Inhibition of Mild Steel Corrosion in 0.5 M Sulphuric Acid Solution by Aspirin Drug

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Abstract— The inhibition of mild steel corrosion in 0.5 M sulphuric acid solution by Aspirin drug as an eco-friendly and commercially available inhibitor was studied at different temperature by weight loss technique. It was found that the test drug has a promising inhibitory action against corrosion of mild steel in the medium investigated. The inhibition efficiency was found to increase with a corresponding increase in the concentration of the inhibitor. It was also found that the adsorption as well as the inhibition process followed a first-order kinetics and Aspirin adsorbs on the steel surface according Langmuir isotherm. Adsorption enthalpy were determined and discussed. Effect of temperature was also investigated and activation parameters were evaluated.

Keywords— Corrosion, inhibitor, acid solutions, Aspirin , adsorption.

I. INTRODUCTION

The studies of carbon steel corrosion in acidic media receive more and more attention both of academics and industrials because of the wide applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes. The electrochemical corrosion is generally caused by dissymmetry potentials between metal and strong acid. The aggressively of hydrogen ion is inevitable in uninhibited acid. $H^+$ and Dissolved $O_2$ are named natural motors of corrosion [1-2]. Facing this problem, the corrosion inhibitors are required. Works on the inhibition are so many so much so that we can not quote them. But scientists are unanimous on the fact that this protection is provided by the adsorption of inhibitors on the metal surface. Then, compounds can adsorb on metal surface and block the active surface sites to reduce the corrosion rate. Many synthetic compounds offer good anticorrosive action; but most of them risk being highly toxic to both human beings and environment. In these later years, researchers reorient their studies to the use of naturally occurring substances.

Plant extracts and oils have became important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention; therefore, finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance [3][4] may give a vivid account of natural products which are used as corrosion inhibitors for various metal and alloys in aggressive media. They stated that natural plant have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency. The studies in these two later years prove that this kind of inhibitor find more and more attention of researchers [5-10]. However, the constitutenets that provide inhibitive action, the mechanisms and the best condition for inhibition are still unclear. But, data on the composition of both oil and extract may give information on the molecules which can adsorb on the metallic surface and hence secure from corrosion. In the present work, inhibitive action of BP extract as a cheap, eco friendly and naturally occurring substance on corrosion behavior of mild steel 0.5M sulphuric acid has been investigated through weigh loss measurements. The study is completed by the comparative action of aspirin drug on the corrosion of mild steel in 0.5M sulphuric acid.

II. EXPERIMENTAL

A. Material:

A commercially available grade of mild steel (purity = 98% Fe) identified and obtained locally was employed in this study. The sheets of metal were mechanically press cut into coupons of 5 cm x 5 cm x 0.5 cm dimensions. A small hole of about 5 mm diameter near the upper edge of the coupons was made to help hold them with glass hooks and suspend them into the corrosive medium.
The inhibitor used in this study was an salicylate drug with common name: Aspirin, while its systematic name is 2-acetoxybenzoic acid. The molecular formula of the drug is C\textsubscript{9}H\textsubscript{8}O\textsubscript{4} with molecular mass of 180.157 g/mol. Aspirin has the chemical structure shown in Figure 1.

![Aspirin Chemical Structure](image)

Figure I Aspirin (2-Acetoxbenzoic Acid)

The tablets of aspirin were obtained from a local pharmacy and were used without further purification or modification. From the mass of the drug samples and its molecular weight relation, appropriate concentrations of the drug were prepared by dilution. The corrosive medium used was 0.5M sulphuric acid. It was prepared by appropriate dilution of analytical grade of the acid reagent with doubly distilled deionised water without further purification.

B. Weight Loss Measurements.

In the weight loss experiment, four glass containers of 250mL capacity were labeled A to D, each containing 0.5M sulphuric acid solution. The first beaker was reserved as blank while each of the three remaining beakers contained the drug at different concentrations all placed at normal temperature (about 30\textdegree C). The metal coupons were immersed in the experimental solutions with the help of glass hooks and monitored after 12 hours. The weights of the specimens were noted before immersion. After every immersion time of 48 hours, the specimens were removed, polished with emery papers, washed in double distilled water, degreased with acetone, dried in warm air, and reweighed. From the initial and final weights of the specimens, the loss of weight was calculated, and the corrosion rate (cm/hr) was computed from the following equation [13, 14]:

\[
CR = \frac{\Delta W}{At\rho} \text{ (cm/hr)} \quad (1)
\]

Where \(\Delta W\) is the weight lost (grams), \(A\) is the surface area of the coupon (cm\(^2\)), \(\rho\) is the density (g/cm\(^3\)), \(t\) is the period of exposure (hours)

C. Evolved-Hydrogen gas Measurements.

Corrosion inhibition performance of inhibitor can be evaluated using the gasometric technique, is more suitable for short term immersion tests. The volume of evolved hydrogen as a function of concentration of inhibitor is defined as the rate of dissolution of mild steel in 0.5M sulphuric acid.

<table>
<thead>
<tr>
<th>Conc. Of Disprine</th>
<th>Blank</th>
<th>1x10\textsuperscript{-3}</th>
<th>2x10\textsuperscript{-3}</th>
<th>3x10\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta W) (gm)</td>
<td>5.70</td>
<td>4.72</td>
<td>2.24</td>
<td>1.61</td>
</tr>
<tr>
<td>Vol.of Hydrogen (lit)</td>
<td>3.419</td>
<td>2.831</td>
<td>1.344</td>
<td>0.965</td>
</tr>
<tr>
<td>Weight of hydrogen (gm)</td>
<td>0.3053</td>
<td>0.2528</td>
<td>0.1200</td>
<td>0.0862</td>
</tr>
</tbody>
</table>

The inhibition efficiency and surface coverage were calculated from the mass loss data according to the Equations 2 and 3, respectively.
Figure 2 shows the inhibition efficiency and corrosion rate in different concentration of the Aspirin and it could be seen that the % IE increases and corrosion rate decreases with the inhibitor concentration.

\[
\theta = 1 - \frac{CR_{inh}}{CR_{blank}} \tag{2}
\]

\[
%IE = \theta \times 100 \tag{3}
\]

Where \( CR_{inh} \) and \( CR_{blank} \) are the corrosion rates in the absence and presence of inhibitor, respectively. It can be observed that the inhibition efficiency increased and the corrosion rate decreased as the inhibitor concentration increased. The maximum value of inhibition efficiency was 71.80%. It could be considered that aspirin. As inhibitor of mild steel to 0.5M sulphuric acid solution given the high level of the inhibition efficiency.

<table>
<thead>
<tr>
<th>Conc. Of Disprine</th>
<th>Blank</th>
<th>1x10^{-3}</th>
<th>2x10^{-3}</th>
<th>3x10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.R.×10^{-4}</td>
<td>52.5</td>
<td>43.5</td>
<td>20.6</td>
<td>14.8</td>
</tr>
<tr>
<td>IE</td>
<td>------</td>
<td>17.14</td>
<td>60.76</td>
<td>71.80</td>
</tr>
<tr>
<td>( \theta )</td>
<td>------</td>
<td>0.1714</td>
<td>0.6076</td>
<td>0.7180</td>
</tr>
</tbody>
</table>

2.3 Adsorption Isotherm behavior

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm, it gives an insight into the adsorption process. Several adsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir, Temkin, Frumkin, Flory-Huggins.

\[
y = -0.085x + 0.65 \quad R^2 = 0.9146
\]

The value of the correlation \( R^2 \) is 0.914, used to determine the best fit isotherm which was obtained for Langmuir. The Langmuir isotherm, which is presented in Equation 4 is most often used to calculate the equilibrium constant \( k \), which is the relationship between surface coverage and the inhibitor concentration.

\[
\frac{C}{\theta} = \frac{1}{k} + c \tag{4}
\]

Where \( C \) is the inhibitor concentration, \( \theta \) is the surface coverage. Figure 4 shows that a plot of \( c/\theta \) versus \( c \) yields a straight line with \( R^2 = 0.914 \). The plot obeys Langmuir adsorption isotherm as the plot has linearity and good correlation coefficient. The \( R^2 \) values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm. From equation 4 the value of rate constant \( K \) is found to be 2.06x10^{2}. The adsorption Gibb’s free energy was calculated using Equation 5

\[
\Delta G = -RT\ln(55.5k) \tag{5}
\]
Where \( R \) is the gas constant (8.314 kJ/mol); and \( T \) is the absolute temperature (313K). The constant value of 55.5 is the concentration of water in solution in mol/L. The value of \( \Delta G_{\text{ads}} \) for the inhibitor on the surface of mild steel is given -24.30 kJ/mol since \( \Delta G_{\text{ads}} \) is below 40 kJ/mol, it corroborates that the adsorption process is physisorption. The negative value of \( \Delta G_{\text{ads}} \) indicated spontaneous adsorption of the inhibitor on the mild steel surface.

2.4 Thermodynamic measurements

Weight loss measurements for mild steel in 0.5M sulphuric acid without and with \( 10^{-3} \) mol L\(^{-1} \) of Aspirin, in the temperature range 303 to 323K at 2 days of immersion, are shown in Table 3.

### Table III
Corrosion Data Of Steel In 0.5 M H\(_2\)SO\(_4\) Solution Without And With 10\(^{-3}\) M Aspirin At The Temperature Range 303k To 323k For 2 Days.

<table>
<thead>
<tr>
<th>Conc.of Inhi.</th>
<th>Temperature [k]</th>
<th>1000/T</th>
<th>C.R.x10(^{-5})</th>
<th>Log(_{10})C.R.</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>303</td>
<td>3.30</td>
<td>52.5</td>
<td>-3.28</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.19</td>
<td>93.3</td>
<td>-3.03</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>3.09</td>
<td>191.7</td>
<td>-2.72</td>
<td>-----</td>
</tr>
<tr>
<td>3x10(^{-3})M Inhibitor</td>
<td>303</td>
<td>3.30</td>
<td>14.8</td>
<td>-3.83</td>
<td>71.80</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.19</td>
<td>26.8</td>
<td>-3.57</td>
<td>71.27</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>3.09</td>
<td>57.9</td>
<td>-3.24</td>
<td>69.79</td>
</tr>
</tbody>
</table>

The activation energies \( (E_a) \) for the corrosion of mild steel in the absence and presence of different concentrations of aspirin drug, were calculated using Arrhenius-type equation:

\[
CR=Ae^{-Ea/RT}
\] (6)

Where \( E_a \) is the activation corrosion energy; \( R \) is the universal gas constant; \( A \) is the Arrhenius pre exponential factor, \( T \) is the absolute temperature and \( CR \) is corrosion rate.

The collected data in Tables 4 indicate that the addition of Aspirin leads to an increase in the activation \( E_a \) and \( \Delta H \) to values greater than that of the solution without inhibitor. Moreover, the average difference value of the \( E_a - \Delta H \) is 2.61 kJ/mol which is approximately equal to the value of \( RT \) (2.60 kJ/mol) at the average temperature (313 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known equation of perfect gas [23]:

\[
E_a - \Delta H = RT
\] (5)

It is pointed out in the literature that positive sign of the enthalpies reflects the endothermic nature of the steel dissolution process. The presence of inhibitors tested reveals that the corrosion process becomes more and more endothermic when compared to blank.

### Table IV
Activation Energy And Enthalpy Of Corrosion Reaction Of Mild Steel In 0.5 M H\(_2\)SO\(_4\) Solution In Absence And Presence Of Aspirin.

<table>
<thead>
<tr>
<th></th>
<th>( E_a ) (KJ/mol)</th>
<th>( \Delta H ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>50.90</td>
<td>48.29</td>
</tr>
<tr>
<td>Inhibitor [3x10(^{-3})M]</td>
<td>53.58</td>
<td>50.97</td>
</tr>
</tbody>
</table>

### III. Conclusion

The study of effect of aspirin on the corrosion of mild steel in 0.5 M \( \text{H}_2\text{SO}_4 \) conducted by weight loss method may draw the following conclusions:

1. The Aspirin acts as an efficient inhibitor for corrosion of mild steel in 0.5 M \( \text{H}_2\text{SO}_4 \); the inhibition efficiency increases with increase of inhibitor concentration to attain a maximum value of 71.80\% at 3x10\(^{-3}\)M aspirin.
2. Addition of isolated molecule of Aspirin also gives an opportunity to use these pharmaceutical compounds as efficient inhibitor for mild steel. Its inhibition attains maximum at 10^{-3}M.

3. Temperature effect shows that Aspirin exhibits constant efficiency until 323K which is recommended for industrial descaling.

4. Aspirin adsors on the metal surface according to the Langmuir isotherm with more probable physisorption phenomenon.

REFERENCES


