INFLUENCE OF ION-ADDITIVES ON INHIBITORY ACTION
OF EXTRACT OF TRIGONELLA FOENUM GRACEUMS SEEDS
FOR AA6063 IN ACID MEDIUM

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ABSTRACT
The effect of some ion-additives on the inhibitive effect of extract of Trigonella foenum graceums seeds (TfgS) on acid corrosion of aluminium alloy (AA6063) was studied. The investigation was carried out for different immersion periods in 0.5 N HCl at room temperature employing weight loss method. An optimum concentration (1.056 g/L) of the inhibitor was used for the 0.05 g/L of various ion-additives (halide and Zn$^{2+}$ ions). Various corrosion parameters were evaluated using weight loss data. The inhibition efficiency was observed to increase synergistically on adding the additives. The TfgS extract is a potential inhibitor for acid-induced corrosion of AA6063.

Key words: Aluminium alloy (AA6063); Weight loss; Acid corrosion; Trigonella foenum graceums seeds (TfgS); Additives; Synergism.

INTRODUCTION
The corrosion of metallic materials in acidic solution causes considerable costs$^{1-2}$. In order to combat the corrosion of metals, several techniques have been applied. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media$^{3-9}$. It has been well established that the organic compounds with hetero-atoms such as oxygen, nitrogen, sulphur, and phosphorus tend to be most effective inhibitors as they get adsorbed on the specimen surface$^{10-11}$. While selecting inhibitors factors like, cost, toxicity, availability and environmental safety need to be focused. Hence, now a day’s researchers are inclined to opt natural products as corrosion inhibitor$^{12-27}$. The plant extracts being biodegradable poses no threat to the environment. Moreover they are the rich source of active chemical constituents having significant inhibitive property, hence can be a good replacement for synthetic organic compounds. The presence of anions and cations in the solution had been found to stabilize the adsorption of some organic cations and anions leading to improved inhibition efficiency. This increased efficiency to retard the corrosion process has been ascribed as synergistic effect$^{12,28-29}$. It has been proposed that formation of intermediate bridges between the metal surface and the positive end of the organic inhibitor are responsible for the improved adsorption of the organic cations. Hence increase in surface coverage arising from ion-pair interactions between the organic cations and the anions improve corrosion inhibition synergism. Synergistic studies have become an increasing important phenomenon and serves as the basic criterion for selection of most modern corrosion inhibitors.

An attempt has been made to evaluate synergism in the inhibitory action of ethanolic extracts of Trigonella foenum graceums seeds (EETfgS) and some ion-additives, viz. halide ions (anions) and zinc ions (cations) for aluminium alloy (AA6063) in 0.5N hydrochloric acid medium for various immersion periods at room temperature.

EXPERIMENTAL
The corrosion inhibition property of different test solutions was investigated by weight loss method at various immersion periods. All the solutions were made in doubly distilled water and the experimentations were carried out at room temperature.
**Weight loss measurements**

Aluminium alloy (AA6063) sheets with 0.016 cm thickness were mechanically press-cut into 3cm × 2.4cm coupons. AnalR grade HCl was employed to prepare standard 0.5 N HCl as the corrodent. The preparations of test coupons, electrolyte test solution and ethanolic extraction of *Trigonella foenum graceums* seeds (EETfgS) were carried out as reported earlier\(^{19,26}\).

**Preparation of test solutions**

The experimentation was carried out in 10 different beakers, labeled S0 to S9; each with a constant volume of aggressive solution (0.5 N HCl). The first beaker, S0, contained only aggressive medium and no plant extract / additives; while an optimum concentration of plant extracts, EETfgS (1.056 g/L) was added to the beakers labeled S1, S3, S5, S7 and S9. In the beakers labeled as S2 and S3; S4 and S5; S6 and S7; S8 and S9 – in a set of two beakers each – a fixed quantity (0.5 g/100 ml) of ion-additive (KI, KCl, KBr and Zn\(^{2+}\) respectively) was added. Thus, the beakers labeled S3, S5, S7 and S9 contained KI+ EETfgS, KCl+ EETfgS, KBr+ EETfgS, and Zn\(^{2+}\) + EETfgS respectively. The experiments were carried out for various immersion periods ranging from 3 h to 72 h at room temperature to evaluate synergism between EETfgS and ion-additives for inhibition towards acid corrosion of AA6063.

**RESULTS AND DISCUSSION**

Corrosion of Al in aqueous solution depends on the concentration of anions in solution\(^{30-31}\) for which general mechanism of dissolution has been suggested as:

\[
\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow [\text{AlOH}]^{2+} + \text{H}^+ \tag{1}
\]

\[
[\text{AlOH}]^{2+} + X^- \leftrightarrow [\text{AlOX}]^+ \tag{2}
\]

The controlling step in the metal dissolution is the complex cation reaction between the hydrated cation and the anion present is the controlling step in the metal dissolution in equation 2; while in the presence of chloride ions the reaction will be:

\[
[\text{AlOH}]^{2+} + \text{Cl}^- \rightarrow [\text{AlOHC}]^+ \tag{3}
\]

Hence, the metal dissolution rate depends on the chloride concentration.

Natural products are rich source of active chemical constituents like tannins, amino acids, alkaloids, and pigments, known to exhibit inhibiting action. The adsorption of these active constituents on the metal surface reduces the surface area available for corrosion. The inhibitive tendency of anions (like halides) depends on their ionic size and charge; the electrostatic field set up by the negative charge of the anion on adsorption sites; nature and concentration of the halide ion\(^{32}\). It has also been reported\(^{33}\) that the inhibitive effect increases in the order Cl\(^-\) (radius: 90pm) < Br\(^-\) (radius: 114pm) < I\(^-\) (radius: 135pm), which indicates that the radii of halide ions have an important role in the synergism.

**Weight loss and corrosion rates**

Using weight loss technique, inhibitive synergism of EETfgS and ion-additives on AA6063 at various immersion periods was studied at room temperature. Corrosion and adsorptive parameters like corrosion rate (\(\rho_{corr} \text{ mmmy}^{-1}\)), percentage inhibition efficiency (IE%), fractional surface coverage (\(\theta\)), have been calculated and tabulated in table 1.

The results reveal that the corrosion rate was reduced sharply on adding EETfgS in the aggressive medium. Similarly, reduction in corrosion rate was observed on adding ion-additives in corro dent solution, indicating the inhibitive property of the ion-additives. The minimum corrosion rate was found in presence of EETfgS, when immersed for 48 h, indicating that the adsorptive tendency of the active constituents of the plant extracts. When coupons were immersed for long hours, due to the increase in dissolution / desorption of the adsorbed constituents, the corrosion rate was increased slightly. Whereas, keeping the coupons for longer period, again a decrease in corrosion rate was seen, which depicts the formation of an adsorbed film over the metal surface. Addition of halide and zinc ions as additives to the solution containing plant extract causes further reduction in the corrosion rate, clearly illustrating synergistic inhibition.
The maximum inhibition efficiency (88.95%) of EETfgS alone was observed at 48 h immersion period; which significantly rises on adding ion-additives, 95.79% for [Br¯ + EETfgS] and 98.95% for [Zn²⁺ + EETfgS]. This substantial rise in IE % shows the synergistic inhibition of EETfgS and ion-additives for AA6063.

The results have been very well analyzed and represented graphically (figures 1 – 3). The variation of mass loss (mg) as a function of immersion time period without and with inhibitors (plant extract /and ion-additives) has been illustrated in figure 1. It’s clear from the graph that in corrorent, a linear increase in weight loss with immersion period and a sharp decline in weight loss in the presence of inhibitor and ion-additives have been observed. The metal dissolution has been slowed down with the addition of inhibitors.

The variation of corrosion rate with immersion time has been depicted graphically by figure 2, which shows a decrease in corrosion rate with immersion time. This behavior could be attributed to the increase in adsorption of inhibitors over the metal surface. Figure 3 illustrates the inhibition efficiency of the inhibitors with immersion time (h). The graph is self explanatory that the addition of ion-additives along with EETfgS leads to a significant rise in the inhibition efficiency. The maximum IE (98.95%) was obtained for test with EETfgS + Zn²⁺ ions immersed for 48 h. This is further validated on the basis of Synergistic parameter (S) (table 2). It has been further observed that the synergistic effect also vary on addition of ions to EETfgS in the order Zn²⁺ > Br > Cl > I.

The protection action of the inhibitors is based on the adsorption ability of their active molecules; the resulting adsorbed film isolates the metal surface from the corrosive medium. Consequently, in inhibited solutions, the corrosion rate is indicative of the number of free corrosion sites left after some sites have been effectively blocked by inhibitor adsorption. It is generally accepted that the first step during the adsorption of an inhibitor molecule over the metal surface involves the replacement of one or more water molecules adsorbed over the metal surface.

\[
\text{Inh} \text{ (sol)} + x \text{H}_2\text{O} \leftrightarrow \text{Inh} \text{ (ads)} + x \text{H}_2\text{O} \text{ (sol)}
\]

The inhibitor may then combine with freshly generated Al³⁺ ions on the aluminium surface, forming metal – inhibitor complexes:

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \\
\text{Al}^{3+} + \text{Inh} \text{ (ads)} \rightarrow [\text{Al} - \text{Inh}]^{3+} \text{(ads)}
\]

The resulting complex could, depending on its relative solubility, either inhibit or catalyze further metal dissolution; hence the integrity depends on the capacity of the environment to dilute it. The adsorption of these inhibitors over the metal surface reduces the exposed surface area available for corrorent.

**The Synergism**

The synergistic parameter, S, was evaluated using the relationship given by Aramaki and Hackerman and reported elsewhere:

\[
S = \frac{1 - I_{A+B}}{1 - I_{A+B}'} = \frac{1 - I_A - I_B + I_AI_B}{(1 - I_{A+B}')} 
\]

Where, \(I_{A+B} = I_A + I_B\); \(I_A\) and \(I_B\) are the inhibition efficiencies of ion-additives and EETfgS respectively, when employed alone and \(I_{A+B} = \) the inhibition efficiency of co-employment of the two inhibitors.

From the value of S thus obtained following inferences can be drawn: if \(S > 1\): the two inhibitors act synergistically; if \(S < 1\): the two inhibitors act antagonistically; and if \(S=1\): there is no interaction between the inhibitor molecules.

The value of S for [EETfgS + ion-additives] has been evaluated and found to be more than unity (table 2), thereby two inhibitors act synergistically.

The mechanism of the synergism can be envisaged as the ion-additives get initially adsorbed over the metal surface; the active components of extracts then get adsorbed by the coulombic attraction over the metal surface where the ion-additives have already been adsorbed and thus suppressing the corrosion rate by the stabilization of the adsorbed ions and by the increase in surface coverage. Since the metal...
surface is positively charged in HCl medium, the extract’s constituents get adsorbed over aluminium\textsuperscript{34}. However, adsorption of ion-additives caused a decrease in the positive charge of Al due to formation of Al-ion surface bond, which produces a negative pole, facilitating the adsorption of the extract’s active constituents\textsuperscript{33}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Weight loss (mg) vs. immersion time (h).
\{for corroden (S0); with EETfgS (1.056g/L) (S1); with ion-additives (0.5 g/100 ml) (Cl\textsuperscript{−} S2 / Br\textsuperscript{−} S4 / I\textsuperscript{−} S6 and Zn\textsuperscript{2+} S8) and with [EETfgS + ion-additives] (S3, S5, S7, and S9)\}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Corrosion rate ($\rho_{corro}$) (mmy\textsuperscript{-1}) vs. immersion time (h)
\{for corroden (S0); with EETfgS (1.056g/L) (S1); with ion-additives (0.5 g/100 ml) (Cl\textsuperscript{−} S2 / Br\textsuperscript{−} S4 / I\textsuperscript{−} S6 and Zn\textsuperscript{2+} S8) and with [EETfgS + ion-additives] (S3, S5, S7, and S9)\}}
\end{figure}
Table-1: Corrosion parameters for corrosion of AA6063 in 0.5N HCl in absence and presence of EETfgS /and ion-additives at different immersion periods (h).

<table>
<thead>
<tr>
<th>Immersion period (h)</th>
<th>0.5 N HCl Test Solution without or with extract / ion-additives</th>
<th>Beaker label</th>
<th>Weight loss (mg)</th>
<th>Corrosion rate (ρ_corro) (mmy⁻¹)</th>
<th>IE (%)</th>
<th>Fractional surface coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Corrodent (blank)</td>
<td>S0</td>
<td>3.0</td>
<td>2.0117</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>EETfgS</td>
<td>S1</td>
<td>1.0</td>
<td>0.6706</td>
<td>66.67</td>
<td>0.6667</td>
</tr>
<tr>
<td></td>
<td>KI</td>
<td>S2</td>
<td>2.4</td>
<td>1.6093</td>
<td>20.00</td>
<td>0.2000</td>
</tr>
<tr>
<td></td>
<td>EETfgS+KI</td>
<td>S3</td>
<td>1.2</td>
<td>0.8047</td>
<td>60.00</td>
<td>0.6000</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>S4</td>
<td>2.0</td>
<td>1.3411</td>
<td>33.33</td>
<td>0.3333</td>
</tr>
<tr>
<td></td>
<td>EETfgS+KCl</td>
<td>S5</td>
<td>0.9</td>
<td>0.6053</td>
<td>70.00</td>
<td>0.7000</td>
</tr>
<tr>
<td></td>
<td>KBr</td>
<td>S6</td>
<td>1.5</td>
<td>1.0058</td>
<td>50.00</td>
<td>0.5000</td>
</tr>
<tr>
<td></td>
<td>EETfgS+KBr</td>
<td>S7</td>
<td>0.8</td>
<td>0.5364</td>
<td>73.33</td>
<td>0.7333</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>S8</td>
<td>1.4</td>
<td>0.9388</td>
<td>53.33</td>
<td>0.5333</td>
</tr>
<tr>
<td></td>
<td>EETfgS+ Zn²⁺</td>
<td>S9</td>
<td>0.5</td>
<td>0.3353</td>
<td>83.33</td>
<td>0.8333</td>
</tr>
<tr>
<td>6</td>
<td>Corrodent (blank)</td>
<td>S0</td>
<td>4.0</td>
<td>1.3411</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>EETfgS</td>
<td>S1</td>
<td>3.0</td>
<td>1.0058</td>
<td>25.00</td>
<td>0.2500</td>
</tr>
<tr>
<td></td>
<td>KI</td>
<td>S2</td>
<td>3.5</td>
<td>1.1735</td>
<td>12.50</td>
<td>0.1250</td>
</tr>
<tr>
<td></td>
<td>EETfgS+KI</td>
<td>S3</td>
<td>2.8</td>
<td>0.9388</td>
<td>30.00</td>
<td>0.3000</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>S4</td>
<td>3.5</td>
<td>1.1735</td>
<td>12.50</td>
<td>0.1250</td>
</tr>
<tr>
<td></td>
<td>EETfgS+KCl</td>
<td>S5</td>
<td>2.4</td>
<td>0.8047</td>
<td>31.43</td>
<td>0.3143</td>
</tr>
<tr>
<td></td>
<td>KBr</td>
<td>S6</td>
<td>2.7</td>
<td>0.9053</td>
<td>32.50</td>
<td>0.3250</td>
</tr>
<tr>
<td></td>
<td>EETfgS+KBr</td>
<td>S7</td>
<td>1.2</td>
<td>0.4023</td>
<td>70.00</td>
<td>0.7000</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺</td>
<td>S8</td>
<td>2.8</td>
<td>0.9388</td>
<td>30.00</td>
<td>0.3000</td>
</tr>
<tr>
<td></td>
<td>EETfgS+ Zn²⁺</td>
<td>S9</td>
<td>1.5</td>
<td>0.5029</td>
<td>62.50</td>
<td>0.6250</td>
</tr>
<tr>
<td></td>
<td>Corrodent (blank)</td>
<td>S0</td>
<td>5.0</td>
<td>0.8382</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig.-3: Inhibition efficiency Vs. immersion time (h) {with EETfgS (1.056g/L) (S1); with ion-additives (0.5 g/100 ml) (Cl⁻ S2 / Br⁻ S4 / I⁻ S6 and Zn²⁺ S8) and with [EETfgS + ion-additives] (S3, S5, S7, and S9)}
Table-2: Synergistic parameter (S) for [EE\textsubscript{Tfg}S + ion-additives] for AA6063 for various immersion periods (h) in 0.5 N HCl at room temperature.

<table>
<thead>
<tr>
<th>Immersion period (h)</th>
<th>EET\textsubscript{Tfg}S + Ion-additives</th>
<th>Synergistic Parameter (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>I\textsuperscript{-}</td>
<td>2.484</td>
</tr>
<tr>
<td></td>
<td>Cl\textsuperscript{-}</td>
<td>2.329</td>
</tr>
<tr>
<td></td>
<td>Br\textsuperscript{-}</td>
<td>2.438</td>
</tr>
<tr>
<td></td>
<td>Zn\textsuperscript{2+}</td>
<td>2.678</td>
</tr>
<tr>
<td>6</td>
<td>I\textsuperscript{-}</td>
<td>2.378</td>
</tr>
<tr>
<td></td>
<td>Cl\textsuperscript{-}</td>
<td>2.864</td>
</tr>
<tr>
<td></td>
<td>Br\textsuperscript{-}</td>
<td>2.595</td>
</tr>
<tr>
<td></td>
<td>Zn\textsuperscript{2+}</td>
<td>2.843</td>
</tr>
<tr>
<td>12</td>
<td>I\textsuperscript{-}</td>
<td>2.747</td>
</tr>
</tbody>
</table>
CONCLUSIONS

On analyzing the investigations on the inhibition efficiency of co-employment of the two inhibitors, EETfgS and ion-additives, following conclusions can be drawn:

1. The co-employment of the two inhibitors [EETfgS + ion-additives] produced promising results.
2. Inhibition efficiency (% IE) was seen synergistically increased on addition of ion-additives.
3. IE for EETfgS (88.95 %) was found to increase significantly on adding ion-additives, viz. $\Gamma^-$ (91.58 %); $\text{Cl}^-\text{Br}^-\text{Zn}^{2+}$ (95.79 %) and $\text{Zn}^{2+}$ (98.95 %).
4. Of all ion-additives, EETfgS when co-employed with $\text{Zn}^{2+}$ ions, show significant rise in inhibitory action for almost all immersion periods.
5. Distinctive synergism has been seen between the two inhibitors, EETfgS and ion-additives, with S values > unity.
6. The synergism vary on addition of ion-additives to EETfgS in the order $\text{Zn}^{2+} > \text{Br}^- > \text{Cl}^- > \text{I}^-$
7. These environmentally friendly inhibitors could find possible applications in metal surface anodizing and surface coating in industries.

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