Egy- dronate drug as promising corrosion inhibitor of C - steel in aqueous medium

ABSTRACT

The effect of Egy – dronate as the corrosion inhibition of Carbon steel (CS) in 1 M HCl was studied by weight loss (WL), hydrogen evaluation (HE), Open circuit potential (E_{ocp}), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), electron frequency modulation (EFM) and surface examination of the specimens by atomic force microscopy (AFM), energy dispersion spectroscopy (EDS) and scanning electron microscopy (SEM). The results of the inhibition efficiency (IE %) increase with increasing the concentration of inhibitor but decreases with raising the temperature. The adsorption of Egy - dronate on the C - steel surface obeys with Langmuir adsorption isotherm. The adsorption process is spontaneous, endothermic and physical adsorption. The polarization curves show that Egy - dronate is a mixed-type inhibitor tends to anodically more. The results obtained from chemical and electrochemical techniques are a good agreement quality and gives the same behavior of the adsorption of Egy - dronate. All techniques have proved the thin film formation adsorbed on the metal surface as a protective coated to prevent the dissolution metal in the corrosive medium, due to electrostatic attraction between unshared electrons of inhibitor molecules and the positive sites on the metal surface.

Keywords: corrosion inhibition, HCl, CS, adsorption, SEM, EDX, AFM.

1. INTRODUCTION

The most methods for protection of metals from corrosion are investigated by utilization of inhibitors that especially in acid medium [1-2]. The well-known acidic inhibitors are drugs and organic compounds that contain O, S, N (N-heterocyclic), long carbon chain and aromatic compounds. The organic inhibitors have many advantages such as high % IE, low cost, friendly to the environment and easy to produce [3-5]. Pharmaceutical drugs like heterocyclic compounds are used for to reduced corrosion process of Fe, Cu and Al [6-16] in various aqueous medium. Adsorption of the drug facilitates the protection of the metal surface [17]. A few medications such as tetracycline, cloxacillin, azithromycin, ampiclox, ampicillin and orphenadrine were discovered to have a great inhibition for corrosion of metals and alloys.

Numerous authors generally concur that medications are inhibitors that can compete favorably with green inhibition of corrosion and that most medications can be synthesized from natural products. A few medications have been discovered to be a great corrosion inhibitors for metals such as: Biopolymer gave 86% (IE) for Cu in NaCl [18], pyromellitic diimide linked to oxadiazole cycle gave 84.6% IE for CS in HCl [19], 2-mercapto-benzimidazole gave 82% (IE) for CS in HCl [20], Antidiabetic Drug Janumet gave 88.7% inhibition efficiency for MS in HCl [21], Januvia gave 79.9% (IE) for Zn in HCl [22], Cefuroxime Axetil gave 89.9% (IE) for Al in HCl [23], Phenytoin sodium gave 79% (IE) for CS in HCl [24], Aspirin gave 71% (IE) for MS in H2SO4 [25], Septazole gave 84.8% IE for Cu in HCl [26] and Chloroquine diphosphate gave 80% (IE) for MS in HCl [27]. Selection of some medication as corrosion inhibitors due to the followings: (1) drug molecules contain oxygen, sulphur and nitrogen as active sites, (2) it is environmentally friendly furthermore vital in organic responses and (3) drugs can be easily produced and purified [28-32].
The scope of this paper is to use Egy-dronate drug as a promising corrosion inhibitor of CS in acid medium by various chemical and electrochemical methods, and to elucidate the mechanism of corrosion inhibition.

2. EXPERIMENTAL TECHNIQUES

2.1. Materials

The CS specimen composition is listed in the following Table 1.

Table 2: The Components and molecular structure of investigated drug

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Active center</th>
<th>Molecular weight</th>
<th>IUPAC Name</th>
<th>Structure</th>
<th>Inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{4}H_{13}NO_{7}P_2</td>
<td>N7O2P</td>
<td>249.097 g/mol</td>
<td>sodium [4-amino-1-hydroxy-1-(hydroxy-oxido-phosphoryl)-butyl]phosphonic acid trihydrate</td>
<td><img src="image" alt="Structure" /></td>
<td>Alendronic acid</td>
</tr>
<tr>
<td>C_{27}H_{44}O_2π</td>
<td>O2π</td>
<td>384.64 g/mol</td>
<td>(3β,5Z,7E)-9,10-secocholesta-5,7,10(19)trien-3-ol</td>
<td><img src="image" alt="Structure" /></td>
<td>Cholecalciferol (Vit. D3)</td>
</tr>
</tbody>
</table>

2.2. Inhibitors

Egy-dronate drug is a mixed inhibitor which consists of two substances Alendronic acid and Cholecalciferol as described in Table 2. The pharmaceutical drugs have been investigated purchased from Sandozinc and Pfizer inc companies.

2.3. Solutions

The corrosive solution was prepared by dilution of analytical grade (37%) HCl with bi-distill water to obtain 1M HCl. The corrosive solution mixed with different concentration range of the Egy-dronate drug that was used between 50 and 300 ppm.

2.4. WL measurements

Seven square CS sheets of 2.0 × 2.0 × 2.0 cm² were abraded by emery paper (grade 600, 800, 1000 and 1200) and then washed by bi-distill water and acetone. After accurate weighting, the specimens were immersed in a 100 ml beaker, which contained 100 ml of 1M HCl with and without adding different doses of investigated drug. All corrosive solutions were opened to air. After three hours, the coins were taken out, washed, dried, and weighed accurately per thirty minutes. The average WL for seven square CS specimens will be obtained.

The % IE and the degree of surface coverage (θ) of Egy-dronate inhibitor for the corrosion of CS were calculated as following [33]:

\[
\% IE = θ \times 100 = \left[1 - \frac{W}{W^0}\right] \times 100
\]

Where, \(W^0\) and \(W\) are the WL, without and with adding deferent doses of investigate drug respectively.

2.5. Gasometric measurements

Measurements of \(V\) were estimation at 25°C, and the \(V\) volume developed every 15 minutes, the \(\Theta\) and the % IE were calculated by (3) and (4).

\[
V = K \times t
\]

Where, \((V)\) is the volume of hydrogen in ml, \((K)\) is rate constant and \((t)\) is time in minute.

\[
\Theta = 1 - \frac{K}{K^0}
\]

Where, \((K^0)\) and \((K)\) are the rate of corrosion in absence and presence drug, which calculated by plotting \((V)\) vs. \((t)\) and \((K)\) value is the slope.

\[
\% IE = \Theta \times 100
\]

2.6. Electrochemical measurements

Electrochemical measurements including EOCPP, PP, EIS and EFM were performed in three
Electrodes at 25°C. The counter electrode is platinum, saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode and the working electrode was in the form of a square cut from CS fixed with epoxy resin of polytetrafluoroethylene (PTFE) except the flat surface acted as the working electrode in 1 cm² area.

Electrochemical estimation performed for four techniques. Impedance measurements were carried out in frequency range from 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using AC signals at open circuit potential. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer \( R_{ct} \) or \( R_{p} \) (diameter of high frequency loop) and the capacity of double layer \( C_{dl} \).

EFM measurement is the techniques that can directly and fast to determination corrosion current data without knowledge of Tafel slopes with a small signal polarization. The % IE_{EFM} was calculated.

The electrode potential was allowed to stabilize for 30 min before starting the measurements. All the experiments were conducted at 25 ± 1°C. Measurements were performed using Gamry (PCI 300/4) Instrument Potentiostat / Galvanostat / ZRA.

2. 7. Surface Examinations

The CS coins used for analysis of morphology surface were prepared in 1M HCl acid (blank) and with 300 ppm of Egy-dronate drug at room temperature for one day (24 h). The performed specimens examined by using SEM, EDX and AFM techniques.

3. RESULT AND DISCUSSION

3.1. WL technique

The WL curves of CS without and with the addition various doses of Egy – dronate drug as an inhibitor in 1M HCl were shown in Figure 1, that the WL values of CS in 1M HCl solution containing the investigated drug, that clarified the % IE, increasing with increasing the concentration of the drug, but decreases with raising temperatures. The results are appearing in the Table 3. This direction may as a result from the fact that the adsorption of the drug on the CS increases with increasing the concentrations of the drug. These means, the inhibitor make thin film in the surface of the metal which protective it from corrosion process [34].

**Table 3.** The rate of corrosion and % IE for WL measurements without and with various concentrations of Egy-dronate drug that was immersion for 120 min in 1M HCl at 25°C

<table>
<thead>
<tr>
<th>Conc. Ppm</th>
<th>Kcorr. ( \text{mg. cm}^{-2} \text{. min}^{-1} )</th>
<th>% IE</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>16.25</td>
<td>-----</td>
<td>Blank</td>
</tr>
<tr>
<td>50</td>
<td>5.83</td>
<td>64.1</td>
<td>Egy – dronate</td>
</tr>
<tr>
<td>100</td>
<td>5.42</td>
<td>66.7</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>5.00</td>
<td>69.2</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>4.58</td>
<td>71.8</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>4.17</td>
<td>74.4</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>3.75</td>
<td>76.9</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)

**Figure 1.** Weight loss – time curves for the corrosion of CS in 1M HCl in the absence and presence of different doses of Egy-dronate drug at 25°C

**Slika 1.** Krive gubitak težine - vreme za koroziju ugleničnog čelika u M HCl u odsustvu i prisustvu različitih doza leka Egi-dronate na 25°C

3.2. Effect of temperature

The effect of temperature of the rate of corrosion for CS in acid medium with various concentrations from Egy – dronate drug was tested by WL measurements over the temperature range from 25 to 45°C. The effect of increasing temperatures on the rate of corrosion and the % IE, calculated. The results of the rate of corrosion were increased as the temperatures increases and decreasing both \( \theta \) and % IE, Figure 2.

The activation energy \( (E_a) \) of the corrosion process was calculated by using Arrhenius equation (5):
$K_{corr} = A \exp (-E_a' / RT)$  \hspace{1cm} (5)

Where, \((k)\) is the rate of corrosion and \((A)\) is the Arrhenius constant or frequency factor, \((R)\) is general gas constant and \((T)\) is absolute temperature. Figure 3, represents the Arrhenius plot in the presence and absence of drug. $E_a'$ values determined from the slopes of these linear plots are shown in Table 4. The linear regression ($R^2$) is close to 1 which indicates that the corrosion of CS in 1 M HCl solution can be obvious that using the kinetic model. Table 4 showed that the value of $E_a'$ for the inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of CS is slow in the presence of inhibitor and can be sure due to physical adsorption. It is known from equation (8), that the higher $E_a'$ values lead to the lower of the rate of corrosion. This is due to the formation of a film on the CS surface serving as an energy barrier for the CS corrosion [35].

![Figure 2. The effect of Egy-dronate % IE at various temperatures](image)

**Slika 2. Uticaj Egy-dronate na % IE na različitim temperaturama**

**Table 4. Activation parameters for CS corrosion in the nonexistence and existence of various doses of Egy-dronate drug in 1 M HCl**

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>Activation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E'a $\text{kJ mol}^{-1}$</td>
</tr>
<tr>
<td>Blank</td>
<td>47.3</td>
</tr>
<tr>
<td>50</td>
<td>55.5</td>
</tr>
<tr>
<td>100</td>
<td>56.8</td>
</tr>
<tr>
<td>150</td>
<td>57.7</td>
</tr>
<tr>
<td>200</td>
<td>61.8</td>
</tr>
<tr>
<td>250</td>
<td>62.5</td>
</tr>
<tr>
<td>300</td>
<td>62.9</td>
</tr>
</tbody>
</table>

**Figure 3. Arrhenius curves for CS dissolution in 1 M HCl in the nonexistence and existence Egy-dronate drug**

**Slika 3. Arreniusove krive za ugljenični čelik u 1 M HCl u odsustvu i prisustvu Egi-dronate droge**

**Figure 4. Log (kcorr. /T) vs. (1/T) for metal in M HCl in existence and nonexistence Egy-dronate drug at various temperatures**

**Slika 4. Log (kcorr. /T) vs. (1/T) za metal u M HCl u prisustvu i odsustvu Egi-dronate leka na različitim temperaturama**

Enthalpy and entropy of activation ($\Delta H^*$, $\Delta S^*$) of the corrosion process was calculated from the transition state equation (6) which listed in the Table 4:

$$K_{corr}/T = (RT / Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT)$$  \hspace{1cm} (6)

Where, \((h)\) is Planck's constant and \((N)\) is Avogadro's number. A plot of log ($K_{corr}/T$) vs. (1/T) for CS in 1 M HCl at different concentrations from investigated drug, gives straight lines as shown in Figure 4. The positive signs of ($\Delta H^*$) refer to the endothermic nature of the CS dissolution process. Large and negative values of $\Delta S^*$ imply that the activated...
complex in the rate-determining step represents an association rather than dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex [36].

3.3. Adsorption isotherm

Inhibitions of corrosion are found to protect of CS from corrosion in acid solution by adsorption on the surface of the CS. Moreover, the adsorption process depends on the chemical composition of the drug molecule, the temperature and the electrochemical potential at the metal and solution interface. The adsorption process involving two types:

1- Physisorption - which involves electrostatic force between ionic charges at the metal and the solution containing inhibitor interface? The heat of adsorption is low and therefore this type of adsorption is stable only at relatively low temperatures.

2- Chemisorption - which involves charge sharing or charge transfer from the inhibitor molecules to the metal surface form a coordinate type bond [37]. Chemisorption is typically by much stronger adsorption energy than physical adsorption. Such bond is therefore more stable at higher temperatures. Various adsorption isotherms including Frumkin, Langmuir, Temkin and Freundlich isotherms were tested to find the best suitable adsorption isotherm for adsorption of the studied inhibitors on the CS surface. Langmuir adsorption isotherm was found to fit the experimental data. The mathematical expression of Langmuir is given as following [38]:

\[ C/\Theta = 1/k_{ads} + C \]  

where, \( k_{ads} \) is the adsorption equilibrium constant.

Plotting (C/Θ) versus (C) of Egy – dronate drug at various temperatures is introduced in Figure 5 recommends that no forces of attraction between the atoms adsorbed on the metal surface. The relationship is linearly with unity slope and intercept equal \((1/k_{ads})\), the adsorption constant being result to the standard free energy of adsorption \(\Delta G_{ads} \) by the relation (8):

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

Where, \( R \) is the universal gas constant, \( T \) is the absolute temperature and 55.5 is the concentration of water in the solution in M/L.

The \(\Delta G_{ads} \) values at all studied temperatures which calculated by above equation (8) and recorded in Table 5. The heat of adsorption \((\Delta H_{ads})\) was calculated according to the Van't Hoff equation [39]:

\[ \log k_{ads} = (-\Delta H_{ads}/2.303RT) + \text{constant} \]  

Plotting (log \( k_{ads} \)) against \((1/T)\) give straight line that shown in Figure 6, the straight line gives slope equal \((-\Delta H_{ads}/2.303R)\), from this slope, the \(\Delta H_{ads} \) value was calculated and listed in Table 5. Then in accordance with the basic equation (10):

\[ \Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads}. \]  

Table 5. Thermodynamic parameters for the adsorption of Egy – dronate drug on CS surface in 1M HCl at various temperatures

<table>
<thead>
<tr>
<th>Temp. oC</th>
<th>Kads M-1</th>
<th>(\Delta G_{ads}) kJ mol-1</th>
<th>(\Delta H_{ads}) kJ mol-1</th>
<th>(\Delta S_{ads}) J mol-1 K-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>62.5</td>
<td>20.12</td>
<td>-1.43</td>
<td>96.7</td>
</tr>
<tr>
<td>30</td>
<td>53.76</td>
<td>20.16</td>
<td>-1.43</td>
<td>95.0</td>
</tr>
<tr>
<td>35</td>
<td>44.84</td>
<td>19.76</td>
<td>-1.43</td>
<td>92.2</td>
</tr>
<tr>
<td>40</td>
<td>42.55</td>
<td>20.22</td>
<td>-1.43</td>
<td>92.2</td>
</tr>
<tr>
<td>45</td>
<td>40.32</td>
<td>20.66</td>
<td>-1.43</td>
<td>92.2</td>
</tr>
</tbody>
</table>

The values of \(\Delta G_{ads} \) and \(\Delta H_{ads} \), the \(\Delta S_{ads} \) were calculated at all studied temperatures by the above equation (10). For all thermodynamic adsorption parameters for Egy - dronate drug on CS from 1M HCl solution, can be concluded that:

1- The experimental data give good curves fitting for the applied adsorption isotherms as the correlation coefficients were in the range (0.99 - 0.98).

2- \( K_{ads} \) values decrease with increasing temperatures from 25 to 45°C.
Abd El-Aziz S. Fouda et al.  Egy- dronate drug as promising corrosion inhibitor of ...

Figure 6. Curve (log kads.) vs. (1/T) for the corrosion of CS in 1M HCl in the presence of Egy - dronate drug at various temperatures

Slika 6. Kriva (log kads.) vs. (1/T) za koroziju ugljeničnog čelika u 1M HCl u prisustvu leka Egy-dronate na različitim temperaturama

3- The negative values of $\Delta G_{ads}$ reflected that the adsorption of Egy – dronate drug on CS surface in 1 M HCl solution is spontaneous process.

4- $\Delta G_{ads}$ slightly increases (becomes less negative) with increasing temperatures which indicated that the occurrence of endothermic process and the adsorption was unfavorable with increasing reaction temperature as a result of the inhibitor desorption from the CS surface [40].

5- The value of $\Delta G_{ads}$ around -20 kJ mol$^{-1}$ or lower indicates the electrostatic attraction between charged metal surface and charge drug molecules in the bulk of the solution i.e. physisorption.

6- The positive sign of $\Delta H_{ads}$ refers to the adsorption of inhibitor molecules is an endothermic process, indicate that the adsorption is physical adsorption. The unshared electron pairs in investigate molecule may attractive with positive center on the surface of CS by electrostatic attraction to produce a protective film which prevent the dissolution process [41].

7- The values of $\Delta S_{ads}$ in the presence of investigate drug as an inhibitor are large and positive that is accompanied with endothermic adsorption process [42].

3.4. HE technique

Plotting the volume of hydrogen against time at various doses between 50 to 300 ppm of Egy - dronate drug gives straight lines in Figure 7. The slope of line equals the rate of corrosion. The great straight lines show vicinity of insoluble film adsorbed on the metal surface. The rate of corrosion ($k_{corr}$), $\theta$ and IE % obtained from hydrogen evolution at various doses are listed in Table 6. As shown, the rate of corrosion reduced with increasing of Egy – dronate drug doses, appearing diminishes conduct for the metal disintegration. The reaction is presented by chemical equation (11) and pointed out that Fe dissociation in acid arrangements relies on hydrogen ion more than the chloride ion [43], this means the Fe$^{2+}$ bonded with Cl and formed FeCl$_2$.

$$Fe(s) + 2H^+ == Fe^{2+} + H_2(g) \quad (11)$$

Table 6. The rate of corrosion for metal nonexistence and existence various doses of Egy - dronate drug

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>$k_{corr}$ ml cm$^{-2}$ min$^{-1}$</th>
<th>$\theta$</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.158</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>50</td>
<td>0.062</td>
<td>0.608</td>
<td>60.8</td>
</tr>
<tr>
<td>100</td>
<td>0.060</td>
<td>0.620</td>
<td>62.0</td>
</tr>
<tr>
<td>150</td>
<td>0.055</td>
<td>0.652</td>
<td>65.2</td>
</tr>
<tr>
<td>200</td>
<td>0.052</td>
<td>0.671</td>
<td>67.1</td>
</tr>
<tr>
<td>250</td>
<td>0.049</td>
<td>0.689</td>
<td>68.9</td>
</tr>
<tr>
<td>300</td>
<td>0.047</td>
<td>0.703</td>
<td>70.3</td>
</tr>
</tbody>
</table>

Figure 7. Hydrogen volume produced versus time arrangements with distinctive centralization of inhibitor at 25°C

Slika 7: Zapremina vodonika proizvedena u odnosu na vremenske aranžmane sa prepoznatljivom centralizacijom inhibitora na 25°C

3.5. Open circuit potential ($E_{op}$)

From the Figure 8 is shown several interesting points:

1. The $E_{op}$ in the blank solution began from -533 mV then shifted anodically and reached the steady state after 300 second indicating that the initial dissolution process and formation oxide film on the metal surface.

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2. The $E_{OCP}$ is started in the existence of Egy-dronate drug, at less negatively potential compared with that in the nonexistence of the drug and then shifted anodically, according to the increasing the doses 50, 100, 150, 200, 250 and 300 respectively, that shown in Table 7. The steady state is attained rapidly, with increasing the doses of the drug comparing with the blank, then it shifted in the potential of $E_{OCP}$ increment in the positive direction and the drug might certainly act as an anodic inhibitor [44]. However, from Figure (8), the shift in $E_{OCP}$ on addition Egy-dronate drug is about 57.5 mV revealing that the present drug acts as anodically drug.

![Graph showing potential vs. time](image)

**Figure 8.** Open circuit potential, EOCP vs. time relations for CS immersed in 1M HCl in the nonexistence and existence of Egy-dronate drug at 25°C

Slika 8. Potencijal otvorenog kola, EOCP vs. vremenu za ugljenični čelik uronjeni u M HCl u odsustvu i prisustvu droge Egi-dronate na 25°C

Table 7. Open circuit potential of CS for without and with various doses of Egy - dronate drug at 25°C

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>-EMin (mV)</th>
<th>-EMax (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>533.0</td>
<td>502.0</td>
</tr>
<tr>
<td>50</td>
<td>551.7</td>
<td>472.1</td>
</tr>
<tr>
<td>100</td>
<td>507.4</td>
<td>464.3</td>
</tr>
<tr>
<td>150</td>
<td>503.9</td>
<td>464.5</td>
</tr>
<tr>
<td>200</td>
<td>500.8</td>
<td>475.2</td>
</tr>
<tr>
<td>250</td>
<td>495.3</td>
<td>465.2</td>
</tr>
<tr>
<td>300</td>
<td>490.5</td>
<td>451.3</td>
</tr>
</tbody>
</table>

3.6. PP technique

Polarization measurement was carried out to obtain Tafel plots in the nonexistence and existence of various doses of Egy - dronate drug at 25°C. The current and potential relationship for CS electrode in different test solutions of Egy-dronate drug is shown in Figure 9. The numerical values of the variation of the corrosion current density (icorr.), the corrosion potential ($E_{corr}$), the anodic Tafel slope ($\beta_a$), the cathodic Tafel slope ($\beta_c$), $\theta$ and % IE are listed in Table (8). The results in this table indicate [u7] that:

1. The icorr diminish in the existence of drug compared to the blank solution and also diminish [u7] with raising doses of drug.
2. Addition of Egy – dronate drug causes diminish in the rate of corrosion that shifted both anodic and cathodic curves to lower values of icorr. This suggests that both the hydrogen evolution at cathodic and at the anodic dissolution reactions of CS electrode are inhibited by adsorption of Egy – dronate drug on the metal surface [45].
3. The anodic and cathodic slopes of Tafel lines ($\beta_a$ and $\beta_c$) were slightly changed by increasing the doses of the tested compound. This indicates that there is no change of mechanism of inhibition in existence and nonexistence of Egy-dronate drug and effects of both anodic and cathodic reaction [46] i.e. mixed type.

Calculation IE % and $\theta$ according to equation (12) [47]:

$$IE\% = \theta \times 100 = \left(1-\frac{icorr(inh)}{icorr(free)}\right) \times 100$$

Where, icorr(free) and icorr(inh) are the corrosion current densities in the nonexistence and existence of drug, respectively.

![Graph showing PP curves](image)

**Figure 9.** PP curves for corrosion of CS in 1M HCl in the nonexistence and existence of various doses of Egy-dronate drug at 25°C

Slika 9. PP krive za koroziju ugljeničnog čelika u 1M HCl u odsustvu i posustvu različitih doza leka Egi-dronate na 25°C
Table 8. PP parameters for the corrosion of CS in 1M HCl in the nonexistence and existence of various doses of Egy – dronate drug at 25°C

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>Icorr. mA/cm²</th>
<th>-Ecorr. mV(SCE)</th>
<th>βa mV dec⁻¹</th>
<th>βc mV dec⁻¹</th>
<th>C. R. Mpy</th>
<th>Z</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>147</td>
<td>480</td>
<td>166</td>
<td>208</td>
<td>67.3</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>50</td>
<td>65.7</td>
<td>470</td>
<td>85.3</td>
<td>107</td>
<td>30.02</td>
<td>0.565</td>
<td>56.5</td>
</tr>
<tr>
<td>100</td>
<td>61.6</td>
<td>459</td>
<td>65.1</td>
<td>108</td>
<td>28.16</td>
<td>0.592</td>
<td>59.2</td>
</tr>
<tr>
<td>150</td>
<td>54.9</td>
<td>467</td>
<td>84.5</td>
<td>132</td>
<td>25.08</td>
<td>0.636</td>
<td>63.6</td>
</tr>
<tr>
<td>200</td>
<td>48.5</td>
<td>459</td>
<td>63.3</td>
<td>128</td>
<td>22.15</td>
<td>0.679</td>
<td>67.9</td>
</tr>
<tr>
<td>250</td>
<td>45</td>
<td>462</td>
<td>53.3</td>
<td>84.0</td>
<td>20.56</td>
<td>0.702</td>
<td>70.2</td>
</tr>
<tr>
<td>300</td>
<td>31.8</td>
<td>459</td>
<td>36.7</td>
<td>72.6</td>
<td>14.51</td>
<td>0.789</td>
<td>78.9</td>
</tr>
</tbody>
</table>

3.7. EIS technique
The EIS collection data was carried out at room temperature in corrosive medium in existence and nonexistence of Egy – dronate drug. The equivalent circuit which used to fit EIS data is shown in Figure 10. Where, Rs, Rct and CPE refer to solution resistance, the change transfer resistance and constant phase element representing the double layer capacitance (Cdl) of the in interface, respectively.

Figure 10. Equivalent circuit model used to fit the impedance spectra

Slika 10. Model ekvivalentnog kola koji se koristi za ispitivanje impedance

A typical example of EIS data obtained for Egy - dronate drug is represented as Nyquist and Bode plots in Figure 11- a, b. The diagram of impedance is characterized by a single full semicircular loop appearance indicating that a charge transfer process controls the corrosion of CS [48]. Small distortion was observed in the diagrams; this distortion has been attributed to frequency dispersion [49]. The obtained diameters of the capacitive loops increase in existence of Egy- dronate drug. The % IE, of corrosion process, contrary to the RDUCEs of the capacity of double layer (Cdl) which is defined as:

\[ Cdl = \frac{1}{2 \pi f_{\text{max}} R_p} \]

where, \( f_{\text{max}} \) is the maximum frequency.

Figure 11. The Nyquist (a) and Bode (b) plots for corrosion of CS in 1M HCl in the nonexistence and existence of various doses of Egy - dronate at 25°C

Slika 11. Nyquist (a) i Bode (b) krive za koroziju ugljeničnog čelika u 1M HCl u odsustvu i prisustvu različitih doza leka Egi-dronata na 25°C
The % IE and θ obtained from the impedance measurements were defined by the following relation:

$$IE \% = \theta \times 100 = [1 - (R^o_p/R_p)] \times 100$$  \hspace{1cm} (14)

Where, $R_{op}$ and $R_p$ are the charge transfer resistance in the absence and presence of Egy-dronate drug, respectively. The analysis of EIS parameters were shown, that the $R_p$ increases with increasing doses of Egy-dronate drug and provides consequently the reduction of the corrosion rate. It is important to emphasize that the values of $C_{dl}$ decrease with increasing the doses of Egy-dronate.

Table 9. EIS data of CS in 2M HCl and in the nonexistence and existence of various doses of test drug at 25°C

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>$R_p$ (Ω cm²)</th>
<th>$C_{dl}$ (µF cm²)</th>
<th>θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>64.73</td>
<td>594.2</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>50</td>
<td>158.4</td>
<td>126.3</td>
<td>0.591</td>
<td>59.1</td>
</tr>
<tr>
<td>100</td>
<td>162.2</td>
<td>112.1</td>
<td>0.601</td>
<td>60.1</td>
</tr>
<tr>
<td>150</td>
<td>170.6</td>
<td>97.69</td>
<td>0.621</td>
<td>62.1</td>
</tr>
<tr>
<td>200</td>
<td>186.4</td>
<td>82.54</td>
<td>0.653</td>
<td>65.3</td>
</tr>
<tr>
<td>250</td>
<td>205.3</td>
<td>72.7</td>
<td>0.685</td>
<td>68.5</td>
</tr>
<tr>
<td>300</td>
<td>301.6</td>
<td>33.16</td>
<td>0.785</td>
<td>78.5</td>
</tr>
</tbody>
</table>

This is due to the gradual replacement of water molecules in the metal interface by the adsorbed drug molecules as an adherent film form on the metal surface as a result of reduces of the local dielectric constant and increases in the thickness of the electrical double layer of the metal solution interface [50]. The obtained Bodes plot for Egy-dronate is shown in Figure 11. The high frequency limits corresponds to ($R_p + R_s$). The low frequency contribution shows the kinetic response or charge transfer reaction [51]. EIS data are listed in Table 9.

3.8. EFM technique

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [52].

The high validly of EFM collection data are seen that have the causality factors similar or equal the hypothetical values of causality factors.

The causality factors CF-2 and CF-3 were calculated from the frequency spectrum of the current responses.

Figure 12. EFM for CS in 1M HCl with and without various doses of the used Egy-dronate drug

Slika 12. EFM za ugljenični čelik u 1M HCl sa i bez različitih doza korišćenog leka Egi-dronate
Figure (12), shows the frequency spectrum (current vs. frequency) of the current response of pure CS in 1 M HCl, contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The EFM Intermodulation spectrums of CS in 1 M HCl acid solution containing (50, 100, 150, 200, 250 and 300 ppm) of the Egy – dronate drug as inhibitor is shown in Figure 12. The harmonic and Intermodulation peaks are clearly visible and are much larger than the background noise. The experimental EFM-data were treated using two different models: complete diffusion control of the cathodic reaction and the “activation” model. The latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode [53]. The large peaks were utilized to calculate the corrosion current density (i_corr), the Tafel slopes (β_a and β_c) and the causality factors (CF-2 and CF-3). These electrochemical parameters were listed in Table 10. The addition of Egy - dronate drug at a given doses in the acidic solution reduces the corrosion current density, indicating that these compounds inhibit the corrosion of CS in 1 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are validity and of good quality [54]. The inhibition efficiencies % IE_EFM increases by increasing the drug doses and were calculated as follows:

$$\% \text{IE} = \left(1 - \frac{I_{corr}}{I_{corr}}\right) \times 100$$  \hspace{1cm} (15)

Where, $I_{corr}$ and $I_{corr}$ are corrosion current densities without and with deferent doses of drug respectively.

### Table 10. Electrochemical kinetic variables occur by EFM method for CS in 1 M HCl nonexistence and existence different doses of Egy-dronate at 25°C

Tabela 10. Elektrokemijske kinetičke varijable dobijene metodom EFM za ugljenični čelik u 1 M HCl u odsustvu i prisustvu različitih doza leka Egi-dronata na 25°C

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Conc. M</th>
<th>i_corr. μAcm$^{-2}$</th>
<th>$B_s \times 10^3$ mVdec$^{-1}$</th>
<th>$B_c \times 10^3$ mVdec$^{-1}$</th>
<th>CF (2)</th>
<th>CF (3)</th>
<th>CR mpy</th>
<th>Θ</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0</td>
<td>350.3</td>
<td>156.4</td>
<td>247.9</td>
<td>1.5</td>
<td>2.9</td>
<td>160.1</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Egy - dronate</td>
<td>50</td>
<td>110.3</td>
<td>134.0</td>
<td>141.6</td>
<td>1.4</td>
<td>4.5</td>
<td>50.4</td>
<td>0.685</td>
<td>68.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>103.1</td>
<td>94.1</td>
<td>109.4</td>
<td>1.8</td>
<td>4</td>
<td>47.1</td>
<td>0.706</td>
<td>70.6</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>96.6</td>
<td>93.4</td>
<td>122.7</td>
<td>2.2</td>
<td>1.9</td>
<td>44.2</td>
<td>0.724</td>
<td>72.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>95.4</td>
<td>133.5</td>
<td>160.0</td>
<td>2</td>
<td>6</td>
<td>43.6</td>
<td>0.728</td>
<td>72.8</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>93.2</td>
<td>102.5</td>
<td>123.1</td>
<td>2.2</td>
<td>1.6</td>
<td>42.6</td>
<td>0.734</td>
<td>73.4</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>89.2</td>
<td>81.0</td>
<td>111.3</td>
<td>1.8</td>
<td>4</td>
<td>40.8</td>
<td>0.745</td>
<td>74.5</td>
</tr>
</tbody>
</table>

### 3.9. EDX spectra

The EDX spectra were used to determine the elements existence on the surface of CS after one day to exposure of the uninhibited and inhibited specimens in 1M HCl. Figure (13), shows the EDX analysis result on the composition of CS only without acid, with acid and with inhibitor treatment. The EDS analysis indicates that only Fe and oxygen were detected, which shows that the passive film contained only Fe_{2}O_{3}. The EDS analysis diagram of CS in 1 M HCl only and in the presence of 300 ppm of pharmaceutical compound. The spectra views additional lines, appearing the existence of C (owing to the carbon atoms of Egy - dronate). These data show that the carbon, oxygen and the electrons density of π bonding formation thin layer that cover the specimen surface. This layer is entirely owing to the inhibitor, because the carbon, iron and oxygen signals are absent on the specimen surface exposed to uninhibited HCl.

It is shown that, in addition of Egy dronate drug gives the signals of C, O and Fe were present in the spectra. A comparable elemental distribution is shown in Table (11).

### Table 11. Surface composition (weight %) of the CS after immersion 24 h in 1M HCl with 300 ppm of the studied inhibitor

Tabela 11. Sastav površine (težina%) ugljeničnog čelika posle potapanja 24 h u 1M HCl sa 300 ppm ispitanog inhibitora

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>98.28</td>
<td>0.78</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Blank</td>
<td>72.1</td>
<td>9.23</td>
<td>17</td>
<td>0.35</td>
</tr>
<tr>
<td>Egy - dronate</td>
<td>75.97</td>
<td>2.08</td>
<td>20.68</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 13. EDS analysis on CS in nonexistence and existence of Egy-dronate drug that immersion one days

Slika 13. EDS analiza ugljeničnog čelika u odsustvu i prisustvu leka Egi-dronate koji se potapaju jedan dan
3.10. SEM microscopy

Figure 14, represents the micrograph is obtained of CS samples after exposure to 1M HCl only and 1M HCl containing 300 ppm Egy-dronate for one day immersion.

It is important to stress out that when the compound is exists in the solution, the morphology of CS alloy surfaces are quite different from the previous one, the specimen surfaces were very smooth. We observed the formation of a film which is distributed in a random way on the whole surface of the CS alloy. This may be interpreted as due to the adsorption of the Egy – dronate drug on the CS alloy surface incorporating into the passive film in order to block the active site present on the CS alloy surfaces. Or due to the involvement of drug molecules in the interaction with the active sites of CS alloy surface, resulting in a decrease in the contact between CS alloy and the corrosive medium and sequentially exhibited excellent inhibition effect [56-57].

3.11. AFM Microscopy

AFM is a powerful tool to investigate the surface morphology of various samples at nano-micro scale that is currently used to study the influence of corrosion inhibitor on metal solution interface. From the analysis, it can be gained regarding the roughness (Ra) on the surface. The roughness profile values play an important role in identifying and report the efficiency of the drug under study. Among the Ra take a role in explanation about the nature of the adsorbed film on the surface [45-46].

Figure (15), shows the 3D images as well as elevation profiles of polished CS in absence and present Egy – dronate drug as an inhibitor. It was observed in Figure (15), that the surface of CS specimen which exposed to corroded solution (a) affects CS surface with large and deep crack but the surface in specimen (b) was covered by thin film. The conclusion, that the adsorption film can protects the surface of the metal from corrosion process. Analysis of the values indicated higher values of roughness parameter reached. The mean roughness (Ra) was found to be (2.60 µm) for the specimen placed in 1M HCl for one day. The observation of the metal surface which immersed in 1M HCl in presence of 300 ppm of Egy - dronate drug possess Ra (738.34 nm) which is very small compared to the blank value. The decrease in the Ra value reflected the adsorption of drug molecules on metal surface thereby reducing the rate of corrosion.
4. CONCLUSIONS

1. The tested Egy–dronate drug establish a very good inhibition for CS corrosion in HCl solution.
2. Egy–dronate inhibit the CS corrosion by adsorption on its surface and make layer film.
3. The inhibition efficiencies of the tested compound increase with increasing of their concentrations.
4. Double layer capacitances decrease with respect to blank solution when the inhibitor added. This fact may explained by adsorption of the inhibitor molecule on the CS surface.
6. The values of inhibition efficiencies obtained from the different independent techniques used showed the validity of the obtained results.

5. REFERENCES


IZVOD

EGIDRONAT KAO PERSPEKTIVNI INHIBITOR KOROZIJE UGLENIČNOG ČELIKA U VODENIM RASTVORIMA

Uticaj Egi-dronata kao inhibitora korozije ugljeničnog čelika u 1M HCl proučavan je gubitkom težine, procenom vodonika, potencijalom otvorenog kola, potentiodinamičkom polarizacijom, elektrohemijskom spektroskopskom impedancijom, modulacijom elektronske frekvencije i ispitivanjem površina uzoraka atomskom mikroskopijom (AFM), spektroskopiom disperzije energije (EDS) i skenirajućom elektronskom mikroskopijom (SEM). Rezultati efikasnosti inhibicije (IE%) povećavaju se s povećanjem koncentracije inhibitora, ali se smanjuju sa podizanjem temperature. Adsorpcija Egidronata na ugljenično-čelilčnoj površini podudara se sa Langmuirovom adsorpcionom izotermom. Proces adsorpcije je spontana, endotermna i fizička adsorpcija. Polarizacijske krive pokazuju da je Egidronat mešoviti inhibitor koji ima tendenciju anodnom tipu. Rezultati dobijeni hemijskim i elektrohemijskim tehnikama su dobar kvalitet odgovora i daju isto ponašanje adsorpcije Egidronata. Sve tehnike su dokazale formiranje tankog filma na površini metala kao zaštitnu oblogu, kako bi se sprečio metal da se razlaže u korozivnom medijumu, zbog elektrostatičke privlačnosti između nerastvornih elektrona molekula inhibitora i pozitivnih mesta na površini metala.

Ključne reči: inhibicija korozije, HCl, ugljenični čelik, adsorpcija, SEM, EDS, AFM.

Naučni rad
Rad primljen: 03. 01. 2018.,
Rad prihvaćen: 25. 01. 2018.
Rad je dostupan na sajtu: www.idk.org.rs/casopis