Potentials of *Hyppocratea pallens planch* leave extract as inhibition towards the corrosion of mild steel in acidic media

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**ABSTRACT**

The inhibiting effect of leaf extracts of *Hyppocratea pallens planch* ex oliv on the corrosion of mild steel in 1.0 M HCl and 0.5 M H₂SO₄ solutions has been investigated by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques. The effect of temperature on the corrosion and inhibition processes was studied in the temperature range 303-333K. The presence of this plant extract reduced considerably the corrosion rate of mild steel in acidic media and the corrosion inhibition efficiency increased with extract concentration up to 1000 mgL⁻¹. The results suggest that the extract inhibited the corrosion reaction via adsorption of the organic matter on the metal surface, following the Langmuir isotherm and inhibited both the anodic and cathodic partial reactions.

**Keywords**: Plant extract, Mild steel, acid inhibition, electrochemical technique

**INTRODUCTION**

Mild steel is widely used in most of the chemical industries for the fabrication of various reaction vessels, pipes, tanks, etc; due to its easy availability and low cost [1,2]. Acids are generally used for the removal of undesirable scales and rust in several industrial processes, including pickling and descaling operations. The use of corrosion inhibitors is one of the most effective and economical methods to protect metal surfaces against corrosion in such aggressive media [3-5]. A number of organic compounds have been reported as effective corrosion inhibitors, especially those containing nitrogen, oxygen, sulphur, phosphorus, and multiple bonds or aromatic rings in their structures [6-8]. The lone pairs and π-electron distribution in these functional groups are the key structural features that control the inhibition efficiency [9,10]. Apart from the electronic structure considerations, there are also economic and toxicity considerations. Therefore, the focus now is to develop inexpensive, readily available and non toxic (benign) corrosion inhibiting additives.

In this regard, immense number of scientific studies have been devoted to the inhibitive action of plant extracts on the corrosion of mild carbon steel in acidic media, showing that these extracts could serve as good corrosion inhibitors; the cited extracts include: *Occimum viridis, Telferia occidentalis, Azadirachta indica, Hibiscus sabdariffa and Garciniakola* [11], *Phyllanthus amarus* [12], *Phaseolus vulgares* L.[13], *Chamaemelum mixtum* L., *Cymbopogon proximus, Nigella sativa* L., and *Zenthoxyllum alatum* [14], *Mentha pulegium* [15], and *Lupinus albus* L [16].
The present study is aimed at investigating the inhibitive and adsorption properties of extracts from the leaves of Hippocratea Pallens planch.ex oliv (HPP) on mild steel corrosion in 1 M HCl and 0.5 M H$_2$SO$_4$ using gravimetric and electrochemical methods. HPP is a perennial plant that belongs to the family Celastraceae. It is widely distributed in many parts of Africa including Zimbabwe, Angola, Nigeria and Senegal. The aqueous extract from the bark, leaves and seeds are used in steam-baths to relieve rheumatic pains and for the treatment of dysentery. Preliminary phytochemical tests confirm the presence of alkaloids flavonoids, saponins and tannins [17]. HPP has never been used for the purpose of corrosion inhibition.

MATERIALS AND METHODS

2.1. Materials preparation

Tests were performed on carbon steel specimens with weight percentage composition as follows; C – 0.05; Mn – 0.6; P – 0.36; Si – 0.3 and the balance Fe. The blank corrodents were respectively 1.0 M HCl and 0.5 M H$_2$SO$_4$ solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground leaves of HPP under reflux for 3 hours in 1.0 M HCl and 0.5 M H$_2$SO$_4$ solutions, respectively. The resulting solutions were cooled and then filtered twice. The amount of plant material extracted into solution was obtained by comparing the weight of the dried residue with the initial weight of the dried plant material before extraction. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range 50–1000 mgL$^{-1}$ in the respective corrodents.

2.2. Weight loss measurements

Mild steel coupons of dimensions 3.0 x 3.0 x 0.2 cm were used in the weight loss experiments. Before each experiment the coupons were abraded using SiC papers (grades 200-800) washed with distilled water and dried in acetone and warm air. The pre-cleaned and weighed coupons were suspended in beakers containing the test solutions using glass hooks and rods. Tests were conducted under total immersion conditions in 300 ml of the aerated and unstirred test solutions. To determine weight loss with respect to time, the coupons were retrieved from test solutions after 6 h, appropriately cleaned, dried and re-weighed. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight. All tests were run in triplicate and the data showed good reproducibility. Average values for each experiment were obtained and used in subsequent calculations.

2.3. Electrochemical experiments

Metal samples for electrochemical experiments were machined into cubic specimens and fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one square surface area of 1 cm$^2$ was left uncovered. The exposed surface was ground with silicon carbide abrasive paper (from grade #200 to #1000), degreased in acetone, rinsed with distilled water and dried in warm air. Electrochemical experiments were conducted in a 3-electrode corrosion cell using a VERSASTAT 400 Complete DC Voltammetry and Corrosion System, with V3 Studio software. A graphite rod was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The latter was connected via a Luggin’s capillary. Measurements were performed in aerated and unstirred solutions at the end of 30 min of immersion at 303 K. Impedance measurements were made at corrosion potentials ($E_{corr}$) over a frequency range of 100 kHz – 10 mHz, with a signal amplitude perturbation of 5 mV. Potentiodynamic polarization studies were carried out in the potential range ± 250 mV versus corrosion potential at a scan rate of 0.333 mV s$^{-1}$. Each test was run in triplicate to verify the reproducibility of the systems.

RESULTS AND DISCUSSION

3.1. Weight loss data

Weight loss measurements were carried out in 1.0 M HCl and 0.5M H$_2$SO$_4$ solutions in the absence and presence of different concentrations of HPP extract. Corrosion rates of the mild steel coupons were calculated from the weight loss data using the equation:

$$C_R (mdd) = \frac{\Delta w}{st}$$

where, $\Delta w$ is mass loss (mg), $s$ is area of specimen (dm$^2$) and $t$ is the immersion time in days.
The degree of surface coverage ($\theta$) and inhibition efficiency (IE%) were calculated as follows:

$$\theta = \frac{W_o - W_1}{W_o}$$  \hspace{1cm} (2)

$$IE\% = \frac{W_o - W_1}{W_o} \times 100$$  \hspace{1cm} (3)

Figure 1 presents the effect of increasing the concentration of HPP extract on the corrosion rate of mild steel. The results show that HPP extract inhibited the corrosion of mild steel in 1.0 M HCl and 0.5 M H$_2$SO$_4$ solutions at all the concentrations studied and the extent of corrosion inhibition depends on the concentration of HPP. Increasing the concentration of the extract decreases the corrosion rate of the metal. The data also reveals higher corrosion susceptibility of the mild steel in 0.5 M H$_2$SO$_4$ solution compared to the HCl solution. The fact that the metal specimen manifests higher corrosion susceptibility in 0.5 M H$_2$SO$_4$ is evident that the acid anions influence the corrosion process in different ways.

Figure 1. Effect of different concentrations of HPP on the corrosion of mild steel in 0.5 M H$_2$SO$_4$ and 1 M HCl at 303 K for 3 h immersion period

Figure 2. Variation of inhibition efficiency with concentration of HPP in 1.0 M HCl and 0.5 M H$_2$SO$_4$ at 303 K for 3 h immersion period
Figure 2 illustrates the trend of inhibition efficiency (IE%) with HPP concentration. It is evident from the plot that the inhibition efficiency increased with increase in inhibitor concentration. This suggests that higher concentrations of the extract lead to higher surface coverage. The plot also shows slightly better performance of HPP in 0.5M H$_2$SO$_4$ solution.

3.2. Impedance data

Electrochemical impedance spectroscopy (EIS) is a well-established and powerful tool in the study of the kinetics and mechanisms of corrosion phenomena [4, 18, 19]. Impedance experiments were undertaken to afford insight into the characteristics and kinetics of electrochemical processes occurring at the Fe/1 M HCl and Fe/0.5 M H$_2$SO$_4$ interfaces in absence and presence of 50mgL$^{-1}$ and 1000 mgL$^{-1}$ HPP extract. The impedance responses of these systems are given in Figures 3a and 3b, while Table 1 summarizes the corresponding impedance parameters.

The Nyquist plots generally comprise of only one depressed semicircle in the high frequency region, corresponding to a single time constant. The ionic conductivity and dielectric properties of the oxide film means that it can be represented as a parallel circuit of a resistor and a capacitor. The observed depression of the Nyquist semicircle with centre under the real axis is typical for solid metal electrodes that show frequency dispersion of the impedance data. When such a non ideal frequency response is present the capacitance of the oxide film is replaced by a constant phase element (CPE). The use of such a CPE accounts for the deviations from ideal dielectric behavior and is related to surface inhomogeneities. The impedance, Z of the CPE is:

$$Z_{CPE} = Q^{-1}(j \omega)^{-n}$$  \hspace{1cm} (4)

Where Q and n stand for the CPE constant and exponent respectively, $j = (-1)^{1/2}$ is an imaginary number, $\omega$ is the angular frequency in rad s$^{-1}$, ($\omega = 2 \pi f$) where f is the frequency in Hz. Using the Zsimpwin software, the Nyquist plot for mild steel in uninhibited and inhibited solutions was appropriately analyzed by fitting to the equivalent circuit model $R_s(C_{dl}R_{ct})$. In this equivalent circuit, $R_s$ is the solution resistance, $R_{ct}$ is the charge transfer resistance and $C_{dl}$ is the double layer capacitance. The capacitance values were calculated using the equation [13, 20]:

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_{ct}}$$ \hspace{1cm} (5)

where $f_{\text{max}}$ is he frequency at which the imaginary component of impedance is maximum. The obtained values of the charge transfer resistance were used in computing the percentage inhibition efficiency IE\% as follows:

$$IE\% = \frac{R_{ct} - R_{ct}'}{R_{ct}} \times 100$$ \hspace{1cm} (6)

where $R_{ct}$ and $R'_{ct}$ are the charge transfer resistance in the presence and absence of inhibitor respectively.

Table 1 reveals that introduction of HPP into the acid corrodents caused the charge transfer resistance to increase, while reducing the double layer capacitance. This effect becomes more pronounced at higher HPP concentration. The increase in $R_{ct}$ values in inhibited solutions indicates improved corrosion resistance due to the corrosion inhibiting action of the extract. The decrease in the $C_{dl}$ which can result from a decrease in local dielectric constant and/ or an increase in the thickness of the electric double layer, presents clear experimental evidence of the adsorption of the organic matter from HPP extract on the metal/solution interface. In other words, the reduction in $C_{dl}$ values was caused by the gradual replacement of water molecules by the adsorption of the extract organic matter with lower dielectric constant [21-23]. This implies that HPP extract reduces the corrosion rate of the mild steel specimen in both 0.5 M H$_2$SO$_4$ and 1 M HCl by adsorption of the extract organic matter on the metal surface.
3.3. Polarization data
Potentiodynamic polarization experiments were undertaken to distinguish the effect of HPP extract on the anodic and cathodic corrosion reactions. The polarization curves for the mild steel sample in 1 M HCl and 0.5 M H₂SO₄ without and with HPP extract presented in Figures 4a and 4b all exhibit active dissolution without any distinctive transition to passivation. Figure 4a shows that the extract did not significantly alter the corrosion potential (Ecorr) in 1
M HCl and functioned more or less as a mixed-type inhibitor, reducing both the anodic and cathodic currents. In 0.5 M H₂SO₄ however, HPP is seen to shift $E_{corr}$ in the cathodic direction and the cathodic polarization is also more pronounced than the anodic polarization, indicating that the corrosion process was predominantly under cathodic control.

Inhibition efficiency was quantified from polarization data as follows:

$$IE_{p} (%) = \frac{i_{corr}^o - i_{corr}^i}{i_{corr}^o}$$  \hspace{1cm} (7)
where \( i_{corr}^i \) and \( i_{corr} \) are the values of the corrosion current density without and with inhibitor respectively. The values of \( i_{corr} \), the corrosion potential (\( E_{corr} \)) and inhibition efficiency (IE\( \% \)) are given in Table 2. Also, it can be clearly seen that the inhibition efficiency of HPP extract increases with inhibitor concentration and follows the same trend as the values computed from gravimetric data; i.e. slightly better efficiency in 0.5 M H\(_2\)SO\(_4\).

Table 2. Potentiodynamic polarization parameters for mild steel in 1.0 M HCl and 0.5 M H\(_2\)SO\(_4\) without and with 50 and 1000mgL\(^{-1}\) HPP extract at 303K

<table>
<thead>
<tr>
<th>System</th>
<th>( i_{corr} ) (µA/cm(^2))</th>
<th>( E_{corr} ) (mV)</th>
<th>IE( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0M HCl</td>
<td>4063</td>
<td>-521.6</td>
<td>-</td>
</tr>
<tr>
<td>50mgL(^{-1})</td>
<td>484.5</td>
<td>-512.8</td>
<td>88.1</td>
</tr>
<tr>
<td>1000mgL(^{-1})</td>
<td>385.1</td>
<td>-531.7</td>
<td>90.5</td>
</tr>
<tr>
<td>0.5M H(_2)SO(_4)</td>
<td>14581</td>
<td>-508.2</td>
<td>-</td>
</tr>
<tr>
<td>50mgL(^{-1})</td>
<td>1952.3</td>
<td>-531.7</td>
<td>86.6</td>
</tr>
<tr>
<td>1000mgL(^{-1})</td>
<td>953.2</td>
<td>-532.2</td>
<td>93.5</td>
</tr>
</tbody>
</table>

3.4. Adsorption considerations

Basic information on metal-inhibitor adsorptive interactions can be provided by the adsorption isotherms, which reflect the relationship between the degree of surface coverage (\( \theta \)) and inhibitor concentration (\( C \)). Assuming a direct relationship between inhibition efficiency and the degree of surface coverage (\( \theta \)) for different inhibitor concentrations, data obtained from gravimetric measurements were adapted to determine the fit to some well known adsorption isotherms including the Langmuir, Temkin, Freundlich and the Flory-Huggins isotherms. The best fit was observed for the Langmuir adsorption isotherm, which is given by Eq. (7) [23, 24], was found to be more suitable.

\[
\frac{C}{\theta} = C + \frac{1}{K}
\]

where \( \theta \) is the fraction of surface coverage, \( C \) is the inhibitor concentration, \( K \) is the equilibrium constant for the adsorption/desorption process. The corresponding linear plots of \( C/\theta \) vs \( C \) are presented in Figure 5 for HPP adsorption from both 1 M HCl and 0.5 M H\(_2\)SO\(_4\) (with slopes of 1.23 and 1.18 respectively). The non-zero intercepts on the y-axes and slopes \( \neq 1.0 \) mean that some of the adsorbed species interact with each other and that the adsorption heat changes with increasing surface coverage.

Figure 5. Langmuir adsorption isotherm plot for the adsorption of HPP extract at 303K in 1.0M HCl and 0.5M H\(_2\)SO\(_4\) on mild steel surface
3.4. Effect of temperature

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the absence and presence of inhibitor gives some insights into the possible mechanism of inhibitor adsorption [11, 25, 26]. Accordingly, the effect of temperature on corrosion and corrosion inhibition processes was studied using the gravimetric technique. Measurements were made in the temperature range 303-333 K in the absence and presence of 50 and 1000 mgL$^{-1}$ HPP for a 3 h immersion period. Figure 6 illustrates the effect of increasing temperature on the corrosion rates of the mild steel in inhibited and uninhibited solutions. Inspection of the data shows that the corrosion rate increased with increase in temperature and this effect was more pronounced in the uninhibited acid solutions. Table 3 illustrates the trend of inhibition efficiency with temperature and shows that inhibition efficiency at low and high HPP concentrations increased with increasing temperature. The observed increase in efficiency with temperature in both acid media is an indication that some of the extract components become increasingly well adsorbed at higher temperature and so contribute more to the overall inhibiting effect.

![Figure 6. Effect of temperature on the corrosion rate of mild steel in (a) 1 M HCl and (b) 0.5 M H$_2$SO$_4$ solutions without and with HPP extract](image)

Table 3. Effect of temperature on the inhibition efficiency of HPP in 1.0M HCl and 0.5M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>System</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M HCl</td>
<td>67.1</td>
<td>66.5</td>
<td>68.7</td>
<td>86.9</td>
</tr>
<tr>
<td>50mgL$^{-1}$</td>
<td>81.0</td>
<td>84.0</td>
<td>95.8</td>
<td></td>
</tr>
<tr>
<td>1000mgL$^{-1}$</td>
<td>70.9</td>
<td>71.0</td>
<td>76.6</td>
<td>77.0</td>
</tr>
<tr>
<td>0.5M H$_2$SO$_4$</td>
<td>83.3</td>
<td>84.12</td>
<td>91.9</td>
<td>93.3</td>
</tr>
</tbody>
</table>
The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation [1, 27-29]:

\[ C_R = A \exp\left(\frac{-E_a}{RT}\right) \] (9)

where \( C_R \) is the corrosion rate, \( A \) is the frequency factor, \( E_a \) is the activation energy of the metal dissolution reaction, \( R \) is the gas constant and \( T \) is the absolute temperature. The \( E_a \) values can be determined from the slopes of Arrhenius plots of \( \log C_R \) versus \( 1/T \), shown in Figure 7. The heat of adsorption, \( Q_{ads} \) was also calculated using equation (10):

\[ Q_{ads} = 2.303R \left[ \log \left( \frac{\theta_2}{1-\theta_2} \right) - \log \left( \frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_1T_2}{T_2-T_1} \] (10)

where \( \theta_1 \) and \( \theta_2 \) are the values of the surface coverage at temperatures \( T_1 \) and \( T_2 \).

Figure 7 Arrhenius plots for mild steel corrosion in (a) 1 M HCl and (b) 0.5 M H₂SO₄ solutions without and with HPP extract.
The calculated values of $E_a$ and $Q_{ads}$ are given in Table 4. $E_a$ decreased in the presence of HPP extract in both 1 M HCl and 0.5 M H$_2$SO$_4$. Such behavior suggests that the extract is capable of retarding corrosion and its efficiency becomes considerably enhanced if the system temperature is increased. This corroborates the data in Table 3. An increase in inhibition efficiency with rise in temperature as well as unchanged or lowered activation energy in inhibited system compared to the blank are indicators that the inhibitor is chemically adsorbed on the corroding metal surface, possibly because some of this energy is used up in chemical reaction [30-32]. In view of that, our results are suggestive of pronounced chemisorption of some of the HPP extract organic matter on the mild steel surface immersed in 1 M HCl and 0.5 M H$_2$SO$_4$. The positive $Q_{ads}$ values also imply that inhibitor adsorption, and hence efficiency, increased with rise in temperature [33]. This observation further confirms chemical adsorption of HPP extract on the mild steel surface in both HCl and H$_2$SO$_4$ solutions.

Table 4. Corrosion activation energies ($E_a$) and heats of adsorption ($Q_{ads}$) for mild steel in HCl and H$_2$SO$_4$ acid solutions without and with HPP extract at 303-333 K

<table>
<thead>
<tr>
<th>System</th>
<th>$E_a$(kJ/mol)</th>
<th>$Q_{ads}$(kJ/mol)</th>
<th>System</th>
<th>$E_a$(kJ/mol)</th>
<th>$Q_{ads}$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>103.2</td>
<td>-</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>89.6</td>
<td>-</td>
</tr>
<tr>
<td>50 mg L$^{-1}$</td>
<td>66.9</td>
<td>33.2</td>
<td>50 mg L$^{-1}$</td>
<td>80.4</td>
<td>9.0</td>
</tr>
<tr>
<td>1000 mg L$^{-1}$</td>
<td>43.14</td>
<td>48.2</td>
<td>1000 mg L$^{-1}$</td>
<td>78.0</td>
<td>28.8</td>
</tr>
</tbody>
</table>

CONCLUSION

The results obtained show that HPP extract is a good corrosion inhibitor for mild steel in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions. The inhibition efficiency increased with increase in concentration and with increase in temperature up to 333 K. The obtained results suggest that the corrosion mechanisms were identical in both acid media and this was not modified by the presence of HPP extract, which manifested slightly higher inhibition efficiency in 0.5 M HCl. Polarization measurements suggest mixed-inhibition mechanism, which the impedance data indicate was achieved via adsorption of the extract organic species on the mild steel surface. The adsorption behavior was approximated by the Langmuir isotherm. The trend of inhibition efficiency with temperature as well as values of the corrosion activation energy in uninhibited and inhibited solutions suggest pronounced chemisorption of the extract organic matter on the corroding mild steel surface.

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REFERENCES