

Effects of Extracts from *Nauclea Latifolia* on the Dissolution of Carbon Steel in H₂SO₄ Solutions

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The effects of ethanol (ENL), alkaloids (ANL) and non-alkaloids (NNL) extracts from the root of *Nauclea latifolia* on the dissolution of carbon steel in H₂SO₄ solutions were studied using gasometric techniques. The extracts showed significant inhibition of the rate of corrosion of the steel and the maximum inhibition efficiencies ($\eta\%$) of the extracts followed the trend ANL>ENL>NNL. $\eta\%$ increased with the extracts concentration but decreased with temperature rise (NNL). The inhibitive action of the plant's extracts is attributed to the adsorption of mainly the alkaloids on the metal surface following Temkin adsorption isotherm.

Keywords: Mild steel; *Nauclea latifolia* extract; Acid corrosion; Alkaloid; Corrosion inhibition; Adsorption

1. INTRODUCTION

Increased awareness of the environmental requirements that is currently imposed on the development of cleaner chemical inhibitors and of the health risks associated with the use of unsafe and toxic inorganic inhibitors have increased interest in the use of natural products (of plant origin) as acid corrosion inhibitors. Though, the use of plant extracts as corrosion inhibitor is not a recent development as records show that in the Middle Ages (i.e from the 5th century to the 15th century) plant extracts (flour, bran, yeast, a mixture of molasses and vegetable oil, and starch) have been used

for pickling of metal articles by master-armourers [1,2] and extracts of bran among other substances used to inhibit the corrosion of iron in acids [3] its use in the new millennium has resulted in enormous data on plant extracts as corrosion inhibitors. Plants aerial parts and roots extracts, exudates gums, vegetable oils and tannins extracts have all been reported as good corrosion inhibitors of metals in aqueous solutions. A summary of plants extracts used as corrosion inhibitors have recently been given in Okafor *et al.* [4] and Raja and Sethuraman [5].

Plant extracts are rich sources of naturally synthesized chemicals and thousands have been identified in these extracts. They constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant [4, 6-10]; as well as its location [11].

Nauclea latifolia commonly known as Pin Cushion Tree is a straggling shrub or small spreading tree that belongs to the family Rubiaceae and to the class Magnoliopsida (Dicotyledons). It is a widely distributed savanna plant native to Africa and Asia and found in the forest and fringe tropical forest. In many African communities, the plant enjoys huge popularity on account of its diverse potential for treating various ailments [12-15]. Phytochemical investigation of the plant revealed the presence of naturally synthesized biological compounds including, monoterpene, triterpene, alkaloids, saponins, flavonoids, steroids, glycosides and traces of inorganic compounds [16-20].

In our previous report [10] ethanol extracts from leaves, bark and roots of *N. latifolia* have been established as green corrosion inhibitor of the acid corrosion of carbon steel in H₂SO₄ solutions. The inhibition efficiencies of the extracts follow the trend: root>leaves>bark and the presence of alkaloids in the root and leaves extracts was assumed to be responsible for the reported inhibition trend. In order to affirm this assumption we present a study on the effects of ethanol (ENL), alkaloids (ANL) and non-alkaloids (NNL) extracts from the root of *N. latifolia* on the dissolution of carbon steel in 5 M H₂SO₄ solutions using gasometric techniques. The root of *N. latifolia* was selected because it exhibited the highest inhibition efficiency.

2. EXPERIMENTAL

The carbon steel coupons (of dimension 2.0 x 0.08 x 5.0 cm and surface area of 21.12 cm²) used for this work were polished with series of emery paper of variable grades starting with the coarsest and proceeding in steps to the finest (600) grade, degreased with absolute ethanol, dipped into acetone and air dried.

2.1. Preparation of plant extracts

The roots of *N. latifolia* were collected as required from a local bush in Calabar, Nigeria in January, 2012. The plant material was identified by a botanist at the Department of Botany, University of Calabar, Calabar, Nigeria. These were cut into small chips, dried in an N53C-Genlab laboratory

oven at 50°C, and ground into powder form. 80.0 g of the powder was extracted continually with 250 cm³ of absolute ethanol in a soxhlet extractor for 24 h. The solvents were evaporated in to afford crude ethanol extract. This was used as ethanol extract (ENL) for the corrosion test. The remaining portion of the ethanol extracts from *N. latifolia* was partitioned between 100 ml of chloroform and 100 ml of 0.1 M HCl solution using a separating funnel. The float fraction was used as the non-alkaloid extract (NNL). The tailing portion of the extracts in the separating funnel was further basified with 100 ml of ammonia and partitioned with 100 ml of chloroform to obtain the alkaloid extract (ANL).

1.5 g of the ethanol extracts (ENL) and the non-alkaloid extract (NNL) were respectively soaked in 0.5 liter of 5.0 M H₂SO₄ solutions for the gasometric test. The resultant solutions were kept for 24 h, filtered and stored. From the stock solutions (3.0 g/L), inhibitor test solutions (concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 g/L) were prepared. The yield of the alkaloid extract was small even after repeated extraction from the ethanol extract. From the quantity extracted, 100 cm³ of 1.0 and 0.5 g/L of the extracts were prepared.

2.2. Gasometric measurements

The gasometric measurements were carried out as previously described [21-22]. However, 5 M H₂SO₄ solutions were used to produce appreciable amount of hydrogen needed for the depression of the paraffin oil in the gasometric assembly. The data presented are means of duplicate determinations.

3. RESULTS AND DISCUSSION

The volume of gas evolved during the corrosion of carbon steel in 5.0 M H₂SO₄ solutions in the absence and presence of the plant extracts was measured as a function of time. In general, for acid solutions, when dissolved oxygen is present both hydrogen evolution and oxygen reduction reactions will be possible. However, in view of the fact that, the concentration of H₃O⁺ in acid solutions, at pH 0, is high, and since this ion has a high rate of diffusion, the contribution made by the hydrogen evolution reaction on the cathodic process will predominant that of oxygen reduction reaction [23]. Thus, it is assumed that the dominant gas evolved during the dissolution of the steel in 5.0 M H₂SO₄ is hydrogen.

The result of the hydrogen evolution obtained in the absence and presence of ENL at 30°C is shown in Figure 1. Similar plots were obtained in the presence of NNL (at 30 and 40°C) and ANL at 30°C. The rates of hydrogen evolution, obtained from the slopes of the plots are presented in Table 1. It is observed that the presence of the extracts decreases the volume of hydrogen evolved during the corrosion reaction compared to the blank system and that the rate of hydrogen evolution decreased with the increase in the extract concentration and with increased in temperature (for NNL). Similar trend has been previously reported for the corrosion of mild steel in 5.0 M H₂SO₄ in the presence of ethanol extract from *N. latifolia* [10]. This trend implies a dependence of the inhibition process on the amount of the inhibiting species present in the system.

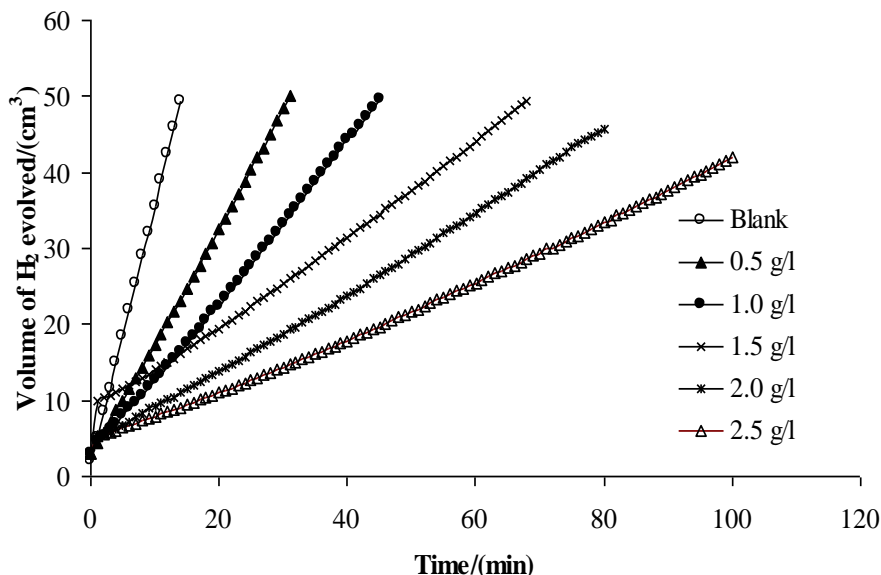


Figure 1. Variation of volume of hydrogen evolved with time for galvanized steel in 5 M H₂SO₄ solution with and without ethanol extracts from *Nauclea latifolia* (ENL) at 30°C

The results also suggest that the inhibition of the rate of hydrogen evolution in the presence of the extracts follow the trend: ANL>ENL>NNL at the concentrations studied.

From the rate of hydrogen evolution values, the inhibitor surface coverage (θ) and efficiencies ($\eta\%$) were determined using Eqs (1) and (2), respectively.

$$\theta = \frac{(R_o - R_{inh})}{R_o} \tag{1}$$

$$\eta\% = \frac{(R_o - R_{inh})}{R_o} \times 100 \tag{2}$$

where R_o and R_{inh} are the rates of hydrogen evolution in the absence and presence of the plant extracts, respectively. It can be seen from the calculated results (Table 1) that the extracts inhibit the dissolution of the steel to an appreciable extent and that the extent of inhibition is dependent on the inhibitor concentration.

Table 1. Kinetics data for the inhibition of galvanized steel dissolution in 5 M H₂SO₄ solution in the presence and absence (blank) of extracts from *Nauclea latifolia*

| Concentration (g/l) | Ethanol extracts | | | Non-alkaloid extracts | | | | | | Alkaloid extracts | | | | |
|---------------------|---------------------------------------|----------|--------|---------------------------------------|----------|--------|---------------------------------------|----------|--------|-------------------------|--------------------------|---------------------------------------|----------|--------|
| | 30°C | | | 30°C | | | 40°C | | | E _a (KJ/mol) | Q _{ad} (KJ/mol) | 30°C | | |
| | R _H (cm ³ /min) | θ | IE (%) | R _H (cm ³ /min) | θ | IE (%) | R _H (cm ³ /min) | θ | IE (%) | | | R _H (cm ³ /min) | θ | IE (%) |
| Blank | 3.407 | - | - | 3.407 | - | - | 14.550 | - | - | 59.07 | - | 3.407 | - | - |
| 0.5 | 1.515 | 0.56 | 55.5 | 1.799 | 0.47 | 47.2 | 11.800 | 0.19 | 18.9 | 76.55 | -54.73 | 1.021 | 0.70 | 70.0 |
| 1.0 | 1.035 | 0.70 | 69.6 | 1.533 | 0.55 | 55.0 | 8.257 | 0.43 | 43.3 | 68.52 | -19.23 | 0.640 | 0.81 | 81.2 |
| 1.5 | 0.605 | 0.82 | 82.3 | 1.331 | 0.61 | 60.9 | 7.871 | 0.46 | 45.9 | 72.33 | -24.80 | - | - | - |
| 2.0 | 0.521 | 0.85 | 84.7 | 1.103 | 0.68 | 67.6 | 7.036 | 0.52 | 51.6 | 75.40 | -27.30 | - | - | - |
| 2.5 | 0.373 | 0.89 | 89.0 | 0.865 | 0.75 | 74.6 | 6.173 | 0.58 | 57.6 | 79.96 | -31.44 | - | - | - |

3.1. Inhibition mechanism

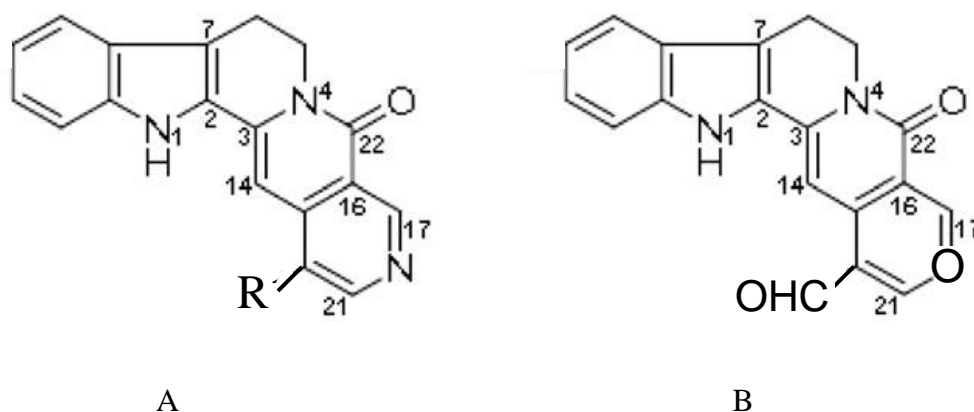
The inhibition process, from a theoretical standpoint, has been regarded as a simple substitution process, in which an inhibitor molecule (I) in the aqueous phase substitutes an x number of water molecules adsorbed on the surface:

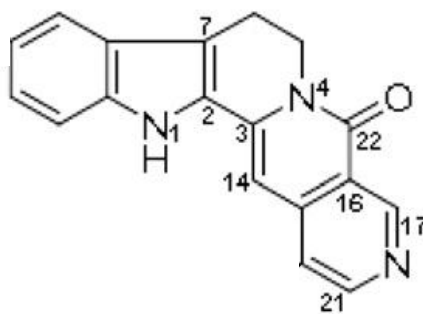


The inhibitor molecules may then combine with Fe^{2+} ions on the metal surface, forming metal-inhibitor complex. The resulting complex could either inhibit or catalyzed further metal dissolution, depending on its solubility [4]. From the results obtained in this present investigation, it follows that the plant extracts form insoluble complexes with the metal ions which inhibit the corrosion reaction.

N. latifolia root extracts contains both alkaloids and non-alkaloids compound. Alkaloids extracted from the roots of *N. latifolia* include naucleoline, naucleidinal, nauclefine, nauclefolinine, nauclefine and naufoline [24-26]. Three dimensional structures of some of these compounds are shown in Figure 2. Most of them are pentacyclic ringed indole alkaloids with polycyclic adsorption sites (including N and O atoms). These characteristics would afford the compounds the abilities to adsorb on the metal/solution interface via, electrostatic attraction between the charged metal and the charged inhibitor molecules, dipole-type interaction between unshared electron pairs in the compounds with the metal, π electrons-interaction with the metal, and a combination of all of the above [23, 27]. The adsorption on the surface of the metal creates a barrier for mass and charge transfer leading to a decrease in the interaction between the metal and the corrosive environment. As a result, the corrosion rate of the metal is decreased.

The non-alkaloidal compounds present in *N. latifolia* include monoterpene, triterpene, saponins, flavonoids, steroids and glycosides [10, 16-19]. These compounds are heterocyclics in nature and contain both N and O atoms in their structures. From the results of the corrosion test (Figure 3) it could be seen that the non-alkaloidal compounds have some inhibiting ability which is probable due to the adsorption of the heterocyclics on the surface of the metal. However, this adsorption is not as effective as those of the alkaloids. From Figure 3 also, it could be observed that mutual effects of the alkaloidal and the non-alkaloidal extracts (total ethanol extract, ENL) enhanced the inhibition ability of NNL but reduced that of ANL at the extracts concentration tested.





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Figure 2. Structure of some indole alkaloids present in *Nauclea latifolia* (a) Nauclefoline, R=CH₃O₂C (b) Naucleidinal (c) Nauclefine

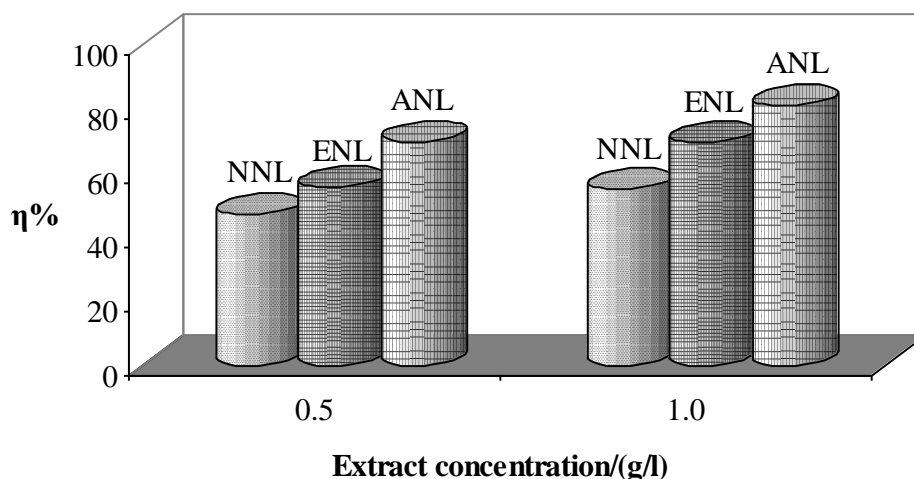


Figure 3. Maximum inhibition efficiency for galvanized steel coupons in 5.0 M H₂SO₄ containing 0.5 and 1.0 g/l ENL, ANL and NNL extracts from *N. latifolia* at 30°C

3.2. Adsorption isotherm

In order to use the rate of hydrogen evolution measurements to calculate the thermodynamic parameters pertaining to the inhibitor adsorption of the plant extract, it is necessary to determine empirically which adsorption isotherm fits best to the surface coverage data. The experimental data from ENL and NNL (at 30 and 40°C) were applied to different adsorption isotherm equations and found to fit the Temkin isotherm (Figure 4) with R² values of 98.43% (for ENL at 30°C) and 95.45% and 94.86% (for NNL at 30 and 40°C, respectively). The Temkin isotherm may be formulated as:

$$\exp(-2a\theta) = kc \quad (4)$$

where θ is the surface coverage, a is the molecular interaction parameter (determined from the slope of the plot in Figure 4) and k (determined from the intercept of the plot in Figure 4) is the

equilibrium constant whose values indicate the binding power of the inhibitor to the steel surface and is related to the standard free energy of adsorption by the equation:

$$k = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^o}{RT}\right) \tag{5}$$

The value of 55.5 being the concentration of water in solution expressed in mole. The calculated values of a , k and $-\Delta G_{ads}^o$ are given in Table 2. The molecular interaction parameter can have both positive and negative values. Positive values of a indicate attraction forces between adsorbed molecules while negative values indicate repulsive forces between the adsorbed molecules [28]. Negative values of a were obtained indicating that repulsion exists between the adsorbed phytochemical molecules. These values can also be interpreted to imply that the interactions between molecules caused a decrease in the adsorption energy with the increase of surface coverage. The negative value of $-\Delta G_{ads}^o$ indicates a spontaneous adsorption of the molecules on the surface of the metal. From the $-\Delta G_{ads}^o$ values obtained, physical type of adsorption is dominated during the adsorption of the extract molecules on the surface of the metal [29-30].

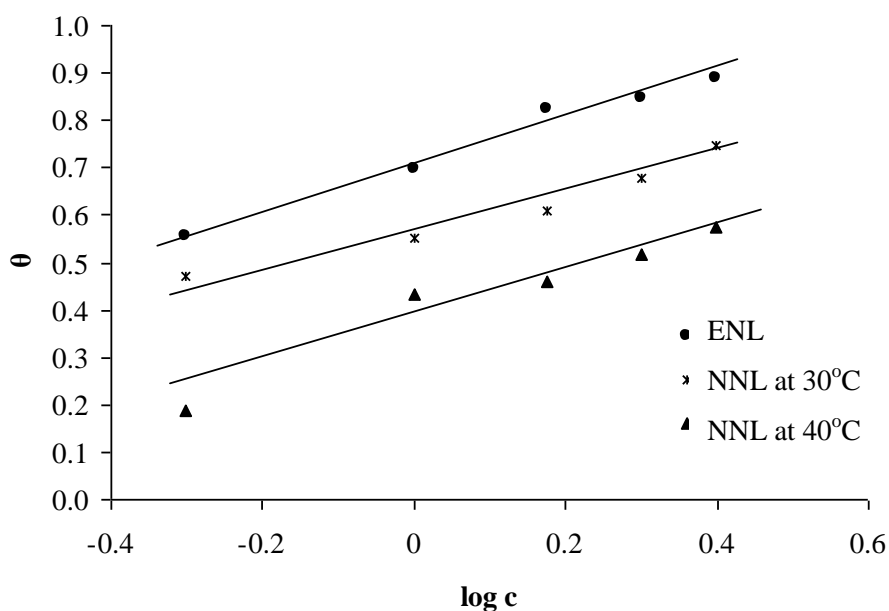


Figure 4. Temkin adsorption isotherm for galvanized steel in 5 M H₂SO₄ solution in the presence of ENL and NNL

Table 2. Adsorption parameters for mild steel in H₂SO₄ solutions containing from extracts from *Nauclea latifolia*

| Parameters | Ethanol extracts | Non-alkaloid extracts |
|-----------------------------|------------------|-----------------------|
| | 30°C | 30°C |
| a | -0.44 | -0.58 |
| k (mol ⁻¹) | 27.55 | 31.84 |
| $-\Delta G_{ads}^o$ kJ/mol) | 18.47 | 18.84 |

4. CONCLUSION

Ethanol (ENL), alkaloids (ANL) and non-alkaloids (NNL) extracts from the root of *Nauclea latifolia* were found to be good inhibitors of the dissolution of carbon steel in H₂SO₄ solutions.

The maximum inhibition efficiencies ($\eta\%$) of the extracts followed the trend ANL>ENL>NNL and $\eta\%$ increases with the extracts concentration but decreases with temperature rise (NNL). The trend confirms previous assumption that the alkaloid content of *N. latifolia* is the principal inhibiting agent in extracts from the plant.

The inhibitive action of the plant's extracts is attributed to the adsorption of the alkaloids and non-alkaloidal components of the plant on the metal surface.

The experimental data obtained in this study fits the Temkin adsorption isotherm.

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