Eco Friendly Green Inhibitor Tinosporacordifolia (Linn.) For The Corrosion Control of Aluminum in Sulfuric Acid Medium

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ABSTRACT: Aqueous extract of stems of Tinosporacordifolia was studied as a corrosion inhibitor for aluminum in sulfuric acid (pH = 3) by using potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS) technique in the temperature range of 30 °C to 50 °C. The concentrations of inhibitor used were in the range of 50-400ppm. Inhibition efficiency was found to increase with increase in inhibitor concentrations and decrease with increase in temperature. Tinosporacordifolia stems extract (TCSE) acted as an anodic type inhibitor and underwent physical adsorption process on the surface of the metal and followed Langmuir adsorption isotherm.

KEYWORDS: Aluminum, potentiodynamic polarisation, Tinosporacordifolia, Sulfuric acid, EIS.

I. INTRODUCTION

Aluminum is one of the most common metals used for industrial and domestic purposes due to its excellent electrical conductivity, good forming properties, low cost and other relatively noble properties [1]. The applications of aluminum and its alloys are often possible because of the natural tendency of aluminum to form a passivating oxide layer. However in aggressive media, the passivating layer can be destroyed and corrosive attack can take place. The protection of aluminum and its oxide films against the corrosive action of sulfate ions have been extensively studied. Sulfuric acid in the pH range of 2-4.5 is mainly used for pickling, chemical and electrochemical etching of aluminum and its alloys. A useful method to protect metals and alloys deployed in service in aggressive environments against corrosion is the addition of inhibitors. A number of organic compounds are known to be applicable as corrosion inhibitors for aluminum and its alloys in acidic environments[2]. Such compounds mainly contain nitrogen, oxygen sulfur or π bonds through which adsorption of the molecules on the metal surface can take place. This creates a barrier between the metal and corrosive and brings down the rate of corrosion.

II. LITERATURE SURVEY

Despite of broad spectrum of organic compounds, the choice of appropriate inhibitor for a particular application is restricted by several factors. These include increased environmental awareness and the need to promote environment friendly processes. There exists a need to develop a new class of corrosion inhibitors with low toxicity and good efficiency. The exploration of natural products of plant origin as non-expensive eco-friendly inhibitor is an essential field study [3]. These plant products are not only eco-friendly, but also readily available, cost effective renewable source of materials and contain organic compounds such as amino acids, tannins and alkaloids which have inhibitive effect. Till date lots of works have been reported for using natural product as corrosion inhibitors [4] for aluminum in acidic media. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically acceptable and possess no threat to the environment. As a part of our research work with natural inhibitors...
for the corrosion control of aluminum and its alloys [5], we report herein, the results of utility of Tinosporacordiofolia stems extracts (TCSE) for the corrosion control of aluminum in sulfuric acid medium of pH=3.0

III. MATERIALS AND METHOD

3.1. Materials: The composition of aluminum is: Si: 0.467%, Fe: 0.163%, Mg: 0.530% and aluminum: Balance. Cylindrical test coupons of 10 mm diameter and approximately 20 mm height were machined from the rods of aluminum and metallographically mounted up to 10mm height using cold setting resin. The exposed flat surface of the mounted part was polished as per standard metallographic practice - belt grinding followed by polishing on emery papers (in the range of 600-2000) and finally disc polished using levigated alumina abrasive. The stock solution of 2 M sulfuric acid was prepared by using analar grade sulfuric acid and double distilled water. Standardization was done by volumetric method. From the standard solution, sulfuric acid solution of required concentration was prepared as and when required. Experiments were carried out at different temperatures using a calibrated thermostat under unstirred conditions.

Tinosporacordiofolia stems extracts (CLE) was prepared by literature method [6]. The stems of Tinosporacordiofolia were cut into pieces. These were completely air-dried at room temperature for 4 weeks. The dried stems were pulverized into fine powder using a domestic mixer grinder. 40 g of the powder was boiled in 500 mL of distilled water for 5 h. It was filtered using a piece of clean white cotton gauze. The filtrate was evaporated to complete dryness at 40 ℃, producing a fine sweet smelling and chocolate color solid residue. The extraction process was repeated 4 times and the solid residue weighed after extraction was pooled together in an air and water-proof container and kept in a refrigerator at 4 ℃. It was characterised by FTIR spectrum. Aqueous solution of the inhibitor of required concentration was prepared freshly as and when required.

3.2 Method

Electrochemical studies were carried out using a potentiostat (CH600D-series, U.S.model with CH Instruments beta software). Studies were done by using conventional three electrode Pyrex glass cell with platinum as counter electrode and SCE as reference electrode. Working electrode was aluminum. Finely polished aluminum specimen was exposed to sulfuric acid (pH=3) at different temperatures (30 ℃ to 50 ℃) and allowed to establish a steady state open circuit potential by immersing the electrodes in corrosive medium for 30 minutes. Potentiodynamic polarisation method and electrochemical impedance spectroscopy studies were carried out as reported earlier [7].

3.3 Result

3.3.1. Fourier transform infrared (FTIR) spectroscopy of TCSE

Absorption at 3425 cm⁻¹ can be assigned to both O-H (overlapped by the strong stretching mode of N-H) and N-H. The 1643 cm⁻¹ band is assigned to the N-H bending. The peak at 1149 cm⁻¹ can be assigned to stretching mode of C-N group of aromatic amines. The band at 1404 cm⁻¹ is attributed to C-C in aromatic ring. The adsorption band at 1026cm⁻¹ is assigned to the C-N stretch of aliphatic amines.

3.3.2. Potentiodynamic polarization (PDP) measurements

Figure 1 shows the potentiodynamic polarization plot for the corrosion of aluminum in sulfuric acid (pH=3) containing different concentrations of TCSE at 30 ℃.
Valuable potentiometric polarization parameters like, corrosion current density ($i_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), anodic Tafelslope ($\beta_a$) and cathodic Tafel slope ($-\beta_c$) were obtained from the potentiodynamic polarization plot. Corrosion rate was calculated using equation (1).

$$C.R. \ (\text{mm Y}^{-1}) = \frac{i_{\text{corr}} \times M \times 3270}{\rho \times Z}$$  \hspace{1cm} (1)

where 3270 is a constant that defines the unit of corrosion rate, $i_{\text{corr}}$ = corrosion current density in A cm$^{-2}$, $\rho$ = density of the corroding material (in g cm$^{-3}$), $M$ = Atomic mass of the metal, and $Z$ = Number of electrons transferred per metal atom. For aluminum $M=27$, $Z=3$ and $\rho = 2.7$

Percentage inhibition efficiency was calculated using the equation (2).

$$I.E \ (%) = \theta \times 100$$  \hspace{1cm} (2)

where $\theta = \frac{i_{\text{corr}} - i_{\text{corr.(inh.)}}}{i_{\text{corr}}}$  \hspace{1cm} (3)

where $i_{\text{corr}}$ and $i_{\text{corr.(inh.)}}$ are the corrosion current densities in the absence and in the presence of inhibitor, respectively.

The experiments were repeated at five different temperatures. Corrosion potential ($E_{\text{corr}}$), corrosion current density ($i_{\text{corr}}$), corrosion rate (CR) and percentage inhibition efficiency (\% I.E) were determined. The results of the potentiodynamic polarization measurement is tabulated in Table 1 for aluminum in sulfuric acid (pH=3).

It was observed that with increase in the concentrations of the TCSE corrosion current density decreased. Inhibition efficiency increased with increasing inhibitor concentration. The observed inhibition efficiency of TCSE may be due to the adsorption of its components on the aluminum surface. The adsorbed molecules may isolate the metal surface from the aggressive medium leading to decreasing the corrosion rate. The anodic and cathodic Tafel slopes remained almost unchanged for the uninhibited and inhibited solutions. This indicates that the inhibitive action of TCSE may be due to simple blocking of the available surface area on the surface of the metal. There was measurable positive shift in corrosion potential ($E_{\text{corr}}$) after the addition of inhibitor. According to Li et al [8], if the displacement in corrosion potential is more than ±85 mV with respect to corrosion potential of the blank, then the inhibitor can be considered distinctively as a cathodic or anodic type. However, the maximum displacement in the present investigations for aluminum in sulfuric acid was more than that of 85mV, towards the positive direction. This observation suggests that constituents of inhibitor molecule may act as anodic type and brings the anodic reaction under control.

### 3.3.3 Electrochemical impedance spectroscopy (EIS) technique

Figure 2 (a) represent the Nyquist plot of aluminum in the sulfuric acid (pH=3) containing various concentrations of aqueous extracts of TCSE at 30 °C. Similar plots are obtained at other temperatures.
The results of both the techniques are tabulated in Table 1. The polarization resistance \( R_p \) and the double layer capacitance \( C_{dl} \) was calculated from equation (4):

\[
C_{dl} = C_1 + C_2
\]

And the polarization resistance \( R_p \) was calculated using the equation (5):

\[
R_p = R_0 + R_1 + R_2
\]

Since \( R_p \) is inversely proportional to the corrosion current and it can be used to calculate the percentage inhibition efficiency using the relation

\[
\eta\% = \frac{R_p\text{blank} - R_p}{R_p\text{blank}} \times 100
\]

The results of both the techniques are tabulated in Table 1.

**Table 1: Results of potentiodynamic polarization measurements and Impedance parameters for the corrosion of aluminum in \( \text{H}_2\text{SO}_4 \) (pH=3) containing different concentrations of TCSE at different temperatures.**

<table>
<thead>
<tr>
<th>Temp. (^\circ\text{C})</th>
<th>[TCSE] ppm</th>
<th>( i_{corr} \times 10^5 \text{ A/cm}^2 )</th>
<th>C.R. (mpmy)</th>
<th>( \beta_p ) (Vdec(^{-1}))</th>
<th>( \beta_c ) (Vdec(^{-1}))</th>
<th>( E_{corr} ) (mV vs SCE)</th>
<th>% I.E.</th>
<th>( C_{dl} \times 10^{10} \text{ F/cm}^2 )</th>
<th>( R_2 ) (ohmcm(^2))</th>
<th>% I.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0</td>
<td>0.705</td>
<td>0.081</td>
<td>0.51</td>
<td>0.51</td>
<td>-837</td>
<td>-----</td>
<td>32.90</td>
<td>6068</td>
<td>-----</td>
</tr>
<tr>
<td>50</td>
<td>0.095</td>
<td>0.031</td>
<td>0.62</td>
<td>0.55</td>
<td>-419</td>
<td>53.00</td>
<td>1.71</td>
<td>12878</td>
<td>52.87</td>
<td>61.22</td>
</tr>
<tr>
<td>100</td>
<td>0.090</td>
<td>0.031</td>
<td>0.67</td>
<td>0.60</td>
<td>-563</td>
<td>62.63</td>
<td>1.15</td>
<td>15653</td>
<td>61.22</td>
<td>61.22</td>
</tr>
<tr>
<td>200</td>
<td>0.083</td>
<td>0.013</td>
<td>0.69</td>
<td>0.61</td>
<td>-547</td>
<td>84.13</td>
<td>0.82</td>
<td>21484</td>
<td>81.75</td>
<td>81.75</td>
</tr>
<tr>
<td>300</td>
<td>0.089</td>
<td>0.011</td>
<td>0.69</td>
<td>0.58</td>
<td>-615</td>
<td>85.99</td>
<td>0.70</td>
<td>32127</td>
<td>82.10</td>
<td>82.10</td>
</tr>
<tr>
<td>400</td>
<td>0.046</td>
<td>0.011</td>
<td>0.72</td>
<td>0.53</td>
<td>-630</td>
<td>86.48</td>
<td>0.33</td>
<td>91387</td>
<td>88.02</td>
<td>88.02</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
<td>0.749</td>
<td>0.086</td>
<td>0.51</td>
<td>0.52</td>
<td>-720</td>
<td>-----</td>
<td>111</td>
<td>6036</td>
<td>-----</td>
</tr>
</tbody>
</table>
It was also observed that the value of constant phase element Q decreases, while the values of R decreased with increasing concentration of inhibitor, indicating that the inhibition efficiency increases with the increase in concentration of aqueous extracts of TCSE. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of inhibitor molecules on the aluminum surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with increase in inhibitor concentrations may be attributed to the formation of a protective layer on the electrode surface. The thickness of this protective layer increased with increase in inhibitor concentration up to their critical concentration of 400 ppm and then decreased. The obtained CPE (Q) values decreased noticeably with increase in the concentration of inhibitors. This may be due to the adsorption of constituents of TCSE on the metal surface as Q is inversely proportional to the thickness of the protective layer

3.3.4. Effect of temperature

Inhibition efficiency increased with increase in the concentrations of the TCSE but decreased with increase in temperature. This can be attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface (or desorption of the inhibitor molecules from the metal surface) at higher temperatures [13]. This suggests physical adsorption mechanism. Physical (electrostatic) adsorption may take place when inhibition efficiency decreases with increase in temperature (where as chemical adsorption takes place when inhibition efficiency increases with increase in temperature) [14]. However, at higher concentrations of inhibitor this decrease was small. The study of effect of temperature was used to calculate energy of activation (E) for the corrosion process in the presence and absence of inhibitor using Arrhenius law[15]. The Arrhenius plot for the aluminum in the presence of inhibitor in sulphuric acid (pH=3) is shown in Figure 3(a).

The enthalpy of activation and entropy of activation (∆H & ∆S) for the dissolution of specimen were calculated from transition state Equation [15]. The plot of (ln (CR/T) versus 1/T) gave straight line with slope = ∆H/R. Intercept = lnR/Nh + ∆S/R. The plot of ln (CR/T) versus 1/T for the aluminum in various concentrations of inhibitor in sulfuric acid (pH=3) is shown in Figure 3(b).
Energy of activation ($E_a$) values increased significantly after the addition of the inhibitor. The increase in activation energy ($E_a$) of inhibited solutions compared to the blank suggests that inhibitor gets adsorbed on the corroding metal surface. The increase in the $E_a$ values, with increasing inhibitor concentration indicates the increase in energy barrier for the corrosion reaction [15]. The adsorption of the inhibitor molecules on the surface of the aluminum blocks the charge transfer during corrosion reaction, thereby increasing the activation energy. The values of $\Delta S_a$ were higher for inhibited solutions than those for the uninhibited solutions. This suggested that an increase in randomness occurred on going from reactants to the activated complex. This might be the results of the adsorption of organic compound present in the TCSE from the acidic solution which could be regarded as a quasi-substitution process between the organic compound in the aqueous phase and water molecules at electrode surface. Thus the increase in entropy of activation was attributed to the increase in solvent entropy [16].

3.3.5 Adsorption Isotherm

Adsorption isotherms are usually employed to explain the mechanism of interaction between an inhibitor (adsorbate) and an adsorbent surface. This is usually achieved by fitting the degree of surface coverage data into various adsorption isotherms or models and the correlation coefficients (highest) used to determine the best fit isotherm which can then be used to describe the inhibitor adsorption mechanism. In this work, the best fitted isotherm was the Langmuir adsorption model which relates the degree of surface coverage ($\theta$) to the concentration of the extracts ($C_{inh.}$) according to equation (7).

$$\frac{\theta}{(1 - \theta)} = K_{ads} C$$

(7)

where $K_{ads}$ is the equilibrium constant of the inhibitor adsorption process and $C$ is the inhibitor concentration, and $\theta$ is the degree of the surface coverage, which is calculated using Equation (3). This model has also been used for other inhibitor systems [17]. The plot of $C_{inh.}/\theta$ versus $C_{inh.}$ gave a straight line (intercept = $1/K$) as shown in Figure 4(a). The correlation regression coefficients were close to unity, and the slopes of straight lines were nearly unity, suggesting that the adsorption of organic compounds present in TCSE obeyed Langmuir’s adsorption isotherm, and there is negligible interaction between the adsorbed molecules [18].
The values of standard free energy of adsorption are related to K by the relation (8).

\[ K = \frac{1}{C_{\text{water}}} \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) \]  

(8)

Where \( C_{\text{water}} \) is the concentration of water in solution expressed in ppm, \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature. It must be noted that the concentration unit of water molecules has to be same as that of the inhibitor (the unit of \( C_{\text{water}} \) is ppm, with the value of approximate \( 1 \times 10^6 \)) [15].

The plot of \( \Delta G_{\text{ads}} \) versus \( T \) in Figure 4(b) was used to calculate the heat of adsorption \( \Delta H_{\text{ads}} \) and the standard adsorption entropy \( \Delta S_{\text{ads}} \) according to the thermodynamic Equation (9). The negative values of \( \Delta G_{\text{ads}} \) suggest the spontaneous adsorption of inhibitor on the surface of metal and the stability of the adsorbed layer on the aluminum.

\[ \Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \]  

(9)

The thermodynamic parameters obtained for aluminum in sulfuric acid (pH=3) are tabulated in Table 3. In general, the standard free energy values of \(-20\) kJ mol\(^{-1}\) or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, resulting in physisorption, and standard free energy values of \(-40\) kJ mol\(^{-1}\) or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, resulting in chemisorption [15]. The \( \Delta G_{\text{ads}} \) values obtained for the studied inhibitor on the aluminum surface in sulfuric acid (pH=3) is less than \(-20\) kJ mol\(^{-1}\) which indicates the adsorption of constituents of TCSE on the surface of aluminum is a physisorption process [19].

The values of thermodynamic parameters for the adsorption of inhibitors can provide valuable information about the mechanism of inhibition. While an endothermic adsorption process (\( \Delta H_{\text{ads}} > 0 \)) is attributed unequivocally to chemisorption, an exothermic adsorption process (\( \Delta H_{\text{ads}} < 0 \)) may involve either physisorption or chemisorptions or a mixture of both the processes. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of adsorption enthalpy. In this process, the enthalpy of a physisorption process is lower than 41.86 kJ mol\(^{-1}\), while that of a chemisorption process approaches 100 kJ mol\(^{-1}\) [14]. In the present case, the calculated value of \( \Delta H_{\text{ads}} \) is \(-40.05\) kJ mol\(^{-1}\), which indicates the adsorption of TCSE on the surface of aluminum is a physisorption process. The \( \Delta S_{\text{ads}} \) value is negative, indicating that an ordering takes place when the inhibitor gets adsorbed on the metal surface [20]. Kinetic and thermodynamic parameters are tabulated in Table 2.
Table 2: (a) Kinetic parameters and (b) Thermodynamic parameters for the adsorption of TCSE on aluminum in H₂SO₄ (pH=3)

<table>
<thead>
<tr>
<th>[TCSE] (ppm)</th>
<th>E_a (kJ mol⁻¹)</th>
<th>ΔH_a (kJ mol⁻¹)</th>
<th>ΔS_a (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36.88</td>
<td>34.28</td>
<td>145.68</td>
</tr>
<tr>
<td>50</td>
<td>78.08</td>
<td>75.48</td>
<td>120.70</td>
</tr>
<tr>
<td>100</td>
<td>49.70</td>
<td>47.12</td>
<td>119.32</td>
</tr>
<tr>
<td>200</td>
<td>46.22</td>
<td>43.62</td>
<td>133.38</td>
</tr>
<tr>
<td>300</td>
<td>40.02</td>
<td>37.42</td>
<td>155.08</td>
</tr>
<tr>
<td>400</td>
<td>52.03</td>
<td>49.43</td>
<td>118.44</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>ΔG_ads (kJ mol⁻¹)</td>
<td>ΔH_ads (kJ mol⁻¹)</td>
<td>ΔS_ads (kJ mol⁻¹ K⁻¹)</td>
</tr>
<tr>
<td>30</td>
<td>3.23</td>
<td>-40.05</td>
<td>-0.16</td>
</tr>
<tr>
<td>35</td>
<td>2.40</td>
<td>-37.70</td>
<td>-0.09</td>
</tr>
<tr>
<td>40</td>
<td>2.43</td>
<td>-36.32</td>
<td>-0.11</td>
</tr>
<tr>
<td>45</td>
<td>0.91</td>
<td>-33.93</td>
<td>-0.10</td>
</tr>
<tr>
<td>50</td>
<td>0.13</td>
<td>-31.54</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

3.3.6. Mechanism of Inhibition

TCSE is composed of numerous naturally organic heterocyclic compounds. Major constituents of the aqueous extract of TCSE are reported to be Berberine, Tembeterine and palmetine[6]. The structures of same are given in Figures 5(a), 5(b) and 5(c).

Surface of aluminum is covered with thin layer of γ alumina which initially thickens on exposure to neutral aqueous solution with the formation of a layer of crystalline hydrated alumina. The aluminum surface has positive charge in acidic environment in contact with sulfuric acid. The mechanism of adsorption can be predicted on the basis of the mechanism proposed for the corrosion of aluminum in sulfuric acid [21].

Anodic reactions

\[
\text{Al(s)} + \text{H}_2\text{O} \rightarrow \text{AlOH}_{\text{ads}} + \text{H}^+ + e^- \\
\text{AlOH}_{\text{ads}} + 5\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Al}^{3+} \cdot 6\text{H}_2\text{O} + 2e^- \\
\text{Al}^{3+} + \text{H}_2\text{O} \rightarrow [\text{AlOH}]^{2+} + \text{H}^+ \\
[\text{AlOH}]^{2+} + X \rightarrow [\text{AlOHX}]^+ 
\]

Cathodic reaction

\[
\text{H}^+ + e^- \rightarrow \text{H(ads)} \\
\text{H(ads)} + \text{H(ads)} \rightarrow \text{H}_2
\]

TCSE acts as an anodic type of inhibitor, by bringing anodic reaction under control. In acid medium, aluminum is positively charged. This may attract negative sulfate ions from the solution, and forms a double layer. In other words, surface of aluminum acquires net negative charge due to the adsorption of sulfate ions. In acidic solution the organic compounds present in the aqueous extract of TCSE containing heteroatom can be easily protonated because of their high electron density. The protonated molecules may be physically attracted to the anions layer which is formed on the metal surface, forming electrostatic protective barrier on the surface of the metal[16]. This barrier will prevent the further dissolution of the metal and prevent the metal from undergoing corrosion. Enhanced corrosion inhibition may be also due to the π electrons of the aromatic ring of the constituents of the extract which also acts as high electron rich centers.

IV. CONCLUSIONS

- TCSE is a green inhibitor, which is readily available and cost effective for the corrosion control of aluminum.
The inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperature. It acted as an anodic inhibitor.

TCSE adsorbed on the aluminum surface via both physiosorption process and followed Langmuir’s adsorption.

REFERENCES


