Corrosion Inhibition, Adsorption Behavior and Thermodynamic Properties of Streptomycin on Mild Steel in Hydrochloric Acid Medium

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Corrosion inhibition in the presence of Streptomycin in 1M HCl was studied using the weight loss technique at 303 to 338 K. The results obtained revealed that the inhibition efficiency decreased with increase in temperature. Inhibition occurred through adsorption of the Streptomycin molecules on the metal surface. The apparent activation energies, enthalpies and entropies of the dissolution process and the free energies and enthalpies for the adsorption process were determined and discussed. The fundamental thermodynamic functions were used to evaluate important inhibitive properties of Streptomycin.

Keywords: Activation energy, Gibb’s Free Energy, Van’t Hoff equation, Streptomycin, mild steel, adsorption.

1. INTRODUCTION

Corrosion of mild steel is one of the most common forms of corrosion in acidic medium. The practical importance of such corrosion is in acid pickling of iron, chemical cleaning of scales of boilers, oil and petrochemical industries. Hydrochloric acids and mild steel are most commonly used in the industries. So this leads to researchers studying the effect of corrosion inhibitors on mild steel in hydrochloric acid environment [1-5]. The inhibition of steel in acid solutions by different type of organic compounds has been extensively studied [6]. Among them very few are environmentally acceptable such as natural products i.e. extracts of various parts of plants, pharmaceutically active compounds i.e. antibiotics, antibacterial etc. [7-16].
Streptomycin is a commercially available first line drug for plague and on combination with other drugs; it is widely used for the treatment of tuberculosis. The present work is the continuation of the previous work reported in literature by Shukla et.al. [17]. In the previous work, performance of Streptomycin has been studied and reported by using electrochemical impedance spectroscopy, potentiodynamic polarization studies and weight loss studies at 308 K only. Adsorption isotherm was obtained only at 308 K for various concentrations of the inhibitor.

In this work, we report the kinetic, activation and adsorption parameters. In addition, the adsorption isotherm for the different temperature range (303-338K) was also obtained to show the adsorption model of the inhibitor. Below is the structure of Streptomycin.

\[ \text{Structure of Streptomycin} \]

2. EXPERIMENTAL

In order to study the temperature effects on the performance of the Streptomycin against mild steel in hydrochloric acid solution without and with different concentrations of the inhibitor at 303-338 K using weight loss method. The weight loss method is probably most widely used method of inhibition assessment [18-20]. Mild steel sample was taken as the same size and composition as reported earlier [17]. Prior to the experiment, all the samples were polished with different grades of emery papers, washed with doubly distilled water and degreased with acetone and dried.

Inhibition efficiencies, corrosion rates and surface coverage were calculated by using following formula:

\[ \eta \, (\%) = \frac{W_o - W_i}{W_o} \times 100 \] \quad (1)

\[ C_t = \frac{87.5 \times W}{A \times t \times D} \] \quad (2)

\[ \theta = \frac{W_o - W_i}{W_o} \] \quad (3)
where, $\eta$ is inhibition efficiency, $W_o =$ weight loss without inhibitor, $W_i =$ weight loss with inhibitor, $C_r =$ corrosion rate in mm$^{-1}$, $W =$ weight loss of the mild steel in mg, $A =$ area of the mild steel sample in cm$^2$, $t =$ time of exposure of the metal sample in hours, $D =$ density of mild steel (i.e. 7.86 g cm$^{-3}$), $\theta =$ surface coverage of inhibitor on mild steel surface.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of temperature on the inhibition efficiency and corrosion rate

**Table 1.** Weight loss data of Streptomycin with mild steel at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Concentration of inhibitor (M)</th>
<th>Weight loss (mg)</th>
<th>Inhibition efficiency ($\eta$) (%)</th>
<th>Corrosion rate ($C_r$) (mm$^{-1}$)</th>
<th>Surface coverage ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>39.01</td>
<td>-</td>
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<td>72.5</td>
<td>65.5</td>
<td>13.47</td>
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<td>5.16$\times$10$^{-4}$</td>
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<td>8.86</td>
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<td>87.1</td>
<td>5.03</td>
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<tr>
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<td>8.60$\times$10$^{-4}$</td>
<td>17.9</td>
<td>91.5</td>
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<td>307.2</td>
<td>-</td>
<td>57.06</td>
<td>-</td>
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<td></td>
<td>3.44$\times$10$^{-4}$</td>
<td>152.2</td>
<td>50.5</td>
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<td>5.16$\times$10$^{-4}$</td>
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<td>19.49</td>
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<td>234.0</td>
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<td>43.47</td>
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<td>-</td>
<td>119.98</td>
<td>-</td>
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<td>95.63</td>
<td>0.20</td>
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<td>31.1</td>
<td>82.66</td>
<td>0.31</td>
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<td>383.1</td>
<td>40.7</td>
<td>71.16</td>
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<td>352.7</td>
<td>45.4</td>
<td>65.51</td>
<td>0.45</td>
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<tr>
<td>338</td>
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<td>799.2</td>
<td>-</td>
<td>148.45</td>
<td>-</td>
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<td></td>
<td>3.44$\times$10$^{-4}$</td>
<td>718.5</td>
<td>10.1</td>
<td>133.46</td>
<td>0.10</td>
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<td>15.5</td>
<td>125.44</td>
<td>0.16</td>
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<tr>
<td></td>
<td>6.88$\times$10$^{-4}$</td>
<td>601.0</td>
<td>24.8</td>
<td>111.64</td>
<td>0.25</td>
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<tr>
<td></td>
<td>8.60$\times$10$^{-4}$</td>
<td>574.6</td>
<td>28.1</td>
<td>106.73</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Data derived from the weight loss study such as weight loss, inhibitor efficiency and surface coverage are listed in Table 1. Corrosion rate curves of mild steel without and with addition of different concentrations of Streptomycin in 1M HCl at 303-338K are shown in Figure 1.

![Corrosion Rate vs Inhibitor Concentration](image1)

**Figure 1.** Effect of Streptomycin concentration on corrosion rate of mild steel in 1M HCl at different temperatures.

![Inhibition Efficiency vs Inhibitor Concentration](image2)

**Figure 2.** Effect of inhibitor concentration on inhibition efficiency of mild steel corrosion in 1M HCl at different temperatures.

A close look at the figure reveals that the corrosion rate decreases as the concentration of inhibitor increases, while the corrosion rate increases with the increase in the temperature. This means
that the inhibitor efficiency decreases with increase in the temperature but inhibitor efficiency increases with increase in the inhibitor concentrations for all the temperature ranges studied as shown in Figure 2. Such behavior of streptomycin in 1M HCl is due to the increase in surface coverage by increasing the inhibitor concentration [21-23]. When the temperature increases, surface coverage reduction causes desorption of streptomycin from the mild steel surface and the mild steel surface is exposed to the acidic medium [24]. This may be due to decrease in the strength of the adsorption process at higher temperature, suggesting the physical adsorption of the inhibitor sample on the mild steel surface [25, 26].

3.2. Activation parameters on the inhibition process

Temperature plays an important role in understanding the inhibitive mechanism of the corrosion process. To assess the temperature effect, experiments were performed at 303 - 338K in uninhibited and inhibited solutions containing different concentrations of streptomycin and the corrosion rate was evaluated as presented in Table 1. The relationship between the corrosion rate \( C_r \) of mild steel in acidic media and temperature \( T \) is expressed by the Arrhenius equation [27-30]:

\[
\log(C_r) = \frac{-E_a}{2.303RT} + \log \lambda
\]

(4)

where, \( E_a \) is the apparent effective activation energy, \( R \) molar gas constant and \( \lambda \) the Arrhenius pre exponential factor.

![Figure 3. Arrhenius plot for mild steel corrosion in 1M HCl in the absence and presence of different concentrations of Streptomycin](image-url)
A plot of log of corrosion rate obtained by weight loss measurement versus $1/T$ gave straight line with regression coefficient close to unity, as shown in Figure 3. The values of apparent activation energy ($E_a$) obtained from the slope ($-E_a/2.303R$) of the lines and the pre exponential factor ($\lambda$) obtained from the intercept (log $\lambda$) are given in Table 2. It is evident from Table 2 that the apparent energy of activation increased on addition of Streptomycin in comparison to the uninhibited solution. The increase in the apparent activation energy suggests physical adsorption. Increase in the activation energy is attributed to appreciable decrease in the adsorption of inhibitor on mild steel surface by increase in the temperature. This decrease in adsorption leads to increase in corrosion rate due to the greater exposed surface area of the mild steel towards 1M hydrochloric acid solution [31].

Table 2. Activation parameters of Streptomycin in 1M HCl

<table>
<thead>
<tr>
<th>Inh. Conc. (M)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\lambda$ (mg cm$^{-2}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta G^*$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>31.81</td>
<td>1.14 × 10$^7$</td>
<td>29.15</td>
<td>-118.54</td>
<td>65.07</td>
</tr>
<tr>
<td>3.44 × 10$^{-4}$</td>
<td>53.82</td>
<td>2.48 × 10$^{10}$</td>
<td>51.16</td>
<td>-54.65</td>
<td>67.71</td>
</tr>
<tr>
<td>5.16 × 10$^{-4}$</td>
<td>62.31</td>
<td>4.57 × 10$^{11}$</td>
<td>59.65</td>
<td>-30.43</td>
<td>68.87</td>
</tr>
<tr>
<td>6.88 × 10$^{-4}$</td>
<td>74.91</td>
<td>8.18 × 10$^{11}$</td>
<td>72.26</td>
<td>5.94</td>
<td>70.46</td>
</tr>
<tr>
<td>8.60 × 10$^{-4}$</td>
<td>82.36</td>
<td>5.03 × 10$^{11}$</td>
<td>79.70</td>
<td>27.80</td>
<td>71.28</td>
</tr>
</tbody>
</table>

Figure 4. Transition state plot for mild steel corrosion in 1M HCl in the absence and presence of different concentrations of Streptomycin
The value of $\lambda$ is also higher for inhibited solution than for the uninhibited solution. It is clear from equation (4) that corrosion rate is influenced by both $E_a$ and $\lambda$. Generally, lower $\lambda$ value and higher $E_a$ value leads to the lower corrosion rate. It is evident that the effect of activation energy on mild steel corrosion is larger than that of the pre exponential factor. Decrease in the corrosion rate by increasing inhibitor concentration in this study suggests that $E_a$ is the deciding factor rather than the $\lambda$. Moreover, increase in concentration of Streptomycin leads to an increase in the value of $E_a$, indicating strong adsorption of the inhibitor molecules at the metal surface.

Experimental corrosion rate values evaluated from the weight loss data for mild steel in 1M HCl in the absence and presence of Streptomycin was used to determine the enthalpy of activation ($\Delta H^*$) and apparent entropy of activation ($\Delta S^*$) for the formation of the activation complex in the transition state equation. An alternative formula for the Arrhenius equation is the transition state equation [32, 33]

$$C_R = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right)$$  \hspace{1cm} (5)

where, $h$ is Planck’s constant, $N$ the Avogadro’s number, $\Delta S^*$ the apparent entropy of activation and $\Delta H^*$ the enthalpy of activation. A plot of $\log (C_R/T)$ versus $1/T$ is shown in Figure4. Straight lines were obtained with slope ($-\Delta H^*/2.303R$) and intercept of $[\log(R/Nh)+[\Delta S^*/2.303R]]$, from which $\Delta H^*$ and $\Delta S^*$ were calculated and listed in Table 2. The positive value of enthalpy of activation ($\Delta H^*$) in the absence and presence of various concentration of inhibitor reflects the endothermic nature of mild steel dissolution process meaning that dissolution of steel is difficult [24]. It is evident from the table that the value of $\Delta H^*$ increased in the presence of the inhibitor than the uninhibited solution indicating higher protection efficiency. This may be attributed to the presence of energy barrier for the reaction; hence the process of adsorption of inhibitor leads to rise in enthalpy of the corrosion process. On comparing the values of entropy of activation ($\Delta S^*$) listed in Table 2, it is clear that entropy of activation increased in the presence of the studied inhibitor compared to free acid solution. In the free acid solution it can be explained as follows: the transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state, so a high value for the entropy of activation is obtained. In the presence of inhibitor, however, the rate determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms. Since the surface is covered with inhibitor molecules, this will retard the discharge of hydrogen ions at the metal surface causing the system to pass from a random arrangement, and hence entropy of activation is increased. Hence, increase in the entropy of activation ($\Delta S^*$) in the presence of inhibitor increases in the disordering on going from reactant to activated complex.

The change in activation free energy ($\Delta G^*$) of the corrosion process can be calculated at each temperature by applying the equation:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$  \hspace{1cm} (6)
The obtained $\Delta G^*$ values are listed in Table 2. The values of $\Delta G^*$ were positive and showed almost no change with increasing temperature, indicating that the activated complex was not stable and the probability of its formation decreased somewhat with rise in temperature. However, $\Delta G^*$ values for inhibited systems reveal that in the course of inhibitor addition, the activated corrosion complex becomes less stable as compared to its absence.

3.3. Adsorption isotherm and adsorption parameters

Adsorption of the organic compound depends upon the charge and the nature of the metal surface, electronic characteristics of the metal surface on adsorption of solvent and other ionic species, temperature of the corrosion reaction and the electrochemical potential at the metal solution interface [34]. Adsorption of the Streptomycin involves two types of the possible interaction with the metal surface. The first one is weak undirected interaction due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of the metal. This interaction is termed physical adsorption or physisorption. The second type of interaction occurs when there is interaction between the adsorbate and adsorbent. This type of interaction involves charge sharing or charge transfer from adsorbate to the atoms of the metal surface in order to form a coordinate type bond and the interaction is termed chemical adsorption or chemisorptions [35].

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include Langmuir, Temkin, Frumkin, Hill deBoer, Parsons, Flory-Huggins, Dhar-Flory-Huggins, Bockris-Swinkels and thermodynamic/kinetic model of El-Awady et.al. [36-38]. The adsorption isotherm provides important clues regarding the nature of the metal-inhibitor interaction. Inhibitor molecules adsorb on the metal surface if the interaction between molecule and metal surface is higher than that of the water molecule and the metal surface [39]. In order to obtain the adsorption isotherm, the degree of surface coverage ($\theta$) for various concentrations of the inhibitors and different temperatures were calculated using equation (3) and listed in the Table1. Langmuir isotherm was tested for its fit to the experimental data. Langmuir adsorption isotherm is given by following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

where, $K_{ads}$ is the equilibrium constant of the adsorption-desorption process, $\theta$ is the degree of surface coverage and $C_{inh}$ is the molar concentration of inhibitor in the bulk solution. The plot of the $(C_{inh}/\theta)$ vs $C_{inh}$ fitted the experimental data at lower range of temperatures as reported earlier [17]. But for the higher temperature range the adsorption process did not follow the Langmuir adsorption isotherm. By testing other adsorption isotherms, it is found that the experimental data fits the El-Awady adsorption isotherm for all the temperature range studied. The characteristic of the isotherm is given by:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y \log C_{inh}$$
where, $C_{inh}$ is molar concentration of inhibitor in the bulk solution, $\theta$ is the degree of surface coverage, $K$ is the equilibrium constant of adsorption process; $K_{ads} = K^{1/y}$ and $y$ represent the number of inhibitor molecules occupying a given active site. Value of $1/y$ less than unity implies the formation of multilayer of the inhibitor on the metal surface, while the value of $1/y$ greater than unity means that a given inhibitor occupy more than one active site [11, 40, 41] Curve fitting of the data to the thermodynamic/kinetic model (El-Awady et. al.) is shown in Figure 5. The plot gives straight lines which shows that the experimental data fits the isotherm. The values of $K_{ads}$ and $1/y$ calculated from the El-Awady et.al. isotherm model is listed in Table 3.

**Table 3. Adsorption Parameters calculated from the El-Alwady isotherm**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_{ads}$ (mol$^{-1}$)</th>
<th>$1/y$</th>
<th>$R^2$</th>
<th>$\Delta G_{ads}$ (kJ mol$^{-1}$)</th>
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</thead>
<tbody>
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<td>-31.0</td>
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<tr>
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<td>0.98608</td>
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<td>0.6987</td>
<td>0.99154</td>
<td>-29.4</td>
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</table>

It is evident from Table 3 that the value of $1/y$ is less than unity showing that there is multilayer adsorption of the inhibitor molecule. $K_{ads}$ represents the strength between adsorbate and adsorbent. Larger values of the $K_{ads}$ imply more efficient adsorption and hence better inhibition efficiency [42, 43]. $K_{ads}$ value decreased in this study with increase in the temperature indicating that adsorption of Streptomycin on the mild steel surface was unfavorable at higher temperature.

**Figure 5.** El-Awady et. al. adsorption isotherm model for mild steel in 1M HCl containing streptomycin at different temperatures.
The equilibrium constant for the adsorption process is related to the standard free energy of adsorption by the expression [28]:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{-\Delta G_{ads}}{RT}\right)$$

(9)

This equation can also be expressed as:

$$\Delta G_{ads} = -2.303 \ RT \log(55.5K_{ads})$$

(10)

where, $\Delta G_{ads}$ is Gibbs free energy of adsorption, $T$ is the temperature in Kelvin and $K_{ads}$ is the equilibrium constant for the adsorption process and 55.5 is the molar concentration of water in solution. $K_{ads}$ value was calculated from the intercept of the Figure 3 and listed in Table 3. The negative values of $\Delta G_{ads}$ indicates the spontaneity of the adsorption process and the stability of the adsorbed species on the mild steel surface [44, 45]. Usually the values around -20 kJ mol$^{-1}$ or lower are consistent with physisorption, while those higher than -40kJ mol$^{-1}$ involve chemisorption [46]. When charged species are adsorbed on the metal surface, there is possibility of coulombic interaction between adsorbed cation and anion thereby causing increase in the Gibb’s free energy even if no chemical bonds are formed [41].

![Figure 6. The relationship between lnK$_{ads}$ and 1/T](image-url)
The values of $\Delta G_{ads}$ for the Streptomycin are listed in Table 3. These values indicate physical adsorption of Streptomycin on mild steel surface. The adsorption is enhanced by means of the presence of nitrogen atoms with lone pair of electrons and $\pi$ electrons in the inhibitor molecule influence it to adsorb electrostatically on the mild steel surface forming the insoluble and stable inhibitor film on metal surface that decreases the metal dissolution.

Assuming the thermodynamic model, corrosion inhibition of mild steel in presence of Streptomycin can be better explained using the enthalpy of adsorption $\Delta H_{ads}^o$ and entropy of adsorption $\Delta S_{ads}^o$ which can be calculated from the integrated van’t Hoff equation [47, 24]:

$$\ln K_{ads} = -\frac{\Delta H_{ads}^o}{RT} + \frac{\Delta S_{ads}^o}{R} + \ln \frac{1}{55.5} \quad (11)$$

To calculate the enthalpy of adsorption $\Delta H_{ads}^o$ and entropy of adsorption $\Delta S_{ads}^o$, $\ln K_{ads}$ was plotted against $1/T$ (Figure 6) and straight line was obtained with slope equal to $(-\Delta H_{ads}^o/R)$ and intercept equal to $(\Delta H_{ads}^o/R + \ln 1/55.5)$. The calculated values of the heat of adsorption and entropy of adsorption are listed in Table 4.

Table 4. Heat of adsorption and entropy of adsorption values calculated by different thermodynamic equations

<table>
<thead>
<tr>
<th>Different thermodynamic equations</th>
<th>$\Delta H_{ads}^o$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_{ads}^o$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van’t Half Equation (eq 11)</td>
<td>-40.5</td>
<td>-29.9</td>
</tr>
<tr>
<td>Gibbs- Helmholtz Equation (eq 12 &amp; 13)</td>
<td>-40.9</td>
<td>-</td>
</tr>
<tr>
<td>Basic Thermodynamic equation (eq 14)</td>
<td>-41.9</td>
<td>34.1</td>
</tr>
</tbody>
</table>

The enthalpy of adsorption can also be calculated from the Gibbs-Helmholtz equation [48]:

$$\left[ \frac{\partial (\Delta G_{ads}^o / T)}{\partial T} \right] = -\frac{\Delta H_{ads}^o}{T^2} \quad (12)$$

which can also be represented as:

$$\frac{\Delta G_{ads}^o}{T} = \frac{\Delta H_{ads}^o}{T} + k \quad (13)$$

The variation of $\Delta G_{ads}^o / T$ vs $1/T$ gives straight line with slope equal to $\Delta H_{ads}^o$ (figure 7).
It can be seen from the figure that the value of $\Delta G_{ads}/T$ decreases with $1/T$ in a linear fashion. The obtained value of $\Delta H_{ads}$ is given in Table 4. The value agrees with the one obtained using van’t Hoff equation. The enthalpy of adsorption $\Delta H_{ads}$ and entropy of adsorption $\Delta S_{ads}$ can also be calculated from the following thermodynamic basic equation [49]:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$  \hspace{1cm} (14)

A plot of $\Delta G_{ads}$ vs $T$ gives straight line (figure 8) with slope equal to $-\Delta S_{ads}$ and intercept $\Delta H_{ads}$. The values of $\Delta S_{ads}$ and $\Delta H_{ads}$ deduced from Figure 8 is presented in the Table 4. The values calculated from the different equations are in good agreement.

The negative value of $\Delta H_{ads}$ indicates that the adsorption of Streptomycin molecules is an exothermic process [50]. If the value of $\Delta H_{ads}$ is less than or around the 40kJ mol$^{-1}$ the adsorption process is physisorption while the value is more than 100 kJ mol$^{-1}$ the adsorption of inhibitor follows chemisorption process [51, 52]. In the present case, $\Delta H_{ads}$ values are around 40kJ mol$^{-1}$ suggesting the physical adsorption (physisorption). The entropy of adsorption obtained from Figures 6 and 8 are large and negative, which suggests the adsorption is an exothermic phenomenon accompanied by the decrease in entropy [53].
4. CONCLUSIONS

Streptomycin acted as a good inhibitor for the corrosion of mild steel in 1M HCl solution. Inhibition efficiency values increased with increase in inhibitor concentration but decreased with increase in temperature. The value of apparent activation energy increased with the increase in the inhibitor concentration. Enthalpy of activation reflects the endothermic nature of the mild steel dissolution process. Entropy of activation increased with increasing inhibitor concentration; hence increase in the disorderliness of the system. The adsorption of Streptomycin on the mild steel follows the El-Awady isotherm model. Gibbs free energy of adsorption, heat of adsorption and entropy of adsorption indicated that the adsorption process is spontaneous and exothermic and the molecules adsorbed on the metal surface by the process of physical adsorption.

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References

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