Original Article

Corrosion inhibition effect of non-toxic $\alpha$-amino acid compound on high carbon steel in low molar concentration of hydrochloric acid

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Abstract

Electrochemical studies of the corrosion inhibition effect of biodegradable 2-amino-4-methylpentanoic acid (LCN) on high carbon steel in 1M HCl acid was evaluated with potentiodynamic polarization technique, weight loss analysis and optical microscopy. Results show the compound to be highly effective with optimal inhibition efficiencies of 87.46% and 85.88% from the electrochemical test with dominant cathodic inhibition behaviour between 0% and 1.88% inhibitor concentration and anodic inhibition behaviour at 2.81% and 5.63% inhibitor concentration due to changes in the effect of lateral repulsion between inhibitor molecules. Thermodynamic calculations showed chemisorption molecular interaction and adsorption onto HCS surface according to Langmuir, Freundlich and Frumkin isotherm models with correlation coefficients of 0.9991, 0.8727 and 0.9782. Statistical analysis showed inhibitor concentration is only relevant variable responsible for inhibition efficiency. Calculated results from predicted corrosion rate values varied at an average value of 53% from experimental results. Optical microscopy images of LCN inhibited and uninhibited HCS samples significantly contrast each.

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1. Introduction

Ferrous alloys are extensively applied in industry such as petrochemical, chemical processing, pharmaceuticals, marine, automobile, mining and extraction, energy and construction industries, etc., as materials of construction for equipment, machines, devices and plants structures. Most industrial environments are highly corrosive to these alloys during application, e.g., hydrochloric acid is used in the petroleum industry for oil well acidizing and in the mining and extraction for pickling and removal of metals from their ores. In most cases, corrosion problems are associated with operating problems and equipment maintenance, leading sometimes to recurrent, partial and even total process shutdown resulting in severe financial and economic losses. They often appear as leaks, rust, pitted holes and deteriorations in tanks, casings, tubing, pipelines, and other equipment. The use of corrosion inhibiting chemicals known as inhibitors has been proven to be one of the most practical techniques of corrosion protection of metals in anion
containing industrial environments such as acid cleaning, oil well acidification, acid pickling and descaling processes [1-4]. Previous research on the use of organic compounds as metallic corrosion inhibitors in acid solutions attests to their generally high performance characteristics; however, their use is limited by their varying levels of toxicity, thus the need for environmentally sustainable substitutes [5-13]. Amino acids belong to the class of non-toxic organic compounds which are highly soluble in aqueous media, rapidly biodegradable and easily produced at high purity with low cost. Their derivatives have been used in previous research experiments to inhibit the corrosion of metals and alloys [14-25]. They contain heteroatoms such as nitrogen, sulphur and oxygen, in addition to multiple bonds in their structure which facilitate adsorption onto metallic surfaces. Their corrosion inhibition performance is subject to their molecular size, molecular mass, internal structure, heteroatoms and adsorption strength. 2-Amino-4-methylpentanoic acid, is an essential branched-chain α-amino acid containing α-amino group, α-carboxylic acid group, an isobutyl side chain and an aliphatic side-chain that is non-linear. It is used in the biosynthesis of proteins in animals and is important for haemoglobin formation. In continuation of inhibitor development and the drive for improved efficiency, this research aims to study and evaluate the electrochemical performance of 2-amino-4-methylpentanoic acid on high carbon steel in dilute hydrochloric acid.

2. Experimental methods

High carbon steel (HCS) obtained commercially has a nominal (wt%) composition as shown in Table 1. The steel specimen were abraded with silicon carbide papers (80, 320, 600, 800 and 1000 grit) after machining, before cleansing with deionized water and acetone, and kept in a desiccator for electrochemical test and corrosion potential measurement according to ASTM G1-03 [26]. The polarization plots were obtained at a scan rate of 0.0015 V/s between potentials of −0.5 V and +1 V according to ASTM G102-89 [27]. A platinum rod was used as the counter electrode and a silver chloride electrode (Ag/AgCl) as the reference electrode. Corrosion current density (Icorr) and corrosion potential (Ecorr) values were obtained using the Tafel extrapolation method. The corrosion rate (C_R) and the inhibition efficiency (η, %) were calculated from the mathematical relationship:

\[ \text{C}_R = \frac{0.0327 \times I_{corr} \times E_{eq}}{D} \]  

(1)

\[ \text{I}_{corr} \] is the current density in A/cm², \( D \) is the density in g/cm³; \( E_{eq} \) is the sample equivalent weight in grams. 0.0327 is a constant for corrosion rate calculation in mm/y [28]. L-2-Amino-4-methylpentanoic acid (LCN) obtained from Sigma Aldrich, USA is a white powdery solid whose molecular structure is shown in Fig. 1. It has a molar mass of 131.17 g/mol. 200 ml of 1 M HCl/0.91%, 1.88%, 2.81%, 3.75%, 4.69% and 5.63% LCN prepared from analar grade of HCl acid (37%) with deionized water. Optical images of steel samples before and after corrosion were analyzed with Omax trinocular metallurgical through the aid of Toupcam analytical software.

Measured HCS coupons separately immersed in 200 ml of the dilute acid test solution for 288 h at 30°C were weighed at 24 h interval according to ASTM G31-72 [29]. Corrosion rate (C_R) is determined as follows as [30];

\[ C_R = \left[ \frac{87.6ω}{\text{DAT}} \right] \]  

(2)

\( ω \) is the weight loss in mg, \( D \) is the density in g/cm³, \( A \) is the total surface area of the coupon in cm² and 87.6 is a constant for corrosion rate determination in mm/y. \( t \) is the time in h. Inhibition efficiency (η) was determined from the equation below;

\[ η = \left[ \frac{ω_2 - ω_1}{ω_1} \right] \times 100 \]  

(3)

\( ω_1 \) and \( ω_2 \) are the mass loss at specific LCN concentrations. Surface coverage was determined from the relationship [31,32]:

\[ θ = \left[ 1 - \frac{ω_2}{ω_1} \right] \]  

(4)

where \( θ \) is the degree of LCN compound, adsorbed per gram of HCS samples. \( ω_1 \) and \( ω_2 \) are the weight loss of each HCS sample at specific concentrations of LCN in the acid solution.

3. Results and discussion

3.1. Potentiodynamic polarization studies

The potentiodynamic polarization scans for the active-passive electrochemical corrosion behaviour of HCS in HCl at 0%-5.63% LCN are shown in Fig. 2. Numerical results of the polarization scans are presented in Table 2. The corrosion potentials of the polarization plots shifts from −0.256 V at 0% LCN to cathodic values of −0.267 V and −0.269 V at low LCN concentrations of 0.91% and 1.88% LCN due to the dominant cathodic inhibiting action of protonated LCN molecules on HCS surface whereby the hydrogen evolution and oxygen reduction reactions are effectively suppressed. This shift in corrosion potential is also due to an active site blocking effect that occurs when an inhibitor is added to a corrosive solution [33]. It is likely the available LCN molecules at the earlier mentioned concentrations precipitated on specific sites on the

<table>
<thead>
<tr>
<th>Element symbol</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Composition (1018CSS)</td>
<td>0.7</td>
<td>0.04</td>
<td>0.05</td>
<td>0.70</td>
<td>98.51</td>
</tr>
</tbody>
</table>
steel’s surface during the inhibition process thereby increasing the surface impedance of the steel. Further increase in LCN concentration (2.81%–5.63% LCN) proportionally shifts the corrosion potential values to anodic potentials probably as a result of total surface coverage by the excess LCN molecules causing inhibition of the surface oxidation of HCS by steric hindrance to the cathodic and mainly the anodic reactions. 

Variation in corrosion rate for HCS at 0% LCN and (0.91%–5.63% LCN) is fundamentally due to the adsorption of LCN compound on HCS surface, thus improving the passivity of the HCS in HCl. The corrosion rates and corrosion current density decreased significantly with increase in LCN concentration. Changes in LCN concentration had no significant effect on the cathodic Tafel slopes between 0.91% and 1.88% LCN. The anodic Tafel slopes are observed to be greater than the respective cathodic Tafel slopes. This is as a result of the anodic exchange-current density values being lesser than those of the cathodic values. The anodic Tafel value at 0% LCN is the product of oxide formation on HCS surface oxides due to the slow electron transfer step [34,35]. Changes in anodic Tafel slope values after 0% LCN and is due to changes in the electrode substrate, rate controlling step and influence of potential controlled conditions resulting from the electrochemical action of LCN. This is further proven from the inhibition efficiency, whose values marginally increased in proportion to concentration. The increase of inhibitor efficiency with increasing of the concentration can be interpreted on the basis of the adsorption amount and the coverage of surfactant molecules, increases with increasing concentrations as earlier mentioned [36]. The maximum change in corrosion potential of HCS for both the anodic and cathodic direction is less than 85 mV; hence LCN is a mixed type inhibitor in HCl solution.

3.2. Inhibition mechanism of LCN

Amino acids are organic compounds containing amine (–NH₂) and carboxyl (–COOH) functional groups, along with a side chain (R group) due to their amphiprotic nature specific to amino acids. LCN being a weak acid releases a proton at low concentrations in the acid solution. During electrochemical reaction the carboxylic acid functional groups (–CO₂H) deprotonates to become negative carboxylates (–CO₂⁻) while the α-amine functional group (NH₃⁺) protonates to become positive α-ammonium groups (+NH₃⁺). The positively charged α-ammonium group predominates at low concentrations while the negatively charged carboxylate ion predominates at higher concentrations. Lone pair of electrons is available on the nitrogen and oxygen atoms; hence coordination of amino acids with metal atoms occurs through these atoms. The flow of electrons from the electron rich centres of LCN to electron deficient centres of HCS metal inhibits the electrochemical processes responsible for corrosion. The observed increase in inhibition efficiency of LCN with increase in concentration, suggests LCN adsorbs on HCS.

3.3. Weight-loss measurement and optical microscopy analysis

Experimental results for weight-loss (\(\omega\)) and corrosion rate (\(C_w\)) of HCS, and LCN inhibition efficiency (\(\eta\)) in 1 M HCl solution at 288 h exposure time are presented in Table 3. Fig. 3(a) and (b) shows the graphical plot of HCS corrosion rate and LCN inhibition efficiency versus exposure time during the exposure period. Optical microscopic images of HCS before corrosion, and after corrosion with and without LCN inhibiting compound are shown from Fig. 4(a) to 5(b) at mag. 40 x. The corrosion rate of HCS at 0% LCN [Fig. 3(a)] decreased for the first 72 h of exposure to 0.0081 mm/y before increasing progressively to 0.0111 mm/y at 288 h during which severe surface oxidation of HCS occurred as depicted by the surface morphology in Fig. 4(b). Numerous micro and macro-pits coupled with a porous texture consisting of hydrated iron (III) oxides and iron (III) oxide-hydroxide. This observation is due to the electrochemical action of Cl⁻ ions, resulting from the disassociation of HCl in H₂O according to the equation below:

\[
\text{HCl(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- (\text{aq})
\]

The Cl⁻ ions in solution reacts with HCS according to the following equation causing the rapid oxidation of HCS:

\[
\text{Fe(s)} + 2\text{HCl(aq)} \rightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2(\text{g})
\]

Continuous deterioration and oxide formation of HCS lead to the formation of pores and channels within the oxide layer which further accelerates the corrosion of the steel. At 0.91% LCN to 5.63% LCN, the corrosion rate of HCS decreased significantly from the onset of the exposure hours (24 h) till 288 h due to the action of LCN molecules in retarding the redox electrochemical reaction of Cl⁻ ions. The optical micrograph in Fig. 5(a) and (b) shows a mildly deteriorated morphology at 0.91% LCN and 5.63% LCN in comparison to Fig. 4(b) due to the electrochemical interaction between the Cl⁻ ions and inhibitor cations. The inhibition efficiency of LCN seems to be more time dependent than its concentration value as its inhibition efficiency tends to increase with time [Fig. 3(b)] at all concentrations studied to peak at values between 72.35% and 85.88% at 288 h. Due to the presence of N and O heteroatom in its molecular structure, the α-amino groups (NH₂⁻) protonates to become positive α-ammonium groups (+NH₃⁺) in the acid solution and inhibits further corrosion of HCS through adsorption via the negatively charged chloride ions, resulting in the pi electrons and unshared electrons pairs forming a strong bond with vacant d-orbital of HCS surface. In the presence of LCN compound, transition from active deterioration of
Table 2 – Potentiodynamic polarization result for HCS in 1 M HCl (0%–5.63% LCN) acid solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LCN conc. (M)</th>
<th>LCN conc. (%)</th>
<th>HCS corrosion rate (mm/y)</th>
<th>LCN inhibition efficiency (%)</th>
<th>Corrosion current (A)</th>
<th>Corrosion current density (A/cm²)</th>
<th>Corrosion potential (V)</th>
<th>Polarization resistance, R_p (Ω)</th>
<th>Cathodic Tafel slope, B_c (V/dec)</th>
<th>Anodic Tafel slope, B_a (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00</td>
<td>0.00</td>
<td>22.13</td>
<td>0.00</td>
<td>2.94E−03</td>
<td>1.91E−03</td>
<td>−0.256</td>
<td>19.65</td>
<td>−7.533</td>
<td>10.770</td>
</tr>
<tr>
<td>B</td>
<td>0.91</td>
<td>6.96E−02</td>
<td>6.22</td>
<td>71.90</td>
<td>8.26E−04</td>
<td>5.36E−04</td>
<td>−0.267</td>
<td>40.61</td>
<td>−7.375</td>
<td>14.950</td>
</tr>
<tr>
<td>C</td>
<td>1.88</td>
<td>1.43E−01</td>
<td>5.36</td>
<td>75.76</td>
<td>7.12E−04</td>
<td>4.62E−04</td>
<td>−0.269</td>
<td>51.25</td>
<td>−7.541</td>
<td>14.080</td>
</tr>
<tr>
<td>D</td>
<td>2.81</td>
<td>2.14E−01</td>
<td>4.37</td>
<td>80.23</td>
<td>5.81E−04</td>
<td>3.77E−04</td>
<td>−0.244</td>
<td>70.65</td>
<td>−8.156</td>
<td>13.380</td>
</tr>
<tr>
<td>E</td>
<td>3.75</td>
<td>2.86E−01</td>
<td>4.08</td>
<td>81.58</td>
<td>5.41E−04</td>
<td>3.51E−04</td>
<td>−0.239</td>
<td>91.26</td>
<td>−8.183</td>
<td>13.230</td>
</tr>
<tr>
<td>F</td>
<td>4.69</td>
<td>3.57E−01</td>
<td>4.92</td>
<td>86.80</td>
<td>3.88E−04</td>
<td>2.52E−04</td>
<td>−0.237</td>
<td>123.67</td>
<td>−8.317</td>
<td>13.850</td>
</tr>
<tr>
<td>G</td>
<td>5.63</td>
<td>4.29E−01</td>
<td>2.78</td>
<td>87.46</td>
<td>3.68E−04</td>
<td>2.39E−04</td>
<td>−0.233</td>
<td>146.91</td>
<td>−8.542</td>
<td>13.420</td>
</tr>
</tbody>
</table>
The inhibition efficiency of chemical compounds is due to the strength of its adsorption on metallic surfaces in corrosive media. Adsorption depends upon the orientation of the inhibitor molecule, and its ionization and polarization. The interaction of inhibitor molecules on metallic surfaces resulting from the aggregation and formation of molecular film on metallic surfaces can be further understood through adsorption isotherms. The isotherms show the phenomenon governing the retention of substances from aqueous solution to solid interphase at a constant temperature and pH. Langmuir, Freundlich and Frumkin gave the best fitting for LCN adsorption on HCS in HCl as shown from Figs. 6–8.

3.4. Adsorption Isotherm

Plots of $C_{LCN}/\theta$ vs $C_{LCN}$ fits with the Langmuir isotherm (Fig. 6), with a correlation coefficient of 0.9991 according to the Langmuir equation below.

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

$\theta$ is the amount of LCN adsorbed per unit gram on HCS surface at equilibrium. $C_{LCN}$ is LCN concentration and $K_{ads}$ is the equilibrium constant of adsorption. The high values of $K_{ads}$ indicate strong adsorption on HCS surface in HCl solution due to the presence of donor atoms of nitrogen in LCN functional groups. Langmuir isotherm assumes that there are fixed number of vacant or adsorption sites available on the metal surface, these sites are of equal dimension and shape on the metal surface, each site can hold a definite amount of molecule resulting in a constant amount of heat energy is released and no lateral interaction between the adsorbed molecules exists.

Table 3 – Results from weight loss analysis at 240 h for HCS in 1 M HCl solution (0%–5.63% LCN).

<table>
<thead>
<tr>
<th>Samples</th>
<th>LCN concentration (%)</th>
<th>LCN concentration (molarity)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mm/y)</th>
<th>LCN inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>1.703</td>
<td>0.0111</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0.91</td>
<td>6.96E−02</td>
<td>0.471</td>
<td>0.0031</td>
<td>72.35</td>
</tr>
<tr>
<td>C</td>
<td>1.88</td>
<td>1.43E−01</td>
<td>0.424</td>
<td>0.0028</td>
<td>75.10</td>
</tr>
<tr>
<td>D</td>
<td>2.81</td>
<td>2.14E−01</td>
<td>0.293</td>
<td>0.0019</td>
<td>82.62</td>
</tr>
<tr>
<td>E</td>
<td>3.75</td>
<td>2.86E−01</td>
<td>0.288</td>
<td>0.0019</td>
<td>83.09</td>
</tr>
<tr>
<td>F</td>
<td>4.69</td>
<td>3.57E−01</td>
<td>0.255</td>
<td>0.0017</td>
<td>85.02</td>
</tr>
<tr>
<td>G</td>
<td>5.63</td>
<td>4.29E−01</td>
<td>0.240</td>
<td>0.0016</td>
<td>85.88</td>
</tr>
</tbody>
</table>

Fig. 3 – Plot of (a) HCS corrosion rate versus exposure time in 1 M HCl. (b) LCN inhibition efficiency versus exposure time in 1 M HCl.

Fig. 4 – Optical microscopic image of HCS at mag. 40× (a) before corrosion, (b) after corrosion in 0% LCN/1 M HCl.
Fig. 5 – Optical microscopic image of HCS at mag. 40× (a) after corrosion in 0.91% LCN/1 M HCl, (b) after corrosion in 5.63% LCN/1 M HCl.

Fig. 6 – Langmuir plot of $\frac{C_{LCN}}{\theta}$ versus LCN concentration in 1 M HCl.

Fig. 7 – Frumkin isotherm plot of $\log[\theta/(1 - \theta)c]$ versus $\theta$ 1 M HCl.

The Frumkin adsorption isotherm assumes metallic surfaces to be heterogeneous and the lateral interaction effect among the adsorbed molecules is apparent according to the equation [42]:

$$\frac{\theta}{1 - \theta} = K_c e^{2x0}. \text{rearranging the equation becomes}$$

$$\log \left[ \frac{\theta}{(1 - \theta)c} \right] = 2.303 \log K + 2a\theta$$

(9)

$\alpha$ is the interaction parameter which describes the molecular interaction in adsorbed layer, and calculated from the slope of the Frumkin isotherm plot. Taking into account, the attraction ($\alpha > 0$), repulsion ($\alpha < 0$) and no interaction ($\alpha = 0$) between the adsorbed species, the isotherm becomes equivalent to the Langmuir isotherm. For +ve $\alpha$, adsorption energy increases with $\theta$, whereas for negative $\alpha$ adsorption energy decreases with $\theta$. $K$ is the adsorption–desorption constant. Plots of $\log[\theta/(1 - \theta)c]$ versus $\theta$ in Fig. 7 showed a correlation coefficient of 0.9782 in HCl.

Freundlich isotherm shows the relationship between adsorbed molecules, their interaction and influence on the adsorption process through molecular repulsion or attraction according to the following equation.

$$\theta = K_c^n$$

(10)

$$\log \theta = n \log C + \log K_{ads}$$

(11)

where $n$ is a constant depending on the characteristics of the adsorbed molecule, $K_{ads}$ is the adsorption–desorption equilibrium constant denoting the strength of interaction in the adsorbed layer. The amount adsorbed on HCS surface represents the sum total of adsorption on the reactive sites [43,44]. The correlation coefficient for Freundlich isotherm plot (Fig. 8) is 0.8727.

3.5. Thermodynamics of the corrosion inhibition mechanism

The strength and type of adsorption of the corrosion inhibition mechanism of LCN on HCS was determined from the thermodynamics of LCN molecular interaction with the steel surface through the equilibrium constant of adsorption of the Langmuir isotherm due to its correlation coefficient approaching unity. Calculated results of Gibbs free energy of adsorption in HCl solution is shown in Table 4, from Eq. (12) [45].

$$\Delta G_{ads} = -2.303 RT \log[55.5K_{ads}]$$

(12)

where 55.5 is the molar concentration of water in the acid solution, $R$ is the universal gas constant, $T$ is the absolute temperature and $K_{ads}$ is the equilibrium constant of adsorption. Negative values of $\Delta G^o_{ads}$ signify spontaneous and stable
adsorption reactions. In HCl solution, the lowest $\Delta G_{\text{ads}}$ value is $-33.64$ kJ mol$^{-1}$, at the highest LCN concentration and the highest $\Delta G_{\text{ads}}$ value of $-36.06$ kJ mol$^{-1}$ occurred at the lowest LCN concentration on HCS surface. These $\Delta G_{\text{ads}}$ values in HCl solution depict chemisorption adsorption reaction mechanisms, i.e., chemical interaction of LCN molecules through charge sharing and covalent bonding on the steel's surface. The chemisorption of the LCN cationic molecules could also occur due to the interaction between the $d$ orbital of the oxidized HCS surface which involved displacement of H$_2$O molecules from the metal surface, and the lone sp$^3$ electron pairs present on the N, atoms of LCN [46,47]. The result also shows that lateral interaction according to Frumkin adsorption isotherm among the inhibitor species tends to be repulsive with increase in LCN concentration hence the decrease in $\Delta G_{\text{ads}}$ value.

3.6. Analysis of variance

Statistical analysis at a confidence level of 95% (significance level of $\alpha = 0.05$) was used to calculate the statistical significance of LCN concentration and time of exposure on LCN inhibition efficiency results from weight loss throughout the exposure period of 288 h according to Eqs. (13)–(15).

The sum of squares among columns (LCN concentration)

$$SS_c = \sum \frac{T^2}{n} - \frac{T^2}{N}$$

(13)

Sum of squares among rows (time of exposure)

$$SS_r = \sum \frac{T^2}{nc} - \frac{T^2}{N}$$

(14)

Total sum of squares

$$SS_{\text{Total}} = \sum x^2 - \frac{T^2}{N}$$

(15)

Results from statistical analysis in Table 5 showed that LCN inhibitor concentration is the only statistically relevant variable responsible for LCN inhibition efficiency results with significance factor value (F-value) of 37.12 in HCl solution [48]. These values are much greater than the control significance factor (significance F) value of 2.42, corresponding to a percentage significance of 119.2. The effect of LCN inhibitor concentration on inhibition efficiency values is deemed unlikely to have occurred by chance, but significantly influenced the performance of LCN inhibitor as against the time of exposure. The results show that changes in LCN concentration has strong influence the electrochemical corrosion behaviour and inhibitor protection of LCN on HCS in contrast to exposure time whose results show it is statistically irrelevant. LCN is a concentration dependent inhibitor.

3.7. Theoretical model for corrosion rate

Corrosion rates values have been known not to be fixed values due to the unpredictable nature of corrosion [49]. Most often the corrosion process is often controlled by stochastic phenomena; as a result, mathematical models with appropriate mathematical equations can be used to accurately predict the corrosion rate of metals before the corrosion occurs. The theoretical corrosion rate model used was developed by dimensional analysis using the Buckingham–Pie technique to obtain the expression for the theoretical corrosion rate model as [50–53];

$$C_{\text{Rm}} = Dl \left( \frac{VT_n}{AD} \right)$$

(16)

where $D$ is the density of the fluid, $V$ is the velocity of the fluid, $\mu$ is the viscosity of the fluid, $T$ is the exposure time and $A$ is the area of the specimen. $D_l$ is the dimensionless corrosion rate parameter.

Table 4 – Results for Gibbs free energy ($\Delta G_{\text{ads}}$), surface coverage ($\theta$) and equilibrium constant of adsorption ($K_{\text{ads}}$) for LCN adsorption on HCS in 1 M HCl solution.

<table>
<thead>
<tr>
<th>Samples</th>
<th>LCN concentration (M)</th>
<th>Surface coverage ($\theta$)</th>
<th>Equilibrium constant of adsorption ($K$)</th>
<th>Gibbs free energy, $\Delta G$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>6.96E–02</td>
<td>0.724</td>
<td>37 620.5</td>
<td>36.06</td>
</tr>
<tr>
<td>C</td>
<td>1.43E–01</td>
<td>0.751</td>
<td>21 994.4</td>
<td>34.63</td>
</tr>
<tr>
<td>D</td>
<td>2.14E–01</td>
<td>0.828</td>
<td>22 647.2</td>
<td>34.78</td>
</tr>
<tr>
<td>E</td>
<td>2.86E–01</td>
<td>0.831</td>
<td>17 182.2</td>
<td>34.12</td>
</tr>
<tr>
<td>F</td>
<td>3.57E–01</td>
<td>0.850</td>
<td>15 878.6</td>
<td>33.92</td>
</tr>
<tr>
<td>G</td>
<td>4.29E–01</td>
<td>0.859</td>
<td>14 183.4</td>
<td>33.64</td>
</tr>
</tbody>
</table>

Table 5 – Analysis of variance for LCN inhibition efficiency on HCS in 1 M HCl at 95% confidence level.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>Mean square ratio (F)</th>
<th>Significance F (min. MSR at 95% confidence)</th>
<th>F (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCN concentration</td>
<td>315 583.48</td>
<td>5</td>
<td>63 116.70</td>
<td>37.12</td>
<td>2.53</td>
<td>119.2</td>
</tr>
<tr>
<td>Exposure time</td>
<td>−144 278.13</td>
<td>11</td>
<td>−13 116.19</td>
<td>−7.71</td>
<td>2.42</td>
<td>−54.5</td>
</tr>
<tr>
<td>Residual</td>
<td>93 530.79</td>
<td>55</td>
<td>1700.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>264 836.15</td>
<td>71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
correction factor expressing in terms of known experimental parameters as follows:

\[ C_{RM\text{mod}} = D_L \left( \frac{m \cdot s \cdot kg/m^2}{A \cdot \rho} \right) = D_L \left( \frac{kg}{s \cdot A \cdot \rho} \right) \]  \hspace{1cm} (17)

\[ C_{RM} = D_L \left( \frac{W_L}{T \cdot A \cdot \rho} \right) \]  \hspace{1cm} (18)

\[ D_L \] can be obtained by writing Eq. (18) in a straight line equation, \( y = mx + c \) as

\[ \ln \left( \frac{1}{C_R} \right) = \ln \left( A_D \right) + \ln \left( \frac{T}{W_L} \right) \]  \hspace{1cm} (19)

\( m \) is the slope of the equation and \( c \) is the intercept which corresponds to \( \ln(A_D/D_L) \). The experimental corrosion rate data of HCS in the acid solution at specific LCN concentrations in **Table 6** was used to plot the graph of \( \ln(1/C_R) \) vs \( \ln(T/W_L) \). The Newton non-linear regression method of polymath was used to fit linear equation to the experimental plots was generated. The intercepts from those equations were equated to obtain the value of dimensionless corrosion rate correction factor \( D_L \) which was substituted in the developed empirical model equation for determining the theoretical corrosion rate values. The corrosion rate predicted by the model equations were plotted and compared with experimental corrosion rate in **Figs. 9–12**. The predicted corrosion rates differed from the experimental corrosion rates by an average value of 53%.

### 4. Conclusion

LCN performed effectively on the corrosion inhibition of high carbon steel in HCl acid solution from potentiodynamic polarization analysis, weight loss test. Corrosion inhibition efficiency results were proportional to inhibitor concentration. The organic compound adsorbed onto the steel through chemisorption mechanism according to the Langmuir, Freundlich and Frumkin adsorption isotherm. Statistical analysis showed inhibitor concentration is the only relevant variable responsible for inhibition efficiency. Calculated results from predicted corrosion rate values varied from experimental results but followed the same trend. Identified functional groups completely adsorbed onto both steels from analysis of the adsorption spectra. The optical images of the inhibited steel samples slightly contrast the images without LCN compound.

### Conflicts of interest

The author declares no conflicts of interest.

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