Inhibiting Effect of Dioctyl Phthalate on the Corrosion of Mild Steel in 1.0 M Hydrochloric Acid Solution

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Abstract

Steel corrosion is a major and costly problem to industrialists and construction workers. The inhibiting effect of dioctyl phthalate on the corrosion of mild steel was carried out in 1.0 M solution of HCl as the corrosion medium using the weight loss method. The adsorption of the dioctyl phthalate on the surface of the mild steel in 1.0 M HCl was found to follow the physisorption mechanism and also follow the first order rate law. The corrosion rate was found to be directly proportional to the temperature of the medium, and inversely proportional to the concentration of the inhibitor in solution. The activation energy increases with increase in the concentration of the inhibitor. Values of standard free energy change, \( \Delta G_{ads}^0 \) are consistently below \(-20 \) kJmol\(^{-1}\). This solidly established that the adsorption mechanism of the dioctyl phthalate on mild steel surface is physisorption. Langmuir and Freundlich adsorption isotherms were used, with Freundlich isotherm as best fit for the modelling of the adsorption process. The value \( n_F \) in Freundlich isotherm which, indicates the intensity of adsorption, was found to be in the average of 0.717 not far from the typical value of 0.6 \( n_F \).

1. Introduction

Corrosion is degradation of materials’ properties due to interactions with their
environments, and corrosion of most metals (and many materials for that matter) is inevitable. While primarily associated with metallic materials, all material types are susceptible to degradation [1]. Degradation of polymeric insulating coatings on wiring has been a concern in aging aircraft. Even ceramics can undergo degradation by selective dissolution. Like death and taxes, corrosion is something we hope to avoid; but ultimately it is something we must learn to deal with [2]. The fundamental cause or driving force for all corrosion is the lowering of a system’s Gibbs energy [3].

There are basically five methods of corrosion control, these are: material selection, coating, inhibitors, design and cathodic protection. For the sake of this research, the method of corrosion control employed is the use of inhibitors. Corrosion inhibitors are substances, which when added to a solution, reduces the rate at which a material mostly metals deteriorate [4]. Corrosion inhibition is often attained by the formation of a coating of the inhibiting material on the surface of the metal. For example, Benzotriazole inhibits corrosion of copper by forming an inert layer of this polymer on the metal’s surface [5].

The study of the mechanism of corrosion and corrosion inhibition of Tin in aqueous solutions containing tartaric acid was conducted by Rabab and Waheed [6]. They discovered that with only the solution of tartaric acid, the dissolution of the tin was enhanced, but an introduction of about 0.02 mol·dm\(^{-3}\) of a naturally occurring glycine inhibits the rate of corrosion by 30%.

Onen, et al. [7] studied the inhibition properties of titanium oxide for aluminium and mild steel using the method of absorbance difference. They found that there is an increase in percentage inhibition as the concentration of the titanium (IV) oxide also increases. They attributed the inhibition efficiency of the titanium (IV) oxide to the presence of lone pair of electrons on the oxygen which is delocalized and provides resonance stability to the compound [7].

Organic inhibitors are the most widely used nowadays, owing to the fact that they are environmentally friendly. The organic type inhibitors studied are the azoles and their derivatives, imidazoles, amines and their derivatives, amino acids—which, are considered the most non toxic organic compounds, highly soluble in aqueous media and produced with high purity and at low cost; triphenylmethane derivatives, thiol group compounds, organic derivatives of phosphates such as inositol hex phosphates, potassium ethyl xanthate, etc. [8].

Dioctyl phthalate (DOP) with IUPAC nomenclature dioctyl benzene-1,2-dicarboxylate, is a clear, colourless, and viscous liquid with a slight, characteristic odor, soluble in ethanol, ether, mineral oil, and the majority of organic solvents, immiscible with water, resistant to hydrolysis and air oxygen activity. The major applications of DOP are found in plastic industry for plasticizing plastic, wood coatings, manufacture of medical and sanitary equipments such as blood bags and dialysis equipments and it is also applicable in the manufacture of capacitors as dielectric fluid, hydraulic liquid and solvent in light stick. It has a molecular weight of 390.6 gmol\(^{-1}\), with a specific gravity of 0.98 at 25°C [9].
This particular compound was selected for this research because, since most of the experiments involving corrosion studies was done using plant extracts. Attributing the inhibiting effect to one compound in the extract is difficult, hence posing difficulty in studying the mechanism of the adsorption. With a pure compound, which is readily available, studying the inhibiting properties will open doors for its application in industries.

2. Method

The method employed for the study of the inhibiting properties of Dioctyl phthalate in HCl is the weight loss method [10]. Coupons of mild steel of size 5 cm by 4 cm were used, and concentration of the inhibitor ranges from 0.01 mol·dm⁻³ to 0.07 mol·dm⁻³, in 1.0 M HCl [10]. The immersion time was 1 - 3 hrs and temperature ranges of 303 K to 313 K.

Determination of Parameters

The percentage inhibition efficiency %IE, the surface coverage θ, and the corrosion rate \( C_r \) were determined from Equations (1)-(3) respectively.

\[
%IE = \left[ 1 - \left( \frac{W_0 - W_t}{W} \right) \right] \times 100
\]

(1)

\[
\theta = 1 - \left( \frac{W_0 - W_i}{W} \right)
\]

(2)

where \( W_0 \) = initial weight of the mild steel before suspending in the solutions, \( W \) = weight of the mild steel without the inhibitor, that is, weight in blank solution, and; \( W_t \) = weight of the mild steel after inhibition the inhibitor

\[
C_r \ (\text{mg} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1}) = \frac{W_0 - W_i}{A T}
\]

(3)

where \( A \) = surface area of the coupon (cm²), \( T \) = time of exposure in hrs, \( W_0 - W_i \) = weight loss.

The inhibitor efficiency gives important information about the performance of the inhibitor in various medium [11].

The activation energy of adsorption \( E_{ads} \), Enthalpy and entropy of adsorption \( H_{ads} \) and \( S_{ads} \), and free energy change of adsorption \( \Delta G_{ads} \) were determined from the following Equations (4)-(6) respectively.

\[
\ln C_r = \ln A - \left( \frac{E_{ads}}{RT} \right)
\]

(4)

where \( C_r \) = rate of corrosion, \( A \) = a frequency factor, \( R \) = Gas constant (Atm. L. mol⁻¹·K⁻¹), \( T \) = temperature (K).

A plot of \( \ln C_r \) against \( 1/T \), gives a straight line, with slope equals to \( E_{ads}/R \) and an intercept of \( \ln A \). [12]. The values of \( E_a \) greater than 20 kJ indicate that the adsorption process is controlled by the surface reactions [13]

\[
\frac{\ln C_r}{T} = \ln R + \left( \frac{\Delta S_{ads}}{R} \right) - \left( \frac{\Delta H_{ads}}{RT} \right)
\]

(5)

where \( R \) = gas constant, \( N \) = Avogadro’s number 6.03 × 10²³ mol⁻¹, \( h \) = the
Planck’s constant $6.62 \times 10^{-34}$ Js

A plot of $\ln C/ T$ against $1/ T$ is a straight line with a slope equal to $\frac{\Delta H_{ads}}{RT}$ and the intercept of the graph is equal to $\ln \frac{R}{N\hbar} + \left(\frac{\Delta S_{ads}}{R}\right)$. The values of $\Delta H_{ads}$ indicates whether the adsorption process absorbed heat ($+\Delta H$) or releases heat ($-\Delta H$) [14]

$$\Delta G_{ads} = -RT (\ln 55.5 K_{ads})$$ (6)

where $K_{ads}$ is the equilibrium constant for the adsorption of the inhibitor on mild steel surface [15].

Other parameters determined are the rate constant for the adsorption process $k$, and the half life of the metal in the presence of the inhibitor according to Equation (7) and Equation (8).

$$\ln w_f = \ln w_i - kt$$ (7)

where $w_i$ and $w_f$ are respectively the weights of the mild steel in blank acid solution and after immersion in the inhibitor solution. This value tells how fast the adsorption process is taking place. A plot of $\ln (w_f/w_i)$ against $t$, gives a straight line with a slope which is equal to $k$.

$$\frac{1}{2} \ln 2 \frac{k}{t_{1/2}} =$$ (8)

where $t_{1/2}$ = half-life of the mild steel.

Freundlich and Langmuir adsorption isotherms (Equation (9), and Equation (10)) were used to model the adsorption process.

Freundlich $\log \theta = \log k + n \log C$ (9)

Langmuir $\left(\frac{C}{\theta}\right) = \frac{1}{k} + C$ (10)

where $k$ is the equilibrium constant, $C$ is the concentration of the inhibitor, $n$ is a constant which tells the intensity of the adsorption process, and have a typical value of 0.6 [16].

3. Results and Discussion

The variation of the rate of corrosion of mild steel at different concentration of inhibitor solution in 1.0 M HCl solution as the corrodat and at different temperatures is shown in Figures 1-3. The Figures show the effect of exposure time, and the concentration of the inhibitor on the corrosion rate of the mild steel. From the Figures, it is clear that corrosion rate decreases with increase in concentration of the inhibitor and decrease with time of exposure to the inhibitor solution [17].

The effect of temperature is shown in Figure 4. Corrosion rate increases with increasing temperature from 303 K to 313 K, and the corrosion rate decreases with increase in the concentration of the inhibitor. This is because as the concentration is increasing, more molecules of the inhibitor become available to
Figure 1. Variation of Corrosion rate with conc. of inhibitor in 1.0 M HCl solution at 303 K.

Figure 2. Variation of Corrosion rate with conc. of inhibitor in 1.0 M HCl solution at 308 K.

Figure 3. Variation of Corrosion rate with conc. of inhibitor in 1.0 M HCl solution at 313 K.

Figure 4. Effect of temperature on corrosion rate in 1.0 M HCl solution after 1 Hr.
cover the surface of the mild steel, preventing it from coming in contact with the corrodant.

1) Thermodynamic Considerations

The activation energy $E_{\text{ads}}$ of the adsorption process is represented in Table 1. Generally, higher values of $E_{\text{ads}}$ in presence of additives support physical adsorption mechanism whereas an unchanged or lower value of $E_{\text{ads}}$ for inhibited systems compared to the blank is indicative of chemisorption mechanism. From Table 1, it can be seen that the values of the activation energies for the inhibited systems increases from 82.96 kJ for the uninhibited system to a maximum of 162.54 kJ for the inhibited system. This is an indication of a physisorption (a process in which the electronic structure of the adsorbed molecule is barely disturbed on adsorption) mechanism of adsorption [18].

The dissolution process of the mild steel is considered difficult if the values of the enthalpy of adsorption $\Delta H_{\text{ads}}$ for the corrosion process in the blank and inhibited solution is found to be positive, indicating an endothermic process [19]. From Table 1, it can be seen that all the values of the $\Delta H_{\text{ads}}$ are positive, hence the dissolution of mild steel in the solution of the inhibitor is difficult. The entropy of the inhibition process $\Delta S_{\text{ads}}$, as shown in Table 1, a higher value of the entropy obtained in the presence of the inhibitor, showed that the recombination step is a more orderly arrangement compared to the initial state without the inhibitor [14]. It can be seen from Table 1 that the values of $Q_{\text{ads}}$ are negative throughout and decreases as the concentration of the inhibitor decreases. This indicates that the adsorption of the inhibitor to the surface of the mild steel is spontaneous, and this is indicative of a strong interaction between the inhibitor and the mild steel [20].

It was also discovered that the values of $E_{\text{ads}}$ increases with increase in the concentration of the inhibitor. The values of $E_{\text{ads}}$ and those of $\Delta H_{\text{ads}}$ varies in a similar manner, and the average values of $E_{\text{ads}} - \Delta H_{\text{ads}}$ equal to 2.41 kJmol$^{-1}$, which is very close to the value of RT (2.51 kJmol$^{-1}$) indicating that the adsorption process is unimolecular in nature [21].

2) Adsorption Studies

The isotherms selected for the adsorption study are Langmuir and Freundlich. The isotherm parameters were calculated from Equation (9) and Equation (10) for Freundlich and Langmuir isotherm respectively. The values obtained are represented in Table 2.

The adsorption equilibrium constant $K_{\text{ads}}$ decreases with increase in experimental temperature in the corrosion media (Table 2), indicating that the interactions between the adsorbed molecules and the metal surface are weakened and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature [22]. The positive adsorption equilibrium constant $K_{\text{r}}$ values are indication of favourable adsorption [23]. The parameter $n_f$ in the Freundlich isotherm relates to intensity of adsorption and it varies with heterogeneity of the material [24],
Table 1. Thermodynamic parameters of the dioctyl phthalate inhibitor in 1.0 M HCl solution at different concentrations of the inhibitor.

<table>
<thead>
<tr>
<th>Concentration of inhibitor (moldm$^{-3}$) in 1.0 M HCl</th>
<th>Activation energy of Adsorption ($E_{ads}$ (kJ))</th>
<th>$R^2$</th>
<th>Heat of Adsorption ($Q_{ads}$ (kJ))</th>
<th>$R^2$</th>
<th>Enthalpy of adsorption and Entropy of Adsorption ($\Delta H_{ads}$ (kJ) $\Delta S_{ads}$ (JK$^{-1}$))</th>
<th>$R^2$</th>
<th>Gibbs Free Energy of Adsorption ($\Delta G_{ads}$ (kJ))</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>82.96</td>
<td>0.962</td>
<td>80.40</td>
<td>−0.57</td>
<td>0.959</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>91.66</td>
<td>0.962</td>
<td>−50.76</td>
<td>0.985</td>
<td>89.10</td>
<td>−0.19</td>
<td>0.960</td>
<td>−51</td>
</tr>
<tr>
<td>0.03</td>
<td>98.28</td>
<td>0.956</td>
<td>−42.23</td>
<td>0.935</td>
<td>95.72</td>
<td>0.94</td>
<td>0.953</td>
<td>−42.23</td>
</tr>
<tr>
<td>0.05</td>
<td>126.82</td>
<td>0.965</td>
<td>−88.74</td>
<td>0.991</td>
<td>124.3</td>
<td>1.4</td>
<td>0.964</td>
<td>−88.74</td>
</tr>
<tr>
<td>0.07</td>
<td>162.52</td>
<td>0.917</td>
<td>−108.12</td>
<td>0.875</td>
<td>160.00</td>
<td>3.01</td>
<td>0.914</td>
<td>−108.12</td>
</tr>
</tbody>
</table>

Table 2. Values for adsorption studies of the inhibitor on mild steel in 1.0 M HCl solutions at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>303</td>
<td>22</td>
<td>0.848</td>
</tr>
<tr>
<td>308</td>
<td>16.4</td>
<td>0.877</td>
</tr>
<tr>
<td>313</td>
<td>13.2</td>
<td>0.619</td>
</tr>
</tbody>
</table>

Key: $K_L$=equilibrium constant for Langmuir isotherm, $K_F$ = equilibrium constant for Freundlich isotherm, $n_F$ = adsorption intensity.

and the value is always positive, but not an integer, with typical value of 0.6 [25]. The average value of $n_F$ is 0.717 for the inhibitor in 1.0 M HCl, a value not far from 0.6, an indication that this adsorption process can reasonably be modelled by Freundlich isotherm and is heterogeneous [23].

3) Standard Free Energy of Adsorption $\Delta G_{ads}^o$

The standard free energy of adsorption, $\Delta G_{ads}^o$, which can characterize the interaction of adsorbed molecules and metal surface, was calculated using Equation 11. The values of $K_{ads}$ were determined from the different isotherm plots, and are represented in Table 3. The negative values of $\Delta G_{ads}^o$ ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface. Generally, the values of $\Delta G_{ads}^o$ below −40 kJ/mol are consistent with physisorption, while those above −40 kJ/mol involve chemisorptions mechanism [26]. From Table 3 all the values of the standard free energy of adsorption are negative. This indicates that the adsorption process is spontaneous. The values also, were found to be below −40 kJ/mol; which concur with the physisorption mechanism earlier proposed for the adsorption process in 1.0 M HCl/inhibitor solutions [27].

4) Kinetic Studies

The corrosion of mild steel follows a first order rate law with respect to the concentration of the inhibitor [28]. A decrease in the rate constant $k$, with
Table 3. Values for the standard free energy of adsorption $\Delta G_{\text{ads}}$ of the solution of the inhibitor in 1.0 M HCl at different temperatures.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Temperature (K)</th>
<th>$K_{\text{ads}}$</th>
<th>$R^2$</th>
<th>$G_{\text{ads}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303</td>
<td>22</td>
<td>0.965</td>
<td>$-17.90$</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>16.4</td>
<td>0.961</td>
<td>$-17.45$</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>13.2</td>
<td>0.857</td>
<td>$-17.17$</td>
</tr>
<tr>
<td>Freunlich</td>
<td>303</td>
<td>1.41</td>
<td>0.782</td>
<td>$-10.98$</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>10.4</td>
<td>0.907</td>
<td>$-16.28$</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.75</td>
<td>0.996</td>
<td>$-13.89$</td>
</tr>
</tbody>
</table>

Table 4. Rate constant $k$, and half-life $t_{1/2}$ of mild steel in the inhibitor/1.0 M HCl solution at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Rate Constant $k$ (hr$^{-1}$)</th>
<th>$R^2$</th>
<th>$t_{1/2}$ (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.083</td>
<td>0.892</td>
<td>8.351</td>
</tr>
<tr>
<td>308</td>
<td>0.056</td>
<td>0.98</td>
<td>12.378</td>
</tr>
<tr>
<td>313</td>
<td>0.034</td>
<td>0.187</td>
<td>20.387</td>
</tr>
</tbody>
</table>

Increase in temperature indicates that the rate of the mild steel corrosion is greatly reduced in the presence of the inhibitor (dioctyl phthalate) in 1.0 M HCl medium. The half-life calculated from Equation (8), and presented in Table 4, indicated that the life span of the mild steel is increased as the temperature increased.

4. Conclusion

The inhibiting effect of dioctyl phthalate on the corrosion of mild steel was carried out in 1.0 M HCl solution and at a temperature range of 303 to 313 K using the weight loss method. The results obtained, showed that dioctyl phthalate is a good corrosion inhibitor of mild steel. The efficiency was found to decrease with increasing temperature and increase with increase in the concentration of the inhibitor in the media. The adsorption of the inhibitor on mild steel was found to be spontaneous. The most suitable isotherm to be used for modelling the corrosion inhibition studies of the dioctyl phthalate is the Freundlich adsorption isotherm. Physisorption mechanism was proposed for the adsorption of dioctyl phthalate in 1.0 M HCl solution on mild steel. It can therefore be recommended that more research should be carried out on the properties of dioctyl phthalate in corrosion inhibition using other methods, other than the weight loss method.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References


