Application of Theophylline Anhydrous as Inhibitor for Acid Corrosion of Aluminum

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The inhibitive effect of theophylline anhydrous on aluminum corrosion in hydrochloric acid solution was investigated using chemical and electrochemical techniques. It was found that the compound acts as good corrosion inhibitor with inhibition efficiency more than 99.9%. The inhibition efficiency was found to increase with inhibitor concentration and exposure time. On the other hand, it decreases by rising the temperature. The inhibition action was discussed in view of adsorption of the organic compound molecules on the aluminum surface. It was found that the adsorption of theophylline anhydrous on aluminum surface follows Langmuir adsorption isotherm. The thermodynamic parameters for the corrosion process in free and inhibited media were calculated and interpreted.

Keywords: Theophylline, Aluminum, Corrosion inhibitor, Electrochemical techniques, Thermodynamic parameters.

Corrosion of metals and alloys is a disaster which causes a large economic loss in different human activities [1]. The corrosion process is thermodynamically spontaneous and cannot be totally stopped anyhow. However, there are continuous trials to develop methods for decreasing the corrosion to its minimum rate. One of the methods used to achieve this goal was using inhibitors. The corrosion inhibitors act either by adsorption on the metal surface or reaction with it producing a passive film. The former ones are most likely organic compounds with atoms in their structures carrying a lone pair of electrons capable of electrostatic attraction of the vacant orbitals of the metal. Recently, there is a great offer by the researchers to find efficient corrosion inhibitors with low hazard impact on the environment and human. Most of them have investigated the plant extracts as well as drugs to achieve this purpose [2-9]. Theophylline anhydrous was tested as an inhibitor for steel corrosion [10-11].

Aluminum is an important metal that is frequently used in industrial applications or household appliances. Although aluminum forms a protective oxide layer on its surface, it suffers from corrosion if brought in contact with acidic media. This behavior is attributed to the formation of soluble salts by the...
reaction of the acid with the oxide layer. This process occurs during the removal of scale from aluminum heat exchangers, tanks, pipes, etc. To avoid the corrosion of aluminum in such cases inhibitor must be added to the cleaning acid. The inhibition of aluminum corrosion in different media has been studied by many researchers either using organic [7, 12-21] or inorganic compounds [22-25].

In the present work, theophylline anhydrous (Fig. 1) was investigated as inhibitors for aluminum corrosion in 2.0 M HCl solution. Theophylline is methylxanthine drug used to treat the symptoms of asthma or other lung conditions, such as emphysema or chronic bronchitis. Theophylline is a natural product found in cocoa beans. Amounts of 3.7 mg/g have been reported in Criollo cocoa beans [26]. Theophylline anhydrous has a formula C7H8N4O2 with a molecular weight of 180.16 g/mol. The chemical structure of theophylline anhydrous (1, 3-Dimethylxanthine, 2,6-Dihydroxy-1,3-dimethylpurine, 3,7-Dihydro-1,3-dimethyl-1H-purine-2,6-dione) is represented in Fig.1. Weight loss and potentiodynamic measurements were used for this purpose. The thermodynamic parameters of the corrosion and inhibition processes were calculated.

Sigma-Aldrich  Pure theophylline anhydrous powder was used as received
Pure aluminum (99.99%) provided by Egypt alum's aluminum plant (Nag Hammady) was used in this study. Approximately 4.0 M hydrochloric acid solution was prepared by diluting the appropriate volume of the concentrated pure grade acid, with distilled water. The concentration of the prepared acid was then checked by titration against the standard solution of sodium carbonate. From this acid solution, exactly 2.0 M HCl was prepared and used in the experiments.

For weight loss experiments, rectangular sheets with 1.0 cm² surface area were used. The aluminum sheet was polished with different grades of emery papers, cleaned with doubly distilled water and degreased with acetone before it was introduced into the test solution. Before each experiment, the specimens

Fig.1. Theophylline anhydrous (1, 3-Dimethylxanthine, 2, 6-Dihydroxy-1, 3-dimethylpurine, 3, 7-Dihydro-1, 3-dimethyl-1H-purine-2,6-dione).

Experimental
were weighed, hanged in 50 mL of test solution using nylon thread. The temperature of the environment was maintained by thermostatically controlled water bath with an accuracy of ±0.1°C under a naturally aerated condition. At the end of every tested time interval, the specimens were taken out for washing, drying, and weighing. The weight loss values were taken as the mean of results was obtained from three different experiments. The corrosion rate was calculated as the loss of weight in grams per square centimeter per time (g.cm⁻².h⁻¹). The inhibition efficiency, IE% and surface coverage (θ), were determined using the following equation:

$$IE\% = [1 - (\frac{W_i}{W_f})] \times 100$$

$$\theta = 1 - \frac{W_i}{W_f}$$

where $w_f$ and $w_i$ are the rates of aluminum coupon corrosion in free and inhibited HCl solutions, respectively.

Three electrodes cell with platinum foil as a counter electrode and saturated calomel electrode was used in the electrochemical experiments. The working electrode was aluminum rod impeded in Araldite with the bottom surface area of 0.38 cm² exposed to the corrosive solution. Before each experiment, the working electrode was polished with different grades of emery papers, washed by water and inserted into the electrochemical cell. The working electrode was immersed for 30 minutes in the test solution to attain its steady state potential before the start of each experiment. Meinsbergerpotentiostat/ Galvanostat with PS6 software was used to carry out potentiodynamic polarization.

Potentiodynamic experiments were performed by scanning the electrode potential from -1800 to 600 mV at 5 mV/sec sweep rate. Tafel lines were extrapolated to the corrosion potential for the calculation of the electrochemical kinetics parameters. The IE% and θ were obtained by using equations (3), (4):

$$IE\% = [1 - (\frac{i_i}{i_f})] \times 100$$

$$\theta = 1 - \frac{i_i}{i_f}$$

where $i_f$ and $i_i$ are the corrosion current densities of aluminum specimen (mA/cm²) in absence and presence of different concentrations of the inhibitor, respectively.

All experiments were carried out in normally aerated solutions at 30°C except those carried out at different temperatures.

Results and Discussion

Weight loss measurements

The corrosion behavior of aluminum in 2.0 M HCl solutions devoid of and containing different concentrations of theophylline anhydrous was studied using weight loss technique at different exposure time intervals. The obtained data are tabulated in Table 1. The data of the table reveal that the addition of theophylline anhydrous markedly decreases the corrosion of aluminum in the acid solution. Therefore, it could be concluded that theophylline anhydrous acts as a good corrosion inhibitor for aluminum corrosion in the acidic medium. The inhibition efficiency reaches to values more than 99.9%.

<table>
<thead>
<tr>
<th>t, h.</th>
<th>Free</th>
<th>0.000005</th>
<th>0.00001</th>
<th>0.00005</th>
<th>0.0001</th>
<th>0.0005</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>r</td>
<td>0.2133</td>
<td>0.0031</td>
<td>0.0024</td>
<td>0.0016</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>IE%</td>
<td>---</td>
<td>98.55</td>
<td>98.87</td>
<td>99.25</td>
<td>99.34</td>
</tr>
<tr>
<td>2</td>
<td>r</td>
<td>0.17375</td>
<td>0.00165</td>
<td>0.0013</td>
<td>0.001</td>
<td>0.00075</td>
</tr>
<tr>
<td></td>
<td>IE%</td>
<td>---</td>
<td>99.05</td>
<td>99.25</td>
<td>99.42</td>
<td>99.57</td>
</tr>
<tr>
<td>3</td>
<td>r</td>
<td>0.132467</td>
<td>0.0012</td>
<td>0.0009</td>
<td>0.000733</td>
<td>0.000533</td>
</tr>
<tr>
<td></td>
<td>IE%</td>
<td>---</td>
<td>99.09</td>
<td>99.32</td>
<td>99.45</td>
<td>99.59</td>
</tr>
<tr>
<td>4</td>
<td>r</td>
<td>0.106975</td>
<td>0.00095</td>
<td>0.0007</td>
<td>0.000575</td>
<td>0.000425</td>
</tr>
<tr>
<td></td>
<td>IE%</td>
<td>---</td>
<td>99.11</td>
<td>99.35</td>
<td>99.46</td>
<td>99.6</td>
</tr>
</tbody>
</table>

The inhibition action of theophylline anhydrous could be interpreted in view of its molecular structure. It is well known now that the adsorption of inhibitor molecules on the corroded metal surface is an essential initial step that should be established for performing the inhibition action. The degree of adsorption of the chemical compound molecules largely depends on its chemical structure. The molecular structure of theophylline anhydrous contains two aromatic rings as well as O, N and S atoms which possess lone pairs of electrons. These features of the structure suggest a high tendency of the molecules to be strongly adsorbed at the metal surface. As the inhibitor molecules are adsorbed on the metal surface, they form a continuous film that acts as a barrier between the metal surface and the corrosive medium. The presence of this film prevents the transfer of mass and charge leading to the decrease of the corrosion process.

Figure 2 represents the relation between inhibition efficiency of theophylline anhydrous and its concentration for aluminum corrosion in 2.0 M HCl solution at different time intervals. The curves of the figure show that, the inhibition efficiency increases as the inhibitor concentration is increased. It is important to note that the inhibition efficiency increases, from the lowest to the highest inhibitor concentration, in a narrow range; about one to two units. This behavior suggests that even the

presence of low concentrations of theophylline anhydrous leads to a high inhibition effect on the acid aluminum corrosion. Such result may refer to the mode of inhibitor molecules adsorption on the metal surface. The high inhibition efficiency achieved by very small concentration is a fair evidence for horizontally adsorbed molecules. It implies that a small number of adsorbed molecules can cover a high surface area which could not be achieved if they are adsorbed vertically.

Further examination of Fig. 2 reveals that, the change of inhibition efficiency is relatively large upon increasing the inhibitor concentration from $5 \times 10^{-6}$ to $10^{-5}$ M. As the concentration reaches $10^{-5}$ M, the inhibition efficiency steadily increases up to a concentration of $5 \times 10^{-4}$ M. This result confirms the above conclusion regarding the adsorption mode of the inhibitor molecules. Thus, it takes no more than a small number of molecules to approach the highest possible inhibition efficiency. Therefore, as such low inhibitor concentration $10^{-5}$ M is reached, the surface is almost completely covered with adsorbed molecules. The small number of molecules needed for almost complete surface coverage supports the idea that the inhibitor molecules are adsorbed horizontally on the surface. Further increasing of inhibitor concentration only leads to a very small increase in the inhibition efficiency.

The little effect of increasing concentration on the inhibition efficiency could be interpreted as follows. At low inhibitor concentrations there are a lot of free sites on the metal surface for inhibitor molecules to adsorb at. Therefore, all the inhibitor molecules find their sites for adsorption and take their parts in the inhibition process. Nevertheless, as the concentration increases there are not enough free sites on the metal surface to all the molecules for adsorption. Thus, a competition between the inhibitor molecules arises to be adsorbed on the free surface site. Such competition for adsorption leads to decrease the impact of high concentration of the inhibitor molecules. The expected result of this is a

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*Fig. 2. Effect of theophylline anhydrous concentration on inhibition efficiency for aluminum corrosion in 2.0 M HCl solution.*

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deviation from the linear relationship between inhibitor concentration and inhibition efficiency as shown in Fig. 2.

**Polarization technique**

The potentiodynamic polarization curves of aluminum corrosion in 2.0 M HCl solutions in the absence and presence of various concentrations of theophylline anhydrous were traced at the scanning rate of 5 mV/sec. The obtained curves were represented in Fig. 3. The corrosion kinetic parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), anodic Tafel slope ($β_a$) and cathodic Tafel slope ($β_c$) deduced from the curves are given in Table 2.

![Potentiodynamic polarization curve](image)

**Fig. 3.** Potentiodynamic polarization of aluminum in 2.0 M HCl solutions containing and devoid of different concentrations of theophylline anhydrous.

Inspection of Fig. 3 reveals that both the anodic and cathodic polarization curves shift toward more negative potential and less current density values upon the addition of theophylline anhydrous. This result suggests the inhibitive action of theophylline anhydrous toward aluminum corrosion in the acidic medium.

Several observations, due to addition of the extract, could be recognized from the data of Table 2:

1. The corrosion potential tends to become more negative by the addition of theophylline anhydrous. This result may refer to a cathodic inhibition mechanism.

ii. The corrosion rate decreases and the inhibition efficiency increases by increasing theophylline anhydrous concentration. Upon increasing the theophylline anhydrous concentration in the bulk solution the number of molecules adsorbed on aluminum surface increases leading to an increase in the inhibition efficiency.

**TABLE 2. Parameters of aluminum corrosion in free and inhibited 2.0 M HCl solutions as revealed from polarization technique.**

<table>
<thead>
<tr>
<th>Conc., M</th>
<th>$-E_{corr}$, mV</th>
<th>$i_{corr}$ mA/cm$^2$</th>
<th>$\beta_c$ mV/decade</th>
<th>$\beta_a$ mV/decade</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000</td>
<td>665</td>
<td>433.89</td>
<td>518</td>
<td>800</td>
<td>----</td>
</tr>
<tr>
<td>0.000005</td>
<td>714</td>
<td>165.47000000</td>
<td>410</td>
<td>790</td>
<td>61.86000</td>
</tr>
<tr>
<td>0.00001</td>
<td>730</td>
<td>113.44000000</td>
<td>324</td>
<td>767</td>
<td>73.86000</td>
</tr>
<tr>
<td>0.00005</td>
<td>740</td>
<td>3.036000000</td>
<td>319</td>
<td>758</td>
<td>99.30000</td>
</tr>
<tr>
<td>0.0001</td>
<td>748</td>
<td>0.00074074</td>
<td>297</td>
<td>764</td>
<td>99.99980</td>
</tr>
<tr>
<td>0.0005</td>
<td>770</td>
<td>0.00050329</td>
<td>280</td>
<td>780</td>
<td>99.99988</td>
</tr>
</tbody>
</table>

There is almost no change in anodic Tafel constant upon the addition of increasing concentrations of the theophylline anhydrous. In contrast, the cathodic Tafel constant value has greatly changed upon the addition of the inhibitor. This result supports the conclusion made by the change of corrosion potential; that theophylline anhydrous acts as a cathodic inhibitor. This type of inhibitor reduces the corrosion rate via inhibition of the cathodic reaction.

**Adsorption behavior**

The corrosion inhibition process is often attributed to the adsorption of inhibitor molecules onto the metal surface. The adsorbed molecules form a film isolating the metal surface from the aggressive medium. The best way to study the adsorption process is through identifying its adsorption isotherm. Several isotherms were postulated for different adsorption behaviors. All the known isotherms have been tried here in the present study to find out the one which is fitted with the obtained results. It is found that Langmuir adsorption isotherm is the best isotherm fitted with the experimental results.

Langmuir adsorption isotherm could be represented by the equation:

$$ \frac{C}{\theta} = \frac{1}{k} + C $$  \hspace{1cm} (5)

where $C$ is the inhibitor concentration, $\theta$ is the fraction of surface coverage and $k$ is the adsorption constant which is identified as:

$$ lnk = \frac{\ln 1}{55.5} - \frac{\Delta G_{ads}^o}{RT} $$  \hspace{1cm} (6)

where \( \Delta G_{\text{ads}} \) is the standard adsorption free energy and 55.5 is the molar concentration of water.

Plotting \( C \) versus \( C/\theta \) gives a straight line with unit slope and unit correlation coefficient as shown in Fig. 4. This indicates that the adsorption of theophylline anhydrous on an aluminum surface in the acidic medium follows Langmuir adsorption isotherm. The value of \( (k) \) was determined by the intercept of the line of Fig. 4 and was used to calculate the standard free energy of adsorption. It was found that standard free energy of adsorption of theophylline anhydrous on the aluminum surface in the acidic medium is \(-48.98\) kJ/mol. The negative sign suggests that the adsorption process is spontaneous and forms a stable film on the aluminum surface.

**Effect of temperature**

The effect of temperature (in the range of 313 – 343 K), on the corrosion of aluminum in 2.0 M HCl solutions devoid of and containing \( 5\times10^{-4} \) M of theophylline anhydrous was studied using weight loss measurements. Table 3 contains the values of inhibition efficiency of \( 5\times10^{-4} \) M theophylline anhydrous toward aluminum corrosion in 2.0 M HCl solutions at different temperatures for different exposure times. Inspection of Table 3 reveals that, as the temperature increases the inhibition efficiencies of all tested extract decrease.

TABLE 3. Values of inhibition efficiency of theophylline anhydrous toward aluminum corrosion in 2 M HCl solutions at different temperatures for different exposure times.

<table>
<thead>
<tr>
<th>t, min</th>
<th>T, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313</td>
</tr>
<tr>
<td>15</td>
<td>88.24</td>
</tr>
<tr>
<td>30</td>
<td>87.48</td>
</tr>
<tr>
<td>45</td>
<td>86.29</td>
</tr>
<tr>
<td>60</td>
<td>84.19</td>
</tr>
<tr>
<td>75</td>
<td>82.22</td>
</tr>
</tbody>
</table>

The corrosion reaction can be regarded as an Arrhenius-type process which follows the equation:

$$\log r = \log A - \frac{E_a}{2.303 RT}$$

(7)

where $r$ represents the rate of corrosion reaction, $A$ is Arrhenius factor and $E_a$ is the apparent activation energy of the corrosion reaction. Plotting of $\log r$ versus $1/T$ gave a straight line, as shown in Fig. 5. The values of activation energies for corrosion reactions of aluminum in free and inhibited acid solutions were presented in Table 3.

![Fig. 5. Arrhenius plot for aluminum corrosion in the free and inhibited 2.0M HCl solutions.](image)

Other activation parameters were calculated using the transition state equation:

$$\log \frac{I_{corr}}{T} = \log \left( \frac{R}{\lambda N} \right) + \left[ \frac{\Delta S^*}{2.303 R} \right] - \frac{\Delta H^*}{2.303 RT}$$

(8)
where, \( R \) is the universal gas constant (8.314 J/mol.K), \( N \) is the Avogadro’s number (6.02 \times 10^{23}) , \( h \) is the Plank’s constant (6.62 \times 10^{-34} \text{ m}^2 \text{ kg} / \text{s} ) where \( \Delta S^* \) and \( \Delta H^* \) are the entropy and the enthalpy changes of activation corrosion energies for the transition state complex, respectively. Plotting \( \log (I_{corr}/T) \) versus \( 1/T \) gives straight lines (Fig. 6) from which the activation parameters are determined and represented in Table 4.

![Transition state plot for aluminum corrosion in free and inhibited 2.0M HCl solutions.](image)

**Fig. 6. Transition state plot for aluminum corrosion in free and inhibited 2.0M HCl solutions.**

The data in Table 4 reveal that the presence of theophylline anhydrous increases the value of apparent activation energy of the corrosion process. The increase of the activation energy means a slowdown of the corrosion reaction. Thus, theophylline anhydrous acts as an inhibitor for acid aluminum corrosion via increasing the activation energy. This suggests that the molecules are adsorbed on the aluminum surface forming a barrier for mass and charge transfer between the metal surface and the corrosive environment. Some authors [2, 5, 27] attributed such result to a physical adsorption process of the inhibitor molecules on the metal surface.

**TABLE 4. Thermodynamic parameters of aluminum corrosion reaction in free and inhibited 2.0 M HCl solutions.**

<table>
<thead>
<tr>
<th>Medium</th>
<th>( E_a ) ( \text{kJ.mol}^{-1} )</th>
<th>( -\Delta S^* ) ( \text{kJ.mol}^{-1}\text{K}^{-1} )</th>
<th>( \Delta H^* ) ( \text{kJ.mol}^{-1} )</th>
<th>( \Delta G^* ) (303 K) ( \text{kJ.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free</td>
<td>12.4</td>
<td>0.263</td>
<td>8.65</td>
<td>88.34</td>
</tr>
<tr>
<td>Inhibited</td>
<td>27.87</td>
<td>0.228</td>
<td>24.1</td>
<td>93.20</td>
</tr>
</tbody>
</table>

The change in the free energy of activation \( (\Delta G^\circ) \) for the corrosion process was calculated at 303 K by applying the well-known thermodynamic equation:

\[
\Delta G^\circ = \Delta H^* - T \Delta S^*
\]

The obtained $\Delta G^*$ values were also listed in Table 4. According to the data recorded in Table 4 $\Delta H^*$ has a positive sign, reflecting the endothermic nature of the activation process, for the corrosion reaction. The negative values of $\Delta S^*$ point out to a greater order produced during the process of activation. This can be achieved by the association or fixation process associated with the formation of activated complex with consequent loss in the degrees of freedom of the system during the process [6]. The values of $\Delta G^*$ were positive indicating that the activated complex is not stable. However, $\Delta G^*$ values for the inhibited systems were somewhat more positive than that for the uninhibited systems. This result reveals that, in the inhibited acid solution the activated complex becomes less stable as compared with that in the free acid one. Thus, the presence of inhibitor decreases the probability of activation complex formation.

Conclusions

It was found that theophylline anhydrous acts as good corrosion inhibitor with inhibition efficiency more than 99.9%. The inhibition efficiency was found to increase with inhibitor concentration and the exposure time but decreases by rising the temperature. The adsorption of theophylline anhydrous on aluminum surface follows Langmuir adsorption isotherm. The calculated thermodynamic parameters for the corrosion process in free and inhibited media show that the corrosion process is endothermic and the transition complex is less stable in the presence of theophylline anhydrous. Moreover, the activation energy increased in the presence of theophylline anhydrous.

References


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