CHAPTER- X

THE INHIBITION EFFICACY OF *ARACHIS HYPOGAEA*

ON BRASS (Cu-40Zn) IN 1.0 N HYDROCHLORIC ACID AND

NATURAL SEA WATER
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Copper and its alloys have wide application and hence are used in many environments mostly in sea water because of their excellent corrosion resistance which is coupled with combination of their desirable properties such as superior electrical and thermal conductivity, ease of fabricating and joining, wide range attainable mechanical properties and resistance to biofouling.

Biofouling is a general term describing all forms of biological growth on surfaces in contact with natural sea water [304]. Characklis defines fouling as the undesirable formation of deposits on equipment surfaces, which significantly decreases equipment performance and or the useful life of the equipment [305]. The microbiologically influenced corrosion (MIC) of copper and its alloys is not very well documented.

The present investigation deals with the study of the dezincification of brass (Cu-40Zn) were protect by using green plant extract namely *Arachis hypogaea* root in 1.0N Hydrochloric acid and Natural sea water.

10.0. RESULTS AND DISCUSSION

10.1. IN 1.0N HYDROCHLORIC ACID

10.1.1. NON-ELECTROCHEMICAL METHOD

10.1.1.1. Weight loss method

The dezincification behaviour of brass in 1.0N Hydrochloric acid containing various concentration of *Arachis hypogaea* root extract (AHR) with various exposure time from 24 to 360hrs were carried out by mass loss method and the values are recorded
in Table- 10.1. In the absence of inhibitor the value of corrosion rate increased from 0.431 to 0.573 mmpy with increase of exposure time. The corrosion rate was tremendously decreased from 0.431 to 0.069 mmpy after 24hrs and 0.573 to 0.231 mmpy after 360hrs exposure in acid media. However the value of corrosion rate was gradually increased from 0.069 to 0.231 mmpy with increase of exposure time at 100ppm of inhibitor concentration. The maximum of 87.90% of inhibition efficiency was attained after 72hrs exposure time. The percentage of inhibition efficiency increased with increase of inhibitor concentration. This may be due to the presence of phytochemical constituents in AHR containing (p-hydroxybenzoicacid, caffeic acid, chlorogenic acid, ferulic acid, catechin, and asparagines) hetero atoms (N and O) in addition to aromatic compounds increased the electron density and hence enhanced the adsorption of active inhibitor molecules on the surface of the metal. Due to this effect the protective film may prevent further dissolution both zinc and copper in the alloy.

10.1.1.2. EFFECT OF TEMPERATURE

The corrosion behaviour of brass containing various concentration of AHR inhibitor in 1.0N Hydrochloric acid at different temperature from 303 to 343K was investigated by mass loss measurement and the calculated values are shown in Table- 10.2. In the absence of inhibitor the value of corrosion rate increased from 1.1032 to 1.9306 mmpy with rise in temperature. The corrosion rate was gradually decreased from 1.1032 to 0.2758 mmpy and 1.9306 to 0.9653 mmpy with increase of inhibitor concentration. The maximum of 74.91% of inhibition efficiency was achieved at 303K. The percentage of inhibition efficiency decreased with rise in temperature was due to physical adsorption mechanism.
Table 10.1 The corrosion parameters of brass (Cu-40Zn) in 1.0N Hydrochloric acid containing various concentration of AHR inhibitor at different exposure time.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Weight loss (mg)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hrs</td>
<td>72 hrs</td>
<td>144 hrs</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>49</td>
<td>95</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>15</td>
<td>33</td>
</tr>
<tr>
<td>50</td>
<td>6</td>
<td>11</td>
<td>29</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
<td>9</td>
<td>26</td>
</tr>
<tr>
<td>100</td>
<td>4</td>
<td>6</td>
<td>21</td>
</tr>
</tbody>
</table>
Table- 10.2 The corrosion parameters of brass in 1.0N Hydrochloric acid containing various concentration of AHR inhibitor at various temperature.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Weight loss (mg)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
<td>313K</td>
<td>323K</td>
</tr>
<tr>
<td>0</td>
<td>8</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>50</td>
<td>4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>70</td>
<td>3</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>
10.1.1.2.1. ACTIVATION ENERGY

The values of Corrosion rate obtained from the mass loss measurement was substituted in Eqn-4.7 and the calculated values of activation energy are presented in Table-10.3. The activation energy increased from 14.975 to 27.066 kJ/mol with increase of inhibitor concentration. The average value of \( E_a \) obtained from the blank (12.090 kJ/mol) was lower than that of the values obtained for a system containing various concentrations of AHR extract. This result indicated that the AHR inhibitor was adsorbed on the surface of brass by physical adsorption process.

Table- 10.3 Calculated values of activation energy (\( E_a \)) and heat of adsorption (\( Q_{ads} \)) of AHR inhibitor on brass (Cu-40Zn) in 1.0N Hydrochloric acid.

<table>
<thead>
<tr>
<th>S.no</th>
<th>Conc. (ppm)</th>
<th>% of I.E ( % )</th>
<th>( E_a ) (kJ/mol)</th>
<th>( Q_{ads} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Blank</td>
<td>--</td>
<td>12.090</td>
<td>---</td>
</tr>
<tr>
<td>2.</td>
<td>10</td>
<td>25.02</td>
<td>14.975</td>
<td>-15.484</td>
</tr>
<tr>
<td>3.</td>
<td>30</td>
<td>37.53</td>
<td>14.977</td>
<td>-08.906</td>
</tr>
<tr>
<td>4.</td>
<td>50</td>
<td>50.04</td>
<td>17.520</td>
<td>-13.374</td>
</tr>
<tr>
<td>5.</td>
<td>70</td>
<td>62.55</td>
<td>21.191</td>
<td>-17.550</td>
</tr>
<tr>
<td>6.</td>
<td>100</td>
<td>75.00</td>
<td>27.066</td>
<td>-23.736</td>
</tr>
</tbody>
</table>

10.1.1.2.2. ADSORPTION STUDIES

(i) Heat of adsorption

The value of heat of adsorption (\( Q_{ads} \)) on Brass in 1N Hydrochloric acid containing various concentration of AHR was calculated using Eqn-4.8. The calculated values of \( Q_{ads} \) are reported in Table- 10.3. These negative values were indicated that the surface coverage (\( \theta \)) was decreased with rise in temperature.

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(ii) Adsorption isotherm

(a) Langmuir adsorption isotherm

According to Langmuir adsorption isotherm from Eqn-4.10, a plot of $\log C/\theta$ versus $\log C$, linear plots were generated (Fig.10.1) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of AHR inhibitor on brass in 1.0N Hydrochloric acid means that there was no interaction between the adsorbed species.

![Langmuir isotherm for the adsorption of AHR inhibitor on brass (Cu-40Zn) in 1.0N Hydrochloric acid.](image)

(iii) Free energy of adsorption

The standard free energy of adsorption $\Delta G_{\text{ads}}$ can be calculated using the Eqn-4.9. The negative values of $\Delta G_{\text{ads}}$ (Table- 10.4) ensured the spontaneity of the adsorption process and the stability of the adsorbed layer.
Table- 10.4 Langmuir adsorption parameters for the adsorption of AHR on brass(Cu-40Zn) in 1.0N Hydrochloric acid.

<table>
<thead>
<tr>
<th>Adsorption Isotherms</th>
<th>Temperature (Kelvin)</th>
<th>Slope</th>
<th>Log &lt;i&gt;k&lt;/i&gt;</th>
<th>&lt;i&gt;R&lt;/i&gt;&lt;sup&gt;2&lt;/sup&gt;</th>
<th>∆&lt;i&gt;G&lt;/i&gt;&lt;sub&gt;ads&lt;/sub&gt; kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303</td>
<td>0.4492</td>
<td>1.8878</td>
<td>0.9962</td>
<td>-10.952</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.4549</td>
<td>1.8339</td>
<td>0.9954</td>
<td>-10.991</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.4391</td>
<td>1.8715</td>
<td>0.9935</td>
<td>-11.754</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.4492</td>
<td>1.8878</td>
<td>0.9962</td>
<td>-12.398</td>
</tr>
</tbody>
</table>

10.1.2. ELECTROCHEMICAL STUDIES

10.1.2.1. Polarisation studies

The Fig.10.2 represents the anodic and cathodic polarisation behaviour of brass (Cu-40Zn) in 1.0N Hydrochloric acid in the presence and absence of AHR inhibitor and the corresponding data are shown in Table- 10.5. The value of corrosion current density was found to decrease from 2.47 to 0.32µA/cm<sup>2</sup> and the corrosion potential (<i>E</i><sub>corr</sub>) was shifted to more negative direction from -269 to -279mV. It very well reveals that the AHR extract inhibit the acid corrosion of brass with predominantly control the cathodic reaction. Therefore this inhibitor behaves as mixed type. The effectiveness of inhibitors increased with concentrations as observed in weight loss data. Which indicate that there was a good correlation between the percentage of inhibition efficiencies observed in the previous measurement.
Fig. 10.2 Polarisation curves for brass (Cu-40Zn) in 1.0N Hydrochloric acid containing various concentration of AHR inhibitor.

10.1.2.2. Electrochemical impedance (EIS) studies

The electrochemical impedance spectroscopy (EIS) measurement for brass (Cu-40Zn) in 1.0N Hydrochloric acid containing various concentration of AHR inhibitor is shown in Fig. 10.3(a) and the corresponding data are reported in Table-10.5. Here the $R_{ct}$ values increased from 180 to 2060Ω with increase of inhibitor concentration. It obvious that the formation of protective film on the metal surface. The $R_{ct}$ value increased with increase of inhibitor concentration and followed by decreased in the dissolution rate of brass.
Table- 10.5 Parameters derived from electrochemical measurements of brass (Cu-40Zn) in 1.0N Hydrochloric acid containing various concentration of AHR inhibitor.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Polarisation studies</th>
<th>Impedance studies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_{corr} (mV vs SCE)</td>
<td>b_a (mV/decade)</td>
</tr>
<tr>
<td>Blank</td>
<td>-269</td>
<td>64.91</td>
</tr>
<tr>
<td>10</td>
<td>-296</td>
<td>63.27</td>
</tr>
<tr>
<td>50</td>
<td>-297</td>
<td>63.02</td>
</tr>
<tr>
<td>100</td>
<td>-279</td>
<td>62.20</td>
</tr>
</tbody>
</table>

In the Bode impedance plot (f vs Z) is shown in Fig.10.3(b). It represented that the value of impedance increased with increase of inhibitor concentration and suggest that the protective film formed on the metal surface was more stable. In Bode phase plot (Fig.10.3(c)) the phase angle at higher frequencies was attributed anticorrosion performance. The phase angle increased with increase of inhibitor concentration.
Fig. 10.3. (a-c) Electrochemical impedance plots, Nyquist (a) Bode impedance plot (b), phase angle plot (c), for brass (Cu-40Zn) in 1.0N Hydrochloric acid containing various concentration of AHR extract.
10.1.3. MORPHOLOGICAL STUDIES

10.1.3.1. UV analysis

Fig. 10.4(a) and (b) show that the UV visible spectrum of the corrosion product on the surface of brass (Cu-40Zn) in the absence and presence of AHR extract in 1 Hydrochloric acid. In the absence of inhibitor, the UV absorption maximum with two band around 278.92nm, 338.00nm and in the presence of inhibitor two band around 281.20nm, 515.50nm were noticed. Thus in the presence of inhibitor both the absorption band shifted to longer wavelength region i.e.; Bathochromic shift (or) red shift. This results revealed that the binding between the active group present in the inhibitor and the surface of the metal.

![UV spectrum of corrosion product on brass(Cu-40Zn) in 1.0N Hydrochloric acid](a) (b)

Fig. 10.4 (a-b), UV spectrum of corrosion product on brass(Cu-40Zn) in 1.0N Hydrochloric acid (a) in the abesence, (b) in the presence of AHR inhibitor.
10.1.3.2. FT-IR analysis

Fig. 10.5(a), (b) and (c) shows that the IR spectrum of the ethanolic crystals of AHR extract, corrosion product formed on brass (Cu-40Zn) in the absence and presence of inhibitor in 1.0N Hydrochloric acid. On comparing spectra (Fig.10.5(a) and(c) ) the –OH stretch was shifted from 3256 cm\(^{-1}\) to 3347.89 cm\(^{-1}\), the –CH (alkane) stretch was shifted 2968 cm\(^{-1}\) to 2909.95 cm\(^{-1}\), the –C=O carbonyl stretch was shifted from1684 cm\(^{-1}\) to 1636.50 cm\(^{-1}\), the aromatic C=C stretch was shifted from 1486 cm\(^{-1}\) to 1430.05 cm\(^{-1}\), the C-O stretch was shifted from 1262 cm\(^{-1}\) to 1361.877 cm\(^{-1}\), the C-N stretch was shifted from 1018 cm\(^{-1}\) to 1060.41 cm\(^{-1}\), the =CH (alkene) stretch was shifted from 674 cm\(^{-1}\) to 613.98 cm\(^{-1}\), indicating that there was a interaction between the inhibitor and surface of the metal. It observed that certain peaks have been disappeared and some have shifted to higher and lower frequency region, providing that some adsorption has been taking place over the metal surface in the presence of green inhibitor.

![Fig.10.5 (a) FT-IR spectrum of alcoholic crystals of AHR inhibitor.](image-url)
Fig. 10.5 (b) FT-IR spectrum of corrosion product on brass (Cu-40Zn) in the absence of AHR inhibitor in 1.0N Hydrochloric acid.

Fig. 10.5 (c) FT-IR spectrum of corrosion product on brass (Cu-40Zn) in the presence of AHR inhibitor in 1.0N Hydrochloric acid.

10.1.3.3. XRD analysis

The Corrosion product formed on brass (Cu-40Zn) surface was examined by XRD studies and this pattern is shown in Fig.10.6. It revealed that the formation of protective film may be combine with rich amount composite such as CuO, CuCO$_3$, ZnCl$_2$, Zn(OH)$_2$ and ZnO formed on the metal surface confirm the co-ordination between the metal atom and the inhibitor molecules.

Fig.10.6. XRD spectrum of corrosion product on brass (Cu-40Zn) in the presence of AHR inhibitor in 1.0N Hydrochloric acid.

10.1.3.4. SEM analysis

The surface morphology of brass was studied by scanning electron microscope (SEM). Fig.10.7(a) and (b) show that the SEM magnification of corrosion surface of brass in hydrochloric acid. This SEM photographs shows that the surface of metal has pits, crevices and severely affected by the corrosive environment but in presence of inhibitor they are minimized on the metal surface as shown in Fig.10.7 (c-d). In Fig.10.7 (c) clearly indicated that the low concentration of inhibitor, the metal completely shielded by spongy like structure of inhibitor molecule. But in the case of higher concentration (Fig.10.7(d)) uniform polished surface was formed. These noticeable variations of the microstructures of the films reflect that the inhibitor adsorbs strongly on the metal surface.
Fig. 10.7 (a-d). SEM image of brass (Cu-40Zn) in 1.0N Hydrochloric acid alone (a-b), SEM image of brass in 1.0N Hydrochloric acid having (c) 10ppm (d) 100ppm of AHR inhibitor.
Table 10.6: The corrosion parameters of brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor at different exposure time.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Weight loss (mg)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.025</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>15</td>
<td>1.15</td>
<td>0.0027</td>
<td>56.25</td>
</tr>
<tr>
<td>30</td>
<td>0.013</td>
<td>0.008</td>
<td>69.25</td>
</tr>
<tr>
<td>50</td>
<td>0.011</td>
<td>0.006</td>
<td>73.66</td>
</tr>
<tr>
<td>70</td>
<td>0.009</td>
<td>0.003</td>
<td>76.14</td>
</tr>
<tr>
<td>100</td>
<td>0.007</td>
<td>0.002</td>
<td>79.63</td>
</tr>
</tbody>
</table>
Table 10.7: The corrosion parameters of brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor at different temperature.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Weight loss (mg)</th>
<th>Corrosion rate (mmpy)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313K</td>
<td>333K</td>
<td>343K</td>
</tr>
<tr>
<td>0</td>
<td>6</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
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<td>30</td>
<td>4</td>
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<tr>
<td>70</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
10.2. IN NATURAL SEA WATER

10.2.1. NON-ELECTROCHEMICAL METHOD

10.2.1.1. Weight loss method

The dezincification behaviour of brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor with different exposure time from 15days to 90days were carried out by mass loss method and the values are recorded in Table- 10.6. In the absence of inhibitor, the value of dezincification of brass increased with increase of exposure time. However in the presence of inhibitor, the corrosion rate was gradually decreased from 0.032 to 0.006mmpy, 0.025 to 0.014mmpy after 15days and 90days exposure time. The value of corrosion rate increased from 0.006 to 0.014mmpy with increase of exposure time at 100ppm of inhibitor concentration. The maximum of 81.25% of inhibition efficiency was attained and the percentage of inhibition efficiency increased with increase of inhibitor concentration and decreased with rise in exposure time. This may be due to the organic matter in the extract adsorbed on the metal surface to create a barrier to charge and mass transfer, thus protecting the alloy surface from corrosive media.

10.2.1.2. EFFECT OF TEMPERATURE

The corrosion behaviour of brass in Natural sea water containing various concentration of AHR inhibitor with rise in temperature from 313 to 343K was investigated by mass loss measurement and the calculated values are shown in Table- 10.7. In the absence of inhibitor, the value of corrosion rate increased from 0.8274 to 1.2411mmpy with increase of temperature. The corrosion rate was significantly decreased with increase of inhibitor concentration from 0.8274 to 0.1378 mmpy, 1.2411 to 0.5515mmpy at 313K and 343K in Natural sea water environment. The maximum of 83.34 % of inhibition efficiency was achieved at 313K. The percentage of inhibition
efficiency decreased with rise in temperature was suggestive of physisorption process mechanism.

10.2.1.2.1. ACTIVATION ENERGY

The values of Corrosion rate obtained from the mass loss measurement were substituted in Eqn-4.7 and the calculated values of activation energy are presented in Table-10.8. The activation energy increased from 13.986 to 41.269 kJ/mol with increase of inhibitor concentration. The average value of $E_a$ obtained from the blank (12.065 kJ/mol) was lower than that of the values obtained for a system containing various concentrations of AHR extract in Natural sea water. This result indicated that the AHR inhibitor adsorbed on the surface of brass by physical adsorption.

10.2.1.2.2. ADSORPTION STUDIES

(i) Heat of adsorption

The value of heat of adsorption ($Q_{ads}$) on brass in Natural sea water containing various concentration of AHR inhibitor was calculated using Eqn-4.8. The calculated values of $Q_{ads}$ are reported in Table-10.8. These negative values indicated that the adsorption of AHR inhibitor on the metal surface was exothermic.

<table>
<thead>
<tr>
<th>S.no</th>
<th>Conc. (ppm)</th>
<th>% of I.E</th>
<th>$E_a$ (kJ/mol)</th>
<th>$Q_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Blank</td>
<td>--</td>
<td>12.065</td>
<td>---</td>
</tr>
<tr>
<td>2.</td>
<td>10</td>
<td>16.68</td>
<td>13.986</td>
<td>-12.870</td>
</tr>
<tr>
<td>3.</td>
<td>30</td>
<td>33.37</td>
<td>16.658</td>
<td>-16.589</td>
</tr>
<tr>
<td>4.</td>
<td>50</td>
<td>50.06</td>
<td>20.626</td>
<td>-21.074</td>
</tr>
<tr>
<td>5.</td>
<td>70</td>
<td>66.75</td>
<td>27.267</td>
<td>-26.914</td>
</tr>
<tr>
<td>6.</td>
<td>100</td>
<td>83.31</td>
<td>41.269</td>
<td>-41.213</td>
</tr>
</tbody>
</table>
(ii) Adsorption isotherm

(a) Langmuir adsorption isotherm

According to Langmuir adsorption isotherm from Eqn-4.10, a plot of logC/θ versus logC, linear plots were generated (Fig.10.8) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of AHR inhibitor on brass surface means that there was no interaction between the adsorbed species.

![Langmuir isotherm for the adsorption of AHR inhibitor on brass (Cu-40Zn) in Natural sea water.](image)

(iii) Free energy of adsorption

The standard free energy of adsorption $\Delta G_{ads}$ can be calculated using the Eqn-4.9. The negative values of $\Delta G_{ads}$ (Table- 10.9), indicating that the inhibitor strongly and spontaneously adsorbed on the surface of the metal.

Table- 10.9 Langmuir adsorption parameters for the adsorption of AHR inhibitor on brass (Cu-40Zn) in Natural sea water.

<table>
<thead>
<tr>
<th>Adsorption Isotherm</th>
<th>Temperature (Kelvin)</th>
<th>Slope</th>
<th>log k</th>
<th>$R^2$</th>
<th>$-\Delta G_{ads}$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>313</td>
<td>0.2994</td>
<td>1.9161</td>
<td>0.9856</td>
<td>11.483</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.2828</td>
<td>1.9440</td>
<td>0.9874</td>
<td>12.023</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.2915</td>
<td>1.9694</td>
<td>0.9899</td>
<td>12.934</td>
</tr>
</tbody>
</table>
10.2.2. ELECTROCHEMICAL STUDIES

10.2.2.1. Polarisation studies

The Fig.10.9 indicates the polarisation behaviour of (Cu-40Zn) brass in Natural sea water containing various concentration of AHR inhibitor and the parameters are given in Table- 10.10. The corrosion current density decreased from 6.53 to 1.04 µA/cm² with increase of inhibitor concentration from 0 to 100ppm. This Figure represented that the corrosion potential was shifted to noble or passive direction i.e., the $E_{corr}$ changed from -263 to -243mV. This may be due to the adsorption of inhibitor molecules on the surface of brass. It very well indicated that the AHR extract inhibited the anodic as well as cathodic reactions, suggesting that the inhibitor was act as mixed type and the inhibition efficiency calculated from the intersection of the anodic and cathodic Tafel slopes were in good agreement with those observed from the mass loss data.

![Polarisation curves for brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor.](image)

Fig.10.9 Polarisation curves for brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor.
10.2.2.2. Electrochemical Impedance (EIS) studies

The Fig.10.10(a) portrays the Nyquist plot for (Cu-40Zn) brass in Natural sea water containing various concentrations of AHR extract. The values of $R_{ct}$ increased from 346 to 2813Ω with increase of inhibitor concentration due to the formation of Metal-Inh complex on the metal surface. The calculated value of inhibition efficiency increased from 72.58 to 87.70% with increase of inhibitor concentration.

Table 10.10 Parameters derived from electrochemical measurements of brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Polarisation studies</th>
<th>Impedance studies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{corr}$ (mV vs SCE)</td>
<td>$b_a$ (mV/decade)</td>
</tr>
<tr>
<td>Blank</td>
<td>-263</td>
<td>67.89</td>
</tr>
<tr>
<td>10</td>
<td>-211</td>
<td>61.26</td>
</tr>
<tr>
<td>50</td>
<td>-220</td>
<td>66.87</td>
</tr>
<tr>
<td>100</td>
<td>-243</td>
<td>70.538</td>
</tr>
</tbody>
</table>

Fig.10.10 (b), the Bode impedance plot indicates that the impedance increased with increase of inhibitor concentration and consequently the inhibition efficiency was increased. Fig. 10.10(c) shows the Bode phase plot in the theta- frequency format for brass in Natural sea water in the presence and absence of AHR inhibitor. It reflected that the phase angle increased and impedance of the double layer decreased with increase of inhibitor concentration.
Fig. 10.10 (a-c) Electrochemical impedance plots, Nyquist (a), Bode impedance plot (b) phase angle plot (c) for brass (Cu-40Zn) in Natural sea water containing various concentration of AHR inhibitor.
10.2.3. MORPHOLOGICAL STUDIES

10.2.3.1. UV analysis

Fig.10.11(a) and (b) show that the UV visible spectrum of the corrosion product on the surface of brass (Cu-40Zn) in the absence and presence of AHR inhibitor in Natural sea water. In the absence of inhibitor, one absorption band around 256.20nm and in the presence of inhibitor one band around 410.00nm were noticed. Thus in the presence of inhibitor the absorption band shifted to longer wavelength region i.e.; Bathochromic shift (or) red shift. This results revealed that the binding between the active group present in the inhibitor and the surface of the metal.

![Fig.10.11. UV spectrum of corrosion product on brass (Cu-40Zn) in Natural sea water (a) in the absence and (b) in the presence of AHR inhibitor.](image)

10.2.3.2. FT-IR analysis

Fig.10.5(a) and 10.12 shows that the IR spectrum of the ethanolic crystals of AHR extract and corrosion product formed on brass (Cu-40Zn) in the presence of inhibitor in Natural sea water. On comparing both spectra the –OH stretch was shifted from 3256cm\(^{-1}\) was 3506.59cm\(^{-1}\), the –CH (alkane) stretch was shifted 2968cm\(^{-1}\) to
2925.26 cm\(^{-1}\), the \(-\text{C}=\text{O}\) carbonyl stretch was shifted from 1684 cm\(^{-1}\) to 1672.82 cm\(^{-1}\), the aromatic \(-\text{C}=-\text{C}\) stretch was shifted from 1486 cm\(^{-1}\) to 1466.96 cm\(^{-1}\), the \(-\text{C}-\text{O}\) stretch was shifted from 1262 cm\(^{-1}\) to 1286.62 cm\(^{-1}\), the \(-\text{C}-\text{N}\) stretch was shifted from 1018 cm\(^{-1}\) to 1118.46 cm\(^{-1}\), the \(=\text{CH}\) (alkene) stretch was shifted from 674 cm\(^{-1}\) to 614.48 cm\(^{-1}\), indicating that there was an interaction between the inhibitor molecules and surface of the metal. It was observed that certain peaks have been disappeared; some have shifted to lower and higher frequency region, providing that some co-ordination takes place over the metal surface and the active inhibitor molecules.

Fig.10.12 (c) FT-IR spectrum of corrosion product on brass (Cu-40Zn) in the presence of AHR inhibitor in Natural sea water.

10.2.3.3. XRD analysis

The corrosion product of brass in the presence of inhibitor was analysed by XRD is shown in Fig.10.13. The corrosion product may be combine with rich amount of \(\text{Cu}_2\text{O}\), \(\text{ZnCl}_2\), \(\text{ZnO}.\text{CO}_2\), and basic \(\text{Cu CO}_3.\text{Cu(OH)}_2\) complex with the surface of the metal atom.
10.2.3.4. SEM images

Surface examination using SEM was carried out to study the effect of inhibitors on the surface morphology of brass metal. In the absence of inhibitors (Fig.10.14(a)), a very rough surface was observed due to rapid corrosion attack of metal by chloride anions present in the Natural sea water. Inspection of figure revealed that the surface was damaged severely in the absence of inhibitor, while in the presence of the inhibitor, the extent of corrosion was much less. These observations confirm that the brass surfaces were covered with the inhibitor molecules and the protective inhibitor layers were formed. The faceting observed in Fig. 10.14(b-d) was gone and the surface was free from pits and it was smooth. It can be concluded that the rate of corrosion was minimized in the presence of inhibitor.

Fig.10.13. XRD spectrum of corrosion product on brass (Cu-40Zn) in the presence of AHR inhibitor in Natural sea water.
Fig.10.14 (a-d), SEM image of stainless steel in Natural sea water alone (a). various magnification of SEM image of stainless steel exposed to Natural sea water having (b - d ) 50ppm, (c) having 100ppm of AHR inhibitor.
From the above investigations, the following conclusions were drawn.

The inhibition effect of *Arachis hypogaea* root (AHR) extract on brass (Cu-40Zn) in 1.0N Hydrochloric acid and Natural sea water environment were studied by Electrochemical and Non-electrochemical method with various exposure time and temperature.

**In Hydrochloric acid**

The corrosion rate increased from 0.431 to 0.573 mmpy with increase of exposure time from 24hrs to 360hrs in the absence of inhibitor.

In the presence on AHR the corrosion rate was significantly reduced from 0.431 to 0.069 and 0.573 to 0.231 with increase of increase of inhibitor concentration from 0 to 100ppm.

The maximum of 87.90% of inhibition efficiency was achieved at 100ppm of inhibitor concentration.

In temperature studies the value of corrosion rate increased with rise in temperature. The maximum 74.91, 50.00% of inhibition efficiency was achieved at 303K and 343K.

The values of activation energy ($E_a$) were found to range from 12.090 to 27.066 kJ/mol, indicating that the adsorption of AHR consistent with the mechanism of physical adsorption.

The value of Heat of adsorption ($Q_{ads}$) were negative (-15.484 to –23.736 kJ/mol) and indicated that the adsorption of AHR extract on the brass surface was exothermic.

The negative value of free energy of adsorption ($\Delta G_{ads}$) suggested that the spontaneous adsorption inhibitor on the surface of metal.
In polarisation studies the value of $I_{\text{corr}}$ decreased from 2.47 to 0.32 µA/cm$^2$ and the value of $E_{\text{corr}}$ was shifted to negative direction.

The impedance method revealed that the value of $R_{\text{ct}}$ increased from 180 to 2060Ω and the maximum of 91.26% of inhibition efficiency was achieved. The electrochemical values are good agreement with mass loss data.

The inhibitor obeys Langmuir adsorption isotherm and behaved as mixed type.

The UV and FTIR spectral analysis may confirm the complex formation on the metal surface and XRD spectra may confirmed the CuO, CuCO$_3$, ZnCl$_2$, Zn(OH)$_2$ and ZnO complex formed on the metal surface.

The SEM images shows that in the absence of inhibitor the surface of the metal was severely affected by pits and crevices and in the presence of inhibitor metal was shielded by spongy like structure of inhibitor molecules. At high concentration of inhibitor uniform polished smooth surface was formed.

**In Natural sea water**

The dezincification behaviour of brass (Cu-40Zn) was increased with increase of exposure time in the absence of inhibitor.

In the presence of AHR inhibitor, the corrosion rate was moderately decreased from 0.032 to 0.006 mmpy, 0.025 to 0.014 mmpy after 15days and 90days exposure time.

The maximum of 81.25% of inhibition efficiency was achieved.

In temperature studies the maximum of 83.34, 55.56% of inhibition efficiency was attained at 313K and 343K respectively. The decrease of inhibition efficiency with rise in temperature was suggestive of physical adsorption mechanism.

The calculated values of activation energy ($E_a$) were also agreed with physisorption process.
The measured value of heat of adsorption \( (Q_{\text{ads}}) \) and free energy of adsorption \( (\Delta G_{\text{ads}}) \) reflected that the adsorption of inhibitor was exothermic and spontaneous process.

In polarisation studies the value of \( I_{\text{corr}} \) decreased from 6.53 to 1.04 \( \mu \text{A/cm}^2 \) and the value of \( E_{\text{corr}} \) shifted to passive direction.

The impedance method reveals that the value of \( R_{\text{ct}} \) increased from 346 to 2813\( \Omega \) and maximum of 87.70\% of inhibition efficiency was achieved. The electrochemical values are also good agreement with mass loss data.

The inhibitor obeyed Langmuir adsorption isotherm.

The corrosion product over the surface of the brass in the presence of inhibitor is characterised by UV and IR studies support that the good performance of AHR inhibitor on the metal surface. The XRD spectra may also confirm that the rich amount of \( \text{Cu}_2\text{O}, \text{ZnCl}_2, \text{ZnO}, \text{CO}_3 \) and basic \( \text{Cu CO}_3\cdot\text{Cu(OH)}_2 \) complex formed on the brass surface.

The SEM structure reflected that the entire surface of the brass covered almost completely, led to reduce the dezincification of brass in Natural sea water media.
Comparison of inhibition efficiency of Green inhibitor

From the above investigation, the inhibition behaviour of various green inhibitors on different electrode in acid and Natural sea water environment were compared and presented in the comparison Table.

It clear that the *Vinca rosea* leaves extract on stainless steel in both environment has greater I.E (even at 100ppm) than *Solanum trilobatum* leaves extract. The maximum of 92.07 and 87.75% of inhibition efficiency was achieved in acid and Natural sea water.

In both environment the *Cynodon dactylon* has better performance than *Hibiscus-rosa sinensis* flower in copper. The maximum of 84.82 and 92.19% of inhibition efficiency was attained in acid and Natural sea water media.

In brass (Cu-40Zn), the *Jatropha curcas* had more effective in Natural sea water media (even at 100ppm) achieved more than 90.62% of I.E was achieved. The *Arachis hypogaea* root extract had more active in acid media (even 100ppm) and to attain 87.90% of inhibition efficiency.

In over all comparison, *Vinca rosea* leaves extract was more active on stainless steel and achieved greater than 92% in Hydrochloric acid media even at 100ppm of inhibitor concentration. The *Cynodon dactylon* and *Jatropha curcas* were better performance on copper and brass in Natural sea water environment. The maximum of 92.19 and 90.62% of I.E was achieved on copper and brass (Cu-40Zn) in natural sea water in CDL and JCL respectively.
## Comparison Table

<table>
<thead>
<tr>
<th>S.no</th>
<th>Inhibitor</th>
<th>Conc. of inhibitor (ppm)</th>
<th>Environment</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Vinca rosea</td>
<td>100</td>
<td>1.0N Hydrochloric acid</td>
<td>92.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>Natural sea water</td>
<td>87.75</td>
</tr>
<tr>
<td>2.</td>
<td>Cynodon dactylon</td>
<td>500</td>
<td>1.0N Hydrochloric acid</td>
<td>84.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>Natural sea water</td>
<td>92.19</td>
</tr>
<tr>
<td>3.</td>
<td>Jatropha curcas</td>
<td>1000</td>
<td>1.0N Hydrochloric acid</td>
<td>80.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>Natural sea water</td>
<td>90.62</td>
</tr>
<tr>
<td>4.</td>
<td>Solanum trilobatum</td>
<td>500</td>
<td>1.0N Hydrochloric acid</td>
<td>84.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>Natural sea water</td>
<td>77.55</td>
</tr>
<tr>
<td>5.</td>
<td>Hibiscus rosa-sinensis</td>
<td>1000</td>
<td>1.0N Hydrochloric acid</td>
<td>84.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>Natural sea water</td>
<td>85.93</td>
</tr>
<tr>
<td>6.</td>
<td>Arachis hypogaea</td>
<td>100</td>
<td>1.0N Hydrochloric acid</td>
<td>87.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>Natural sea water</td>
<td>81.25</td>
</tr>
</tbody>
</table>
GENERAL MECHANISM

The following mechanism proposed for the corrosion of steel in acid and Natural sea water.

Anodic dissolution process

\[
\text{Fe} + \text{Cl}^- \rightarrow (\text{FeCl}^-)_{\text{ads}} \quad \text{(1)}
\]

\[
(\text{FeCl}^-)_{\text{ads}} \rightarrow (\text{FeCl}^+)_{\text{ads}} + e^- \quad \text{(2)}
\]

\[
(\text{FeCl}^+)_{\text{ads}} \rightarrow (\text{Fe}^{2+})_{\text{ads}} + \text{Cl}^- \quad \text{(3)}
\]

Cathodic reduction process

\[
\text{Fe} + \text{H}^+ \rightarrow (\text{FeH}^+)_{\text{ads}} \quad \text{(4)}
\]

\[
(\text{FeH}^+)_{\text{ads}} + e^- \rightarrow (\text{FeH})_{\text{ads}} \quad \text{(5)}
\]

\[
(\text{FeH}^+)_{\text{ads}} + \text{H}^+ + e^- \rightarrow \text{Fe} + \text{H}_2 \quad \text{(6)}
\]

The protonated inhibitor molecules are adsorbed at cathodic sites in competition hydrogen ions and hence reduced the H\(_2\) gas evolution.

The mostly accepted reaction of the first step in the adsorption of an organic inhibitor on a metal surface usually involved the replacement of one or more water molecules adsorbed at the metal surface.

\[
\text{Inh}_{\text{(sol)}} + x \text{H}_2\text{O}_{\text{(ads)}} \leftrightarrow \text{Inh}_{\text{(ads)}} + x \text{H}_2\text{O} \quad \text{(7)}
\]

The inhibitor may combine with freshly generated Fe\(^{2+}\) ions on steel surface, forming metal inhibitor complexes.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(8)}
\]

\[
\text{Fe}^{2+} + \text{Inh}_{\text{(ads)}} \rightarrow [\text{Fe-Inh}]_{\text{ads}} \quad \text{(9)}
\]

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution.
The following mechanism proposed for the corrosion of copper and its alloy in acid and Natural sea water

The theories on the anodic dissolution (dezincification) mechanism of brass were studied by Holliday et.al. and Pickering et.al. [306-307]. They suggested the participation of [OH\(^-\)] ions directly during the dissolution of brass in both alkaline and acidic and neutral solutions. Anodic dissolution of brass in acidic solutions may be written as,

\[
(Cu - Zn) + Cl^- + H_2O \rightleftharpoons [CuCl OH^-]_{ads} + H^+ + e^- \tag{10}
\]

\[
[CuCl OH^-]_{ads} \rightarrow [CuCl OH^-] + e^- \tag{11}
\]

\[
[CuCl OH^-] + H^+ \rightarrow Cu^{++} + Cl^- + H_2O \tag{12}
\]

\[
Cu^{++} + Zn \rightarrow Zn^{++} + Cu \tag{13}
\]

In the presence of inhibitor

\[
Cu-Zn + Inh \rightarrow [Cu - Inh]_{ads} + [Zn Inh]_{ads} \tag{14}
\]

\[
[CuCl OH^-]_{ads} + [Cu - Inh]_{ads} \rightarrow [CuCl OH^- Inh Cu]_{ads} \tag{15}
\]

\[
[CuCl OH^- InhCu]_{ads} \rightleftharpoons [CuCl OH Inh Cu] + e^- \tag{16}
\]

\[
[CuCl OH Inh Cu] \rightleftharpoons [Cu OH Cl] + [Cu Inh]_{ads} \tag{17}
\]

\[
[Cu OH Cl] + H^+ \rightarrow Cu^{++} + Cl^- + H_2O \tag{18}
\]

\[
Cu^{++} + Zn \rightarrow Zn^{2+} + Cu \tag{19}
\]

The formation of [Cu OH Cl] complex was possible as they are formed rapidly as intermediate in the dissolution process. The rapid formation of the [Cu OH Cl] complex led to their accumulation and adsorption on the alloy surface. The [Cu OH Cl] films formed were not stable and underwent film decomposition to the highly soluble Cu\(^{2+}\) compounds, leading to the observed copper appearance on the alloy surface.

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2Cu⁺ → Cu + Cu (II)  \[\text{(20)}\]

The Cu(II) species formed the highly soluble CuCl₂ leaving copper patches on the brass surface. Alloy dezincification enhanced the decomposition of the adsorbed [Cu OH Cl] film by shifting reaction 19 to right due to the reaction of zinc with formed Cu⁺⁺ compounds. [Cu⁺⁺ + Zn → Zn⁺⁺ + Cu]. In the presence of inhibitor, in acidic and natural sea water the chloride solution inhibition efficiencies increased with a decrease of [H⁺] and [Cl⁻] ion concentrations. The reduction of dissolution rate of copper and zinc in presence of inhibitor may be due to the formation of Cu(I)-Inh complex along with zinc complex on the brass surface.

2Cu⁺ → Cu + Cu(II)  \[\text{(21)}\]

The Cu (II) species formed the highly soluble CuCl₂ leaving copper patches on the brass surface. Alloy dezincification enhanced the decomposition of the adsorbed [Cu OH Cl] film by shifting reaction 9 to right due to the reaction of zinc with formed Cu⁺⁺ compounds. [Cu⁺⁺ + Zn → Zn⁺⁺ + Cu]. In the presence of inhibitor, in acidic chloride solution inhibition efficiencies increased with a decrease of [H⁺] and [Cl⁻] ion concentrations. The reduction of dissolution rate of copper and zinc in presence of inhibitor may be due to the formation of Cu(I)-Inh complex along with zinc complex on the brass surface. The increase of surface coverage suggest that the inhibition mechanism of anodic dissolution of brass by the inhibitor follow simple adsorption mode without affecting the dissolution.