Corrosion Behavior of Aluminum Electrode in Absence and in Presence of Sodium Chloride at Different pH Solutions using Toludine as Inhibitor

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Abstract: The electrochemical behavior and the corrosion rate of aluminum electrode have been evaluated in different pH solutions in absence and presence of aggressive anion, using open-circuit potential measurements and potentiodynamic polarization technique. Also, the corrosion inhibiting effects of ortho, meta and para toludine in a solution of pH4 containing 0.1M sodium chloride was investigated using potentiodynamic polarization measurements. [Journal of American Science 2010;6(8):476-486]. (ISSN: 1545-1003).

Keywords: corrosion; aluminum electrode; pH; anion; sodium chloride; potentiodynamic polarization

1. Introduction

Aluminum and aluminum alloys represent an important category of materials due to their high technological value and wide range of industrial applications especially in aerospace and household industries. The use of these materials in light weight installation is widespread. Aluminum and its alloys, however, are reactive materials and prone to corrosion. Passivation and activation can occur depending on the potential, the pH and the Cl\(^{-}\) concentration. Rather than the potential for pitting initiation, the pitting potential of aluminum appears to be the point at which the passivation phenomena become very low\(^{[1,2]}\).

The variation of OCP of aluminum with time of immersion in NaCl solution has been also studied\(^{[3,4]}\). The electrochemical behavior of aluminum and some of its alloys was investigated\(^{[5]}\) in buffer solution of different pH. The inhibition of corrosion of these materials using inorganic passivators like sulphates, molybdates was discussed showing that inhibition efficiency is independent on the concentration of the passivating anion in the solution. The corrosion and passivation behavior of aluminum in alkaline solution in pH range from 2-11 has attracted the attention of many investigators\(^{[6-10]}\). Results indicated that increasing pH changing the cathodic reaction, and increasing Cl\(^{-}\) ion concentration decreased the cathodic reaction rate. On the other hand, the anodic reaction rate increased with increase in Cl\(^{-}\) concentration. The open circuit corrosion potential and the pitting potential shifted in the active (negative) direction with increasing pH and Cl\(^{-}\) ion concentration. The electrochemical and surface properties of Al in citric acid solutions of pH2-8 by OCP, potentiodynamic polarization and potentiostatic current-time transient measurements were investigated\(^{[11]}\). The corrosion kinetic parameters E\(_{\text{corr}}\), I\(_{\text{corr}}\) and \(b_a\) suggest that surface processes are involved in the dissolution kinetics, especially in the pH range 3-6. Corrosion inhibition of Al in HCl solution was investigated in the presence of different concentration of tetrazole derivative. The adsorption of these compounds on the Al surface obeys a langmuir adsorption isotherm and has a mixed physisorption and chemisorption mechanism\(^{[12]}\). The aim of the present work is to study the electrochemical behavior of aluminum metal in different pH of aggressive NaCl solution and also to study the inhibitive effect of adding o, m and p toludine with different percent.

2. Experimental

The aluminum sample selected for the study was of high purity (99.99 %). Prior to each electrochemical experiment, the electrode surface was polished with emery paper [from 400-1200 grade], degreased with acetone and finally rinsed with doubly distilled water. For the OCP against time measurements, pH-meter-millivoltameter type WGPYE model 290 was used. Electrochemical polarization measurements were made using EG&G PARC model 350A corrosion measurement system, in all measurements the reference electrode was a saturated calomel electrode (SCE). The exposed area of the working electrode was 1cm\(^2\).Two carbon electrodes were used as counter electrodes. The experiments were carried out in different pH using buffer acetic and sodium acetate in acid medium and buffer boric acid and sodium borate in alkaline medium, free and containing NaCl with concentration ranging between 0.01M and 0.5 M. The effect of toludine as inhibitor was studied using different percent of o, p and m toludine.
3. Results and Discussion:

III.1-OCP measurements:

The aluminum electrode was immersed in aerated different pH solutions at 30°C and the variation of OCP was followed as a function of time till attainment of the steady state value (Ecorr). Two main trends can be seen for the variation of OCP with time. The first one includes solutions of pH 2-7 (some representative examples are given in Fig.1). The second trend is related to solutions of pH 8 and 9. In Fig.1 some representative examples of OCP-time curves, which illustrate both types of behavior are shown. These results indicate a significant change of the surface oxide film during the immersion time. In this respect a similar behavior were reported for aluminum electrode in acetate solutions and in mixtures of acetate and oxalate solutions for Al- 7075 alloy in oxalate solutions and for Al-3003 and Al-5052 alloys in citrate and acetate buffer solutions. On the other hand the marked increase in the OCP with decrease of pH denotes an ongoing surface oxide film growth and aging of the aluminum oxide film, therefore in solutions of pH4 and pH5 the very slow reaching of steady-state potential of aluminum electrode means that beside the electrochemical process, surface coordination processes also play an important role.

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} &= \text{AlOH}_2^+ + \text{H}^+ \\
\text{Al}^{3+} + 2\text{H}_2\text{O} &= \text{Al(OH)}_3^+ + 2\text{H}^+ \\
\text{Al}^{3+} + 3\text{H}_2\text{O} &= \text{Al(OH)}_3 + 3\text{H}^+
\end{align*}
\]

The second shape of potential-time curves observed in the solutions of pH8 and pH9 is quite different from those recorded in solutions of pH4 and pH5. It is clear from Fig.1 that the potential of aluminum electrode decreases in a relatively short time and reaching a steady-state value after about one hour from the moment of immersion. This behavior indicates the instability of the pre-immersion air-formed aluminum oxide film on the metal surface.

3.2- Potentiodynamic polarization measurements:

Fig.2 show some examples of the potentiodynamic polarization curves performed on aluminum electrode in different pH solutions at 30°C with a scan rate of 0.5 mV/sec starting from -0.250 V with respect to SCE (in the so called Tafel region).

All the potentiodynamic polarization curves have similar shapes. The corrosion kinetic parameters Ecorr, icorr, b\text{a} and b\text{c} determined from polarization curves in the Tafel region are summarized in Table (1).

The cathodic reaction occurring at the Al-oxide/acetate solution interface was hydrogen evolution. Table (1) shows that the cathodic slopes (b\text{c}) are much greater than that expected for H\text{2} evolution according to Volmer-Tafel mechanism (-118 mV (decade)) at 30°C. Such large cathodic Tafel slopes are not unexpected for aluminum, and have previously been reported for H\text{2} evolution reaction on Al oxide-covered electrodes. The presence of the oxide film can markedly influenced the surface reduction process, by affecting the energetics of the reaction at the double layer, or by imposing a barrier to change transfer through the oxide film, or both.

The anodic Tafel slopes (b\text{a}) are much greater than the expected 40 mV (decade) for the uniform anodic dissolution of aluminum via hydrated Al\text{3+} ions. The observed (b\text{a}) values are in agreement with the b\text{a} values reported for an Al oxide-covered electrode, which clearly indicates the presence and growth of a passive oxide film. However the b\text{a} is greater than those for the simple aluminum dissolution mechanism (Al -> Al\text{3+} + 3e), it can also be attributed to the precipitation of some side reactions (e.g., surface coordination reactions) in anodic oxide film growth.

<table>
<thead>
<tr>
<th>pH</th>
<th>Ecorr (V)</th>
<th>icorr (A/cm²)</th>
<th>b\text{a} (mV)</th>
<th>b\text{c} (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.415</td>
<td>1.75</td>
<td>190</td>
<td>137</td>
</tr>
<tr>
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</tr>
<tr>
<td>4</td>
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<td>144</td>
</tr>
<tr>
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<td>2.15</td>
<td>173</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>-0.562</td>
<td>2.23</td>
<td>170</td>
<td>153</td>
</tr>
<tr>
<td>7</td>
<td>-0.620</td>
<td>2.35</td>
<td>156</td>
<td>162</td>
</tr>
<tr>
<td>8</td>
<td>-0.720</td>
<td>4.24</td>
<td>146</td>
<td>173</td>
</tr>
<tr>
<td>9</td>
<td>-0.828</td>
<td>6.40</td>
<td>140</td>
<td>187</td>
</tr>
</tbody>
</table>

3.3- Effect of solution pH on corrosion potential and corrosion current:

It is evident from Fig.3 that the values of corrosion potential (Ecorr) of aluminum electrodes decreases with increase in pH. On the Ecorr vs pH curve three different regions were distinguished. The first are corresponds to the pH range 2-3 in which Ecorr changed relatively slowly towards more negative values. It is apparent therefore, that at this range of pH the concentration of the H\text{2} ions is sufficiently high and oxygen is eliminated from solutions, the dissolution of aluminum is under the control of electrochemical processes. This means that the main cathodic reaction is a reduction of H\text{2} ions whereas
The main anodic reaction is the dissolution of aluminum in the form of Al^{3+} aqueous complexes. The second region extending from pH3 to pH6, where $E_{corr}$ changes approximately linearly with pH, and the slope of $E_{corr}$ against pH curve was 59.66 mV/unit pH. This behavior can be explained as follows: In aqueous solutions Al- oxide surface is significantly hydrated. The hydration of aluminum-oxygen bonds on the oxide film leads to the formation of surface-OH groups. Subsequent amphoteric dissociation of -OH groups leads to the development of a charge on the oxide surface [19]. Therefore, an acid-base equilibrium is established on the surface which controls the surface charge and the surface processes on an oxide covered Al-electrode. $E_{corr}$ against pH behavior in the pH region 6-9 was characterized by a strong negative shift of $E_{corr}$ with increase in pH. At the same time, the corrosion current density $i_{corr}$ increased significantly with increase in pH Fig. [3], especially in solution of pH8. Thus the dissolution of aluminum increases significantly from pH7 to pH9. Such behavior is in agreement with the fact that aluminum dissolves relatively strongly at these pH values as aluminate AlO_2^- or Al(OH)_4^- ions [23]. It is seems that the electrochemical corrosion mechanism (evolution of hydrogen, dissolution of aluminum as aluminate ion) proceeds in this pH range, especially at pH8 and pH9.

### 3.4- Influence of chloride ion concentration at different pH solutions:

The variation of the OCP with time of immersion for aluminum electrode at various pH (4 and 5 (acetic acid + sodium acetate and pH 8 and 9 (boric acid and sodium borate solutions) solutions containing (0.01 M – 0.5 M) sodium chloride at 30C are shown in Fig.4(a-d). In each experiment the potential was followed at intervals for 4 hours. The steady-state potential ($E_{st}$) obtained were plotted against the logarithm of the molar chloride concentration at different pH solutions, and are represented in Fig.5.

As evident from Figs.4(a,b) the OCP values were changed rapidly at the beginning towards positive potential then reached stationary potential after about one hour in absence of Cl^- ion, but in presence of different chloride concentrations the OCP values were changed toward negative potential and reached steady-state value after about half an hour and the same behavior is observed in pH8 and pH9 as shown in Figs.4(c,d).

Fig.5 shows the effect of variation of salt concentration on steady-state potential of aluminium electrode at different pH solutions. The OCP is shifted in the negative direction with increase in pH and chloride ion concentration. The shift in the OCP towards more negative values is attributed to the adsorption of negative chloride ion on the surface of the metal [20], (the adsorption of ions on the metal surface is responsible for change in its potential).

Fig.6(a-d) show potentiodynamic polarization curves for aluminum electrode in various pH 4, 5, 8 and 9 solutions free and containing various chloride ion concentrations. The behavior of aluminum in chloride containing solution of pH4 and pH5 is different from those recorded at pH8 and pH9.

In case of pH4 and pH5 free and containing different chloride ion concentrations we observed the absence of pitting potential due to the presence of acetic acid which resists the pitting corrosion [21].

In case of pH8 and pH9 in absence of chloride ions there is no pitting potential because the presence of OH^- ions dissolved aluminum metal, but in the presence of chloride ions the curves exhibit an apparent active region with passivity at intermediate value of potential and pitting at and beyond the pitting potential due to the presence of chloride ions.

The values of the corrosion potential ($E_{corr}$), anodic Tafel slope, ($b_a$), cathodic Tafel slope ($b_c$) are given in Table (2), (3) and (4) respectively.

### Table (2): Effect of various chloride concentrations on the corrosion potential of aluminum in different pH solutions.

<table>
<thead>
<tr>
<th>Conc. of NaCl (M)</th>
<th>Corrosion Potential, $E_{corr}$, (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetic acid + sodium acetate</td>
</tr>
<tr>
<td></td>
<td>pH4</td>
</tr>
<tr>
<td>0</td>
<td>-0.515</td>
</tr>
<tr>
<td>0.01</td>
<td>-0.535</td>
</tr>
<tr>
<td>0.05</td>
<td>-0.598</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.628</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.690</td>
</tr>
</tbody>
</table>

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Table (3): Effect of various chloride concentrations on the anodic Tafel slope of aluminum in different pH solutions

<table>
<thead>
<tr>
<th>Conc. of NaCl (M)</th>
<th>Anodic Tafel Slope ( b_a ) (mV)</th>
<th>Acetic acid+ sodium acetate</th>
<th>Boric acid +sodium borate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH4</td>
<td>pH5</td>
<td>pH8</td>
</tr>
<tr>
<td>0</td>
<td>143</td>
<td>150</td>
<td>173</td>
</tr>
<tr>
<td>0.01</td>
<td>140</td>
<td>154</td>
<td>170</td>
</tr>
<tr>
<td>0.05</td>
<td>142</td>
<td>152</td>
<td>166</td>
</tr>
<tr>
<td>0.1</td>
<td>148</td>
<td>150</td>
<td>160</td>
</tr>
<tr>
<td>0.5</td>
<td>146</td>
<td>156</td>
<td>165</td>
</tr>
</tbody>
</table>

Table (4): Effect of various chloride concentrations on the cathodic Tafel slope of aluminum in different pH solutions

<table>
<thead>
<tr>
<th>Conc. of NaCl (M)</th>
<th>Cathodic Tafel Slope ( b_c ) (mV)</th>
<th>Acetic acid+ sodium acetate</th>
<th>Boric acid +sodium borate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH4</td>
<td>pH5</td>
<td>pH8</td>
</tr>
<tr>
<td>0</td>
<td>-190</td>
<td>-180</td>
<td>-165</td>
</tr>
<tr>
<td>0.01</td>
<td>-195</td>
<td>-175</td>
<td>-160</td>
</tr>
<tr>
<td>0.05</td>
<td>-201</td>
<td>-170</td>
<td>-164</td>
</tr>
<tr>
<td>0.1</td>
<td>-204</td>
<td>-182</td>
<td>-168</td>
</tr>
<tr>
<td>0.5</td>
<td>-205</td>
<td>-187</td>
<td>-160</td>
</tr>
</tbody>
</table>

Increase in pH from 4 to 9 and/or chloride ion concentration shifted \( E_{corr} \) in the active direction. This shift is a result of the shift in the cathodic curve as hydrogen ion concentration decreases. Increase in pH of the solution changed the slope of the cathodic curve. This change is attributed to the change in the cathodic reaction at different pH levels. Increase in chloride ion concentration decreased the cathodic reaction rate, but the slope of the curve remained almost the same.

At pH 8 and pH 9 the increase in chloride ion concentration shifted the passive region of the anodic curve to higher current density. The height of the passive region also varied with pH but was not affected by increasing in chloride concentration (e.g. for pH8 passive region extends for about \(-0.102\) mV, corresponding value for pH9 is \(-0.212\) mV). Also, the increase in chloride concentration shifted \( E_{pit} \) to more negative values.

The passive region observed in all cases is attributed to the formation of a thin oxide film on the surface of the metal which causes the metal to stop interaction with the surrounding media\(^{[21]}\).

Fig. 7 shows the plot of corrosion rate (MPY), calculated using \( I_{corr} \) values obtained from polarization curves, against the logarithm of molar chloride concentration at different pH. At all pH values the corrosion rate increase with increasing chloride ion concentration and it was found to be significance at pH9.

The increase in corrosion rate with increasing chloride ion concentration is due to the participation of this ion in the metal dissolution reaction. This kind of mechanism has been predicted by\(^{[22-24]}\).

The corrosion rate was found to be enhanced at acidic pH values; this result was in agreement with the enhanced solubility of aluminum oxide at low pH values.

At pH 9 the oxide film is highly soluble and this leads to a higher corrosion rate, the dissolution equilibrium is governed by the equation:

\[
Al^{+3} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+ \\
Al(OH)_4^- . 2H_2O \rightleftharpoons AlO_2^- + 3e^{-}
\]

The results obtained for increasing amount of sodium chloride in aqueous solution were also consistent with the suggestion that the chloride ions are responsible for the attack and subsequent dissolution of the oxide layer. Thus the rate of corrosion increases rapidly with increasing chloride concentration in solution. This is attributed to the adsorption of chloride to weak parts of the oxide film leads to the formation of film / solution interface of transitional chloride ion containing complex by the reaction

\[
Al + nCl^- \rightleftharpoons AlCl(n-3)^- + 3e^{-}
\]

These complexes are much more soluble than the complex formed in the absence of chloride.
ion. The dissolution of the complex leads to the breakdown of passivity and hence pitting.

3.5-Toludine as Inhibitor for Acidic Chloride Corrosion of Aluminum.

Examples of potentiodynamic polarization curves for aluminum in a solution of pH4 containing 0.1 M sodium chloride without and with various para-toludine concentrations are shown in Fig.8. Ortho and meta toludine show similar behavior as para toludine. In all cases, addition of toludine induced a negligible decrease in the anodic current and a significant decrease in the cathodic current. The observed decrease in the cathodic current was the greatest for 0.1% m-toludine. The value of \( E_{\text{corr}} \) was not significantly affected by the addition of inhibitors. None of the inhibitors affected the anodic Tafel slope which was around 64 mV. The cathodic Tafel slope of approximately \( 190 \text{ - 197mV} \) was observed in presence and in absence of inhibitors i.e is independent of inhibitor concentration Table (5). This fact can be classified the inhibitor as cathodic inhibitor.

Table (5) contains the values, corrosion potential \( (E_{\text{corr}}) \) cathodic Tafel slope \( (b_c) \) corrosion \( (i_{\text{corr}}) \) and exchange \( (i_e) \) current densities, percentage decreases in each, polarization resistance \( (R_p) \), degree of surface coverage \( (\theta) \) and the percentage inhibition \( (P) \) as a function of inhibitors concentrations. The percentage decreases in the exchange current density equals that in the corrosion current density within the limits of experimental error.

The cathodic Tafel slopes \( (b_c) \) were above 180 mV, this indicate that hydrogen evolution reaction takes place at the metal covered by a surface layer, probably an oxide or an oxide-inhibitor complex, which acts as a potential energy barrier to the charge carriers\[^{[18,25]}\]. Polarization resistances, \( R_p \), for aluminum in a solution of pH4 containing 0.1 M sodium chloride free and in the presence of different toludine (o, m, and p) at various concentrations were determined. Generally \( R_p \) values increased with increasing inhibitor concentration and were greatest in 0.1% m-toludine. A comparison of the inhibiting efficiencies and corrosion rate obtained using the polarization technique shows that \((\text{NH}_2)\) group in meta position is much more effective than in the para and ortho position.

Fig.9a shows the plot of corrosion rate (MPY), calculated using \( i_{\text{corr}} \) values obtained from polarization curves, of aluminum electrode versus the logarithm of different toludine ( o, m and p ) of various concentrations in a solution of pH4 containing 0.1M sodium chloride. The corrosion rate decreases as the inhibitors concentrations increases and the corrosion rate follows the sequence ortho > para > meta. The efficiency of a certain corrosion inhibitor is measured by the percentage inhibition \((P\%)\)^{[26]}.

\[
P = 100 \left( 1 - \frac{W_2}{W_1} \right)
\]

Where \( W_1, W_2 \) are the corrosion rates in absence and presence of inhibitor, respectively. Fig.9b shows a plot of percentage protection \( P \) versus the logarithm of different concentrations of various toludine in a solution of pH4 containing 0.1 M sodium chloride. It is seen that the percentage protection increase with increasing inhibitor concentration approaching 88% in case of meta, 86% in case of para and 83% in case of ortho. This is may be due to the adsorption of a complete monolayer of toludine on the surface. The degree of surface coverage \( \theta \) was calculated from the shift in the cathodic Tafel lines caused by the presence of inhibitors. For inhibitors which causes a parallel shift of the cathodic Tafel line, a comparison can be made at constant potential thus,

\[
\begin{align*}
E &= a_1 - b \log (i_{\text{c1}}) \quad \text{Without inhibitor} \\
E &= a_2 - b \log (i_{\text{c2}}) \quad \text{With inhibitor} \\
\text{and} \quad (i_{\text{c2}}) &= (1- \theta) (i_{\text{c1}})
\end{align*}
\]

By comparing the current densities in presence \((i_{\text{c1}})\) and in absence \((i_{\text{c2}})\) of a blocking adsorption inhibitor, the degree of coverage can be calculated\[^{[27]}\]. The only requirement for the above equation to hold is that the presence of inhibitor does not change the Tafel slope, a condition which is fulfilled here.

It is now commonly believed that the first step in the corrosion inhibition is an adsorption process. Therefore, it is of interest to determine the type of adsorption isotherm which best explains the adsorption data.

The Langmuir isotherm is

\[
\frac{\theta}{1-\theta} = KC
\]

Where \( \theta \) is the degree of coverage, \( K \) is the absorbability and \( C \) is the concentration of inhibitor. Taking logarithms of the above equation gives.
\[
\log \frac{\theta}{1 - \theta} = \log k + \log C
\]

Alternatively, a plot of \( \log \left( \frac{\theta}{1 - \theta} \right) \) versus \( \log C \) should be a straight line with unit slope.

Fig. 10a shows such a plot of \( \log \left( \frac{\theta}{1 - \theta} \right) \) versus the logarithm of different concentrations of various toludine for aluminium in a solution of pH4 containing 0.1 M sodium chloride. The figure shows that a good straight line relation is obtained which indicates that the adsorption of inhibitor on aluminium follows langimuir isotherm. However the slope of the straight line are about 0.62, 0.72 and 0.82, for meta, para and ortho respectively, which is less than unity this may be attributed to the effects of lateral interaction between the adsorbed inhibitor molecules.

Fig. 10b shows the relation between \( \log \left( \frac{P}{1-P} \right) \) versus inhibitors concentrations. Again the relation is a straight line with a slope of 0.64, 0.77 and 0.93 for meta, para and ortho respectively. These values are sufficiently close to the values of 0.62, 0.72 and 0.82. It is then concluded that the adsorption does not change the mechanism of the hydrogen evolution reaction, even though, it significantly reduced its rate. This supports the view that toludine blocks a fraction of the electrode surface hence it reduces the surface area available for hydrogen evolution, this reduce the rate of hydrogen evolution and consequently the rate of the overall corrosion reaction. From Table (5) it is clear that the percentage decreases in \( i_{corr} \), \( i_p \) and \( \theta \) and \( P \) are all equal within experimental error. It can be concluded that the cathodic (hydrogen evolution) reaction is the rate determining step and the fractional of the surface area covered with toludine does not participate in the corrosion reaction. This is strongly suggested that toludine is a cathodic corrosion inhibitor of a blocking adsorption type. The general conclusion is that toludine is an excellent inhibitor for the corrosion of aluminum in acidic chloride solution and meta-toludine shaving marked efficiency than para and ortho toludine at comparable concentration. The reactivity of toludine follows the order:

\[ m\text{-toludine} > p\text{-toludine} > o\text{-toludine} \]

This order of reactivity can be explained on the basis of basicity of toludine as aromatic amine. The low basicity of the amino group (\(-\text{NH}_2\)) in ortho and para position results from the resonance (+R) effect where nitrogen atom shares its lone pair of electrons with the aromatic ring and consequently acquires a positive charge. The lower reactivity of o-toludine attributed to the lower basicity of the amino group results from both its + R effect and to the ortho effect where steric hindrance is exerted by the bulky methyl group located at the ortho position to the amino group.

4. Conclusion

The OCP for pH 4-5 varies in the noble direction at the moment of immersion then decrease slowly after 50 minute till steady state values. In pH 8&9 the OCP decrease in a relatively short time reaching a steady-state value after one hour.

In the presence of \( \text{Cl}^- \) ion the OCP are shifted towards negative direction with increasing pH and \( \text{Cl}^- \) concentrations.

Potentiodynamic polarization of Al electrode in different pH solutions similar shapes with shift of the passive region to higher current density with increasing pH. In presence of \( \text{Cl}^- \) we observed the absence of pitting potential at pH4 and pH5 due to presence of acetic acid which resist the pitting corrosion.

At pH8 and 9 all the curves exhibit an active region with passivity at intermediate value of potential and pitting at and beyond the pitting potential due to presence of \( \text{Cl}^- \) ion.

The variation of the corrosion rate as a function of the logarithm of molar chloride concentration show that the corrosion rate increases with increasing \( \text{Cl}^- \) ion concentration and pH of the solutions.

The corrosion rate decrease as the inhibitor concentrations increase following the sequence o,m and p and the percentage protection with increasing inhibitor concentrations due to the toludine on the surface.
Table (5): The effect of inhibitor concentration on corrosion potential, cathodic Tafel slope, corrosion and exchange current densities, percentage decreases in each, polarization resistance, degree of surface coverage and percentage protection.

<table>
<thead>
<tr>
<th>Conc (Wt. %)</th>
<th>Log C</th>
<th>$-E_{corr}$ (V)</th>
<th>$bc$ (m V)</th>
<th>$i_o$ (nA/cm$^2$)</th>
<th>% decrease in $i_o$</th>
<th>$i_{corr}$ (nA/cm$^2$)</th>
<th>% decrease in $i_{corr}$</th>
<th>$R_p$</th>
<th>$\theta$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-2</td>
<td>3.6620.672</td>
<td>190</td>
<td>7.638x10$^{-4}$</td>
<td>-</td>
<td>4.59x10$^{-5}$</td>
<td>-</td>
<td>9.2x10$^{2}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>-2</td>
<td>3.640.646</td>
<td>187, 195, 198</td>
<td>4.53x10$^{-4}$</td>
<td>41</td>
<td>50.4</td>
<td>64.6</td>
<td>1.76x10$^{-3}$</td>
<td>61</td>
<td>52</td>
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<tr>
<td>0.025</td>
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<td>3.668.642</td>
<td>195, 198</td>
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<td>60</td>
<td>66</td>
<td>79</td>
<td>2.78x10$^{-4}$</td>
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<td>67</td>
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<td>-1</td>
<td>3.6640.648</td>
<td>196, 197, 198</td>
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<td>1.24x10$^{-4}$</td>
<td>2.58x10$^{-4}$</td>
<td>1.24x10$^{-4}$</td>
<td>3.64x10$^{2}$</td>
<td>60</td>
<td>66</td>
</tr>
</tbody>
</table>

Fig. (1): Variation of the OCP with time for aluminium electrode in different pH solutions.

Fig. (2): Potentiodynamic polarization curves of aluminum electrode in different pH solutions.
Fig. (3): Dependence of corrosion potential ($E_{corr}$) and corrosion current densities ($i_{corr}$) of aluminium electrode, determined from Tafel plots, on various pH values.

Fig. (4): Variation of the OCP with time for aluminium electrode in a solution of a) pH 4  b) pH 5 c) pH 8 d) pH 9 free and containing different concentrations of sodium chloride

Fig. (5): Effect of variation of salt concentration on steady-state potential of aluminium electrode at different pH solutions.
Fig. (6): Potentiodynamic polarization curves of aluminium electrode in a solution of (a) pH 4 (b) pH 5 (c) pH 8 (d) pH 9 free and containing various sodium chloride concentrations.

Fig. (7): Variation of the Corrosion rate of aluminium electrode with logarithm of molar chloride concentration at different pH values.
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5. References

Fig.(8): Potentiodynamic polarization curves of aluminium electrode in a solution of pH4 containing 0.1M sodium chloride in absence and in presence of various o-toludine concentrations.
Fig. (9): Effect of o,p and m-toludine concentrations as inhibitors on a) corrosion rate b) percentage protection of aluminium in a solution of pH4 containing 0.1 M sodium chloride.

Fig. (10): Plot of a) $\log \frac{\theta}{1-\theta}$ b) $\log \frac{P}{1-P}$ vs. log concentrations of o,p and m toludine in a solution of pH4 containing 0.1 M sodium chloride.