The Effect of Expired Acyclovir and Omeprazole Drugs on the Inhibition of Sabic Iron Corrosion in HCl Solution

M. Abdallah1,2,*, A. Fawzy1,3, A. Al Bahir1,4

1 Chemistry Department, Faculty of Applied Science, Umm Al-Qura University, Makkah, Saudi Arabia
2 Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
3 Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt
4 Chemistry Department, Faculty of Science, King Khalid University, Abha, Saudi Arabia
*E-mail: metwally555@yahoo.com

Received: 13 January 2020 / Accepted: 18 March 2020 / Published: 10 April 2020

Acyclovir (ACV) and Omeprazole (OMP) are two expired drugs examined as an inhibitors for the dissolution of Sabic iron in 1.0 M HCl using weight loss, electrochemical impedance and two types of polarization; galvanostatic and potentiodynamic measurements. Increase the concentration of expired ACV and OMP increases the efficacy of inhibition that also decreases with temperature. These drugs acts as mixed inhibitors that was detected by galvanostatic polarization studies. The inhibition activity of expired ACV and OMP increases the efficacy of inhibition that also decreases with temperature. These drugs acts as mixed inhibitors that was detected by galvanostatic polarization studies. The inhibition activity of expired ACV and OMP owing to its horizontal adsorption of them on the Sabic iron surface because of the presence of several active centers. The adsorption follows Langmuir isotherm. The impedance data demonstrated one capacitive loop suggesting that the charge transfer control the corrosion reaction. The expired ACV and OMP performed as an efficient pitting corrosion inhibitor by moving the pitting potential to more noble values.

Keyword: Sabic iron; Expired drugs; Corrosion Inhibitors; Kinetic parameters; Pitting potential

1. INTRODUCTION

Many industrial applications may get important benefits from the inhibition effect of Sabic iron in HCl solution through the use inhibitors because they are a simple and important method, and are therefore of interest to scientific research. Pickling, chemical and electrochemical etching of iron produced by HCl solution.

Organic compounds that contain different hetero atoms and many bonds in molecules utilized as inhibitors for the corrosion of iron alloys by its adsorption on the iron surface [1-10]. There are many factors that determine the adsorption capacity of inhibitors including the kind of material surface, the corrosive solutions type, the chemical structure of inhibitors, the existence the functional group and the
probable interaction between inhibitors with d-orbital iron atom which accelerates absorption of the inhibitor molecule [11-16].

Acyclovir (ACV) and Omeprazole (OMP) are two expired drugs that are used in this study to inhibit the corrosion of Sabic iron in HCl solution. Among the most important characteristics of these compounds are they are environmentally friendly and not harmful to human health, and their economical cost is few and easy to manufacture with a high degree of purity and also from their chemical composition, we find that they contain many active centers that facilitate the adsorption process. The inhibiting activity of ACV and OMP drugs against Sabic iron corrosion in 1.0 M HCl solution was explored using weight loss, (WL) galvanostatic polarization (GAP), potentiodynamic anodic polarization (PAP) and electrochemical impedance spectroscopy (EIS) measurements. The activation thermodynamic parameters of the corrosion of the Sabic iron in the free 1.0 M HCl solution and in the presence of the expired ACV and OMP were computed, the demonstration of all these subjects is the goal of our manuscript. It was detected that the adsorption isotherms type fits the experimental results. Also, the inhibition of the pitting corrosion of Sabic iron in chloride solutions was studied.

2. EXPERIMENTAL

2.1. Measurements

Sabic iron produced by the Saudi Arabia basic industry company (Sabic) has a purity of 99.99%. Coupons with dimensions of 1x4x0.4 cm$^3$ were used for WL measurement. For electrochemical techniques such as GAP, PAP and EIS; For electrochemical techniques such as GAP, PAP and EIS, the electrode is cylindrical shape and immersed in araldites with exposed surface area of 0.54 cm$^2$.

Sabic iron surface was furished in various grades of wet abrasive papers through 500-2000 grade. and then washed with double distilled water and acetone finally dried by filter papers all this for the treatment of the electrode or the coupons. All chemicals used were class AR and were used as they were provided. As shown previously, weight loss tests are performed at different temperatures using an air thermostat[17,18]

For the electrochemical measurements, a three-compartment cell was used comprising Sabic Fe as working electrode (WE), Saturated calomel electrode (SCE) as reference electrode, Pt counter electrode. PGSTAT30 potentiostat /galvanostat in a cell used for conducting the measurements, using a thermostat control system to detect measurements at an adjusted temperature. In a potentiodynamic polarization technique, the electrode potential was changed in a potential range of -200 mV to +200 mV vs. OCP at a scan rate of 2.0 mV/s. In a frequency range of 100 kHz to 0.1 Hz with an amplitude of 4.0 mV peak-to-peak, EIS measurements were done. At 25±1°C by using air thermostat, all the above experiments were performed.

2.2. Inhibitors

ACV and OMP are two expired antibacterial drugs produced from Pfizer Pharmaceutical Company, Riyadh - Saudi Arabia. Their structures are listed in Table 1.
Table 1. The names and structures of expired drugs used.

<table>
<thead>
<tr>
<th>Name</th>
<th>3D shape</th>
<th>Chemical structure</th>
<th>Molecular Weight g mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acyclovir (ACV)</td>
<td><img src="image" alt="3D structure of ACV" /></td>
<td><img src="image" alt="Chemical structure of ACV" /></td>
<td>222.12</td>
</tr>
<tr>
<td>Omeprazole (OMP)</td>
<td><img src="image" alt="3D structure of OMP" /></td>
<td><img src="image" alt="Chemical structure of OMP" /></td>
<td>343.265</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. WL Measurements

3.1.1. The Influence of Expired ACV and OMP Concentrations

The influence of the diverse concentrations (100–500 ppm) of ACV and OMP on the WL versus immersion time curves of Sabic iron in 1.0 M HCl solution is represented by Fig.1(a& b). The inhibition of the corrosion of Sabic iron by two drugs is confirmed by the fact that the WL decreases with the increase in the concentration of ACV and OMP. No insoluble surface film during corrosion detected by the obtained straight line.

From the next equation [19]:

\[
CR \text{ (mpy)} = \frac{K W}{A t d} \tag{1}
\]

where, \(K\) is a constant, \(W\) is the weight loss in grams, \(A\) is the surface area subjected to the solution in cm², \(t\) is time in hour and \(d\) is the density of iron.

\[
\% \text{ IE} = \Theta \times 100 = \left[ 1 - \frac{CR_{inh}}{CR} \right] \times 100 \tag{2}
\]

The inhibition efficiency (% IE) and the degree of surface coverage (\(\Theta\)) of the expired ACV and OMP drugs on the corrosion of Sabic iron were computed, in the above equation [20]. \(CR\) and \(CR_{inh}\) are corrosion rate values in free and with the presence of the expired drugs, respectively.

The CR, % IE and \(\Theta\) values were computed and registered in Table 1, Obviously with increasing the concentration of expired ACV and OMP decreases the values of \(R_{corr}\) but increases the values of IE% and \(\Theta\) all this improves the inhibitory effect of the these drugs on Sabic iron corrosion in 1.0 M HCl
solution due to increased adsorption of expired drugs on the surface of Sabic iron. ACV shows lower % IE than Omp, that will be explained later.

**Figure 1.** Weight loss (WL) versus immersion time for the corrosion of Sabic iron in free 1.0 M HCl solution (blank) and with various concentrations of expired A) ACV and, B) Omp at 25 °C.

**Table 2.** Effect of increasing concentrations of expired ACV and OMP drugs on the corrosion parameters obtained from WL measurements in the corrosion of Sabic iron in 1.0 M HCl solution.

<table>
<thead>
<tr>
<th>Inh. Conc. (ppm)</th>
<th>25</th>
<th>35</th>
<th>45</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10^3 CR mg cm^2 min^-1</td>
<td>% IE</td>
<td>CR mg cm^2 min^-1</td>
<td>% IE</td>
</tr>
<tr>
<td>-</td>
<td>0</td>
<td>1.70</td>
<td>---</td>
<td>1.90</td>
</tr>
<tr>
<td>ACV</td>
<td>100</td>
<td>0.35</td>
<td>79.4</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.33</td>
<td>80.5</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.29</td>
<td>82.9</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.25</td>
<td>85.3</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.22</td>
<td>87.0</td>
<td>0.87</td>
</tr>
<tr>
<td>OMP</td>
<td>100</td>
<td>0.29</td>
<td>82.9</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.27</td>
<td>84.1</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.23</td>
<td>86.5</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.21</td>
<td>87.6</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.19</td>
<td>88.8</td>
<td>0.89</td>
</tr>
</tbody>
</table>
3.2. Effect of raising temperature

The effect of a raising temperature on the WL for the corrosion of Sabic iron in 1.0 M HCl solution including diverse concentrations of the expired ACV and OMP was investigated. Similar figures to figure 1 were obtained but do not appeared. The corrosion parameters gained from the WL were registred in Table 2, the values of CR increases and those of %IE and O declines with the increase in temperature so it is apparent that the inhibition lowered at high temperatures, suggest the adsorption of ACV and OMP on the surface of Sabic iron is physical.

3.2.1. Kinetics Parameters

The activation energy of the corrosion process can be determined from the Arrhenius equation as follows [21,22]:

\[ \ln CR = \ln A - \frac{E_a^*}{RT} \]  

(3)

where, \( E_a^* \) is the activation energy and A is the Arrhenius constant.

The relationship between log CR and 1/T for the corrosion of Sabic iron in 1.0 M HCl solution and including diverse concentrations of ACV and OMP is illustrated by Figure 2. From the slope of the straight lines we can calculate the values of \( E_a \) and are given in Table 2. The existence of ACV and OMP drugs increases the values of \( E_a \) increase more than with those in 1.0 M HCl solutions donating a vigor adsorption of ACV and OMP on the Sabic iron surface. This adsorption has weakened at elevated temperature and thus increased the reaction rate due to a larger area of the Sabic iron surface is exposed to a corrosive solution [23].

![Figure 2](image)

**Figure 2.** Plots of log CR versus 1/T for the corrosion of Sabic iron in 1.0 M HCl solution and including various concentrations of drugs: A) ACV and B) OMP.

The enthalpy (\( \Delta H^* \)) and entropy (\( \Delta S^* \)) for the activation process were determined from the transition state equation [21,22]:

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

(4)
where, \( N \) is Avogadro’s number and \( h \) are Planck’s constant.

The plots of \( \ln (CR / T) \) vs. \( 1 / T \) of Sabic iron are presented in 1.0 M HCl and containing various concentrations of ACV and Omp drugs are given in Fig. 3. The values of \( \Delta H^* \) and entropy \( \Delta S^* \) were computed from the slope and intercept of the straight lines and are listed in Table 4. The positive sign of \( \Delta H^* \) indicating the endothermic behavior of Sabic iron corrosion. The negative values of \( \Delta S^* \) imply that the activated complex in the rate determining step represents binding rather than dissociation [24].

**Figure 3.** Plots of \( \ln (CR/T) \) versus \( 1/T \) for the corrosion of Sabic iron in 1.0 M HCl solution and containing some concentrations of the expired drugs: A) ACV and B) Omp.

**Table 3.** Thermodynamic activation parameters for the corrosion of Sabic iron in 1.0 M HCl and containing some concentrations of the expired drugs: ACV and Omp.
3.3. Adsorption Isotherms

Expired ACV and OMP inhibit the Sabic iron corrosion in 1.0 M HCl is mainly due to its ability to form a protective adsorbed layer on the iron surface. Adsorption can be considered as replacement process where expired drugs in aqueous phase, Drug(aq.), replace an (x) the number of water molecules adsorbed, H$_2$O(ads.) on the Sabic iron. x is defined as the number of adsorbed water molecules exchanged by a single drug molecule. The adsorption process can be represented as follow [25]:

\[
\text{Drug}^{\text{(aq.)}} + x\text{H}_2\text{O}_{\text{ads.}} \rightarrow \text{Drug}_{\text{ads.}} + x\text{H}_2\text{O}_{\text{aq.}} \tag{5}
\]

A number of adsorption isothermal relationships have been applied to match the experimental data for this work. We found that Langmuir isotherm is the most appropriate isotherm that matches the experimental data according to the following equation:

\[
\frac{C}{\theta} = \frac{C_{\text{inh}}}{K_{\text{ads}}} + 1/K_{\text{ads}} \tag{6}
\]

where, C is the concentration of expired drugs: ACV, OMP and $K_{\text{ads}}$ is the equilibrium constant of the adsorption.

The relationship between $C/\theta$ versus C (Langmuir isotherm) of expired ACV and Omp on Sabic iron in 1.0 M HCl solutions at different temperatures is shown by Figure 4. A. straight lines with slope nearly equal unit were obtained. This indicates that the monolayer of adsorbed drug is placed on the surface of Sabic iron that there is no interaction between adsorbed species.

The values of $K_{\text{ads}}$ can be computed from the intercept of Langmuir relation at different temperatures and recorded in Table 4. Clearly, increased temperature leads to lower the values of $K_{\text{ads}}$ and decreased adsorption strength, while lower temperature leads to strong absorption of expired drugs: ACV and OMP on the Sabic iron surface.

3.3.1. Thermodynamic parameters for adsorption

The study the thermodynamic parameters for the adsorption of the expired ACV and OMP on the surface of the Sabic iron is important explain the expired drug inhibition mechanism. The standard free energy of adsorption ($\Delta G^o_{\text{ads.}}$) was computed from the next equation [26]:

\[
55.5 K = \exp \left[ -\frac{\Delta G^o_{\text{ads}}}{RT} \right] \tag{7}
\]

Table 4 shows the computed values of $\Delta G^o_{\text{ads}}$ at various concentrations of expired of ACV and OMP. The adsorption of expired ACV and OMP. is spontaneous and the film absorbed on the iron surface is stable due to the values of $\Delta G^o_{\text{ads}}$ appear to be negative. Inspection of Table 4 the values of $\Delta G^o_{\text{ads}}$ ranged from -33.60 kJ mol$^{-1}$ to -36.89 kJ mol$^{-1}$indicating the adsorption of expired drugs on the Sabic iron surface is mixed from the chemical and physical adsorption [27,28].

The standard enthalpy of the adsorption ($\Delta H^o_{\text{ads}}$) was determined from Van't Hoff equation [29]:

\[
\ln K_{\text{ads}} = \frac{\Delta H^o_{\text{ads}}}{RT} + C \tag{8}
\]

where C, is constant. Fig.4 symbolizes the relationship between $\ln K_{\text{ads}}$ and 1/T. The values of $-\Delta H^o_{\text{ads}}$ were gained from the slope of the straight lines and are inserted in Table 4.

The negative values of $\Delta H^o_{\text{ads}}$ indicating the adsorption of expired ACV and OMP on the surface of Sabic iron is an exothermic process. The standard entropy for adsorption process ($\Delta S^o_{\text{ads}}$) can be
computed from Gibbs–Helmholtz equation and inserted into Table 4. According to the following equation:

$$T \Delta S_{ads}^\circ = (\Delta H_{ads}^\circ - \Delta G_{ads}^\circ)$$  \hspace{1cm} (9)

The values of $\Delta S_{ads}^\circ$ are positive indicating the disorder increases in the iron interface/solution during adsorption of the expired drugs ACV and OMP on the Sabic iron surface.

**Figure 4.** The relationship between $C/\theta$ versus $C$ for the adsorption of ACV and OMP drugs on Sabic iron surface in 1.0 M HCl solution at different temperatures (Langmuir isotherm)

**Table 4.** The thermodynamic parameters for adsorption process for Sabic iron corrosion in free 1.0 M HCl solution and including of expired ACV and OMP at different temperatures.

<table>
<thead>
<tr>
<th>Inh.</th>
<th>Temperature ($^\circ$C)</th>
<th>$10^{-3} K_{ads}$ 1 mol$^{-1}$</th>
<th>$\Delta G_{ads}^\circ$ kJ mol$^{-1}$</th>
<th>$\Delta H_{ads}^\circ$ kJ mol$^{-1}$</th>
<th>$\Delta S_{ads}^\circ$ J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACV</td>
<td>25</td>
<td>17.90</td>
<td>-34.21</td>
<td>-8.15</td>
<td>34.24</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>13.51</td>
<td>-34.64</td>
<td></td>
<td>34.67</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>11.69</td>
<td>-35.38</td>
<td></td>
<td>35.41</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>13.51</td>
<td>-36.89</td>
<td></td>
<td>36.91</td>
</tr>
<tr>
<td>OMP</td>
<td>25</td>
<td>25.15</td>
<td>-35.05</td>
<td>-1.33</td>
<td>35.05</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>21.65</td>
<td>-35.84</td>
<td></td>
<td>35.84</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>25.50</td>
<td>-37.44</td>
<td></td>
<td>37.44</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>25.15</td>
<td>-38.58</td>
<td></td>
<td>38.58</td>
</tr>
</tbody>
</table>

**3.4. GAP Measurement**

Figure 5 displays the GAP measurements of Sabic iron in 1.0 M HCl solutions and in the presence of some concentration's ranges from (100 to 500ppm) of the expired drugs: ACV and OMP. The values of corrosion current densities($I_{corr}$) was obtained from the extrapolation of the cathodic and
anodic Tafel lines of the polarization curves with the corrosion potentials \(E_{\text{corr}}\). The inhibition efficiency was determined from the relation:

\[
\% \text{ IE} = \left[1 - \frac{R_{\text{add}}}{R_{\text{free}}}\right] \times 100
\]

where, \(R_{\text{free}}\) and \(R_{\text{add}}\) are the rate of corrosion in 1.0 M HCl and with different concentrations of expired ACV and OMP., respectively. The computed corrosion parameters such as anodic \((\beta_a)\), cathodic \((\beta_c)\), \(E_{\text{corr}}\), \(I_{\text{corr}}\), rate of corrosion \((R_{\text{corr}})\) and inhibition efficiency \((\% \text{IE})\) are listed in Table 5.

\(E_{\text{corr}}\) values slightly changed, \(I_{\text{corr}}\) values are reduced, and thus the values of \(\% \text{IE}\) increase demonstrate the inhibitory action of expired drugs.

As a results of adding expired drugs: ACV and OMP to the blank 1.0 M HCl solution, the anodic and cathodic polarization curves have varied to lower current density indicating the retard the Sabic iron corrosion and delaying the reaction of hydrogen evolution. Also, the values of \(\beta_a\) and \(\beta_c\) are varied towards the more positive and negative values proving the expired ACV and OMP acts as mixed inhibitors but the cathode is greater polarized when external current is utilized i.e., the values of \(\beta_c\) are greater than \(\beta_a\). So, the expired ACV and OMP are considered as mixed inhibitors but the cathode is more polarized. The values of \(E_{\text{corr}}\) are changed slightly, the values of \(I_{\text{corr}}\) are reduced and hence the values of \(\% \text{IE}\) increases proving the inhibitory action of the expired drugs. At the same concentration of the examined expired drugs, the \(\% \text{IE}\) values of OMP is more than ACV.

Figure 5. GAP polarization curves for the corrosion of Sabic iron in 1.0 M HCl solution and containing different concentrations of the expired drugs: A) ACV and B) OMP
Table 5. GAP data for Sabic iron corrosion in 1.0 M HCl solution and with different concentrations of the expired drugs: ACV and OMP at 25 °C.

<table>
<thead>
<tr>
<th>Inh. Conc. (ppm)</th>
<th>-E_{corr} (mV (SCE))</th>
<th>β_α (mV/decade)</th>
<th>β_β (mV/decade)</th>
<th>I_{corr} (µA/cm²)</th>
<th>R_{corr} (mpy)</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0</td>
<td>540</td>
<td>302</td>
<td>502</td>
<td>0.0760</td>
<td>34.549 ---</td>
</tr>
<tr>
<td>ACV</td>
<td>100</td>
<td>486</td>
<td>288</td>
<td>499</td>
<td>0.0133</td>
<td>6.046</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>440</td>
<td>460</td>
<td>492</td>
<td>0.0112</td>
<td>5.091</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>375</td>
<td>589</td>
<td>486</td>
<td>0.0085</td>
<td>3.864</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>335</td>
<td>785</td>
<td>474</td>
<td>0.0062</td>
<td>2.818</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>324</td>
<td>886</td>
<td>468</td>
<td>0.0042</td>
<td>1.909</td>
</tr>
<tr>
<td>OMP</td>
<td>100</td>
<td>532</td>
<td>298</td>
<td>480</td>
<td>0.0076</td>
<td>3.457</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>500</td>
<td>480</td>
<td>473</td>
<td>0.0065</td>
<td>2.955</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>480</td>
<td>589</td>
<td>463</td>
<td>0.0048</td>
<td>2.182</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>462</td>
<td>788</td>
<td>457</td>
<td>0.0040</td>
<td>1.818</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>430</td>
<td>883</td>
<td>443</td>
<td>0.0036</td>
<td>1.636</td>
</tr>
</tbody>
</table>

3.5. EIS Measurements

The corrosion behavior of Sabic iron in 1.0 M HCl solution and its inhibition by expired drugs namely, ACV and OMP was examined by EIS measurements. The Nyquist plots of Sabic iron in free 1.0 M HCl solution and with some concentrations of ACV and OMP at 25°C, was symbolized in Figure 5. The impedance diagram does not display a complete semicircle. This behavior owing to the roughness and homogeneity of the iron surface [30]. The impedance spectra of Nyquist plots were analyses by convenient the experimental data to a simple equivalent circuit [31]. Devoid of and including expired drugs also demonstrated the same plots. No significant change in the corrosion process mechanism occurs due to the presence of an expired ACV and OMP that only reduces corrosion by increasing the surface coverage by forming a adsorbent inhibitor film. The relationship between the real component of impedance versus the imaginary component is discovered at different frequencies by the Nyquist schemes. Half-circle intersections with the axis of the real component can give the values of charge transfer resistance (R_{ct}). Double layer capacity (C_{dl}) and the values of %IE are set from next equations:

\[ C_{dl} = \frac{1}{2\pi f_{\text{max}} R_{ct}} \]  

\[ \%\text{IE} = \left[ 1 - \frac{R_{ct}}{R_{ct(\text{inh})}} \right] \times 100 \]  

Where f is the frequency, R_{ct} and R_{ct(\text{inh})} are the charge transfer resistance in free 1M HCl solution and with the presence of the expired drugs: ACV and OMP. Table 5 shows the values of C_{dl}, R_{ct} and %IE. Inspection of Table 5. Obviously, the more expired ACV and OMP concentrations, the lower C_{dl} values and higher R_{ct} values, so the values of %IE increase.
Figure 6. Nyquist plots for the corrosion of Sabic iron in 1.0 M HCl solution and including some concentrations of the expired drugs: A) ACV and B) OMP at 25 °C.

The increase in $R_{ct}$ increases indicates that the corrosion of Sabic iron is mainly controlled by a charge transfer process and formation of a protective film on the iron surface interface [32]. On the other hand, $C_{dl}$ values are reduced by substituting water molecules by adsorption of the expired drugs on the Sabic iron surface. Therefore, corrosion rate is reduced and the %IE increased. This mention that the inhibitory impact of the two expired ACV and OMP is mainly by adsorption into the Sabic iron / solution interface.

Table 6. EIS parameters for Sabic iron corrosion in 1.0 M HCl solution and with different concentrations of the expired drugs: ACV and OMP at 25 °C.

<table>
<thead>
<tr>
<th>Inh.</th>
<th>Inh. Conc. (ppm)</th>
<th>$R_{ct}$ ($\Omega$ cm$^2$)</th>
<th>$C_{dl}$ ($\mu$F cm$^{-2}$)</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>0</td>
<td>50.3</td>
<td>217</td>
<td>--</td>
</tr>
<tr>
<td>ACV</td>
<td>100</td>
<td>311</td>
<td>185</td>
<td>83.90</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>353</td>
<td>174</td>
<td>85.72</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>419</td>
<td>167</td>
<td>88.00</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>600</td>
<td>158</td>
<td>91.65</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>813</td>
<td>147</td>
<td>93.82</td>
</tr>
<tr>
<td>OMP</td>
<td>100</td>
<td>460</td>
<td>182</td>
<td>89.13</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>610</td>
<td>175</td>
<td>91.80</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>803</td>
<td>168</td>
<td>93.77</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>860</td>
<td>153</td>
<td>94.18</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1111</td>
<td>146</td>
<td>95.50</td>
</tr>
</tbody>
</table>
3.6. Inhibition of Pitting Corrosion

PAP measurements are used to test expired drugs: ACV and OMP as pitting corrosion inhibitors. Fig. 7 displays the PAP curves of Sabic iron in 1.0 M HCl + 0.5 M NaCl solutions devoid of and containing some concentrations of expired drugs: ACV and OMP at scan rate 1.0 mV s\(^{-1}\). NaCl solution was used as pitting corrosion agent. It is clear that there is no any anodic dissolution peaks during the anodic polarization. This proves that the stability of the passive film formed at the iron surface. The passive film formed on the surface of the Sabic iron is penetrated by the chloride ions causing rapid increase in the current. The potential at which current increases is defined as the pitting potential \(E_{\text{pit}}\) [33,34].

It is obvious that when the concentrations of expired ACV and OMP increases, the values of \(E_{\text{pit}}\) is moved to positive direction (noble direction). This indicates that the tested two expired drugs increase the resistance to the pitting attack. Figure 8 elucidates the relationship between \(E_{\text{pit}}\) and the logarithm of the concentration of the expired drugs. According to the following equation [33,34]:

\[
E_{\text{pit}} = n + m \log C_{\text{inh}}
\]

(13)

where, \(n\) and \(m\) are constants depending on the kind of metals and additive used.

The expired ACV and OMP acted as pitting corrosion inhibitors are indicated by the detected Broken lines and \(E_{\text{pit}}\) is moved to positive direction indicting. It was concluded that \(E_{\text{pit}}\) depended on the concentration of expired drugs from the lines obtained from Fig.8. The change in \(E_{\text{pit}}\) toward the positive direction is low at low concentrations of the expired drugs whereas \(E_{\text{pit}}\) rapidly turns into the positive direction at high concentrations of the expired drugs, indicated inhibition of localized attack by chloride ions.

**Figure 7.** PAP curves of Sabic iron corrosion in 1.0 M HCl + 0.5 M NaCl solution and including various concentrations of the expired drugs: A) ACV and B) OMP, at scan rate 1.0 mV s\(^{-1}\).
3.7. Mechanism of Corrosion Inhibition

The inhibitory effect of two expired drugs ACV and OMP toward the corrosion of Sabic iron in 1.0 M HCl was investigated using chemical and electrochemical tests. The acquired results indicated that %IE of all techniques used depended on the concentration of expired drugs. The increase in the concentration of the expired drugs is accompanied by a decrease in WL, a decrease in the value of corrosion rate, an increase in $\theta$, the $I_{corr}$ values reduced, $R_{ct}$ increased, $C_{dl}$ values reduced, and the values of %IE increased.

These results demonstrate that the explanation for the inhibitory effect of expired drugs is due to adsorption on Sabic iron / solution interface. The nature of interaction of expired drug with the Sabic iron surface during corrosion inhibition can be explained in terms of its adsorption properties. The presence of many active center such the presence of nitrogen , oxygen, sulfur atoms , the occurrence of electro donating groups such as OH and NH$_2$ groups  All of these increase the electro density of these drugs and thus facilitates the adsorption process and hence the values of %IE increases. The high molar of mass of OMP (343.265 g.mol$^{-1}$) than the molar mass of ACV (222.12 g.mol$^{-1}$) resulted in a large coverage filled by the inhibitor. Therefore, % IE of OMP drug is more effective than ACV.

4. CONCLUSIONS

1. Acyclovir (ACV) and Omeprazole (OMP) are two expired drugs that act as effective inhibitors for Sabic iron corrosion in 1.0 M HCl solution.
2. With higher ACV and OMP expired drug concentration and lower temperatures lead to higher % IE values.

3. GAP has proven that expired ACV and OMP drugs act as mixed inhibitors.

4. The adsorption of expired ACV and OMP drugs on Sabic iron surface obeyed Langmuir isotherm.

5. The horizontal adsorption of these drugs causes their inhibition on the Sabic iron surface

6. The charge transfer process controls dissolution reaction.

7. Expired ACV and OMP drugs act as inhibitors for pitting corrosion of Sabic iron.

8. %IE values obtained from all measurements used are good and consistent.

ACKNOWLEDGEMENT
This work was funded by Research and Development Grants Program for National Research Institutions and Centers (GRANTS), Graduate Research Program, King Abdulaziz (Grant no 1-18-01-007-0020).

References


© 2020 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).