Corrosion inhibition of zinc in hydrochloric acid solution using Ampicillin

Khulood A.saleh, Khalil S. Khalil*
Department of Chemistry, College of science, University of Baghdad, Baghdad, Iraq.

Abstract
The corrosion behavior of Zn in 0.1 M HCl solution containing various concentration of Ampicillin range (2 x 10^-4 – 1x 10^-3) M was investigated. The corrosion rates were measured by using weight loss measurement and polarization curve. The results of polarization method obtained showed that the rate of corrosion of zinc increased with increasing the temperature from 293K to 323K and the values of inhibition efficiency of ampicillin increased with increasing the temperature and AMP concentrations, the results showed that AMP caused to protection efficiency reached to 88.8% when (1x10^-3) M AMP concentration was used in 323K. The coverage (θ) of metal surface by AMP could be obtained from the rate of corrosion in the presence and absence of AMP in the acid solution. A linear relationship was found to exist between the value of (C/θ) and the corresponding AMP concentration (C) indicating that the inhibition action to occur via adsorption mechanism. Changes in the free energy, enthalpy and entropy associated with AMP adsorption have been determined. Apparent energies of activation have been calculated for the corrosion process of zinc in the acid from corrosion rates and Arrhenius Plots.

Key word: corrosion, inhibition, ampicillin, zinc, acidic solution.

Introduction
Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation [1]. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is very slow [2]. Zinc is a metal with numerous industrial applications

*Email: Khalel5010@yahoo.com
and is mainly used for the corrosion protection of steel [3]. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous [4]. The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research [5]. Many researchers report that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on [6,7]. Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators [8-13]. It has been found that most of the organic inhibitors act by adsorption on the metal surface [14]. The use of inhibitors is one of the best methods of protecting metals against corrosion [15]. In order to study the corrosion of metals, several techniques have been applied. The use of chemical inhibitors is one of the most practical methods for the protection against corrosion in acidic media. Most of the excellent acid inhibitors are organic compounds containing nitrogen [16-18], oxygen [19-22], phosphorus [23] and sulphur [24,25]. Studies of the relation between adsorption and corrosion inhibition are of considerable importance. In the present paper, the corrosion inhibition of zinc in 0.1M HCl solutions by ampicillin has been studied. The chemical structure of AMP is as shown in Figure-1. From the structure, it can be seen that ampicillin \{(7-(2-amino-2-phenyl-acetyl) amino-3,3 dimethyl-6-oxo-2-thia-5-azabicyclo- [3,2,0] heptane-4-carboxylic acid\}. Has hetero atoms in their heterocyclic structure and it is therefore expected to be a good corrosion inhibitor [26].

![Figure 1- structure of AMP](image)

**Experimental**

1. **Materials and reagents**
   Zinc 99.99% sheet were used for electrochemical and gravimetric studies. The zinc samples were mechanically polished using different grades of emery paper, washed with distilled water, and dried at room temperature. Appropriate concentration of aggressive solutions used (0.1M HCl) was prepared using distilled water. Sensitive balance. Ampicillin 99.99% was obtained from (SID) samara Drugs industry.

2. **Weight loss method**
   In the weight loss experiments, a clean weighed zinc coupon was immersed completely in a 75 ml beaker containing the corrodent and inhibitors. The coupons were retrieved at 1 h interval progressively for 5h immersed in 0.1M HCl (specific gravity: 1.18) and different concentrations of ampicillin at room temperature. Each 2 min to remove the corrosion product, scrubbed with bristle brush under running water, dried in acetone and weighed. The zinc specimens were rectangular in the form \(2 \times 1.5 \times 0.06\) cm.

3. **Potentiostatic polarization measurements**
   The polarization can be carried by using a potentiostat (M lab Potentiostat / galvanostat 200 (2007) (Germany) was obtained from Bank Elektronik –Intelligent Controls GmbH. Three electrode are required: the working electrode (WE) (that is the metal), the reference electrode (the potential of the WE is measured relative to this potential), and counter or auxiliary electrode (that the majority of the current passes through). Anodic and cathodic polarization of zinc was carried out under potentiostatic conditions in 0.1M HCl in the absence as well as in the presence of different concentrations of inhibitor from \((2\times 10^{-4} – 1\times 10^{-3})\) M at different temperature (293-323) K. The working electrode was
immersed in the test solution during 5 minutes until a steady state open circuit potential ($E_{ocp}$) was obtained. The inhibition efficiency depends on many factors including number of adsorption sites or functional groups, basicity, and molecular size. In the present case, the S- atom and the N-atom and the O-atom probably act as the centers of adsorption.

**Result and discussion**

1. **Weight loss measurement**

   Different experimental techniques have been used to evaluate inhibition efficiency of the AMP. Gravimetric is one of the simplest. Determination of the weight loss allows the calculation of the inhibition efficiency ($\%I$) using Eq. (1). The variation of inhibition efficiency with increasing in inhibitor concentrations is shown in Figure-2. It was observed that AMP inhibits the corrosion of zinc in 0.1M HCl solution, at all concentrations used in study, i.e. from $2 \times 10^{-4}$ to $1 \times 10^{-3}$ M. Maximum inhibition efficiency was shown at $1 \times 10^{-3}$ M concentration of the inhibitor in 0.1M HCl at 290 K and it reached to 75%. It is evident from table-1 that the corrosion rate is decreased with increasing concentration of AMP. The value of percentage inhibition efficiency ($\%I$) and corrosion rate obtained from weight loss method at different concentrations of AMP in 0.1M HCl at 290 K are summarized in table -1.

![Figure 2- Variation of inhibition efficiency for zinc with different concentrations of AMP inhibitor in 0.1M HCl at 290K.](image)

This result suggests that the increase in efficiencies with increasing in inhibitors concentration because of increases the number of molecules adsorbed onto Zinc surface and reduces the surface area that is available for the direct acid attack on the metal surface [27]. Therefore, AMP is an adsorption inhibitor for the corrosion of zinc in 0.1 M HCl solutions [28]. The results obtained from weight loss are in good agreement with electrochemical studies. The corrosion rates of the zinc coupons have been determined for 1h immersion period at 290K from mass losses, using Eq. (1) where $\Delta m$ is the mass loss, S is the area and t is the immersion period [29]. The percentage protection efficiency ($\%I$) and coverage degree was calculated according the relationships Eq. (2) and (3) respectively [30].

\[
W = \frac{\Delta m}{S} \Delta t
\]  
\[\% I = \frac{W_0 - W_i}{W_0} \times 100
\]  
\[\Theta = 1 - \frac{W_i}{W_0}
\]

Where $W_0$ and $W_i$ are the Weight loss data of the metal coupons in the absence and presence of the inhibitor respectively. $\Theta$ is the surface coverage.
Table 1- Corrosion parameters of zinc in aqueous solution of 0.1M HCl in absence and presence of different concentrations of AMP from weight loss measurements at 290K.

<table>
<thead>
<tr>
<th>Conc. AMP (M)</th>
<th>W(mg/cm².h)</th>
<th>%I</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>AMP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 x 10⁻⁴</td>
<td>0.2</td>
<td>50</td>
<td>0.555</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>0.177</td>
<td>55.7</td>
<td>0.637</td>
</tr>
<tr>
<td>8 x 10⁻⁴</td>
<td>0.145</td>
<td>63.7</td>
<td>0.75</td>
</tr>
<tr>
<td>1x10⁻³</td>
<td>0.1</td>
<td>75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

2. Potentiostatic polarization measurements

Anodic and cathodic galvenostatic polarization curves for zinc in 0.1 M HCl acid, alone and containing different concentration of AMP at 303K is shown in figure-3 The curves show polarization of both, the cathodes as well as anodes. The extrapolation method for the polarizations curves was applied and the data for corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), cathodic and anodic Tafel slopes ($b_c$ and $b_a$) and percentage inhibition efficiency (%I) are show in table-2. In almost all these cases, the %I from Tafel plots agree well with the values obtained from weight loss data. In the case of polarization method the relation determines the inhibition efficiency (%I) eq.4 [31]:

$$\% I = \left(1 - \frac{i_{corr \, un}}{i_{corr \, i}}\right) 100$$ (4)

Where $i_{corr \, un}$ and $i_{corr \, i}$ are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

![Figure 3- Polarization plots of zinc in 0.1M HCl for various concentrations of AMP at 303K.](image-url)

The tafel plots Figure-3 reveal that the corrosion potential ($E_{corr}$) of the working electrode in the solution containing corrosion inhibitor shift to higher position, compared to that of blank, implying that the corrosion inhibitor act as anodic-type inhibitor [32]
Table 2- Corrosion data of zinc in 0.1M HCl at absence and presence different AMP concentrations at temperature ranges 293-323K.

<table>
<thead>
<tr>
<th>AMP / M</th>
<th>TK</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ $\mu$A/cm$^2$</th>
<th>$-b_t$ mV/Dec</th>
<th>$b_t$ mV/Dec</th>
<th>$\theta$</th>
<th>%I</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl Blank</td>
<td>293</td>
<td>-995</td>
<td>358.14</td>
<td>173.1</td>
<td>78.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-998.7</td>
<td>729.24</td>
<td>124.1</td>
<td>128.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-998.8</td>
<td>1160</td>
<td>129.5</td>
<td>122.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-999</td>
<td>1760</td>
<td>156.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2x10$^4$</td>
<td>293</td>
<td>-904.8</td>
<td>177.14</td>
<td>104.6</td>
<td>76.1</td>
<td>0.505</td>
<td>50.5</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-918.3</td>
<td>215.15</td>
<td>107.1</td>
<td>85.6</td>
<td>0.704</td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-924.4</td>
<td>264.31</td>
<td>110.2</td>
<td>86.8</td>
<td>0.772</td>
<td>77.2</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-917</td>
<td>308.4</td>
<td>131.4</td>
<td>77.1</td>
<td>0.824</td>
<td>82.4</td>
</tr>
<tr>
<td>5x10$^4$</td>
<td>293</td>
<td>-928.6</td>
<td>169.3</td>
<td>122</td>
<td>78.6</td>
<td>0.527</td>
<td>52.7</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-942.3</td>
<td>197.02</td>
<td>137.3</td>
<td>76.4</td>
<td>0.729</td>
<td>72.9</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-939.7</td>
<td>201.5</td>
<td>139</td>
<td>80.2</td>
<td>0.826</td>
<td>82.6</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-908</td>
<td>226.56</td>
<td>123.3</td>
<td>88.6</td>
<td>0.871</td>
<td>87.1</td>
</tr>
<tr>
<td>8x10$^4$</td>
<td>293</td>
<td>-902</td>
<td>149.71</td>
<td>131.4</td>
<td>71.7</td>
<td>0.581</td>
<td>58.1</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-924.7</td>
<td>188.75</td>
<td>149.8</td>
<td>81.4</td>
<td>0.741</td>
<td>74.1</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-936.6</td>
<td>195.67</td>
<td>155.1</td>
<td>79.7</td>
<td>0.831</td>
<td>83.1</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-931.5</td>
<td>221.18</td>
<td>134.8</td>
<td>68.3</td>
<td>0.874</td>
<td>87.4</td>
</tr>
<tr>
<td>1x10$^3$</td>
<td>293</td>
<td>-915.4</td>
<td>132.54</td>
<td>126.8</td>
<td>68.1</td>
<td>0.629</td>
<td>62.9</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-926.7</td>
<td>148.86</td>
<td>127.4</td>
<td>71.4</td>
<td>0.795</td>
<td>79.5</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-936.9</td>
<td>152.04</td>
<td>131.4</td>
<td>72.6</td>
<td>0.868</td>
<td>86.8</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-936.9</td>
<td>196.21</td>
<td>130.1</td>
<td>70.5</td>
<td>0.888</td>
<td>88.8</td>
</tr>
</tbody>
</table>

2.1. Kinetic of corrosion and thermodynamic activation parameters

In order to study the effect of temperature on the inhibition efficiencies of AMP, potentiostatic polarization measurements were carried out in the temperature range 293–323K in absence and presence of inhibitor at different concentration. The various corrosion parameters obtained are listed in table-3. The data obtained suggests that AMP get adsorbed on the zinc surface at all temperatures and corrosion rates increased in absence and presence of inhibitor with increasing in temperature in 0.1M HCl solutions. In acidic media, corrosion of metal is generally accompanied with evolution of H$_2$ gas; rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal. Inspection of table-2, showed that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of AMP increased with temperature. In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (5 and 6) and transition state Eq. (7 and 8) were used [33]:

$$\text{CR} = A \exp^{(-E_a/RT)}$$  \hspace{1cm} (5)

$$\log \text{CR} = \log A - E_a/2.303RT$$ \hspace{1cm} (6)

$$\text{CR} = \frac{RT}{Nh} \exp^{(\Delta S_a/2R)} \exp^{(-\Delta H_a/RT)}$$  \hspace{1cm} (7)

$$\log (\text{CR}/T) = \log R/Nh + \Delta S_a/2.303R - \Delta H_a/2.303RT$$ \hspace{1cm} (8)

Where C.R is the corrosion rate, R the gas constant, T the absolute temperature, A the pre exponential factor, h the Plank's constant and N is Avogadro's number, E$_a$ the activation energy for corrosion process, $\Delta H_a$ the enthalpy of activation and $\Delta S_a$ the entropy of activation. The apparent activation energy ($E_a$) at optimum concentration of AMP was determined by linear regression between logCR and 1/T, figure-4, and the result is shown in table-3.
Figure 4- Arrhenius Plot of log CR versus 1/T for the corrosion of zinc in 0.1 M HCl containing various concentrations of AMP.

The linear regression coefficient was close to 1, indicating that the zinc corrosion in hydrochloric acid can be elucidated using the kinetic model. Inspection of table-3 showed that the value of $E_a$ determined in 0.1M HCl containing different AMP concentrations. The inhibition efficiency of AMP slightly increases with temperature and its increase leads to decrease the apparent activation corrosion energy. This reduction probably was attributed to chemisorption of AMP on the zinc surface [34]. Figure-5, showed a plot of log (CR/T) versus 1/T. The straight lines are obtained with a slope (-$\Delta H_a/RT$) and an intercept of (Ln R/Nh + $\Delta S_a/R$) from which the values of the values of $\Delta H_a$ and $\Delta S_a$ are calculated and are given in table-3. Inspection of these data revealed that the thermodynamic parameters ($\Delta H_a$ and $\Delta S_a$) for dissolution reaction of zinc in 0.1M HCl in the presence of AMP is lower. The positive sign of $\Delta H_a$ reflect the endothermic nature of the zinc dissolution process suggesting that the dissolution of zinc is slow [35], respectively, also indicate that the activated complex may be the rate-determining step and represents association (increasing degree of orderliness) rather than dissociation (disorderliness) [33].

Figure 5- Arrhenius plots of log CR/T vs. 1/T for Zinc in 0.1M HCl in the absence and the presence of AMP at optimum concentration.

Table 3- Activation parameters $E_a$, $\Delta H_a$ and $\Delta S_a$ for the zinc dissolution in 0.1M HCl in the absence and the presence of AMP at optimum concentration.
2.2. Adsorption isotherm

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at metal/solution interface. Basic information on the adsorption of inhibitors on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm, the fractional surface coverage values ($\theta$) as a function of inhibitor concentration must be obtained. The values of $\theta$ can be easily determined from the weight loss measurements by the ratio $\%I/100$, where $\%I$ is inhibition efficiency obtained by weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitors on the zinc surface. Several adsorption isotherms (viz., Frumkin, Langmuir, Temkin, Freundlich) were tested and the Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior of this inhibitor. The Langmuir isotherm is given by following equation [36] as shown in table-4:

$$\theta/1-\theta = K_{ads} C$$

(9)

The rearrangement gives the following equation:

$$C/\theta = 1/K_{ads} + C$$

(10)

Where $C$ is the concentration of inhibitor, $K_{ads}$ is the equilibrium constant of the adsorption process, and $\theta$ is the surface coverage. Plot $C/\theta$ versus $C$ yields a straight line, figure-6, with regression coefficient, $R^2$, almost equal to 1. This suggests that AMP in present study obeyed the Langmuir isotherm and there is negligible interaction between the adsorbed molecules. Free energy of adsorption was calculated using the relation [37]:

$$K_{ads} = 1/55.55 \exp(-\Delta G_{ads}/RT)$$

(11)

Where $R$ is the universal gas constant and $T$ is the absolute temperature. The value 55.55 in the above equation is the concentration of water in solution in mol L$^{-1}$.

![Figure 6- Langmuir isotherm plot for the adsorption of AMP on the surface of zinc.](image)

**Table 4-** Langmuir adsorption parameters for the adsorption of AMP on the surface of zinc.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>K(M$^1$)</th>
<th>$-\Delta G$ (kJ.mol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>5000</td>
<td>30.537</td>
<td>0.990</td>
</tr>
<tr>
<td>303</td>
<td>12500</td>
<td>33.888</td>
<td>0.995</td>
</tr>
<tr>
<td>313</td>
<td>16666</td>
<td>35.755</td>
<td>0.998</td>
</tr>
<tr>
<td>323</td>
<td>33333</td>
<td>38.759</td>
<td>0.999</td>
</tr>
</tbody>
</table>

The free energy of adsorption ($\Delta G_{ads}$), is calculated from Eq. (11). The negative value of the free energy of adsorption and the high values of the adsorption constant indicate a spontaneous adsorption of these inhibitors on zinc and increase as the percentage inhibition increases. This means that the
inhibitive action of this substance results from the chemical adsorption of these molecules on the surface of zinc. This is also supported by the fact that the inhibition efficiency of the investigated inhibitor increases at higher temperature (323K) [38].

**Conclusion**

1) The performance of this inhibitor can be optimized by taking advantages of the operating temperature and concentration of the inhibitor.

2) AMP acts as a good inhibitor for the corrosion of zinc in 0.1M HCl.

3) Potentiostatic curves reveal that AMP is an anodic type of inhibitor.

4) The results obtained from weight loss and polarization studies are in good agreement with each other.

5) The adsorption of AMP on zinc surface obeyed Langmuir adsorption isotherm.

**Reference**


