

Evaluation Of The Inhibitive Properties And Adsorptive Parameters Of Ethanol Leaf Extract Of *Mucuna Pruriens* For The Corrosion Inhibition Of Aluminium In 2 M H₂SO₄ Solution

¹Ahile, U. J*, ¹Gbertyo, J. A., ²Anzene, J. S., ³Ajegi, J. O. and ¹Oche, E. J.

¹Department of Chemistry, Benue State University, Makurdi-Nigeria

²Directorate of Advancement and Linkages, Nasarawa State Polytechnic, Lafia-Nigeria

³Department of Chemistry, College of Education Oju, Benue State-Nigeria

Abstract

The hindering action of ethanol leaf extract of *Mucuna pruriens* on the corrosion of aluminium in 2 M H₂SO₄ solution was monitored isothermally (301 K, 305 K, 309 K and 313 K) using weight loss studies. The corrosion rate and degree of surface coverage, θ , increased with increase in the inhibitor concentration and temperature. The increase in the degree of surface coverage with rise in temperature suggests that strong chemical bond exist between the extracts and the adsorbent. The highest degree of surface coverage was 0.6610 at 313 K and 0.5 g/dm³ concentration of the adsorbate. Free energy of adsorption, ΔG_{ads} , ranged from -9.90 kJmol⁻¹ to -15.60 kJ/mol⁻¹, indicative of spontaneous adsorption process and these values are supportive of a physical adsorption mechanism. The heats of adsorption values were all positive implying that the accumulation of the adsorbate on the coupon surface was endothermic. The values of activation energy, E_a ranged from 23.59 kJmol⁻¹ to 78.12 kJmol⁻¹, further supporting physisorption. The mean entropy value of -43.39 Jmol⁻¹ suggests that the entire adsorption process might be controlled by the activated complex. The negative entropy informs that the mechanism was associative rather than dissociative. More so, the data obtained fitted best to Freundlich, Temkin, Langmuir and Adejo-Ekwenchi adsorption isotherms. The increase in parameter b in the Adejo-Ekwenchi isotherm supports chemical adsorption; calculated values of adsorption equilibrium constant from the Langmuir isotherm plot (3.013, 2.805, 1.815 and 1.49) are all positive signifying favourable adsorption of the inhibitor onto the metal surface. The average value of parameter n in the Freundlich isotherm is 0.869, slightly higher than the typical value of 0.6, indicating that the adsorption of this extract onto the surface of the metal may not be reasonably modeled by this isotherm despite the good R² values.

Key words: Corrosion inhibition, Weight loss method, Adsorption Isotherm

1. Introduction

The present regime of environmental consciousness, prudence and transparency has made green chemicals to be sought for in scientific and engineering circles now. Chemical weapons, insecticides, fertilizers, industrial effluents, paints and organic solvents have changed the health of planets and world inhabitants to the point that the very existence of life is threatened. The

industrial cycle is now becoming more careful due to strict environmental regulation, competition, good business sense and fear of depletion of the natural resources. The realization of the negative impacts of how our activities have affected the world has made man to search and go for green chemicals.

Aluminum has many applications in industry, due to its qualities including its good thermal and electrical conductivities, high ductility, good corrosion resistance and low density. It is used widely in the aviation and automobile industry, household appliances, electronic devices and containers [1, 2]. Aluminium is able to resist corrosion as a result of its ability to form a natural oxide film on its surface in a wide variety of media [2–6].

One of the most practical methods for protecting metals against corrosion is the use of inhibitors especially in acid solutions to prevent unexpected metal dissolution and acid consumption [7]. Studies have shown some organic compounds as effective corrosion inhibitors [8-10]. But, most of these organic compounds are highly toxic and harmful to both human being and the environment. Because of the known harmful effects of most synthetic organic inhibitors and restrictive environmental regulations, researchers have now focused on the need to develop cheap, non-toxic and environmentally friendly natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from herbs, spices and medicinal plants.

Plant extracts are a rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in the environment. In this work, the inhibitive properties of ethanol extract of *Mucuna pruriens* leaves on corrosion reaction of aluminium in H_2SO_4 solution was investigated. Adsorption mechanisms were deduced through adsorption isotherms using data obtained there from.

2. Materials and Methods

2.1 Materials

Aluminium wires were bought from the market and taken to the Department of Mechanical Engineering University of Agriculture Makurdi where they were melted in a furnace and moulded into sheets of desired sizes, they were later mechanically press-cut into coupons, with dimension of 2.1 cm x 2.1 cm and 0.35 cm each, with a tiny hole drilled at the edge of each coupon for suspension in the corrosive. The coupon surfaces were thoroughly polished to mirror finish using abrasive paper of different grades and then washed in absolute ethanol to degrease, dried with acetone, and preserved in a dessicator [11]. Subsequently, the initial weight of each coupon was carefully measured [12], using an ADAM Electric Weighing Balance (ADAM P W & PGW series; Max: 180 g, d = 0.0001 g). A 2 M H_2SO_4 solution was prepared which served as corrosive. All reagents used were analytical grade, while doubly distilled water was used for the

preparation of the solutions. *Mucuna pruriens* leaves were air dried, grounded to fine powder and 20 g was weighed and soaked in 200 cm³ of ethanol for 48 hours. This extract was filtered and freed of ethanol by evaporation in a water bath at 321 K. The concentrated stock of the extract obtained was used in preparing 0.1, 0.2, 0.3, 0.4 and 0.5 g of 2 M of H₂SO₄ respectively.

2.2 Weight Loss Measurement Method

80 mL of the 2 M H₂SO₄ which served as the corrosive, was taken in a 100 mL beaker and placed in the thermostated water bath maintained at 301 K. A coupon of known initial weight was wholly immersed in the corrosive suspended with the aid of a thread tied to a retort stand for 8 hours. At retrieval it was immediately dipped into a saturated solution of ammonium acetate to quench the corrosion reaction, and carefully washed in absolute ethanol, rinsed in distilled water and then kept in the desiccator to cool to ambient temperature and reweighed.

The weight loss of the coupon was obtained as the difference in weight before and after the immersion. Triplicate results were used in each case and the mean values reported for each of these temperatures. The same procedure was repeated after the introduction of various concentrations of the extract into the corrosive maintained at same temperatures. The weight loss was calculated thus;

$$W_L = W_i - W_f \quad 1$$

Where W_L is the weight loss of the coupon, W_i is the initial weight and W_f is the weight after retrieval. The percentage inhibition was obtained through equation 2 as shown,

$$IE \% = 1 - \frac{W_{inh}}{W_{blank}} \times 100 \quad 2$$

where, W_{inh} and W_{blank} are the weight losses in grams of the coupon in the presence and absence of the inhibitor respectively. The degree of surface coverage, θ , is given by equation 3

$$IE \% = 1 - \frac{W_{inh}}{W_{blank}} \quad 3$$

The corrosion rate of the metal was determined for the immersion period from weight loss through equation 4 as;

$$CR (mgcm^{-2}h^{-1}) = \frac{W_L}{At} \quad 4$$

where W_L is the weight loss in milligrams (mg). A is the coupon surface area in cm² and t is the immersion time in hours.

3. Results and Discussion.

3.1 Results

An average of triplicate values were recorded and used to calculate the weight loss from where the degree of surface coverage of *Mucuna pruriens* extract was computed and reported in table 1. The rate of corrosion at each studied temperature was evaluated using equation 4 above and also reported in table 1 below. These were used as the basis for determination of other parameters in tables 2 and 3.

Table 1 Degree of Surface Coverage (θ) and Corrosion rate(CR) $\text{gcm}^{-2}\text{h}^{-1}$

Conc (g/dm^3)	Surface Coverage (θ)				Corrosion rate ($\text{gcm}^{-2} \text{h}^{-1}$)			
	301 K	305 K	309 K	313 K	301 K	305 K	309 K	313 K
Blank					0.000100	0.000110	0.00023	0.000290
0.1	0.2264	0.2264	0.3840	0.5841	0.000069	0.000071	0.00093	0.000113
0.2	0.2381	0.2381	0.4828	0.5944	0.000068	0.000073	0.00090	0.000111
0.3	0.2857	0.2857	0.5320	0.6231	0.000063	0.000070	0.00084	0.000100
0.4	0.2976	0.3041	0.5419	0.6321	0.000062	0.000068	0.00082	0.000990
0.5	0.3214	0.3861	0.5563	0.6610	0.000060	0.000061	0.00079	0.000950

Table 2. Values of activation energy, E_a and thermodynamic parameters for extract of *Mucuna pruriens* stem as inhibitor for aluminium corrosion.

Conc. (g/dm^3)	E_a (kJmol^{-1})	ΔH (kJmol^{-1})	$-\Delta S$ (Jmol^{-1})	$-\Delta G$ (kJmol^{-1})			
				301 K	305 K	309 K	313 K
Blank	82.88	86.80	39.91				
0.1	78.12	74.05	49.57	12.70	12.70	13.60	13.70
0.2	76.17	65.09	13.53	11.02	11.30	14.30	15.60
0.3	77.62	52.24	78.40	10.80	10.90	13.70	14.90
0.4	78.12	40.02	36.84	10.50	10.40	13.10	14.20
0.5	23.59	31.49	38.61	9.900	10.80	12.70	13.90

Table 3. values of parameters of linearised various adsorption isotherms for adsorption of the extract on the aluminium surface.

Isotherm	Temp (K)	R ²	Slope	K _{ads}		-ΔG _{ads} (kJ/mol)
Langmuir	301	0.940	0.36	3.0130		4.84
	305	0.910	0.34	2.8054		4.83
	309	0.780	0.18	1.8150		4.48
	313	0.990	0.05	1.4990		4.35
Temkin					α	
	301	0.920	0.14	2.2690	0.163	4.57
	305	0.710	0.16	2.4604	0.187	4.71
	309	0.960	0.25	4.4055	0.287	5.34
Adejo-Ekwenchi					b	
	301	0.870	0.26	33.650	0.260	7.120
	305	0.710	0.34	42.600	0.340	7.750
	309	0.980	0.91	362.20	0.910	9.620
Freundlich					n	
	301	0.920	0.225	0.3581	0.920	2.830
	305	0.717	0.232	0.4009	0.717	2.970
	309	0.943	0.232	0.6776	0.943	3.520
	313	0.894	0.075	0.6854	0.894	3.580

4 Discussion

The degree of surface coverage of *Mucuna pruriens* extract on the aluminium coupons' surface increased with both concentration and temperature. This behaviour has long been attributed to the formation of chemical bond (Chemisorption) in the adsorbate-adsorbent interaction. Other researchers also reported that in addition, Chemisorption may also require energy of activation, and although the adsorption equilibrium must always shift towards the desorbed state as temperature rises, the extent of adsorption observed after a given time before equilibrium often increases with rising temperature and it is expected that the values of activation energy should be above 80 kJ/mol while physisorption has its values below 80 kJ/mol. The Ea values were just slightly below the threshold value except at 313 K and thus represents physical adsorption mechanism going by this axis of consideration [31].

The corrosion rate in both uninhibited and inhibited acid increases with rise in temperature but decreased with increase in inhibitor concentration which suggest chemical adsorption. The optimum inhibitor efficiency was approximately 66.1% which corresponds to 0.5g/dm³ *Mucuna pruriens* extract in 2 M H₂SO₄ at 8hours.

The value of activation energy, E_a , was calculated using the Arrhenius equation as given by equation (5)

$$CR = A \exp^{-E_a/RT} \quad 5$$

where CR is the corrosion rate of aluminium, A is Arrhenius constant or Pre-exponential factor, R is the universal gas constant and T is absolute temperature. Linearization of equation (5) gives equation (6).

$$\ln CR = \ln A + \frac{E_a}{RT} \quad 6$$

A plot of CR against $1/T$ gave a slope of $-E_a/R$, from where the values of activation energy were evaluated. [32].

The values of heat of adsorption, ΔH_{ads} , were obtained using an alternative formulation of Arrhenius equation, the transition state equation [32].

$$\ln \left(\frac{CR}{T} \right) = \ln \left(\frac{R}{Nh} \right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad 7$$

Where h is the Planck's constant, N is Avogadro's number, ΔS is the entropy of activation and ΔH is the enthalpy of activation. A plot of $\log (CR/T)$ vs. $1/T$ gave a straight line with the slope of $-\Delta H/R$ and the intercept of $\ln (R/Nh) + \Delta S/R$, from which the values of ΔS and ΔH were calculated and given in table 2. The positive signs of enthalpy (ΔH) reflect the endothermic nature of dissolution process meaning that dissolution of Aluminium is difficult. The negative values of ΔS in the presence of the inhibitor imply that the activated complex in the rate determining step represents association rather than dissociation, meaning that disordering decreases on going from reactants to the activated complex [31].

The change in activation free energy (ΔG) of the corrosion process was calculated at each temperature by applying equation.

$$\frac{E_a}{R} = Slope \quad 8$$

The obtained values of ΔG are listed in table 2,

The results also revealed that values of ΔG_{ads} are more negative at higher temperatures indicating that the spontaneity of adsorption and hence stability of the adsorbed layer is higher with rise in temperature [32]. It is of note that ΔG_{ads} up to -20kJmol^{-1} are consistent with interactions between charged molecules and the charged metal surface which is an indication of physical adsorption, while ΔG_{ads} values more negative than -40kJmol^{-1} involve charge sharing or transfer from the indicator molecules to the metal surface which is chemisorption [33]. However,

ΔG values were all negative which indicate a spontaneous adsorption of the inhibitor molecules, also the values were less than -40 kJ/mol which shows that the inhibitor functioned by physically adsorbing on the surface of the aluminium.

4.2 Adsorption isotherms

Freundlich isotherm plot of $\log \theta$ versus $\log C$ gave a straight line with slope equal to n and intercept $\log K$. The positive adsorption equilibrium constant, K , values are indication of favourable adsorption. The parameter, n , in the Freundlich isotherm is related to intensity of adsorption and it varies with heterogeneity of the material [29] and the value is always positive but not an integer, with a typical value of 0.60 [25]. The values of parameter n are all greater than 0.6, an indication that this adsorption process cannot be reasonably modeled by this isotherm. Values of ΔG_{ads} obtained through this isotherm are all below 20 kJ/mol, supporting physical adsorption mechanism.

The Temkin isotherm better models chemical adsorption. The positive sign of parameter α is an indication of attractive interaction of molecules within the adsorbed layer; a fact which is supported by increase in the degree of surface coverage in table 1 with rise in temperature. The R^2 values also indicate good fitting, as they are fairly close to unity. Also, values of ΔG_{ads} are in agreement with those obtained through the conventional method (all are below 20 kJ/mol). Therefore, it can be deduced that this adsorption models Temkin isotherm [29].

Thermodynamic parameters can be used to determine the adsorption behaviour of a pure compound with known molecular mass but not for a crude extract. The Adejo-Ekwenchi adsorption isotherm has been published to tackle the anomalies usually encountered in resolving adsorption processes of plant extracts involving several compounds of varying molecular masses. Increase in parameter b in this isotherm with temperature implies chemical adsorption, and for this data it was observed to be consistent with chemisorption from 301 K to 309 K [27, 28]. The “out of phase” value at 313 K may imply that desorption processes dominated the adsorption-desorption equilibrium process.

5. Conclusion

This work has shown that ethanol leaf extract of *Mucuna pureins* inhibited the corrosion of Aluminium in 2 M H_2SO_4 . The corrosion rate decreased with increase in the extract concentration and the efficiency increased with increase in both concentration of the extract and rise in temperature.

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