A thermometric study on the kinetics of the acid dissolution of aluminium in the presence of Napoleonaea imperialis seeds extract and iodide ions

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Abstract. The dissolution of aluminum alloy AA 1060 in 0.5 M and 1.0 M HCl was investigated using thermometric measurements. The reaction number of the aluminum coupons varied linearly with the concentration of the acid. Addition of Napoleonaea imperialis seed extract to the dissolving aluminum coupons lowered the reaction number in both concentrations of HCl by inhibiting the dissolution process. The inhibition efficiency of Napoleonaea imperialis seed extract was enhanced to a considerable extent in the presence of iodide ions with the synergistic parameter S > 1. The adsorption of Napoleonaea imperialis extract on the aluminium surface best aligned with the Langmuir adsorption isotherm model. The values of the free energy, ∆G_ads, for the adsorption process revealed the process to be spontaneous and physisorptive.

Keywords: aluminium, temperature, reaction number, Napoleonaea imperialis, inhibition efficiency, adsorption isotherm.

1. Introduction

Metals and alloys have numerous applications in industrial installations and equipment, however these metals and alloys are often attacked by corrosion. Metals and alloys are prone to corrosion either by man-made fluids or by natural fluids [1-3]. These reactions may damage the metal simultaneously with consequent loss of cohesive strength. The surface of metallic structures is attacked through the migration of ions away from the surface, resulting in material loss over time [2-5].

According to ASM International 2012, aluminium is an important metal in many industries owing to its many excellent characteristics especially its good electrical and thermal conductivities, low density, high ductility, low cost and availability for the fabrication and construction industries. It is widely used as materials for automobiles, aviation, household appliances, containers, electronic devices, pipes, machinery, and chemical batteries [6, 3-5].

It has been reported that the oxide film on aluminium can readily undergo dissolution in chloride environments. Suitable inhibitors must be used if the life span of this valuable metal must be guaranteed. For this reason the corrosion mechanism of aluminium in chloride solutions has been investigated in a number of studies [7-14]. This has brought about the use of inhibitors which can counteract the corrosive action of such aggressive environments.

Corrosion inhibitors are chemical substances that when added in small concentration to an environment, effectively decreases the corrosion rate [15-20].

Though the use of inhibitors has been one of the best means of protecting metals and alloys against corrosion, however, most of these inhibitors are toxic to the environment [15-20]. In an attempt to find inhibitors which are environmentally friendly, safe and readily available, attention has been drawn to the use of natural products such as plant extracts as corrosion inhibitors [7, 10, 11, 13-16, 18-22]. Napoleonaea imperialis (NI) seed extract contains some saponins, alkaloids, glycosides and proteins [23]. These phytochemicals have structures similar to those of conventional corrosion inhibitors hence their potential to inhibit the corrosion of metals/ alloys in corrosive environments.

This study sets to investigate the dissolution of aluminum in HCl in the presence of NI seeds extract and iodide ions using thermometric measurements.

2. Experimental

2.1. Materials

The reagents used in experiments were purchased from Emole Nigeria Limited, while the aluminium sheet, AA 1060 type and purity 98.5 per cent was obtained from Eastern Chase Aluminium Company, Avu Owerri, in Nigeria.

2.2. Preparation of aluminium coupons

The sheet of aluminium, AA 1060 type and purity 98.5 per cent used for this study was mechanically pressed cut into 3 x 2 cm coupons. These coupons were used as cut without further polishing. However, they were degreased in ethanol, dried in acetone and stored in a moisture free desiccator before their use in the studies.

2.3. Preparation of plant extract

Fresh ripe fruits of NI were harvested from Obinze in Owerri Capital Territory, Imo State, Nigeria. The plant was identified and authenticated by Mr. J. Opayemi, Department of Plant Science & Biotechnology, University of Port Harcourt and voucher sample, UPH 147, deposited at University of Port Harcourt Herbarium. The seeds were separated from their rinds and were air-

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dried, and then crushed to coarse powder at room temperature and weighed. 243 g of the coarse powder was extracted with n-butanol by cold maceration for 48 hours [23].

The process was repeated 5 times using fresh solvent each time. Extracts obtained were combined and concentrated to dryness using a rotary evaporator to yield 24.05 g of sticky dark brown extract.

2.4. Preparation of inhibitor solution
Five different concentrations of NI seed extract (0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L, and 1.0 g/L) were prepared in 0.5 M and 1.0 M HCl solution respectively and were used for the measurements. A blank was also prepared without the inhibitor. The effect of iodide ions on the inhibition efficiency of NI extract was investigated by adding 5 mM KI the different concentrations of NI extract [8, 9, 13, 18].

2.5. Thermometric method
The solutions of HCl were prepared by dilution of analytical grade HCl with distilled water and used as corrodiot. The reaction vessel is a well lagged calorimeter to prevent heat losses. The corrodiot solution was varied at 1.0 M and 0.5 M, while the halide (KI) used had its concentration to be 0.001 M, 0.002 M, 0.003 M, 0.004 M and 0.005 M (for synergism) respectively. The volume of the test solution used was 100 mL. The progress of the corrosion reaction was monitored by determining the changes in temperature with time (each minute for the first five minutes, each five minutes for the next twenty five minutes and each ten minutes for the last thirty minutes) using a calibrated thermometer (0 – 100°C) to the nearest ±0.05 °C. The data was generated for a period of one hour. From the rise in temperature per minute, the reaction number (RN) was calculated using Eq. 1 and 2 [9, 13, 24]:

\[
RN \ (K \ min^{-1}) = \frac{Tm-Ti}{t} \quad (1)
\]

where \( Tm \) is the maximum temperature attained by the system, \( Ti \) is the initial temperature, both in Kelvin, and \( t \) is the time in minutes required to reach the maximum temperature.

From the above equation, the inhibition efficiency (IE) of the used inhibitor was computed using equation (2):

\[
IE\% = \frac{RNf-RNi}{RNf} \times 100 \quad (2)
\]

where \( RNf \) is the reaction number of aqueous acid in the absence of inhibitor, and \( RNI \) is the reaction number of aqueous acid in the presence of inhibitor [9, 13, 24].

3. Results and discussion
3.1. Effect of corrodiot concentration on the corrosion of aluminium
Figure 1 presents the variation of temperature with time for the corrosion of aluminium coupons in 0.5 and 1.0 M HCl respectively. From the plot, it is observed that the dissolution of aluminium starts after a certain time known as the incubation period, from the immersion of the aluminium coupon in the test solution. The incubation time is the time needed by the acid to destroy the pre-immersion oxide film on the surface of the aluminium before a gradual rise in temperature with time to a maximum temperature, \( Tm \). There was a decrease in temperature values after reaching a maximum temperature in the 1.0 M HCl solution.

From Figure 1, it can be observed that the corrosion of aluminium in 1.0 M HCl released more heat resulting in a higher value of \( Tm \) of 322 K (49 °C) at 25 min compared to a \( Tm \) of 311 K (38 °C) at 50 min in 0.5 M HCl. Also, the dissolution of aluminium in 1.0 M HCl took a shorter time of 25 min to attain \( Tm \) as against 50 min in 0.5 M HCl. This is in accordance with the fact that thermodynamically, an increase in HCl concentration gives rise to a corresponding increase in the concentrations of active species as well as increase in the rate of dissolution of aluminium [9, 13, 24].

The reaction number is directly proportional to the corrosion rate of a metal or alloy [13, 24]. Figure 2 shows that the reaction number of aluminium in 0.5M HCl is lower compared its reaction number in 1.0 M HCl. This signifies that an increase in concentration of the corrodiot increased the rate of corrosion of aluminium and hence, the reaction number.

![Figure 1. Variation of temperature (K) with time (min) for the corrosion of aluminium coupons in 0.5 and 1.0 M HCl respectively.](image1)

![Figure 2. Effect of corrodiot concentration on reaction number, RN (K min⁻¹) for the dissolution of aluminium in HCl.](image2)

3.2 Effect of NI seed extract on the corrosion of aluminium in 0.5 and 1.0 M HCl
Figures 3 and 4 present the variation of temperature with time for the corrosion of aluminium coupons in the absence and presence of NI extract in 0.5 and 1.0 M HCl respectively. From the plots, it can be observed that the addition of NI extract to the acid solutions released less

\[
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\text{respectively.}
\]

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\text{number, RN (K min⁻¹) for the dissolution of aluminium in}
\text{HCl.}
\]

\[
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\]

\[
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\text{respectively. From the plots, it can be observed that the}
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\]
heat than was observed in the blank solution (absence of NI). This is reflected in the lower temperature values that were observed and a decreased in $Tm$ values compared to the uninhibited acid solutions. The maximum temperature measured in the uninhibited 0.5 M and 1.0 M HCl solutions were 311 K (38 °C) and 324 K (51 °C) attained after 40 min and 25 min respectively. This corresponds to a RN of 0.45 and 0.76 K/min respectively in both acid concentrations.

Addition of NI extract to the acid solutions caused a decreased in the maximum temperature (307 K and 317 K) and an increase in the time required to reach it (60 mins for both concentrations). This implies that the dissolution of aluminium coupons in the acid solutions was slowed down on addition of NI extract resulting in the inhibition of the corrosion process. This was possible by the adsorption of the seed extract on the surface of the aluminium coupons thereby blocking further attack by the corrosive species [9-11]. Furthermore, increasing the concentration of NI extract led to a decrease in $Tm$, the RN of aluminium and an increase in the inhibition efficiency of NI extract in both 0.5 M and 1.0 M HCl solutions.

Table 1 presents the values of reaction number, inhibition efficiency and surface coverage ($\Theta$) for the dissolution of aluminium in the presence of different concentrations of NI extract in 0.5 M and 1.0 M HCl respectively.

From the results presented on Table 1, it can be observed that the presence of the NI seed extract reduced the reaction number of aluminium thereby inhibiting the corrosion of aluminium in both 0.5 and 1.0 M HCl respectively. The inhibition efficiency of the seed extract was concentration dependent. Inhibition efficiency was found to be 66.70 % and 71.05 % at the optimum concentration of 1.0 g/L in 0.5 M and 1.0 M HCl respectively. This suggests that as the concentration of the plant extract increased, there was an increase in surface coverage of the adsorbed extract on the aluminium coupons which provided a barrier and prevented further dissolution. This result is in agreement with previous studies [7-11, 18, 19].

Table 1. Values of reaction number, inhibition efficiency and surface coverage for the corrosion of aluminium in 0.5 M and 1.0 M HCl with various concentrations of NI extract.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>RN 0.5 M HCl</th>
<th>RN 1.0 M HCl</th>
<th>IE% 0.5 M HCl</th>
<th>IE% 1.0 M HCl</th>
<th>$\Theta$ 0.5 M HCl</th>
<th>$\Theta$ 1.0 M HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.20</td>
<td>0.76</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2 g/L</td>
<td>0.1</td>
<td>0.32</td>
<td>50.00</td>
<td>58.00</td>
<td>0.50</td>
<td>0.58</td>
</tr>
<tr>
<td>0.4 g/L</td>
<td>0.1</td>
<td>0.32</td>
<td>50.00</td>
<td>58.00</td>
<td>0.50</td>
<td>0.58</td>
</tr>
<tr>
<td>0.6 g/L</td>
<td>0.0833</td>
<td>0.23</td>
<td>58.35</td>
<td>69.74</td>
<td>0.58</td>
<td>0.70</td>
</tr>
<tr>
<td>0.8 g/L</td>
<td>0.1</td>
<td>0.25</td>
<td>50.00</td>
<td>67.11</td>
<td>0.50</td>
<td>0.67</td>
</tr>
<tr>
<td>1.0 g/L</td>
<td>0.0666</td>
<td>0.22</td>
<td>66.70</td>
<td>71.05</td>
<td>0.67</td>
<td>0.71</td>
</tr>
</tbody>
</table>

3.3 Effect of KI on the dissolution of aluminium

Figures 5 and 6 present the variation of temperature with time for the corrosion of aluminium coupons in various concentrations of KI in 0.5 and 1.0 M HCl respectively. From the plots, it can be observed that the corrosion of aluminium in the presence of KI gave lower temperature values and $Tm$ than the free acid solution. This implies that KI inhibited the corrosion of aluminium in both concentrations of HCl.

Table 2 presents values of reaction number, inhibition efficiency and surface coverage for the corrosion of aluminium in the presence of various concentrations of KI in 0.5 and 1.0 M HCl respectively.
3.4. Effect of KI and NI seed extract mixture on the corrosion of aluminium

Iodide ion (I\textsuperscript–) is characterized by its strong adsorbability onto the metal surface due to its large ionic radius. This process changes the electrical double layer at the solution side of the interface from positive to negative. This change in the electrical double layer facilitates physical adsorption of the inhibitor cations [25, 26]. Consequently, the protonated phytochemicals in NI extract are able to adsorb electrostatically on the aluminium (electrode) surface covered primarily by adsorbed I\textsuperscript– ions.

Figures 7 and 8 present the variation of temperature with time for the corrosion of aluminium coupons in the absence and presence of various concentrations of NI extract and 5 mM KI solution mixture in 0.5 and 1.0 M HCl respectively. From the plots, it can be observed that the corrosion of aluminium in the presence of NI extract with 5 mM KI solution gave lower temperature values and $T_m$ than the uninhibited solution.

Table 3 presents values of reaction number, inhibition efficiency and surface coverage for the corrosion of aluminium in the presence of various concentrations of NI extract and 5 mM KI solution mixture in 0.5 and 1.0 M HCl respectively.

The values of IE presented on Table 3 shows that the inhibition efficiency of NI seed extract and 5 mM KI mixture were higher at all the concentrations investigated than were obtained for the various concentrations of the seed extract alone (Table 1). This implies that the presence of the iodide ions enhanced the inhibitive and adsorptive behaviour of NI seed extract thereby resulting in higher inhibition efficiency values. Similar results have also been reported by other researchers [8, 13, 18, 25, 26].

**Table 2. Values of reaction number, inhibition efficiency and surface coverage for the corrosion of aluminium in 0.5 and 1.0 M HCl with various concentrations of KI.**

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>RN</th>
<th>IE%</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.133</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>0.001</td>
<td>0.1</td>
<td>0.42</td>
<td>23.08</td>
</tr>
<tr>
<td>0.002</td>
<td>0.0833</td>
<td>0.50</td>
<td>35.92</td>
</tr>
<tr>
<td>0.003</td>
<td>0.0833</td>
<td>0.40</td>
<td>35.92</td>
</tr>
<tr>
<td>0.004</td>
<td>0.0666</td>
<td>0.38</td>
<td>48.77</td>
</tr>
<tr>
<td>0.005</td>
<td>0.0666</td>
<td>0.40</td>
<td>48.77</td>
</tr>
</tbody>
</table>

**Table 3. Values of reaction number, inhibition efficiency and surface coverage for the corrosion of aluminium in the presence of various concentrations of NI seed extract and 5 mM KI solution mixture in 0.5 and 1.0 M HCl respectively.**

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>RN</th>
<th>IE%</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.1333</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>0.001</td>
<td>0.1</td>
<td>0.42</td>
<td>23.08</td>
</tr>
<tr>
<td>0.002</td>
<td>0.0833</td>
<td>0.50</td>
<td>35.92</td>
</tr>
<tr>
<td>0.003</td>
<td>0.0833</td>
<td>0.40</td>
<td>35.92</td>
</tr>
<tr>
<td>0.004</td>
<td>0.0666</td>
<td>0.38</td>
<td>48.77</td>
</tr>
<tr>
<td>0.005</td>
<td>0.0666</td>
<td>0.40</td>
<td>48.77</td>
</tr>
</tbody>
</table>
3.5. Synergism
Synergism is a combined action of a compound greater in total effect than the sum of individual effects. It has become one of the most important factors in inhibition process and serves as a basis for all modern corrosion inhibitor formulation. Synergism of corrosion inhibitors is either due to interaction between components of the inhibitors or due to interaction between the inhibitor and one of the ions present in aqueous solution [8, 9, 13, 18, 25, 26].

Synergistic studies were carried out on the combination of the inhibitor-plant extract (0.2, 0.4, 0.6, 0.8, 1.0 g/L) with 5 mM KI in HCl (0.5 M, 1.0 M) respectively. Synergism parameter (S) of the inhibitor due to halide was calculated using Eq. 3 [8, 9, 13]:

\[
S = \frac{1 - I_a - I_b + I_{ab}}{1 - I_{ab}}
\]

where \(I_a\) and \(I_b\) are inhibition efficiencies of the inhibitor and halide, respectively, and \(I_{ab}\) is the inhibition efficiency of the inhibitor, when it is combined with halide. Values of S calculated are recorded in Table 4.

S approaches 1 when no interaction between the inhibitor compounds exists. When S < 1, the antagonistic interaction prevails, this may be attributed to competitive adsorption [8, 9, 13]. In this study, the values were found to be greater than unity indicating that the adsorption of KI on the surface of aluminium enhanced the adsorption of \(Napoleonaea\) imperialis seed extract on the aluminium surface. From the results obtained (Tables 4), it is obvious that I\(^-\) ions promoted the physical adsorption of NI seed extract on the aluminium surface in both 0.5 M and 1.0 M HCl.

3.6. Adsorption consideration
Adsorption isotherms provide information about the interaction among adsorbed molecules themselves as well as their interactions with the metal surface. The adsorption characteristics of NI seed extract on the aluminium surface was investigated using different adsorption isotherm models. Assuming a direct relationship between inhibition efficiency and surface coverage, surface coverage values for the various concentrations, obtained from the thermometric study were found to align best with the Langmuir adsorption isotherm.

Langmuir adsorption isotherm relates the degree of surface coverage to the concentration of the inhibitor in the bulk electrolyte according to Equation 4:

\[
\frac{C}{\theta} = \frac{1}{k_{ads}} + C
\]

where \(\theta\) is the degree of surface coverage of the inhibitor, \(C\) is the concentration of the inhibitor in the bulk electrolyte and \(k_{ads}\) is the adsorption equilibrium constant [11, 27].

Figures 9 and 10 show the plots of \(C/\theta\) versus concentration for both NI extract and NI + KI. Linear plots were obtained for both plots with the values of \(R^2\) very close to unity (\(R^2 > 0.90\)).

### Table 3. Values of reaction number, inhibition efficiency and surface coverage, for various concentrations of NI seed extract + 5 mM KI mixtures.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>0.5 M HCl</th>
<th>1.0 M HCl</th>
<th>0.5 M HCl</th>
<th>1.0 M HCl</th>
<th>0.5 M HCl</th>
<th>1.0 M HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.15</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0.07</td>
<td>0.1</td>
<td>53.33</td>
<td>75.00</td>
<td>0.53</td>
<td>0.75</td>
</tr>
<tr>
<td>0.4</td>
<td>0.03</td>
<td>0.05</td>
<td>80.00</td>
<td>87.5</td>
<td>0.80</td>
<td>0.88</td>
</tr>
<tr>
<td>0.6</td>
<td>0.025</td>
<td>0.025</td>
<td>83.33</td>
<td>93.75</td>
<td>0.83</td>
<td>0.94</td>
</tr>
<tr>
<td>0.8</td>
<td>0.02</td>
<td>0.022</td>
<td>86.67</td>
<td>94.00</td>
<td>0.87</td>
<td>0.94</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0166</td>
<td>0.02</td>
<td>88.93</td>
<td>95.00</td>
<td>0.89</td>
<td>0.95</td>
</tr>
</tbody>
</table>

### Table 4. Synergism parameter for NI extract + 5 mM KI mixture for the corrosion aluminium in HCl.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>0.5 M HCl</th>
<th>1.0 M HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>48.47</td>
<td>34.94</td>
</tr>
<tr>
<td>0.4</td>
<td>32</td>
<td>29.89</td>
</tr>
<tr>
<td>0.6</td>
<td>30.91</td>
<td>33.43</td>
</tr>
<tr>
<td>0.8</td>
<td>29.61</td>
<td>33.50</td>
</tr>
<tr>
<td>1.0</td>
<td>38.29</td>
<td>33.60</td>
</tr>
</tbody>
</table>

### Figure 9. Langmuir plot for the adsorption of NI extract on aluminium surface.

### Figure 10. Langmuir plot for the adsorption of NI extract + 5 mM KI on aluminium surface.

The equilibrium constant for adsorption \(K_{ads}\) was evaluated from the intercept of the plots. \(K_{ads}\) is related to the free energy of adsorption according to Eq. 5:
\[ \Delta G_{\text{ads}} = -2.303 \times RT \log(55.5 \, K_{\text{ads}}) \]  

(5)

where \( K_{\text{ads}} \) is the adsorption equilibrium constant, \( R \) is the gas constant (8.314 J K\(^{-1}\)mol\(^{-1}\)), \( T \) is the absolute temperature in Kelvin and the value 55.5 is the concentration of water in solution expressed in mol L\(^{-1}\).

\[ \Delta G_{\text{ads}} \] and \( K_{\text{ads}} \) are presented on Table 5.

Table 5. Langmuir parameters for the adsorption of NI seed extract on aluminium surface in 0.5 M and 1.0 M HCl respectively.

<table>
<thead>
<tr>
<th></th>
<th>( K_{\text{ads}} )</th>
<th>( R^2 )</th>
<th>( \Delta G_{\text{ads}} ) (kJ mol(^{-1}))</th>
<th>( K_{\text{ads}} )</th>
<th>( R^2 )</th>
<th>( \Delta G_{\text{ads}} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI</td>
<td>5.8823</td>
<td>0.905</td>
<td>-14.34</td>
<td>0.991</td>
<td>-15.33</td>
<td></td>
</tr>
<tr>
<td>NI+KI</td>
<td>6.4516</td>
<td>0.993</td>
<td>-14.57</td>
<td>16.1290</td>
<td>0.999</td>
<td>-16.84</td>
</tr>
</tbody>
</table>

The low values of \( K_{\text{ads}} \) presented on Table 5 signifies weak interaction between the inhibitor molecules and the aluminium surface while the negative values of \( \Delta G_{\text{ads}} \) shows the spontaneous adsorption of NI extract and NI+KI on the aluminium surface [8, 9, 11, 27].

Also, values of \( \Delta G_{\text{ads}} \) for both NI extract and NI+KI were negatively less than the threshold value of -40 kJ mol\(^{-1}\) required for the mechanism of chemical adsorption. Thus, the adsorption of NI extract and NI+KI on the aluminium surface is not only spontaneous but is consistent with the electrostatic interaction between charged molecules and the charged metal/alloy surface or physisorption [8, 9, 11, 18, 27, 28].

4. Conclusion

The findings of this study showed that Napoleonaea imperialis seeds extract inhibited the corrosion of aluminium in 0.5 M and 1.0 M HCl respectively. The inhibition efficiency of NI seed extract was due to the presence of saponins, flavonoids, cardiac glycosides, alkaloids and proteins. The higher the contaminant (HCl) concentration the higher the rate of aluminium corrosion and reaction number. The adsorption of NI seed extract on the aluminium surface was exothermic and spontaneous. The values of the energetic parameter obtained were found to be greater than unity signifying that the adsorption of the iodide ions on the aluminium surface enhanced the adsorption of NI seed extract on the aluminium surface. The Langmuir isotherm model best described the adsorption of NI seed extract and NI seed extract + KI mixture on the aluminium surface. The adsorptions of NI seed extract and NI + KI mixture on the aluminium surface were spontaneous and physisorptive.

Conflict of interest

The authors confirm that this article content has no conflicts of interest.

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