14.76	71.8	53.2	0.718	0.532
80.0	1.58	12.58	78.4	60.1	0.784	0.601
100.0	1.01	9.96	86.3	68.4	0.863	0.684

The observed retardation of the aluminium corrosion could be attributed to the adsorption of components of components of *B. axillaris* extracts namely, saponins, phenolic compounds, eugenic oils, glycosides and tannins [4] to the aluminium surface. A layer of adsorbed molecules is probably formed, which would isolate the metal surface from the aggressive acid medium by displacing water molecules and forming coordinate covalent bond with the metal [7]. The components present in the extracts include substances with active adsorption sites such as oxygen, nitrogen, multiple bonds, heteroatoms, heterocyclic and aromatic moieties. These are all electron rich components and potential adsorption sites onto the metal surface via back-donation of electrons. However, assigning inhibitive effect to a particular component is difficult at this stage except if surface analytical techniques and spectroscopic analysis of the corrosion products are employed to enable proper characterization/identification of the active components since these components respectively contribute their characteristic different adsorptive potentials to the overall inhibitive effect so observed.

The observed decrease in %I with increase in temperature suggests physical adsorption of the *B. axillaris* extract onto the aluminium surface. Similar trends have been reported in literature [7, 8] and it is usually associated with the reduction in stability of the adsorbed film at elevated temperatures, leading to a shift in inhibitor-metal interfacial equilibrium [8,9] The inhibition is probably a result of replacement of water molecules from the metal surface by the molecules of *B. axillaris* phytochemicals.

Adsorption Considerations

For a substance to be an effective metal corrosion inhibitor, it must be effectively adsorbed on the metal surface forming a thin protective layer for the metal. The adsorption can be physical (physisorption) or chemical (chemisorption) adsorption. Physically adsorbed molecules essentially retard metal dissolution by inhibiting the cathodic reaction, whereas chemisorped molecules inhibit anodic adsorption site [10]. The adsorption of the inhibitor may be influenced by the nature of the metal, the charge on the metal, the chemical nature of the inhibitor, distribution of charge on the molecule and the type of electrolyte, i.e. aggressive medium [11].

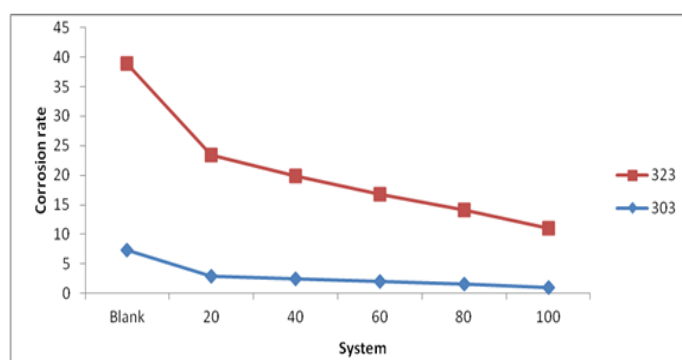


Figure 1 (a): variation of corrosion rate with the concentrations of the systems investigated at 303 and 323 K.

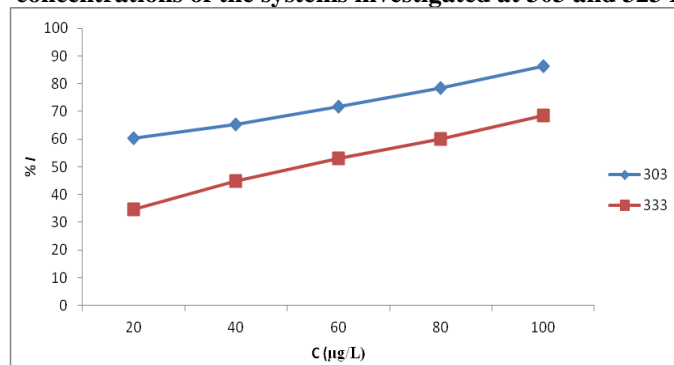


Figure 1 (b): variation of inhibition efficiency with the concentrations of the systems investigated at 303 and 323 K.

In order to describe properly the interaction between the inhibitor molecule and the metal surface, the degree of surface coverage (Θ) values for the different concentrations of the extracts obtained from weight loss measurement ($\Theta = I/100$) were being fitted into different adsorption isotherm/models and correlation coefficients (R^2) were used to determine the best fit, with the assumption that a direct relationship exists between the surface coverage and the inhibition efficiency. The data best fitted the Langmuir and Temkin adsorption isotherm with $R^2 > 0.970$

Respectively, the Temkin and Langmuir adsorption isotherms are given by Equations 8 and 9

$$\Theta = 2.303f \log K_{ads} + 2.303f \log C \quad \text{---} \quad (8)$$

$$C/\Theta = n/K_{ads} + nC \quad \text{---} \quad (9)$$

Where C is the concentration of the extracts, f is the heterogeneity factor which is related to the molecular interaction parameter " a " ($f = -2a$) and K_{ads} is the equilibrium constant for adsorption related to Gibbs free energy change (ΔG_{ads}^*) as follows:

$$\Delta G_{ads}^* = -RT \ln(55.5K_{ads}) \quad (10)$$

Figures (2) and (3) show the Temkin and Langmuir adsorption isotherms for the inhibition of aluminium dissolution in 1.0 M HCl in the presence of different concentrations of *B. axillaris* extracts at 303 and 323K.

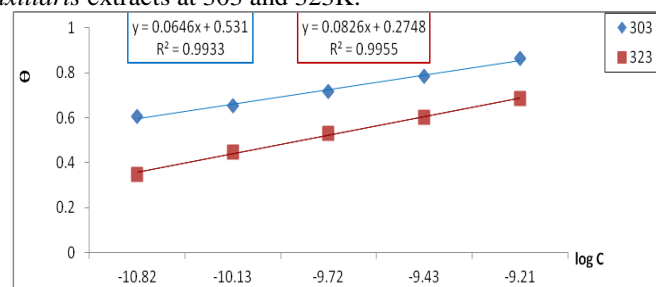


Figure 2: Temkin adsorption isotherm for the inhibition of aluminium dissolution in 1M HCl containing different concentrations of *B. axillaris* extracts at 303 and 323K.

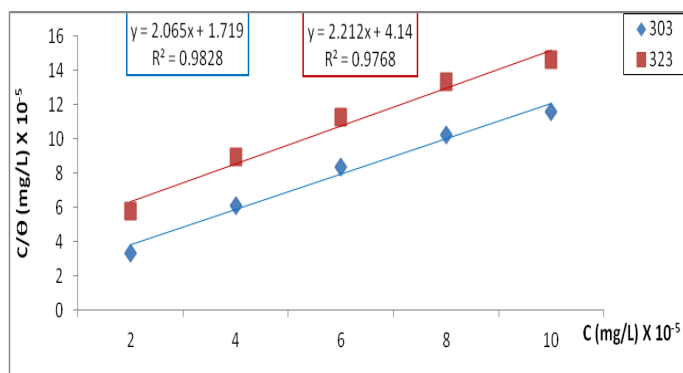


Figure 3: Langmuir adsorption isotherm for the inhibition of aluminium dissolution in 1.0 M HCl containing different concentrations of *B. axillaris* extracts at 303 and 323 K.

Table (2) shows the adsorption parameters deduced from Temkin and Langmuir adsorption isotherms. The equilibrium constant of adsorption, K_{ads} , denotes the strength of inhibitor-metal surface interaction. In practice, a decrease in values of K_{ads} with increase in temperature (as obtained in this study) usually indicates that the inhibitor is physically adsorbed onto the metal surface and that desorption of the inhibitor occurs when temperature is elevated. The values of ΔG_{ads}^* obtained are less negative than -20 kJ/mol indicating that the active molecules of the extracts are physically adsorbed onto the metal surface. The heterogeneity factor (f) is used to describe the nature of interaction between the adsorbed molecules: $f < 0$ implies that repulsion occurs in the adsorbed layer and vice versa for $f > 0$ (i.e. attraction occurs in the adsorbed layer) The values of ' f ' obtained (table 3) are all positive at all temperatures studied, indicating attraction between the adsorbed molecules.

Table 2: Adsorption Parameters deduces from Temkin and Langmuir Adsorption Isotherms

Parameter	303K	323K
K_{ads} (kJ/mol)	1.201	0.534
ΔG_{ads}^* (kJ/mol)	-10.58	-9.10
n	2.065	2.212
f	0.028	0.036
α	-0.014	-0.018

Kinetic/ Thermodynamic Considerations

The experimental values of the corrosion rates obtained were fitted into Arrhenius equation in order to estimate kinetic information as well as further elucidate the inhibitor adsorption mechanism. Arrhenius equation is expressed in equation (11) below:

$$\log(R_2/R_1) = \{E_a/2.303R\} \{1/T_1 - 1/T_2\} \quad (11)$$

where R_1 and R_2 are the corrosion rates at temperatures T_1 and T_2 respectively, E_a is the activation energy and R is the universal gas constant. The heat of adsorption was estimated from the trend of surface coverage with temperature as follows:

$$Q_{ads} = 2.303R \{ \log(\Theta_2/1-\Theta_2) - \log(\Theta_1/1-\Theta_1) \} \times \{ T_2 T_1 / (T_2 - T_1) \} \quad (12)$$

Where Θ_1 and Θ_2 are the degrees of surface coverage at T_1 and T_2 respectively. The calculated values are shown in table (3)

Concentration ($\mu\text{g/L}$)	Q_{ads} (kJ/mol)	E_a (kJ/mol)
Blank	-	2.47
20	-5.181	3.23
40	-4.118	3.27
60	-5.149	3.34
80	-4.305	3.51
100	-5.228	3.88

When %I increases with increase in temperature and E_a (inhibited solution) $<$ E_a (uninhibited solution), then the mechanism of adsorption is usually physisorption, otherwise, chemisorptions. Increase in E_a with concentration of the extract denotes increased energy barrier over which the acid molecules must pass in order to reach the active corrosion site of the metal

and effect dissolution. In other words, the acid molecules need higher energy in the presence of the extract, leading to slowed rate of metal corrosion. The standard heat of adsorption is negative, indicating the exothermic nature of the process.

Conclusion

On the basis of our investigation, the following conclusions are drawn:

- the extracts of *B. axillaries* acts as an effective an efficient inhibitor against aluminium corrosion in the acid medium at all temperatures studied, with greatest efficiency at 303 K
- corrosion rate increases with temperature both in the absence and presence of the inhibitor but significantly decreased further in the presence of the extracts
- the inhibition prowess of *B. axillaries* extracts is probably due to the adsorption of the active components of extracts on to the aluminium surface and thus blocking the corrosion active sites of the aluminium by the physical adsorption mechanism.
- the inhibition behavior of aluminium corrosion by the extracts is approximated by Temkin and Langmuir adsorption modesl at all the concentrations and temperatures studied
- the adsorption process is exothermic as inferred from negative values of enthalpy of adsorption.

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