Inhibition of aluminium corrosion by *Commelina diffusa* leaf extract in 2 M HCl solution

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Abstract

The effect of *Commelina diffusa* leaf extract on the corrosion of aluminium in 2 M HCl solution was studied using weight loss, thermometric and hydrogen evolution methods. *Commelina diffusa* leaf extract appreciably inhibited the corrosion of aluminium in HCl solution. The inhibition efficiency increased with increase in extract concentration and temperature. The experimental data conformed to the modified Langmuir adsorption isotherm. The spontaneity of the adsorption process was revealed by the negative values of standard free energy obtained. Chemisorption process has been proposed for the adsorption of *Commelina diffusa* leaf extract onto aluminium surface.

Keywords: *Commelina diffusa*, Corrosion inhibition, extract, Langmuir isotherm, Chemisorption

1. Introduction

The use of aluminium and its alloys in the fabrication of domestic and industrial equipment/machinery is increasing. Aluminium and its alloys are particularly good where high strength-to-weight ratio is required [1]. Under normal conditions, aluminium is very resistant to corrosion attack, due to a thin oxide layer on its surface. This oxide layer, being amphoteric, dissolves in high concentrations of acids and alkalis [2]. In order to reduce the loss of the metal in contact with aggressive environments such as during pickling, oil well acidizing, acid descaling, etc, corrosion inhibitors are usually employed.

In line with strict environmental protection laws in many countries, eco-friendly corrosion inhibitors are now in high demand, as replacement for the traditional inhibitors (inorganic and synthesized organic compounds) since many of them are toxic to plants and animals. Fortunately, eco-friendly inhibitors can be extracted from natural products. Several leaves extracts [3-6] have been reported as potential inhibitors of aluminium corrosion in acidic media. Since corrosion inhibitors are known to be specific in their action, there is the need to empirically test each extract to determine its inhibitory effect on a given metal in a particular medium.

*Commelina diffusa* Burm. f. (English name: Spreading day flower; Ibibio name: Ekpa ekpa ikpaha) is a medicinal plant belonging to the family Commelinaceae. The traditional medicinal use of *Commelina diffusa* by the people of eastern Nigeria have been documented [7]. The preliminary phytochemical screening of *Commelina diffusa* leaf extract reveal the presence of alkaloids, anthraquinones, ketonic compounds and terpenoids [8]. There is no reported work on the use of *Commelina diffusa* leaf extract as corrosion inhibitor for aluminium in acidic medium. The aim of this research was to assess the inhibitory effect of *Commelina diffusa* on aluminium corrosion in hydrochloric acid solution.

2. Materials and Methods

2.1 Test Materials

The chemical composition of aluminium sheet used for this study was as follows (weight %): Al (99.60), Cu (0.03), Si (0.13), Mn (0.05), Mg (0.10) and, Fe (0.09). The sheet was mechanically press - cut into 4 cm x 5 cm coupons, and polished to mirror finish using different grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dipped in acetone before air-drying. They were then stored in a moisture – free desiccator before use in corrosion studies [9].
2.2 Preparation of Commelina diffusa leaf extract
Commelina diffusa leaves were collected from a farm in Uyo, Akwa Ibom State, Nigeria and authenticated by a plant taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Nigeria. They were washed and air-dried at 30°C for seven days and ground to powder. The Commelina diffusa leaf extract was obtained following standard procedure reported previously [10–11].

2.3 Weight loss method
The aluminium coupons were suspended with the aid of glass hooks and rods and immersed in 100 cm³ of 2 M HCl solution (blank) and in 2 M HCl solution containing 1.0 g/L – 4.0 g/L Commelina diffusa leaf extract (inhibitor) in open beakers. One aluminium coupon per beaker was used in each experiment. The beakers were then placed in a thermostatic water bath maintained at 30°C, 40°C, 50°C, and 60°C, respectively. The aluminium coupons were retrieved from the test solutions after 30 minutes and scrubbed with bristle brush under running water. They were dipped in acetone and air-dried before reweighing.

The inhibition efficiency IWL (%) was computed using the formula [12]:

\[ I_{WL} = \left( \frac{W_0 - W_1}{W_0} \right) \times 100 \]  \hspace{1cm} (1)

where \( W_0 \) and \( W_1 \) are the weight losses of the aluminium coupons in the absence and presence of extract, respectively, in 2 M HCl at the same temperature.

The corrosion rate (CR) of aluminium in 2 M HCl solution was calculated using the formula:

\[ CR = \frac{W}{A t} \]  \hspace{1cm} (2)

Where \( W \) is the weight loss (mg), A is the total surface area (cm²) while \( t \) is the exposure time (hours).

2.4 Thermometric Method
The aluminium coupons were suspended with the aid of glass hooks and rods and immersed in 100 cm³ of 2 M HCl solution (blank) and in 2 M HCl solution containing 1.0 g/L – 4.0 g/L Commelina diffusa leaf extract (inhibitor) in open beakers. One aluminium coupon per beaker was used in each experiment. The beakers were then placed in a thermostatic water bath maintained at 30°C, 40°C, 50°C, and 60°C, respectively. The aluminium coupons were retrieved from the test solutions after 30 minutes and scrubbed with bristle brush under running water. They were dipped in acetone and air-dried before reweighing.

The reaction number (RN) is defined as [14]:

\[ RN = \frac{T_m - T_i}{t} \]  \hspace{1cm} (3)

where \( T_m \) and \( T_i \) are the maximum and initial temperatures, respectively, while \( t \) is the time (min) taken to reach the maximum temperature.

The inhibition efficiency, \( I_{TM} \) (%) was calculated using the formula:

\[ I_{TM} = \left( \frac{RN_0 - RN_I}{RN_0} \right) \times 100 \]  \hspace{1cm} (4)

where \( RN_0 \) is the reaction number in the absence of inhibitors (blank) and \( RN_I \) is the reaction number in the presence of studied inhibitor.

2.5 Hydrogen Evolution Method
The hydrogen evolution tests were done following standard procedure reported by other workers [13]. The reaction vessel contained 100 cm³ of 2 M HCl solution. One 4 cm x 5 cm aluminium coupon was dropped into the 2 M HCl solution (blank) and the reaction vessel quickly closed. The volume of \( H_2 \) gas evolved from the corrosion reaction was recorded every 60 seconds for 30 minutes. The experiment was repeated using 1.0 g/L – 4.0 g/L Commelina diffusa leaf extract in 2 M HCl solution.

The hydrogen evolution rate \( R_H \) (cm³ min⁻¹) was evaluated using the formula [16]:

\[ R_H = \frac{V_t - V_i}{t_i - t_i} \]  \hspace{1cm} (5)

Where \( V_t \) and \( V_i \) are the volumes of hydrogen evolved at time \( t_t \) and \( t_i \), respectively.

The inhibition efficiency \( I_{HE} \) (%) was calculated using the equation [3]:

\[ I_{HE} = \left( \frac{R_{H0} - R_{HI}}{R_{H0}} \right) \times 100 \]  \hspace{1cm} (6)

Where \( R_{H0} \) and \( R_{HI} \) are the hydrogen evolution rates in the absence and presence of inhibitor, respectively, at a specified time.

3. Results and Discussion
3.1 Effect of Commelina diffusa leaf extract concentration on inhibition efficiency
Fig. 1 shows that the inhibition efficiency by the weight loss method increased with increase in Commelina diffusa leaf extract concentration, at a particular temperature. Fig. 2 reveals a marked reduction in the volume of hydrogen gas evolved in the presence of Commelina diffusa leaf extract compared to the blank. The inhibition efficiency by the hydrogen evolution method (Table 1) depicts an increase in the inhibition efficiency with increase in the leaf extract concentration. The results of the thermometric tests (Fig. 3) depict an increase in the time taken to reach maximum temperature in addition to a reduction in the maximum temperature attained in the presence of the extract relative to the blank, which translates to inhibition of aluminium corrosion in the corroding by the extract. The inhibition efficiency by the thermometric method (Table 2) also shows an increase in the inhibition efficiency with increase in the extract concentration. The data obtained by the three methods reveal that Commelina diffusa leaf extract functioned effectively as an inhibitor of aluminium corrosion in HCl solution. Additionally, an increase in the inhibition efficiency with increase in Commelina diffusa leaf extract concentration reveals that the extract inhibits the corrosion process by adsorbing on the metal surface and reducing/blocking the electron transfer processes on the metal surface [17].
Fig 1: Effect of *Commelina diffusa* leaf extract concentration on the inhibition efficiency of aluminium corrosion in 2 M HCl solution at 30°C and 40°C (weight loss measurements)

Fig 2: Variation of volume of H$_2$ gas evolved (cm$^3$) with time (min) for aluminium corrosion in 2 M HCl in the absence and presence of *Commelina diffusa* leaf extract at 30°C

Fig 3: Variation of temperature (°C) with time (min) for aluminium corrosion in 2 M HCl in the absence and presence of *Commelina diffusa* leaf extract

Table 1: Hydrogen evolution data for aluminium corrosion in 2 M HCl solution in the absence and presence of *Commelina diffusa* leaf extract

<table>
<thead>
<tr>
<th>Extract concentration</th>
<th>H$_2$ evolution rate (cm$^3$ min$^{-1}$)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 M HCl</td>
<td>0.8900</td>
<td></td>
</tr>
<tr>
<td>1.0 g/L</td>
<td>0.2800</td>
<td>68.54</td>
</tr>
<tr>
<td>2.0 g/L</td>
<td>0.2133</td>
<td>76.03</td>
</tr>
<tr>
<td>3.0 g/L</td>
<td>0.1733</td>
<td>80.53</td>
</tr>
<tr>
<td>4.0 g/L</td>
<td>0.1467</td>
<td>83.52</td>
</tr>
</tbody>
</table>
3.2 Effect of temperature on inhibition efficiency
Table 3 reveals that an increase in temperature led to an increase in the inhibition efficiency of aluminium corrosion in HCl solution by Commelina diffusa leaf extract. An increase in inhibition efficiency with increase in temperature shows a strong interaction between the metal surface and inhibitor as well as a chemical adsorption mechanism \[^3\]. Therefore, it can be proposed that the interaction between aluminium surface and Commelina diffusa leaf extract probably occurred by a chemisorption mechanism.

Table 3: Weight loss data for aluminium corrosion in 2 M HCl solution in the absence and presence of Commelina diffusa leaf extract at 30°C and 40°C

<table>
<thead>
<tr>
<th>Extract conc. (g/L)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mg cm(^{-2}) hr(^{-1}))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>40°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 M HCl</td>
<td>0.0187</td>
<td>0.01169</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.6914</td>
<td>4.3213</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0092</td>
<td>0.0072</td>
<td>50.80</td>
</tr>
<tr>
<td></td>
<td>0.1858</td>
<td>0.1311</td>
<td>73.13</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0072</td>
<td>0.0045</td>
<td>61.50</td>
</tr>
<tr>
<td></td>
<td>0.1311</td>
<td>0.7194</td>
<td>81.04</td>
</tr>
<tr>
<td>3.0</td>
<td>0.0049</td>
<td>0.0306</td>
<td>73.80</td>
</tr>
<tr>
<td></td>
<td>0.0804</td>
<td>0.5025</td>
<td>88.37</td>
</tr>
<tr>
<td>4.0</td>
<td>0.0046</td>
<td>0.0288</td>
<td>75.40</td>
</tr>
<tr>
<td></td>
<td>0.0574</td>
<td>0.3588</td>
<td>91.70</td>
</tr>
</tbody>
</table>

The activation energies (E\(_a\)) of the corrosion of aluminium in HCl solution in the absence and presence of Commelina diffusa leaf extract were calculated using the Arrhenius equation \[^{18}\]:

\[
\log \left( \frac{CR_2}{CR_1} \right) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]  
(7)

where CR\(_1\) and CR\(_2\) are corrosion rates at temperatures T\(_1\) (K) and T\(_2\) (K), respectively, while R is the universal gas constant. The values of heat of adsorption (Q\(_{ads}\)) were evaluated using the formula \[^{19}\]:

\[
Q_{ads} = 2.303R \left[ \log \left( \frac{\theta_2}{1-\theta_2} \right) - \log \left( \frac{\theta_1}{1-\theta_1} \right) \right] \times \left[ \frac{T_1T_2}{T_2-T_1} \right]
\]  
(8)

where R is the universal gas constant while \(\theta_1\) and \(\theta_2\) are the degrees of surface coverage at T\(_1\) (K) and T\(_2\) (K), respectively.

The values of activation energy (E\(_a\)) obtained using equation (7) are presented in Table 4. Table 4 reveals that the E\(_a\) values in the presence of Commelina diffusa leaf extract were lower than that of the blank (284.70 kJ mol\(^{-1}\)). Lower E\(_a\) values in the presence of inhibitor relative to the blank in addition to an increase in the inhibition efficiency with increase in temperature could be attributed to chemisorption of inhibitor on the metal surface \[^{20}\]. The Q\(_{ads}\) values for the corrosion of aluminium in 2 M HCl solution as contained in Table 4 are positive. Positive values of Q\(_{ads}\) indicate that the adsorption of Commelina diffusa leaf extract onto aluminium surface and hence the inhibition efficiency increased with increase in temperature \[^{21}\].

Table 4: Calculated values of activation energy and heat of adsorption for aluminium corrosion in 2 M HCl solution in the absence and presence of Commelina diffusa leaf extract

<table>
<thead>
<tr>
<th>Extract concentration</th>
<th>E(_a) (kJ mol(^{-1}))</th>
<th>Q(_{ads}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 M HCl (Blank)</td>
<td>284.70</td>
<td>-</td>
</tr>
<tr>
<td>1.0 g/L</td>
<td>237.02</td>
<td>76.43</td>
</tr>
<tr>
<td>2.0 g/L</td>
<td>228.85</td>
<td>77.61</td>
</tr>
<tr>
<td>3.0 g/L</td>
<td>220.71</td>
<td>78.27</td>
</tr>
<tr>
<td>4.0 g/L</td>
<td>198.92</td>
<td>101.13</td>
</tr>
</tbody>
</table>

3.3 Adsorption isotherm
The best fit of the experimental data obtained for the adsorption of Commelina diffusa leaf extract onto aluminium surface was found to conform to the modified Langmuir adsorption isotherm defined as \[^{22}\]:

\[
\frac{C}{\theta} = n \frac{1}{K_{ads}} + nC
\]  
(9)

where \(\theta\) is the degree of surface coverage, C is the inhibitor concentration and K\(_{ads}\) is the adsorption equilibrium constant.

Linear plot of C/\(\theta\) vs. C was obtained (Fig. 4), confirming that the adsorption of Commelina diffusa leaf extract onto aluminium surface obeyed the Langmuir adsorption isotherm. The values of K\(_{ads}\) presented in Table 5 were evaluated from the intercept of the graph. The standard free energy of adsorption, \(\Delta G_{ads}\), was calculated using the formula \[^{23}\]:

\[
\Delta G_{ads} = -RT \ln(55.5K_{ads})
\]  
(10)

where R is the universal gas constant, T is the absolute temperature while 55.5 is the molar concentration of water in the solution. The negative values of \(\Delta G_{ads}\) obtained reveal the spontaneity of the adsorption of Commelina diffusa leaf extract onto aluminium surface.
adsorption of the extract was spontaneous.

Due to negative values of $\Delta G^\circ$, the aluminium surface conformed to the modified Langmuir adsorption isotherm. Due to negative values of $\Delta G^\circ$, the adsorption of the extract onto aluminium surface, based on an increase in the inhibition efficiency with increase in temperature coupled with a decrease in the $E_a$ value in the extract relative to the blank. The adsorption of Commelina diffusa leaf extract onto aluminium surface conformed to the modified Langmuir adsorption isotherm. Due to negative values of $\Delta G^\circ$, the adsorption of the extract was spontaneous.

**Table 5: Langmuir adsorption isotherm data for aluminium corrosion in 2 M HCl solution containing Commelina diffusa leaf extract**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>R$^2$</th>
<th>n</th>
<th>$1/K_{ads}$ (g L$^{-1}$)</th>
<th>$K_{ads}$ (g$^{-1}$ L)</th>
<th>$\Delta G^\circ$ ads (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>0.9931</td>
<td>1.08</td>
<td>9.420 x 10$^{-3}$</td>
<td>1.062</td>
<td>-10.269</td>
</tr>
<tr>
<td>40°C</td>
<td>0.9986</td>
<td>0.99</td>
<td>4.203 x 10$^{-4}$</td>
<td>2.379</td>
<td>-12.707</td>
</tr>
</tbody>
</table>

**Conclusion**

Based on this work, the following conclusions could be made: Commelina diffusa leaf extract is a good inhibitor of aluminium corrosion in hydrochloric acid solution. The inhibition efficiency increased with increase in Commelina diffusa leaf extract concentration and temperature. Chemical adsorption is proposed to account for the adsorption of the extract onto aluminium surface, based on an increase in the inhibition efficiency with increase in temperature coupled with a decrease in the $E_a$ value in the extract relative to the blank. The adsorption of Commelina diffusa leaf extract onto aluminium surface conformed to the modified Langmuir adsorption isotherm. Due to negative values of $\Delta G^\circ$, the adsorption of the extract was spontaneous.

**References**


