Effect of Temperature on the Performance of Aloe Extract and Azadirachta Indica Extract in Absence and Presence of Iodide Ions on Aluminum Corrosion in Hydrochloric Acid

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Abstract
The effect of temperature in the range (20-60)°C on the corrosion of aluminum in 0.5 M hydrochloric acid have been investigated using chemical (hydrogen evolution (HE) and mass loss (ML) and electrochemical (potentiodynamic polarization (PDP) and el measurements in the absence and the presence of Aloe and/or Azadirachta Indica (AZI) extract without and with iodide ions. It was found that, the inhibition efficiency (Inh.%) of Aloe extract and/or AZI extract increase with rising temperature, this indicate that Aloe extract and AZI extract are good inhibitors. The synergistic effect between iodide and the molecules of extract (Aloe and/or AZI) due to the stability of insoluble complex formed on aluminum surface.

Keywords: Corrosion, Aloe plant, Azadirachta Indica, Effect of temperature, Aluminum.

Introduction
Corrosion of metals is very common problem that has economic implications costing billions of dollars each year. Corrosion environment can be broadly classified as atmospheric, underground/soil waste, acidic, alkaline or combinations of these. A wide variety of acid or alkaline conditions are encountered in common environments. Many of several corrosion problems encountered in the industries involves acids and in certain cases due to alkalis and solvents. Hence corrosion inhibition programs are now required in many industries such as oil and gas exploration and production, petroleum refining, chemical manufacturing and the product additive industries.

Recently, many plant extracts are widely used as corrosion inhibitors for some metals and alloys in cleaning and pickling processes. Several authors [1-9] have been studied the corrosion inhibition of aluminum and its alloys by natural organic inhibitors. Like most chemical reactions, the corrosion rate of metals in aqueous acid solutions increases with increasing temperature, especially when evolution of hydrogen accompanied corrosion, e.g., during dissolution of aluminium and zinc in alkaline or of mild steel in acids. If oxygen takes part in a cathodic reaction during corrosion, the relationship between corrosion rates and temperature becomes more complicated owing to the lower stability of oxygen at elevated temperature [10].

The effect of temperature in the range (20-60)°C on the performance of Aloe extract and Azadirachta Indica (AZI) extract in the absence and presence of iodide ions (NaI) on the corrosion of aluminium in hydrochloric (HCl) acid was carried out using chemical and electrochemical studies.

2. Materials and methods
2.1. Aluminium
The utilized aluminium has the following composition: 95.277%Al, 0.009%Mn, 0.043%Ni, 0.765%Fe, 0.014%Pb, 2.242%Si, 1.621%Zn and 0.009%Cr.
2.2. Solutions
The studied solutions (HCl and NaI) were prepared with analytical grade reagents (A.R.). The concentration of the inhibitors (extracts) was 48%v/v for Aloe extract and 24%v/v for AZI extract. Deionised water was used throughout for the preparation of solutions. Temperature was adjusted to ± 0.02 °C using ultra-thermostat (Julabo U3 No 8311). The solutions were deaerated with pure nitrogen for 15 minutes before starting electrochemical experiments.

2.3. Methods
Details of chemical and electrochemical cell and measuring instruments are given elsewhere [11,12]. Before measurements, the electrode was mechanically polished with a series of emery papers of the type (231Q wet-dry empirical Pape asoc) as previously described [13-15].

3. Results and discussion
The effect of temperature in the range (20-60)° C on the corrosion of aluminium in 0.5 M HCl was tested by chemical ((HE) and (ML)) and electrochemical ((PDP) and (EIS)) measurements and in 0.5 M HCl containing 48%v/v of Aloe extract and 24%v/v of AZI extract in the absence and presence of 0.01M iodide ions by electrochemical measurements.

3.1. Effect of temperature on the corrosion of aluminium in 0.5 M HCl
3.1.1. Chemical methods:
Figure (1) shows the results of HE for the corrosion of aluminium in 0.5 M HCl at 30, 40, 50 and 60 °C, and Figures (2a, b) show the relation between corrosion rates (R' and R) for aluminium in 0.5 M HCl with temperature from both ML (Figure 2a) and HE (Figure 2b) methods, respectively. Corrosion rates R' and R are recorded in Table (1).

![Figure 1: The relation between hydrogen volume and time for the corrosion of Al in 0.5M HCl at different temperatures](image1)

![Figure 2: The relationship between corrosion rates (a)R’, (b)R of Al corrosion in 0.5M HCl at different temperatures](image2)
It is clear that, the corrosion rate of aluminium increases rapidly with rising temperature, i.e., the slope of the straight lines is increased (Figure (1)). And at 50°C and 60°C, the lines give a steady state at the long time of immersion, (above 50 min.), this is may be due to chemisorption of chloride ions in HCl solution on aluminium surface at high temperatures, which led to inhibit the metal dissolution.

Arrhenius plots are shown in Figures (3 a, b), which illustrate the relation between (log(R' or R)) vs. (1/T). Activation energy (E*) values were calculated from the slopes of the straight lines according to the relation [16]:

$$\log (R' \text{ or } R) = \log A - \frac{E_0}{2.303RT}$$  \hspace{1cm} (1)

where, A is the Arrhenius constant, R is the ideal gas constant and T is absolute temperature. E* values are recorded in table (2).

**Table 1: Corrosion rates (R' and R) of aluminium in 0.5 M HCl at different temperatures**

<table>
<thead>
<tr>
<th>t°C</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>4.433x10^-6</td>
<td>2.380x10^-5</td>
<td>3.360x10^-5</td>
<td>5.469x10^-5</td>
<td>9.230x10^-5</td>
</tr>
<tr>
<td>R</td>
<td>-</td>
<td>7.917x10^-3</td>
<td>6.907x10^-2</td>
<td>1.628x10^-1</td>
<td>2.782x10^-1</td>
</tr>
</tbody>
</table>

An alternative form of Arrhenius equation is the transition state equation [17-21]:

$$R \text{ or } R' = \frac{RT}{Nh} \exp(\Delta S/R) \exp(-\Delta H^*/RT)$$  \hspace{1cm} (2)

$$\log(R/T) = \log(R/Nh) + \Delta S^*/2.303R - \Delta H^*/2.303RT$$  \hspace{1cm} (4)

where, h is blank’s constant, N is Avogadro’s number, $\Delta S^*$ is the entropy of activation and $\Delta H^*$ is the enthalpy of activation.

The plots of log (R/T) and/or log(R/T) vs. (1/T) will give a straight lines (Figures (4 a, b)), with a slope of $-\Delta H^*/2.303R$ and an intercept of $\log(R/Nh)+\Delta S^*/2.303R$. The values of $\Delta H^*$ and $\Delta S^*$ are calculated from ML and HE and recorded in table (2). From Table (2), it is clear that, $E_a$ values approximately agree with that obtained by a number of authors [17, 21-23]. But ($E_a$)ML is greater than ($E_a$)HE, this attributed to that the hydrogen evolution reaction is easier than the dissolution reaction. The values of $E_a$ and $\Delta H^*$ are approximately equal, which indicate that the dissolution of aluminium will occur without changing in the reaction mechanism at different temperatures.

**3.1.2. Electrochemical methods:**

The electrochemical behavior of aluminium in 0.5 M HCl was studied using PDP and EIS measurements, Figures (5 a, 5b), respeitively. Figure (5a) represents the displacement in the anodic and cathodic Tafel lines and shift $E_{corr}$ to more negative values when the temperature rises from 20 to 60°C as a result to lowering the hydrogen evolution over potential. This means the corrosion rate of aluminium is increased with rising temperature. Nyquist plots were illustrate in Figure (5b), it is clear that there are a gradual decrease in the diameters of the semicircles with rising temperature which indicates that the increase in the corrosion rate of aluminium in 0.5 M HCl with rising temperature will occur. At 60°C, Nyquist plots give semicircle with inductive loop due to pitting corrosion as a result of the presence of chloride ions within HCl solution which contain adsorbed layer on aluminium surface.

Table (3) gives the electrochemical parameters obtained from the polarization and impedance measurements. It is clear that corrosion current ($I_{corr}$) and corrosion resistance ($R_{corr}$) are increased and the
charge transfer resistance \((R_{ct})\) decreased, which indicates that the corrosion rate increases with rising temperature. Figures (6 a, b) give the relations: \(\log I_{corr}\) vs. \(1/T\) and \(\log (I_{corr}/T)\) vs. \(1/T\) from PDP method.

Activation energy \((E_a)\), enthalpy \((\Delta H^*)\) and entropy \((\Delta S^*)\) were calculated and recorded in Table (2). It is obvious that the values obtained from polarization (PDP) is grater than that from chemical methods (ML and HE), this attributed to that the electrochemical methods give instantaneous corrosion values, whereas the values obtained from chemical methods are intermediate values [24].

**Figure 3:** Arrhenius plots for the corrosion rate a) \((R')\) b) \((R)\) of Al in 0.5M HCl solution

**Figure 4:** Plots of (a) \(\log (R'/T)\) (b) \(\log (R/T)\) Vs. \((10^3/T)\) for the corrosion of Al in 0.5 M HCl solution

**Table 3:** Electrochemical parameters and inhibition efficiency for Al corrosion in 0.5 M HCl at different temperatures

<table>
<thead>
<tr>
<th>Temp. (^\circ C)</th>
<th>(-E_{corr}) (mV)</th>
<th>(b_a) (V dec(^{-1}))</th>
<th>(-b_c) (V dec(^{-1}))</th>
<th>(I_{corr}) (mA cm(^{-2}))</th>
<th>(R_{corr}) (mm day(^{-1}))</th>
<th>(R_{sol}) ((\Omega) cm(^2))</th>
<th>(R_{ct}) ((\Omega) cm(^2))</th>
<th>(C_{dl}) ((\mu F))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>694.21</td>
<td>30.647</td>
<td>118.37</td>
<td>3.32</td>
<td>45.60</td>
<td>2.098</td>
<td>109.9</td>
<td>29.55</td>
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<tr>
<td>30</td>
<td>726.57</td>
<td>44.550</td>
<td>131.22</td>
<td>7.28</td>
<td>79.30</td>
<td>0.584</td>
<td>42.52</td>
<td>102.5</td>
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<tr>
<td>40</td>
<td>722.09</td>
<td>76.615</td>
<td>10896</td>
<td>25.90</td>
<td>282.66</td>
<td>2.227</td>
<td>11.89</td>
<td>24.51</td>
</tr>
<tr>
<td>50</td>
<td>713.13</td>
<td>72.270</td>
<td>139.151</td>
<td>26.71</td>
<td>290.92</td>
<td>2.272</td>
<td>6.421</td>
<td>30.77</td>
</tr>
<tr>
<td>60</td>
<td>719.12</td>
<td>83.171</td>
<td>84.540</td>
<td>31.82</td>
<td>346.53</td>
<td>1.065</td>
<td>1.101</td>
<td>38.22</td>
</tr>
</tbody>
</table>
Figure 5: Electrochemical behavior of Al corrosion in 0.5M HCl at different temperatures from (a) Polarization, (b) Impedance

3.2. Effect of temperature on the corrosion of Al in the presence of constant concentration of Aloe extract:

The effect of temperature in the range (20-60)° C on the corrosion rate of aluminium in 0.5 M HCl solution in the presence of (48%/v/v) of Aloe extract was studied using electrochemical (PDP and EIS) measurements. Tafel plots and Nyquist diagrams are shown in Figures (7 a, b) and the electrochemical parameters are listed in Table (4), which exhibit that the corrosion current density (I_{corr.}) increased more rapidly with rising temperature, where decreased in the presence of Aloe extract than that in absence (Table(3)). Figure (7a) shows the displacement of the cathodic, anodic curves and E_{corr.} shifts to the negative direction with rising temperature, which indicates that thinning oxide film formed on aluminium surface and the increasing I_{corr.} values due to the decrease in hydrogen over potential with rising temperature, also it is shows that the presence of inflection at the beginning of the cathodic polarization due to the accumulation of hydrogen gas which increase with rising temperature. The presence of steady state in the anodic direction due to the formation of protection layer adsorbed on aluminium surface.

Table 4: Electrochemical parameters and inhibition efficiency for Al corrosion in 0.5M HCl in presence of 48% v/v of Aloe Vera extract at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>E_{corr.} (mV)</th>
<th>b_a (V dec^{-1})</th>
<th>-b_c (V dec^{-1})</th>
<th>I_{corr.} (mA cm^{-2})</th>
<th>R_{corr.} (mm day^{-1})</th>
<th>Inh. %</th>
<th>R_{sol.} (Ω cm^2)</th>
<th>R_{ct.} (Ω cm^2)</th>
<th>C_{dl.} (μF)</th>
<th>Inh. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>705.60</td>
<td>30.04</td>
<td>86.40</td>
<td>1.33</td>
<td>14.43</td>
<td>59.9</td>
<td>1.775</td>
<td>324.00</td>
<td>33.26</td>
<td>66.08</td>
</tr>
<tr>
<td>30</td>
<td>728.81</td>
<td>45.69</td>
<td>75.44</td>
<td>2.16</td>
<td>23.49</td>
<td>70.3</td>
<td>1.198</td>
<td>200.40</td>
<td>50.55</td>
<td>75.05</td>
</tr>
<tr>
<td>40</td>
<td>729.70</td>
<td>97.31</td>
<td>71.82</td>
<td>3.00</td>
<td>32.60</td>
<td>88.4</td>
<td>1.710</td>
<td>93.93</td>
<td>55.02</td>
<td>87.33</td>
</tr>
<tr>
<td>50</td>
<td>747.42</td>
<td>33.40</td>
<td>71.00</td>
<td>3.08</td>
<td>33.56</td>
<td>88.4</td>
<td>2.949</td>
<td>64.00</td>
<td>39.31</td>
<td>89.98</td>
</tr>
<tr>
<td>60</td>
<td>759.46</td>
<td>44.77</td>
<td>21.77</td>
<td>3.08</td>
<td>33.49</td>
<td>90.3</td>
<td>1.310</td>
<td>15.50</td>
<td>13.82</td>
<td>92.91</td>
</tr>
</tbody>
</table>
As shown in Table (4) and Figure (7b), $R_{ct}$ values and the diameters of semicircles decrease when rising temperature which indicates that Aloe extract acts as good inhibitor for aluminium corrosion at different temperatures. The increase in inhibition efficiency with increasing temperature can be explained due to: slowness of motion of Aloe extract molecules which have large size compared with that of adsorbed water molecules on aluminium surface. At high temperatures, the motion of Aloe molecules is less than that of water molecules which lead to desorption of water molecules from aluminium surface and adsorbed a lot of Aloe molecules which lead to increase of surface coverage and inhibition efficiency [25,26].

Figure (8a) represents Arrhenius plot (log $I_{corr}$/vs.1/T) for aluminium in 0.5 M HCl containing 48%v/v of Aloe extract from polarization measurements. It was found that the value of activation energy ($E_a$) is equal to 13.69 kJ.mol$^{-1}$ which agrees with previous studies [27]. The decrease of the activation energy in the presence of Aloe extract indicates to chemisorption of the extract molecules on aluminium surface. Surface coverage ($\Theta$) increases with rising temperature as a result of increasing in the desorption process of H$_2$O molecules with rising temperature [28-30] which lead to an increase in the adsorption process of the inhibitor. The results were in good agreement with those reported previously for aluminium [31, 32].

A plot log ($I_{corr}/T$) vs. 1/T gives a straight lines (Figure 8b) with slope of ($-\Delta H^*/2.303R$) and an intercept of ($\log((R/Nh)+\Delta S^*/2.303R)$), the values of $E_a$, $\Delta H^*$ and $\Delta S^*$ were calculated and listed in Table (5). The data shows that the thermodynamic activation functions ($E_a$ and $\Delta H^*$) for the corrosion of aluminium in 0.5 M HCl in the presence of Aloe extract are less than those in acid solutions. The entropy of activation $\Delta S^*$ has large negative value, this indicates that the formation of activated complex is the rate determining step represents an association rather than dissolution step, this means, a decrease in disordering takes place on going from reactants to the activated complex [33].
Figure 8: Plots of a) log $I_{corr}$, b) log $I_{corr}/T$ Vs. ($10^3/T$) for the corrosion of Al in 0.5 M HCl solution in the presence of 48% of Aloe Vera extract.

Table 5: Thermodynamic parameters of Al sample in 0.5 M HCl in the presence of studied extracts without and with iodide ions at different temperatures from polarization method.

<table>
<thead>
<tr>
<th>Solution</th>
<th>48% Aloe</th>
<th>48% Aloe+0.01MNaI</th>
<th>24% AZI</th>
<th>24% AZI+0.01MNaI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ kJ.mol.$^{-1}$</td>
<td>13.69</td>
<td>17.23</td>
<td>28.15</td>
<td>35.61</td>
</tr>
<tr>
<td>$\Delta H^\ddagger$ kJ.mol.$^{-1}$</td>
<td>11.36</td>
<td>14.36</td>
<td>25.08</td>
<td>33.89</td>
</tr>
<tr>
<td>$\Delta S^\ddagger$ J.mol.$^{-1}$K.$^{-1}$</td>
<td>-179.88</td>
<td>-172.28</td>
<td>-150.88</td>
<td>-120.82</td>
</tr>
</tbody>
</table>

3.3. Effect of temperature on the corrosion of Al in the presence of constant concentration of Aloe extract and constant concentration of iodide ions

The electrochemical behaviour for aluminium in 0.5 M HCl in the presence of 48% v/v of Aloe extract and 0.01 M NaI at different temperatures (20-60)$^\circ$ C was studied using polarization and impedance measurements, Figure (9 a, b) and Table (6). It is clear that displacements of the cathodic and anodic Tafel lines, shift $E_{corr}$ to more negative values (Figure 9a) and a gradual decrease in the diameter of half circle (Figure 9b) with rising temperature from 20$^\circ$ C to 60$^\circ$ C, i.e., the corrosion rate of aluminium decreases and increases in resistance with rising temperature.
Figure 9: Electrochemical behavior of Al corrosion in 0.5 M HCl in the presence of 48% of Aloe Vera extract + 1x10^{-2} M NaI at different temperatures from (a) Polarization, (b) Impedance

Table 6: Electrochemical parameters and inhibition efficiency for corrosion of Al in 0.5 M HCl in the presence of 48% of Aloe Vera extract + 1x10^{-2} M NaI at different temperatures

<table>
<thead>
<tr>
<th>$T^\circ C$</th>
<th>$E_{corr}$ (mV)</th>
<th>$b_a$ (V dec$^{-1}$)</th>
<th>$b_c$ (V dec$^{-1}$)</th>
<th>$I_{corr}$ (mA cm$^{-2}$)</th>
<th>$R_{corr}$ (mm day$^{-1}$)</th>
<th>Inh. (%)</th>
<th>$R_{sol}$ (Ω cm$^2$)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (μF)</th>
<th>Inh. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>695.70</td>
<td>87.55</td>
<td>95.00</td>
<td>2.13</td>
<td>23.15</td>
<td>35.84</td>
<td>1.133</td>
<td>147.10</td>
<td>4.964x10^{-5}</td>
<td>25.29</td>
</tr>
<tr>
<td>30</td>
<td>732.05</td>
<td>71.89</td>
<td>15.14</td>
<td>2.68</td>
<td>29.16</td>
<td>63.20</td>
<td>0.525</td>
<td>87.23</td>
<td>5.780x10^{-5}</td>
<td>52.23</td>
</tr>
<tr>
<td>40</td>
<td>707.75</td>
<td>103.71</td>
<td>113.79</td>
<td>3.90</td>
<td>42.46</td>
<td>84.94</td>
<td>2.051</td>
<td>44.26</td>
<td>6.821x10^{-5}</td>
<td>73.10</td>
</tr>
<tr>
<td>50</td>
<td>761.55</td>
<td>32.14</td>
<td>39.80</td>
<td>3.64</td>
<td>39.61</td>
<td>86.37</td>
<td>1.449</td>
<td>27.04</td>
<td>1.024x10^{-5}</td>
<td>76.11</td>
</tr>
<tr>
<td>60</td>
<td>735.40</td>
<td>33.23</td>
<td>25.87</td>
<td>3.41</td>
<td>37.11</td>
<td>89.28</td>
<td>1.813</td>
<td>10.68</td>
<td>2.988x10^{-5}</td>
<td>89.71</td>
</tr>
</tbody>
</table>
Table (6) shows the increase in $I_{\text{corr.}}$ and $R_{\text{corr.}}$ values with rising temperature and also the inhibition efficiency in the presence of iodide ions is higher than that in the absence, this indicates that the synergistic effect between Aloe extract and iodide ions lead to increase the inhibition efficiency. This attributed to the formation of complex between iodide and Aloe molecules through the electrostatic attraction which adsorb on aluminium surface and becomes more stable with rising temperature, the increase in temperature lead to high kinetic energy for molecules in solution with less weight and the large Aloe molecules moves far from aluminium surface and then, the formed complex becomes more stable which gives high inhibition efficiency.

Figures (10 a, b) show Arrhenius plots which for aluminum corrosion in 0.5 M HCl in the presence of constant concentration of Aloe extract and iodide ions. The values of $E_a$, $\Delta H^*$ and $\Delta S^*$ were calculated and listed in Table (5). The data shows that the thermodynamic activation functions ($E_a$ and $\Delta H^*$) are higher than those in the presence of Aloe extract alone. This result shows that the uses of inhibitors in the presence of iodide ions for protection of metals from corrosion is linked to high adsorption on the surface [34], which include the formation of physical protective layer of stable (insoluble) complex between the metal and corrosive medium [35], this layer will effect on the corrosion reaction.

### 3.4. Effect of temperature on the corrosion of aluminium in the presence of constant concentration of Azadirachta Indica (AZI) extract

The corrosion of aluminium in 0.5 M HCl containing 24% v/v of AZI extract has been studied over the temperature range (20-60)°C using PDP and EIS measurements.

Figures (11a, b) show the effect of temperature on the polarization Tafel lines and Nyquist plots for aluminium in 0.5 M HCl in the presence of 24% v/v of AZI extract. A general trend was observed in this Figure, as the temperature increases, the cathodic and anodic Tafel lines are shifted towards high current and
E$_{\text{corr}}$ values. The values of the inhibition efficiency and the electrochemical parameters are listed in Table (7). It was noted that:
- the values of $I_{\text{corr}}$ and $R_{\text{corr}}$ were increased with rising temperature and then decreased, this indicates that the corrosion rate decreases with rising temperature.
- $E_{\text{corr}}$ shifting to more negative values indicates to formation of thin layer on aluminum surface.
- a gradual decrease in the diameter of half circles with rising temperature in the presence of constant concentration of AZI extract, while, its obvious that there is a gradual increase in the diameter of the circles and decrease the values of charge transfer resistance ($R_{\text{ct}}$) in the absence of AZI extract.

![Figure 11](image)

*Figure 11*: Electrochemical behavior of Al corrosion in 0.5 M HCl in presence of 24% of AZI extract at different temperatures from (a) Polarization, (b) Impedance.

These results attribute to the increase in the thickness of passive oxide layer which lead to increase in the inhibition efficiency as a result of adsorption of AZI extract molecules on aluminium surface, which attributed to desorption of water molecules and replacement with the large AZI molecules with rising temperature.

The apparent activation energy $E_a$ was calculated from the relation between log $I_{\text{corr}}$ vs. $1/T$ (Figure (12a)). It was found that $E_a$ value equal to 28.15 kJ mol$^{-1}$, which agrees with previous study [3]. $\Delta H^*$ and $\Delta S^*$ values obtained from the relation between log $I_{\text{corr}}/T$ vs. $1/T$, Figure (12b) and recorded in Table (5).
Table 7: Electrochemical parameters and inhibition efficiency for Al corrosion in 0.5M HCl in the presence of 24% of Azadirachta Indica extract at different temperatures

<table>
<thead>
<tr>
<th>C V/V</th>
<th>( \eta_{\text{corr.}} ) (mV)</th>
<th>( b_a ) (V dec(^{-1}))</th>
<th>( b_c ) (V dec(^{-1}))</th>
<th>( I_{\text{corr.}} ) (mA cm(^{-2}))</th>
<th>( R_{\text{corr.}} ) (mm day(^{-1}))</th>
<th>Inh. %</th>
<th>( R_{\text{sol.}} ) (( \Omega ) cm(^2))</th>
<th>( R_{\text{ct.}} ) (( \Omega ) cm(^2))</th>
<th>( C_{\text{dl.}} ) (( \mu F ))</th>
<th>Inh. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
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<td>23.85</td>
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<td>24.82</td>
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<td>6.263</td>
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<td>66.80</td>
<td>1.904</td>
<td>25.90</td>
<td>87.73</td>
<td>54.04</td>
</tr>
<tr>
<td>50</td>
<td>735.84</td>
<td>63.49</td>
<td>141.59</td>
<td>8.83</td>
<td>96.11</td>
<td>66.94</td>
<td>1.707</td>
<td>14.42</td>
<td>106.0</td>
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</tr>
<tr>
<td>60</td>
<td>754.22</td>
<td>125.45</td>
<td>144.84</td>
<td>9.03</td>
<td>98.36</td>
<td>71.62</td>
<td>4.008</td>
<td>9.106</td>
<td>137.7</td>
<td>87.94</td>
</tr>
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</table>

Figure 12: Plots of a) \( \log I_{\text{corr}} \), b) \( \log I_{\text{corr.}}/T \) Vs. \((10^3/T)\) for the corrosion of Al in 0.5 M HCl solution HCl in the presence of 24% AZI extract.

The results show that the lower \( E_a \) value in the presence of AZI extract attributed to chemisorption of AZI molecules on aluminium surface with rising temperature and form the adsorbed layer at aluminium/HCl solution interface which lead to increase Inh.%. The \( E_a \) and \( \Delta H^* \) for the corrosion of aluminium in 0.5 M HCl in the presence of AZI extract gave in lower values than in 0.5 M HCl only, and showed higher values than in the presence of Aloe extract, this attributed to the concentration which chose from the extract and to the large size of AZI molecules. Also, it was found that the value of \( \Delta S^* \) in the presence of AZI extract has high negative value, this indicates that the activated complex formed in the determination step was accumulation rather than dissolution which lead to lower the disruption [33]. This is agrees with the results obtained in the case of Aloe extract.

3.5. Effect of temperature on the corrosion of aluminium in the presence of constant concentration of AZI extract and constant concentration of iodide ions

Figure (13a) shows polarization curves, for aluminium in 0.5 M HCl in the presence of 24% v/v AZI extract and 0.01M NaI at different temperatures, it is clear that shift in the cathodic and anodic Tafel lines and
$E_{\text{corr}}$ values to more negative values with rising temperature from $20^\circ$ C to $60^\circ$ C, i.e., the corrosion rate decreased. Figure (13b) shows a gradual decrease in the diameter of half circles which indicates that decrease in corrosion rate and the resistance with rising temperature.

![Figure 13](image)

**Figure 13:** Electrochemical behavior of Al corrosion in 0.5 M HCl in the presence of 24% of AZI extract $+1\times10^{-2}$ M NaI at different temperatures from (a) Polarization, (b) Impedance

Table (8) shows the electrochemical parameters obtained from polarization and impedance measurements. $I_{\text{corr}}$ and $R_{\text{corr}}$ values are increased with rising temperature which attributed to the adsorption of AZI extract and iodide ions through the chemisorption of $\text{ExI}_2$ complex. It obvious that the inhibition efficiency in the absence of iodide ions (i.e., in presence of AZI extract only) decreases which indicates that the addition of iodide lead to decrease of the inhibition efficiency of AZI extract, but at $30^\circ$ C, the Inh.% was decreased comparing with that at $20^\circ$ C and $40^\circ$ C, this can interpret as: at $20^\circ$ C, the molecules will adsorb on aluminium surface by physical adsorption and change to chemisorption at $40^\circ$ C, which produce with rise the temperature from $20^\circ$ C to $30^\circ$ C desorption of AZI molecules lead large area of aluminium surface to corrosion media [9], after that the physical adsorption will change to chemisorption and increases the inhibition efficiency with rising temperature, but it will be less in the range $(40-60)^\circ$ C. This can be explained by that the active complex formed at the aluminium/HCl interface will be able to soluble at low temperatures, and with rising temperature the adsorbed layer become insoluble, which is the result to the reaction occur between the complex and aluminium surface and then the chemical adsorption of AZI molecules and iodide ions which occur with constant rate.
Table 8: Electrochemical parameters and inhibition efficiency for Al corrosion in 0.5 M HCl in the presence of 24% of AZI extract + 1×10⁻² M of NaI at different temperatures

<table>
<thead>
<tr>
<th>Conc V/V</th>
<th>Polarization</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-E_{corr.} (mV)</td>
<td>b_{a} (V dec⁻¹)</td>
</tr>
<tr>
<td>20</td>
<td>727.51</td>
<td>40.82</td>
</tr>
<tr>
<td>30</td>
<td>732.82</td>
<td>56.04</td>
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<tr>
<td>40</td>
<td>756.58</td>
<td>48.20</td>
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<td>50</td>
<td>733.81</td>
<td>79.33</td>
</tr>
<tr>
<td>60</td>
<td>750.89</td>
<td>83.99</td>
</tr>
</tbody>
</table>

The activation energy E_{a} equal to 35.61 kJ mol⁻¹. Figure (14 a, b) illustrates the relation between log I_{corr} vs. 1/T and the relation log(I_{corr}/T) vs. 1/T, respectively for aluminium in 0.5 M HCl. Values of E_{a}, ΔH° and ΔS° are recorded in Table (5).

![Figure 14: Plots of a) log I_{corr}. b) log(I_{corr}/T) Vs. (10^°T) for corrosion of Al in 0.5M HCl in the presence of 24% AZI extract+1×10⁻² M NaI](image)

The results show that the higher values of E_{a} and ΔH° for the corrosion of aluminium in 0.5 M HCl in the presence of AZI and iodide ions than that in the presence of AZI extract only, and ΔS° value have large positive value indicate to the formation of stable adsorbed layer on aluminium surface at high temperatures.

From pervious results it is obvious that the Inh.% of Aloe plant extract increases in presence of I⁻ ions, and AZI extract have high Inh.% with rising temperature in absence of I⁻ ions, and this makes it a good inhibitors at high temperatures.

It will be noted that the Aloe plant extract and AZI plant extract are good inhibitors for aluminum corrosion at high temperatures.

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Conclusion
The effect of temperature on the corrosion of aluminum in 0.5 M hydrochloric acid in the absence and the presence of Aloe and/or Azadirachta Indica extract and iodide ions have been investigated using chemical and electrochemical measurements, it can be concluded that:

1. The corrosion rate of aluminum sample in 0.5 M HCl solution increased with rising temperature.
2. The inhibition efficiency of Aloe extract and AZI extract for aluminum sample in 0.5 M HCl solution increased with rising temperature, this indicates that Aloe and AZI extracts are good inhibitors in acidic solutions at higher temperatures.
3. Aloe and AZI extracts molecules adsorb on aluminium surface by chemical adsorption.
4. The addition of iodide ions on the corrosive medium in the presence of Aloe extract and/or AZI extract leads to increasing inhibition efficiency greater than in the absence. This indicates a synergistic effect between iodide ions and Aloe and/or AZI extract molecules.

References