Study of dithiocarbamates compounds in corrosion inhibition of aluminium in 1M NaCl polarization resistance

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The polarization resistance ($R_p$) has been used to monitor the corrosion of aluminium in aqueous solutions in the pH range 1-13 and in the presence of 1M NaCl. The effects of time, nitrogen, temperature and some dithiocarbamates have been studied. The $R_p$-pH curves in air and nitrogen saturated solutions are bell shaped showing its lowest value at pH 13. In solutions without inhibitors, the $R_p$ has been found to change with temperature according to the relationship $R_p = a - bt$, while in the presence of inhibitors the relationship is more complicated. The effect of inhibitor concentration is found to depend on the type of inhibitor and pH. The kinetic parameters have been evaluated for uninhibited and inhibited reactions.

The electrochemical polarization resistance technique is an excellent method of measuring corrosion rate. This technique is performed by applying a controlled potential scan over a small range, typically ±20 mV relative to corrosion potential. The theoretical background for polarization resistance measurements have been provided by Stern and Geary and this method has been reviewed by Mansfield. The $R_p$ method has attracted considerable attention where it has been used in determination of corrosion rates, inhibition efficiency and corrosion mechanism.

There is very little information available on the corrosion inhibition of aluminium by dithiocarbamate compounds. Moreover, these compounds have three adsorption sites, i.e., the amine group, the double bond and the sulphur atom. Therefore, it is expected that these compounds would be good inhibitors. This investigation is aimed to study the corrosion behaviour of aluminium in 1M NaCl in absence and presence of the dithiocarbamate compounds at different conditions and evaluating some kinetic parameters, using polarization resistance technique.

Experimental Procedure

Triply distilled water was used throughout the experiments. Chemicals were the products of BDH or Merck (Analar grade). Commercial grade Al was used in this work. Sodium methyl, ethyl, propyl and butyl dithiocarbamates (SMD, SED, SPD, SBD) were prepared in the laboratory according to the method of Moore and Crossly.

Their purities were checked by analysis for C, H, and N. In addition, the purity of the prepared compounds was also checked using NMR and IR spectroscopy.

The pH of solutions was adjusted using HCl or NaOH as appropriate. Polarization curves for Al electrode were obtained using the corrosion measurement system model 350 A (EG & GPARC (Princeton Applied Research)).

The electrode has an area of 1 cm² and was prepared by cleaning the surface with 180 emery paper followed by 600 and finally with 1000, washed with tap water, triply-distilled water and finally with acetone and then air dried. In case of oxygen free experiments, nitrogen was bubbled for 20 min before the start of experiments and the bubbling continued during the measurement.

The polarization resistance technique is performed by applying a controlled-potential scan over a small range, typically ±20 mV with respect to $E_{corr}$ with scan rate of 1 mV/s starting from the cathodic to the anodic potential. The resulting current is linearly plotted versus potential. The slope of this potential-current plot is the polarization resistance, $R_p$.

The inhibition efficiency was calculated by Eq. (1):

$$\text{Inhibition efficiency} = \frac{R_p - R_{p0}}{R_p} \times 100 \ldots (1)$$

where $R_{p0}$ and $R_p$ are the polarization resistance before and after adding the additives, respectively.
Results and Discussion

Aluminium in NaCl—The variation of $R_p$ with pH is shown in Fig. 1. It shows that $R_p$ increases with the increase of pH and it attains maximum in the pH range 5-9. It then decreases where it has the lowest value at pH 13. It was observed that the electrode surface at pH 1 and 13 becomes grey with slow evolution of gases at pH 1 but at pH 13, the evolution of gases is very vigorous. At other pH values, no change in surface colour takes place and no gases are evolved.

The variation of $R_p$ with time at three selected pH in aerated 1M NaCl is shown in Fig. 2. It is clear that at pH 1, $R_p$ increases with time to ~3 folds of its value immediately after immersion and this maximum value is reached after ~1 h, then it decreases in an exponential manner. At pH 7, $R_p$ is much higher than that at pH 1 and it increases slowly but linearly with time as shown in Fig. 2.

The variation of $R_p$ with pH in the presence of nitrogen is almost identical to that of aerated solutions as can be seen in Fig. 1. It is observed that $R_p$ at pH 1, 5 and 13 are little higher in comparison with those of aerated solutions while at pH 7 it is slightly less and at pH 13 it is about the same.

The variation of $R_p$ with temperature was studied in the temperature range 10-40°C and the results are shown in Fig. 3. As can be seen, $R_p$ decreases with temperature which indicates an increase in the rate of corrosion. It was found that the following relationship is held reasonable.

$$R_p = a - bt$$

where $a$ and $b$ are constants. It is also obvious that at all temperatures $R_p$ has its lowest values at pH 13 followed by pH 1 and the highest values are obtained in the range 5-9.

An attempt has been made to compare the corrosion behaviour of Al by $R_p$ method and weight loss measurement. The comparison was found to be rather difficult due to the fact that the corrosion behaviour in the latter case is very complex especially in the pH range 3-11, as can be seen in Fig. 4. It is clear from Fig. 4b that at pH 13, the corrosion rate is much higher in comparison with pH 1. However, at longer times the rate of change at pH 1 is higher than at pH 13.

The plot of weight loss against pH, after 45 days immersion is shown in Fig. 5. It is obvious that this figure is the reverse of that obtained from $R_p$ measurements (Fig. 1). It was observed that at pH 1, there was a slow evolution of hydrogen and the specimens became light grey and a grey precipitate was observed at the bottom of the flask. In the pH range 3-11 and in sea water, the behaviour is as observed at pH 1 except there was no gas evolution and the amount of the precipitate is much less. At pH 13, the reaction was vigorous with evolution of gases and an appreciable grey precipitate was formed which is strongly adhering to the bottom of the flask. Moreover, pH of solution changes to different extents depending on initial pH. In the acid side of the pH scale, the change in pH is towards higher values while in the alkaline side the change is towards lower values as can be seen in Fig. 6. However, at pH 13 the pH is almost constant.

![Fig. 1](image_url)

Fig. 1—Variation of $R_p$ of Al electrode with pH in 1M NaCl (O-Air and □-N₂)

![Fig. 2](image_url)

Fig. 2—Variation of $R_p$ with time of Al electrode at various pH in 1M NaCl (O-pH 1, □-pH 7 and △-pH 13)

![Fig. 3](image_url)

Fig. 3—Variation of $R_p$ of Al electrode with temperature at different pH. (O-pH 1, □-pH 5, △-pH 7, ○-pH 9 and ▲-pH 13)
Fig. 4—Variation of weight loss with time for Al electrode at different pH (●-pH 1, ○-pH 3, □-pH 5, △-pH 7, ◇-pH 9, ⬤-pH 11 and ■-pH 13)

Fig. 5—Dependence of weight loss on pH at fixed time

Fig. 6—Change of pH with time using weight loss method (a) for pH 1 and 13, and (b) for pH 3-11 (●-pH 1, ○-pH 3, □-pH 5, △-pH 7, ◇-pH 9, ⬤-pH 11 and ■-pH 13)

Effect of inhibitors—The variation of $R_p$ with pH in the presence of $10^{-3}\, M$ of various additives is shown in Fig. 7a. It is clear that at the pH investigated $R_p$ in the presence of different additives are higher than their corresponding values in additive free solutions. This indicates that these additives are inhibitors in this pH range.

The range of efficiencies was found to be almost the same in the pH range studied. In addition, SBD was found to be the most efficient inhibitor at all pH, while SED has the least efficiency.

Table 1 shows the inhibition efficiencies in the presence of different concentrations of SMD. The
higher inhibition efficiency varies between 20-60%. The lower values were observed in the intermediate range of concentration at pH 5 and 7, while at pH 9 the lowest efficiency was observed at high concentration. For SPD and SBD the efficiencies reach 70% and these values were obtained at pH 5, 7 and 9. For the last two additives the efficiencies are generally a little higher at certain pH than for SMD and SED. The inhibition efficiencies in the presence of nitrogen at different concentrations of additives are generally less at similar conditions except at pH 7 where it is close to 90% at high concentration.

The effect of temperature on the behaviour of $R_p$ for various additives and at different pH is shown in Fig. 8. It is clear that the general behaviour is similar at pH 5, 9 and 13 where the curves for inhibitor free solutions lay below those of inhibited solutions. In addition, all curves have an upward curvature. At pH 7 the behaviour is different, where the curve for inhibitor free has the least values of $R_p$ at 10°C while SBD has a higher value. At other temperatures, inhibitor free curves are similar to other pH. In addition, at pH 7 the $R_p$ temperature curves for SMD, SPD and SBD show downward curvature. In all cases, except at pH 7, the efficiency increases with decrease in temperature. It is to be pointed out that Eq. (2) which is applicable to inhibitor free solutions is not suitable for inhibited solutions.

The corrosion rate expressed as current density $I_{corr}$ is related to $R_p$ by the following equation:

$$I_{corr} = \frac{\beta_a \beta_c}{2.3 (\beta_a \beta_c)} \cdot \frac{1}{R_p}$$

where $\beta_a$ and $\beta_c$ are anodic and cathodic Tafel constants, respectively.

Fig. 9 shows the familiar plot of ln $1/R_p$ against ln [OH]. The three straight lines covering the pH range 1-5, 5-9 and 9-13 for acidic and alkaline regions satisfy the following general equations:

$$\ln \text{(rate)} = a \pm b \ln C$$
Table 2—Activation parameters for Al electrode in 1 M NaCl under different conditions

<table>
<thead>
<tr>
<th>Additive</th>
<th>pH</th>
<th>1</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>13</th>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>ΔH*</td>
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<td>33.3</td>
<td>13.5</td>
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<td>-83.4</td>
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<tr>
<td>E*</td>
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<td>30.5</td>
<td>28.4</td>
<td>15.7</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td>ΔH*</td>
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<td>52.4</td>
<td>47.7</td>
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<td></td>
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<tr>
<td>SMD</td>
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<td>9.1</td>
<td>12.3</td>
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<td></td>
</tr>
<tr>
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<td>7.6</td>
<td>19.7</td>
<td>26.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔH*</td>
<td>43.3</td>
<td>15.6</td>
<td>50</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SED</td>
<td>ΔS*</td>
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<td>-85.5</td>
<td>30</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
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<td>7.6</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ΔH*</td>
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<td>19.4</td>
<td>31.3</td>
<td>9.5</td>
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<tr>
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<td></td>
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<td>E*</td>
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<td>6.8</td>
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<tr>
<td>ΔH*</td>
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<td>2.9</td>
<td>3.9</td>
<td>24</td>
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<td></td>
</tr>
<tr>
<td>SBD</td>
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<td>-12.8</td>
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<tr>
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<td>21.3</td>
<td>24.3</td>
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</table>

Al oxidation. This value lies in between that reported by Cha and Savinell, i.e. 1.0 at 60°C and that reported by Brown and Whitely, i.e., 0.5 at 22°C using the electrochemical methods. It must be pointed out that these values are in Cl- free alkaline solutions.

In the presence of additives, similar kinetic treatment was used, i.e., the plot of ln 1/Rp against ln C gave a fairly good straight line and typical plots are shown in Fig. 10. From these plots, the order of reaction and the apparent rate constant were calculated. The orders of reactions are found to be very small and almost close to zero.

The rate constants for uninhibited solutions depend on pH and the highest value was obtained in alkaline solutions. In the presence of inhibitors, the rate constants are different from inhibitor free solutions and they are generally very low (6 x 10⁻⁵-6 x 10⁻³).

The activation energies for corrosion and inhibited reactions were obtained using the following equation:

\[ \ln \left( \frac{R_p}{T} \right) = \frac{E^*}{T} + \text{constant} \]  

where the constant includes, Arrhenius factor, gas constant, the Faraday transfer coefficients and the number of electrons involved in the rate determining step in cathodic and anodic reactions.

The plot of LHS of Eq. (7) against 1/T gave straight lines from the slopes of which E* was obtained and the activation energy values are shown in Table 2. For the corrosion reaction, E* de-
creases with increase in pH while for inhibitor, $E^*$ depends, to certain extent, on the additive and pH.

Other activation parameters, namely, $\Delta H^*$ and $\Delta S^*$ were obtained using the transition state equa­tion12 and the results are shown in Table 2.

In the presence of Cl$^-$, the passivity of the Al is broken and this could be attributed to the ability of Cl$^-$ to penetrate the oxide film through pores or defects on the lattice or colloidal disperse the oxide film and increase its permeability hence make it more susceptible to acid attack. It is also possible that Cl$^-$ is adsorbed on the metal surface in competition which dissolved O$_2$. This may be represented as

$$\text{Al} + \text{O}_2 = \text{Al}:\text{O}_2_{ads} \quad \ldots (8)$$

$$\text{Al} + \text{Cl}^- = \text{AlCl}^-_{ads} \quad \ldots (9)$$

Reaction (8) favours a decrease in rate of corrosion, while reaction (9) favours hydration of metal ions according to the reaction:

$$\text{AlCl}^-_{ads} + \text{H}_2\text{O} = \text{Al}(\text{H}_2\text{O})_{\lambda}^{3+} + \text{Cl}^- + 3\text{e}^- \quad \ldots (10)$$

This reaction increases the rate with which metal ions enter into solutions. This is because once in contact with metal surface, Cl$^-$ favours hydration of metal ions and increases the lase with which metal ions enter into the solutions. In addition to reaction (10) another dissolution reaction may occur which is Cl$^-$ catalysed and is shown as:

$$\text{AlCl}^-_{ads} + \text{Cl}^- = \text{AlCl}_2^- + 3\text{e}^- \quad \ldots (11)$$

Reactions (10) and (11) were reported to be the rate determining step13,14 and suggest that the Al surface is covered by either O$_2$ or Cl$^-$ or both, depending on the prevailing conditions.

According to Fig. 9, there are different corrosion mechanisms depending on pH. Thus, at low pH, the main cathodic reaction is the reduction of hydrogen ion. These ions are first adsorbed by aluminium15 and then reduced as

$$\text{H}^+_\text{ads} + \text{e}^- \rightarrow \text{H}^-_{ads} \quad \ldots (12)$$

The initial increase in $R_p$ observed at pH 1 may be attributed to the adsorbed hydrogen atoms which cover the electrode surface. At a later stage the H$^-_{ads}$ will combine to form molecular hydrogen which may also be adsorbed on the surface. When the gas evolves it will leave the surface exposed to the media where Cl$^-$ will be chemisorbed onto the oxide surface and acts as a reaction partner aiding the dissolution via the formation of oxychloride complexes16, e.g.,

$$\text{Al}^{3+} + 2\text{Cl}^- + 2\text{OH}^- \rightarrow \text{Al(OH)}_2\text{Cl}_2^- \quad \ldots (13)$$

This reaction is expected to lead to a decrease in $R_p$ and hence an increase in corrosion rate. It is also possible to attribute the decrease in $R_p$ at pH 1 after one hour to the formation of AlCl$_4^-$ which results from reaction (7) followed by the reaction:

$$\text{AlCl}_2^- + \text{Cl}^- \rightarrow \text{AlCl}_3^- + 3\text{e}^- \quad \ldots (14)$$

This compound will behave as the product of reaction (10).

It is of interest to mention that Brett16 working with acidic chloride solutions has proposed that the corrosion of Al in this media is due to the thinning of the oxide film which gives rise to a high electric field strength permitting the occurrence of ionic migration across the layer and hence to relatively high corrosion rate, i.e., low $R_p$ value. The proposed reactions are:

**Al/Oxide interface**

$$\text{Al} \rightarrow \text{Al}^{3+} + \text{e}^- \quad \ldots (15)$$

**Oxide/Electrolyte interface**

$$\text{Al}^{3+} \rightarrow \text{Al}^{3+} + 2\text{e}^- \quad \ldots (16)$$

The final product in this mechanism (Al$^{3+}$) will react as mentioned above.

At pH 7, $R_p$ was found to be almost constant with time (Fig. 2). This behaviour may be explained by assuming two sets of competing reactions. The first set of reactions leads to passivation and they are reaction (9) and:

$$\text{Al} + \text{OH}^- \rightarrow \text{AlOH}^-_{ads} \quad \ldots (17)$$

$$2\text{AlOH}^-_{ads} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 4\text{H}^+ + 5\text{e}^- \quad \ldots (18)$$

The second set of reactions leads to the dissolution of Al and these include reactions (10)-(12).

Since $R_p$-pH diagrams have been shown to be almost identical in presence and absence of air and for the whole pH range, it may be possible to conclude that reaction (8) has probably a minor contribution to the passivity of Al and that reactions (17) and (18) may account for the passivity of Al in the neutral and near neutral solutions.

The fact that the rate of corrosion in acid solutions is much faster than in neutral and near neutral solutions, does not exclude that O$_2$ may be adsorbed on the surface of Al which has greater affinity of O$_2$ than for Cl$^-$. But the fact that [Cl$^-$] is ~1000 fold higher than [O$_2$] the adsorption of Cl$^-$ will be more favourable and hence the passivity will break.
In alkaline solution, the reaction of Al with OH\(^-\) ions are:

\[
\begin{align*}
    \text{Al} + \text{OH}^- & \rightarrow \text{AlOH}_{\text{ads}}^- + \text{H}_2\text{O} \\
    \text{AlOH}_{\text{ads}}^- + \text{OH}^- & \rightarrow \text{Al(OH)}_{2,\text{ads}}^- + \text{H}_2\text{O} \\
    \text{Al(OH)}_{2,\text{ads}}^- + \text{OH}^- & \rightarrow \text{Al(OH)}_3^- + \text{H}_2\text{O}
\end{align*}
\]

\[\cdots (19)\]
\[\cdots (20)\]
\[\cdots (21)\]

Moreover, the corrosion inhibition of Al seems to be affected by dissolved \(\text{O}_2\), \(\text{Cl}^-\), \(\text{OH}^-\) and organic molecules. Therefore, the mechanism of action of an inhibitor may vary with factors such as its concentration, the \(pH\) of the solution, the nature of anion and other species present in the solution, structure of the organic compounds, latter interactions and charge on the metal.

**References**