CHAPTER - IV

RESULTS AND DISCUSSION

This chapter includes the experimental results and discussion of the present study on corrosion inhibitive action of the five different leaves extracts for aluminium corrosion in 1M NaOH solution. The individual behaviour of each plant leaves extract as corrosion inhibitor may briefly be analyzed before attempting a comparative evaluation.

4.1. Corrosion inhibition of aluminium in alkaline medium using Coleus aromaticus leaves extract (CALE)

4.1.1. Weight loss measurements

The weight loss results obtained for the corrosion of aluminium specimen for different concentrations of the Coleus aromaticus leaves extract (CALE) ranging from in 1M NaOH solution at 303 ± 0.5 K are given in Table 4.1. It is observed that increase in inhibitor concentration decreased the corrosion rate and therefore the corrosion inhibition strengthened. The increase in inhibition efficiency may result from the fact that adsorption and surface coverage increase with increase in concentration. As concentration increases more number of inhibitor molecules are adsorbed on the metal surface, thus resulting in larger surface coverage. The increase in inhibition efficiency with increase in concentration of the extract shown in Table 4.1. further suggested that the inhibitor molecules are adsorbed on the aluminium/solution interface and the adsorbed inhibitor molecules automatically screen the coated part of the metal surface from the action of the corroden tal. Hence the dissolution of aluminium decreases with increase in concentration of extract because the aluminium surface is efficiently separated from the alkaline medium. Furthermore, such enhanced adsorption at higher concentration suggests that the adsorption intermediate, formed on the metal surface at lower concentration of CALE is probably a soluble complex leading to low surface coverage. At higher inhibitor concentrations, however the complex becomes insoluble resulting in improved inhibition due to higher surface coverage. Similar observations are reported for inhibition of aluminium corrosion in alkaline and acid media using plant extracts [1-5].
Table 4.1. Corrosion parameters for aluminium in 1M NaOH solution in the presence and absence of CALE at 303K.

<table>
<thead>
<tr>
<th>Concentration of CALE (gL⁻¹)</th>
<th>Weight loss (g/cm²)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
<th>Surface coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0689</td>
<td>183.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0156</td>
<td>41.48</td>
<td>77.3</td>
<td>0.77</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0105</td>
<td>27.92</td>
<td>84.7</td>
<td>0.84</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0079</td>
<td>21.00</td>
<td>88.5</td>
<td>0.88</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0056</td>
<td>14.89</td>
<td>91.8</td>
<td>0.91</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0050</td>
<td>13.29</td>
<td>92.7</td>
<td>0.92</td>
</tr>
</tbody>
</table>

4.1.1.1. Effect of immersion time

The corrosion rate and inhibition efficiency data obtained from weight loss results for the aluminum specimen at different immersion time intervals explained the effectiveness of the inhibitor action over a period of immersion time (Table 4.2.). The variation in inhibition efficiency of different concentrations of the leaves extract for increasing immersion time is shown in Figure 4.1. The data obtained from the study showed that the weight loss of aluminum in 1M NaOH varied linearly with immersion period both in uninhibited and inhibited solutions.

![Figure 4.1. Plot of weight loss against time for aluminium corrosion in 1M NaOH without and with CALE at 303 K.](image)

The curves indicate the progressive corrosion reaction in solution. The weight loss at different intervals of time indicated the existence of a film on the
corroding surface. Even in the presence of a film the corrosion reaction seemed to be uniform since the weight loss varied linearly with immersion time. The lines obtained in the presence of inhibitor solutions, fall well below that of blank. The inhibition efficiency of CALE is found to be increased with the addition of inhibitor concentration at different immersion time intervals of the aluminium specimen in 1M NaOH solution. The maximum inhibition efficiency obtained for all the immersion periods tested describe that effective inhibition on aluminium surface is observed with 1.5 gL\(^{-1}\) inhibitor concentration. When the immersion period is increased from 1 h to 4 h corrosion rate increases and inhibition efficiency decreases. As the immersion time increases the physisorbed layer becomes thicker and this partially collapses (due to thickness) exposing the metal surface and hence inhibition efficiency decreases. So it can be inferred that the effectiveness of the inhibitor decreased with increase in immersion time [6-10].

Table 4.2. Effect of immersion time on inhibition efficiency of CALE solution for aluminium corrosion in 1M NaOH.

<table>
<thead>
<tr>
<th>Concentration of CALE (gL(^{-1}))</th>
<th>Weight loss (g / cm(^2))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1h</td>
<td>2h</td>
</tr>
<tr>
<td>blank</td>
<td>0.0689</td>
<td>0.1576</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0156</td>
<td>0.0397</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0105</td>
<td>0.0300</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0079</td>
<td>0.0233</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0056</td>
<td>0.0157</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0050</td>
<td>0.0155</td>
</tr>
</tbody>
</table>

4.1.1.2. Effect of temperature

The effect of temperature on inhibition efficiency of the inhibitor was determined in 1M NaOH containing 0.3, 0.6, 0.9, 1.2, and 1.5 gL\(^{-1}\) of the leaves extract at different temperatures ranging from 303 to 333K for an immersion period of 1 h and the results are given in Table 4.3. The results indicate that the corrosion rate increases with increasing temperature and obeys Arrhenius law in the temperature range studied. The inhibition efficiency of all concentrations of the extract is found to decrease with
increasing temperature (303-333K) as a result of fast dissolution of aluminium at higher temperature [11, 12]. This may be attributed to the fact that a higher temperature would bring desorption of adsorbed molecules. So increase of temperature could lessen the inhibitor performance to a greater extent and this supports physical adsorption mechanism of CALE on aluminium surface. Temperature influences the structure and thickness of the adsorbed film on metal [13-15].

Table 4.3. Effect of temperature on inhibition efficiency of CALE for aluminium corrosion in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of CA .E (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>0.3</td>
<td>77.3</td>
</tr>
<tr>
<td>0.6</td>
<td>84.7</td>
</tr>
<tr>
<td>0.9</td>
<td>88.5</td>
</tr>
<tr>
<td>1.2</td>
<td>91.8</td>
</tr>
<tr>
<td>1.5</td>
<td>92.7</td>
</tr>
</tbody>
</table>

In order to have a better understanding about the effect of temperature on the rate of corrosion reaction, the logarithm of the corrosion rate (CR) is plotted against the reciprocal of the absolute temperature 1/T using Arrhenius equation [16,17].

\[ k = A \ e^{-\frac{E_a}{RT}} \] ............................. (4.1)

straight lines are obtained for the plot of log CR against 1/T (Figure 4.2.) and \( E_a \) values are calculated from the slopes. Enthalpy of activation (\( \Delta H^* \)) and entropy of activation (\( \Delta S^* \)) are calculated from the slope and intercept of the line obtained from the plot of log k/T versus 1/T using transition state equation[18-20]. The values of \( E_a, \Delta H^* \) and \( \Delta S^* \) for aluminium in 1M NaOH in the presence and absence of different concentrations of CALE are given in Table 4.4. It is evident that for the corrosion of aluminium in 1M NaOH the \( E_a \) value is 48.35kJ/mol and for the different concentrations of the inhibitors the \( E_a \) values are higher ranging from 61.11 to 78.56 kJ/mol. High values of activation energy indicate that the corrosion process is controlled by the surface reaction.
Figure 4.2. Arrhenius plot for aluminium corrosion in 1M NaOH in the absence and presence of CALE.

Table 4.4. Activation parameters for aluminium in 1M NaOH in the absence and presence of various concentrations of CALE.

<table>
<thead>
<tr>
<th>Concentration of CALE (g·L⁻¹)</th>
<th>Eₐ (kJ·mol⁻¹)</th>
<th>ΔH (kJ·mol⁻¹)</th>
<th>-ΔS(J·K⁻¹·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>48.35</td>
<td>45.70</td>
<td>49.81</td>
</tr>
<tr>
<td>0.3</td>
<td>61.11</td>
<td>58.47</td>
<td>18.00</td>
</tr>
<tr>
<td>0.6</td>
<td>66.82</td>
<td>64.18</td>
<td>19.25</td>
</tr>
<tr>
<td>0.9</td>
<td>70.11</td>
<td>67.47</td>
<td>21.26</td>
</tr>
<tr>
<td>1.2</td>
<td>78.12</td>
<td>75.48</td>
<td>27.82</td>
</tr>
<tr>
<td>1.5</td>
<td>78.56</td>
<td>75.92</td>
<td>28.31</td>
</tr>
</tbody>
</table>

Analysis of the temperature dependence of inhibition efficiency and comparison of activation energies in the absence and presence of inhibitor suggests the possible mechanism of inhibitor adsorption on the metal surface. A decrease in inhibition efficiency with rise in temperature, and corresponding increase in corrosion activation energy (Eₐ) in presence of inhibitor compared to its absence is often considered as an adsorption film of physical (electrostatic) nature. Scrutiny of the results obtained at higher temperatures suggests physisorption of inhibitor species on aluminium surface. It also suggests that the addition of CALE decreases the metal dissolution in alkali solution by increasing the energy barrier for the
corrosion reaction by the adsorption of organic molecules present in the active principles of CALE on the aluminium surface. Hence CALE can be included in group-I of inhibitors as designated by Putilova [21, 22].

The results revealed that $E_a$ and $\Delta H^*$values increase in presence of CALE indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the aluminium corrosion reaction. The positive values of enthalpies reflect the endothermic nature of aluminium dissolution process. Furthermore, the entropy of activation in the presence and absence of the inhibitor is small and negative. This may be attributed to the fact that the adsorption process is rather slow and activated complex in the rate determining step represents association rather than dissociation step, which means that a decrease in disordering occurs on going from reactants to activated complex. Thus orderliness increases as reactants are converted to activated complex [23-25].

4.1.1.3. Adsorption isotherms

It is generally assumed that adsorption of inhibitor molecules on metal surfaces is the important step in the mechanism of inhibition. Establishment of isotherms that manifest the adsorption behaviour of corrosion inhibitors are necessary because they provide information about the nature of metal inhibitor interaction. Inhibitors generally are adsorbed on the surface of the metal and thereby prevent access of the metal to the corrosive medium. The molecular structure and electronic properties of the organic compounds and the distribution of charges in the inhibitor molecules play a significant role in adsorption of inhibitor molecules on a metal surface. The inhibition efficiency is correlated to surface coverage and a 100% efficiency suggesting to full coverage ($\theta = 1$). The degree of surface coverage values calculated from weight loss measurements ($\theta = \% I/100$), are used to determine its adsorption characteristics in 1M NaOH solution.

The interaction between the inhibitor molecule and metal surface can be provided by means of adsorption isotherm. To ascertain the nature of adsorption, the surface coverage values of CALE obtained at 303K-313K are tested with different adsorption isotherms which include Langmuir [26], Freundlich [27], and Temkin [28]. The correlation coefficient ($R^2$) is used to determine the best fit isotherm.
Langmuir and Temkin adsorption isotherms are found to fit well with the experimental data (Figures 4.3. and 4.4.). The slopes of the isotherms show deviation from the value of unity that would be obtained for the ideal Langmuir adsorption isotherm. The plot of C/θ versus C gives straight lines with slope values equal to unity. All the regression coefficients are very close to one which indicates that adsorption of organic molecules of CALE on the aluminium surface obeys Langmuir adsorption isotherm [29,30]. The isotherm is based on the assumption that all adsorption sites are equivalent and the adsorption of molecule occurs independently from nearby sites being occupied or not. Therefore it is assumed that there is no interaction between the adsorbed species. The inhibiting species of CALE cover adsorption sites at the metal/solution interface.

The reciprocal of the intercept values obtained from the plot are used to calculate standard free energy adsorption ΔG_{ads}. The adsorption constant K_{ads} is related to the standard free energy of adsorption, ΔG_{ads} with the following equation [31, 32].

\[
\Delta G_{ads} = -RT \ln (55.5 \times K_{ads})
\]

where 55.5 is the water concentration of the solution in mol\(^{-1}\).

Table 4.5. Adsorption parameters of CALE on aluminium in 1M NaOH at different temperatures.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T (K)</th>
<th>K_{ads}</th>
<th>-ΔG_{ads} (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M NaOH</td>
<td>303</td>
<td>11.12</td>
<td>16.18</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>9.16</td>
<td>16.21</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>9.11</td>
<td>16.71</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>8.09</td>
<td>16.90</td>
</tr>
</tbody>
</table>
Figure 4.3. Langmuir adsorption isotherm for the adsorption of CALE on aluminium in 1M NaOH solution at different temperatures.

Figure 4.4. Temkin adsorption isotherm for CALE on aluminium in 1M NaOH at 303 - 333 K
The values of $K_{ads}$ are low and decreasing with increase in temperature. This suggests the fact that adsorption strength decreases at higher temperatures and this is due to physical adsorption of inhibitor molecules on aluminium metal surface. The negative values of $\Delta G_{ads}$ obtained indicate the spontaneity of the adsorption process and the stability of the adsorbed layer on Al surface [33-35].

4.1.2. Gasometric technique

The inhibitor action with increasing concentration is closely observed by the changes in $H_2$ gas evolution using gasometric technique. Figure 4.5. shows the variation of the volume of hydrogen gas evolved as a function of time when an aluminium specimen reacts with 1M NaOH in the absence and presence of different concentrations of CALE. $H_2$ evolution rates increased with time for about 15 min after the corrosion reaction has begun and then decreased slowly. There was no change in volume of hydrogen gas evolved after 15 min. The corrosion rate of aluminium in sodium hydroxide decreased gradually after 15 min and the volume of $H_2$ evolved remained constant. The rate of hydrogen evolution is equivalent to the rate of aluminium dissolution and hence the inhibition efficiency is calculated from the volume of hydrogen gas evolved. Plots of the inhibitor solutions fall below that of free alkali solution [36-39]. These plots indicate that the studied inhibitor CALE can behave as a potential inhibitor even at trace concentrations. Table 4.6. shows that the inhibition efficiency values increases with increasing concentrations of CALE.

Table 4.6. volume of hydrogen gas evolved and inhibition efficiency of CALE.

<table>
<thead>
<tr>
<th>Concentration of CALE (g/L)</th>
<th>Volume of hydrogen evolution (mL/cm²)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>22.6</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>4.9</td>
<td>78.32</td>
</tr>
<tr>
<td>0.6</td>
<td>3.6</td>
<td>84.07</td>
</tr>
<tr>
<td>0.9</td>
<td>2.9</td>
<td>87.17</td>
</tr>
<tr>
<td>1.2</td>
<td>2.1</td>
<td>90.07</td>
</tr>
<tr>
<td>1.5</td>
<td>1.8</td>
<td>92.03</td>
</tr>
</tbody>
</table>

88
The volume of hydrogen gas evolved varies linearly with reaction time according to the relation [40]:

\[ V = kt \]  

(4.3)

Where \( V \) is the volume of hydrogen evolved at time \( t \) and \( k \) is the specific rate constant of the corrosion reaction.

![Figure 4.5](image)

Figure 4.5. Plot of volume of hydrogen gas evolved against time for aluminium corrosion in 1M NaOH solution in the absence and presence of CALE at room temperature.

Corrosion rate of aluminium determined by monitoring the \( \text{H}_2 \) gas evolution rate can provide information concerning the chemical nature of the surface film in situ at the metal corrodeant interface.

4.1.3. Potentiodynamic polarisation studies

The cathodic and anodic polarisation curves for aluminium corrosion in 1M NaOH in the absence and presence of different concentrations of leaves extract are shown in Figure 4.6. The scan rate is 1 mV/s and the measurements are made from -1700 to -1300 mV. Electrochemical parameters such as \( E_{\text{corr}} \), \( I_{\text{corr}} \), anodic and cathodic Tafel slopes (\( \beta_a \) and \( \beta_c \)) obtained by extrapolation of the Tafel lines are given in Table 4.7.
**Potential / V vs SCE**

Figure 4.6. Polarisation curves for aluminium in 1M NaOH without and with CALE.

Table 4.7. Tafel polarisation parameters for the corrosion of aluminium in the absence and presence of CALE in 1M NaOH.

<table>
<thead>
<tr>
<th>Concentration of CALE gL⁻¹</th>
<th>(-E_{corr}) (mV)</th>
<th>(I_{corr}) mA.cm⁻²</th>
<th>Tafel slope (mV/decade)</th>
<th>(R_{corr}) mmpy</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>158.8</td>
<td>5.421</td>
<td>185</td>
<td>313</td>
<td>209.01</td>
</tr>
<tr>
<td>0.3</td>
<td>155.9</td>
<td>1.107</td>
<td>174</td>
<td>260</td>
<td>42.6974</td>
</tr>
<tr>
<td>0.6</td>
<td>154.4</td>
<td>0.7200</td>
<td>169</td>
<td>250</td>
<td>27.7622</td>
</tr>
<tr>
<td>0.9</td>
<td>152.8</td>
<td>0.6776</td>
<td>172</td>
<td>245</td>
<td>26.1112</td>
</tr>
<tr>
<td>1.2</td>
<td>152.9</td>
<td>0.5980</td>
<td>178</td>
<td>224</td>
<td>23.0378</td>
</tr>
<tr>
<td>1.5</td>
<td>152.3</td>
<td>0.5547</td>
<td>175</td>
<td>218</td>
<td>21.3614</td>
</tr>
</tbody>
</table>
In the presence of different concentrations of inhibitor the corrosion current density was lowered significantly and this confirms the inhibitive nature of the leaves extract. The cathodic and anodic curves are shifted down in the presence of inhibitor and the shift is dependent on inhibitor concentration. The addition of CALE hinders the alkali attack on aluminium. Comparison of the curves recorded in the absence and presence of inhibitor shows that increasing concentrations of the inhibitor gives rise to a consistent decrease in cathodic and anodic current densities.

The values of anodic and cathodic Tafel slopes for various concentrations of the inhibitor are found to be lower than the values obtained for blank solution. This indicates that the inhibitor influences kinetics of both anodic dissolution of aluminium and cathodic hydrogen evolution reaction[41-43]. It also suggests that the extract inhibits the corrosion process by adsorption of its molecules on both anodic and cathodic sites and accordingly it behaves as mixed type inhibitor. It can be noticed that the concentration of inhibitor produces a little change on values of cathodic Tafel constant ($\beta_c$) whereas it makes more marked change on the values of anodic Tafel constant ($\beta_a$). It can be assumed that inhibitor may influence to a greater extent the mechanism of anodic dissolution process than the cathodic hydrogen evolution reaction. The values of inhibition efficiency increase with increase in inhibitor concentration. It reveals that a higher surface coverage is obtained with a solution of maximum inhibitor concentration. $E_{corr}$ values are shifted to more positive side in the presence of inhibitor solutions indicating mixed-type behavior of the inhibitor with predominant anodic action. According to literature report [44, 45] the inhibitor can be classified as a cathodic or anodic type if the displacement in corrosion potential is more than ±85 mV with respect to the corrosion potential of the blank solution. In the present study, the maximum displacement observed is less than ±10mV with respect to the corrosion potential of the blank solution which indicates that CALE acts as a mixed type inhibitor.

4.1.4. AC Impedance studies

The mechanism of inhibitor action of CALE for the corrosion of aluminum in 1M NaOH is predicted by conducting impedance experiments. Figure 4.7. shows the Nyquist plots recorded in the absence and presence of different concentrations of leaves extract. The corresponding impedance results are given in Table 4.8. The impedance diagrams are not perfect semicircles. This feature is assigned to
frequency dispersion of interfacial impedance [46]. The charge transfer resistance 
($\text{R}_{\text{ct}}$) values are calculated from the difference in impedance at the lower and higher 
 frequencies[47-49]. The general shape of the curves is almost same for all 
 concentrations of the additive. Similarity of the shapes maintained for the whole 
 concentration range manifest that no change in the corrosion inhibition mechanism 
 occurred on the addition of CALE. The increasing $\text{R}_{\text{ct}}$ values and decreasing $\text{C}_{\text{dl}}$ 
 values confirmed the inhibitive nature of the CALE. The values of charge transfer 
 resistance ($\text{R}_{\text{ct}}$) increase with increase in concentrations of CALE showing that 
 inhibition efficiency of the extract molecules increases when their concentrations are 
 increased. The diameter of the capacitive loop increased with increase in the 
 concentration of the inhibitor. It indicated that the impedance of the aluminium 
 surface increased with the increase in inhibitor concentration. It is evident from 
 figure that the depressed capacitive loop corresponds to surface in homogeneity 
 which may be the result of surface roughness, dislocation, distribution of active sites 
 or adsorption of inhibitor molecules. Inspection of Table 4.8. shows that $\text{R}_{\text{ct}}$ and 
 double layer capacitance $\text{C}_{\text{dl}}$ values have opposite trends over the whole 
 concentration range. The decrease in capacitance with increase in extract 
 concentration may be attributed to the formation of a protective layer on the 
 electrode surface. Decrease in $\text{C}_{\text{dl}}$ values with increase in inhibitor concentration is 
 attributed to decrease in local dielectric constant and/or an increase in the thickness 
 of double layer. It also suggests that the inhibitor molecules function by adsorption 
 at the metal/solution interface [50]. Thickness of the protective layer increases 
 because more inhibitor molecules adsorb on the metal surface. This trend is in 
 accordance with Helmholtz model, given by equation [51]:

$$C_{\text{dl}} = \frac{\text{ne}^0 \text{A}}{d} \quad \text{................................................. (4.4)}$$

where $d$ is the thickness of the protective layer, $\varepsilon$ is the dielectric constant of the 
 medium, $\varepsilon_0$ vacuum permittivity and $A$ is the effective surface of the electrode. The 
 same trend is shown for corrosion of aluminium in acidic and alkaline media by 
 several authors.
Figure 4.7. Nyquist plots for aluminium corrosion in 1M NaOH without and with CALE.

Table 4.8. Electrochemical impedance parameters for aluminium corrosion in the absence and presence of CALE in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of CALE (gL⁻¹)</th>
<th>$R_{ct}$ (Ωcm²)</th>
<th>$C_{dl}$ (μF/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.09</td>
<td>88.76</td>
<td>----</td>
</tr>
<tr>
<td>0.3</td>
<td>14.18</td>
<td>7.77</td>
<td>78.1</td>
</tr>
<tr>
<td>0.6</td>
<td>20.00</td>
<td>6.04</td>
<td>84.5</td>
</tr>
<tr>
<td>0.9</td>
<td>29.22</td>
<td>5.50</td>
<td>89.4</td>
</tr>
<tr>
<td>1.2</td>
<td>41.14</td>
<td>4.20</td>
<td>92.4</td>
</tr>
<tr>
<td>1.5</td>
<td>42.11</td>
<td>4.16</td>
<td>92.6</td>
</tr>
</tbody>
</table>
The change in charge transfer and double layer capacitance values is due to gradual replacement of water molecules by the anions of the alkali and adsorption of inhibitor molecules on the metal surface, which reduces the extent of metal dissolution [52]. The numerical values of $R_c$ and $C_d$ are determined by analysis of complex plane impedance plot and the equivalent circuit model by means of Zsimpwin 3.21 software fit program. Computer fitting of the spectrum allows understanding of the elements of circuit analog. The equivalent circuit model used to fit the experimental data is shown in Figure 4.8. This circuit is generally used to describe the metal/solution interface model. In the electric circuit $C_d$ is double layer capacitance, $R_c$ is the interfacial charge transfer resistance and $R_s$ is the solution resistance.

![Figure 4.8. Equivalent Randle’s circuit for the electrochemical cell.](image)

4.1.1.5. FT-IR spectral study

The IR spectra of CALE and corrosion product scratched from aluminium specimen in the presence of CALE recorded using KBr pellet method are shown in Figure 4.9. The broad and strong band ranging from 3200 to 3500 cm$^{-1}$ observed is due to overlapping of $-\text{OH}$ stretching vibrations. A peak observed at 1076 cm$^{-1}$ is assigned to alcoholic O-H bending vibration, shows the presence of hydroxyl group in CALE. Normally carbonyl group vibrations occur in the region 1850 – 1600 cm$^{-1}$ [53]. In the present study, C=O stretching vibrations are observed at 1650 and 1387 cm$^{-1}$ in figure 4.9(a). The peaks corresponding to C=O stretching frequency are shifted to 1609 cm$^{-1}$ and 1384 cm$^{-1}$ in the Figure 4.9(b). The changes in peak positions confirmed the adsorption of organic molecules of C. aromaticus on aluminium surface.
Figure 4.9. (a) IR spectrum of CALE
Figure 4.9. (b) IR spectrum of CALE protective film on aluminium surface.
Comparison of the peaks obtained in IR spectra, reveals that the studied leaves extract acts as an inhibitor for the alkaline corrosion of aluminium by adsorption of its active species over the aluminium surface.

The absorption peaks indicate that CALE contains mixtures of organic compounds. Noticeable changes in the peak values are seen at wave numbers of 3200-3500, 1650–1600, 1100-1050 cm\(^{-1}\) for the FT-IR spectrum of corrosion product scratched after CALE adsorption on aluminium surface. These regions may be assigned to O–H (well broad), C–H (variable) and C–O stretching respectively. It is clear that certain peaks are found to disappear completely, while some are shifted to higher or lower frequency region, which imply that adsorption is taking place over the solid surface. These shifts reveal the interaction that occurred between the CALE molecules and Al surface. The peak at 2396 cm\(^{-1}\) assigned as aromatic –C-H is missing in the spectrum of the corrosion product because of the interaction of n electrons of the aromatic ring with metal.

Table 4.9. FT-IR spectral data of CALE and aluminium with CALE protection film.

<table>
<thead>
<tr>
<th>Peaks from FT-IR spectra</th>
<th>Possible groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>CALE</td>
<td>Al with CALE protection film</td>
</tr>
<tr>
<td>712.3 -931.1</td>
<td>669.80</td>
</tr>
<tr>
<td>1076.23</td>
<td>1083.59</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1387.53</td>
<td>1384.81</td>
</tr>
<tr>
<td>1650.02</td>
<td>1609.95</td>
</tr>
<tr>
<td>2396.89</td>
<td>-</td>
</tr>
<tr>
<td>3209.57</td>
<td>3415.41</td>
</tr>
</tbody>
</table>

As aluminium is unlikely to be attached to a carbon atom, these changes suggest the possibility that the oxygen atoms in the hydroxyl groups of CALE are involved in this adsorption process as well. The FT-IR study thus reveals that functional groups like –OH, –COOH, C=O, C–O present in the constituents of
CALE are involved in adsorption on aluminium surface via hydrogen bonding and/or weak van der Waals forces suggesting the formation of CALE-Al$^{3+}$ complex formed on the metal surface.

4.1.6. Metallurgical microscope analysis.

The surface morphology of aluminium is examined by comparing the micrographs taken using metallurgical microscope (Gippon Inc. Japan) after immersion in the test solution in the absence and presence of CALE at room temperature for 1h. Figures 4.10 (a) and (b) showed the images of aluminium specimen in 1M NaOH without inhibitor, and in the presence of inhibitor. The formation of interfacial voids during immersion in NaOH is possibly related to the high solubility and rapid dissolution of the oxide film in alkali solution. As can be seen from the micrographs the surface is damaged by the aggressive alkali solution when aluminium is immersed in 1M NaOH without CALE (Figure 4.10.a).

Close observation of the micrograph taken for aluminium in 1M NaOH shows the deposits of aluminium hydroxide on the surface of aluminium. Further it reveals degradation of aluminium suffering from uniform corrosion attack in sodium hydroxide. Comparing Figures 4.10 (a) and (b) it is observed that no damage is caused to the metal surface in the presence of 1.5 gL$^{-1}$ of CALE and it confirms the inhibition ability.

From the surface micrographs it is evident that the inhibition of aluminium corrosion in 1M NaOH is mainly due to the formation of protective film formed by adsorption of CALE molecules on aluminium surface and it confirms the inhibiting potential of CALE. Accordingly, it is concluded that the adsorption film of the inhibitor can effectively retard the corrosion of aluminium.
Figure 4.10. Micrographs of aluminium in a) 1M NaOH
b) 1M NaOH with 1.5gL$^{-1}$ of CALE.
4.1.1.7. Inhibitive action of Coleus aromaticus leaves extract

The inhibition mechanism of the studied inhibitor is a combination of surface blockage and electrostatic repulsion between adsorbed surface layer and the aggressive OH'ions. On accounting for the observed protective effect of a natural inhibitor examined in the form of leaves extract it should be noted that the extract comprises a mixture of organic and resinous matter. It is generally accepted that the corrosion inhibition occurs due to adsorption of organic molecules at the metal/solution interface. The adsorption of organic inhibitor molecules from the aqueous solution is a substitution adsorption process between the organic compound in the aqueous phase [\text{Org}_{(sol)}] and water molecules on the metal surface [\text{H}_2\text{O}_{(ads)}].

\[
\text{M(nH}_2\text{O)}_{(ads)} + 1 \rightarrow \text{M}_{(ads)} + \text{nH}_2\text{O}_{(sol)}
\]

where x is the size ratio, the number of water molecules replaced by one organic inhibitor.

Preliminary phytochemical analysis of CALE carried out for the leaves extract revealed the presence of alkaloids, glycosides, flavonoids, and phenolic compounds. Leaves of Coleus aromaticus are reported to contain carvacrol, β-carophyllene, caffeic acid, chlorogenic acid, salvegenin, luteolin, and apigenin as major phytochemical constituents [54]. The various phytoconstituents of Coleus aromaticus make it rather difficult to predict the inhibiting action to a particular constituent or group of constituents. A close examination of the structure of chief constituents of Coleus aromaticus such as carvacrol, β-carophyllene, caffeic acid, chlorogenic acid, salvegenin, luteolin, and apigenin reveals that these active principles are mainly responsible for the corrosion inhibition process [55]. Figure 4.11. shows the structures of the various active components present in CALE.
Figure 4.11. Structures of active components present in Coleus aromaticus.

The reason being these compounds contain phenolic groups, -C-O, C=C, C-H groups, and aromatic rings which fulfill the general requirements of typical corrosion inhibitors. The adsorption of these compounds on Al surface reduces the surface area that is available for the attack of the aggressive ion from the alkaline medium. Therefore the inhibition potential of CALE is due to the synergistic effect of the active principles that are involved in the adsorption process on aluminium surface. Studies have shown that plant extracts that contain flavonoids, alkaloids, tannins, triterpenoids, saponins, amino acids, phenols, glycosides, essential oils and carotenoids can be used as corrosion inhibitors. It is therefore expected that the presence of naturally occurring metal-binding compounds of interest such as carvacrol, β-carophyllene, caffeic acid, chlorogenic acid, salvegenin, luteolin, and apigenin in CALE along with other constituents be responsible for the inhibition of corrosion of aluminium in 1M NaOH. The adsorbate inhibitor molecules on the metal surface constitute a barrier to charge and mass transfer between the metal and the corrodent and thus protect the metal surface from corrosion attack.
4.1.8. Comparison of inhibition efficiency of CALE

The inhibition efficiency values obtained in all the four techniques adopted to test the effectiveness of the inhibitor for aluminium corrosion in 1M NaOH are found to be in good agreement. The inhibition efficiency values are given in Table 4.10. The inhibition efficiency determined by the four different methods increases with increase in the concentration of the inhibitor and the trend obtained from chemical and electrochemical measurements are comparable and run parallel with one another.

It is concluded that the corrosion rate depends on the chemical nature of the aggressive medium rather than the applied technique. It also indicates the validity of the results. Thus the protection efficiency of CALE against aluminium corrosion in sodium hydroxide solution has been proved.

Table 4.10. Comparison of inhibition efficiency of CALE

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration of CALE (g/L)</th>
<th>Inhibition efficiency (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Weight loss</td>
<td>Hydrogen evolution</td>
<td>Tafel extrapolation</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>0.3</td>
<td>77.3</td>
<td>78.32</td>
<td>79.5</td>
<td>78.1</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>84.7</td>
<td>84.07</td>
<td>86.7</td>
<td>84.5</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>88.5</td>
<td>87.17</td>
<td>87.5</td>
<td>89.4</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>91.8</td>
<td>90.07</td>
<td>88.9</td>
<td>92.4</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>92.7</td>
<td>92.03</td>
<td>89.7</td>
<td>92.6</td>
</tr>
</tbody>
</table>
4.2. Corrosion inhibition of aluminium in alkaline medium with Solanum nigrum leaves extract (SNLE)

4.2.1. Weight loss measurements

4.2.1.1. Corrosion rate and inhibition efficiency

The weight loss results obtained for the corrosion of aluminium specimen for different concentrations of the Solanum nigrum leaves extract (SNLE) in 1M NaOH solution at 303 ± 0.5 K are given in Table 4.11. The results revealed that weight loss values of aluminium in 1M NaOH solution containing SNLE decreased as the concentration of inhibitor is increased. Inspection of the Table 4.11. reveals that the variation of the corrosion parameters for different concentration of SNLE is consistent with each other. The corrosion inhibition of SNLE strengthened with the increase in concentration. As concentration increases more inhibitor molecules are adsorbed on the metal surface, thus resulting in larger surface coverage. The inhibition efficiency increases with increase in extract concentration and reaches a maximum value of 86.18% with 1.5 g/L extract concentration. It denotes that the dissolution of aluminium decreases with increase in concentration of extract. The corrosion inhibition can be attributed to adsorption of inhibitor molecules such as alkaloids, flavanoids, and tannins present in the phytoconstituents of SNLE on aluminium surface. Several factors could contribute to this, which includes the presence of a mixture of organic and resinous matter in the extract composition [56, 57].

Table 4.11. Corrosion parameters for aluminium in 1M NaOH solution containing various concentrations of SNLE at 303 K.

<table>
<thead>
<tr>
<th>Concentration of SNLE (gL⁻¹)</th>
<th>Weight loss (gcm⁻²)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
<th>Surface coverage (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0557</td>
<td>207.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0123</td>
<td>41.53</td>
<td>77.91</td>
<td>0.78</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0116</td>
<td>35.93</td>
<td>79.17</td>
<td>0.79</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0097</td>
<td>30.73</td>
<td>82.58</td>
<td>0.82</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0084</td>
<td>22.04</td>
<td>84.92</td>
<td>0.85</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0077</td>
<td>12.64</td>
<td>86.18</td>
<td>0.86</td>
</tr>
</tbody>
</table>
The inhibition efficiency increases with increase in extract concentration and reaches a maximum value of 86.18% with 1.5 g/L extract concentration. The adsorption of these compounds on the aluminium surface reduces the surface area available for the attack of the aggressive OH\textsuperscript{-} ions from the alkaline solution for corrosion. The degree of protection increases with increase in extract concentration due to a higher degree of surface coverage resulting from enhanced inhibitor adsorption. The increase in inhibition efficiency tends to saturate at higher concentration of SNLE because there is no much difference at higher concentrations.

4.2.1.2. Effect of immersion time

Table 4.12. displays the weight loss of aluminium in 1M NaOH without and with SNLE for different immersion period. From these data, it is clear that the weight loss (and hence the rate of corrosion) of aluminium enhances with the immersion time. Initially the rate of aluminium dissolution is slow and then it increases with the immersion time as seen from the increasing weight loss and it is attributed to disappearance of the inhibitor film formed on the metal surface. Weight loss vs time plot given in Figure 4.12. shows that SNLE inhibits aluminium corrosion in the alkaline environment. Rate of corrosion in inhibited systems decreased with increasing concentration of SNLE suggesting that the inhibiting effect of the extract on aluminium corrosion is concentration dependent. The % inhibition increases with concentration due to the increase in the surface area covered with the additive [58].

Table 4.12. Effect of immersion time on aluminium corrosion rate in free and inhibited 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of S \textsuperscript{1}LE (gL\textsuperscript{-1})</th>
<th>Weight loss (g/cm\textsuperscript{2})</th>
<th>1(h)</th>
<th>2(h)</th>
<th>3(h)</th>
<th>4(h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td>0.0557</td>
<td>0.1258</td>
<td>0.2968</td>
<td>0.3245</td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td>0.0123</td>
<td>0.0319</td>
<td>0.0805</td>
<td>0.0988</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>0.0116</td>
<td>0.0291</td>
<td>0.0745</td>
<td>0.0964</td>
</tr>
<tr>
<td>0.9</td>
<td></td>
<td>0.0097</td>
<td>0.0249</td>
<td>0.0612</td>
<td>0.0897</td>
</tr>
<tr>
<td>1.2</td>
<td></td>
<td>0.0084</td>
<td>0.0220</td>
<td>0.0593</td>
<td>0.0773</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>0.0077</td>
<td>0.0207</td>
<td>0.0507</td>
<td>0.0708</td>
</tr>
</tbody>
</table>
4.2.1.3. Effect of temperature

Temperature study is carried out to get more information about the effectiveness of SNLE at higher temperatures, the nature of adsorption and thereafter to evaluate the activation process. Weight loss measurements are done in the temperature range of 303 – 333 K, without and with inhibitor at different concentrations during 1 h immersion period. From Table 4.13, it is clear the increase in temperature leads to an increase in the corrosion rate of aluminium without or with inhibitor. It also shows that inhibition efficiency (% IE) decreased with increasing temperature as a result of fast dissolution of aluminium at higher temperature.

This may be attributed to the fact that a higher temperature could quench the inhibitor performance to a large extent and this suggests physical adsorption mechanism of SNLE on aluminium surface. Activation energy, E_a is calculated with the help of the Arrhenius plot shown in Figure 4.13.
Figure 4.13. Arrhenius plot for aluminium corrosion in 1M NaOH in the presence of SNLE.

Table 4.13. Effect of temperature on aluminium corrosion rate in free and inhibited 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of SNLE (g/L)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>0.3</td>
<td>80.0</td>
</tr>
<tr>
<td>0.6</td>
<td>82.7</td>
</tr>
<tr>
<td>0.9</td>
<td>85.2</td>
</tr>
<tr>
<td>1.2</td>
<td>89.4</td>
</tr>
<tr>
<td>1.5</td>
<td>93.9</td>
</tr>
</tbody>
</table>
Higher $E_a$ values in the presence of the inhibitor compound compared to that in the blank solution indicates that the inhibitor will be effective at ordinary temperature but the efficiency will be considerably diminished at higher temperatures. It also suggests that the process is activation controlled [59, 60]. Enthalpy of activation ($\Delta H^*$) and entropy of activation ($\Delta S^*$) are calculated from the slope and intercept of the line obtained by plotting $\ln CR/T$ versus $1/T$ shown in Figure 4.14. The values of $E_a$, $\Delta H^*$ and $\Delta S^*$ for aluminium corrosion in 1M NaOH in presence and absence of different concentrations of SNLE are given in Table 4.14. It can be seen from the Table 4.14. that the activation parameters $\Delta H^*$ and $\Delta S^*$ of aluminium dissolution reaction in 1M NaOH are higher in the presence of SNLE than in the absence of extract. The positive values of enthalpy reflect the endothermic nature of aluminium dissolution process. The large and negative values of entropy imply the decrease in disordering takes place on moving from reactants to activated complex. Orderliness increases as reactants are converted to activated complex [61, 62].

<table>
<thead>
<tr>
<th>Concentration of SNLE (gL$^{-1}$)</th>
<th>$E_a$(kJ mol$^{-1}$)</th>
<th>$\Delta H^*$(kJ mol$^{-1}$)</th>
<th>$\Delta S^*$(JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>50.78</td>
<td>52.93</td>
<td>25.92</td>
</tr>
<tr>
<td>0.3</td>
<td>67.38</td>
<td>72.76</td>
<td>-27.09</td>
</tr>
<tr>
<td>0.6</td>
<td>70.81</td>
<td>72.53</td>
<td>-25.72</td>
</tr>
<tr>
<td>0.9</td>
<td>73.71</td>
<td>75.94</td>
<td>-35.46</td>
</tr>
<tr>
<td>1.2</td>
<td>76.89</td>
<td>78.64</td>
<td>-43.28</td>
</tr>
<tr>
<td>1.5</td>
<td>88.56</td>
<td>79.01</td>
<td>-43.8</td>
</tr>
</tbody>
</table>
4.2.1.4. Adsorption isotherms

Since it is important to understand the inhibition mechanism the adsorptive behaviour of an inhibitor must be well described with the help of an adsorption isotherm study. Basic information about the interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm. The degree of surface coverage values for various concentrations of SNLE from the weight loss measurements obtained are used to determine the adsorption characteristics of SNLE in 1M NaOH solution. Different adsorption isotherms are tested to fit the surface coverage data obtained from weight loss data to understand the mechanism of adsorption. The experimental data fitted well with Langmuir adsorption isotherm as shown in Figure 4.15. and the adsorption parameters are given in Table 4.15. The negative values of $\Delta G_{ads}^0$ obtained indicate the spontaneous adsorption of the inhibitor and are usually characteristic of strong interaction with the metal surface. It is found that the $\Delta G_{ads}$ values are less than $-40$KJ/mole indicating that inhibitor molecules are physically adsorbed on the metal surface [63].

Figure 4.14. Plot of ln CR/T vs 1/T for aluminium corrosion in 1M NaOH in the presence of SNLE.
Figure 4.15. Langmuir adsorption isotherm for SNLE on aluminium in 1M NaOH solution at different temperature.

Table 4.15. Adsorption parameters for SNLE on aluminium in 1M NaOH at different temperatures.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T (K)</th>
<th>$K_{ads}$</th>
<th>$\Delta G_{ads}$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303</td>
<td>14.85</td>
<td>16.92</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>313</td>
<td>11.48</td>
<td>16.81</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>10.69</td>
<td>17.15</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>7.05</td>
<td>16.53</td>
</tr>
</tbody>
</table>
4.2.2. Gasometric technique

Figure 4.16. shows the variation of the volume of hydrogen gas evolved as a function of time when an aluminium specimen reacts with 1M NaOH in presence of different concentrations of SNLE. The volume of the hydrogen gas evolved is characterized by a sharp rise and approximately linear increase for the blank solution. The curves obtained in the presence of SNLE displayed a marked reduction in the rate of hydrogen evolution. The straight lines obtained for the inhibitor shown in Figure 4.16. indicate immediate breakdown of the oxide film in alkaline medium and absence of incubation period. Increase in inhibition efficiency values are obtained for increasing concentrations of SNLE [64, 65].

![Volume-time curve for aluminium in 1M NaOH solution with SNLE at room temperature.](image)

Figure 4.16. Volume-time curves for aluminium in 1M NaOH solution with SNLE at room temperature.
Table 4.16. Variation of hydrogen evolution with concentration of SNLE for aluminium corrosion in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of SNLE (gL⁻¹)</th>
<th>Volume of hydrogen evolution (mL/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>22.7</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>6.1</td>
<td>73.12</td>
</tr>
<tr>
<td>0.6</td>
<td>5.5</td>
<td>75.77</td>
</tr>
<tr>
<td>0.9</td>
<td>4.5</td>
<td>80.17</td>
</tr>
<tr>
<td>1.2</td>
<td>3.2</td>
<td>85.9</td>
</tr>
<tr>
<td>1.5</td>
<td>3.0</td>
<td>86.78</td>
</tr>
</tbody>
</table>

4.2.3. Polarisation curves

Polarisation curves of aluminium corrosion in 1M NaOH solution without and with different concentrations of SNLE are shown in Figure 4.17. It can be observed that both the anodic and cathodic reactions are suppressed by the addition of SNLE. It suggests that the inhibitor exerted an efficient inhibitory activity both on anodic dissolution of metal and on cathodic hydrogen reduction reaction. Most of the inhibitor molecules adsorbed on the anodic active sites at low concentration of SNLE. However at high concentrations of the inhibitor, the remaining molecules blocked other sites of the electrode, and the inhibition is achieved by geometric blocking. The corrosion current density decreases to a greater extent by the addition of SNLE. Electrochemical parameters such as $E_{corr}$, $I_{corr}$, anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$) are obtained from polarization studies. It can be seen from Table 4.17. that the corrosion potential is not shifted significantly in the presence of the extract. Cathodic Tafel slopes are larger than 120mV/decade, while the anodic Tafel slopes are much higher. The reason probably lies in the growth and dissolution of surface film on the electrode and the reaction of the subvalent aluminum ion ($\text{Al}^+$ or $\text{Al}^{2+}$). A model is proposed by Macdonald et al., [66, 67] to explain the electrochemical features of aluminum in concentrated alkaline media. Adsorbed $\text{Al(OH)}_n$ (n < 3) species are envisaged as intermediates. It indicates that SNLE controls both anodic and cathodic reactions to inhibit the corrosion of aluminium by blocking active sites on the aluminium surface. Hence it is inferred that the inhibition action is of mixed type with predominant anodic action.

111
Potential / V vs SCE

Figure 4.17. Polarization curves for aluminium in 1M NaOH without and with SNLE

Table 4.17. Polarisation parameters for aluminium corrosion in 1M NaOH in the absence and presence of SNLE.

<table>
<thead>
<tr>
<th>Concentration of SNLE (gL⁻¹)</th>
<th>-E&lt;sub&gt;corr&lt;/sub&gt; (mV)</th>
<th>I&lt;sub&gt;corr&lt;/sub&gt; (mA/cm²)</th>
<th>Tafel slope (mV/decade)</th>
<th>Corrosion rate (mpmy)</th>
<th>I.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>β&lt;sub&gt;a&lt;/sub&gt;</td>
<td>β&lt;sub&gt;c&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>158.8</td>
<td>5.421</td>
<td>313</td>
<td>185</td>
<td>209.01</td>
</tr>
<tr>
<td>0.3</td>
<td>158.02</td>
<td>1.159</td>
<td>232</td>
<td>167</td>
<td>44.93</td>
</tr>
<tr>
<td>0.6</td>
<td>157.97</td>
<td>1.071</td>
<td>240</td>
<td>170</td>
<td>41.30</td>
</tr>
<tr>
<td>0.9</td>
<td>157.65</td>
<td>0.9234</td>
<td>229</td>
<td>174</td>
<td>35.61</td>
</tr>
<tr>
<td>1.2</td>
<td>156.29</td>
<td>0.9090</td>
<td>235</td>
<td>159</td>
<td>35.05</td>
</tr>
<tr>
<td>1.5</td>
<td>155.77</td>
<td>0.8299</td>
<td>236</td>
<td>163</td>
<td>32.00</td>
</tr>
</tbody>
</table>
The inverse relationship between the corrosion current density and polarisation resistance \( (R_p) \), with the increasing concentration of the SNLE, suggests that the adsorption of the inhibitor molecules on metal/solution interface makes a physical barrier for the mass and charge transfer. Thus a high degree of protection is given to the metal surface at 1.5 gL\(^{-1}\) concentration of SNLE.

4.2.4. AC impedance measurements

The corrosion behaviour of aluminium in 1M NaOH in the absence and presence of SNLE is investigated by AC impedance method to find out the charge transfer resistance \( (R_a) \) and double layer capacitance \( (C_d) \). Figure 4.19. shows the Nyquist plots for aluminium in 1M NaOH in the absence and presence of different concentrations of SNLE. The corresponding impedance parameters are given in Table 4.18.

Impedance plots are semicircles both in the absence and in the presence of the inhibitor. The plots show that the impedance changes according to the change in inhibitor concentration. It can be seen from the figure that the obtained Nyquist plots are almost semicircle in nature with a high frequency loop followed by an inductive loop at the low frequency region. The semicircular nature of the Nyquist plot is due to the charge transfer process which mainly controls the corrosion of aluminium and to the formation of oxide layer. The oxide film is assumed to be a parallel circuit of a resistor due to the ionic conduction in the oxide film and a capacitor due to its dielectric properties. The low frequency inductive loop is due to the growth and dissolution of the surface film. In fact the presence of SNLE enhanced the value of \( R_a \) in alkaline solution. The values of double layer capacitance are brought down to the maximum extent in the presence of inhibitor. The maximum \( R_a \) value of is obtained at the concentration of 1.5 gL\(^{-1}\) of SNLE [68].

The recorded impedance values are found to increase with increasing the inhibitor concentration indicating that the metal surface is more protected. It is important to develop the appropriate circuit model for the impedance which can be used to fit the experimental data and determine the parameters which characterize the corrosion process.
The equivalent circuit model used to fit the experimental data is shown in Figure 4.18. In the electric circuit $C_{dl}$ is double layer capacitance, $R_{ct}$ is the interfacial charge transfer resistance and $R_s$ is the solution resistance. The numerical values of $R_{ct}$ and $C_{dl}$ are determined by analysis of complex plane impedance plot and the equivalent circuit model by means of a computer program.

Figure 4.18. Equivalent electric circuit for the electrochemical cell.
Figure 4.19. Nyquist plot for aluminium in 1M NaOH without and with different concentrations of SNLE.

Table 4.18. Electrochemical impedance parameters for aluminium in 1M NaOH solution in the absence and presence of different concentrations of SNLE.

<table>
<thead>
<tr>
<th>Concentration of SNLE (gL⁻¹)</th>
<th>R_{cl} (Ω cm²)</th>
<th>C_{dl} (µF/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.09</td>
<td>88.76</td>
<td>----</td>
</tr>
<tr>
<td>0.3</td>
<td>14.17</td>
<td>10.61</td>
<td>78.17</td>
</tr>
<tr>
<td>0.6</td>
<td>15.84</td>
<td>9.61</td>
<td>80.47</td>
</tr>
<tr>
<td>0.9</td>
<td>17.34</td>
<td>8.40</td>
<td>82.16</td>
</tr>
<tr>
<td>1.2</td>
<td>19.68</td>
<td>6.55</td>
<td>84.28</td>
</tr>
<tr>
<td>1.5</td>
<td>21.89</td>
<td>5.26</td>
<td>85.87</td>
</tr>
</tbody>
</table>
4.2.5. FT-IR spectral analysis

The adsorption film of SNLE on aluminium is further confirmed by comparing the IR spectra of vacuum dried SNLE with the spectra of its adsorbed film over aluminium surface in 1M NaOH for 1 h immersion period. Identification of different functional groups from the IR spectra (Figures 4.20.a & b) enables to understand the adsorption mechanism. The FT-IR analysis of SNLE reveals the presence of different functional groups ranging from 4000 to 400 wave number. Figure 4.20.(a) revealed the presence of C=O, C-H, C≡C and C-O bond stretching. Generally O-H stretching will be present in all phenolic compounds and C-N is commonly found in all types of alkaloids. The spectral data are in good agreement with the previous reports on Solanum nigrum [69].

The peaks in the range 500 – 800 cm⁻¹ correspond to C-H out of plane bending. A peak at 1617 cm⁻¹ is assigned to C≡C stretching. The peaks in the range of 1000-1300 cm⁻¹ indicate the presence of C-O stretching. The peak at 1617 cm⁻¹ is assigned to C-C stretching of alkyl group. The absorption bands below 1000 cm⁻¹ correspond to aliphatic and aromatic C–H group. From Figure 4.20.(b) it is clear that changes occur in the intensity of the main bands of Al- SNLE sample and shift in the peak positions are also noticed. These FT-IR measurements indicated that Al³⁺ on the surface of the sample can bond directly with SNLE molecules via O and N atoms and form Al(SNLE)₃ films on the sample [70-72]. FT-IR spectra indicate that SNLE contains O and N atoms in functional groups (O-H, C-N, C-O-C) that are involved in corrosion inhibition activity.
Figure 4.20. (a) FT-IR spectrum of SNLE powder
Figure 4.20. (b) FT-IR spectrum of SNLE film on aluminium
(after immersion for 1h in IM NaOH + 1.5gL⁻¹ SNLE).
4.2.6. Surface examination

The changes in surface topographies of the aluminium specimen due to corrosion process before and after SNLE addition are examined using metallurgical microscope. Figures 4.21.(a) and (b) show the variation in the surface structure due to corrosion inhibition of aluminium surface by SNLE.

Figure 4.21 (a) shows the image of metal surface with corrosion products formed on it. In the presence of SNLE (Figure 4.21.b) the metal surface is devoid of ridges and corrosion products. The protective coating film seen on aluminium surface is attributed to the corrosion resistance of the metal. Hence these images reveal the fact that the adsorbed inhibitor film present on the aluminium surface controlled the dissolution of the base metal effectively.
Figure 4.21. Micrographs of aluminium exposed to (a) 1M NaOH (b) 1M NaOH solution with 1.5 gL$^{-1}$ of SNLE.
4.2.7. Explanation for corrosion inhibition behaviour of SNLE

The qualitative screening tests carried out for the phytochemical constituents of leaf extract of Solanum nigrum showed positive results for alkaloids, saponins, and proteins. The presence of these phytochemicals in SNLE are supported by other reports [73, 74]. The inhibition behaviour can be explained by considering the interaction of the inhibitor molecules with the metal. The adsorption of inhibitor molecules are greatly influenced by their molecular weight, structure, steric and electronic effects. The major constituent present in the leaves of SNLE are the steroidal alkaloid solasodine found in the family Solanaceae especially genus Solanum. Inspection of the chemical structures shown in Figure 4.22. revealed that the compound can adsorb on the aluminium surface via the lone pair of electrons present on their oxygen and nitrogen atoms. Corrosion inhibition is attributed to the formation of protective film by adsorption of these molecules of SNLE onto the aluminium surface [75].

![Chemical structures of Solasodine and Diosgenin](image)

Figure 4.22. Active principles of SNLE.

4.2.8. Comparison of inhibition efficiency of SNLE

The inhibition efficiency determined by the four different techniques increases with increase in concentration of the inhibitor. From Table 4.19, it is clear that the different techniques gave good agreement as to the order of inhibition of SNLE concentration. Slight variation in the values may be due to the difference in the working conditions under which each technique is carried out. It is therefore
concluded that SNLE acts as a potential corrosion inhibitor for aluminium in alkaline medium.

Table 4.19. Comparison of inhibition efficiency of SNLE.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration of SNLE (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
<td>Hydrogen evolution</td>
</tr>
<tr>
<td>0.3</td>
<td>77.91</td>
<td>73.12</td>
</tr>
<tr>
<td>0.6</td>
<td>79.17</td>
<td>75.77</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>0.9</td>
<td>82.58</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>84.92</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>86.18</td>
</tr>
</tbody>
</table>

4.3. Corrosion inhibition of aluminium in alkaline medium using Moringa oleifera leaves extract (MOLE)

4.3.1. Weight loss measurements

4.3.1.1. Corrosion rate

The weight loss results of the aluminium specimens in 1M NaOH without and with various concentrations of the leaves extract after 1h immersion are given in Table 4.20. Aluminium specimen corroded very fast in 1M NaOH and showed very high corrosion rate with large weight loss. Corrosion rate of aluminium is found to decrease when the concentration of inhibitor increased and correspondingly an increase in inhibition efficiency of the extract is noticed. A maximum inhibition efficiency of 84% is obtained for 1.5 gL⁻¹ concentration of the extract. The increase in inhibition efficiency obtained at higher inhibitor concentrations indicate that the adsorption process enhances with increasing additive concentration. Furthermore it reveals that more inhibitor molecules and their complexes are adsorbed on the aluminium/solution interface, thus blocking the available surface area from the action of the corrodent [76].
Table 4.20. Corrosion parameters of aluminium in 1M NaOH with various concentrations of MOLE.

<table>
<thead>
<tr>
<th>Concentration of MOLE (gL⁻¹)</th>
<th>Weight loss (gcm⁻²)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
<th>Surface coverage (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0527</td>
<td>140.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0202</td>
<td>53.72</td>
<td>61.5</td>
<td>0.61</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0172</td>
<td>45.74</td>
<td>67.2</td>
<td>0.67</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0133</td>
<td>35.37</td>
<td>74.7</td>
<td>0.74</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0108</td>
<td>28.72</td>
<td>79.5</td>
<td>0.79</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0084</td>
<td>22.34</td>
<td>84.0</td>
<td>0.84</td>
</tr>
</tbody>
</table>

4.3.1.2. Effect of immersion time

Figure 4.23. shows the variation of weight loss with time for the corrosion of aluminium in 1M NaOH in the absence and presence of MOLE. The curves obtained by plotting weight loss versus time displayed the gradual increase in weight loss that occurred for the increasing immersion time. Corrosion inhibition of aluminium in strong alkaline solutions is hindered by the high rates of hydrogen gas evolution from the corrosion reaction. With increasing immersion time hydrogen gas evolution results in agitation of the solution which prevents the adsorption of the inhibitor at the metal/solution interface. So the surface covered by the inhibitor molecules is low and the inhibition efficiency is also low. At higher concentrations, surface coverage is higher and the adsorption film is thick and becomes insoluble. The decrease in weight loss is significant at low concentration of MOLE but it varied only slightly at higher concentrations [77]. The data obtained for variation of weight loss with increasing time is given in Table 4.21. The decrease in inhibition efficiency for increasing immersion time is depicted in Figure 4.24.
Table 4.21. Effect of immersion time on corrosion rate of aluminium in 1M NaOH and inhibited with MOLE.

<table>
<thead>
<tr>
<th>Concentration of MOLE (gL⁻¹)</th>
<th>Weight loss (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1(h)</td>
</tr>
<tr>
<td>Blank</td>
<td>0.0527</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0202</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0172</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0133</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0108</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0084</td>
</tr>
</tbody>
</table>

Figure 4.23. Variation of weight loss with time for aluminium corrosion in 1M NaOH and inhibited solution.
4.3.1.3. Effect of temperature

Temperature has more pronounced effect on the electrochemical corrosion reaction of aluminium. Corrosion rate increases exponentially with temperature and corrosion reactions are considered as Arrhenius processes. Figure 4.25. represents the Arrhenius plot drawn for the corrosion of aluminium in 1M NaOH in the absence and presence of MOLE. The increase in corrosion rate and decrease in inhibition efficiency may be attributed to possible shift of the adsorption-desorption equilibrium towards desorption of adsorbed inhibitor due to increased solution agitation. The results obtained for the effect of temperature on inhibition efficiency are given in Table 4.22. Therefore as temperature increases there is an increased rate of desorption leading to decrease in inhibition efficiency. It is also considered that the whole process is governed by surface reaction because the $E_a$ values obtained for the corrosion process in the absence and presence of MOLE are greater than 20 kJ mol$^{-1}$ [78].

Figure 4.24. Variation of inhibition efficiency of MOLE with time for aluminium corrosion in 1M NaOH at 303 K.
Table 4.22. Effect of temperature on aluminium corrosion rate in 1M NaOH solution containing various concentrations of MOLE.

<table>
<thead>
<tr>
<th>Concentration of MOLE (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>303K 313K 323K 333K</td>
</tr>
<tr>
<td>0.6</td>
<td>61.54 51.07 43.56 34.01</td>
</tr>
<tr>
<td>0.9</td>
<td>67.21 56.27 48.27 39.55</td>
</tr>
<tr>
<td>1.2</td>
<td>74.75 64.99 56.73 47.17</td>
</tr>
<tr>
<td>1.5</td>
<td>79.46 70.08 62.91 53.26</td>
</tr>
<tr>
<td></td>
<td>83.92 74.11 68.44 59.48</td>
</tr>
</tbody>
</table>

Figure 4.25. Arrhenius plot for aluminium corrosion in 1M NaOH in the absence and presence of MOLE.
The enthalpy and entropy values for the activation process are calculated using transition state equation and the data are given in Table 4.23. The positive sign of enthalpies reflect the endothermic nature of aluminium dissolution process. The large and negative values of entropy of activation in the absence and presence of MOLE reveal that the rate determining step for the activated complex formation involves an association step rather than dissociation. It also indicates that decrease in disorderliness takes place on moving from reactants to activated complex.

Table 4.23. Activation parameters for aluminium corrosion in 1M NaOH in the absence and presence of various concentrations of MOLE.

<table>
<thead>
<tr>
<th>Concentration of MOLE (gL(^{-1}))</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(\Delta H^*) (kJ mol(^{-1}))</th>
<th>(\Delta S^*) (JK(^{-1})mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>52.56</td>
<td>49.923</td>
<td>35.308</td>
</tr>
<tr>
<td>0.3</td>
<td>67.47</td>
<td>64.833</td>
<td>-6.096</td>
</tr>
<tr>
<td>0.6</td>
<td>69.54</td>
<td>66.905</td>
<td>-11.691</td>
</tr>
<tr>
<td>0.9</td>
<td>72.18</td>
<td>70.349</td>
<td>-20.887</td>
</tr>
<tr>
<td>1.2</td>
<td>75.18</td>
<td>72.541</td>
<td>26.449</td>
</tr>
<tr>
<td>1.5</td>
<td>77.80</td>
<td>75.164</td>
<td>-33.258</td>
</tr>
</tbody>
</table>

4.3.1.4. Adsorption isotherms

The most frequently used adsorption isotherms namely Langmuir, Temkin, Frumkin and Freundlich are tested graphically to fit the experimental data obtained from weight loss measurements. The experimental data is found to fit well with Langmuir (Figure 4.26) and Temkin (Figure 4.27) adsorption isotherms. The best fit is obtained for Langmuir adsorption model and the isotherm is used for calculating adsorption parameters. The calculated values of \(\Delta G_{ads}\) at all the temperatures studied are presented in Table 4.24. The value of \(K_{ads}\) decreases with increase in temperature, suggesting that the inhibitor is physically adsorbed on the aluminium surface and the desorption processes are enhanced at higher temperatures [79].
Table 4.24. Adsorption parameters for MOLE on aluminium in 1M NaOH at different temperatures.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T(K)</th>
<th>K_{ads}</th>
<th>-\Delta G_{ads} (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M NaOH</td>
<td>303</td>
<td>4.75</td>
<td>14.04</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.35</td>
<td>13.16</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>2.36</td>
<td>12.28</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>1.63</td>
<td>11.36</td>
</tr>
</tbody>
</table>

Figure 4.26. Langmuir adsorption isotherm for the adsorption of MOLE on aluminium in 1M NaOH.
4.3.2. Gasometric technique

Since aluminium is readily soluble in aqueous alkalis with liberation of hydrogen, the rate of aluminium dissolution in 1M NaOH is measured as a function of time. Plots of the additive solutions are found below that of the blank solution. These plots indicate that the tested inhibitor MOLE behaves as effective inhibitor. It is postulated that corrosion occurs only at the free sites of aluminium metal that are unoccupied by the inhibitor molecules. Figure 4.28. shows the effect of MOLE concentration on the volume–time curves obtained for dissolution of aluminium in 1M NaOH solution at 303 K. The % IE increases with increase in the concentration of the inhibitor and the values are given in Table 4.25. It is clear that the dissolution of aluminium increases linearly with time from the initial point, because the incubation periods are absent. The curves are typical zero order kinetic ones with a slope representing the reaction rate at any time [80, 81].
Figure 4.28. Effect of MOLE concentration on volume-time curves for aluminium in 1M NaOH.

Table 4.25. Variation of hydrogen gas evolution with concentration of MOLE for aluminium corrosion in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of MOLE (gL⁻¹)</th>
<th>Volume of hydrogen evolution (mL/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>23.3</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>9.0</td>
<td>61.37</td>
</tr>
<tr>
<td>0.6</td>
<td>8.3</td>
<td>64.37</td>
</tr>
<tr>
<td>0.9</td>
<td>6.9</td>
<td>70.38</td>
</tr>
<tr>
<td>1.2</td>
<td>6</td>
<td>74.24</td>
</tr>
<tr>
<td>1.5</td>
<td>5</td>
<td>78.54</td>
</tr>
</tbody>
</table>
4.3.3. Polarisation curves

Polarisation curves of aluminium in 1M NaOH solution without and with different concentrations of MOLE are shown in Figure 4.29. Inspection of the curves reveals that the corrosion potential shifts to less negative values upon addition the inhibitor. It is clear that corrosion potential is almost independent of inhibitor concentration. Curves of the inhibitor containing systems fall below that of the free alkali solution. It could be observed that both of the cathodic and anodic curves show lower corrosion current density for various concentrations of the inhibitor. It is obvious that both anodic and cathodic reactions are suppressed by the addition of MOLE. The electrochemical parameters such as corrosion potential ($E_{\text{corr}}$), corrosion current density ($i_{\text{corr}}$), cathodic Tafel slope ($\beta_c$), and anodic Tafel slope ($\beta_a$) obtained from polarization curves are listed in Table 4.26. The slopes of the cathodic and anodic Tafel lines show a slight change upon addition of the inhibitors and it indicates that the used inhibitor act by blocking the available surface area. Thus the inhibitor decreases the active surface area available for corrosion without affecting the mechanism of corrosion [82].
Figure 4.29. Polarisation curves of aluminium in 1M NaOH solution without and with different concentrations of MOLE.

Table 4.26. Polarisation parameters for aluminium in 1M NaOH in the absence and presence of MOLE.

<table>
<thead>
<tr>
<th>Concentration of MOLE (gL⁻¹)</th>
<th>-Ecorr (mV)</th>
<th>Icorr (mA/cm²)</th>
<th>Tafel slopes (mV/decade)</th>
<th>Rcorr mmpy</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>βc</td>
<td>βa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>158.8</td>
<td>5.421</td>
<td>185</td>
<td>313</td>
<td>209.01</td>
</tr>
<tr>
<td>0.3</td>
<td>158.7</td>
<td>2.076</td>
<td>215</td>
<td>218</td>
<td>80.04</td>
</tr>
<tr>
<td>0.6</td>
<td>158.1</td>
<td>1.881</td>
<td>198</td>
<td>218</td>
<td>72.54</td>
</tr>
<tr>
<td>0.9</td>
<td>158.1</td>
<td>1.450</td>
<td>201</td>
<td>210</td>
<td>55.90</td>
</tr>
<tr>
<td>1.2</td>
<td>157.5</td>
<td>1.203</td>
<td>196</td>
<td>206</td>
<td>46.41</td>
</tr>
<tr>
<td>1.5</td>
<td>157.3</td>
<td>1.055</td>
<td>185</td>
<td>204</td>
<td>40.69</td>
</tr>
</tbody>
</table>
The significant change in the values of anodic Tafel slope (βₐ) is probably due to the adsorption of MOLE molecules on aluminium surface. These results indicated that active components present in the extract block the available surface area for corrosion process. Addition of MOLE decreases the active surface area of corrosion without changing the mechanism of corrosion of aluminium. The inhibitor showed more effect on anodic curves than cathodic curve of the corrosion process and did not shift the corrosion potential (Eᵣ) values significantly. It suggests the inhibitor behaves as a mixed type inhibitor with predominant anodic inhibition [83].

4.3.4. Impedance measurements

The results of corrosion behaviour of aluminium in 1M NaOH solution in the absence and presence of MOLE studied at room temperature using EIS experiments are shown in Figure 4.31. as Nyquist representations.

In presence of the inhibitor MOLE, the value of Rₑₙ increases and the value of Cₐₑ decreases. The decrease in Cₐₑ shows that the adsorption process is enhanced by increasing additive concentration in alkali solution [84]. The electrochemical theory shows that Cₐₑ is proportional to the corrosion rate. The corrosion resistance of aluminium electrode is increased by the gradual increase in MOLE concentration. It is evident from Table 4.27. that increase in the value of Rₑₙ led to increase in the inhibition efficiency of MOLE. This results show good agreement with the results obtained from polarisation method. An appropriate circuit model for impedance is drawn (Figure 4.30.) to fit the experimental data to find the parameters that describe the corrosion process in solution [85].

Figure 4.30. Equivalent electrochemical cell.
Figure 4.31. Nyquist plots of aluminium in 1M NaOH without and with different concentrations of MOLE.

Table 4.27. Electrochemical impedance parameters for aluminium corrosion in 1 M NaOH solution in the absence and presence of MOLE.

<table>
<thead>
<tr>
<th>Concentration of MOLE (g/L⁻¹)</th>
<th>R_ct</th>
<th>C_dl</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.09</td>
<td>88.76</td>
<td>----</td>
</tr>
<tr>
<td>0.3</td>
<td>7.745</td>
<td>28.62</td>
<td>60.06</td>
</tr>
<tr>
<td>0.6</td>
<td>9.371</td>
<td>18.98</td>
<td>66.99</td>
</tr>
<tr>
<td>0.9</td>
<td>11.63</td>
<td>0.9725</td>
<td>73.40</td>
</tr>
<tr>
<td>1.2</td>
<td>14.12</td>
<td>0.8998</td>
<td>78.09</td>
</tr>
<tr>
<td>1.5</td>
<td>16.56</td>
<td>0.8428</td>
<td>81.32</td>
</tr>
</tbody>
</table>
4.3.5. FT-IR spectral studies.

The transmission spectra of MOLE and the stripped film after 1h immersion in 1M NaOH containing 1.5gL⁻¹ of MOLE are depicted in Figures 4.32.(a) and (b). The FT-IR spectra of the stripped film of the aluminium metal surface containing 1.5 gL⁻¹ of MOLE show significant and marked variation in absorption compared to the spectrum of pure MOLE powder. The peaks identified in the frequency range 650 – 900 cm⁻¹ are assigned as Al-O of the corrosion product and it can also be assigned to aromatic C-H bending. Comparison of the absorption bands in Figures 4.32. (a) and (b) reveals the shifting of bands from their original positions. Interactions between major functional groups of MOLE on the surface of Al are established through these shifts in the wavelength. However none of the functional groups on the MOLE spectrum are missing in the spectrum of the protection film indicating that all of them are involved in bonding with Al³⁺ on the aluminium surface. Thus FT-IR spectral analysis support the other experimental findings that aluminium corrosion inhibition in the alkaline medium is due to the adsorption of MOLE molecules on the metal surface [86, 87].

Table 4.28. FT-IR transmittance spectral data of MOLE and aluminium with MOLE protection film.

<table>
<thead>
<tr>
<th>Original frequency in MOLE</th>
<th>Shifted frequency in Al with MOLE protection film</th>
<th>Possible groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>668.48, 604.72</td>
<td>400-700</td>
<td>C–H bending</td>
</tr>
<tr>
<td>887.23, 840.11</td>
<td>841.54</td>
<td>C–N stretching</td>
</tr>
<tr>
<td>1077.33</td>
<td>1078.15</td>
<td>C–O stretching,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=S stretching</td>
</tr>
<tr>
<td>1419.48</td>
<td>1388.41</td>
<td>C–N stretch</td>
</tr>
<tr>
<td>1635.88</td>
<td>1609.96</td>
<td>C=O stretch,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=N stretch</td>
</tr>
<tr>
<td>3169.23</td>
<td>3411.58</td>
<td>O–H stretch or</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N–H stretch</td>
</tr>
</tbody>
</table>
Figure 4.32. FT-IR transmittance spectrum of (a) MOLE
Figure 4.32. FT-IR transmittance spectrum of (b) MOLE film stripped from aluminium surface.
4.3.6. Surface study

Metallurgical microscope images of the surface of the samples taken before and after the inhibition process are given in Figure 4.33. (a) and (b). Deep corrosion and considerable loss of the surface material is observed when aluminium specimen is immersed in 1M NaOH as shown in Figure 4.33.(a). Surface morphology is retained up to marked extent by the inhibitor film formed on the surface (Figure 4.33. b) which prevents the attack of the aggressive anions of the solution. Thus a significant reduction in the loss of surface material is noticed when the specimen is subjected to corrosion process in presence of inhibitor (1.5gL⁻¹) for the same period as carried out with free alkali.
Figure 4.33. Microscopic images for surface morphology of aluminium a) after corrosion in 1M NaOH and b) in the presence of MOLE (1.5gL⁻¹) in 1M NaOH.
4.3.7. Corrosion inhibition of aluminium by MOLE

Generally inhibitive action of the leaves extract is attributed to the presence of certain organic compounds containing nitrogen, oxygen, and/or sulphur atoms in a conjugated system that are available in the phytoconstituents of the aqueous leaves extracts. The phytochemical constituents present in MOLE, mainly the alkaloids, flavonoids, anthocyanins, proanthocyanins and cinnamates [88] enabled the leaves extract to act as an adsorption inhibitor. The inhibition efficiency of MOLE depends on the number of adsorption sites and their basicity. It is clear that the hetero centers O, N, and S of the alkaloids, flavonoids, anthocyanins, and saponins are the sites that are responsible for the adsorption of MOLE on aluminium surface.

![Structures](image)

Figure 4.34. Structures of active principles of Moringa oleifera.
4.3.8. Comparison of inhibition efficiency of MOLE

Inspection of Table 4.29 shows that inhibition efficiency obtained for MOLE from electrochemical and non-electrochemical methods ranges range from 60% to 84% for the corrosion of aluminium in 1M NaOH solution. The values obtained from the four different methods are in good correlation with each other.

The little discrepancies noticed may be accounted for the specific experimental conditions that are included for the particular measurement. Thus the corrosion resistance of aluminium in alkaline solution is enhanced to a greater extent in the presence of MOLE inhibitor.

Table 4.29. Inhibition efficiency of MOLE

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration of MOLE (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
<td>Hydrogen evolution</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>0.3</td>
<td>61.5</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>67.2</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>79.5</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>84.0</td>
</tr>
</tbody>
</table>
4.4. Corrosion inhibition of aluminium in alkaline medium using Vitex negundo leaves extract (VNLE)

4.4.1. Weight loss measurements

The weight loss results obtained for the corrosion of aluminium specimen for different concentrations of the Vitex negundo leaves extract (VNLE) in 1M NaOH solution at 303 ± 0.5 K are given in Table 4.30. It is observed that the used inhibitor retards the corrosion rate of aluminium in 1M NaOH at all concentrations under study. Corrosion rate is found to depend up on concentration of VNLE and IE (%) increases with increase in concentration [91].

Table 4.30. Corrosion parameters for aluminium in 1M NaOH solution in the absence and presence of VNLE at 303 K.

<table>
<thead>
<tr>
<th>Concentration of VNLE (gL⁻¹)</th>
<th>Corrosion rate (mm/year)</th>
<th>Inhibition efficiency (%)</th>
<th>Surface coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M NaOH</td>
<td>212.21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>93.34</td>
<td>56.0</td>
<td>0.56</td>
</tr>
<tr>
<td>0.6</td>
<td>83.23</td>
<td>60.7</td>
<td>0.60</td>
</tr>
<tr>
<td>0.9</td>
<td>71.80</td>
<td>66.1</td>
<td>0.66</td>
</tr>
<tr>
<td>1.2</td>
<td>63.29</td>
<td>70.1</td>
<td>0.70</td>
</tr>
<tr>
<td>1.5</td>
<td>46.27</td>
<td>78.1</td>
<td>0.78</td>
</tr>
</tbody>
</table>

4.4.1.1. Effect of immersion time

Figure 4.35 shows plots of weigh loss versus time in 1M NaOH without and with VNLE at 303 ± 0.5 K. and the variation in inhibition efficiency of different concentrations of VNLE for increasing immersion time. The results show that the weight loss in uninhibited and inhibited solutions increased with time (Table 4.31). The curves of inhibited solutions showed similar trend for the increasing concentration and increasing immersion time [92]. The inhibition efficiency of VNLE decreased with increase in immersion time and the plot is shown in Figure 4.36. The curves fall one below another for increasing concentration of VNLE.

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Table 4.31. Effect of immersion time on inhibition efficiency of VNLE for aluminium corrosion in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of VNLE (g L(^{-1}))</th>
<th>Weight loss (g / cm(^2))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1h</td>
<td>2h</td>
</tr>
<tr>
<td>Blank</td>
<td>0.0798</td>
<td>0.1491</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0351</td>
<td>0.0693</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0313</td>
<td>0.0614</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0270</td>
<td>0.0532</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0238</td>
<td>0.0453</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0174</td>
<td>0.0356</td>
</tr>
</tbody>
</table>

Figure 4.35. Plot of weight loss against time for aluminium corrosion in 1M NaOH without and with VNLE at 303 K
Figure 4.36. Effect of immersion time on inhibition efficiency of VNLE.

4.4.1.2. Effect of temperature

The effect of temperature on inhibition efficiency of the inhibitor was determined for 1M NaOH containing 0.3, 0.6, 0.9, 1.2, and 1.5g/L of the leaves extract at different temperature ranging from 303 to 333 K. Inhibition efficiency decreases with increasing temperature as a result of fast dissolution of aluminium at higher temperature. The film on aluminium surface varies with temperature and becomes thinner at higher temperatures. So it becomes easier for the transfer of OH\(^{-}\) ions thorough the film and hence rate of aluminium dissolution is increased and the effect is shown in Figure 4.37 [93, 94].

Figure 4.37 Variation of inhibition efficiency and VNLE concentration at 303-333 K.
Table 4.32. Effect of temperature on inhibition efficiency of VNLE for aluminium corrosion in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of VNLE (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>0.3</td>
<td>56.0</td>
</tr>
<tr>
<td>0.6</td>
<td>60.7</td>
</tr>
<tr>
<td>0.9</td>
<td>66.1</td>
</tr>
<tr>
<td>1.2</td>
<td>70.1</td>
</tr>
<tr>
<td>1.5</td>
<td>78.1</td>
</tr>
</tbody>
</table>

Figure 4.38. Arrhenius plot for aluminium corrosion in 1M NaOH and inhibited solution.
Figure 4.39. Transition state plot for aluminium corrosion in 1M NaOH and inhibited solution.

Table 4.33. Activation parameters obtained for various concentrations of VNLE

<table>
<thead>
<tr>
<th>Concentration of VNLE (gL⁻¹)</th>
<th>E_(a) (kJ mol⁻¹)</th>
<th>ΔH° (kJ mol⁻¹)</th>
<th>ΔS° (JK⁻¹mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>40.25</td>
<td>37.61</td>
<td>-75.36</td>
</tr>
<tr>
<td>0.3</td>
<td>49.88</td>
<td>47.23</td>
<td>-50.44</td>
</tr>
<tr>
<td>0.6</td>
<td>46.89</td>
<td>44.25</td>
<td>-60.96</td>
</tr>
<tr>
<td>0.9</td>
<td>46.02</td>
<td>43.38</td>
<td>-65.06</td>
</tr>
<tr>
<td>1.2</td>
<td>48.11</td>
<td>45.47</td>
<td>-59.33</td>
</tr>
<tr>
<td>1.5</td>
<td>51.09</td>
<td>48.45</td>
<td>-52.20</td>
</tr>
</tbody>
</table>
Plotting log CR against 1/T gave straight lines (Figure 4.38). The $E_a$ values calculated from the slopes are given in the Table 4.33. For the corrosion of aluminium in 1M NaOH the $E_a$ value is 40.25 kJ/mol and for the different concentrations of the inhibitors the $E_a$ values are higher ranging from 49.88 to 51.09 kJ/mol. The higher values obtained for the inhibited solutions indicated the raised energy barrier for the aluminium dissolution process. The values of enthalpy of activation $\Delta H^*$ and entropy of activation $\Delta S^*$ are obtained from the transition state equation and the plot is given in Figure 4.39.

Positive values for enthalpy of activation reveal the endothermic nature of aluminium corrosion reaction. Furthermore, the entropy of activation in the presence and absence of the inhibitor is large and negative and activated complex in the rate determining step represents association rather than dissociation step. It implies that a decrease in disordering occurs on going from reactants to activated complex [95-97].

4.4.1.3. Kinetic and thermodynamic studies

Inhibitors generally are adsorbed on the surface of the metal and thereby preventing access of the metal to the corrosive medium. The inhibition efficiency is correlated to surface coverage and a 100% efficiency suggesting to full coverage ($\theta=1$). The degree of surface coverage values calculated from weight loss measurements ($\theta = \% I/100$), are used to determine VNLE adsorption characteristics in 1M NaOH solution. To ascertain the nature of adsorption, the surface coverage values of VNLE obtained at 303-333 K are fitted into Langmuir, Freundlich and Temkin adsorption isotherms. The data fitted well with Langmuir (Figure 4.40) and freundlich isotherm (Figure 4.41) models. The correlation coefficient $R^2$ was used to determine the best fit isotherm. The best fit is obtained for Langmuir’s model and the isotherm is considered to propose adsorption mechanism. The adsorption equilibrium constant calculated from the intercept of the Langmuir adsorption isotherm and $\Delta G_{ads}$ calculated from the value of $K_{ads}$ are given in Table 4.34. The values of $K_{ads}$ are low and decreasing with increase in temperature. This suggests the fact that adsorption strength decreases at higher temperatures and this is due to physical adsorption of inhibitor molecules on aluminium metal surface. The negative values of $\Delta G_{ads}$ obtained indicate the spontaneity of the adsorption process [99].
Figure 4.40. Langmuir adsorption isotherm for VNLE on aluminium in 1M NaOH at different temperatures.

Figure 4.41. Freundlich adsorption isotherm for VNLE on aluminium in 1M NaOH at different temperatures.
Table 4.34. Adsorption parameters of VNLE on aluminium in 1M NaOH at different temperatures.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T (K)</th>
<th>K_{ads}</th>
<th>^{\circ} \Delta G_{ads} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.90</td>
<td></td>
<td>13.35</td>
</tr>
<tr>
<td>40</td>
<td>3.05</td>
<td></td>
<td>13.36</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>50</td>
<td>2.25</td>
<td>12.96</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2.30</td>
<td>13.43</td>
</tr>
</tbody>
</table>

4.4.2. Gasometric technique

Figure 4.42. shows the variation of the volume of hydrogen gas evolved as a function of time when an aluminium specimen reacts with 1M NaOH in the absence and presence of different concentrations of VNLE. The inhibition efficiency values (Table 4.35.) increased with increasing concentrations of VNLE and it indicates the decrease in corrosion rate of aluminium. The plots illustrate lesser rates of H₂ gas evolution on introduction on VNLE to the corrodent.

Figure 4.42. Hydrogen evolution during corrosion of aluminium in 1M NaOH solution in the absence and presence of VNLE at room temperature.
Table 4.35. Variation of hydrogen evolution with concentration of VNLE for aluminium corrosion in 1M NaOH solution.

<table>
<thead>
<tr>
<th>Concentration of VNLE (gL⁻¹)</th>
<th>Volume of hydrogen evolution (mL)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>22.9</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>12</td>
<td>47.59</td>
</tr>
<tr>
<td>0.6</td>
<td>9.8</td>
<td>57.20</td>
</tr>
<tr>
<td>0.9</td>
<td>8.7</td>
<td>62.01</td>
</tr>
<tr>
<td>1.2</td>
<td>7.0</td>
<td>69.43</td>
</tr>
<tr>
<td>1.5</td>
<td>5.5</td>
<td>75.98</td>
</tr>
</tbody>
</table>

4.4.3. Potentiodynamic polarisation studies

The cathodic and anodic polarisation curves for the corrosion of aluminium in the absence and presence of different concentrations of VNLE are shown in Figure 4.43. Electrochemical parameters such as $E_{\text{corr}}$, $I_{\text{corr}}$, anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$) obtained by extrapolation of the Tafel lines are given in Table 4.36. In the presence of different concentrations of VNLE the corrosion current density is lowered significantly and this confirms the inhibitive nature of the leaves extract. The cathodic and anodic curves are shifted down in the presence of inhibitor and the shift is dependent on inhibitor concentration. The addition of VNLE hinders the alkali attack on aluminium. Comparison of the curves recorded in the absence and presence of inhibitor shows that increasing concentrations of the inhibitor gives rise to a consistent decrease in cathodic and anodic current densities. The positive shift of $E_{\text{corr}}$ values and the corresponding decrease in the current densities with increasing of VNLE reveal the mixed-type behavior of the inhibitor with predominant anodic action [102].
Figure 4.43. Polarisation curves for aluminium in 1M NaOH without and with VNLE

Table 4.36. Polarisation parameters for aluminium in 1M NaOH in the absence and presence of VNLE.

<table>
<thead>
<tr>
<th>Concentration of VNLE gL⁻¹</th>
<th>-E&lt;sub&gt;corr&lt;/sub&gt; (mV)</th>
<th>I&lt;sub&gt;corr&lt;/sub&gt; (mA cm⁻²)</th>
<th>Tafel slopes (mV/decade)</th>
<th>R&lt;sub&gt;corr&lt;/sub&gt; (mm/py)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>β&lt;sub&gt;c&lt;/sub&gt;</td>
<td>β&lt;sub&gt;a&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>158.8</td>
<td>5.421</td>
<td>185</td>
<td>313</td>
<td>209.01</td>
</tr>
<tr>
<td>0.3</td>
<td>154.0</td>
<td>2.574</td>
<td>165</td>
<td>294</td>
<td>99.23</td>
</tr>
<tr>
<td>0.6</td>
<td>154.7</td>
<td>2.003</td>
<td>162</td>
<td>293</td>
<td>77.21</td>
</tr>
<tr>
<td>0.9</td>
<td>154.5</td>
<td>1.634</td>
<td>163</td>
<td>286</td>
<td>63.01</td>
</tr>
<tr>
<td>1.2</td>
<td>154.4</td>
<td>1.407</td>
<td>167</td>
<td>280</td>
<td>54.25</td>
</tr>
<tr>
<td>1.5</td>
<td>154.2</td>
<td>1.231</td>
<td>169</td>
<td>277</td>
<td>47.47</td>
</tr>
</tbody>
</table>
The values of anodic and cathodic Tafel slopes for various concentrations of the inhibitor are found to be lower than that of blank solution. This indicates that the inhibitor influences kinetics of both anodic dissolution of aluminium and cathodic hydrogen evolution reaction. The values of inhibition efficiency increase with increase in inhibitor concentration, and it reveals that a higher surface coverage is obtained with a solution of maximum inhibitor concentration.

4.4.4. AC Impedance studies

Figure 4.44. shows the Nyquist plots recorded in the absence and presence of different concentrations of leaves extract. The corresponding impedance results are given in Table 4.37. The semicircle is characteristic of the parallel arrangement of the double layer capacitance and charge transfer resistance corresponding to the aluminium dissolution reaction. The increasing $R_d$ values and decreasing $C_d$ values confirmed the inhibitive nature of the VNLE. Decrease in $C_d$ values with increase in inhibitor concentration is attributed to decrease in local dielectric constant and/or an increase in the thickness of double layer. It suggests that the inhibitor molecules function by adsorption at the metal/solution interface.

The increase in $R_d$ values revealed that the extent of adsorption increase with increase in VNLE concentration. In the Nyquist plots phase angle increases with increase in VNLE concentration and it is ascribed to decrease in surface inhomogeneity. The presence of VNLE increases the impedance but does not alter the other aspects of corrosion mechanism [103-105]. The capacitive and inductive loops showed in the Nyquist plots reveal the formation of metal inhibitor complex at metal/solution interface. The decrease in the thickness of double layer charges is due to the formation of a complex at the metal surface. The equivalent circuit model used to fit the experimental data is shown in Figure 4.45. In the electric circuit model $C_d$ is double layer capacitance, $R_d$ is the interfacial charge transfer resistance and $R_s$ is the solution resistance. The numerical values of $R_d$ and $C_d$ are determined by simulation of complex plane impedance plot and the equivalent circuit model by means of a computer program.
Figure 4.44. Nyquist plots for aluminium corrosion in 1M NaOH without and with VNLE

Table 4.37. Electrochemical impedance parameters for aluminium in 1 M NaOH solution in the absence and presence of VNLE

<table>
<thead>
<tr>
<th>Concentration of VNLE (gL⁻¹)</th>
<th>$R_{cl}$ (Ω cm²)</th>
<th>$C_{dl}$ (μF/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.09</td>
<td>88.76</td>
<td>----</td>
</tr>
<tr>
<td>0.3</td>
<td>8.04</td>
<td>15.54</td>
<td>54.0</td>
</tr>
<tr>
<td>0.6</td>
<td>9.26</td>
<td>11.39</td>
<td>60.2</td>
</tr>
<tr>
<td>0.9</td>
<td>11.23</td>
<td>10.53</td>
<td>67.2</td>
</tr>
<tr>
<td>1.2</td>
<td>12.13</td>
<td>9.18</td>
<td>69.6</td>
</tr>
<tr>
<td>1.5</td>
<td>18.19</td>
<td>8.00</td>
<td>79.7</td>
</tr>
</tbody>
</table>
4.4.5. FT-IR spectral study

Figure 4.46. (a) and (b) show the FT-IR spectrum recorded for the crude VNLE and reaction product formed on aluminium surface containing 1.5gL⁻¹ of VNLE in 1M NaOH respectively. Comparison of the peaks revealed significant and prominent variation between the two spectra. Adsorption of VNLE molecules on aluminium surface is established from the different absorption bands and shifts in wavelengths. The peaks identified in the range 650 – 950 cm⁻¹ are assigned as Al-O of the corrosion product scraped from Al surface [106]. The same frequency range can also be assigned for aromatic ring bending. Generally aromatic ring stretching vibrations occurred in the range 1400 -1600 cm⁻¹. The peak that appeared at 1409 cm⁻¹ (Figure 4.46.a) is assigned for aromatic ring stretching and the peak is shifted to 1385cm⁻¹ (Figure 4.46.b). The peaks observed at 2922 and 2852 cm⁻¹ in Figure 4.46 (b) are assigned as asymmetric C-H vibration ( aliphatic or aromatic). The O-H stretching at 3359 cm⁻¹ is shifted to 3430. The shifting of C=O and C-O stretching frequency from 1636 to 1621 cm⁻¹ and from cm⁻¹1046 to 1096 cm⁻¹ respectively confirmed the adsorption of organic molecules of VNLE on aluminium surface. Interaction between major functional groups of MPLE and the surface of aluminium are revealed through these shifts in the wavelength.
Figure 4.46. (a) FT-IR spectrum of VNLE powder
Figure 4.46. (b) FT-IR spectrum of scraped film of VNLE from aluminium surface.
Identification of new bands in Figure 4.46.(b) indicated likely products of functional group interactions that are not originally present in VNLE spectrum. Nevertheless, all the functional group bands that are found in VNLE spectrum are present in the scraped film of VNLE indicating all of them are likely used for bonding with aluminium. Comparison of Figures 4.46. (a) and (b) justifies the inhibition property of VNLE for corrosion of aluminium in alkaline solution.

4.4.6. Surface analysis

Figure 4.47.(a) shows the surface structure of aluminium after immersion in 1M NaOH. Figure 4.47.(b) represents the surface after treatment with VNLE inhibitor for 1 h. Comparison of the micrographs revealed that Figure 4.47(a), has corroded aluminium surface with uniform attack by sodium hydroxide. The degradation of the metal occurs with deposition of aluminium hydroxide precipitates on the surface.

Close observation of Figure 4.47.(b) shows that there is an improvement in the surface morphology possibly due to diminished corrosion rate. A protective film is formed on aluminium surface covering the flawed areas. The ridges seen in Figure 4.44.(a) are reduced in the presence of inhibitor. These observations indicate the corrosion inhibiting nature of VNLE in 1M NaOH [107].
Figure 4.47. Micrographs of aluminium exposed to (a)1M NaOH (b)1M NaOH solution with 1.5 gL⁻¹ of VNLE.
4.4.7. Corrosion inhibition of VNLE

Preliminary phytochemical screening of VNLE revealed the presence of phenolic compounds, flavonoids and alkaloids. Earlier reports on phytochemical analysis of the leaves extract of Vitex negundo available in literature also confirmed the presence of many polyphenolic compounds, terpenoids, glycosidic iridoids and alkaloids the chief chemical constituents. The plant Vitex negundo contains 5 hydroxy-7, 4′ dimethoxy flavone derivatives, 7, 8 dimethyl herbacetin 3-rhamnoside, negundoside, agnuside, and vitegnoside. Figure 4.48. shows the structures of the active principles of VNLE [108,109].

![Structures of active principles in VNLE](image)

Figure 4.48. The active principles present in VNLE.

A close examination of the structures (Figure 4.48) of the organic compounds reveals that these active principles are involved in the corrosion inhibition process. The reason is these compounds contain many hydroxyl groups, -C=O groups, electron releasing methyl, methoxy group subtituents, and aromatic rings with extended conjugation. The polar centers of these groups via their electron rich centers can form complexes with Al^{3+} on the metal surface. Therefore the
inhibition potential of VNLE is due to the synergistic effect of the active principles that are involved in the adsorption process on aluminium surface.

4.4.8. Comparison of inhibition efficiency of VNLE

It is worth noting from Table 4.38. that the inhibition efficiency values determined from chemical and electrochemical measurements are comparable and are in good agreement with each other. The results obtained revealed that VNLE effectively inhibits the corrosion of aluminium in 1M NaOH solution. Little difference obtained from both chemical and electrochemical measurements are also reported earlier [110].

Table 4.38. Comparison of inhibition efficiency of VNLE

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration of VNLE (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
<td>Hydrogen evolution</td>
</tr>
<tr>
<td>0.3</td>
<td>56.0</td>
<td>47.59</td>
</tr>
<tr>
<td>0.6</td>
<td>60.7</td>
<td>57.20</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>0.9</td>
<td>66.1</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>70.1</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>78.1</td>
</tr>
</tbody>
</table>

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4.5. Inhibitive effect of Mentha piperita leaves extract (MPLE)

4.5.1. Weight loss measurements

4.5.1.1. Effect of inhibitor concentration

The data of percentage inhibition efficiency (% IE) and corrosion rate (CR) obtained from weight loss method at different concentrations of MPLE in 1M NaOH at 303 ± 0.5 K are summarized in Table 4.39. It shows that the magnitude of inhibition depends on concentration of inhibitor. The inhibition efficiency increases with increasing MPLE concentration in 1N NaOH medium. It is due to the fact that adsorption process enhances and hence the dissolution of aluminium decreases with increase in concentration of extract.

Table 4.39. Corrosion parameters for aluminium in 1M NaOH containing various concentrations of MPLE.

<table>
<thead>
<tr>
<th>Concentration of MPLE (gL⁻¹)</th>
<th>Weight loss (g/cm²)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
<th>Surface coverage (Θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0891</td>
<td>236.95</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0472</td>
<td>125.56</td>
<td>47.0</td>
<td>0.47</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0443</td>
<td>117.85</td>
<td>50.2</td>
<td>0.50</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0426</td>
<td>113.33</td>
<td>52.1</td>
<td>0.52</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0398</td>
<td>105.84</td>
<td>55.3</td>
<td>0.55</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0305</td>
<td>81.13</td>
<td>65.7</td>
<td>0.65</td>
</tr>
</tbody>
</table>

4.5.1.2. Effect of immersion time

Aluminium is immersed for different time intervals in 1M NaOH containing different concentrations of MPLE at 303K is shown in Table 4.40. The loss in weight of aluminium specimen is plotted in Figure 4.49. as a function of time for various concentrations of the additive. Curves having the same character were obtained for the free and inhibited alkali solutions. The lowest inhibition efficiency is observed with the lowest MPLE addition examined in the alkaline medium. The %IE of MPLE decreases with increasing immersion period. This indicates that the protective film formed on the metal surface is broken by the corrosive environment and the film is dissolved in the solution [111].
Table 4.40. Effect of immersion time on corrosion inhibition of MPLE.

<table>
<thead>
<tr>
<th>Concentration of MPLE (gL⁻¹)</th>
<th>Weight loss (g/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1 (h)</td>
<td>2 (h)</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0472</td>
<td>0.0740</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0443</td>
<td>0.0723</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0426</td>
<td>0.0680</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0398</td>
<td>0.0634</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0305</td>
<td>0.0500</td>
</tr>
</tbody>
</table>

Figure 4.49. Weight loss vs time curves for aluminium in 1M NaOH containing different concentrations of MPLE at 303 K.
4.5.1.3. Effect of temperature

The effect of temperature on the corrosion rate of aluminium is studied in free alkali and in the presence varying concentrations of MPL3E in the temperature range of 303-333K using weight loss experiments. It is found that rates of aluminium corrosion increases with increase in temperature both for free and inhibited alkali solution. The %IE of the extract calculated in the temperature range shows a corresponding decrease for the increase in temperature (Table 4.41). These observations indicate physical adsorption of inhibitor compounds on aluminium surface.

<table>
<thead>
<tr>
<th>Concentration of MP.E (gL(^{-1}))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>0.3</td>
<td>47.0</td>
</tr>
<tr>
<td>0.6</td>
<td>50.2</td>
</tr>
<tr>
<td>0.9</td>
<td>52.1</td>
</tr>
<tr>
<td>1.2</td>
<td>55.3</td>
</tr>
<tr>
<td>1.5</td>
<td>65.7</td>
</tr>
</tbody>
</table>

Activation energy calculated using Arrhenius equation, ln CR = A – E/RT for corrosion reactions in free and inhibited alkali are given in Table 4.42, and the plot of logarithm of the corrosion rate versus the reciprocal of absolute temperature is shown in Figure 4.50. It is obvious that the energy of activation is greater for inhibited solution than for free alkali. So the rate of corrosion reaction is decreased in presence of extract [112].

4.5.1.4. Determination of activation parameters

The activation functions of the corrosion of aluminium in 1M NaOH calculated from the Arrhenius (Figure 4.50) and transition state plots (Figure 4.51.) show that E\(_a\) and ΔH\(^\ddagger\) in the presence of MPL3E is greater than the values obtained for the free alkali solution.
Figure 4.50. Plot of log CR vs 1/T for aluminium corrosion in free and inhibited alkali.

Figure 4.51. Plot of log (CR/T) vs 1/T for various concentrations of VNLE in 1M NaOH.
The adsorption of MPLE molecules is assumed to occur in the higher energy states, which leads to blocking of the active sites. The enhanced $E_a$ and $\Delta H^*$ in the presence of 0.3 - 1.5 gL$^{-1}$ concentrations of MPLE indicates the rise in energy barrier attained in the presence of MPLE. The entropy of activation $\Delta S^*$ in the absence and presence of the inhibitor is large and negative. It means that increase in orderliness takes place on going from reactants to the activated complex (Table 4.42.).

Table 4.42. Activation parameters for aluminium corrosion in 1M NaOH in the absence and presence of various concentrations of MPLE.

<table>
<thead>
<tr>
<th>Concentration of MPLE (gL$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>40.25</td>
<td>37.61</td>
<td>-75.36</td>
</tr>
<tr>
<td>0.3</td>
<td>49.88</td>
<td>47.23</td>
<td>-50.44</td>
</tr>
<tr>
<td>0.6</td>
<td>46.89</td>
<td>44.25</td>
<td>-60.96</td>
</tr>
<tr>
<td>0.9</td>
<td>46.02</td>
<td>43.38</td>
<td>-65.06</td>
</tr>
<tr>
<td>1.2</td>
<td>48.11</td>
<td>45.47</td>
<td>-59.33</td>
</tr>
<tr>
<td>1.5</td>
<td>51.09</td>
<td>48.45</td>
<td>-52.20</td>
</tr>
</tbody>
</table>

4.5.1.5. Application of adsorption isotherms

The most frequently used adsorption isotherms namely Frndlich, Langmuir, Frumkin, and Temkin isotherms have been tested to understand the mechanism of adsorption MPLE on aluminium surface. The best fitted one follows Langmuir isotherm. Straight lines are obtained when ($C_{inh}/\Theta$) plotting against concentration ($C_{inh}$) on a double logarithmic scale as shown in Figure 4.52. The values of $K_{ads}$ calculated from the intercepts of the straight lines are given in Table 4.43. and the values decreased when the reaction temperature increased from 303-333 K. This indicates that physical adsorption of MPLE on aluminium and hence strength of adsorption decreased with increasing temperature. The values of $\Delta G_{ads}$ are -12.96, -12.95, -12.70 and -12.32 KJ/mol for the studied temperature range and these values reveal that the adsorption process is spontaneous [113-115].
Figure 4.52. Plot of ($C/\Theta$) vs $C$ for various concentrations of MPL in 1M NaOH.

Table 4.43. Adsorption parameters of MPL on aluminium in 1M NaOH at different temperature.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T (K)</th>
<th>$K_{ads}$</th>
<th>$\Delta G_{ads}^{0}$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303</td>
<td>3.09</td>
<td>12.96</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>313</td>
<td>2.61</td>
<td>12.95</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>2.04</td>
<td>12.70</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>1.54</td>
<td>12.32</td>
</tr>
</tbody>
</table>
4.5.2. Gasometric measurement

Inspection of the plots (Figure 4.53.) suggested the absence of incubation period that corresponds to the break down of pre-immersion oxide film. Plots of this type are generally obtained for H₂ gas evolution in alkaline medium. The volume of gas evolution varied linearly with time. Introduction of MPLE into the corrosive medium resulted in decrease of hydrogen gas evolution as shown in Table 4.44. It indicates the corrosion inhibition afforded by MPLE in sodium hydroxide. The corrosion rate decreases with increasing MPLE concentration. So it is clear that the inhibiting action of MPLE is concentration dependent [116].

![Graph showing volume-time curves for aluminium corrosion in 1M NaOH in the absence and presence of MPLE.](image)

**Figure 4.53.** Volume-time curves for aluminium corrosion in 1M NaOH in the absence and presence of MPLE.
Table 4.44. Volume of hydrogen gas evolved and inhibition efficiency of MPL.

<table>
<thead>
<tr>
<th>Concentration of MPL (g/L)</th>
<th>Volume of hydrogen evolution (mL/cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>23.3</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>12.6</td>
<td>45.92</td>
</tr>
<tr>
<td>0.6</td>
<td>11.3</td>
<td>51.50</td>
</tr>
<tr>
<td>0.9</td>
<td>10.4</td>
<td>55.36</td>
</tr>
<tr>
<td>1.2</td>
<td>9.8</td>
<td>57.93</td>
</tr>
<tr>
<td>1.5</td>
<td>8.9</td>
<td>61.8</td>
</tr>
</tbody>
</table>

4.5.3. Polarisation measurements

Potentiodynamic polarisation curves of aluminium electrode are recorded in solutions of 1M NaOH devoid of and containing different concentrations of MPL (Figure 4.54.). Inspection of Table 4.45. shows that the corrosion potential of aluminium is shifted to higher and lower values upon addition of MPL. However, the corrosion potential is independent of MPL concentration. It is also noted that MPL addition decreased corrosion current and both anodic and cathodic Tafel constants. These observations reveal the ability of MPL to suppress the corrosion of aluminium in 1M NaOH by the adsorption of the active ingredient of the extract on both anodic and cathodic sites. Thus adsorption of MPL on aluminium surface leads to decrease the exposed surface area necessary for aluminium dissolution and hydrogen evolution and it acts as a mixed type inhibitor [117-119].
Figure 4.54. Polarisation curves for aluminium in 1M NaOH without and with MPLE.

Table 4.45. Polarisation parameters of aluminium corrosion in 1M NaOH solution without and with MPLE.

<table>
<thead>
<tr>
<th>Concentration of MPLE gL⁻¹</th>
<th>(-E_{corr}) (mV)</th>
<th>(I_{corr}) mA.cm⁻²</th>
<th>Tafel slopes (mV/decade)</th>
<th>(R_{corr}) mmpy</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>158.8</td>
<td>5.421</td>
<td>185</td>
<td>313</td>
<td>209.01</td>
</tr>
<tr>
<td>0.3</td>
<td>154.4</td>
<td>2.789</td>
<td>179</td>
<td>285</td>
<td>107.51</td>
</tr>
<tr>
<td>0.6</td>
<td>155.0</td>
<td>2.764</td>
<td>176</td>
<td>280</td>
<td>106.55</td>
</tr>
<tr>
<td>0.9</td>
<td>159.0</td>
<td>2.710</td>
<td>166</td>
<td>246</td>
<td>104.47</td>
</tr>
<tr>
<td>1.2</td>
<td>156.2</td>
<td>2.360</td>
<td>179</td>
<td>246</td>
<td>90.98</td>
</tr>
<tr>
<td>1.5</td>
<td>156.3</td>
<td>1.911</td>
<td>182</td>
<td>236</td>
<td>73.76</td>
</tr>
</tbody>
</table>
4.5.4. EIS measurements

Figure 4.56. represents Nyquist plots of aluminium in the absence and presence of different concentrations of MPLE and the corresponding impedance data are given in Table 4.46. The curves showed that increase in size of the capacitive semicircles occurred with increase in concentration of MPLE. These changes indicated the increasing charge transfer resistance and decreasing corrosion rate [120-122]. The proposed equivalent circuit shown in Figure 4.55. has been used to analyze the impedance spectra for aluminium in alkaline solutions.

![Electrical equivalent circuit for the system](image)

Figure 4.55. Electrical equivalent circuit for the system
Figure 4.56. Nyquist plots for aluminium corrosion in 1M NaOH in the absence and presence of MPLE.

Table 4.46. Electrochemical impedance parameters for aluminium corrosion in 1 M NaOH solution in the absence and presence of MPLE.

<table>
<thead>
<tr>
<th>Concentration of MPLE (gL(^{-1}))</th>
<th>(R_\text{ct}) (Ω cm(^2))</th>
<th>(C_\text{dl}) (μF/cm(^2))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>3.09</td>
<td>88.76</td>
<td>----</td>
</tr>
<tr>
<td>0.3</td>
<td>5.61</td>
<td>18.8</td>
<td>44.8</td>
</tr>
<tr>
<td>0.6</td>
<td>6.16</td>
<td>17.18</td>
<td>49.8</td>
</tr>
<tr>
<td>0.9</td>
<td>6.84</td>
<td>16.45</td>
<td>54.8</td>
</tr>
<tr>
<td>1.2</td>
<td>7.39</td>
<td>15.76</td>
<td>58.1</td>
</tr>
<tr>
<td>1.5</td>
<td>9.29</td>
<td>12.32</td>
<td>66.7</td>
</tr>
</tbody>
</table>
4.5.5. FT-IR spectral analysis

The FT-IR spectra of the MPLP powder and aluminium surface treated with 1.5 g L\(^{-1}\) MPLP in 1M NaOH solution provided information about the interactions between MPLP and aluminium surface, the strength of the bonds between atoms and the structure of the molecules. A broad band in the range of 3000-3600 cm\(^{-1}\) and a band at found in Figure 4.57.(a) is assigned to O-H stretching, and intramolecular hydrogen bonding of aqueous extract of MPLP. The broad band observed for O-H is seemed to be reduced in band width in Figure 4.57.(b) and it is attributed to Al-MPLE complex formation. The band at 1669 cm\(^{-1}\) is assigned to the bending mode of absorbed water, since plant extracts are known to have a strong affinity for water. These bands are shifted to 3377 cm\(^{-1}\) and at 1611 cm\(^{-1}\), and the changes in the peak positions indicate the interaction of hydroxyl groups of menthol with the aluminium surface. The peak observed at 1422 cm\(^{-1}\) in the spectrum of MPLP is assigned to aromatic ring stretching and it is shifted to 1413 cm\(^{-1}\) in Figure 4.57.(b). The absorption regions for the alcoholic –C-O group due to its stretching vibrations are 1000 – 1200 cm\(^{-1}\) and hydrogen bonding has the effect of decreasing the frequency of this band slightly. The peaks at 1033 and 1080 cm\(^{-1}\) are assigned as alcoholic –C-O stretching vibration of the hydroxyl group present in menthol [123].
Figure 4.57. (a) FT-IR spectrum of MPLE powder
Figure 4.57. (b) FT-IR spectrum of aluminium surface treated with 1.5 gL$^{-1}$ MPLE in 1M NaOH.
4.5.6. Surface study

Microscopic images of aluminium specimen immersed in inhibitor free alkali and alkali solution containing 1.5 gL$^{-1}$ of MPLE are shown in Figure 4.58. (a) and (b). The aluminium surface structure recorded after immersion in inhibitor free alkali solution (Figure 4.58 a) reveals the progressive corrosion reaction. It contains a loose porous layer formed by the aggressive corroding medium. Figure 4.58. (b) shows the retardation of corrosion rate caused by the MPLE inhibitor which forms deposits on aluminium surface.
Figure 4.58. Micrographs of aluminium surface (a) in 1M NaOH
(b) in 1M NaOH solution with 1.5 gL⁻¹ of MPLF.
4.5.7. Explanation for corrosion inhibition of MPLC

Preliminary phytochemical screening of the crude extract of MPLC revealed the presence of terpenoids. In literature it is reported that Mentha piperita contains menthol, menthyl acetate and menthone as its main components. The structure of these organic compounds are given in Figure 4.59.

![Menthol, Menthone, and Methyl acetate structures]

Figure 4.59. Structure of chief constituents of MPLC.

Corrosion inhibition capability of MPLC is attributed to adsorption of these chemical constituents on aluminium surface. The protection efficiency of MPLC is supported by similar report on corrosion inhibition of Mentha species for different metal and medium available in literature [124,125].

4.5.8. Evaluation of inhibition efficiency of MPLC

The inhibition efficiency values obtained from weight loss, hydrogen evolution, polarization curves and Nyquist diagrams are summarized in Table 4.47. The trend seen for each concentration of MPLC from each measurement is in good agreement with other measurements. It is therefore concluded that MPLC acted as a good inhibitor for aluminium corrosion in alkaline medium.

Table 4.47. Comparison of inhibition efficiency of MPLC

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration of MPLC (gL⁻¹)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
<td>Hydrogen evolution</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>0.3</td>
<td>47.0</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>50.2</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>52.1</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>55.3</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>65.7</td>
</tr>
</tbody>
</table>
4.6. Comparative study of inhibitors

A comparative evaluation of the IE of CALE, SNLE, MOLE, VNLE, and MPLE obtained from chemical and electrochemical methods is done to assess the order of inhibiting ability of the leaves extracts.

Table 4.48. IE obtained from WL method

<table>
<thead>
<tr>
<th>Concentration (gL⁻¹)</th>
<th>CALE</th>
<th>SNLE</th>
<th>MOLE</th>
<th>VNLE</th>
<th>MPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>80.03</td>
<td>77.91</td>
<td>61.5</td>
<td>56.0</td>
<td>47.0</td>
</tr>
<tr>
<td>0.6</td>
<td>82.72</td>
<td>79.17</td>
<td>67.2</td>
<td>60.7</td>
<td>50.2</td>
</tr>
<tr>
<td>0.9</td>
<td>85.22</td>
<td>82.58</td>
<td>74.7</td>
<td>66.1</td>
<td>52.1</td>
</tr>
<tr>
<td>1.2</td>
<td>89.4</td>
<td>84.92</td>
<td>79.5</td>
<td>70.1</td>
<td>55.3</td>
</tr>
<tr>
<td>1.5</td>
<td>93.92</td>
<td>86.18</td>
<td>84.0</td>
<td>78.1</td>
<td>65.7</td>
</tr>
</tbody>
</table>

Inspection of IE (%) values obtained from weight loss method reveals that all tested leaves extracts appeared to act as inhibitors over the studied concentration range. Two inhibitor concentrations considered as typical of high and low inhibition effectiveness are 1.5 gL⁻¹ and 0.2 gL⁻¹ respectively. The corrosion rate values calculated from weight loss method in the presence of five leaves extracts indicated that CALE has a greater inhibition effect on the dissolution of aluminium in alkaline medium. The data shown in Table 4.48, indicates that the protection ability of the inhibitors, decreases in the order: CALE > SNLE > MOLE > VNLE > MPLE.

Table 4.49. IE obtained from HE method

<table>
<thead>
<tr>
<th>Concentration of leaves extract (gL⁻¹)</th>
<th>CALE</th>
<th>SNLE</th>
<th>MOLE</th>
<th>VNLE</th>
<th>MPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>78.32</td>
<td>73.12</td>
<td>61.37</td>
<td>47.59</td>
<td>45.92</td>
</tr>
<tr>
<td>0.6</td>
<td>84.07</td>
<td>75.77</td>
<td>64.37</td>
<td>57.20</td>
<td>51.50</td>
</tr>
<tr>
<td>0.9</td>
<td>87.17</td>
<td>80.17</td>
<td>70.38</td>
<td>62.01</td>
<td>55.36</td>
</tr>
<tr>
<td>1.2</td>
<td>90.07</td>
<td>85.9</td>
<td>74.24</td>
<td>69.43</td>
<td>57.93</td>
</tr>
<tr>
<td>1.5</td>
<td>92.03</td>
<td>86.78</td>
<td>78.54</td>
<td>75.98</td>
<td>61.8</td>
</tr>
</tbody>
</table>
The data of hydrogen evolution rate given in Table 4.49. shows the comparative inhibitive effects of each of the inhibitors employed for the study. H₂ evolution rates measured in sodium hydroxide solution for all the inhibitors indicated the following order: CALE > SNLE > MOLE > VNLE > MPLE. The inhibitive effects of the leaves extracts are found to follow the same order as shown in weight loss measurements.

Table 4.50. IE obtained from TP method

<table>
<thead>
<tr>
<th>Concentration (gL⁻¹)</th>
<th>CALE</th>
<th>SNLE</th>
<th>MOLE</th>
<th>VNLE</th>
<th>MPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>79.5</td>
<td>78.62</td>
<td>61.70</td>
<td>52.5</td>
<td>48.5</td>
</tr>
<tr>
<td>0.6</td>
<td>86.7</td>
<td>80.24</td>
<td>65.30</td>
<td>63.0</td>
<td>49.0</td>
</tr>
<tr>
<td>0.9</td>
<td>87.5</td>
<td>82.96</td>
<td>73.25</td>
<td>69.8</td>
<td>50.0</td>
</tr>
<tr>
<td>1.2</td>
<td>88.9</td>
<td>83.23</td>
<td>77.8</td>
<td>74.0</td>
<td>56.4</td>
</tr>
<tr>
<td>1.5</td>
<td>89.7</td>
<td>84.69</td>
<td>80.53</td>
<td>77.2</td>
<td>64.7</td>
</tr>
</tbody>
</table>

% IE results obtained from polarisation measurements given in Table 4.50. are in good correlation with the results obtained from chemical methods. The order of inhibition shown by the leaves extracts is CALE > SNLE > MOLE > VNLE > MPLE.

Table 4.51. IE obtained from EIS method

<table>
<thead>
<tr>
<th>Concentration of extract (gL⁻¹)</th>
<th>CALE</th>
<th>SNLE</th>
<th>MOLE</th>
<th>VNLE</th>
<th>MPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>78.1</td>
<td>78.17</td>
<td>60.06</td>
<td>54.0</td>
<td>44.8</td>
</tr>
<tr>
<td>0.6</td>
<td>84.5</td>
<td>80.47</td>
<td>66.99</td>
<td>60.2</td>
<td>49.8</td>
</tr>
<tr>
<td>0.9</td>
<td>89.4</td>
<td>82.16</td>
<td>73.40</td>
<td>67.2</td>
<td>54.8</td>
</tr>
<tr>
<td>1.2</td>
<td>92.4</td>
<td>84.28</td>
<td>78.09</td>
<td>69.6</td>
<td>58.1</td>
</tr>
<tr>
<td>1.5</td>
<td>92.6</td>
<td>85.87</td>
<td>81.32</td>
<td>79.7</td>
<td>66.7</td>
</tr>
</tbody>
</table>
The %IE of all the examined inhibitors derived from impedance measurements are given in Table 4.51. The results obtained from the impedance measurements are in good agreement with those obtained from weight loss, hydrogen evolution and polarisation methods. The IE of used inhibitors follows the order: CALE > SNLE > MOLE > VNLE > MPL. Results obtained for IE of all the inhibitors from the other three methods also followed the same order.

It is worth noting that the IE values obtained from chemical and electrochemical measurements are comparable with each other. The data from each type of experiment are seemed to be self-consistent. The little differences found in results obtained from both chemical and electrochemical measurements are also reported by several authors [76, 78, 103]. However discrepancies observed in the values of IE are probably due to the different conditions under which the techniques are carried out.

The corrosion inhibiting potential of CALE and SNLE investigated in the present study is compared with that of other natural inhibitors already reported for aluminium corrosion in sodium hydroxide medium. It is observed that the % IE of CALE and SNLE are greater than the % IE of the natural inhibitors Ipomoea involcrata, Hibiscus sabdairiffa, Hibiscus rosasinensis, Euphorbia hirta and Adathoda vasica. Hence it is concluded that the present investigation is successful in identifying new efficient natural inhibitor for aluminium corrosion in sodium hydroxide medium.

4.6.1. Mechanism of corrosion inhibition of aluminium in alkaline medium with leaves extracts

The plausible mechanism for inhibition of aluminium corrosion in alkaline medium is proposed to explain the inhibitive action of all the studied leaves extracts. The general mechanism of corrosion reaction of aluminium in alkaline solution is given as follows:

$$\text{Al} + 3\text{H}_2\text{O} + \text{OH}^- \rightarrow 3\text{H}_2\text{O} + \text{Al(OH)}_3^- \quad \ldots \quad (4.6)$$

It is assumed that corrosion inhibition occurs through adsorption of inhibitor molecules at the metal / solution interface. When the organic compound approaches
and adsorbs at the metal solution interface, the molecule orients in such a way to facilitate coordinate linkage between the inhibitor molecule and Al$^{3+}$ ions present in the metal surface. Electron rich centres of the inhibitor molecule due to electrostatic forces of attraction donate π electrons to Al$^{3+}$ ion, get adsorbed on the metal surface forming Al$^{3+}$-LE complexes. Thus the entry of anions to the metal surface is prevented. In the above process, the inhibitor I adsorbs on the metal and displaces n water molecules initially adsorbed on the metal. Adsorption of the inhibitor on the metal is due to greater interaction energy between the metal and inhibitor than the interaction energy between the metal and the water molecules [126].
REFERENCES