Magnolia Champaca- Stem Extracts as Corrosion Inhibitor for Mild Steel In Acid Medium

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Abstract

The corrosion inhibitive action of flower extracts of Magnolia champaca stem on mild steel corrosion in 1 M HCl solution was studied using weight loss method, potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in 1 M HCl solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.

Key words: Inhibitor, Impedance, Polarization, Magnolia champaca

1. Introduction

Many of the several corrosion problems encountered in chemical inhibitors by inhibitors obtained from natural the industries involves acids and in certain cases due to sources is required to keep the environment more healthy, alkalis and solvents. Hence corrosion inhibition programs safely and under pollution control. Various natural are now required in many industries such as oil and gas products, e.g. Artemisia oil (Bouyanzer and Hammouti, exploration and production, petroleum refining, chemical 2004), Lawsonia extract (El-Etre et al., 2005), Telfaria manufacturing and the product additive industries. occidentalis extract (Oguzie, 2005), Ammi majus L. fruit The corrosion inhibition is achieved by the
addition extracts (Arab et al., 2005), juice of Prunus cerasus of inhibitors to the system that prevent corrosion from (Ashassi-Sorkhabi and Seifzadeh, 2006), Pennyroyal oil taking place on metal surface. Inhibitors are chemicals that from Mentha oulegium (Bouyanzer et al., 2006), Occimum often work by adsorbing themselves on the metallic viridis extract (Oguzie, 2006) etc. have been reported to be surface, protecting the metal surface by forming a film. good inhibitors for steel in acidic solutions. The use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers in recent time [1-7]. The aim of this study was to investigate the inhibition effect of Magnolia champaca stem extract as a cheap, raw and non-toxic corrosion inhibitor on steel corrosion in hydrochloric acid. The electrochemical measurements were used to evaluate the inhibition efficiencies.

2.0 MATERIAL AND METHODS:

2.1 Preparation of Magnolia champaca stem extract:
An aqueous extract of Magnolia champaca stem extract was prepared by grinding 5g of plant stem, with distilled water, filtering the suspending impurities, and making up to 100 ml. The extract was used as corrosion inhibitor in the present study.

2.2 preparation of specimens
Carbon steel specimens (0.022% S, 0.038% Mn, 0.027%P, 0.086 C) of dimension 1.0 cm *4.0cm*0.2cm were polished to a mirror finished with the emery sheets of various grades and degreased with trichloroethylene.

2.3 Weight loss method.
Carbon steel specimens in triplicate were immersed in 100 mL of the inhibited and uninhibited 1 M HCl solutions in the presence and absence of TBAB for two hours. The weight of each specimen before and after immersion was
determined using shimadzu balance, model Ay 62. The inhibition efficiency (IE) was then calculated using the expression:

\[ \text{IE}\% = \left( \frac{W_1 - W_2}{W_1} \right) \times 100 \]

Where \( W_1 \) and \( W_2 \) are the corrosion rates in the absence and presence of the inhibitor, respectively.

2.4 Electrochemical impedance measurements

The impedance measurements were performed using a computer–controlled potentiostat (model Solartron SI-1260) and the data were analysed using gain phase analyser electrochemical interface (Solartron SI-1287). A three electrode set up was employed with Pt foil as the auxiliary electrode and a saturated calomel electrode as the reference electrode. The Teflon coated mild steel rod, with the surface prepared as described in the weight loss experimental method, served as the working electrode. The measurements were carried out in the frequency range \( 10^6 \)–\( 10^{-2} \) Hz at the open circuit potential by superimposing sinusoidal AC signal of small amplitude, 10 mV, after an immersion period of 30 min in the corrosive media. The double layer capacitance \( (C_{dl}) \) and charge transfer resistance \( (R_{ct}) \) were obtained from the impedance plots as described elsewhere[8]. Because \( R_{ct} \) is inversely proportional to corrosion current density, it was used to determine the inhibition efficiency (IE\%) using the relationship:

\[ \text{IE}\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \]
Where $R_{ct}$ and $R_{ct}^0$ are the charge transfer resistance values in the inhibited and uninhibited solutions respectively.

### 2.5. Polarization measurements

The potentiodynamic polarization curves were recorded using the same cell setup employed for the impedance measurements. The potentials were swept at the rate of 1.66mV/s, primarily from a more negative potential than $E_{ocp}$ to a more positive potential than $E_{ocp}$ through $E_{corr}$. The inhibition efficiencies were calculated using the relationship [9];

$$IE\% = \frac{I_{corr}^0 - I_{corr}}{I_{corr}} \times 100$$

Where $I_{corr}^0$ and $I_{corr}$ are the corrosion current densities in the absence and in the presence of inhibitor, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1 Analysis of results of mass loss method

The corrosion rates and inhibition efficiency values, calculated using weight loss data, for various concentrations of Magnolia champaca extract in the presence and absence of TBAB the corrosion of carbon steel in 1 M HCl solution are presented in Table.1. It is apparent that the inhibition efficiency increased with the increase in inhibitor concentration in the presence and absence of TBAB. This behavior can be explained based on the strong interaction of the inhibitor molecule with the metal surface resulting in adsorption. The extent of adsorption increases with the increase in concentration of the inhibitor leading to increased inhibition efficiency. The maximum inhibition efficiency was observed at an inhibitor concentration of 100 ppm. Generally, inhibitor molecules suppress the metal dissolution by forming a protective film adsorbed to the metal surface and separating it from the corrosion medium. The corrosion suppressing ability of the inhibitor molecule originates
from the tendency to form either strong or weak chemical bonds with Fe atoms using the lone pair of electrons present on the O and π electrons in benzene ring. It is also seen from table.1 that the stem extract of Magnolia champaca at 2 mL and 10mL concentrations shows 45.28 % and 75.47 % inhibition efficiencies respectively, Then the values increased to 87.74 % after adding 25 ppm of TBAB solution in 1 M HCl solutions containing 10mL of plant extract respectively. This showed a good synergistic effect between Magnolia champaca stem extract and TBAB.

Table1. Corrosion rate (CR) of mild steels in 1 M HCl solutions the absence and presence of inhibitor and the inhibition efficiency (IE) obtained by mass loss method.

<table>
<thead>
<tr>
<th>Inhibitor concentration (mL)</th>
<th>TBAB (0) ppm</th>
<th>CR (mg cm⁻² h⁻¹)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>106</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>58</td>
<td>45.28</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>47</td>
<td>35.66</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>35</td>
<td>66.98</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>29</td>
<td>72.64</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>26</td>
<td>75.47</td>
</tr>
</tbody>
</table>

3.2 Influence of TBAB on the inhibition efficiency of magnolia champaca stem

<table>
<thead>
<tr>
<th>Inhibitor concentration (mL)</th>
<th>TBAB (25) ppm</th>
<th>CR (mg cm⁻² h⁻¹)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mL+25ppmTBAB</td>
<td>13</td>
<td>13</td>
<td>87.74</td>
</tr>
</tbody>
</table>
3.3 Electrochemical impedance spectroscopic measurements (EIS)

Impedance spectra obtained for corrosion of mild steel in 1 M HCl contains two semicircles in which the second one represents the interaction of metal surface with the corrosive environment. The first semicircle represents the nature of the corrosive media. Since the conductivity of the corrosive medium is very low, this also behaves like a leaky capacitor. The CR-CR model best describes this situation. The second semicircle in the impedance plots contain depressed semicircles with the centre below the real axis. The size of the semicircle increases with the inhibitor concentration, indicating the charge transfer process as the main controlling factor of the corrosion of mild steel. It is apparent from the plots that the impedance of the inhibited solution has increased with the increase in the concentration of the inhibitor. The experimental results of EIS measurements for the corrosion of mild steel in 1 M HCl in the absence and presence of inhibitor are given in Table 3. Said that sum of charge transfer resistance ($R_{ct}$) and adsorption resistance ($R_{ad}$) is equivalent to polarization resistance ($R_p$).

Table 3. Impedance parameters obtained from electrochemical impedance studies.

<table>
<thead>
<tr>
<th>Inhibitor concentration mL</th>
<th>$R_{ct}$ Ohm cm$^2$</th>
<th>$C_{dl}$ µF</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.8</td>
<td>$12.31 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>62.98</td>
<td>$2.889 \times 10^{-6}$</td>
<td>76.5</td>
</tr>
<tr>
<td>10+ 25ppm(TBAB)</td>
<td>108.03</td>
<td>$1.687 \times 10^{-6}$</td>
<td>86.3</td>
</tr>
</tbody>
</table>
Table 3. Impedance parameters obtained from electrochemical impedance studies

3.4 Potentiodynamic Polarization studies:

Fig 2. Potentiodynamic polarization curves of mild steel immersed in 1 M HCl solution in the absence and presence of inhibitors
Table. 4  Corrosion parameters in the presence and absence of inhibitor obtained from polarization measurements.

<table>
<thead>
<tr>
<th>Inhibitor concentration ppm</th>
<th>$-E_{corr}$ (mV)</th>
<th>$\beta_c$ (mV)</th>
<th>$\beta_a$ (mV)</th>
<th>$I_{corr} \times 10^6$ µA</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>436</td>
<td>151</td>
<td>90</td>
<td>1.88</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>424</td>
<td>127</td>
<td>71</td>
<td>0.449</td>
<td>76.1</td>
</tr>
<tr>
<td>$10+$ 25ppm(TBAB)</td>
<td>420</td>
<td>159</td>
<td>67</td>
<td>0.265</td>
<td>85.9</td>
</tr>
</tbody>
</table>

The polarization curves obtained for the corrosion of mild steel in the inhibited (100 ppm) and uninhibited 0.5 M H$_2$SO$_4$ solutions in the absence and presence of KI are shown in Fig.2. Electrochemical parameters such as corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), cathodic and anodic tafel slopes ($\beta_c$ and $\beta_a$) and percentage inhibition efficiency according to polarization studies are listed in table 4. Here $I_{corr}$ decreased with increasing inhibitor concentration. From the figures, it can be interpreted that the addition of this inhibitor to corrosive media changes the anodic and cathodic tafel slopes. The changes in slopes showed the influence of the inhibitor both in the cathodic and anodic reactions. However, the influence is more pronounced in the cathodic polarization plots compared to that in the anodic polarization plots. Even though $\beta_c$ and $\beta_a$ values (table.3) change with an increase in inhibitor concentrations, a high $\beta_c$ value indicates that the cathodic reaction is retarded to a higher extent than the anodic reaction[9].

From Fig.2 it is also clear that the addition of the inhibitor shifts the cathodic curves to a greater extent toward the lower current density when compared to the
anodic curves. The $E_{corr}$ value is also shifted to the more negative side with an increase in the inhibitor concentration. These shifts can be attributed to the decrease in the rate of the hydrogen evolution reaction on the mild steel surface caused by the adsorption of the inhibitor molecule to the metal surface[10]. It has been reported that a compound can be classified as an anodic and cathodic type inhibitor on the basis of shift of $E_{corr}$ value. If displacement of $E_{corr}$ value is greater than 85 mV, towards anode or cathode with reference to the blank, then an inhibitor is categorized as either anodic or cathodic type inhibitor otherwise inhibitor is treated as mixed type[11,12]. In our study, maximum displacement in $E_{corr}$ value was around 16 mV, indicating the inhibitor is a mixed type and more anodic nature and does not alter the reaction mechanism. The inhibition effect has occurred due to simple blocking of the active sites, thereby reducing available surface area of the corroding metal [13, 14,15]. The increase in inhibitor efficiency of inhibited (10mL) 1M HCl solution for the corrosion of mild steel after adding 25 ppm TBAB shows synergism between inhibitor molecules and TBAB.

4. CONCLUSIONS
Results obtained from both electrochemical methods showed that the Magnolia champaca stem extract acts as an inhibitor for corrosion of steel in 1M HCl media. Corrosion inhibition action of Magnolia champaca stem extract increased as its concentration increases. Inhibition of steel in 1M HCl solution by Magnolia champaca stem extract is attributed to adsorption of the phytochemical compounds in this extract.

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References