Understanding the mechanism of corrosion of steel in acidic environments along with the accompanying quest for corrosion inhibitors that are nontoxic to the environment is of significant industrial concern. This work sets to investigate the corrosion of mild steel in 1.0 M solution of HCl in the presence of Euphobia tirucalli gums (ET) using weight loss and linear polarization measurements. The study was carried out within the inhibitor concentration range of 0.2-1.0 g L\(^{-1}\) and at the temperature range of 303 - 333 K. From the results obtained, it was observed that ET gums inhibited the dissolution of mild steel in the acid medium. Thermodynamic parameters obtained from the studies revealed the corrosion inhibition process to be spontaneous, exothermic and physisorptive. The adsorption of ET gums on the steel surface aligned well with the Langmuir, Freundlich and Temkin isotherm models. Linear polarization results revealed that ET functioned as a mixed-type inhibitor by inhibiting both the cathodic and anodic reactions on the mild steel surface.

Introduction

Corrosion is the process through which metals/alloy deteriorates. The presence of moisture, acids, bases, salts, aggressive metal polishes and electrolytes generally would lead to the deterioration of most metals/alloys. According to Ahmad and Roberge,\(^{1,2}\) the tendency of a metal/alloy to corrode to a large extent is a function of the type of metal/alloy and the aqueous medium.

Mild steel is known for its widespread industrial applications due to its structural and mechanical properties. It is, however, susceptible to corrosion when it gets in contact with electrolytes resulting in a relatively short life span.\(^{1,2}\) Corrosion of steel structures and pipes result in significant losses of products in industries, environmental pollution and ecological disasters which have attracted much attention and investigations.\(^{3,4}\)

A substance is said to be a corrosion inhibitor when on its addition to a corrosive environment, it either slows down or prevents corrosion. These substances can function by adsorbing both physically and chemically at the metal/solution interface thereby serving as a barrier between the metal and the corrosive species in the environment.\(^{5,7}\) Peter et al. and Ramyan et al.,\(^{5,8}\) described corrosion inhibitors as usually possess heteroatoms such as oxygen, nitrogen and sulfur that have hydrocarbon parts that are typically attached to or part of a polar group, an aromatic ring or a conjugated system.

Many inorganic and organic compounds have been used and are still being employed in mitigating corrosion of metals and alloys. However, most of these compounds are expensive coupled with the fact that they pose health and environmental challenges hence the quest for cheap and environmentally friendly inhibitors as substitutes.\(^{5,7,8}\)

Plant gums have been reported as good corrosion inhibitors against the dissolution of steel in acidic environments.\(^{9-14}\) Umorer has investigated the inhibitive effects of plant gum exudates from Raphia hookeri (RH) against the corrosion of mild steel in H\(_2\)SO\(_4\)and Ebenso.\(^{9}\) The results obtained revealed that RH acted as a suitable corrosion inhibitor for the corrosion of mild steel in sulphuric acid medium. Abdallahi\(^{10}\) investigated the potential of Guar gum (GG) as a corrosion inhibitor for carbon steel in 1.0 M H\(_2\)SO\(_4\) solution using weight loss and Tafel polarization techniques. The results showed that GG inhibited the corrosion of carbon steel in the acid medium and acted as a mixed type inhibitor. In other studies, other gums such as Gum arabic (GA), Albizia zygia (AZ), Anogessus leiocarpus(Al) and Ficus platphylla (FP) have also been reported to be good corrosion inhibitors.\(^{11-14}\)

The results of phytochemical and pharmacological studies carried out by Prabha et al., and Prashant and Shital on Euphobia tirucalli (ET) gum exudates showed that the gum exudates contain triterpenes, diterpene esters, steroids, alkaloids, flavonoids, tannins, phenols, anthraquinones and cardiac glycosides which are sources of heteroatoms.\(^{15,16}\)

This study sets to investigate the kinetics and thermodynamics of the dissolution of mild steel in 1.0 M solution of HCl in the absence and presence of Euphobiatirucalli gums using weight loss and linear polarization measurements.

Experiments

Mild steel coupons of dimension 3x2 cm\(^2\) and percentage composition: Si-0.03 %, P-0.04 %, S-0.04 %, Mn- 0.60 % and the rest Fe, were used for this study. Analar grade reagents were used for the study.
**Purification of Euphobia tirucalli gum.**

The procedure adopted for the purification of gum has been reported elsewhere by Femi et al., and other researchers. The gums were oven dried at 40 °C for two hours after which they were pulverized with a blender and hydrated in chloroform water of double strength for five days with intermittent stirring such that all the gums particles dissolve completely. A 75 μm sieve was used to strain the hydrated gums to obtain a pure slurry which was allowed to sediment. Absolute ethanol was used to precipitate the gum sediment from the slurry which was later filtered and defatted using diethyl ether. The precipitate was dissolved in acetone and reweighed. The average loss in weight was taken as the difference between the initial and final weights of the mild steel (in duplicates).

The corrosion rate of mild steel as a function of time was investigated by carrying out the experiment for 24 – 168 hours. This was done in the absence and presence of ET gum exudates. Temperature studies were done in a similar manner for three hours with the water bath maintained at 303- 333 K.

By carrying out the necessary substitutions in equations 1 to 3, weight loss data were used to evaluate the weight loss (g h⁻¹), corrosion rate (g h⁻¹ cm⁻²), inhibition efficiency (% IE) and the degree of surface coverage (θ).

\[
CR = \frac{\Delta W}{At} \quad \text{(1)}
\]

\[
IE(\%) = 100 \left(1 - \frac{W_2}{W_1}\right) \quad \text{(2)}
\]

\[
\theta = 1 - \frac{W_1}{W_2} \quad \text{(3)}
\]

where \(\Delta W = W_2 - W_1\) is the weight loss of mild steel after time, \(t\), \(W_1\) and \(W_2\) are the weight loss (g) of mild steel with and without the inhibitor, respectively. \(\theta\) is the extent of surface coverage of the inhibitor, \(A\) is the area of the metal coupon (in cm²) and \(t\) is the immersion period (in hours).

**Linear polarization measurements**

The coupons of 3 x 2 cm² dimension were sealed with epoxy resin in such a way that only 1 cm² was left exposed. A three-electrode system consisting of mild steel as working electrode, platinum (Pt) as an auxiliary electrode and saturated calomel electrode (SCE) as a reference electrode was used. Linear polarization studies were carried out using Metrohm Autolab AUT50280 in the potential range of -1500 to 1500 mV with a scan rate of 0.012 V s⁻¹ at room temperature.

The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (\(I_{corr}\)). The % IE was obtained from the equation below:

\[
\% IE = 100 \left(\frac{I_{corr(\text{blank})} - I_{corr(\text{inh})}}{I_{corr(\text{blank})}}\right) \quad \text{(4)}
\]

where \(I_{corr(\text{blank})}\) is the corrosion current density of MS in the free acid solution and \(I_{corr(\text{inh})}\) is the corrosion current density of MS in the inhibited acid solution.

**Optical microscopy**

The morphologies of the surface of the polished mild steel coupons before immersion in the test solutions and after immersion in the test solutions were investigated using a metallurgical microscope (Tsvieh digital metallurgical microscope, model: Tucsen 0923502).

**Results and discussion**

The corrosion rate of mild steel and inhibition efficiency of ET gums

Figure 1 showed the rate of corrosion of mild steel in the free acid and inhibited 1.0 M HCl solution as a function of immersion time. It can be observed from the plot in Figure 1 that the rate of corrosion of the steel decreased with immersion time and as the concentrations of ET gums increased.

Figure 2 illustrates the trend of inhibition efficiency (% IE) of various concentrations of ET gums with immersion time. Inhibition efficiency of the gums increased as the concentrations of ET gums increased with % IE > 98 up to the immersion time of 96 h before decreasing.

This trend may be due to the desorption of the constituents of ET gums from the surface of the steel over a prolonged exposure resulting in the inhibition efficiency been lowered as observed in the plots.

Olasehinde et al., and Momoh-Yahaya et al. in previous studies reported the decrease in inhibition efficiency of Nicotiana tabacum extracts and adenine.
molecules in acidic environments at more extended immersion periods.

The plot of the inhibition efficiency of ET gums as a function of temperature (303-333 K) is presented in Figure 4. The plot shows a decrease in inhibition efficiency of ET gums as the temperature of the system was increased. This could be attributed to the agitation of adsorbed ET gums and consequent desorption of ET gums from the mild steel surface as temperature increased.\textsuperscript{20-22} The lowering of inhibition efficiency values with increasing temperature is associated with a physisorptive mechanism of adsorption as reported in other works.\textsuperscript{20-24}

The relationship between the corrosion rate of mild steel in the various test solutions and the temperature was evaluated using the Arrhenius equation (equation 5). Taking logarithm of both sides of equation 5, equation 6 is obtained.

\begin{equation}
CR = A \exp \left(\frac{-E_a}{RT}\right)
\end{equation}

\begin{equation}
\log CR = \log A - \frac{E_a}{2.303RT}
\end{equation}

where $CR$ is the rate of corrosion of the metal, $A$ is the Arrhenius or pre-exponential factor, $E_a$ is the apparent effective activation energy, $R$ is the universal gas constant and $T$ is the absolute temperature of the system (K).
A plot of log CR versus 1/T represented on Figure 5 gave a straight line graph with a slope of \((-E_a/2.303RT)\) and an intercept of \([\log A]\) from which the values of the apparent activation energy \((E_a)\) were evaluated.\(^{21,23,24}\) The values of \(E_a\) are shown in Table 1. It is evident from Table 1 that the value of \(E_a\) in the uninhibited system increased on the addition of ET gums as reflected in the values of \(E_a\) in the inhibited systems. This behavior is suggestive of a physisorptive kind of adsorption mechanism whereby an increase in temperature leads to the desorption of the adsorbed inhibitor from the steel surface thereby exposing the mild steel surface to the acid solution and leading to an increase in temperature leads to the desorption of the mild steel surface to the acid solution and leading to a rise in the rate of corrosion of the steel as reported by Szauer and Brandt along with other researchers.\(^{25,23,24}\)

Enthalpy \((\Delta H^0)\) and entropy \((\Delta S^0)\) of activation of the corrosion inhibition were calculated using the Eyring equation;

\[
\log \frac{CR}{T} = \left[ \log \left( \frac{R}{nh} \right) + \left( \frac{\Delta S^0}{2.303R} \right) \right] - \frac{\Delta H^0}{2.303RT} \tag{7}
\]

where \(CR\) is the corrosion rate at temperature \(T\), \(R\) is the molar gas constant, \(n\) is Avogadro’s constant \(6.0225 \times 10^{23}\) and \(h\) is the Planck’s constant \((6.6261 \times 10^{-34} \text{ J s})\). A plot of \(\log CR/T\) versus \(1/T\) as shown in Figure 6 is a straight line graph with a slope of \((-\Delta H^0/2.303R)\) and an intercept of \([\log(R/nh) + \Delta S^0/2.303R]\) from which the values of \(\Delta H^0\) and \(\Delta S^0\) were calculated.\(^{21,23,24}\)

The results presented in Table 1 show that the enthalpies of activation are all negative which reveals the exothermic nature of the dissolution process of the mild steel. Also, the entropies of activation were all negative for the gums.\(^7\) Negative values of \(\Delta S^0\) have been reported by Refat and Shokar\(^25\) to represent the association mechanism of the corrosion process whereby a decrease in disorder takes place ongoing from the reactants to the activated complex. Shukla and Eboso corroborate this explanation in their findings on corrosion process whereby a decrease in disorder takes place ongoing from the reactants to the activated complex.

The values of \(\Delta S^0\) in this study (Table 1) aligns with the findings of Shukla\(^{23}\) and Refat.\(^{25}\) The entropy of activation, \(\Delta S^0\) in this present study increased in the presence of ET gums. This may be as a result of the adsorption of ET gums on the surface of the steel thereby slowing the discharge of hydrogen ions on the surface of the mild steel and the rate of corrosion of the steel.\(^{23,25}\)

**Table 1. Thermodynamic parameters of the corrosion of mild steel in 1.0 M HCl in the presence and absence of ET gums at 303-333 K.**

<table>
<thead>
<tr>
<th>Concentration, g L(^{-1})</th>
<th>(E_a), kJ mol(^{-1})</th>
<th>(\Delta H^0), kJ mol(^{-1})</th>
<th>(\Delta S^0), J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>16.280</td>
<td>-4.509</td>
<td>-132.0</td>
</tr>
<tr>
<td>0.2</td>
<td>20.104</td>
<td>-5.569</td>
<td>-113.6</td>
</tr>
<tr>
<td>0.4</td>
<td>20.736</td>
<td>-5.774</td>
<td>-108.1</td>
</tr>
<tr>
<td>0.6</td>
<td>22.457</td>
<td>-6.220</td>
<td>-66.01</td>
</tr>
<tr>
<td>0.8</td>
<td>25.941</td>
<td>-7.185</td>
<td>-75.45</td>
</tr>
<tr>
<td>1.0</td>
<td>29.018</td>
<td>-8.037</td>
<td>-68.69</td>
</tr>
</tbody>
</table>

**Adsorption isotherms**

Surface coverage (\(\Theta\)) values derived from weight loss measurements were adapted into various adsorption isotherms in order to know the adsorption characteristics of ET gums. The Langmuir, Freundlich and Temkin isotherms were found to give good descriptions of the adsorption characteristics of ET gums with all the plots having linear slopes and regression coefficients values \(R^2 \geq 0.9\).\(^{5,23}\) The functionalized and linear forms of the Langmuir, Freundlich and Temkin isotherm models are the followings:

**Isotherm Functional form**

- **Langmuir**
  \[ k_{ads}C = \frac{\theta}{1-\theta} \]
- **Freundlich**
  \[ k_{ads}C^n = 0 \quad (0 < n < 1) \]
- **Temkin**
  \[ k_{ads}C = \exp(f\theta) - 2a\theta = 2.303(logk_{ads} - \log C) \]

**Linear form**

- **Langmuir**
  \[ \frac{C}{\theta} = C + \frac{1}{k_{ads}} \]
- **Freundlich**
  \[ \log \theta = \log k_{ads} - n \log C \]
- **Temkin**
  \[ \log C = \exp(\theta) - 2a\theta = 2.303(logk_{ads} - \log C) \]
where $C$ is the concentration of the inhibitor in the bulk electrolyte, $K_{\text{ads}}$ is the adsorption equilibrium constant, $\Theta$ is the degree of surface coverage of the inhibitor and $\alpha$ is the molecular interaction parameter.\textsuperscript{20} Table 2 presents the adsorption parameters evaluated from the plots.

The adsorption equilibrium constant, $K_{\text{ads}}$ is related to the standard free energy of adsorption, $\Delta G_{\text{ads}}$ as showed in equations 8 and 9,

$$\log K_{\text{ads}} = -1.744 - \frac{\Delta G_{\text{ads}}^0}{2.303RT} (8)$$

$$\Delta G_{\text{ads}} = -2.303RT \log(55.5K_{\text{ads}}) (9)$$

where $\Delta G_{\text{ads}}$ is the standard free energy of adsorption of ET gums on the mild steel surface, $R$ is the universal gas constant, 55.5 is the concentration of water in solution in mol L\textsuperscript{-1} and $K_{\text{ads}}$ is the equilibrium constant of adsorption. The values of $\Delta G_{\text{ads}}^0$ were negative and less than -20 kJ mol\textsuperscript{-1} for all the three adsorption models.

This implies that the adsorption of ET gums on the surface of the mild steel coupon is spontaneous and physisorptive.\textsuperscript{7} The values of $\Delta G_{\text{ads}}^0 \leq -20$ kJ mol\textsuperscript{-1} and $\Delta G_{\text{ads}} \geq -40$ kJ mol\textsuperscript{-1} have been reported in studies conducted by Momoh-Yahaya et al. and Oguzie et al. to signify the mechanisms of physisorption and chemisorption respectively.\textsuperscript{21,5}

Figure 7. Langmuir isotherm for the adsorption of ET gums on mild steel surface at 303 K and 333 K respectively.

Figure 8. Freundlich isotherm for the adsorption of ET on mild steel surface at 303 K and 333 K respectively.

Figure 9. Temkin isotherm for the adsorption of ET on mild steel surface at 303 K and 333 K respectively.

Linear polarization

Linear polarization plots for the corrosion of mild steel in the various test solutions are shown in Figure 10 while Table 3 presents all the linear polarization parameters derived from the polarization plots and inhibition efficiency values.

The corrosion current density is a function of the reactivity of a metal in an aqueous environment. The higher the values of $I_{\text{corr}}$, the higher the dissolution of the metal and vice versa. Addition of ET gums is observed to reduce the anodic and cathodic current densities and the corresponding corrosion current density ($I_{\text{corr}}$) by shifting the corrosion potential ($E_{\text{corr}}$) toward more negative (cathodic) values.

Figure 10. Linear polarisation plots of mild steel in 1.0 M HCl in the absence and presence of ET.

These shifts in the corrosion potential ($E_{\text{corr}}$) are more pronounced at higher ET concentrations, and the cathodic inhibiting effect becomes more significant. This implies that the gums functioned as a mixed-type inhibitor, with predominant cathodic effect.
Table 2. Adsorption parameters of ET gums on mild steel surface in 1.0 M HCl

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Slopes</th>
<th>Intercepts</th>
<th>$R^2$</th>
<th>$\alpha$</th>
<th>$K_{ads}$</th>
<th>$\Delta G_{ads}, \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303</td>
<td>0.904</td>
<td>0.169</td>
<td>0.991</td>
<td>-</td>
<td>5.921</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>1.076</td>
<td>0.276</td>
<td>0.990</td>
<td>-</td>
<td>3.376</td>
</tr>
<tr>
<td>Freundlich</td>
<td>303</td>
<td>0.625</td>
<td>-0.2264</td>
<td>0.977</td>
<td>-</td>
<td>1.684</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>1.050</td>
<td>-0.608</td>
<td>0.976</td>
<td>-</td>
<td>4.051</td>
</tr>
<tr>
<td>Temkin</td>
<td>303</td>
<td>0.324</td>
<td>0.778</td>
<td>0.934</td>
<td>0.324</td>
<td>11.04</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.292</td>
<td>0.535</td>
<td>0.949</td>
<td>0.292</td>
<td>6.23</td>
</tr>
</tbody>
</table>

Table 4. Linear polarisation parameters for the corrosion of mild steel in 1.0 M HCl in the absence and presence of ET.

<table>
<thead>
<tr>
<th>Conc., g L$^{-1}$</th>
<th>$E_{corr}$, mV</th>
<th>$I_{corr}, \mu Acm^{-2}$</th>
<th>$\beta_a, V dec^{-1}$</th>
<th>$\beta_c, V dec^{-1}$</th>
<th>CR, mmyr$^{-1}$</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-843.79</td>
<td>299.86</td>
<td>0.47551</td>
<td>0.31335</td>
<td>348.44</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>-513.90</td>
<td>135.76</td>
<td>0.64010</td>
<td>0.54541</td>
<td>157.75</td>
<td>54.73</td>
</tr>
<tr>
<td>0.4</td>
<td>-844.30</td>
<td>266.10</td>
<td>0.52436</td>
<td>0.29977</td>
<td>147.12</td>
<td>57.78</td>
</tr>
<tr>
<td>0.6</td>
<td>-836.65</td>
<td>22.93</td>
<td>0.35607</td>
<td>0.32226</td>
<td>26.643</td>
<td>92.35</td>
</tr>
<tr>
<td>0.8</td>
<td>-1620.4</td>
<td>17.81</td>
<td>0.25595</td>
<td>0.28927</td>
<td>20.692</td>
<td>94.06</td>
</tr>
<tr>
<td>1.0</td>
<td>-1315.2</td>
<td>20.31</td>
<td>0.26930</td>
<td>0.23854</td>
<td>23.599</td>
<td>93.23</td>
</tr>
</tbody>
</table>

The values of $b_a$ and $b_c$ changed as the inhibitor concentration increased, signifying the influence of ET gum exudates on both the dissolution of the mild steel in 1.0 M HCl and the kinetics of hydrogen evolution. This is revealed in similar studies by Oguzie et al. and others.3-5,30

**Linear polarization**

Linear polarization plots for the corrosion of mild steel in the various test solutions are shown in Figure 10 while Table 3 presents all the linear polarization parameters derived from the polarization plots and inhibition efficiency values.

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These shifts in the corrosion potential ($E_{corr}$) are more pronounced at higher ET concentrations, and the cathodic inhibiting effect becomes more significant. This implies that the gums functioned as a mixed-type inhibitor, with predominant cathodic effect. The values of $b_a$ and $b_c$ changed as the inhibitor concentration increased, signifying the influence of ET gum exudates on both the dissolution of the mild steel in 1.0 M HCl and the kinetics of hydrogen evolution. This is revealed in similar studies by Oguzie et al. and others.3-5,30

**Optical microscopy**

Plates I, II and III show the micrographs of the polished mild steel, the polished steel after immersion in the uninhibited acid solution and the polished steel after immersion in the inhibited acid solution respectively. Plate II shows a steel surface that is relatively damaged compared to Plates I and III. This is as a result of the rust formed on it after undergoing corrosion in 1.0 M solution of HCl in the absence of the inhibitor. The micrograph of mild steel surface in Plate III shows no pits and cracks except some polishing lines and the presence of an excellent protective film.

This further confirms the adsorption of the constituents of ET gums on the mild steel surface and the inhibitive property of ET gums against the corrosion of mild steel in 1.0 M solution of HCl.
Corrosion of mild steel in the presence of Euphorbia Tirucalli gum

Conclusion

The results obtained from this study have shown that Euphorbia tirucalli gum exudates acted as a useful and efficient inhibitor against the dissolution of mild steel in 1.0 M HCl. Inhibition efficiency of the gums was found to be concentration dependent. However, the inhibition efficiency of the gums decreased with immersion time and rose in temperature. Values of $E_a$, $\Delta H^*$ and $\Delta G_{ads}$ obtained showed that the adsorption of Euphorbia tirucalli gums exudates on the steel surface was physisorptive, exothermic and spontaneous. Linear polarization measurements showed that Euphorbia tirucalli gum exudates functioned as a mixed corrosion inhibitor by inhibiting and retarding the rates of both the anodic metal dissolution and cathode hydrogen ion reduction reactions. Optical micrographs confirm the adsorption of Euphorbia tirucalli gum exudates on the surface of the mild steel.

References

Corrosion of mild steel in the presence of Euphobia Tirucalli gum


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