EVALUATION OF ADSORPTION ISOTHERMS ON INHIBITION OF CORROSION BY BRAZILIAN PLANT EXTRACTS AND CONSTITUENTS

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ABSTRACT: This study reports the ability of amino compounds contained in extracts of plants from Northeastern Brazil of inhibiting corrosion. For this the following were evaluated: potentiodynamic linear polarization (PLP), the mass loss measure and electrochemical impedance spectroscopy (EIS). A phytochemical study of alkaloid extract leads to the isolation of a compound, whose structure was determined by nuclear magnetic resonance spectroscopy. The chromatography techniques were used to isolate the amino compound, which was identified as 4-(N-methylamino)-benzoic acid by ¹³C - and ¹H-NMR spectroscopy. This compound showed a superior anticorrosion performance than crude phenolic extracts and superior efficiency compared with inorganic inhibitors, such as sulfate N-methyl-p-aminophenol (Metol), offering superior efficiency, operating satisfactorily at much lower concentrations. From the Langmuir isotherm showed that the absorption phenomena is purely physical and impute a positive influence on corrosion inhibition. The Temkin adsorption isotherms showed that the lateral interaction between the adsorbed molecules on the metal surface is repulsive.

Keywords: Organic coatings; Acid corrosion; Adsorption.

1. INTRODUCTION

The problem of corrosion is common and occurs in various sectors, such as chemical industry, petrochemical, shipbuilding, construction, automotive, aviation, railway, maritime and others. The consequences of corrosion can result in economic loss, for example, the oxidation of residential pipes, vehicles and metal materials in general, but can also result in serious accidents, causing damage to both nature and man, for example, degradation in pipeline systems, bridge failures, and others. (Rani, 2012; El-Garber, 2009)

The search for environmentally friendly corrosion inhibitors is certainly a current need, where the most common in industry are toxic. For example, ion chromium VI is an excellent inhibitor of iron corrosion and its alloys, however, its irritating to mucous membranes and carcinogenic. Many organic compounds are known to be applicable as steel and copper corrosion inhibitors in acid environments. Usually, corrosion inhibitors are organic compounds that contain sulfur and oxygen nitrogen atoms linked to aromatic rings in a conjugated system, because these atoms or groups give the electronegative sites to the molecule to interact with the metal surface, through adsorption over the metal surface, forming a protective layer.

The aim of this work was to investigate the effects of etanolic extract in five plants from Northeastern Brazil as a corrosion inhibitor for carbon steel in HCl 0.1 M. (Matos, 2004; Chidiebere, 2012).

2. MATERIALS AND METHODS

2.1. Preparation of plant extracts
The leaves of the species *Senna cana* (Nees & Mart.) HS Irwin & Barneby, *Byrsonima sericea* DC, *Dimorphandra gardneriana* Tul. and *Mangifera indica* L. and branches of *Zanthoxylum syncarpum* Tull. were collected in the state of Ceará, Brazil and plant extracts were obtained by maceration in aqueous ethanol (70:30) using 500 grams in each sample. The respective extracts were EESCL, EEBSL, EEDGL, EEMIL and EEZSB.

### 2.2. Obtaining the alkaloid fraction

The extract EEZSB was subjected to acid-base extraction. (Kawanishi, Uhara and Hashimoto, 1985). The results were interpreted using thin layer chromatography (TLC), with Dragendorff reagent for revealing.

After this, the alkaloid extract was subjected to column chromatography on silica gel with Na₂CO₃ (5%) impregnated and using as eluents: hexane, chloroform, ethyl acetate and methanol in different proportions with increasing gradient of polarity. The obtained fractions were submitted to TLC with mobile phase for specific alkaloids: ethyl acetate, ethyl methyl ketone, formic acid and water (50: 30: 10: 10). (Wagner and Bladt, 1996).

The fraction obtained in ethyl acetate and methanol (50:50) was purified by chromatography on Sephadex® column using ethyl acetate as the eluent and revealed with Dragendorff reagent. A compound was identified by ¹H and ¹³C NMR spectroscopy.

After all of the described steps an ethanolic extract alkaloidal fraction of *Zanthoxylum syncarpum* branches (EEZSB - AF) was obtained.

### 2.3. Corrosion tests

The corrosion behavior was evaluated by potentiodynamic linear polarization (PLP) with a scan rate of 1 mV.s⁻¹, potential scan between -1.5 and 0 V. (Oguzie et al, 2006; Bard, 2001).

Electrochemical impedance spectroscopy was performed in open circuit with a sine wave of 10 mV amplitude at frequencies ranging from 100 kHz to 10 mHz. The impedance results are represented by Nyquist diagrams. All electrochemical measurements were obtained using potentiostat PGSTAT30 model (AUTOLAB, Metrohm - Eco Chemie). The substrates were immersed in a solution of HCl 0.1 M in the absence and in the presence of extracts at a concentration of 20% in HCl extract. The working electrode was a carbon steel disc inserted in 1020 in epoxy resin with exposed area of about 1 cm². Platinum was used as an auxiliary electrode and the reference electrode (Ag/AgCl).

The corrosion rates for samples were obtained according to ASTM G1-90 (ASTM, 1999) whose calculation of corrosion rates in mm. year⁻¹.

### 3. RESULTS AND DISCUSSION

#### 3.1. Potentiodynamic Linear Polarisation

The effect of the ethanolic extracts of the species tested were evaluated from the polarization curves obtained by PLP, represented in Figure 1, wherein a change in corrosion potential to more positive values can be seen. Simultaneously, there is a decrease in the current density values in the anode and cathode sides of the curves obtained in the presence of the extracts compared with that obtained in their absence. These results indicate all extracts act as mixed type inhibitors (or adsorption inhibitors), which they act as protective films forming the cathode regions by inhibiting the reduction of oxygen and anodic minimizing the oxidation of the steel. Some silicates and phosphates which in neutral media with low chloride content and in the presence of oxygen, cause passivation of the steel (anodic inhibitor) and precipitate the cathode regions (cathode inhibitors) and organic film formers compounds (adsorption inhibitor) with two functional groups or mixture of compounds, some inhibitors acting as anode, cathode and the other acting as protective films. (Azambuja, 1999).
Figure 1. Polarization potentiodynamic curves for carbon steel immersed in HCl 0.1 M a) Crude extract to all species. b) EEZS (crude extract) vs. EEZS - AF.

From the Tafel curves in the PLP, the polarization resistance ($R_p$) can be obtained using the Stern – Geary equation (Eq. 1) (Stert and Geary, 1957) where this resistance value is inversely proportional to the corrosion current, therefore, an important parameter to be analyzed.

$$I_{corr} = \frac{\beta_a \times \beta_c}{\log(2.303(\beta_a + \beta_c))} \times \frac{1}{R_p}$$  \hspace{1cm} (01)

Where $\beta_a$ and $\beta_c$ are respectively the anodic and cathodic Tafel slopes. $I_{corr}$ is corrosion rate or corrosion current density in mA.cm$^{-2}$.

The $R_p$ values (table 1), show that EEZSB-AF has the highest value of this variable (3.82 KΩ.cm$^{-2}$). As the polarization resistance is inversely proportional to the corrosion current, this inhibitor has a lower corrosion kinetics compared with other inhibitors investigated. (Stert and Geary, 1957). According to Matos (2004), Lima-Neto et al (2006) and Abdullah (2011), this superiority of amino compounds may be related to the presence of organic compounds with O, N and S in its structure.

For calculating inhibition efficiency from PLP, the following formula was used:

$$\eta(\%) = \frac{I_0 - I_{inh}}{I_0} \times 100 \hspace{1cm} (02)$$

where $I_0$ is the corrosion current density in the absence of an inhibitor and $I_{inh}$ is the corrosion current density in the presence of an inhibitor. The corrosion current density ($I$) is determined from the intercept of extrapolated cathodic and anodic Tafel slopes.

Table 1. Corrosion rates and electrochemical parameters derived from PLP.

<table>
<thead>
<tr>
<th>Working Solution</th>
<th>$R_p$ (kΩ.cm$^{-2}$)</th>
<th>$I_{corr}$ (A.cm$^{-2}$)</th>
<th>$\eta$%*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 0.1 M</td>
<td>2.10</td>
<td>0.0074</td>
<td>-</td>
</tr>
<tr>
<td>EEZCL</td>
<td>3.11</td>
<td>0.0025</td>
<td>66.21</td>
</tr>
<tr>
<td>EEZSB</td>
<td>3.40</td>
<td>0.0015</td>
<td>79.72</td>
</tr>
<tr>
<td>EEZSB-AF</td>
<td>3.82</td>
<td>0.0013</td>
<td>82.43</td>
</tr>
<tr>
<td>EEBSL</td>
<td>3.13</td>
<td>0.0030</td>
<td>59.45</td>
</tr>
<tr>
<td>EEDGL</td>
<td>3.05</td>
<td>0.0034</td>
<td>54.05</td>
</tr>
<tr>
<td>EEMIL</td>
<td>2.79</td>
<td>0.0036</td>
<td>51.35</td>
</tr>
</tbody>
</table>

* $\eta$%: Inhibition efficiencies obtained from Tafel curves on PLP.

3.2. Weight Loss

The inhibition efficiencies (table 2) for weight loss tests were evaluated using the following formula:

$$\eta(\%) = \frac{W - W_i}{W} \times 100 \hspace{1cm} (03)$$

where $W$ is the weight loss in the absence of an inhibitor and $W_i$ is the weight loss in the presence of an inhibitor.

The Corrosion Velocity ($V_{corr}$) on millimeters per year for carbon steel samples (table 2) were obtained according to ASTM G1-90
when the mass loss is known can be given by the following equation:

$$V_{corr} = \frac{3.65 \times \Delta m}{S \times t \times \rho}$$  \hspace{1cm} (04)$$

whose $\Delta m$ is Loss of weight, in mg; $S$ is exposed area in cm$^2$; $t$ is exposure time in days and $\rho$ is Specific mass of the material in g.cm$^{-3}$.

### Table 2. Corrosion rates derived from Weight Loss tests.

<table>
<thead>
<tr>
<th>Working Solution</th>
<th>$\Sigma$ Mass (g)*</th>
<th>$V_{corr}$ (mm.y$^{-1}$)</th>
<th>$\eta$%*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 0.1 M</td>
<td>0.0214g ± 0.0011</td>
<td>0.0074</td>
<td>-</td>
</tr>
<tr>
<td>EESCL</td>
<td>0.0058g ± 0.0004</td>
<td>0.0025</td>
<td>72.89</td>
</tr>
<tr>
<td>EEZSB</td>
<td>0.0041g ± 0.0004</td>
<td>0.0015</td>
<td>80.84</td>
</tr>
<tr>
<td>EEZSB-AF</td>
<td>0.0038g ± 0.0003</td>
<td>0.0013</td>
<td>82.24</td>
</tr>
<tr>
<td>EEBSL</td>
<td>0.0061g ± 0.0003</td>
<td>0.0030</td>
<td>71.49</td>
</tr>
<tr>
<td>EEDGL</td>
<td>0.0052g ± 0.0005</td>
<td>0.0034</td>
<td>75.70</td>
</tr>
<tr>
<td>EEMIL</td>
<td>0.0092g ± 0.0003</td>
<td>0.0036</td>
<td>57.01</td>
</tr>
</tbody>
</table>

* $\Sigma$ Mass: Mass loss(g) by immersion tests in HCl 0.1 M.
* $\eta$%: Inhibition efficiencies obtained from Mass loss tests.
* mm.y$^{-1}$: Velocity on corrosion per year from the immersion tests.

The Weight Loss tests confirms that compounds rich in alkaloids exhibited higher efficiency. This characteristic is justified by the presence of aromatic rings and heteroatoms with conjugated double bonds present in isolated alkaloid (4-methylamino) benzoic acid (Praveen, 2009; Maciel et al, 2014; Russin and Kassim, 2010). These results show superior efficiency compared with inorganic inhibitors, such as sulfate N-methyl-p-aminophenol (metol), which have maximum inhibition efficiency of 81.9% to 27.5 g.dm$^{-3}$ (27000 ppm) (Praveen, 2009). However, the concentrations used in this study (1000 ppm) were much lower than the inorganic inhibitor, this associated toxicity of these compounds shows importance based corrosion inhibitors natural products.

### 3.3. Electrochemical Impedance Spectroscopy

The Nyquist diagram, obtained by EIS (Figure 2), compares the efficiency in inhibiting corrosion of samples, wherein resistance to current passage of each sample is represented by a curve where the increase in slope of this curve indicates an increase in resistance charge transfer at the electrode / solution interface and results in a decrease in the tendency to corrode.

![Figure 2. Nyquist diagram for phenolic and amino species.](image)

From the Nyquist diagram (Figure 2), there is a significant increase in resistance for all species in comparison to the solution without extract (blank), so that the increased capacitive arc occurs more efficiently in amino compounds, particularly EEZSB - AF, emphasizing the relevant corrosion inhibiting ability of this species.

Table 3, show the parameters obtained from EIS, wherein the charge transfer resistance ($R_{ct}$) was obtained by the difference between the impedances at lower and higher frequencies, the real axis intercept ($Z_{in}$ = 0)

$$C_{dl} = \frac{1}{2\pi f_{max}R_{ct}}$$  \hspace{1cm} (05)$$

Where $f_{max}$ is the frequency value at which the imaginary component of the impedance is maximum.

The fraction of the surface that was covered by adsorbed molecules was calculated according to equation 06: (Deyab and Abd El-Rehim, 2013)
\[ \theta = (1 - \frac{C_{dl}}{C_{dl}^0}) \]  

Where \( C_{dl} \) and \( C_{dl}^0 \) is the capacitance of the double layer determined with and without the presence of the extract in the solution, respectively.

The inhibition efficiency (\( \eta_{inh} \% \)), was calculated using Eq. 7:

\[ \eta(\%) = \frac{R_{ct} - R_{ct \text{(inh)}}}{R_{ct \text{(inh)}}} \times 100 \]  

where \( R_{ct} \) and \( R_{ct \text{(inh)}} \) are referred to as the charge transfer resistance without and with the addition of the inhibitor, respectively.

**Table 3.** Impedance data of carbon steel surface in 1020 in HCl 0.1 M and solutions containing plant extracts.

<table>
<thead>
<tr>
<th>Working Solution</th>
<th>( R_{ct} ) (( \Omega ).cm(^2))</th>
<th>( C_{dl} ) (( \mu F ).cm(^{-2}))</th>
<th>( \eta_{inh} % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 0.1 M</td>
<td>26.55</td>
<td>90.28</td>
<td>--</td>
</tr>
<tr>
<td>EEMIL</td>
<td>112.02</td>
<td>17.20</td>
<td>76.30</td>
</tr>
<tr>
<td>EEBSL</td>
<td>125.38</td>
<td>19.12</td>
<td>78.82</td>
</tr>
<tr>
<td>EEDGL</td>
<td>132.28</td>
<td>14.57</td>
<td>79.92</td>
</tr>
<tr>
<td>EESCL</td>
<td>144.17</td>
<td>14.57</td>
<td>81.58</td>
</tr>
<tr>
<td>EEZSB</td>
<td>159.12</td>
<td>16.63</td>
<td>83.31</td>
</tr>
<tr>
<td>EEZSB-AF</td>
<td>167.21</td>
<td>12.11</td>
<td>84.12</td>
</tr>
</tbody>
</table>

The data presented in Table 3 shows a behavior similar to that observed in Tafel curves and mass loss. From the values obtained from \( R_{ct} \) and \( C_{dl} \), it is observed that the plant extracts decrease the capacitance of the double layer and increases the resistance to charge transfer, since there is an increased diameter of the semi-circle observed in the Nyquist diagrams. The adsorption may be responsible for lower capacitance in the presence of the inhibitor. The double layer formed at the electrode - solution interface is considered an electrical capacitor, where a decrease in capacitance is due to the formation of a protective barrier for organic molecules on the surface of the steel, which reduces the area available for reaction to occur in the carbon steel surface. (Abd El-Khalek, Abd El-Nabeyb and Abd El-Gaberb, 2012).

3.3.1. Adsorption Isotherm: To evaluate the adsorption process to extract that showed the best efficiency in inhibiting corrosion (EEZSB - AF), the adsorption isotherms of Langmuir and Temkin were obtained, from the coverage fraction (\( \theta \)), calculated for different concentrations of EEZSB - AF presented in Table 4.

**Table 4.** Electrochemical parameters and grade of coverage for different concentrations of EEZSB - AF on HCl 0.1 M.

<table>
<thead>
<tr>
<th>Working Solution</th>
<th>(g.L(^{-1}))</th>
<th>( R_{ct} ) (( \Omega ).cm(^2))</th>
<th>( C_{dl} ) (( \mu F ).cm(^{-2}))</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 0.1 M</td>
<td>3.65</td>
<td>26.55</td>
<td>90.28</td>
<td>--</td>
</tr>
<tr>
<td>EEZSB-AF</td>
<td>0.4</td>
<td>129.53</td>
<td>15.77</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>107.27</td>
<td>20.02</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>93.41</td>
<td>25.66</td>
<td>0.71</td>
</tr>
</tbody>
</table>

\[ \text{Y} = A + BX \]

- **Langmuir**
  - \( A = 2.443 \)
  - \( B = 4.391 \)
  - \( R^2 = 0.9801 \)

\[ \log \left( \frac{\theta}{1 - \theta} \right) = A + B \log C \]

- **Temkin**
  - \( A = 7.128 \)
  - \( B = -5.692 \)
  - \( R^2 = 0.9842 \)
Figure 3. Langmuir adsorption isotherm (a) and Temkin adsorption isotherm (b) for carbon steel in HCl 0.1 M in different concentrations EEZSB - AF.

With the data obtained in the electrochemical impedance tests (Table 4) for the concentrations studied, it was possible to determine the grade of the coverage, making it possible to evaluate the Langmuir adsorption isotherm (Figure 3a).

The adsorption free energy for EEZSB-AF was calculated from the data obtained from the Langmuir adsorption isotherms, applied to the equation 08:

$$K_{ads} = \frac{1}{55.5} \exp \left( \frac{-\Delta G^\circ}{RT} \right)$$

Where 55.5 is the concentration of water in the solution in mol L$^{-1}$, R is the gas constant (8.3147 J.mol$^{-1}$.K$^{-1}$), T is the temperature in K and $\Delta G^\circ$ it is the standard free energy adsorption.

Therefore, a value for $\Delta G_{ads} = -20.78$ kJ.mol$^{-1}$ was obtained. However, the module of the values for $\Delta G^\circ$ are less than 25 kJ.mol$^{-1}$, concluding that the adsorption is purely physical. (Bammou et al., 2012).

This parameter is a relevant factor for the evaluation of the substance efficiency that acts as an inhibitor. When the anions present in solution, such as chloride ions are adsorbed on the metal surface, there is the increased adsorption of organic cations on them, and then this is the way the inhibitor can be adsorbed on the metal surface. (Bammou et al., 2012; Abd El-Khalek, Abd El-Nabeby and Abd El-Gaberb, 2012).

For the lateral grade of interaction, which was obtained from analysis of the results adjusted to Temkin adsorption isotherms (Figure 3b) showed $g = -5.692$. The negative value indicates that the lateral interaction between the adsorbed molecules on the metal surface is repulsive. (Noor and Al-Moubaraki, 2008).

4. CONCLUSION

The electrochemical analysis showed that extracts containing amino compounds displayed superior corrosion inhibiting properties than extracts without this. These results also show superior efficiency compared with inorganic inhibitors, such as sulfate N-methyl-p-aminophenol (Metol), offering superior efficiency, operating satisfactorily at much lower concentrations. With the determination of free energy of adsorption ($\Delta G_{ads} = -20.78$ kJ mol$^{-1}$) calculated from the Langmuir isotherm, it can be concluded that the adsorption is purely physical.

The grade of lateral interaction, obtained from the Temkin adsorption isotherms showed a value of $g = 5.692$. The negative value indicates that the lateral interaction between the adsorbed molecules on the metal surface is repulsive.

The isolated compound (4-methylamino) benzoic acid showed the best results, suggesting that efficient inhibition of Z. syncarpum extract could be due to its presence.

5. REFERENCES


