Inhibitive and Adsorption Properties of Ethanolic Extract of Allium Cepa for the Corrosion of α-Brass in HNO₃ Solutions

Abd El-Aziz S. Fouda, Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt
Ashraf M. Nofal, Institute of Studies and Research Environment, Sadat City University, Egypt
Reham Maher, Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract
Ethanol extract of allium cepa has been evaluated as a green corrosion inhibitor for α-brass in HNO₃ solutions using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Potentiodynamic polarization measurements showed that this extract acts as a mixed type inhibitor. The inhibition efficiency increases with increasing the extract concentration, but decreases with raising the temperature. The adsorption of allium cepa on the α-brass surface follows Temkin adsorption isotherm. From EFM the causality factors are very close to theoretical values which indicate that the measured data are of good quality. Nyquist plots show a single capacitive loop in uninhibited and inhibited solutions. Allium cepa has antifungal and antibacterial effect.

Keywords: Corrosion inhibition; α-brass; allium cepa extract; EIS; EFM, HNO₃

Introduction
Corrosion is the deterioration of metal by chemical attack or reaction with environment. Green corrosion inhibitors are biodegradable and don’t contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Several reports are available on the various natural products used as green inhibitors. Extracts of Gnetum africanum, Raphia hookeri, exudate gum, gum arabic, Datura metel, Andrographis paniculata, Carica papaya, Occinum viridis, Telfairia occidentalis, Vernonia amygdalina, mango juice, Rosmmarius officinalis, Azadirachta indica, Lasiandra africana, Aloe vera, Musa sapientum, and tobacco leaves 1-30 have been investigated for their corrosion inhibition potential. It has been established that the inhibitory actions of plant extracts are due to the presence of some organic compounds such as saponin, tannin, alkaloid, steroids, glycosides, and amino acids 30. Most of these compounds have centers for p-electrons and functional groups (such as – C=C-, –OR, –OH, –COOH-NR₂, –NH₂, and –SR), which provide electrons that facilitate the adsorption of the inhibitor on the metal surface. Also, the presence of hetero atoms such as N, P, O, and S enhances the adsorption (which is the initial mechanism of inhibition) of the inhibitor on the metal surface. Recent researches have also indicated that amino acid contents of the plant extracts have a significant role to play in the corrosion inhibition mechanism of plant extracts 31-40.

Preparation of plant Extract
Plant materials were dried in the shade at room temperature, ground using electrical mill into fine powder and extracted by soaking in methanol at the rate of 1:1(w/v) for 48 hours. The extracts were filtrated through cheese cloth under a strong hand pressure and the solvent was dried under vacuum at 60-65°C using a rotary evaporator. The extracted residue was dissolved in dimethyl sulfoxide (1mg/ml). The crude extracts were preserved under refrigeration until use 41.

Experimental
Materials
The experiments were performed with local commercial α-brass (Helwan Company of Non-Ferrous Industries, Egypt) with the following composition (weight %) Cu 60, Zn 40.

Solutions
The aggressive solutions, 1 M HNO₃ were prepared by dilution of analytical grade (70 %) HNO₃ with bi-distilled water.

Weight Loss Measurements
Seven parallel α-brass sheets of 2 × 2 × 0.6 cm were abraded with emery papers up to 1200 grit grade and then washed with bi-distilled water and acetone. After accurate weighing, the specimens were immersed in a 100 ml beaker, which contained 100 ml of HNO₃ with and without addition of different concentrations of allium cepa extract. All the aggressive acid solutions were open to air. After 3 h, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of the seven parallel α-brass sheets could be obtained. The inhibition efficiency (% IE) and the degree of surface coverage (θ) of investigated extract for the corrosion of α-brass in HNO₃ were calculated from Eq. (1) 42.

% IE = θ x 100 = [1- (W / W°)] × 100

1
where $W^0$ and $W$ are the values of the average weight losses without and with addition of the inhibitor, respectively.

**Electrochemical Measurements**

Electrochemical experiments were performed using a typical three-compartment glass cell consists of the α-brass specimen as working electrode (1 cm$^2$), saturated calomel electrode (SCE) as a reference electrode and a platinum foil (1 cm$^2$) as a counter electrode. The reference electrode was connected to a Luggin capillary and the tip of the Luggin capillary is made very close to the surface of the working electrode to minimize IR drop. All the measurements were done in solutions open to atmosphere under unstirred conditions. Prior to every experiment, the electrode was abraded with successive different grades of emery papers, degreased with acetone and washed with bi-distilled water and finally dried.

Tafel polarization curves were obtained by changing the electrode potential automatically from -0.5 to 0.5 V vs. SCE at open circuit potential with a scan rate of 1 mVs$^{-1}$. The determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives log $i_{corr}$ and the corresponding corrosion potential ($E_{corr}$) for inhibitor free acid and for each concentration of inhibitors. Then $i_{corr}$ was used for calculation of inhibition efficiency ($%\ IE$) and surface coverage ($\theta$) from Eq. (2):

$$%\ IE = \theta \times 100 = \left[1 - \left(\frac{i_{corr,\text{free}}}{i_{corr,\text{inh}}}\right)\right] \times 100 \tag{2}$$

Impedance measurements were carried out in frequency range from 100 kHz to 0.1Hz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer $R_o$ and the capacitance of double layer $C_{dl}$. The inhibition efficiencies ($%\ IE$) and the surface coverage ($\theta$) obtained from the impedance measurements are defined by Eq. (3):

$$%\ IE = \theta \times 100 = \left[1 - \left(\frac{R_{o,c}}{R_o}\right)\right] \times 100 \tag{3}$$

Electrochemical frequency modulation (EFM) was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The Intermodulation spectra contain current responses assigned for harmonic and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_c$ and $\beta_a$) and the causality factors $CF_2$ & $CF_3$ $^{45,44}$. The electrode potential was allowed to stabilize for 30 min before starting the measurements. All the experiments were conducted at 25°C.

Electrochemical measurements were performed using Gamry Instrument Potentiostat/ Galvanostat/ ZRA (PCI4-G750). This includes a Gamry framework system v 6.03 Gamry applications include DC 105 software for DC corrosion measurements, EIS300 software EIS and EFM140 for EFM measurements along with a computer for collecting data. Echem analyst v 6.03 software was used for plotting, graphing, and fitting data.

**Surface Examinations**

The surface films were formed on the α-brass specimens by immersing them in inhibitor solution for a period of 24 h. After the immersion period, the specimens were taken out, dried and the nature of the film formed on the surface of the metal specimen was analyzed by EDX and SEM techniques. Examination of α-brass surface after 24 h exposure to the 1 M HNO$3$ solution without and with inhibitor was carried out by JOEL JSM-6510LV Scanning Electron Microscope. Rough elemental analyses for the exposed surface were conducted by EDX technique.

**Results And Discussion**

**Chemical Method (Weight-loss measurements)**

Figure 1 shows the weight loss-time curves for α-brass in 1M nitric acid in the presence and absence of different concentrations of allium cepa extract at 25°C. These curves are characterized by a sharp rise in weight loss from the beginning. Curves for additives containing system fall below that of the free acid. These curves indicated that, the weight loss of α-brass depends on concentration of the extract. Increase in bulk concentration and consequently increase of surface coverage by the additive increases the inhibition efficiency towards α-brass dissolution. The results of the Table 1 show that the inhibition efficiency of the extract increases with the increase of its concentration in the corrosive medium. It is thus obvious that increase of bulk concentration and consequently, increase of surface area coverage by the additive retards the dissolution of α-brass.
Table 1. Values of inhibition efficiencies (% IE) and surface coverage (θ) of allium cepa for the corrosion of α-brass in 1 M HNO₃ from weight-loss measurements at different concentrations and at 25°C

<table>
<thead>
<tr>
<th>ppm</th>
<th>Allium cepa extract</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.140</td>
<td>14.0</td>
</tr>
<tr>
<td>100</td>
<td>0.289</td>
<td>28.9</td>
</tr>
<tr>
<td>150</td>
<td>0.368</td>
<td>36.8</td>
</tr>
<tr>
<td>200</td>
<td>0.437</td>
<td>43.7</td>
</tr>
<tr>
<td>250</td>
<td>0.528</td>
<td>52.8</td>
</tr>
<tr>
<td>300</td>
<td>0.816</td>
<td>81.6</td>
</tr>
</tbody>
</table>

Figure 1. Weight loss-time curves for the corrosion of α-brass in 1 M HNO₃ in the absence and presence of different concentrations of allium cepa at 25 °C

3.2 Effect of Temperature
The effect of temperature on the corrosion rate of α-brass in 1M HNO₃ and in presence of different extract concentrations was studied in the temperature range of 298–318K using weight loss measurements. As the temperature increases, the rate of corrosion increase and the inhibition efficiency of the extract decreases as shown in Table 2 for allium cepa extract. The adsorption behavior of extract on α-brass surface occurs through physical adsorption.
Table 2. Values of inhibition efficiency (% IE) and corrosion rate (CR) of allium cepa extract for the corrosion of α-brass in 1 M HNO₃ from weight-loss measurements at different concentrations at different temperatures

<table>
<thead>
<tr>
<th>[inh] Ppm</th>
<th>298K C.R</th>
<th>303K % IE</th>
<th>308K C.R</th>
<th>308K % IE</th>
<th>313K C.R</th>
<th>313K % IE</th>
<th>318K C.R</th>
<th>318K % IE</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.37</td>
<td>14.0</td>
<td>0.55</td>
<td>12.0</td>
<td>0.78</td>
<td>11.3</td>
<td>0.85</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>28.9</td>
<td>0.52</td>
<td>28.8</td>
<td>0.65</td>
<td>21.3</td>
<td>0.72</td>
<td>17.5</td>
</tr>
<tr>
<td>5</td>
<td>0.30</td>
<td>39.2</td>
<td>0.50</td>
<td>39.2</td>
<td>0.57</td>
<td>29.9</td>
<td>0.69</td>
<td>24.4</td>
</tr>
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<td>7</td>
<td>0.27</td>
<td>50.8</td>
<td>0.48</td>
<td>50.3</td>
<td>0.51</td>
<td>40.5</td>
<td>0.65</td>
<td>33.1</td>
</tr>
<tr>
<td>9</td>
<td>0.21</td>
<td>65.3</td>
<td>0.33</td>
<td>65.3</td>
<td>0.43</td>
<td>49.9</td>
<td>0.62</td>
<td>42.6</td>
</tr>
<tr>
<td>11</td>
<td>0.18</td>
<td>81.6</td>
<td>0.24</td>
<td>75.1</td>
<td>0.28</td>
<td>57.5</td>
<td>0.59</td>
<td>52.8</td>
</tr>
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</table>

Adsorption Isotherms

It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism. To calculate the surface coverage ($\theta$) it was assumed that the inhibitor efficiency is due mainly to the blocking effect of the adsorbed species and hence % IE = $100 \times \theta$. In order to gain insight into the mode of adsorption of the extract on α-brass surface, the surface coverage values from weight loss measurements were theoretically fitted into different adsorption isotherms and the values of correlation coefficient ($R^2$) were used to determine the best-fit isotherm. Fig. 2 shows the plot log C vs $\Theta$ which is typical of Temkin adsorption isotherm. Perfectly linear plot was obtained with regression constant ($R^2$) > 0.99. The Temkin isotherm is given as:

$$a \Theta = \ln K_{ads} C$$  \hspace{1cm} (4)

where C is the inhibitor concentration and $K_{ads}$ is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption $\Delta G^°_{ads}$ by Eq. (5)

$$K_{ads} = 1/55.5 \exp (-\Delta G^°_{ads}/RT)$$  \hspace{1cm} (5)

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature.

The calculated $\Delta G^°_{ads}$ values were also given in Table 3. The negative values of $\Delta G^°_{ads}$ ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the α-brass surface. It is well known that values of $\Delta G^°_{ads}$ of the order of $-40$ kJ mol$^{-1}$ or higher involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond (chemisorption); those of order of $-20$ kJ mol$^{-1}$ or lower indicate a physical adsorption. The calculated $\Delta G^°_{ads}$ values (Table 3) are more negative than $-20$ kJ mol$^{-1}$ indicate, therefore, that the adsorption mechanism of the investigated compound on α-brass in 1 M HNO₃ solution is typical physical adsorption.
Table 3. Thermodynamic parameters for the adsorption of allium cepa extract on α-brass surface in 1 M HNO₃ at different temperatures

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>K_adsx10⁻³ M⁻¹</th>
<th>-ΔG°_ads kJ mol</th>
<th>-ΔH°_ads kJ mol</th>
<th>-ΔS°_ads KJ mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>5.4</td>
<td>14.1</td>
<td>103.8</td>
<td>300.8</td>
</tr>
<tr>
<td>30</td>
<td>5.22</td>
<td>14.3</td>
<td>295.3</td>
<td>289.9</td>
</tr>
<tr>
<td>35</td>
<td>5.09</td>
<td>14.5</td>
<td>284.2</td>
<td>278.2</td>
</tr>
<tr>
<td>40</td>
<td>5.35</td>
<td>14.8</td>
<td>284.2</td>
<td>278.2</td>
</tr>
<tr>
<td>45</td>
<td>5.87</td>
<td>15.3</td>
<td>284.2</td>
<td>278.2</td>
</tr>
</tbody>
</table>

Kinetic –Thermodynamic Corrosion Parameters
The activation parameters for the corrosion process were calculated from Arrhenius-type plot according to Eq (6):

\[ k_{\text{corr}} = A \exp \left( \frac{E^*}{RT} \right) \]  

(6)

where \( E^* \) is the apparent activation corrosion energy and \( A \) is the Arrhenius pre-exponential constant. Values of apparent activation energy of corrosion for α-brass in 1 M HNO₃ are shown in Table 4, without and with various concentrations of allium cepa extract determined from the slope of \( \log (k_{\text{corr}}) \) versus \( 1/T \) plots are shown in Figure.3. Inspection of the data show that the activation energy have lower values but its values in presence of extract still higher than in its absence. This is may be due to the formation of energy barrier on the alloy surface. The alternative formulation of transition state equation is shown in Eq. 7:

\[ k_{\text{corr}} = \frac{(RT/Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT)}{A} \]  

(7)

where \( k_{\text{corr}} \) is the rate of metal dissolution, h is Planck’s constant, N is Avogadro’s number, \( \Delta S^* \) is the entropy of activation and \( \Delta H^* \) is the enthalpy of activation. Straight lines are obtained with slopes equal to \( (\Delta H^*/2.303R) \) and intercepts are \( \log \left( \frac{R/Nh + \Delta S^*}{2.303R} \right) \).
Figure 4. Plots of \((\log k_{corr}/T)\) against \((1/T)\) in the presence and absence of different concentrations of allium cepa extract in 1 M HNO₃.

Table 4. Activation parameters for α-brass corrosion in the absence and presence of various concentrations of allium cepa extract in 1 M HNO₃

<table>
<thead>
<tr>
<th>Compound</th>
<th>[inh], ppm</th>
<th>(E_a^*) kJ mol(^{-1})</th>
<th>(\Delta H^*) kJ mol(^{-1})</th>
<th>(-\Delta S^*) J mol(^{-1})K(^{-1})</th>
<th>(A \times 10^7) g cm(^2) min(^{-1})</th>
</tr>
</thead>
<tbody>
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<td>Blank</td>
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<td>4.5</td>
<td>1.5</td>
<td>149.0</td>
<td>2.4</td>
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<tr>
<td>Allium cepa</td>
<td>50</td>
<td>6.0</td>
<td>2.3</td>
<td>73.0</td>
<td>961</td>
</tr>
<tr>
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<td>6004</td>
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<td>87.6</td>
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<td></td>
<td>250</td>
<td>8.1</td>
<td>3.5</td>
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<td>733212</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>8.8</td>
<td>3.6</td>
<td>92.5</td>
<td>4718132</td>
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</table>

3.5 Potentiodynamic Polarization Measurements

Figure 5 shows the anodic and cathodic Tafel polarization curves for α-brass in 1M HNO₃ in the absence and presence of varying concentrations of allium cepa at 25°C, respectively. From Fig. 5, it is clear that both anodic metal dissolution and cathodic H₂ reduction reactions were inhibited when investigated inhibitor were added to 1 M HNO₃ and this inhibition was more pronounced with increasing inhibitor concentration. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the investigated inhibitors. This behavior indicates that the undertaken additives act as mixed-type inhibitors [49].
The results in Table 5 show that the increase in inhibitor concentration leads to decrease the corrosion current density ($i_{corr}$), but the Tafel slopes ($\beta_a$, $\beta_c$) are approximately constant indicating that the retardation of the two reactions (cathodic hydrogen reduction and anodic metal dissolution) were affected without changing the dissolution mechanism [50].

Table 5. Corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), Tafel slopes ($\beta_a$, $\beta_c$), degree of surface coverage ($\Theta$), and inhibition efficiency (% IE) of $\alpha$-brass in 1 M HNO$_3$ at 25°C for allium cepa

<table>
<thead>
<tr>
<th>[inh] Ppm</th>
<th>$E_{corr}$ (mv vs SCE)</th>
<th>$i_{corr}$ ($\mu$A cm$^{-2}$)</th>
<th>$\beta_a$ (mV dec$^{-1}$)</th>
<th>$\beta_c$ (mV dec$^{-1}$)</th>
<th>C.R mpy</th>
<th>$\Theta$</th>
<th>% IE</th>
</tr>
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<tbody>
<tr>
<td>Blank</td>
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<td>914</td>
<td>57</td>
<td>189</td>
<td>549.8</td>
<td>-----</td>
<td>-----</td>
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<tr>
<td>50</td>
<td>10</td>
<td>800</td>
<td>64</td>
<td>190</td>
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<td>0.125</td>
<td>12.5</td>
</tr>
<tr>
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<td>58</td>
<td>172</td>
<td>475.2</td>
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<td>12</td>
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<td>442.7</td>
<td>0.624</td>
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<tr>
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<td>198</td>
<td>34.92</td>
<td>0.923</td>
<td>92.3</td>
</tr>
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</table>

Electrochemical Impedance Spectroscopy (EIS)

The effect of inhibitor concentration on the impedance behavior of $\alpha$-brass in 1 M HNO$_3$ solution at 25°C is presented in Fig. 6 (a, b). The curves show a similar type of Nyquist plots (Fig.6a) for $\alpha$-brass in the presence of various concentrations of allium cepa. The existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules.

Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance, which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitor, and
formation of porous layers and in homogenates of the
electrode surface51.

Inspections of the data reveal that each impedance
diagram consists of a large capacitive loop with one capaci-
tive time constant in the Bode–phase plots (Fig.6b). The
electrical equivalent circuit model is shown in Figure 7. It
used to analyze the obtained impedance data. The
model consists of the solution resistance ($R_s$), the charge-
transfer resistance of the interfacial corrosion reaction
($R_{ct}$) and the Constant phase element (CPE). Excellent fit
with this model was obtained with our experimental da-
ta. The values of the interfacial capacitance $C_{dl}$ can be
Calculated from CPE parameter values $Y_0$ and $n$ using
the expression52:

$$C_{dl} = Y_0 (\omega_{max})^{n-1}$$

where $Y_0$ is the magnitude of the CPE, $\omega_{max}$ is the angu-
lar frequency at which the imaginary component of the
impedance reaches its maximum values and $n$ is the de-
viation parameter of the CPE: $-1 \leq n \leq 1$. EIS data (Table
6) show that the $R_{ct}$ values increases and the $C_{dl}$ values
decreases with increasing the inhibitor concentrations.
This is due to the gradual replacement of water mole-
cules by the adsorption of the inhibitor molecules on the
metal surface, decreasing the extent of dissolution reac-
tion. The higher ($R_{ct}$) values, are generally associated
with slower corroding system53.

![Figure 6a](image1)

**Figure 6a:** The Nyquist plots for the corrosion of α-brass in 1 M HNO$_3$ in the absence and presence of different concentra-
tions of allium cepa extract at 25°C

![Figure 6b](image2)

**Figure 6b.** The Bode plots for the corrosion of α-brass in 1 M HNO$_3$ in the absence and presence of different concentra-
tions of allium cepa at 25 °C
Table 6. EIS data of α-brass in 1 M HNO₃ and in the absence and presence of different concentrations of allium cepa extract at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>[inh], ppm</th>
<th>Rₑ, Ω cm²</th>
<th>Rₓ, Ω cm²</th>
<th>Cₓ, µF cm⁻²</th>
<th>Θ</th>
<th>% IE</th>
</tr>
</thead>
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<td>1.27</td>
<td>0.775</td>
<td>77.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7: Electrical equivalent circuit model used to fit the results of impedance

3.7 Electrochemical frequency modulation measurements (EFM)
The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants like EIS; it is a small ac signal. It is generally accepted that in most cases, the corrosion rates determined with the EFM technique, are much higher than the values determined with other techniques exhibiting low corrosion rates. The modulation frequencies that are used in the EFM technique are in the capacitive region of the impedance spectra. The calculated corrosion kinetic parameters at different concentrations of allium cepa in 1 M HNO₃ at 25 °C (i_corr, βₐ, βₓ, CF-2, CF-3 and % IE) are given in Table 7. From Table 7, the corrosion current densities decrease by increasing the concentration of investigated compound and the efficiency of inhibition increases by increasing investigated compound concentrations. The causality factors in Table 7 are very close to theoretical values which according to EFM theory should guarantee the validity of Tafel slopes and corrosion current densities. Values of causality factors in Table 7 indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might be due to the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough. Another possible explanation is that the inhibitor is not performing very well. The obtained results showed good agreement of corrosion kinetic parameters obtained with the EFM, Tafel extrapolation and EIS methods.

Table 7. Electrochemical kinetic parameters obtained by EFM technique for α-brass in the absence and presence of different concentrations of allium cepa extract in 1 M HNO₃ at 25°C

<table>
<thead>
<tr>
<th>[inh], ppm</th>
<th>i_corr, µA cm⁻²</th>
<th>βₓ, mV dec⁻¹</th>
<th>βₐ, mV dec⁻¹</th>
<th>CF-2</th>
<th>CF-3</th>
<th>C.R, mpy</th>
<th>Θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>70.03</td>
<td>64</td>
<td>115</td>
<td>1.858</td>
<td>2.924</td>
<td>34.56</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>37.57</td>
<td>29</td>
<td>68</td>
<td>1.79</td>
<td>2.952</td>
<td>49.64</td>
<td>0.464</td>
<td>46.4</td>
</tr>
<tr>
<td>100</td>
<td>27.46</td>
<td>28</td>
<td>74</td>
<td>1.805</td>
<td>2.751</td>
<td>36.28</td>
<td>0.601</td>
<td>60.1</td>
</tr>
<tr>
<td>150</td>
<td>25.17</td>
<td>30</td>
<td>62</td>
<td>1.795</td>
<td>3.087</td>
<td>33.26</td>
<td>0.641</td>
<td>64.1</td>
</tr>
<tr>
<td>200</td>
<td>22.57</td>
<td>29</td>
<td>59</td>
<td>1.795</td>
<td>2.917</td>
<td>29.83</td>
<td>0.678</td>
<td>67.8</td>
</tr>
</tbody>
</table>
Figure 8. Intermodulation spectrum for α-brass in 1 M HNO₃ solutions without and with various concentrations of allium cepa extract at 25°C.
Table 7. Electrochemical kinetic parameters obtained by EFM technique for α-brass in the absence and presence of different concentrations of allium cepa extract in 1 M HNO₃ at 25°C

<table>
<thead>
<tr>
<th>[inh], ppm</th>
<th>$i_{corr}$ [µA cm⁻²]</th>
<th>$\beta_a$, mV dec⁻¹</th>
<th>$\beta_c$, mV dec⁻¹</th>
<th>CF-2</th>
<th>CF-3</th>
<th>C.R., mpy</th>
<th>Θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>70.03</td>
<td>64</td>
<td>115</td>
<td>1.858</td>
<td>2.924</td>
<td>34.56</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>37.57</td>
<td>29</td>
<td>68</td>
<td>1.79</td>
<td>2.952</td>
<td>49.64</td>
<td>0.464</td>
<td>46.4</td>
</tr>
<tr>
<td>100</td>
<td>27.46</td>
<td>28</td>
<td>74</td>
<td>1.805</td>
<td>2.751</td>
<td>36.28</td>
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<td>60.1</td>
</tr>
<tr>
<td>150</td>
<td>25.17</td>
<td>30</td>
<td>62</td>
<td>1.795</td>
<td>3.087</td>
<td>33.26</td>
<td>0.641</td>
<td>64.1</td>
</tr>
<tr>
<td>200</td>
<td>22.57</td>
<td>29</td>
<td>59</td>
<td>1.795</td>
<td>2.917</td>
<td>29.83</td>
<td>0.678</td>
<td>67.8</td>
</tr>
<tr>
<td>250</td>
<td>20.29</td>
<td>29</td>
<td>68</td>
<td>1.850</td>
<td>2.892</td>
<td>26.80</td>
<td>0.710</td>
<td>71.0</td>
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<td>300</td>
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<td>1.769</td>
<td>2.686</td>
<td>22.88</td>
<td>0.753</td>
<td>75.3</td>
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</tbody>
</table>

SEM/EDX Examination

In order to verify if the investigated compound molecules are in fact adsorbed on α-brass surface, both SEM and EDX experiments were carried out. The SEM micrographs for α-brass surface alone and after 24 h immersion in 1 M HNO₃ without and with the addition of 300 ppm of allium cepa are shown in Figures (9a-c). The corresponding EDX profile analyses are presented in Figures (10a-c). As expected, Figure 9a shows metallic surface is clear, while in the absence of the investigated compound, the α-brass surface is damaged by HNO₃ corrosion (Figure9b). In contrast, in presence of the investigated compound Figure 9c, the metallic surface seems to be almost no affected by corrosion. The corresponding EDX data are presented in Figures (10a-c) and Table8. It is clear from the EDX spectra of α-brass in the presence of investigated compounds, the existence of C and O peaks Figure10c which suggest the adsorption of investigated compounds on the α-brass surface and confirm the formation of a thin film of investigated compounds observed in SEM micrograph, thus protecting the surface against corrosion.
Figure 9 (a-c) SEM micrographs of α-brass surface (a) before of immersion in 1 M HNO₃, (b) after 24 h of immersion in 1 M HNO₃, (c) after 24 h of immersion in 1 M HNO₃+ 300 ppm of allium cepa at 25±1 °C.

Figure 10 (a-c). EDX spectra of α-brass surface (a) before of immersion in 1 M HNO₃, (b) after 24 h of immersion in 1 M HNO₃, (c) after 24 h of immersion in 1 M HNO₃+ 300 ppm of allium cepa at 25°C.
Table 8. Surface composition (weight %) of α-bass before and after immersion in 1 M HNO₃ without and with 300 ppm of allium cepa at 25°C

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>As</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Mass %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free</td>
<td>60.78</td>
<td>32.72</td>
<td>0.79</td>
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<td>1.13</td>
<td>0.70</td>
<td>0.40</td>
<td>----</td>
</tr>
<tr>
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<td>25.78</td>
<td>0.78</td>
<td>10.41</td>
<td>7.85</td>
<td>----</td>
<td>0.61</td>
<td>----</td>
</tr>
<tr>
<td>Allium cepa extract</td>
<td>55.07</td>
<td>26.40</td>
<td>-----</td>
<td>11.79</td>
<td>7.00</td>
<td>----</td>
<td>0.24</td>
<td>----</td>
</tr>
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</table>

Mechanism of Corrosion Inhibition

Results of the present study have shown that this extract inhibits the acid corrosion of α-brass by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of the metal, extract concentration, and temperature as well as inhibitor adsorption abilities which is so much dependent on the number of adsorption sites. The results show that the inhibition efficiency of allium cepa extract increases with increase in extract concentration suggests that some of the molecules of the extract are adsorbed on the metal surface thereby protecting the “covered” surface from further corrodes attack. Increasing the extract concentration increases the degree of surface coverage, θ, of the metal surface. Allium cepa extract consists of a mixture of complex organic compounds including quercetin, fructose, quercetin-3-glucoside, isorhamnetin-4-glucoside, xylose, galactose, glucose, mannose, organosulfur compounds, allysulfides, flavonoids, flavanols, S-alk(en)yl cysteine sulfoxides, cycloallin, selenium, thiosulfinates, and sulfur and seleno compounds. Also, from the point of view of corrosion inhibition, it is evident that these phytochemicals are expected to be good corrosion inhibitors because they are organic compounds having heteroatoms in aromatic systems. Therefore, the inhibition of the corrosion of α-brass by ethanolic extract of allium cepa extract is due to the formation of chelates between copper in the alloy and some phytochemicals constituents of the extract.

Conclusions

Allium cepa extract acts as an inhibitor for corrosion of α-brass in nitric acid solutions. The inhibition efficiency increases with increase in the concentration of the extract. The inhibition is due to the adsorption of the extract components on the metal surface. The adsorption of this extract on the metal surface follows Temkin adsorption isotherm. This extract has antifungal and antibacterial effect.

References


