Inhibition of Carbon Steel Corrosion in Perchloric Acid Solution by Povidone Iodine

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In this study, the influence of Povidone iodine (PVP-I) on the corrosion behavior of carbon steel in perchloric acid solution has been investigated using weight loss method and scanning electron microscopy (SEM). The effects of temperature, immersion time, and concentration of inhibitor on the corrosion of carbon steel were also studied. The effect of temperature on corrosion behavior in the presence of inhibitor was studied in the temperature range of 20-60 °C. The inhibition efficiency increases with increased inhibitor concentration and reaches its maximum of 97.09%. Scanning electron microscopy (SEM) was used to investigate the morphology of the carbon before and after immersion in 1.0 M HClO\textsubscript{4} solution containing 130 mg l\textsuperscript{-1} of Povidone iodine. Surface analysis revealed improvement of corrosion resistance in the presence of PVP-I. The kinetic and thermodynamic parameters (E\textsubscript{a}, K, ΔG\textsubscript{ads}, ΔH\textsubscript{ads} and ΔS\textsubscript{ads}) were evaluated. Adsorption of PVP-I on the carbon steel surface follows the Langmuir isotherm model.

Keywords: Carbon steel, Povidone iodine, Weight loss, Adsorption isotherm, Thermodynamic parameters

INTRODUCTION

Corrosion is one of the major problematic damages to metal and alloy structures provoking economic results in terms of environmental pollution, safety, product losses, repair and replacement [1]. In industry, the carbon steel materials are extensively used because of their relatively low costs, and those of stainless metals, constructability and availability [2] and owing to the fact that of the increased industrial applications of aqueous solution, the study of carbon steel corrosion phenomena has become major in acidic media [3,4,5]. The best techniques of protecting metals require the inhibitors slowing down the rate of corrosion [6]. The inhibition process is a surface reaction; the corrosion is stopped or controlled when the inhibitor is added in a small quantity to the metal. Adsorption isotherms allow information about the interaction of the adsorbed molecules with the electrode surface [7]. On the other hand, the adsorption of inhibitors on the metal/solution interface depends on the chemical nature of the inhibitors, metal and its surface, and the aggressive middle [8]. There are two main types of interaction in adsorption of the inhibitors: physical adsorption and/or chemical adsorption [9]. The inhibition efficiency takes down the different parameters, aggressive electrolyte, pH, temperature, immersion time, metal nature and the chemistry of inhibitor [10]. The Povidone iodine belongs to the group of active pharmaceutical ingredients used in finished pharmaceutical products. PVP-I is used in both antiseptics and disinfectants [11]. Preparations containing povidone iodine are used in acute surgical care for the prevention and control of infections in various indications [12].

The aim of the present study is to investigate the inhibition of carbon steel corrosion by Povidone iodine (PVP-I) in aerated, unstirred 1 M HClO\textsubscript{4} solutions. The thermodynamic parameters were evaluated and a mechanism is proposed to explain the inhibitory action of this corrosion inhibitor. Surface analyses were performed on
the corroded surfaces using scanning electronic microscopy (SEM).

EXPERIMENTAL

Material Preparation

Corrosion tests were performed on a carbon steel of the following percentage composition (wt.%): C 0.37%, Mn 0.68%, Cr 0.077%, Ni 0.059%, Si 0.023%, S 0.016%, Ti 0.011%, Co 0.009%, Cu 0.16%, and iron is the remainder. The test pieces were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed, 400 to 1200 grade). Each specimen was weighed using an analytical balance of 0.0001 g accuracy.

Weight Loss Method

Weight loss measurements were performed on the carbon steel samples with a rectangular form in Perchloric acid solution with and without addition of different concentrations of Povidone iodine. Every sample was weighed by an electronic balance and then placed in the acid solution (50 ml). The duration of the immersion was 2 h at the temperature range from 293-323 K. After immersion, the surface of the specimen was cleaned by double distilled water followed by rinsing with acetone, and the sample was weighed again in order to calculate inhibition efficiency \( IE(\%) \) and the corrosion rate \( (C_R) \). The experiments were done in triplicate, and the average value of the weight loss was noted. For each experiment, a freshly prepared solution was used, and the solution temperature was thermostatically controlled at a desired value. The aggressive solutions (1 M HClO₄) were prepared by dilution of an analytical grade HClO₄ with double distilled water. The corrosion rate \( (C_R) \) was calculated from the formula [13]:

\[
C_R = \frac{W_p - W_a}{S \cdot t}
\]  

(1)

where \( S \) is the total area of the specimen (cm²), \( t \) is the exposure time (h), \( W_p \) and \( W_a \) are the weight losses (mg cm⁻²) in the presence and absence of inhibitor, respectively.

The degree of surface coverage (\( \theta \)) and the inhibition efficiency were calculated using the following equations [13]:

\[
\theta = \frac{C_{R(blank)} - C_{R(inh)}}{C_{R(blank)}}
\]  

(2)

\[
IE(\%) = 100 \times \theta
\]  

(3)

where \( C_{R(blank)} \) and \( C_{R(inh)} \) are the corrosion rates of carbon steel samples in the absence and presence of Povidone-iodine compound, respectively.

RESULTS AND DISCUSSION

Effect of Concentration

Gravimetric measurements of carbon steel subjected to the effects of 1 M HClO₄ acid solution in the absence and in the presence of various concentrations of PVP-I were taken at 303 K for 2 h immersion period. The effect of the inhibitor concentration (mg l⁻¹) on the inhibition efficiency (%) and corrosion rates (mg cm⁻² h⁻¹) was examined; detailed experimental results were graphically represented in Fig. 1. A general trend is observed in the presence of the investigated inhibitor, a decrease in the weight loss of carbon steel in the presence of Povidone iodine even at low concentration (50 mg l⁻¹) compared to the blank. By increasing the concentration of the inhibitor, a further decrease in weight loss of carbon steel was observed. The maximum inhibition efficiency (96.5%) was observed at a concentration of 250 mg l⁻¹ of polyaminophenol, and it was 90% for 1 g l⁻¹ of polypropylene glycol [14,15]. In this study, the inhibitor showed maximum inhibition efficiency of 97.09% at the optimum concentration of 130 mg l⁻¹.

Effect of Immersion Time

The weight loss measurements were performed in 1 M HClO₄ in the absence and presence of inhibitor at 130 mg l⁻¹ for 30 min to 24 h immersion time at temperature 303 K. The weight loss of inhibitor is plotted against immersion time as seen in Fig. 2. The inhibition efficiency of inhibitor was more than 45.13% at half an hour and increased with the increase of immersion time to 97.09% in 2 h and
Fig. 1. Variation of inhibition efficiency and corrosion rate vs. inhibitor concentration for carbon steel after 2 h of exposure.

Fig. 2. Variation of inhibition efficiency and corrosion rate vs. immersion time for carbon steel at 130 mg l⁻¹.
stabilized between 70.50% to 78.20% in an immersion time period of 4 to 24 h, the decreased of the inhibition efficiency after 2 h may be linked to desorption or dissolution of adsorbed inhibitor molecules [16]. The increase in inhibition efficiency and decreasing of corrosion rate with the increment of immersion time implied that the composite inhibitor has a long-term effect as a potent inhibitor. This might be due to the good quality of the compact and intact protective layer formed on the steel surface in the initial time and the formation of the protective film needed a period of time. This indicates that as long as the steel is kept in touch with the inhibitor the film-formation process continues.

Effect of Temperature
The effect of temperature on the corrosion of carbon steel in 1 M HClO$_4$ solution in the absence and presence of 50 to 150 mg L$^{-1}$ of the aqueous PVP-I was studied using weight loss measurements in the range of 293-333 K for 2 h of immersions.

The values of inhibition efficiency obtained from weight loss method are shown in Fig. 3. The decreased inhibition efficiency on elevating the solution temperature might be due many changes occurring on the metal surface such as rapid etching, desorption of inhibitor. The inhibitor itself may undergoes decomposition [17].

Thermodynamic and Kinetic Parameters
The Arrhenius equation can be used successfully to explain the effect of temperature on the inhibition performance of the studied compounds. It is represented by the following equation [18]:

$$C_a = A + \exp \left( - \frac{E_a}{RT} \right)$$  \hspace{1cm} (4)

where $C_a$ is the corrosion rate of carbon steel, $A$ is Arrhenius pre-exponential factor, $E_a$ is the activation energy, $R$ is the gas constant, and $T$ is the temperature.

The values of $E_a$ (Table 1) for carbon steel in 1 M HClO$_4$ without and with various concentrations of inhibitors were obtained from the slope of the plot of log$C_R$ vs. 1/T (Fig. 4).

An alternative Arrhenius plots of log$C_a$/T vs. 1/T (Fig. 5) for carbon steel dissolution in 1 M HClO$_4$ medium in the absence and presence of different concentrations of inhibitor were used to calculate the values of activation thermodynamic parameters such as the enthalpy of activation ($\Delta H_a$) and entropy of activation ($\Delta S_a$) using the following equation [19]:

$$C_a = \left( \frac{RT}{Nh} \right) \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( - \frac{\Delta H_a}{RT} \right)$$  \hspace{1cm} (5)

where $R$ is the universal gas constant, $T$ is the absolute temperature, $N$ is the Avogadro’s number, $h$ is the Planck’s constant.

The values of $\Delta H_a$ and $\Delta S_a$ were obtained from the slope and intercept of the above plot, and are presented in Table 1. The change in activation free energy ($\Delta G_a$) of the corrosion process can be calculated at each temperature by applying the thermodynamic equation [20,21]:

$$\Delta G_a = \Delta H_a - T\Delta S_a$$  \hspace{1cm} (6)

The positive value of activation free energy (Table 1), meaning non-spontaneous corrosion reaction, increases with increasing the concentration of inhibitor. In corrosion context, the activation Gibbs free energy is the excess energy needed to transform metal atoms at the metal surface into solvated metal ions [22].

It was found that $E_a$ values for inhibited systems are higher than those for the uninhibited systems. The increase in activation energy in the presence of optimum concentration results in the decrease of corrosion rate of carbon steel hence high corrosion inhibition efficiency. Moreover, values are increased with the increase in concentration indicating that inhibition process is mainly controlled by activation energy [23]. With increasing temperature there is an appreciable decrease in the adsorption of the inhibitors on the metal surface and a corresponding rise in the corrosion rate. The negative values of $\Delta S_a$ imply that the disorderness is increased on going from reactant to product. The positive values of $\Delta H_a$ reflect the endothermic nature of the carbon steel dissolution process. Further, the $\Delta H_a$ values obtained from the alternative Arrhenius and those values obtained from equation $\Delta H_a = E_a - RT$ are in good agreement with each other.
Fig. 3. Variation of inhibition efficiency with temperature in 1 M HClO₄ solution, at various PVP-I concentrations.

Fig. 4. Alternative Arrhenius plots for carbon steel dissolution in 1 M HClO₄ medium in the absence and presence of Povidone iodine.
The efficiency of a corrosion inhibitor mainly depends on its adsorption ability on the metal surface. So, it is necessary to know the mechanism of adsorption and the adsorption isotherm that can give valuable information on the interaction of inhibitor and metal surface. The Langmuir
adsorption isotherm model was taken into account since equilibrium adsorption of inhibitor concentration was found to obey this adsorption isotherm model on carbon steel in 1 M HClO₄ medium. In this study, the degree of surface coverage values (θ) for various concentrations (50, 80, 110, 130 and 150 mg l⁻¹) of the inhibitor in acidic media was evaluated from weight loss values.

The plots of $C_{inh}/\theta$ against $C_{inh}$ (Fig. 6) yield a straight line with approximately unit slope, indicating that the inhibitor under study follows the Langmuir adsorption

Table 2. Thermodynamic Parameters for Adsorption of Inhibitor on Carbon Steel in 1 M HClO₄ at Different Temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$R^2$</th>
<th>$10^3 \times K_{ads}$ (M⁻¹)</th>
<th>$\Delta H_{ads}$ (KJ mol⁻¹)</th>
<th>$\Delta S_{ads}$ (J mol⁻¹ K⁻¹)</th>
<th>$\Delta G_{ads}$ (KJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1</td>
<td>5.13</td>
<td>90.24</td>
<td>-41.81</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>1</td>
<td>3.11</td>
<td>-15.37 (Eq. (6))</td>
<td>87.82</td>
<td>-41.98</td>
</tr>
<tr>
<td>313</td>
<td>1</td>
<td>2.73</td>
<td></td>
<td>88.34</td>
<td>-43.02</td>
</tr>
<tr>
<td>323</td>
<td>1</td>
<td>2.86</td>
<td>-15.62 (Eq. (9))</td>
<td>90.27</td>
<td>-44.53</td>
</tr>
<tr>
<td>333</td>
<td>1</td>
<td>2.05</td>
<td></td>
<td>88.95</td>
<td>-44.99</td>
</tr>
</tbody>
</table>
isotherm. According to this isotherm, $\theta$ is related to $C_{\text{inh}}$ by [24]:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}}$$  \hspace{1cm} (7)

The $K_{\text{ads}}$ values can be calculated from the intercept lines on the $C_{\text{inh}}/\theta$ -axis. This is related to the standard free energy of adsorption ($\Delta G_{\text{ads}}$) with the following equation [25]:

$$\Delta G_{\text{ads}} = -RT \ln(55.5 \ K_{\text{ads}})$$ \hspace{1cm} (8)

55.5 is a constant for molar concentration of water in the solution, $R$ is the universal gas constant, $T$ is the absolute temperature and $K_{\text{ads}}$ is the equilibrium constant of adsorption.

To obtain the adsorption heat ($\Delta H_{\text{ads}}$), the regression between $\ln(K_{\text{ads}})$ and $1/T$ was dealt with and straight line obtained with slope equal to $(-\Delta H_{\text{ads}}/R)$. The adsorption heat could be calculated according to the Van‘t Hoff equation [26].

$$\ln K_{\text{ads}} = \left(\frac{-\Delta H_{\text{ads}}}{RT}\right) + \text{Const}$$ \hspace{1cm} (9)

It can be seen that the value of enthalpy of adsorption in basic thermodynamic equation (Eq. (6)) agrees with the one obtained using van’t Hoff equation (Eq. (9)).

The obtained results (Table 2) indicate that the adsorption of compound under consideration on carbon steel/adhic solution interface follows the Langmuir adsorption isotherm, this model is the most favorable to clarify interaction between the inhibitor and metal surface [27].

The regression factor is equal to 1 which confirms the application of the Langmuir model. High value of $K_{\text{ads}}$ at lower temperature reflects the high adsorption ability of the PVP-I on carbon steel surface.

In the present case, the negative values of the enthalpy of adsorption ($\Delta H_{\text{ads}} = -15.62$ KJ mol$^{-1}$) indicate that the adsorption of the tested compounds is an exothermic process. The value of $\Delta S_{\text{ads}}$ is positive in the adsorption process indicating that the presence of inhibitor increases the solvent entropy [28]. The negative value $\Delta G_{\text{ads}}$ shows that the adsorption of PVP-I is a spontaneous process under the experimental conditions described and also the strong interaction between inhibitor molecules and the metal surface [29]. Generally, the values of adsorptive free enthalpy up to -20 KJ mol$^{-1}$ are consistent with the electrostatic interaction between the charged molecules and the charged metal (physiosorption), while those negative values higher than -40 KJ mol$^{-1}$ involve sharing or transfer of electrons from the inhibitors to the metal surface to form a coordinate type of bond (chemisorption) [30,31].

The magnitude of $\Delta G_{\text{ads}}$ values obtained from weight loss measurements was in the range of -41.81 to -44.99 KJ mol$^{-1}$ which also shows chemisorptions of the inhibitor.

**Scanning Electron Microscopy**

SEM images were obtained for abraded carbon steel specimens not exposed and exposed to free 1 M HClO$_4$ solution, and that containing inhibitor for 24 h. Figure 7 shows the micrographs of carbon steel coupons in (a) unexposed polished state, (b) exposed to the corroder, (c) immersed in acid solution containing 130 mg l$^{-1}$ PVP-I for 24 h. It was found that the corroded carbon steel surface (Fig. 7b) contains a large number of pits compared to the smooth surface of the coupon in unexposed state (Fig. 7a). However, SEM images of carbon steel surface in the presence of inhibitors (Fig. 7c) were observed to be smoother than that of carbon steel surface in 1 M HClO$_4$ alone. These observations reveal that the PVP-I forms protective layer on the carbon steel surface, which prevents the attack of acid as well as the dissolution of carbon steel by forming surface adsorbed layer and thereby reducing the corrosion rate.

**CONCLUSIONS**

In the present study, the corrosion inhibition efficiency of the Povidone iodine on the surface of steel has been evaluated. PVP-I was found to inhibit the corrosion of carbon steel in 1 M HClO$_4$ solution and the extent of inhibition was concentration dependent. The inhibition efficiencies increased with inhibitor concentration but were reduced proportionally with temperature. The adsorption of inhibitor on the carbon steel surface in 1 M HClO$_4$ solution obeyed the Langmuir’s adsorption isotherm and kinetic
Fig. 7. SEM images of carbon steel samples. (a) after polishing, (b) after immersion in 1 M HClO₄, (c) after immersion in 1 M HClO₄ + 130 mg l⁻¹ PVP-I.
model. The high negative value of $\Delta G_{\text{ads}}$ indicates the spontaneous adsorption and suggests that the inhibitive effect of PVP-I is due to the formation of a chemisorbed film on the metallic surface.

REFERENCES


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