Adsorption inhibitive properties of *Rosmarinus officinalis* L. on aluminium AA8011 Alloy in 1.0M HCl

**ABSTRACT**

The adsorption mechanism of *Rosmarinus officinalis* L. as corrosion inhibitor for Al AA8011 alloy in 1.0M HCl was studied using gravimetric method and thermodynamics studies at 303, 313, 323 and 333K. Inhibitor concentrations ranged between 0 and 1000mg/L. Results show that the adsorption mechanism of *Rosmarinus officinalis* L. is via physisorption, generally endothermic and accompanied by a resulting decrease in disorder. Inhibitor efficiency largely decreased with increase in temperature, and decrease in concentration of the extract. The presence of an external magnetic field enhanced the dissolution of passivating Al$_2$O$_3$ films, thereby increasing corrosion rate.

**Keywords:** aluminum; weight loss; acid corrosion; laangmuir; magnetic field

1. **INTRODUCTION**

Aluminium and its alloys are extensively used in construction, transportation and food packaging industries, it is the choice material in fabricating reaction and pressure vessels for chemical and petrochemical applications. This wide range of applications is due to the low price, high strength-to-weight ratio [1] and the readiness of Al to passivate by forming a thin, corrosion resistant, oxide film on its surface, when exposed to the atmosphere [2–6]. However, this protective, oxide film is destroyed when Al comes in contact with very aggressive acidic media like seawater or hydrochloric acid solutions in industries during processes like pickling. Such processes lead to significant metal loss to the presence of Cl$^-$ ions in such media. The addition of small quantities of plant (roots, fruits, leaves or stems) extracts like *Ananas sativum* (pineapple) by [7], *Papaya* peel by [3], *Terminalia ivorensis* (black afara) by [8] and *Rosmarinus officinalis* L. (rosemary plant, which is aromatic, perennial and native to the Mediterranean climate) by [2] into various concentrations of HCl media has been reported to significantly inhibit acid corrosion of Al. These organic inhibitors contain polar atoms like O, P, N and S [9–11] help serve as reaction sites on the adsorbent (metal) surface by displacing water molecules, thereby inhibiting further corrosion [12,13].

The present report is focused on investigating the corrosion inhibition potentials of rosemary leaves (*Rosmarinus officinalis* L.) extract on Aluminium alloy (AA8011) in 1.0M HCl, and the effect of a magnetic field. This study attempts to extend and compare the findings reported in [2] – where *Rosmarinus officinalis* L. with concentrations of up to 1000mg/L was found to be a moderate inhibitor for the Al AA8011 alloy in 0.25M HCl, with an inhibition efficiency of up to 68% – to a solution of 1.0M HCl under the same parameters, i.e. using the gravimetric technique under an exposure time of 3 hours, with inhibitor concentration ranging from 50 to 1000mg/L, and at temperatures of 303K, 313K, 323K and 333K.

2. **EXPERIMENTAL**

The commercial Aluminum sheet used in this study is the AA8011 alloy. On analysis via optical emission spectrometry, its chemical composition in percent weight is: Al–97.856%, Fe–0.901%, Si–
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0.375%, Mg–0.374%, Zn–0.209%, Cu–0.157%, Mn–0.111%, Cr–0.009%, Ti–0.005%, Ni–0.004%, and other trace elements. The Al sheet was cut into specimens of roughly 30mm×30mm×1mm in dimension, each housing a 02mm hole. Each specimen was hand-polished using emery paper, degreased in acetone, rinsed in ethanol, left to dry at room temperature, and their initial weight (\(w_i\)) was obtained using an electronic balance having an accuracy of ±0.001g.

The hydrochloric acid solution used was of analytical grade. A 1.0M concentration was prepared as the corroding media and it had a pH of 0.0 using a pH tester. Freshly harvested rosemary leaves weighing 25g after being left to room-dry were ground using a manual blender and mixed with 300ml of methanol. The resulting mixture was carefully sieved, and the volume of the filtrate was obtained. Concentrations of 50mg/L, 150mg/L, 250 mg/L, 500mg/L and 1000mg/L of the methanolic extract of the rosemary leaves were obtained by introducing measured amounts of the extract into glass vessels containing 300mL of 1.0M HCl.

Using the gravimetric technique, the blank and inhibited experiments were carried out in the glass vessels over a water bath at temperatures of 303K, 313K, 323K and 333K. After an exposure time of 3hours, the specimens were undipped from the HCl solution, quenched in 2.0M solution of Nitric acid, degreased in acetone and rinsed in ethanol, and left to room-dry. Each specimen was re-weighed, to obtain their final weight (\(w_f\)) and then the weight loss (\(\Delta w\)) was computed as:

\[
\Delta w = w_f - w_i
\]

The values for the gravimetric corrosion rate (CR) were obtained using the expression:

\[
CR = \frac{k\Delta w}{\rho At}
\]

where \(\Delta w\), \(\rho\), \(A\), \(t\) and \(k\) are the weight-loss in grams(g), the average density of all the coupons in mm\(^3\), area of the Al coupon in mm\(^2\), exposure time in hours and a constant of 8.75x10\(^{-3}\) respectively.

The surface coverage (\(\theta\)) which quantifies the area of Al specimen covered by the rosemary inhibitor is obtained by:

\[
\theta = \frac{I.E.}{100}
\]

where I. E. is the efficiency of the rosemary extract as a corrosion inhibitor for the Al specimen.

3. RESULTS AND DISCUSSION

3.1, The Gravimetric Method

Figure 1 shows the corrosion rate versus exposure time for Al immersed in 1.0M HCl solution in the absence of an inhibitor for up to 10 days. It can be observed that Al corrosion rate decreases with increase in exposure time as shown in Table 1 and tends to take on a more linear relationship. A similar result was reported by [14].

![Figure 1](image-url)

*Figure 1. Plot of corrosion rate against exposure time for Al alloy in 1.0M HCl solution*

*Slika 1. Kriva brzine korozije u odnosu na vreme izlaganja za Al leguru u rastvoru 1,0M HCl*
3.2. Thermodynamic Studies

Straight lines were obtained from the linearized form of the Arrhenius equation:

$$\ln(CR) = \ln A - \frac{E_a}{RT}$$

As values of $ln(CR)$ were plotted against $\frac{1}{T}$, values for enthalpies ($\Delta H$) and entropies ($\Delta S$) were obtained from the gradient and intercept respectively. Calculated values for $E_a$, $\Delta H$ and $\Delta S$ are recorded in Table 2. It is observed that; values for $E_a$ generally increased with increase in concentration of the *Rosmarinus officinalis* L. leaves extract and $E_a$ were higher than the $E_a$ on the absence of the extract, this indicates a physisorption process. Values of $\Delta H > 0$ obtained were found to be higher in the presence of *Rosmarinus officinalis* L. leaves extract than in its absence. This suggests that the Al dissolution process is endothermic [17] and agrees with results obtained by [16,18].

Small values of $\Delta S < 0$ indicates a decrease in entropy at the transition state. This means the interaction between molecules of the inhibitor and that of the absorbent Al surface is associative rather than dissociative owing to the decrease in disorder. This result is similar to that reported by [19].

![Table 1. Calculated values for the corrosion rate for Al alloy corrosion in 1.0M HCl solution at room temperature for an exposure time of 1 to 10 days](image)

<table>
<thead>
<tr>
<th>Exposure time (days)</th>
<th>Corrosion rate (mm/yr)</th>
<th>Exposure time (days)</th>
<th>Corrosion rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>139.88</td>
<td>6</td>
<td>25.64</td>
</tr>
<tr>
<td>2</td>
<td>82.27</td>
<td>7</td>
<td>22.22</td>
</tr>
<tr>
<td>3</td>
<td>44.11</td>
<td>8</td>
<td>20.20</td>
</tr>
<tr>
<td>4</td>
<td>36.65</td>
<td>9</td>
<td>17.93</td>
</tr>
<tr>
<td>5</td>
<td>30.37</td>
<td>10</td>
<td>15.04</td>
</tr>
</tbody>
</table>

![Table 2. Activation parameters of Al alloy in 1.0M HCl for blank and different concentrations of Rosmarinus officinalis L.](image)

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H^\theta$ (kJ/mol)</th>
<th>$\Delta S^\theta$ (kJ/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.13</td>
<td>-1.51</td>
<td>-0.28</td>
</tr>
<tr>
<td>50</td>
<td>2.16</td>
<td>-0.48</td>
<td>-0.43</td>
</tr>
<tr>
<td>150</td>
<td>6.23</td>
<td>3.59</td>
<td>-1.09</td>
</tr>
<tr>
<td>250</td>
<td>7.58</td>
<td>4.94</td>
<td>-1.31</td>
</tr>
<tr>
<td>500</td>
<td>9.42</td>
<td>6.78</td>
<td>-1.59</td>
</tr>
<tr>
<td>1000</td>
<td>11.66</td>
<td>9.02</td>
<td>-1.95</td>
</tr>
</tbody>
</table>

3.3. Adsorption Studies

The Langmuir isotherm model provided a good fitting for the corrosion data. Using the linearized form of the model as:

$$\ln\left(\frac{C_0}{\theta}\right) = \ln C - \ln k$$

where $C$ and $k$ are the inhibitor concentration and equilibrium constant, respectively.

Figure 2 shows a plot of $\ln\left(\frac{C_0}{\theta}\right)$ against $\ln C$ with values the equilibrium constant ($k$) calculated from the intercept. The Gibb’s free energy was the computed using the expression [20]:

$$\Delta G_{ads} = -RT \ln(S5.5k)$$

where $R$ and $T$ are the molar gas constant and the kelvin temperatures respectively.
Figure 2. Langmuir adsorption isotherm plot for Al alloy corrosion in 1.0M HCl solution for Rosmarinus officinalis L. extract at different temperatures

Slika 2. Langmuir-ov dijagram izoterme adsorpcije za koroziju legure Al u rastvoru 1.0M HCl za ekstrakt Rosmarinus officinalis L. na različitim temperaturama

Good values for the correlation coefficient ($R^2 > 0.998$) and gradients of unity were obtained in Table 3, this indicates a high correlation between the corrosion data and the Langmuir model. We also observe that the values of the equilibrium constant ($k$) decreased with temperature. This suggests that the potency of Rosmarinus officinalis L. extract molecules as a corrosion inhibitor for Al decreased with increase in temperature in a 1.0M HCl solution.

Table 3. Parameters of linear regression from the Langmuir Isotherm plot for Al alloy corrosion in 1.0M HCl solution for Rosmarinus officinalis L. extract at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
<th>Slope</th>
<th>$\ln(k)$</th>
<th>$k$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-11.14</td>
<td>1.1127</td>
<td>-0.40641</td>
<td>1.5014</td>
<td>0.999</td>
</tr>
<tr>
<td>313</td>
<td>-10.84</td>
<td>1.05007</td>
<td>-0.15111</td>
<td>1.1631</td>
<td>0.998</td>
</tr>
<tr>
<td>323</td>
<td>-8.06</td>
<td>1.11268</td>
<td>1.01349</td>
<td>0.3630</td>
<td>0.999</td>
</tr>
<tr>
<td>333</td>
<td>-8.35</td>
<td>1.04531</td>
<td>1.00187</td>
<td>0.3672</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Calculated values of the Gibb’s free energy ($\Delta G$) were negative, thereby signifying a spontaneous adsorption process. This is indicative of physisorption since values of $|\Delta G_{ads}| \leq 20$ kJ/mol have typically been attributed to weak Van der waals or electrostatic forces of interaction between the molecules of the Rosmarinus officinalis L. extract and active sites on the Al alloy surface.

One of the shortcomings of the Langmuir Isotherm model is that it assumes a monolayer adsorption of the inhibitor on the adsorbent surface. For cases where the slope may deviate markedly from unity, we apply the model by Villamil et. al. [21], whose linearized form is given as:

$$\frac{C}{\theta} = \frac{n_w}{k} + n_wC$$

where $n_w$ is number of displaced water molecules from the adsorbent surface. Figure 3 is a plot for values of $C/\theta$ against $C$ where straight lines were obtained from which values of $n_w$ were computed.
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Figure 3. Villamil et. al. adsorption isotherm plot for Al alloy corrosion in 1.0M HCl solution for Rosmarinus officinalis L. extract at different temperatures

Slika 3. Villamil et. al. dijagram izoterme adsorpcije za koroziju Al legure u rastvoru 1,0M HCl za ekstrakt Rosmarinus officinalis L. na različitim temperaturama

On inspection of Table 4, values for the correlation coefficient (\( R^2 > 0.91 \)) are indicative that the Villamil et. al. model is a moderate fit in predicting the corrosion inhibitive behavior of the *Rosmarinus officinalis* L. extract for Al in 1.0M HCl. Values obtained for \( n_w \) increased with increase in temperatures up to 323K, that is to say numerous molecules of water were displaced from adsorbent surface by molecules of the adsorbate. This could also suggest that increasing the temperature can favour multilayer adsorption of the inhibitor molecules at higher concentration of the acidic medium. This agrees with results reported by [2].

Values for the Gibb’s free energy, \( |\Delta G^w_{ads}| \leq 20\text{kJ/mol} \) were obtained, thereby signifying that the molecules of the inhibitor adsorbed on the adsorbate via physical means.

Table 4. Parameters of linear regression from the Villamil et. al. isotherm plot for Al alloy corrosion in 1.0M HCl solution for Rosmarinus officinalis L. extract at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \Delta G_{ads} ) (kJ/mol)</th>
<th>( n_w )</th>
<th>intercept</th>
<th>( k )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>5.08</td>
<td>2.23</td>
<td>927.92</td>
<td>0.0024</td>
<td>0.910</td>
</tr>
<tr>
<td>313</td>
<td>3.37</td>
<td>4.14</td>
<td>837.65</td>
<td>0.0049</td>
<td>0.931</td>
</tr>
<tr>
<td>323</td>
<td>–2.42</td>
<td>11.11</td>
<td>250.70</td>
<td>0.0443</td>
<td>0.996</td>
</tr>
<tr>
<td>333</td>
<td>3.04*</td>
<td>–247.81</td>
<td>41191.40</td>
<td>–0.0060</td>
<td>0.915</td>
</tr>
</tbody>
</table>

Value(s) with asterisks (*) represent the real part of complex numbers.

The negative values for \( n_w \) and \( k \) at \( T=333K \) suggests that very high temperatures greatly limit the area of adsorbent surface on which the molecules of the inhibitor can cover at high concentrations of the corrodant.

The Freundlich model could be applied to multilayer adsorption systems and assumes a heterogeneous adsorbent surface with its active
sites possessing non-uniform affinities for molecules of the adsorbate. However, this model was not a good fit for the corrosion data and this can be due to the limitations of this model as lacks a fundamental thermodynamic basis [22] and not suitable for adsorption data having a wide range of concentration [23].

The Temkin isotherm is another empirical model that is excellent for predicting gas phase equilibrium [22]. It ignores the extremely low and high value of the concentrations and makes up for the limitations of the Langmuir model with the introduction of the interaction parameter.

Figure 4. shows values of $\theta$ against $\ln C$ were plotted for 0.25M, 0.5M, and 1.0M HCl solutions, from which the value for the interaction parameter ($f$), and the equilibrium constant ($k$) were obtained from the gradient and intercept respectively.

![Temkin adsorption isotherm plot for Al alloy corrosion in 1.0M HCl solution for Rosmarinus officinalis L. extract at different temperatures](image)

Table 5. Parameters of linear regression from the Temkin Isotherm plot for Al alloy corrosion in 1.0M HCl solution for Rosmarinus officinalis L. extract at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta C_{ads}$ (kJ/mol)</th>
<th>Slope</th>
<th>$f$</th>
<th>intercept</th>
<th>$k$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-1.31</td>
<td>0.0923</td>
<td>-10.8</td>
<td>-0.3227</td>
<td>0.0303</td>
<td>0.985</td>
</tr>
<tr>
<td>313</td>
<td>-3.10</td>
<td>0.0430</td>
<td>-23.3</td>
<td>-0.1215</td>
<td>0.0593</td>
<td>0.443</td>
</tr>
<tr>
<td>323</td>
<td>-10.36</td>
<td>0.0126</td>
<td>-79.4</td>
<td>-0.0020</td>
<td>0.8532</td>
<td>0.014</td>
</tr>
<tr>
<td>333</td>
<td>30.01</td>
<td>0.0021</td>
<td>-476.2</td>
<td>-0.0312</td>
<td>3.53E-07</td>
<td>0.325</td>
</tr>
</tbody>
</table>

Low $R^2$ values (asides T=273K) as recorded in Table 5 show that the Temkin model is not a good fit for corrosion data.
Negative values for the interaction parameter \( (f) \) were generally negative thereby indicative of lateral repulsion in the adsorbed layer.

**The Effect of an External Magnetic Field**

A variable magnetic field source was used to test for the effect of the presence of a magnetic on the corrosion rate of Al AA8801 alloy in 1.0M HCl. Increase in the input voltage \( (V) \) of the magnetic field source corresponds to an increase in the magnetic field strength \( (B) \) \([2]\):

\[
B = V
\]

Using input voltages of 15.0, 20.0 and 25.0 volts, values of the corrosion rate in various concentrations of the inhibitor obtained were recorded as shown in Table 6.

**Table 6. Values of the corrosion rate at room temperature both in the absence and absence of a magnetic field in 1.0M HCl solution for blank and at various concentration of the inhibitor**

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( B=0 )</td>
</tr>
<tr>
<td></td>
<td>( V=0.0)volts</td>
</tr>
<tr>
<td>Blank</td>
<td>1082.92</td>
</tr>
<tr>
<td>50</td>
<td>1043.54</td>
</tr>
<tr>
<td>150</td>
<td>943.76</td>
</tr>
<tr>
<td>250</td>
<td>862.03</td>
</tr>
<tr>
<td>500</td>
<td>806.67</td>
</tr>
<tr>
<td>1000</td>
<td>751.31</td>
</tr>
</tbody>
</table>

A plot of corrosion rate versus concentration is given in Figure 5 and the results suggest an increase in the corrosion rate of Al in the presence of an externally applied magnetic field than in the absence of it. A similar result was reported by \([24]\).

Furthermore, a concentration of the acid as high as 1.0M could have enhanced the dissolution of passivating \( \text{Al}_2\text{O}_3 \) films \([25]\) thereby leading to a higher corrosion rate in the presence of the magnetic field.

**Figure 5. Plot of corrosion rate against concentration for Al alloy at room temperature both in the absence and absence of a magnetic field in 1.0M HCl solution**

**Slika 5. Krive brzine korozije u odnosu na koncentraciju za Al leguru na sobnoj temperaturi i u odsustvu i u prisustvu magnetnog polja u rastvoru 1,0M HCl**
4. CONCLUSION

The aim of this research was to use thermodynamic parameters and adsorption isotherms to study the corrosion inhibition mechanism of the methanolic extract of Rosmarinus officinalis L. on aluminum AA8801 alloy in 1.0M HCl. The effect of an external magnetic field on the corrosion rate was also studied.

At higher concentration and lower temperature, the extract functioned well as corrosion inhibitor. The $E_a$ values in the presence of the inhibitor were higher than that for the blank, this indicates a physical adsorption process, while increasingly positive values for $\Delta H^o$ suggests the adsorption process took on an endothermic nature, and small, negative values for $\Delta S^o$ characterize a decrease in disorder.

The experimental data fitted well to the Langmuir model ($R^2 > 0.998$) and was a moderate fit to the Villamil et al. isotherm model ($R^2 > 0.91$), but not a good fit for the Freundlich and Temkin models, while the effect of the presence of an external magnetic field served to raise the corrosion rate.

5. REFERENCES


IZVOD

INHIBITORSKA SVOJSTAVA EKSTRAKTA Rosmarinus officinalis L. NA KOROZIJU LEGURE AA8011 U 1,0M HCl

Mekhanizam adsorpcije Rosmarinus officinalis L. kao inhibitora korozije legure Al AA8801 u 1,0 M HCl proučavan je gravimetrijskom metodom i termodinamičkim studijama na 303, 313, 323 i 333 K. Koncentracije inhibitora su se kretale između 0 i 1000 mg/L. Rezultati pokazuju da se mehanizam adsorpcije Rosmarinus officinalis L. odvija putem fiziorspcije, generalno endotermne i praćena je rezultirajućem smanjenjem poremećaja. Efikasnost inhibitora je u velikoj meri opadan sa povećanjem temperature i smanjenjem koncentracije ekstrakta. Prisustvo spoljašnjeg magnetnog polja pojačalo je rastvaranje pasivizirajućih Al2O3 filmova, čime je povećana brzina korozije.

Ključne riječi: aluminijum, gubitak težine, korozija, Langmuir, magnetno polje