A Study of the Corrosion Inhibition of Mild Steel in 0.5M Tetraoxosulphate (VI) acid by Alstonia boonei Leaves Extract as an Inhibitor at Different Temperatures.

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Abstract—A comparative study of the corrosion inhibition performance of Alstonia boonei leaves extract in 0.5M tetraoxosulphate (VI) acid at different temperatures (30°C, 50°C and 70°C) was undertaken. The results showed that Alstonia boonei leaves extract was more efficient as a corrosion inhibitor at 30°C compared to temperatures of 50°C and 70°C. The adsorption of Alstonia boonei leaves extract was found to obey Langmuir adsorption isotherm at all temperatures (30°C, 50°C and 70°C), but did not obey Freundlich adsorption isotherm at all temperatures. A study of the effect of temperature on corrosion rate and inhibition efficiency showed that corrosion rate increased with increase in temperature, while the inhibition efficiency decreased with increase in temperature.

Keywords—Adsorption, Corrosion, Efficiency, Inhibition, Isotherm.

I. INTRODUCTION

One of the commonest methods of mitigating the corrosion of metals and alloys in corrosive environments is by the use of inhibitors. A corrosion inhibitor is a substance which when added in small concentrations to an environment, effectively reduces the corrosion rate of the metal exposed to that environment [1]. Corrosion inhibitors are commonly added in small concentrations to acids, cooling water, steam and other environments; either continuously or intermittently to reduce corrosion. Corrosion inhibitors reduce the rate of corrosion by adsorption of ion molecules onto the metal surface, increasing or decreasing the anodic and/or cathodic reaction, decreasing the diffusion rate for reactants to the surface of the metal and decreasing the electrical resistance of the metal surface [2]. Chemical based corrosion inhibitors have been successfully used to control the corrosion of metals and alloys in various media [3-5]. However, due to the high toxic nature of chemical based corrosion inhibitors [6], there is need to develop environmentally acceptable and inexpensive green corrosion inhibitors. Green corrosion inhibitors are cheap, ecologically friendly and possess no threat to the environment [7]. There are numerous reports on the use of extracts from plants to control the corrosion of mild steel in several media. The leaves of Nyctanthes arbor-tristis acted as good corrosion inhibitor for mild steel in tetraoxosulphate (VI) acid medium [8]. The inhibition efficiency increased with increase in the concentration of the extract and maximum inhibition efficiency of 90% was obtained at inhibitor concentration of 1% v/v. Extract of Citrus aurantium found to be effective in 1M hydrochloric acid with efficiency of up to 97.51 % [9]. Ethanol extract of Andrographis paniculata inhibited the corrosion of mild steel in hydrochloric acid solution through the mechanism of physical adsorption [10]. Alcoholic extracts of eight plants (Lycium shawii, Teucrium oliverianum, Ochradenus baccatus, Anvillea garcinii, Cassia italica, Artemisia sieberi, Carthamus tinctorius and Tripleurospermum auriculatum) inhibited the corrosion of mild steel in acidic media through adsorption and acted as mixed type inhibitors [11]. Aqueous extracts of damissa lupine and half – bar retarded the partial cathodic reaction of the corrosion of 7075 – T6 aluminium alloy in aqueous solution of 0.5 M sodium chloride [12]. Lupine extract had
the highest inhibition efficiency while half – bar extract had the lowest inhibition efficiency.

The inhibitive action of plant extracts could be attributed to the presence of phytochemical constituents present in the extracts [11-14]. Most of these phytochemical constituents have complicated molecular structures, large molecular weights and significant number of oxygen, sulphur and nitrogen atoms incorporated in their structures [11-14]. These compounds can adsorb on the metal surface via the lone pairs of electrons present in their oxygen, sulphur and nitrogen atoms [11-15]. The adsorption of such compounds decreases the surface area of contact with the corrodent, thereby reducing the corrosion of the metal. Extract of Uncaria gambir could serve as an effective corrosion inhibitor of mild steel in aqueous solution [16]. Electrochemical studies showed that the corrosion inhibition of mild steel in aqueous solution of Uncaria gambir extract was highest at a concentration of 150 ppm in solution with a pH of 5 [16].

Though, numerous plants have been studied and proven to possess corrosion inhibition potentials, there are still many that have not been studied for their anticorrosion potentials [11]. In order to increase the number of plants that possess anticorrosion potentials, we report the corrosion inhibition potentials of Alstonia boonei leaves extract. To the best of our knowledge, Alstonia boonei has not been studied for its corrosion inhibition properties, therefore the need to undertake the study. Phytochemical analyses of ethanolic extract of Alstonia boonei revealed the presence of the following phytochemical compounds: saponins, general glycosides, flavonoids, terpenoids and steroids, carotenoids, coumarins, alkaloids, anthraquinones and glycosides [17]. These phytochemical constituents are mostly responsible for the corrosion inhibition of plants [11–14]: therefore Alstonia boonei has anticorrosion potentials. In line with this, it became necessary to compare the corrosion inhibition performance of Alstonia boonei leaves extract at various temperatures (30°C, 50°C and 70°C). Secondly, to study the effect of temperature on the corrosion of mild steel in tetraoxosulphate (VI) acid medium using Alstonia boonei leaves extract as an inhibitor. This will be accomplished using Arrhenius and Eyring’s equations.

Chemical reaction kinetics is the study of the rates of chemical processes [18]. It includes investigations of how different experimental conditions can influence the rate of a chemical reaction and yields information about the reaction mechanism, as well as the construction of mathematical models that can describe the characteristics of chemical reaction [19].

II. METHOD

2.1 Materials and Equipment

The materials used for the study were: mild steel sheet, Alstonia boonei leaves, absolute ethanol, 0.5M tetraoxosulphate (VI) acid and distilled water. Equipment used were: Electronic balance, electric oven, stopwatch, beakers, abrasive papers and reflux condenser.

2.2 Preparation of corrosion test specimen

Mild steel sheet was mechanically press cut to produce corrosion test specimens each of dimensions 30 mm × 15 mm × 1.2 mm. A 3 mm diameter hole was drilled on each specimen to facilitate easy suspension and withdrawal from the corrodent. The surfaces of the test specimens were polished with abrasive papers to produce smooth surfaces. For surface treatment, the test specimens were decreased in absolute ethanol, washed in distilled water. The washed specimens were cleaned with cotton wool and oven dried. The dried specimens were weighed to obtain the initial weights and stored in a desiccator.

2.3 Preparation of plant extract

The leaves of Alstonia boonei were obtained from Uramuuruwa Onuga forest in Umude Avuvu, Ikeduru, Imo State, Nigeria. The leaves were identified in the Department of Plant Science and Biotechnology, Imo State University, Owerri, Nigeria. The leaves were shade dried for two weeks. The leaves were grounded into powdery form and stored in airtight containers. A stock solution of the plant extract was obtained by refluxing 25 grammes of the powdered Alstonia boonei leaves in 500 mL of 0.5M tetraoxosulphate (VI) acid for three hours. The refluxed solution was filtered to remove any contaminant which might be present. The required concentrations of the extract (2.5 g/L, 5.0 g/L, 10.0 g/L, 25 g/L and 50 g/L) needed for corrosion studies were prepared from the stock solution.

2.4 Experimental

The weight loss measurements were carried out as previously described by [20]. However, weight loss measurements were conducted at temperatures of 30°C, 50°C and 70°C respectively. The mild steel specimens were each suspended and totally immersed in 0.5M tetraoxosulphate (VI) acid without and with different concentrations (2.5 g/L, 5.0 g/L, 10 g/L, 25 g/L and 50 g/L) with the aid of strings and rods for ten hours, washed thoroughly in ethanol, rinsed in distilled water, dried and weighed to obtain the final weight. The weight loss was obtained by computing the difference between the initial weight and final weight. From the weight loss results, the corrosion rate was computed using equation (1) [7]:

\[
\text{Corrosion rate (mm/yr) = \frac{87.6W}{\rho At}} \quad (1)
\]
Where \( W \) is the weight loss in grammes, \( \rho \) is the density of the specimen in g cm\(^{-3}\), \( A \) is the area of the specimen in cm\(^2\) and \( t \) is the exposure time in hours. The inhibition efficiency (I \%) of *Alstonia boonei* leaves extract was computed using equation (2) [7]:

\[
I\% = (1 - \frac{W_i}{W_o}) \times 100 \ldots (2)
\]

\( W_i \) = weight loss in the presence of inhibitor
\( W_o \) = weight loss in the absence of inhibitor

### III. RESULTS AND DISCUSSION

#### 3.1 Comparison of the corrosion inhibition performance of the extract at different temperatures.

This is undertaken with a view to establish the temperature at which *Alstonia boonei* leaves extract will function optimally as a corrosion inhibitor in 0.5M tetraoxosulphate (VI) acid medium. Presented in Fig.1 are the calculated values of corrosion rates (mm/yr) of mild steel in 0.5M tetraoxosulphate(VI) acid in the presence of *Alstonia boonei* leaves extract at temperatures of 30\( ^\circ \)C, 50\( ^\circ \)C and 70\( ^\circ \)C. The corrosion rate decreased as the concentration of the extract increased from 0.25 g/L to 50 g/L. A comparison of the corrosion rates at 30\( ^\circ \)C, 50\( ^\circ \)C and 70\( ^\circ \)C revealed that the corrosion rates obtained at 30\( ^\circ \)C were lower compared to the corrosion rates at temperatures of 50\( ^\circ \)C and 70\( ^\circ \)C. Maximum values of corrosion rates were obtained at temperature of 70\( ^\circ \)C. Also presented in Fig.2 are the calculated values of inhibition efficiency (I \%) of

#### 3.2 Adsorption isotherm

The adsorption process of organic inhibitor molecules occurs due to the replacement of water molecules adsorbed on metallic surface as represented by equation (3):

\[
\text{Org} \text{(sol)} + x\text{H}_2\text{O} \rightarrow \text{Org(ads)} + \text{H}_2\text{O} \ldots (3)
\]

Where \( x \) is the number of \( \text{H}_2\text{O} \) molecules replaced by one organic molecule.

The degree of surface coverage (\( \Theta \)) obtained from the weight loss measurements were used to evaluate the isotherm that best fits the data. The degree of surface coverage (\( \Theta \)) was computed using equation (4) [7]:

\[
\Theta = 1 - \frac{W_i}{W_o} \ldots (4)
\]

Where \( W_i \) and \( W_o \) are the weight losses in the presence and absence of the inhibitor respectively. Values of linear correlation coefficients obtained from the plots were used to determine the isotherm most applicable to the experimental data [21].

The Langmuir adsorption isotherm model is based on the assumption that the adsorption takes place at specific homogeneous sites within the adsorbent [14]. The Langmuir adsorption isotherm model is represented by equation (5) [14, 22]:

\[
\frac{C_{\text{inh}}}{\Theta} = \frac{1}{K_{ads}} + C_{\text{inh}} \ldots (5)
\]
Where $K_{ads}$ (g$^{-1}$) is the adsorption equilibrium constant and $C_{inh}$ is the inhibitor concentration. Fig. 3 shows the Langmuir adsorption isotherm plots for the adsorption of Alstonia boonei leaves extract at temperatures of 30°C, 50°C, and 70°C. Straight lines were obtained with $R^2$ close to unity at each temperature. This is an indication that the adsorption of the extracts at temperatures of 30°C, 50°C and 70°C obeyed Langmuir adsorption isotherm [23]. It also indicates that Alstonia boonei extract species occupies typical adsorption sites at the metal/solution interface [24]. The values of the Langmuir

\[
y = 1.1621x + 0.2247 \\
R^2 = 0.9997
\]

Concentration (g/L)

\[
y = 1.5814x + 2.9008 \\
R^2 = 0.9972
\]

\[
y = 1.453x + 1.7866 \\
R^2 = 0.9987
\]

\[
y = 1.1621x + 0.2247 \\
R^2 = 0.9997
\]

\[
y = 1.5814x + 2.9008 \\
R^2 = 0.9972
\]

\[
y = 1.453x + 1.7866 \\
R^2 = 0.9987
\]

Fig. 3: Langmuir adsorption isotherm plots for the corrosion of mild steel in 0.5M H$_2$SO$_4$ in the presence of the extract at different temperatures.

Table 1: Langmuir adsorption isotherm parameters for the corrosion of mild steel in H$_2$SO$_4$ in the presence of the extract.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$K_{ads}$</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.46</td>
<td>-21.17</td>
<td>0.999</td>
</tr>
<tr>
<td>50</td>
<td>0.56</td>
<td>-17.00</td>
<td>0.998</td>
</tr>
<tr>
<td>70</td>
<td>0.36</td>
<td>-16.79</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Adsorption isotherm parameters obtained from the plots are presented in Table 1. The adsorption equilibrium constant ($K_{ads}$) decreased with increase in temperature from 30°C to 70°C. Since the efficiency of an inhibitor is a function of the magnitude of the adsorption constant ($K_{ads}$), large values of $K_{ads}$ is an indication of better and stronger interaction between the inhibitor molecules and the metal, whereas small values of $K_{ads}$ mean weak interaction [25]. The value of the adsorption equilibrium constant ($K_{ads}$) obtained at 30°C is higher compared to the values obtained at 50°C and 70°C. This implies that Alstonia boonei leaves extract was more efficient as an inhibitor at 30°C compared to the other temperatures (50°C and 70°C).

The Freundlich isotherm is mostly used for heterogeneous surface energy systems (non-uniform distribution of sorption heat) [26]. The Freundlich adsorption isotherm is defined by equation (6) [27]:

\[
\log\Theta = \log K_{ads} + n \log[C] \quad (0<n<1) \ldots (6)
\]

Fig. 4 shows the Freundlich adsorption isotherm plots for the adsorption of Alstonia boonei extract at temperatures of 30°C, 50°C and 70°C. Straight lines were obtained with $R^2$ values presented in TABLE 2. The values of $n$ and $K_{ads}$ were evaluated from the slopes and intercepts of the plots [27]. These values are presented in TABLE 2. The adsorption equilibrium constant ($K_{ads}$) decreases as the temperature increased from 30°C to 70°C. The highest value of $K_{ads}$ was obtained at a temperature of 30°C which is to further confirm that Alstonia boonei extract was more efficient at 30°C compared to temperatures of 50°C and 70°C. The n values lie between 0 and 1 at all temperatures which signifies strong bond between the extract and metal surface [28]. However, the $R^2$ values obtained were not close to unity, therefore poor fit was obtained with Freundlich isotherm.

\[
y = 0.0436x - 0.13 \\
R^2 = 0.655
\]

\[
y = 0.1762x - 0.4377 \\
R^2 = 0.825
\]

\[
y = 0.2087x - 0.5364 \\
R^2 = 0.9318
\]

Fig. 4: Freundlich adsorption isotherm plots for the corrosion of mild steel in the presence of Alstonia boonei extract.

Table 2: Freundlich adsorption isotherm parameters for the adsorption of Alstonia boonei leaves extract on the metal surface.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$K_{ads}$</th>
<th>$n$</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.741</td>
<td>0.043</td>
<td>-16.65</td>
<td>0.655</td>
</tr>
<tr>
<td>50</td>
<td>0.366</td>
<td>0.176</td>
<td>-27</td>
<td>0.825</td>
</tr>
<tr>
<td>70</td>
<td>0.291</td>
<td>0.208</td>
<td>-16.18</td>
<td>0.931</td>
</tr>
</tbody>
</table>

The adsorption equilibrium constant ($K_{ads}$) is related to the free energy of adsorption ($\Delta G_{ads}$) by equation (6) [14]:

\[
\log K_{ads} = -\log C_{H_2O} \cdot \frac{\Delta G_{ads}}{R T} \ldots (6)
\]

Where $C_{H_2O}$ is the concentration of water in solution expressed in g/L, R is the universal gas constant, T is the absolute temperature. The free energy of adsorption ($\Delta G_{ads}$) obtained using equation (6) are presented in TABLES 1 and
2. The results are negative in all cases which imply that the adsorption of *Alstonia boonei* extract on the metal surface is a spontaneous process [7, 15]. Values of $\Delta G_{\text{ads}}$ up to $-20$ KJ/mol are consistent with electrostatic interaction between charged inhibitor molecules and a charged metal (physical adsorption) [7, 23]. Therefore *Alstonia boonei* leaves extract inhibit the corrosion process by physically adsorbing onto the metal surface.

3.3 Effect of temperature.

The effect of temperature on corrosion rate and inhibition efficiency are presented in Figs. 4 and 5 respectively. The corrosion rate increased with increase in temperature and the inhibition efficiency decreased with increase in temperature. This could be attributed to the fact that at high temperatures, the desorption of the *Alstonia boonei* extract occurs and causes mild steel to be exposed to the corrodent [21].

Where CR is the corrosion rate, R is the gas constant and T is the absolute temperature. Fig.5 represents the plot of LogCR versus 1/T for the corrosion of mild steel in 0.5M H$_2$SO$_4$ in the absence and presence of various concentrations of *Alstonia boonei* extract. Straight lines were obtained. The values of the apparent activation energy ($E_{\text{app}}$) were obtained from the slopes of the plots [7, 15] and are presented in TABLE 3. The values of the apparent energy of activation ($E_{\text{app}}$) in the presence of various concentration of *Alstonia boonei* leaves extract were higher compared solution to the value obtained in the blank (0.0 g/L). Similar results were also gotten by [7, 15]. This could be attributed to the desorption of the inhibitor molecules (*Alstonia boonei* leaves extract) which occurs on the surface of the metal as temperature increases [21]. The increase in activation energy in the presence of the extract signifies physical adsorption [7, 21].

$$\ln CR = \ln A - \frac{E_{\text{app}}}{2.303RT} \ldots \ldots (7)$$

$$-\ln \frac{R}{RT} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \ldots \ldots 8$$

Table 3: Activation energy parameters for the corrosion of mild steel in 0.5M H$_2$SO$_4$ in the presence and absence of *Alstonia boonei* extract

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>$E_{\text{app}}$(KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.74</td>
</tr>
<tr>
<td>2.5</td>
<td>39.10</td>
</tr>
<tr>
<td>5.0</td>
<td>45.09</td>
</tr>
<tr>
<td>10</td>
<td>43.92</td>
</tr>
<tr>
<td>25</td>
<td>41.15</td>
</tr>
<tr>
<td>50</td>
<td>40.44</td>
</tr>
</tbody>
</table>

The enthalpy of activation ($\Delta H^*$) and the entropy of activation ($\Delta S^*$) were computed using Eyring’s equation given in (8) [27]
Where h is the Plank’s constant, N is the Avogadro’s number, T is the absolute temperature, R is the gas constant, \( R_b \) is the corrosion rate.

Presented in Fig. 6 is the plot of \(-\frac{lnK_b}{R_T} \) versus \( \frac{1}{T} \). \( K_b \) is Boltzmann constant and equals the term \( \frac{R}{N} \) [27]. Straight lines were obtained. The activation parameters obtained from the slopes and intercepts [27] are presented in TABLE 4.

![Graph showing the relationship between activation energy and temperature for corrosion inhibition.](image)

**Fig 6:** Eyrings plot for the corrosion of mild steel in 0.5M \( H_2SO_4 \) in the absence and presence of the extract.

The enthalpy of activation (\( \Delta H^\ddagger \)) in the presence of various concentrations of the extract was higher compared to the value obtained in the absence of the extract. This implies that the energy barrier of corrosion reaction increases with the concentration of the extract and activated complex can be formed faster in the blank solution [28, 29]. The positive values of \( \Delta H^\ddagger \) is an indication that the adsorption of the extract on the metal surface is an endothermic process [28]. The negative values of \( \Delta S^\ddagger \) in the presence and absence of the inhibitor is an indication that the activated complex in the rate determining step represents an association rather than a dissociation step [29]. This implies that there is more disorderliness in the solution without any extract [29].

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>( \Delta H^\ddagger ) (KJ/mol)</th>
<th>( \Delta S^\ddagger ) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.16</td>
<td>-119.47</td>
</tr>
<tr>
<td>2.5</td>
<td>36.52</td>
<td>-65.58</td>
</tr>
<tr>
<td>5.0</td>
<td>42.51</td>
<td>-49.44</td>
</tr>
<tr>
<td>10</td>
<td>41.35</td>
<td>-54.12</td>
</tr>
<tr>
<td>25</td>
<td>38.57</td>
<td>-63.92</td>
</tr>
<tr>
<td>50</td>
<td>37.86</td>
<td>-65.71</td>
</tr>
</tbody>
</table>

**Table 4:** Activation parameters for the corrosion of mild steel in 0.5M \( H_2SO_4 \) in the absence and presence of the extract.

Based on the experimental results obtained, *Alstonia boonei* leaves extract inhibited the corrosion of mild steel in tetraoxosulphate (VI) acid. Therefore, plant materials could replace synthetic chemicals as inhibitors. They are cheaper, readily available, renewable sources of materials, environmentally friendly and ecologically acceptable. The use of extracts from plants to control corrosion will lead to a reduction in maintenance cost. This is because the incessant breakdown of equipment will be greatly reduced, thereby reducing the frequency of replacing broken down equipment.

**REFERENCES**


