Adsorption Study of *Sorghum Vulgare* as the Corrosion Inhibitor of Mild Steel in Tetraoxosulphate (VI) Acid Medium

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Abstract: *This study deals with inhibition of corrosion of mild steel in tetraoxosulphate (vi) acid environment using the leaves of Sorghum vulgare*. Extraction of Sorghum vulgare was done by cold maceration method. The extract was subjected to corrosion inhibition study using various concentration of the extract from 0.1g/l to 0.5g/l in 1M H₂SO₄ on the mild steel at the 50°C and 70°C using weight loss method. The results obtained revealed that the weight loss of the mild steel decreases as the concentration of the inhibitor increases while the temperature decreases. Inhibition efficiency calculated showed an increase from 28.29% to 72.03% at 50°C as the concentration of the inhibitor increases. From the weight loss data, kinetic and thermodynamic parameters such as Ea, ΔH_ads, and ΔG_ads were calculated, the result showed that the mechanism of adsorption of Sulghum vulgare on the surface of the mild steel is by physical adsorption and it obeys Langmuir and Freundlich adsorption isotherms.

Keywords: Adsorption, Desorption, Tetraoxosulphate (VI), *Sorghum vulgare*

1. Introduction

Most industries have been employing the use of acid solution in cleaning, descaling, pickling of steel structures and oxidation of oil well. The end products of these services from the acid solution result in corrosion of the metals that is in contact with this acid solution. The heavy loss of metals as a result of its contact with the acid can be minimized to a great extent by the use of corrosion inhibitors. An inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate [1]. There are several classes of inhibitors, namely: (a) passivators, (b) organic inhibitors, including slush compounds and pickling inhibitors, and (c) vapor - phase inhibitors. Passivators are usually inorganic oxidizing substances (such as chromates, nitrites, and molybdates) that passivate the metal and shift the corrosion potential several tenths volt in the noble direction. Non-passivating inhibitors are pickling inhibitors, usually organic substances. The practice of corrosion inhibition is in vague because of new regulations that have been developed about toxicity and environmental effects resulting from the use of inorganic inhibitors. For example, there is a trend to replace some widely used inhibitors, especially those that contain hexavalent chromium, Cr⁶⁺, known to cause cancer [1, 2]. Therefore, these carcinogenic and other relate unfriendly inhibitors are facing decline in usage hence the need for eco-friendly inhibitors [3-8]. Some of the eco-friendly inhibitors that has been used are *Curcuma* extract [9], leaves extracts of Wrightiatinctoria, Clerodendrumphilomidis, and Ipomeaeatriloba [10], leaves extract of *Emilia sonchifolia* [11], leaves extract of *Vitex doniana* [12], leaves extract of *Senna alata* [13], *Flacourtia Jangomas* extract [14] and *Persea Americanap leave extract* [15].These eco-friendly inhibitors are always use because they are environmentally friendly, cheap, renewable, and biodegradeable. This study investigates the use of *Sorghum vulgare* (SV), as corrosion inhibitor of mild steel in 1M H₂SO₄ at 50°C and 70°C using weight loss method.

2. Materials and Methods

Preparation of the sample

The leaves of the plant, *Sorghum vulgare* (SV) which is locally known as “Oka Aghirigha” was collected from Ndiakwu Otolo community from Nnewi north local government area, Anambra state, Nigeria. It was air dried for 24days, ground into powdered form. 500g of the ground leaves of *sorghum vulgare* were taken into 1000ml round bottom flasks and enough quantity of ethanol was added as solvent for the extraction. The round bottom flask was covered with a stopper and left for 48hrs, then it was filtered and the filtrate was concentrated to remove the solvent by using rotary evaporator. From this concentrated extract a solution of 0.1-0.5g/l was made.

Specimen preparation

The mild steel was bought from the bridge head market Onitsha, Anamba state, Nigeria. It has a thickness of 0.132cm and mechanically cut into coupons of 4.0x3.0cm, a small hole was drilled at one end of the coupon for easy hooking. They were degreased in absolute ethanol and dried in acetone and finally stored in a desiccator.

Test Solution Preparation

All the chemicals used were of Analytical grade. Solution was prepared by using double distilled water. Different concentration of the corrodent which is H₂SO₄ (0.2, 0.4, 0.6, 0.8 & 1.0M) were prepared with a distilled water.

Gravimetric method (weight loss method)

This study was carried out at a temperature of 50°C and 70°C. The mild steel coupons of 4.0x3.0x0.132cm were weighed and inserted into a 250ml beakers containing 200ml
of different concentration of H₂SO₄ (0.2, 0.4, 0.6, 0.8 & 1.0M) with the help of a thread and put in a thermostat water bath. The coupon was removed at 24 hours interval for 3days (72hrs), it was washed several times in 20% NaOH with a brittle brush, then rinsed with distilled water, dried in acetone and re-weighed. This procedure was repeated using 100ml of various concentrations of extract (0.1-0.5g/l) in 100ml of 1M H₂SO₄ solution. The differences in the weight of the coupons were taken as weight loss which was used to compute the corrosion rate in the different concentration of inhibitor [16-18].

3. Theory

Corrosion rate was calculated to determine the extent of corrosion in different concentration of acid and when different concentration of the inhibitor was added using equation (1) [18].

Corrosion rate (mpy) mils per year

\[ CR = \frac{534W}{rAT} \]  

(1)

Where W is weight loss (g), r is the density of specimen (g/cm³), A is surface area of the specimen (cm²) and T is the time of immersion (days).

Inhibition efficiency

The inhibition efficiency (I %) of different concentration of inhibitor was calculated using the below formula [19]

\[ I\% = \frac{(W_o-W_l)}{W_l} \times 100 \]  

(2)

Where W₀ and W₁ are the weight loss of mild steel in the absence and presence of inhibitor in 1.0M H₂SO₄ medium at the temperature of 50°C and at 70°C.

Degree of surface coverage

Degree of surface coverage (Θ) was also calculated using the equation below [20].

\[ \Theta = \frac{(W_o-W_l)}{W_l} \]  

(3)

Where W₀ and W₁ still remain weight loss of mild steel in the absence and presence of inhibitor in 1.0M H₂SO₄ medium at the temperature of 50°aand at 70°C.

Kinetics and Thermodynamic studies

The apparent activation energies, Ea, heat of adsorption (∆H_ads) and free energy of adsorption (ΔG_ads) for the dissolution of mild steel in 1.0M H₂SO₄ in the absence and presence of the inhibitor were calculated from their various equations as below.

Activation energy, \( E_a \)

Activation energy is calculated from condensed Arrhenius equation as follows [21]

\[ \log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]  

(4)

Where CR₁ and CR₂ are the corrosion rates at temperature T₁ and T₂ respectively [21]. Ea is the activation energy of the reaction in KJ/mol, R is the gas constant (8.314KJ/mol/K) and T is the temperature (K).

Heat of adsorption

Heat of adsorption (ΔH_ads) was obtained from the surface coverage (Θ) and temperatures as in equation 5 [22].

\[ \Delta H_{ads} = 2.303R \left( \log \frac{\Theta_2}{\Theta_1} \right) - \left( \log \frac{\Theta_2}{\Theta_1} \right) \times \left( \frac{T_1T_2}{T_2 - T_1} \right) \]  

(5)

Where \( \Theta_1 \) and \( \Theta_2 \) are the degree of surface coverage at temperature T₁ and T₂ respectively.

Free energy of adsorption (ΔG_ads)

The equilibrium constant of adsorption of ethanol extract of SV is related to the free energy of adsorption (ΔG_ads) according to the following equation 6 [21]

\[ \Delta G_{ads} = -2.303RT\log(55.5k) \]  

(6)

Where ΔG is free energy of adsorption (KJ/mol), R is the gas constant (8.314Jmol⁻¹K⁻¹), T is the temperature(K), k is the equilibrium constant of adsorption equal to 55.5 which is the molar heat of adsorption of water. Values of k are obtained from the intercept of Langmuir and Freundlich isotherms and they were used to compute values of ΔG_ads according to equation 10.

Adsorption study

Langmuir adsorption isotherm

Assumption of Langmuir adsorption isotherm can be expressed by equation 7 [23]

\[ C/\Theta = C + 1/k \]  

(7)

Where C is the concentration of the inhibitor in the electrolyte, Θ is the degree of surface coverage of the inhibitor and K is the equilibrium constant of adsorption. Taking logarithm of both sides of equation 7, equation 8 is obtained [23].

\[ \log C/\Theta = \log C - \log k \]  

(8)

The plot of log(C/Θ) versus logC was made and the result obtained is as shown in Fig.5.

Freundlich adsorption isotherm

Freudlich’s adsorption isotherm of SV extract on the surface of the mild steel is given by the equation 9 and 10 [24].

\[ \frac{x}{m} = kc^{1/n} \]  

(9)

\[ \log \frac{x}{m} = \log k + \frac{1}{n} \log c \]  

(10)

The fraction \( \frac{x}{m} \) in equation 10 has been found to be approximately equal with the inhibition efficiency (I%) of the inhibitor, k and n are constant. While slope is equal to \( \frac{1}{n} \) and intercept = \( \log k \).

4. Result and Discussion

Effect of the corrodent on the corrosion

Fig. 1 and 2 show the effect of different concentration of H₂SO₄ acid on the corrosion of the mild steel at 50°C and 70°C. It can be inferred from the graph that the higher the concentration of the acid, the higher the weight loss of mild steel at both temperatures. From the same graphs the highest weight loss was recorded at 1M, this is because concentration is how much solute is dissolved in a solution.
if a greater concentration of reactant is present; there is a higher chance that collision between particles of the solute will increase. More collision means a higher reaction rate. Thus, increasing the concentration of reactants will result in a higher weight loss. Again, increasing the temperature causes the particles of the reactants to collide more effectively, leading to more frequent and energetic collisions. This increased reaction rate causes the particles of the reactants to react more quickly, thereby increasing the corrosion rate at higher concentrations of the inhibitor. Furthermore, increasing the temperature can increase the chance of collisions between particles of the solute, leading to more rapid corrosion at higher concentrations of the inhibitor.

Effect of different concentrations of inhibitor at 50°C

The effects of inhibitors on the corrosion of mild steel were studied in 1.0M H₂SO₄ solution and the results obtained are in Fig. 3 and 4. Fig. 3 and 4 revealed that there was a decrease in weight loss as the concentration of the inhibitor increases from 0.1 to 0.5g/l, which indicates that the ethanol extract of *Sorghum vulgare* has inhibited corrosion. The reduction in weight loss value upon addition of inhibitor is a result of the following actions performed by the inhibitor: (a) the inhibitor adsorbs itself on the metal surface, protecting the metal surface by forming a film. (b) The protective film or coating prevents the tetraoxosuphate (vi) ion from reaching the mild steel or reduces the corrosion of mild steel by acting as an oxygen barrier. (c) The inhibitor extended the time before corrosion began [27, 28].

**Figure 3:** A variation of weight loss (g) of mild steel with time (days) for different concentrations of SV in 1.0M H₂SO₄ solution at 50°C

**Figure 4:** A variation of weight loss (g) of mild steel with time (days) for different concentrations of SV in 1.0M H₂SO₄ solution at 70°C

**Effect of temperature on inhibition efficiency**

The relationship between temperatures, concentrations of the inhibitor and inhibition efficiency are shown in the Table 2. It depicts that the inhibition efficiency increases with an increase in concentration of the inhibitor but slight decrease with increase in temperature. The slight decrease in inhibition efficiency with rise in temperature suggest possible desorption of the adsorbed SV inhibitor from the metal surface at high temperature. Such behaviour shows that the inhibitor was physically adsorbed on the metal surface, since in chemical adsorption, increasing temperature increases inhibition efficiency [29-33]. The reduction in the inhibition efficiency may again be due to competition between forces of adsorption and desorption.

**Table 1:** Corrosion rate of different concentration of H₂SO₄ at temperatures 50°C and 70°C

<table>
<thead>
<tr>
<th>Concentration of H₂SO₄ (M)</th>
<th>Corrosion rate at 50°C (mpy)</th>
<th>Corrosion rate at 70°C (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.12</td>
<td>1.14</td>
</tr>
<tr>
<td>0.4</td>
<td>1.19</td>
<td>1.21</td>
</tr>
<tr>
<td>0.6</td>
<td>1.28</td>
<td>1.30</td>
</tr>
<tr>
<td>0.8</td>
<td>1.67</td>
<td>1.70</td>
</tr>
<tr>
<td>1.0</td>
<td>2.58</td>
<td>2.62</td>
</tr>
</tbody>
</table>

**Table 2:** Inhibition efficiency (1%) and degree of surface coverage at different concentration of inhibitor extract.

<table>
<thead>
<tr>
<th>Concentration of leaves extract (g/l)</th>
<th>Inhibition efficiency %</th>
<th>Degree of surface coverage σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>50°C</td>
<td>70°C</td>
</tr>
<tr>
<td>0.1</td>
<td>28.29</td>
<td>30.55</td>
</tr>
<tr>
<td>0.2</td>
<td>43.25</td>
<td>40.54</td>
</tr>
<tr>
<td>0.3</td>
<td>51.54</td>
<td>49.48</td>
</tr>
<tr>
<td>0.4</td>
<td>61.46</td>
<td>59.91</td>
</tr>
<tr>
<td>0.5</td>
<td>72.03</td>
<td>70.04</td>
</tr>
</tbody>
</table>
Kinetic and Thermodynamic studies

Activation energy, \( E_a \)

The result of calculated \( E_a \) is shown in Table 3. It can be inferred from Table 3 that activation energy shows a significant increase as the concentration of the inhibitor increases; this actually proved that the extract of SV inhibited the corrosion of the mild steel. This behaviour is also attributed to the physical adsorption of the component of the extract on the surface of the mild steel [34-36].

Heat of adsorption \( \Delta H_{ads} \)

Table 3 also includes the result of calculated \( \Delta H_{ads} \). The values of \( \Delta H_{ads} \) were negative and ranged from -0.225 KJmol\(^{-1}\) to -0.761 KJmol\(^{-1}\) indicating that the adsorption of extract of SV on the surface of mild steel is exothermic [37, 38].

Free energy of adsorption (\( \Delta G_{ads} \))

The degree of linearity (\( R^2 \)) as in Table 4, were found to be close to unity indicating strong adherence of adsorption of SV extract on the surface of the mild steel to Langmuir and Freundlich adsorption isotherms. From the result in Table 4, \( \Delta G_{ads} \) values were found to be negative and less than the threshold value of -40 KJmol\(^{-1}\) required for chemical adsorption hence the adsorption of ethanol extract of SV on the surface of mild steel is spontaneous and follows physical adsorption mechanism [39-42].

Adsorption study

Langmuir adsorption isotherm

Figure 5 shows Langmuir adsorption isotherm plot. It can be observed from Figure 5 that the adsorptions of SV extract on the surface of the mild steel obeyed Langmuir adsorption isotherm. Values of adsorption parameters deduced from Langmuir adsorption plot are shown in Table 4.

Figure 6: Freundlich adsorption isotherm for the adsorption of the ethanol extract of SV on the surface of the mild steel

Freundlich adsorption isotherm

Using equation 10, a plot of \( \log I\% \) versus \( \log C \) produce a straight line that obeyed Freundlich adsorption isotherm in Fig. 6 [17, 37, 42].

Table 4: Langmuir and Freundlich adsorption isotherm parameters for adsorption of extract of SV on the surface of mild steel

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Log k</th>
<th>Slope</th>
<th>( \Delta G ) (kJmol(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-0.0169</td>
<td>0.4351</td>
<td>-10.6822</td>
<td>0.8180</td>
</tr>
<tr>
<td>70</td>
<td>0.0102</td>
<td>0.4734</td>
<td>-11.5224</td>
<td>0.9790</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.0238</td>
<td>0.5710</td>
<td>-23.3073</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>1.9837</td>
<td>0.5146</td>
<td>-24.4835</td>
<td>-</td>
</tr>
</tbody>
</table>

5. Conclusion

SV extract showed inhibitive effect on corrosion of mild steel in acidic environment. Inhibition efficiency increases with an increase in inhibitor concentration. The inhibition efficiency of SV extract decreases as the temperature increases, which depicts that adsorption process of SV, is by physical mechanism. The adsorption of SV extracts on the surface of mild steel obeyed Langmuir and Freundlich adsorption isotherms. Physical adsorption of the extract was confirmed from the calculated values of \( E_a \), \( \Delta H_{ads} \), and \( \Delta G_{ads} \), obtained.

6. Acknowledgment

The authors wish to appreciate the effort of Prof. V.I.E. Ajiwe who read and corrected this work and also the laboratory technologists of the Department of Pure and Industrial Chemistry, Unizik, Nigeria, for the job well done during the course of the experiment.

References


