



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

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ABSTRACT

The adsorption and inhibition of Aluminium corrosion in 1.0 M HCl by different concentrations of extracts of *Baissea axillaris* (BXE) 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, but the presence of extract reduced corrosion rate. 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. Spontaneous physical adsorption mechanism was proposed. Activation Energy was deduced from the Arrhenius equation while thermodynamic approach yielded the heat of adsorption. BXE was found to have potentials of increasing lifespan of aluminium roofing materials if used as an inhibitor or incorporated into its paints.

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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

Aluminium roofing sheets collected from a building site in 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 washed in absolute ethanol, 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 concentrations by dissolving appropriate mass of the extracts in freshly prepared the acid respectively.

Weight loss technique

Pre-weighed aluminium coupons were totally immersed in about 200 ml of the acid 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 loss in weight was recorded progressively for 10 hours. The corrosion rate, R , and inhibition efficiency, % I were computed using equations (1) and (2) respectively:

$$R = (W_0 - W_t)/AT \quad (1)$$

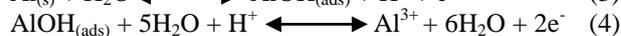
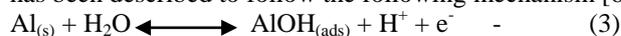
$$\%I = 100(R_b - R_i)/R_b \quad (2)$$

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 (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. Corrosion rate (R), inhibition efficiency (% I) and the degree of surface (Θ) obtained at the studied temperatures (table 1). 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 implied that the addition of BXE reduced the corrosion rate of aluminium compared to that of the free acid solution. However, for both the free acid and the inhibited solutions, corrosion rate increased with increase in temperature but decreased with increase in the concentration of the extract. The inhibition efficiency increased with increase in concentration of BXE. The addition of even a very small amount (20 $\mu\text{g/L}$) of BXE to the acid solution retarded the corrosion rate of the aluminium, the extent of retardation being both concentration and temperature dependent.

Table 1: Corrosion rate, inhibition efficiency and surface coverage in the absence and presence of BXE

Conc ($\mu\text{g/L}$)	R ($\text{mgcm}^{-2}\text{h}^{-1}$)		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, eugenol oils, glycosides and tannins [4] to the aluminium surface. Formation of an adsorbed layer isolates the metal surface from the aggressive acid medium by displacing water molecules and forming coordinate covalent bond with the metal [7]. The phytochemicals 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.

The observed decrease in % I with increase in temperature suggests physical adsorption of the BXE onto the aluminium surface. Similar trends have been reported [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 BXE 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].

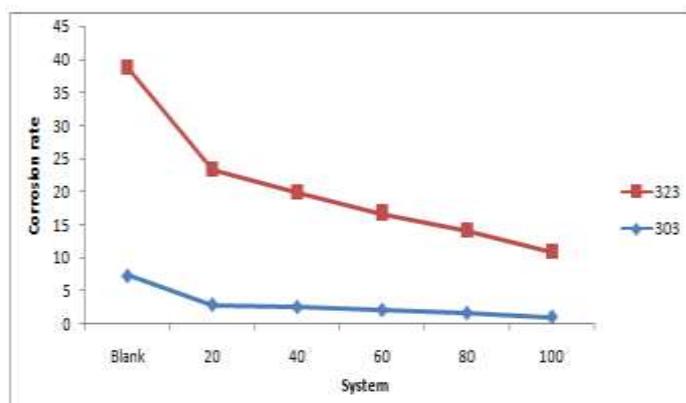


Figure 1 (a): Variation of corrosion rate with the concentrations of the systems investigated at 303 and 323 K.

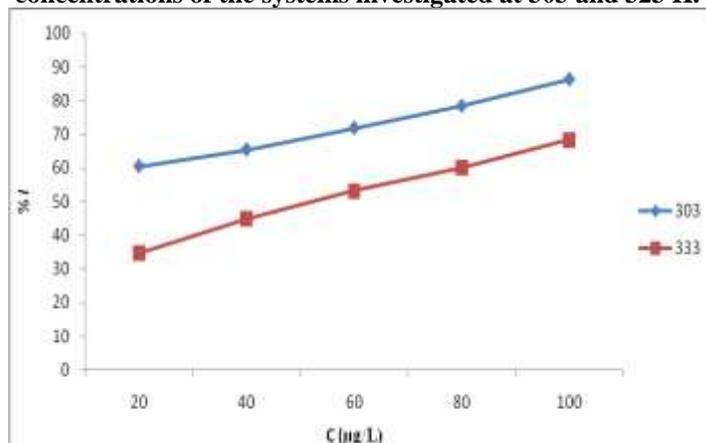


Figure 1 (b): variation of inhibition efficiency with the concentrations of the systems investigated at 303 and 323 K.

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]. 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 fitted into different adsorption 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

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

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

Where C is the concentration of BXE, 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:

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

Temkin and Langmuir adsorption isotherms (figures 2 and 3) was plotted for the inhibition of aluminium dissolution in 1.0 M HCl in the presence of different concentrations of BXE at 303 and 323K.

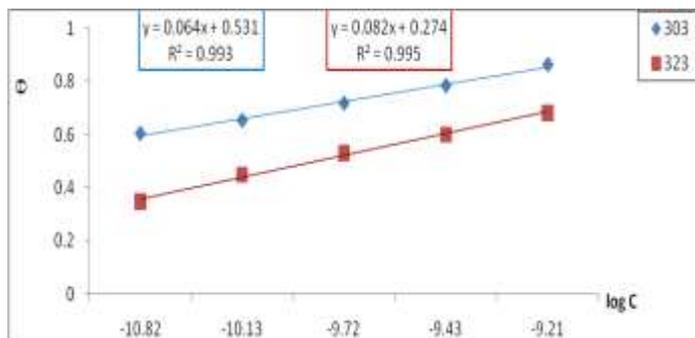


Figure 2: Temkin adsorption isotherm

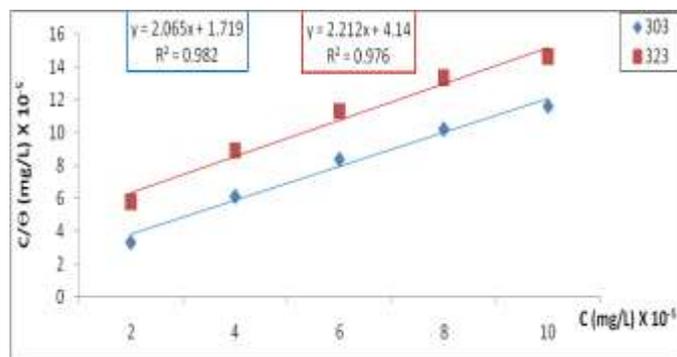


Figure 3: Langmuir adsorption isotherm

Temkin and Langmuir adsorption isotherms afforded some adsorption parameters (table 2). 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 occurred in the adsorbed layer and vice versa for $f > 0$ (i.e. attraction occurred 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 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
a	-0.014	-0.018

Kinetic/ Thermodynamic Considerations

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

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

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 computed activation parameters (table 3) are used to further describe the adsorption process.

Table 3: Activation energy and heat of adsorption

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 [5]. According to collision theory, increase in E_a with concentration of the extract denotes increased energy barrier over which the acid molecules must pass in order to collide with the metal surface and dissolve it. 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 were drawn:

- the BXE acted as an effective and efficient inhibitor against aluminium corrosion in the acid medium at all temperatures studied, with greatest efficiency at 303 K
- the inhibition prowess of BXE was 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 was best approximated by Temkin and Langmuir adsorption models at all the concentrations and temperatures studied
- the adsorption process is spontaneous and exothermic
- BXE is recommended for use as corrosion inhibitor for aluminium structural materials

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