Corrosion Inhibition of Aluminum in NaOH Solutions using some Bidentate Azo Dyes Compounds and Synergistic Action with some Metal Ions

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The inhibition effect of three compounds of bidentate azo dyes of 1-(4-aminophenyl)propan-1-one toward the corrosion of aluminum in 0.1 M NaOH solution was studied using weight loss and galvanostatic polarization measurements. The percentage inhibition efficiency was found to increase with increasing the concentration of inhibitors, decreasing the temperature and the presence of the electron-donating groups in the chemical structure of inhibitors. The inhibiting effect of the investigated compounds is due to its adsorption on the aluminum surface. The adsorption obeys Temkin isotherm. The polarization data showed that the bidentate azo dyes compounds act as mixed type inhibitors. The addition of Mg\textsuperscript{2+}, Ca\textsuperscript{2+} and Ba\textsuperscript{2+} ions to the additives enhanced the inhibition efficiency due to synergistic effect. Some activated thermodynamic parameters were computed and explained.

Keywords: Bidentate azo dyes compounds, Aluminum, Synergistic effect, Corrosion inhibitors

1. INTRODUCTION

Corrosion of aluminum and aluminum alloys has been a subject of numerous studies due to the importance of these materials in contemporary civilization due to its great industrial applications\cite{1-2}. Aluminum generally exhibits passive behavior which influence its corrosion susceptibility. The adhesive passivating surface oxide film is amphoteric and consequently the metal dissolve readily in acidic and basic solutions\cite{3}. It is very important to add a corrosion inhibitor to decrease the corrosion rate of aluminum and its alloys in such solutions.
Most of corrosion inhibitors are organic compounds that contain mainly nitrogen, sulfur or oxygen atoms, multiple bonds or aromatic rings in their structure and they block the active sites and accordingly, decreasing the corrosion rate [4-16].

Generally, inhibitor compounds may either adsorb physically or chemically onto a corroding metal surface. The strength of adsorption process depend on several factors including the nature and number of potential adsorption sites present in organic molecule, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface[17,18].

The present study aimed to investigate the inhibitive action of three bidentate azo dyes of 1-(4-aminophenyl)propan-1-one compounds toward the corrosion of Al in 0.1 M NaOH solution using weight loss and galvanostatic polarization measurements. The effect of addition of some metal chloride e.g. CaCl₂, BaCl₂ and MgCl₂ on the corrosion inhibition was studied. Also, the effect of rising temperature on the corrosion rate was studied in order to calculate some activated thermodynamic parameters related to the corrosion process.

2. EXPERIMENTAL TECHNIQUES

Aluminum (Al) metal with purity 99.99% provided by "Aluminum Company of Egypt, Nagh Ammad" was used in present study as working electrode. The test Al sheets having dimension 2.0x2.0 x 0.1 cm³ were used in weight loss measurements. The sheets were first polished with different grades of emery paper in order to obtain a smooth surface, and then degreasing with acetone and then rinsed with distilled water, dried between two filter papers. The procedure method of weight loss measurements were carried out as described elsewhere[19].

The percentage inhibition efficiency (% IE) and a parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules were calculated using the following equations:

\[
\%\ IE = \left[1 - \frac{W_{\text{add}}}{W_{\text{free}}}\right]100
\]

\[
\theta = \left[1 - \frac{W_{\text{add}}}{W_{\text{free}}}\right]
\]

where, \(W_{\text{free}}\) and \(W_{\text{add}}\) are the weight loss of Al coupons in absence and presence of inhibitors, respectively.

For galvanostatic polarization measurements, a cylindrical rod embedded in araldite with exposed surface of 0.62 cm² was used. Galvanostatic anodic and cathodic polarization measurements were carried out using a PS remote potentiostat with PS6 software to calculate the corrosion parameters. Three compartment cell with a saturated calomel reference electrode and platinum foil auxiliary electrode was used. The polishing, degreasing and washing of the Al electrode as explained in the above techniques. Solutions were not deaerated to make the conditions identical to weight loss measurements. All the experiments were carried out at 25±1°C by using ultra circulating thermostat.
The percentage inhibition efficiency (%IE) was calculated from corrosion current density values using the equation.

\[
\% \ IE = \left( 1 - \frac{I_{\text{add}}}{I_{\text{free}}} \right) \times 100
\]

(3)

where, \(I_{\text{free}}\) and \(I_{\text{add}}\) are the corrosion current densities in absence and presence of inhibitors. The following three compounds of bidentate azo dyes compounds were prepared by method described earlier [20].

1. \(1-(4-((2\text{-}\text{hydroxy}\text{-}3\text{-}\text{nitrophenyl})\text{diazenyl})\text{phenyl})\text{propan-1-one}\)

2. \(1-(4-((3\text{-}\text{amino}\text{-}2\text{-}\text{hydroxyphenyl})\text{diazenyl})\text{phenyl})\text{propan-1-one}\)

3. \(1-(4-((2,4,6\text{-}\text{trihydroxyphenyl})\text{diazenyl})\text{phenyl})\text{propan-1-one}\)

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Figure 1 shows the weight loss-time curves of Al sheet in 0.1M NaOH in absence and presence of compound III as an example of the studied azo dyes compounds(similar curves were obtained in presence of the other two inhibitors, but not shown).
Figure 1. Weight-loss as a function of time for aluminum in 0.1 M NaOH solution in absence and presence of compound III at 30 °C. 1) Blank 2) 1x10^-6 M 3) 3x10^-6 M 4) 5x10^-6 M 5) 7x10^-6 M 6) 9x10^-6 M 7) 11x x10^-6 M

Inspection of the curve of Fig.1 shows that the weight loss values of Al in 0.1M NaOH solution containing investigated inhibitor decreases as the concentration of the inhibitor increases; i.e., the corrosion inhibition strengthens with the inhibitor concentration,. The linear variation of weight loss with time in uninhibited and inhibited in 0.1M NaOH indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed onto the metal surface and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.

Table 1. Values of inhibition efficiency efficiencies (%IE) for bidentate azo dyes compounds for the corrosion of aluminum in 0.1 M NaOH after 75 minutes immersion at 30 °C.

<table>
<thead>
<tr>
<th>Conc., M x10^-6</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound I</td>
<td>30.66</td>
<td>38.82</td>
<td>40.35</td>
<td>46.21</td>
<td>50.34</td>
<td>54.44</td>
</tr>
<tr>
<td>Compound II</td>
<td>40.68</td>
<td>44.86</td>
<td>48.85</td>
<td>52.32</td>
<td>58.44</td>
<td>62.34</td>
</tr>
<tr>
<td>Compound III</td>
<td>60.24</td>
<td>65.74</td>
<td>69.33</td>
<td>72.64</td>
<td>75.32</td>
<td>78.12</td>
</tr>
</tbody>
</table>

This trend may result from the fact that the adsorption of inhibitor on the Al increases with the inhibitor concentration thus the Al surface is efficiently separated from the medium by the formation of a film on its surface[21].

The calculated values of % IE at 30°C are listed in Table 1. The order of decreasing inhibition efficiency of the investigated compounds is as follows:
Compound III > Compound II > Compound I
This sequence will be discussed later in the inhibition mechanism section.

3.2. Effect of temperature

The effect of rising temperature on the corrosion rate of aluminum in 0.1 M NaOH solutions in absence and presence of $5 \times 10^{-6}$ M of the bidentate azo dyes compounds was studied using weight loss measurements. Similar curves were obtained to figure 1 (not shown). It is clear that, the rate of corrosion increases as the temperature increases. This indicates that the rising of temperature decrease the inhibition processes and the best inhibition efficiency is obtained at 30 °C.

![Figure 2](image-url)

**Figure 2.** log corrosion rate vs. $1/T$ curves for aluminum in 0.1 M NaOH solution in absence and presence of $5 \times 10^{-6}$ M of bidentate azo dyes compounds derivatives. (a) Free (b) in presence of: 1) compound I 2) compound II 3) compound III

The apparent activation energy ($E_a^*$) of the corrosion of aluminum in 0.1 M NaOH solutions in the absence and presence of the bidentate azo dyes compounds at different temperatures were calculated from the Arrhenius equation [22].

$$R_{corr} = A \exp\left(-\frac{E_a^*}{RT}\right)$$  \hspace{1cm} (4)

where, $R_{corr}$ is the rate of corrosion, $A$ is the Arrhenius pre-exponential constant, $E_a$ is the activation energy, $R$ is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and $T$ is the absolute temperature (K).
Fig. (2) represents the plots of logarithm of corrosion rate (log $R_{\text{corr}}$), with reciprocal of absolute temperature ($1/T$) for aluminum corrosion in 0.1M NaOH solution in absence and presence of $5\times10^{-6}$ M bidentate azo dyes compounds.

The values of $E_a$ can be obtained from the slope of the straight lines and given in Table 2. Inspection of the data in Table 2, it is clear that, the values of $E_a$ increases with increasing the concentration of inhibitor. This means that, the presence of additives induce an energy barrier for the corrosion reaction and this barrier increases with increasing the concentration of these compounds. The kinetic of Al corrosion process acquires the character of a diffusion process in which at lower temperature the quantity of inhibitor present at the metal surface is greater than that at higher temperature.

The entropy of activation ($\Delta S^*$) and the enthalpy of activation ($\Delta H^*$) for dissolution of Al in 0.1M NaOH solution in absence and presence of $5\times10^{-6}$ M bidentate azodyes of each used compound were obtained by applying the transition state equation [22].

$$R_{\text{corr}} = \frac{(RT/Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT)}{10^3 \exp (1/T)}$$

where, $h$ is the Planck’s constant ($6.6261\times10^{-34}$ Js), $R$ is the universal gas constant and $N$ is the Avogadro’s number ($6.0225\times10^{23}$ mol$^{-1}$).

![Figure 3](image-url)  

**Figure 3.** log corrosion rate/T vs. 1/T curves for aluminum in 0.1 M NaOH solution in absence and presence of bidentate azo dyes compounds (a) Free (b) in presence of : 1) compound I 2) compound II 3) compound III

Fig. (3) represents the relation between the logarithm of (log $R_{\text{corr}} / T$) with reciprocal of absolute temperature ($1/T$) for aluminum 0.1M NaOH containing $5\times10^{-6}$ M of the studied compounds. Straight lines were obtained with a slope of $(-\Delta H^*/2.303 \, R)$ and an intercept $[\log (R/Nh -\Delta S^*/2.303R)]$. Values of $\Delta H^*$ and $\Delta S^*$ were calculated from the slope and intercept of the straight lines,
respectively, and given in Table 2. The positive values of $\Delta H^*$ both in the absence and presence of inhibitor reflect the endothermic nature of the aluminum dissolution process which reflects the difficulty of aluminum dissolution [23]. Large and negative values of $\Delta S^*$ in the absence and presence of inhibitor indicates that the activation complex in the rate determining steps includes association rather than dissociation step. The negative values of $\Delta S^*$ are expected as the adsorption process is accompanied by a decrease in the disorder of the system due to the adsorption of the free bulky inhibitor molecules onto the electrode surface.

**Table 2.** Activation parameters of the dissolution of aluminum in 0.1 M NaOH in the absence and presence of $5 \times 10^{-6}$ M bidentate azo dyes compounds.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$E_a^*$, kJ mol$^{-1}$</th>
<th>$\Delta H^*$, kJ mol$^{-1}$</th>
<th>$-\Delta S^*$, J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free NaOH</td>
<td>28.63</td>
<td>26.66</td>
<td>234.56</td>
</tr>
<tr>
<td>Compound I</td>
<td>31.42</td>
<td>28.83</td>
<td>208.74</td>
</tr>
<tr>
<td>Compound II</td>
<td>33.46</td>
<td>34.02</td>
<td>198.65</td>
</tr>
<tr>
<td>Compound III</td>
<td>34.84</td>
<td>36.18</td>
<td>188.23</td>
</tr>
</tbody>
</table>

3.3. Adsorption isotherm

![Figure 4](image.png)

**Figure 4.** Typical Temkin adsorption isotherm obtained from weight loss measurements for adsorption of studied bidentate azo dyes compounds on the Al surface. 1) compound I 2) compound II 3) compound III

The adsorption of an inhibitor is a substitutional process in which the adsorbed water molecule is being replaced by inhibitor molecules according to the following equation:

$$\text{Dyes}_{\text{sol}} + n\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{Dyes}_{\text{ads}} + n\text{H}_2\text{O}_{\text{sol}}$$  \hspace{1cm} (6)
where \( \text{Dyes}_{\text{sol}} \) and \( \text{Dyes}_{\text{ads}} \) are the bidentate azodyes compounds in the aqueous solution and that adsorbed on the metal surface, respectively. \( \text{H}_2\text{O}_{\text{ads}} \) is adsorbed water molecules and \( n \) is the number of water molecules replaced by one inhibitor molecule. Adsorption isotherms can provide the basic information on the interaction between the inhibitor and the aluminum surface. Four types of adsorption may take place involving organic molecules at the metal solution interface: (i) electrostatic attraction between charged molecules and the charged metal, (ii) interaction of unshared electron pairs in the molecule with the metal, (iii) interaction of \( p \)-electrons with the metal and (iv) a combination of the above, i.e., Inhibitor can function by physical adsorption, chemisorption or by complexation with the metal.

Attempts were made to fit experimental data to various isotherms including Langmuir, Temkin, Frumkin, Freundlich and Flory–Huggins isotherms. It has been found that the experimental results in this study for the inhibitors accord with Temkin isotherm, which can be expressed by the following equation [24]:

\[
\exp(-2a\theta) = KC
\]

where \( \theta \) is the degree of surface coverage (determined from the weight loss shown above), \( C \) is the inhibitor concentration, \( a \) the molecular interaction parameter and \( K \) is the equilibrium constant of the adsorption process. Fig. (4) represents the plots of surface coverage \( (\theta) \) versus \( \log C \). Straight lines were obtained indicating that the adsorption of the bidentate azo dyes compounds on the Al surface obeys Temkin isotherm.

The equilibrium constant of the adsorption process is related to the standard free energy of adsorption process by the following equation [25]:

\[
\Delta G_{\text{ads}} = -RT \ln(55.5K)
\]

where, 55.5 is the concentration of water expressed in mol dm\(^{-3}\). The values of \( K \) are equal to 2.2 \( \times 10^2 \), 3.4 \( \times 10^2 \) and 4.4 \( \times 10^2 \) for compounds I, II and III, respectively. The high value of \( K \) indicates that the strong adsorption of non ionic surfactants compounds on the Al surface. The calculated values of \( \Delta G_{\text{ads}}^0 \) for bidentate azo dyes compounds on the aluminum surface are equal to \(-35.24 \), \(-36.26 \) and \(-37.48 \) kJ mol\(^{-1}\) for compounds I, II, and III, respectively. The negative values of \( \Delta G_{\text{ads}} \) reveal a spontaneous adsorption process. Generally, values of free energy of adsorption up to \(-20 \) kJ mol\(^{-1}\) are consistent with electrostatic interaction between charged molecules and a charged metal while those more negative than \(-40 \) kJ mol\(^{-1}\) involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond. The obtained values of free energy of adsorption (\( \Delta G_{\text{ads}} \)) are negative and lies between \(-35.24 \) to \(-37.48 \) kJ mol\(^{-1}\); This indicates that the adsorption of the studied inhibitors on the Al surface involves physical adsorption and chemical adsorption (mixed adsorption) [26]. In fact the adsorption process could not be classified either as purely physical or chemical. Moreover, the criteria of adsorption type obtained from the change of activation energy, shown above, cannot be taken as a decisive due to competitive adsorption with water molecules, whose removal from the surface requires also some activation energy [27,28]. Therefore, it is concluded that, the adsorption of molecules on the Al surface in 0.1M NaOH solution takes place through both physical and chemical processes simultaneously.
3.4. Synergistic Effect

The corrosion of Al in 0.1M NaOH solution in presence and absence of the bidentate azo dyes compounds with addition of specific concentration (1x10^{-3} M) of Mg^{2+}, Ca^{2+} and Ba^{2+} ions was studied by the weight loss method. Similar curves were obtained to figure 1 (not shown).

The values of percentage inhibition efficiency (%I.E) for various concentrations of inhibitors in the presence of specific concentration of these cations at 30°C are given in Table (3). From these values it is observed that the addition of Mg^{2+}, Ca^{2+} and Ba^{2+} ions improves the inhibitive action of the bidentate azo dyes compounds in alkaline solutions. This may be due to the fact that these cations are chemisorbed on the aluminum surface in alkaline solution, as has already been proved by radio-tracer study[29].

Table 3. Percentage inhibition efficiency (%IE) of different bidentate azo dyes compounds in the presence of 1x10^{-3} M MCl_{2} for the corrosion of aluminum in 0.1M NaOH after 90 minutes immersion at 30°C.

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>x10^{-3} M [MCl_{2}],</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{2+}</td>
<td>Compound I</td>
<td>70.24</td>
<td>72.80</td>
<td>74.52</td>
<td>76.45</td>
<td>79.26</td>
<td>82.13</td>
</tr>
<tr>
<td></td>
<td>Compound II</td>
<td>74.53</td>
<td>76.87</td>
<td>80.22</td>
<td>82.34</td>
<td>84.89</td>
<td>87.33</td>
</tr>
<tr>
<td></td>
<td>Compound III</td>
<td>78.68</td>
<td>80.75</td>
<td>83.90</td>
<td>85.34</td>
<td>87.42</td>
<td>89.84</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>Compound I</td>
<td>73.34</td>
<td>76.26</td>
<td>78.42</td>
<td>80.18</td>
<td>82.43</td>
<td>84.33</td>
</tr>
<tr>
<td></td>
<td>Compound II</td>
<td>78.42</td>
<td>82.02</td>
<td>83.98</td>
<td>86.14</td>
<td>88.49</td>
<td>90.26</td>
</tr>
<tr>
<td></td>
<td>Compound III</td>
<td>82.43</td>
<td>85.27</td>
<td>86.44</td>
<td>89.33</td>
<td>91.51</td>
<td>92.22</td>
</tr>
<tr>
<td>Ba^{2+}</td>
<td>Compound I</td>
<td>78.26</td>
<td>82.19</td>
<td>85.91</td>
<td>87.42</td>
<td>89.35</td>
<td>91.66</td>
</tr>
<tr>
<td></td>
<td>Compound II</td>
<td>82.71</td>
<td>84.62</td>
<td>86.51</td>
<td>87.23</td>
<td>89.38</td>
<td>92.72</td>
</tr>
<tr>
<td></td>
<td>Compound III</td>
<td>87.51</td>
<td>88.74</td>
<td>89.95</td>
<td>90.10</td>
<td>92.82</td>
<td>94.22</td>
</tr>
</tbody>
</table>

Table 4. Synergism parameter (S_{θ}) of different bidentate azo dyes compounds in the presence of 1x10^{-3} M MCl_{2} for the corrosion of aluminum in 0.1M NaOH after 90 minutes immersion at 30°C.

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>10^{-6} [MCl_{2}], M</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{2+}</td>
<td>Compound I</td>
<td>1.004</td>
<td>1.040</td>
<td>1.051</td>
<td>1.063</td>
<td>1.112</td>
<td>1.152</td>
</tr>
<tr>
<td></td>
<td>Compound II</td>
<td>0.985</td>
<td>1.030</td>
<td>1.057</td>
<td>1.065</td>
<td>1.124</td>
<td>1.183</td>
</tr>
<tr>
<td></td>
<td>Compound III</td>
<td>0.839</td>
<td>0.861</td>
<td>0.860</td>
<td>0.908</td>
<td>0.901</td>
<td>0.950</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>Compound I</td>
<td>1.029</td>
<td>1.054</td>
<td>1.086</td>
<td>1.098</td>
<td>1.134</td>
<td>1.184</td>
</tr>
<tr>
<td></td>
<td>Compound II</td>
<td>1.045</td>
<td>1.123</td>
<td>1.149</td>
<td>1.165</td>
<td>1.220</td>
<td>1.278</td>
</tr>
<tr>
<td></td>
<td>Compound III</td>
<td>0.909</td>
<td>0.937</td>
<td>0.932</td>
<td>0.897</td>
<td>0.917</td>
<td>0.975</td>
</tr>
<tr>
<td>Ba^{2+}</td>
<td>Compound I</td>
<td>1.099</td>
<td>1.141</td>
<td>1.110</td>
<td>0.932</td>
<td>0.911</td>
<td>0.972</td>
</tr>
<tr>
<td></td>
<td>Compound II</td>
<td>1.154</td>
<td>1.103</td>
<td>1.143</td>
<td>1.377</td>
<td>1.490</td>
<td>1.127</td>
</tr>
<tr>
<td></td>
<td>Compound III</td>
<td>1.088</td>
<td>1.124</td>
<td>1.132</td>
<td>1.204</td>
<td>1.260</td>
<td>1.417</td>
</tr>
</tbody>
</table>
The percentage inhibition efficiency of bidentate azo dyes compounds increases in presence of these cation than in absence. This behavior could be interpreted on the basis that the inhibitor (In⁻) at high concentration tends to withdraw the cations on the surface of the aluminum into the solution [30]. Hence coadsorption of cations and inhibitor ions is possible (In M²⁺ or M²⁺In⁻), the extent of desorption of cations from the surface depends on the extent of adsorption of inhibitor ion (In⁻), which is a function of the concentration of the inhibitor.

From the results obtained the order of decreasing inhibition efficiency is Ba²⁺ > Ca²⁺ > Mg²⁺. This coincide with to the increasing atomic weights of these cations and it may be explained on the basis of their basicity which increases by increasing atomic weights.

The synergistic inhibition effect was evaluated using a parameter, $S_\theta$, obtained from the surface coverage values ($\theta$) of the anion, cation and both. Aramaki and Hackerman [31] calculated the synergism parameter $S_\theta$ using the following equation.

$$S_\theta = 1 - \theta_{1+2} / 1 - \theta'_{1+2}$$

where:

$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$;

$\theta_1 =$ surface coverage by anion;

$\theta_2 =$ surface coverage by cation;

$\theta'_{1+2} =$ measured surface coverage by both the anion and cation.

The synergism parameters was calculated from the above equation and the corresponding values are shown in Table (4). It is clear from this table that, the values of $S_\theta$ are nearly equal to unity, which suggest that the enhanced inhibition efficiencies caused by the addition of cations to the selected organic compounds is due mainly to the synergistic effect.

3.5. Galvanostatic polarization measurement

Fig. 5. represents the anodic and cathodic polarization curves of Al electrode in 0.1M NaOH solution in absence and presence of compound III as an example the studied bidentate azo dyes compounds. Similar curves were obtained for the other two compounds not shown.

The corrosion parameters such as, corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), anodic Tafel slope ($\beta_a$), cathodic Tafel slope ($\beta_c$) and percentage inhibition efficiency (% IE) were calculated and are given in Table 5. The corrosion current density ($I_{corr}$) was determined by the intersection of the extrapolating anodic and cathodic Tafel lines with stationary (corrosion) potential ($E_{corr}$).

Inspection of Table 5, As the concentration of bidentate azo dyes compounds increases it is clear that.

i. The $E_{corr}$ is shifted to more negative direction and $I_{corr}$ decreases. Hence the values of % IE increases indicating the inhibiting effect of these compounds.
ii. The anodic and cathodic Tafel lines are shifted to more positive and negative potentials, respectively. The values of $b_a$ and $b_c$ are increased indicating that these compounds act mainly as mixed type inhibitors, but the anode is more polarized when an external current was applied ($\beta_a > \beta_c$).

iii. The percentage inhibition efficiency bidentate azo dyes compounds by the galvanostatic polarization measurements decreases in the following order: Compound III > Compound II > Compound I

This sequence is in accordance with that obtained from weight loss measurements. This proves the validity of these tools in the measurements of the investigated inhibitors.

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**Figure 5.** Galvanostatic polarization curves for dissolution of aluminum in 0.1 M NaOH solution in absence and presence of compound III at 30°C. 1) Blank 2) 1x10⁻⁶ M 3) 3x10⁻⁶ M 4) 5x10⁻⁶ M 5) 7x10⁻⁶ M 6) 9x10⁻⁶ M 7) 11x10⁻⁶ M

**Table 5.** Effect of different bidentate azo dyes compounds on the free corrosion potential ($E_{corr.}$), corrosion current density ($i_{corr.}$), Tafel slopes ($\beta_a$ & $\beta_c$), inhibition efficiency (%IE) and degree of surface coverage ($\theta$) of aluminum in 0.1M NaOH at 30°C.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration, x10⁶ M</th>
<th>$-E_{corr.}$ mV(SCE)</th>
<th>$i_{corr.}$ μAcm⁻²</th>
<th>$\beta_a$ mV dec⁻¹</th>
<th>$\beta_c$ mV dec⁻¹</th>
<th>$\theta$</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1170</td>
<td>998.82</td>
<td>4897</td>
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### 3.6. Mechanism of inhibition

The inhibition action of three compounds of bidentate azo dyes of 1-(4-aminophenyl)propan-1-one toward the corrosion of Al in 0.1M NaOH was found to depend on the concentration and nature of the inhibitor, number of adsorption active centers in the molecule, their charge density, molecular size, and mode of interaction with metal surface. It is generally believed that the adsorption of the inhibitor at the Al/OH\textsuperscript{-} interface is the first step in the mechanism of inhibitor action in aggressive alkaline solution. The adsorbed layer acts as a barrier between the metal surface and aggressive solution leading to a decrease in the corrosion rate. The inhibition process of bidentate azo dyes compounds can be attributed to the formation of stable insoluble complex with Al\textsuperscript{3+} ion due to the formation of six membered ring in the complex according to the following

\[
\begin{align*}
\text{Al}^{3+} &\quad \text{N}\text{C}\text{O} \quad \text{CH}_2\text{H}_3\text{C}\text{N}\text{HO} \quad \text{O}\text{OH} \\
\text{H}_2\text{O} &\quad \text{H}_2\text{O}
\end{align*}
\]

The order of the percentage inhibition efficiency of bidentate azo dyes compounds obtained by weight loss and galvanostatic measurements decreases in the following order: compound III > compound II > compound I
Compound III gives the highest inhibition efficiency than compounds II and I due to the presence of three OH group which are electron-donating groups, hence the basicity increases and the adsorption is enhanced. The electro donation increase the localization of lone pair of electron and electron density on N-atom. This led to formation of stable complex. The inhibition efficiency of compound III is more efficient than compound II which co contains two electron-donating groups (OH and NH₂) while compound I contains one electron-donating group (OH) and one electron-withdrawing group (NO₂).

4. CONCLUSION

1. Bidentate azodyes compounds inhibit the corrosion of aluminum in 0.1 M NaOH solution using weight loss and galvanostatic polarization measurements.
2. The percentage inhibition efficiency increases with increasing the concentration of inhibitors, decreasing the temperature and the presence of the electron-donating group in the chemical structure of inhibitors.
3. The inhibiting effect of bidentate azodyes compounds was explained due to the adsorption of stable complex formed on the aluminum surface.
4. The adsorption obeys Temkin isotherms.
5. The efficiencies obtained from the weight loss were in good agreement with that obtained from galvanostatic polarization technique. This proves the validity of these tools in the measurements of the investigated inhibitors.

References


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