Electrochemical Corrosion Behavior of Aluminum in Perchloric Acid

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ABSTRACT
The effects of acetate, citrate, benzoate, tetra-ethylammonium iodide (TEA) and 1,4,8,11 tetra-azacyclo-tetradecane (cyclam) on the corrosion behavior of aluminum in 1 M HClO₄ at 40°C were studied by potentiodynamic polarization technique. Acetate, citrate, and benzoate inhibited the corrosion of aluminum and shifted the breakdown potential to positive direction. Cyclam was investigated as a macrocyclic organic inhibitor to the acid corrosion of aluminum. The addition of cyclam to the corroding medium showed a pronounced effect on the anodic but not on the cathodic part of the polarization curve. The addition of TEA to the medium enhanced the corrosion rate and shifted the breakdown potential to more negative value as the concentration increased. The results were discussed on the basis of the adsorption mechanism and the nature of the adsorbed species.

Keywords: Metals; Electrochemical Techniques; Corrosion

1. Introduction
Corrosion and passivation of aluminum are a subject of tremendous technological importance due to the increased industrial applications of these materials [1,2]. The widespread use of aluminum arises from its different physical and chemical properties, namely, it has low specific gravity, good thermal and electrical conductivity and relatively low toxicity [3]. It also exhibits significant resistance to corrosion because of the rapid formation of a passive oxide film [4]. However, because of the general aggression of acid solutions, inhibitor is commonly used to reduce corrosive attack on metallic surface [5]. There are two types of inhibitors; passivators and pickling inhibitors. Passivators have the property of shifting the corrosion potential to more anodic values. Pickling inhibitors, in spite of leaving the corrosion potential virtually unaffected, cause a significant decrease in the corrosion rate [6]. A large number of investigations have been reported on adsorption of anions on aluminum corrosion and their inhibition or stimulation effects on aggressive acid media [7-13]. Recent study has been concerned with the effects of various inorganic additives, such as nitrate, nitrite, thiocyanate and chromate on the corrosion of aluminum in 1 M HClO₄ at 40°C [14]. In the present work, potentiodynamic polarization technique was used to study the effect of different organic additives vis., acetate, citrate, benzoate, tetraethyl ammonium iodide and cyclam on the electrochemical corrosion behavior of aluminum in 1 M HClO₄ at 40°C and their adsorption mechanism.

2. Experimental
Experiments were performed with highly pure aluminum (99.99%) specimens, in the form of rods, were cut to give an area 1.13 cm² and subsequently mechanically polished using emery paper up to 1200 grade. The specimens were then washed, degreased with acetone, dried and finally left to equilibrate for 5 min. at room temperature prior to testing. This procedure gave good reproducibility of results.

All solutions were prepared from Analar perchloric acid and doubly distilled water. Various organic additives namely: acetate, citrate, and benzoate and organic compounds 1,4,8,11-tetra-aza-cyclo-tetradecane (cyclam) and Tetra-ethyl-ammonium-iodide (TEA) were commercial laboratory grade reagents and were prepared without
further purification.

An ASTM [15,16] electrochemical cell containing a platinum coil counter electrode and a saturated calomel reference electrode inserted into a luggin capillary was used to conduct the tests. The working electrode was the specimens to be tested. Electrochemical corrosion tests were carried out in deaerated, unstirred solutions using purified nitrogen gas.

Before polarisation, the working electrode was introduced into the solution and left for 10 min at the open circuit potential. Polarization was then carried out at a rate of 0.03 Vmin⁻¹ using a Wenking potentiostat. Cathodic polarization was first carried out to ensure reduction of air formed native oxides and cleaning of the surface before shifting the potential towards more positive values. No corrections for IR drops were carried out since the Luggin probe tip was properly aligned to the electrode surface (1 - 3 mm). A constant temperature of 40°C (±0.5°C) was maintained using a thermostatically controlled water bath. The investigated compounds are shown in Figure 1.

3. Results and Discussion

3.1. Effect of Benzoate, Citrate and Acetate

Typical potentiodynamic polarization curves for aluminum in 1 M HClO₄ at 40°C in the presence and the absence of different concentration of benzoate ion is shown in Figure 2. As seen, addition of benzoate ions predominantly affects the anodic part of the polarization curves rather than the cathodic part of the curves. Inspection of the anodic part of the polarization curves reveals that it consists of three different regions. On passing from open circuit towards more anodic potentials an active region for dissolution of aluminum takes place, subsequent by a passive region where a nearly constant current density is observed, finally the transpassive region, where a sharp increase in the current density is noticed. The passive region demonstrates the growth of the passive oxide film.

Acetate and citrate ions gave similar behavior on the corrosion of aluminum in HClO₄ at 40°C. The effect of increasing citrate, benzoate, and acetate concentration on

![Figure 1. The investigation compounds.](image-url)
the breakdown potential $E_p$ and corrosion potential $E_{corr}$ as well as corrosion current density $i$, are given in Table 1. The selected data indicate that addition of citrate ions to perchloric acid solutions shifts $E_{corr}$ to significantly more anodic values. On the other hand, addition of Benzoate and acetate ions has a small influence on $E_{corr}$. The breakdown potential, at any given concentration, is found to be in the order acetate > benzoate > citrate. The corrosion current density obtained by Tafel extrapolation of the active region decreases for all tested anions with increasing the concentration inhibitor.

Figure 3 shows the protection efficiency $\%P$ vs. the logarithmic concentration of citrate, benzoate, and acetate. $\%P$ were estimated using the equation

$$\%P = \left[1 - \left(\frac{i}{i_o}\right)\right] \times 100$$

where, $i$, and $i_o$ is the corrosion current density in the absence and the presence of additives, respectively.

All the plots have S-shaped adsorption isotherm. This suggests that these anions inhibit the acid dissolution by adsorption at the aluminum—acid solution interface. Inspection of this figure shows that citrate has the highest inhibition efficiency, while acetate has the lowest one. Similar observation is obtained by Scully and Rude [17] for the corrosion of aluminum in 0.08 M NaCl at pH 8.

<table>
<thead>
<tr>
<th>Additives</th>
<th>[C], mol/L</th>
<th>$E_{corr}$, V</th>
<th>$i$, $\mu$A/cm$^2$</th>
<th>$E_p$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-0.00</td>
<td>-0.712</td>
<td>66</td>
<td>-0.460</td>
</tr>
<tr>
<td></td>
<td>0.010</td>
<td>-0.578</td>
<td>16.1</td>
<td>-0.418</td>
</tr>
<tr>
<td>Citrate</td>
<td>0.050</td>
<td>-0.656</td>
<td>12.1</td>
<td>-0.405</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>-0.640</td>
<td>8.5</td>
<td>-0.393</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>-0.685</td>
<td>45.3</td>
<td>-0.438</td>
</tr>
<tr>
<td>Benzoate</td>
<td>0.03</td>
<td>-0.665</td>
<td>24.5</td>
<td>-0.415</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>-0.650</td>
<td>19.1</td>
<td>-0.396</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>-0.684</td>
<td>46.7</td>
<td>-0.450</td>
</tr>
<tr>
<td>Acetate</td>
<td>0.030</td>
<td>-0.669</td>
<td>34.7</td>
<td>-0.425</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>-0.666</td>
<td>26.7</td>
<td>-0.420</td>
</tr>
</tbody>
</table>

Figure 4 shows the variation of pitting potential $E_{pit}$ with the logarithm of the concentration of the three organic anions. Inspection of this figure indicates that the pitting potential shifted to the positive direction as the concentration of the three organic anions increased. Therefore, it could be concluded that the efficiency of
Figure 3. Relationship between inhibition efficiency and logarithm of concentrations of citrate, benzoate and acetate.

Figure 4. Relationship between $E_p$ and logarithm of concentrations of citrate, benzoate and acetate.
retarding pitting corrosion of aluminum in 1 M HClO₄ is ordered in the sequence citrate > benzoate > acetate.

These results are interpreted as due to structure effect, where the higher efficiency of the first inhibitor citrate is interpreted as due to the presence of three carboxylic groups (−COO⁻) which increase the adsorption on the surface of the aluminum metal in 1 M HClO₄. On the other hand, Benzoate more efficient than acetate is interpreted as due to the presence of phenyl group attached to the carboxylic group (−COO⁻), leading to increase of the electron density and then increase the adsorption on the aluminum metal [18].

Compounds containing the carboxylic groups may be considered to have affected the surface of the specimens in two ways: a) by adsorption and subsequent formation of stable surface complexes and b) by blocking of the active sites for the dissolution of the oxide layers [19].

**Adsorption Isotherms**

To clarify the nature of adsorption, theoretical fitting of different isotherms, Langmuir, Frumkin, Flory-Huggins and the kinetic-thermodynamic model are tested.

The degree of surface coverage of the metal surface by an adsorbed anion is calculated using the equation

\[
\theta = 1 - \left(\frac{1}{i_n}\right)
\]

The adsorption of an organic inhibitor adsorbed on the surface of a metal is regarded as a substitution adsorption process between the organic compound in the aqueous phase, Org[ (aq)], and the water molecule adsorbed on the electrode surface H₂O(ₘ) [20]

\[
\text{Org}^{−}_{(aq)} + x \text{H}_2\text{O}^{−}_{(s)} = \text{Org}_{(s)} + x \text{H}_2\text{O}^{−}_{(aq)}
\]

where, \(x\) is the size ratio which is the number of water molecules replaced by one molecule of an organic adsorbate.

The Langmuir isotherm is given by [21]:

\[
\frac{\theta}{(1-\theta)} = K[C]
\]

where \(K\) is the binding constant representing the interaction of the additives with metal surface and \(C\) is the concentration of the additives.

Frumkin isotherm is given by [22]:

\[
\frac{\theta}{(1-\theta)} \exp^{-2\alpha\theta} = K[C]
\]

where, \(\alpha\) is a molecular interaction parameter depending on the molecular interaction in the adsorption layer and on the degree of heterogeneity of the surface. It can have both positive and negative values and is a measure of steepness of the adsorption isotherm. The more positive value of, \(\alpha\), increase the steepness of the adsorption isotherm. This has been interpreted [23] to imply that the interaction between molecules with positive, \(\alpha\), value causes an increase in the adsorption energy with increase of \(\theta\).

Flory-Huggins isotherm is given by [24]:

\[
\theta \left[ x(1-\theta)^{\alpha} \right] = K[C]
\]

where \(x\) is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

And the kinetic-thermodynamic model is given by [25]:

\[
\log \left[ x(1-\theta)^{\alpha} \right] = \log K' + y \log C
\]

where, \(y\) is the number of inhibitor molecules occupying one active site. The binding constant \(K\) is given by

\[
K = K'^{e(1/y)}
\]

Since, \(1/y\) is the number of active sites occupied by one single inhibitor molecule.

**Figures 5 and 6** show Langmuir and Frumkin isotherms. It is clear that, Langmuir and Frumkin isotherms are not applicable to fit the data of citrate anion indicative that there might be non-ideal behavior in the adsorption processes of this anion on the aluminum surface at 40°C. **Figure 7** displays the curves fitting of the corrosion data of aluminum to the Flory-Huggins isotherm. The results show that the isotherm is applicable to fit only the data of citrate anion. The size parameter \(x\) for citrate indicates that the bulky citrate ion molecule could replace two molecules of water at the surface of aluminum. **Figure 8** shows curve fitting of the corrosion data of the three anions citrate, benzoate and acetate to the kinetic-thermodynamic model. The three organic anions show a reasonable fit is obtained to the kinetic-thermodynamic model. The number of active sites occupied by one single inhibitor molecule \((1/y)\) and binding constant, \(K\), were calculated and collected in **Table 2**.

As the binding constant, \(K\), being function on of the nature of the inhibitor, The extremely high value of \(K\) of citrate ion could be explained on the basis of the mechanism that suggest adsorption of the citrate ions on the surface of the native film acting as a film forming species decreasing the active area available for ClO₄⁻ attack. The lower binding constant values of \(K\) for benzoate and acetate with respect to that of citrate is predictable since citrate anion contain more active centers than benzoate and acetate. Benzoate has an observed slight higher \(K\) value than acetate, this may be benzoate could acts as blocking inhibitor by forming insoluble precipitates [17], in addition, phenyl ring in benzoate anion could bound to the metal by means of π-π bond resulting from overlap of π electrons bond in the benzene ring and d-orbital in the metal.
Figure 5. Langmuir adsorption isotherm for the citrate, benzoate and acetate.

Figure 6. Frumkine adsorption isotherm for citrate, benzoate and acetate.
Figure 7. Flory Huggins adsorption isotherm for citrate, benzoate and acetate.

Figure 8. Kinetics model adsorption isotherm for citrate, benzoate and acetate.
3.2. Effect of Cyclam

1,4,8,11 tetra-azacyclo-tetradecane (cyclam) was investigated as organic inhibitor to the acid corrosion of aluminum. Figure 9 represents the potentiodynamic polarization curves of aluminum in 1 M HClO₄ at 40°C in the absence and presence of different concentrations of cyclam. Inspection of this figure shows that the addition of cyclam to the corroding medium (1.0 M HClO₄) has a pronounced effect on the anodic but not on the cathodic part of the polarization curve.

The electrochemical corrosion parameters obtained from these curves are given in Table 3. The data show that the corrosion current density decreases as the concentration of cyclam increases. It clears that the presence of cyclam retards the corrosion of aluminum.

Figure 10 shows the variation of the inhibition efficiency % P with the logarithm of the cyclam concentration. The curve has the characteristics of S-shaped adsorption isotherm indicative of an adsorption mechanism for the inhibition process.

Figure 11 shows the relationship between pitting potential $E_p$ and logarithm of concentration of cyclam. This indicates that the pitting potential $E_p$ appreciably increases as the concentration of cyclam increases.

Adsorption Isotherms Analysis of Cyclam

The experimental corrosion data of 1,4,8,11-tetraazacyclotetradecan (cyclam) to various adsorption isotherm:

Table 2. Curve-fitting data of the adsorption isotherm of citrate, benzoate and acetate.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Langmuir</th>
<th>Flory-Huggins</th>
<th>Kinetic-Thermodynamic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K$</td>
<td>$x$</td>
<td>$K$</td>
</tr>
<tr>
<td>Citrate</td>
<td>-</td>
<td>2.37</td>
<td>990</td>
</tr>
<tr>
<td>Benzoate</td>
<td>49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetate</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical parameters of aluminum in perchloric acid in absence and presence of different concentrations of cyclam.

<table>
<thead>
<tr>
<th>[I] mole/L</th>
<th>$E_{corr}$ V</th>
<th>$I$ μA/cm²</th>
<th>$E_p$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.712</td>
<td>66.0</td>
<td>0.46</td>
</tr>
<tr>
<td>0.003</td>
<td>0.709</td>
<td>39.8</td>
<td>0.456</td>
</tr>
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<td>0.005</td>
<td>0.707</td>
<td>35.5</td>
<td>0.452</td>
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<tr>
<td>0.007</td>
<td>0.702</td>
<td>28.0</td>
<td>0.445</td>
</tr>
<tr>
<td>0.01</td>
<td>0.701</td>
<td>19.0</td>
<td>0.439</td>
</tr>
<tr>
<td>0.02</td>
<td>0.700</td>
<td>17.8</td>
<td>0.431</td>
</tr>
<tr>
<td>0.03</td>
<td>0.700</td>
<td>15.8</td>
<td>0.422</td>
</tr>
</tbody>
</table>

Langmuir, Frumkin and Flory-Huggins are studying the theoretical curves yields several significant findings:

Langmuir and Frumkin isotherms are failed to fit the experimental data of the cyclam, indicative that there might be non-ideal behavior in the adsorption process of cyclam molecules on the aluminum surface. The results show a fairly good agreement between the kinetic model and Flory-Huggins isotherms. The size parameter $x$ or the number of surface water molecule replaced by a single inhibitor molecules, the number of active sites $1/y$ occupied by one single inhibitor molecule and binding constant $K$ were calculated and collected in Table 4. The fractional values of the active sites was discussed according to a physical interpretation in which an adsorbed molecule may make it more or less difficult for another molecule to get adsorbed on a neighboring site (steric effect), and a chemical interpretation in which a change in the geometry of the macrocyclic ligand from planar arrangement to folded geometry (structure effect) is also possible [23,25].

3.3. Effect of Tetraethylammonium Iodide

The potentiodynamic polarization curves of aluminum in 1 M HClO₄ in the absence and presence of different TEA concentrations, Figure 12, reveals that addition of TEA affects both cathodic and anodic part of the polarization curves but with different degrees. The data presented in Table 5 clarify that the addition of TEA enhances the corrosion current density of aluminum and $E_{corr}$ was slightly shift to negative value as the corrosion of TEA increased. This increase is attributed to the presence of tetra ethyl ammonium moiety rather than iodide ions since in a previous study [14] the iodide ion did not show any significant effect and did not alter the shape of the blank curve.

Figure 13 shows the relation between breakdown potential $E_p$ and logarithm of TEA concentration. The breakdown potential shifted to more negative value as the concentration increased. The accelerating effect of TEA could be discussed on the basis of the-corrosion characteristics of aluminum that depends on the presence of the protective oxide layer (Al₂O₃). From this point of view, It was proposed that, to cause acceleration for the corrosion process, an aggressive anion must 1) adsorb at the oxide film—solution interface, 2) penetrate or dissolve through the oxide film and 3) react locally with the
Figure 9. Potentiodynamic polarization curves of aluminum metal in 1.0 M HClO₄ containing different concentrations of cyclam.

Figure 10. Relationship between inhibition efficiency and logarithm of concentration of cyclam.
Figure 11. Relationship between $E_p$ and logarithm of concentrations of cyclam.

Figure 12. Potentiodynamic polarization curves of aluminum metal in 1.0 M $\text{HClO}_4$ containing different concentrations of TEA.
4. Conclusions

1) Citrate, benzoate, and acetate anions affect the breakdown potential and the corrosion current density of aluminum in perchloric acid. The breakdown potential was found to be in the order acetate $>$ benzoate $>$ citrate. Citrate has the highest inhibition efficiency, while acetate has the lowest one.

2) Citrate anion contains multi-active centers. It was adsorbed on the metal surface acting as a film forming species decreasing the active area available for $\text{ClO}_4^-$ attack, whereas benzoate inhibits the corrosion by forming insoluble precipitates. The phenyl rings in benzoate anion that could bind to the metal by means of $\pi$-$d$ bond.

3) The macrocyclic organic molecule, cyclam, retards the corrosion of aluminum. The fractional value of the active sites occupied by a single molecule was explained on the basis of steric and structure effect.

4) The enhancement of the corrosion rate of aluminum in presence of TEA is attributed to the presence of tetraethylammonium moiety rather than iodide ions. Tetraethylammonium increases the solubility of the oxide underlying metal [9]. Therefore, the enhancement of the corrosion rates of the aluminum metal. This behavior can be discussed on the basis that the greater solubility of the oxide film in this medium. This effect may be due to the fact that the polarity of this compound help in the breakage of the water aggregates adsorbed on the alumina $\text{Al}_2\text{O}_3$ making it more susceptible to acid attack.

<table>
<thead>
<tr>
<th>[I] mole/L</th>
<th>$-E_{corr}$ V</th>
<th>$I_{corr}$ $\mu$A/cm$^2$</th>
<th>$-E_p$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
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<td>0.460</td>
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<td>0.005</td>
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<td>0.465</td>
</tr>
<tr>
<td>0.010</td>
<td>0.720</td>
<td>69.0</td>
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</tr>
<tr>
<td>0.030</td>
<td>0.721</td>
<td>71.0</td>
<td>0.476</td>
</tr>
<tr>
<td>0.050</td>
<td>0.726</td>
<td>78.0</td>
<td>0.482</td>
</tr>
<tr>
<td>0.070</td>
<td>0.730</td>
<td>83.0</td>
<td>0.486</td>
</tr>
<tr>
<td>0.100</td>
<td>0.732</td>
<td>83.0</td>
<td>0.494</td>
</tr>
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</table>
layer and makes aluminum metal more susceptible to acid attack.

REFERENCES


