Synthesis and Application of 1,7− bis (2-Hydroxy Benzamido)-4-Azaheptane an Corrosion Inhibitor of Mild Steel in Molar Hydrochloric Acid Medium

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The inhibitor effect of 1,7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃ on the corrosion of mild steel in 1M hydrochloric acid (HCl) has been investigated at 308 K using weight loss measurements and electrochemical techniques (impedance spectroscopy and polarisation curves). Inhibition efficiency is dependent upon the 1,7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃ concentration and its inhibition efficiency increases with the increase of concentration of inhibitor to attain 96 % since 10⁻³M. Polarisation curves indicate that 1,7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃ act essentially as mixed inhibitors. EIS measurements show an increase of the transfer resistance with the inhibitor concentration. The temperature effect on the corrosion behaviour of steel in 1M HCl without and with the inhibitor at 10⁻³M was studied in the temperature range from 308 to 333 K, the associated activation energy have been determined. Adsorption of 1,7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃ on the mild steel surface in 1M HCl follows the Langmuir isotherm model. Significant correlations are obtained between inhibition efficiency with the calculated chemical indexes, indicating that variation of inhibition with structure of the inhibitor may be explained in terms of electronic properties.

Keywords: Benzamide; steel; Hydrochloric acid; Corrosion inhibition; Adsorption

1. INTRODUCTION

An important practical application of such phenomena is corrosion inhibition. Numerous investigations have been performed on the inhibition of iron and steel alloy by using of organic
compounds [1-13]. Molecular structure of inhibitors has clearly been established as a major influence on corrosion inhibition. Organic compounds containing electronegative functional groups and π-electron in triple or conjugated double bonds are usually good inhibitors [3, 14, 15]. Heteroatom’s as oxygen, nitrogen, phosphorus and sulfur as well as aromatic ring in their structure are the major adsorption centres. Unfortunately, most corrosion inhibitors used in aqueous heating and cooling systems are health hazards. Their toxic properties are caused by the aromatic and N-containing heterocyclic compounds, which are used widely in pickling processes and in the oil industry [16-18]. Research has focused on the other types of nontoxic compounds organic compounds have been used as good corrosion inhibitors [19-24].

Of practical interest in the general field of organic inhibitors are the nature of the chemical bond at the metal surface and an explanation of why these substances often provide such excellent protection when adsorbed. Therefore, they minimise the direct interaction between the metal and corrosive agents. In some cases, the coordination of the inhibitor molecules to the surface is weak, and their presence in the corrosive solutions required maintaining the desired concentration of these agents to attain a minimal protection of the metal [19-21, 25, 26]. The inhibition effectiveness might be due to the formation of thin layers of iron-inhibitor complexes [27-35]. To this subject, in the past few decades numerous investigations were performed using the traditional electrochemical methods [36-41].

In the present work, we aimed at investigating the corrosion inhibition of steel in 1M HCl by 7− bis (2-hydroxy benzamido)-4-azaheptane H4L3 organic compounds (schema 1) and to observe any correlation between molecular structure of 7− bis (2-hydroxy benzamido)-4-azaheptane H4L3 and their inhibit rice action. The behaviour of steel in 1M HCl without and with 7− bis (2-hydroxy benzamido)-4-azaheptane H4L3 was studied using gravimetric, electrochemical impedance and potentiodynamic measurements.

2. EXPERIMENTAL DETAILS

2.1. Inhibitors

The organic compound tested as corrosion inhibitors is characterised by NMR and IR techniques. 1,7– bis (2-hydroxy benzamido)-4-azaheptane H4L3 is prepared in the laboratory of Laboratory of Inorganic Chemistry and Environment (LCIE), faculty of Sciences, Tlemcen, Alger, according to a previously described procedures, respectively. Microanalyses were performed by Perkin–Elmer 2400 elemental analyzer. IR spectra were measured in the 400–4000 cm-1 range on a 9800 FTIR spectrometer (Perkin–Elmer). Samples were run as KBr pellets and 1H NMR spectra on an AC 250 FT spectrometer Bruker. Chemical shifts are given in ppm versus TMS (1H) using DMSO-d6 as the solvent [42]. The ligands were characterized by 1H and by 13C NMR in DMSO-d6 (d, ppm; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets; q, quadruplet).

The Synthesis of 1,7– bis (2-hydroxy benzamido)-4-azaheptane H4L3. A mixture of phenylsalicylate (0.0428 g, 2.10⁻⁴ mol), 3,3’-diamino-bis-propylamine instead (0.011 g, 10⁻⁴ mol) and
N-(2-aminoethyl)-1,3 propane diamine, (1 g, 1 \( \cdot 10^{-2} \) mol) in 2-propanol (40 mL), were used as purchased. High-grade solvents (acetonitrile, diethyl ether, DMSO, 2-propanol and methanol) were used for the syntheses of the ligands without further purification. The 7− bis (2-hydroxy benzamido)-4-azaheptane \( \text{H}_4\text{L}_3 \) compound was stirred at 75°C for 2h to give \( \text{H}_4\text{L}_3 \) as an oily product. Yield: 72%.

Anal. Calc. for \( \text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_4 \): C, 64.67; H, 6.78; N, 11.31. Found: C, 64.70; H, 6.71; N, 11.28%. \( ^1\text{H} \) NMR (250 MHz, 20 °C) \( \delta \): 9.11 (s, 2H, OCNH), 7.94 (dd, J = 1.5 and 8 Hz, 2H, C(6)H), 7.47 (td, J = 1.5 and 8 Hz, 2H, C(4)H), 7.00 (d, J = 8 Hz, 2H, C(3)H), 6.98 (t, J = 8 Hz, 2H, C(5)H), 3.52 (q, J = 6.4 Hz, 4H, OCNHCH\(_2\)), 2.89 (t, J = 6.4 Hz, 4H, NHCH\(_2\)), 1.81 (q, J = 6.8 Hz, 4H, CH\(_2\)). \( ^{13}\text{C}\{^1\text{H}\} \) NMR (62.896 MHz, 20_C): d 39.3 (s, CH\(_2\)NHCO), 47.1 (s, CH2NH), 116.1 (s, ArC), 117.8 (s, ArC(5)H), 119.3 (s, ArC(3)H), 132.1 (s, ArC(6)H), 133.5 (s, ArC(4)H), 154.4 (s, ArC(2)OH), 166.0 (s, OCNH). Characteristic IR absorptions, (thin film): 3445, 3220, 1613 cm\(^{-1}\). The molecular formula of the inhibitor is shown in schema 1.

![Scheme 1. Structure of 1,7− bis (2- hydroxy benzamido)-4-azaheptane (H4L3)](image)

2.2. Methods and materials

Prior each gravimetric or electrochemical experiment, the surface of the specimens was abraded successively with emery paper. The specimens are then rinsed with acetone and bid stilled water. Weight loss was measured on sheets of steel of 2cm\(^2\) apparent surface area. The samples were
polished successively with different emery paper up 1000 grade, washed with distilled water, degreased and dried before being weighed and immersed in 100 ml of the corrosive medium. The aggressive solution (1M HCl) was prepared by dilution of analytical-grade 37% HCl with doubly distilled water. All tests were obtained in magnetically stirred and deaerated solutions. The immersion time for the weight loss measurements was 6 hours at 308K. The chemical composition of mild steel is given in Table 1:

<table>
<thead>
<tr>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%S</th>
<th>%P</th>
<th>%Cu</th>
<th>%Ni</th>
<th>%Cr</th>
<th>%N</th>
<th>%O</th>
<th>%Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.012</td>
<td>0.01</td>
<td>0.07</td>
<td>0.006</td>
<td>0.008</td>
<td>0.025</td>
<td>0.020</td>
<td>0.015</td>
<td>0.042</td>
<td>0.072</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Electrochemical impedance spectroscopy (EIS) and is carried out with a voltalab PGZ 100 electrochemical system at $E_{\text{corr}}$ after immersion in solution. After determination of the steady-state current at a given potential, sine wave voltage (10mV) peak to peak, at frequencies between 100 kHz and 10 mHz is superimposed on the rest potential. Computer programs automatically controls the measurements performed at rest potentials after 30 min of exposure. EIS diagrams are given in the Nyquist representation.

The potentiodynamic current-voltage characteristics are recorded also with a voltalab PGZ 100, piloted by ordinate, at a scan rate of 1 mV/s. The potential started from cathodic to anodic potential. Before recording each curve, the working electrode is maintained with its free potential of corrosion for 30 min. We used for all electrochemical tests a cell with three electrodes thermostats with double wall (Tacussel Standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode are used as reference and Auxiliary electrodes, respectively. The working electrode is in form of disc from steel of the surface 1 cm$^2$.

2.3. Computational Chemistry

All calculations are performed using ArgusLab 2.0, Chem3D Ultra 8.0 and Gaussian 98 package software’s. The following quantum chemical indices are considered: the energy of the highest occupied molecular orbital ($E_{\text{HOMO}}$), the energy of the lowest unoccupied molecular orbital ($E_{\text{LUMO}}$), $\Delta = E_{\text{HOMO}} - E_{\text{LUMO}}$, total charge density calculated by extended Huckel, and the dipole moment ($\mu$).

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The effect of addition of 1,7– bis (2- hydroxy benzamido)-4-azaheptane H$_2$L$^3$ compound tested at different concentrations on the corrosion of steel in 1M HCl solution was studied by weight loss at 308K after 6h of immersion period. Inhibition efficiency ($E_w$ %) is calculated as follows:
\[
E_w = 100 \times \left(1 - \frac{W_{\text{corr}}}{W_0^{\text{corr}}} \right) \quad (1)
\]

\(W_{\text{corr}}\) and \(W_0^{\text{corr}}\) are the corrosion rates of steel in the presence and absence of the organic compounds, respectively.

**Table 2.** Corrosion parameters obtained from weight loss measurements for mild steel in 1 M HCl containing various concentrations of \(\text{H}_4\text{L}^3\) at 308 K at 6h.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>(W_{\text{corr}}) (mg/cm².h)</th>
<th>EW%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>2,150</td>
<td>-</td>
</tr>
<tr>
<td>10-3</td>
<td>0,075</td>
<td>96,51</td>
</tr>
<tr>
<td>5.10-4</td>
<td>0,112</td>
<td>94,79</td>
</tr>
<tr>
<td>10-4</td>
<td>0,144</td>
<td>93,30</td>
</tr>
<tr>
<td>5.10-5</td>
<td>0,197</td>
<td>90,83</td>
</tr>
<tr>
<td>10-5</td>
<td>0,264</td>
<td>87,72</td>
</tr>
<tr>
<td>10-6</td>
<td>0,331</td>
<td>84,60</td>
</tr>
</tbody>
</table>

Table 2 shows the inhibition efficiency for different concentrations of 1,7− bis (2- hydroxy benzamido)-4-azaheptane \(\text{H}_4\text{L}^3\) organic compound studied in 1M HCl. It’s clear that the addition of 1,7− bis (2- hydroxy benzamido)-4-azaheptane \(\text{H}_4\text{L}^3\) reduces the corrosion rate in HCl 1M solution. The inhibitory effect increases then with the increase of 1,7− bis (2- hydroxy benzamido)-4-azaheptane \(\text{H}_4\text{L}^3\) concentrations. E% reaches a maximum of 96.5% at \(10^{-3}\) mol/l for \(\text{H}_4\text{L}^3\). The plausible mechanism for corrosion inhibition of mild steel in 1M HCl by \(\text{H}_4\text{L}^3\) may be explained on the basis of adsorption behaviour. The adsorption of the \(\text{H}_4\text{L}^3\) molecule with the metal surface is through the already adsorbed [43-46].

The adsorption of the 1,7− bis (2- hydroxy benzamido)-4-azaheptane \(\text{H}_4\text{L}^3\) molecules could occur due to the formation of links between the d-orbital of iron atoms, involving the displacement of water molecules from the metal surface, and the lone electron pairs. It was shown that the protective properties of such compounds depend upon their ability to reductive corrosion rate and are enhanced at higher electron densities around the nitrogen atoms specially [3, 14, 16-18]. The 1,7− bis (2- hydroxy benzamido)-4-azaheptane \(\text{H}_4\text{L}^3\) compound containing electron negative function groups and \(\pi\) electrons conjugated are usually good inhibitors. They reported that the nitrogen atoms is the adsorption centres for their interaction with the metal surface [3, 4, 14, 47-53]. The inhibition efficiencies of 1,7− bis (2- hydroxy benzamido)-4-azaheptane \(\text{H}_4\text{L}^3\) compound are understandable from the delocalisation \(\pi\) electron who permitted essentially to reinforce this interaction.

Figure.1 illustrates the variation of the inhibition efficiency, \(E_w\)\%, versus the concentration of \(\text{H}_4\text{L}^3\). Inspection of these data reveals that the protection efficiency increases with increasing the concentration of the inhibitor and reaches a maximum (96.5 \%) at \(10^{-3}\) M. The corrosion inhibition can be attributed effectively to the adsorption of \(\text{H}_4\text{L}^3\) molecule at the steel acid solution interface.
Figure. 1. Variation of the inhibition efficiency with the logarithmic concentration of H₄L³ for the steel in 1M HCl

It is found from this table that 1,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ who have a nitrogen atom in their cyclic part act as a good inhibitor at a concentration of 10⁻³M. We may conclude that 1,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ is a best inhibitor of mild steel corrosion in 1M HCl solution.

3.2. Polarisation measurements

Current–potential characteristics resulting from cathodic and anodic polarisation curves of steel in 1M HCl in presence of the 1,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ at various concentrations are evaluated. The cathodic Tafel plots of 1,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ are shown in Figure 2, Table 3, collects electrochemical parameters and inhibition efficiencies (Eᵢ) are determined by:

\[
Eᵢ\% = \left(1 - \frac{I_{corr}}{I^{o}_{corr}}\right) \times 100
\]  

(2)

I_{corr} and I^{o}_{corr} are the corrosion current density values with and without the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.
Figure 2. Cathodic and anodic polarisation curves of iron in 1M HCl at different content of 1,7– bis (2- hydroxy benzamido)-4-azaheptane H₄L₃.

The cathodic and anodic polarisation curves of steel in hydrochloric acid in the absence and presence of 1,7– bis (2- hydroxy benzamido)-4-azaheptane H₄L₃ at different concentrations of the tested inhibitors are shown in Figures 2. Table 3 gives the corresponding electrochemical parameters values of corrosion potentials E_{corr}, corrosion current I_{corr}, cathodic Tafel slope b_c, b_a and inhibition efficiencies E% for different concentrations of compounds derived from the potentiodynamic polarisation curves.

Table 3. Polarisation parameters and the corresponding inhibition efficiency of mild steel corrosion in 1M HCl containing different concentrations of H₄L₃ at 308 K.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (mol/l)</th>
<th>Ecorr (mV/SCE)</th>
<th>b_c (mV/dec)</th>
<th>b_a (mV/dec)</th>
<th>Icorr (mA/cm²)</th>
<th>EI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanc</td>
<td>HCl 1M</td>
<td>-470</td>
<td>118</td>
<td>61,3</td>
<td>0,2102</td>
<td>-</td>
</tr>
<tr>
<td>H4L3</td>
<td>10-3</td>
<td>-449</td>
<td>115</td>
<td>53,1</td>
<td>0,005</td>
<td>97,62</td>
</tr>
<tr>
<td></td>
<td>5.10-4</td>
<td>-449</td>
<td>124</td>
<td>57,5</td>
<td>0,0106</td>
<td>94,96</td>
</tr>
<tr>
<td></td>
<td>10-4</td>
<td>-468</td>
<td>133</td>
<td>73,6</td>
<td>0,0722</td>
<td>65,65</td>
</tr>
<tr>
<td></td>
<td>10-5</td>
<td>-488</td>
<td>124</td>
<td>78,3</td>
<td>0,1054</td>
<td>49,85</td>
</tr>
<tr>
<td></td>
<td>10-6</td>
<td>-479</td>
<td>127</td>
<td>61,8</td>
<td>0,1439</td>
<td>31,54</td>
</tr>
</tbody>
</table>

E_{corr} values for different systems obtained under free condition are given in table 2. All concentration of ,7– bis (2- hydroxy benzamido)-4-azaheptane H₄L₃ not affect significantly E_{corr}. It
reported out that if the inhibition is due to the geometric blocking effect the shift of corrosion potential will be negligible ($\Delta E_{corr}$ will be zero) as the inhibitor is added to the solution [14, 15, 33, 54, 55].

The inhibition for this system cannot be caused by the active sites blocking effect, but may be due in the main to the geometric blocking effect. Positive values of E% indicated corrosion inhibition, and negative values showed corrosion acceleration [16-18, 56, 57].

It is obvious that only in the case of the geometric blocking effect does the inhibition efficiency (E%) equal the coverage of the adsorbed inhibitive species ($\theta$) on the metal surface.

Table I shows that the values of $I_{corr}$ decrease with the rise of H4L3 concentration. We note that the corrosion current densities were significantly reduced in the presence of H4L3 and it became only 0.005mAcm$^{-2}$ to 0.1439mAcm$^{-2}$ respectively at 10$^{-3}$M and at 10$^{-6}$M. The addition of ,7− bis (2-hydroxy benzamido)-4-azaheptane H$_4$L$_3$ at different concentrations led to a decrease in the cathodic current densities, which was pronounced at 10$^{-3}$M, its E% value was maximum (97.6%).

The anodic and cathodic Tafel slopes of 118 and 127mV/dec. for cathodic and anodic Tafel slopes, respectively. The Tafel slope was sensibly no affected by addition of different concentrations of ,7− bis (2- hydroxy benzamido)-4-azaheptane H$_4$L$_3$. The parallel Tafel lines indicated that the mechanism of the hydrogen discharge reaction was not modified in ,7− bis (2- hydroxy benzamido)-4-azaheptane H$_4$L$_3$-containing solution [1-3, 14, 47, 48].

The parallel Tafel curves obtained indicate that hydrogen evolution reaction is activation controlled and the addition of H$_4$L$_3$ does not modify the mechanism of this process. Being weakly basic, the peptides, rapidly protonated in acid solutions, exist in their cationic form. Due to electrostatic attraction, the inhibitors are strongly adsorbed onto the electron-rich areas blocking the cathodic sites. This is in agreement with increase of the cathodic over potential and shift of the steady corrosion potential to less noble direction in presence of inhibitors.

The anodic curves without and with 7− bis (2- hydroxy benzamido)-4-azaheptane H$_4$L$_3$ show that the inhibition mode depended upon electrode potential. In the case where the corrosion inhibition depends on the potential of the electrode, the observed phenomena is generally described as corrosion inhibition of the interface associated with the formation of a protective layer of adsorbed inhibition species at the electrode surface [15-18, 42, 56-59].

We conclude that the 7− bis (2- hydroxy benzamido)-4-azaheptane H$_4$L$_3$ has effect on the cathodic and anodic behaviour of steel. Then, we may conclude that 7− bis (2- hydroxy benzamido)-4-azaheptane H$_4$L$_3$ acts as a mixed inhibitor.

3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) becomes a very important tool in the study of the inhibition of corrosion of metals. This method permits to impose a small sinusoidal excitation to an applied potential and then the electrochemical interface metal/solution offers impedance. From the various impedance data, interfaces are often described by equivalent circuits involving resistors, capacitors and sometimes inductances. The various electrochemical reactions involve the formation of electrical double layer.
The inhibitive performances of organic inhibitors are widely discussed on the basis of EIS characteristics [14, 47, 48]. EIS technique has been used to evaluate the efficiency of some organic substances as inhibitors for corrosion of iron in acids and others [1-3, 14, 47, 48].

Encouraging results obtained by weight loss and stationary methods have incited us to study the inhibitory effect of 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ in mild steel in 1M HCl solution by the use of EIS measurements. The corrosion behaviour of steel, in the absence and presence of 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ compound is also investigated by the electrochemical impedance spectroscopy (EIS) at 308 K after 30 min of immersion. The charge-transfer resistance (Rₜ) values were calculated from the difference in impedance at lower and higher frequencies. The charge transfer-resistances (Rₜ) values were calculated from the difference in impedance at low and high frequencies [1-3, 14, 47]. The double layer capacitance (Cₜ) was obtained at the frequency fₘ at which the imaginary component of the impedance is maximal (Z_i, max) by the equation (4):

$$C_{dl} = \frac{1}{2 \pi f_m R_t}$$  \hspace{1cm} (3)

The inhibition efficiency obtained from the charge transfer-resistance was determined by:

$$E_{Rt} (%) = \frac{R'_t - R_t}{R'_t} \times 100$$  \hspace{1cm} (4)

Where Rₜ and R't are, respectively, the transfer-resistances values without and with addition of inhibitor.

![Figure 3](image-url)

**Figure 3.** Impedance diagrams of iron in 1M HCl at $E_{corr}$ with and without 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ at different concentrations.
Typical Nyquist diagrams obtained in the presence of 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ compound at 10⁻³M are shown in Figure 3. the deduced impedance parameters as transfer-resistance Rₜ (Ω.cm²), frequency fₘ (Hz), double layer capacitance C₉ (F/cm²) and corresponding inhibition efficiency (E₉%) are gathered in table 4. It is seen from this figure (3), the impedance diagrams do show perfect semi-circles. We remark that the increase of Rₜ and decrease of double-layer capacitance (C₉) and the efficiency increases when the concentration 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ increases.

The obtained impedance diagrams almost a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of mild steel. In fact, the presence of 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ compound enhances the value of Rₜ in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of 7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ and the decrease in the values of C₉ follow the order similar to that obtained for I₉ in this study.

The decrease in C₉ may be due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solution [16-18].

Table 4. Characteristic parameters evaluated from EIS diagrams with and without H₄L³ at different concentrations.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C (mg/l)</th>
<th>Rₜ (Ω.cm²)</th>
<th>C₉ (µF/cm²)</th>
<th>E₉ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 1M</td>
<td>-</td>
<td>55.87</td>
<td>50.83</td>
<td></td>
</tr>
<tr>
<td>H₄L³</td>
<td>10-6</td>
<td>158,</td>
<td>63,67</td>
<td>64,79</td>
</tr>
<tr>
<td></td>
<td>10-5</td>
<td>227,6</td>
<td>45,26</td>
<td>75,45</td>
</tr>
<tr>
<td></td>
<td>5.10-5</td>
<td>451,9</td>
<td>36,32</td>
<td>87,64</td>
</tr>
<tr>
<td></td>
<td>10-4</td>
<td>545,9</td>
<td>49,96</td>
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<td></td>
<td>5.10-4</td>
<td>918,5</td>
<td>30,20</td>
<td>93,92</td>
</tr>
<tr>
<td></td>
<td>10-3</td>
<td>1404</td>
<td>20,38</td>
<td>96,03</td>
</tr>
</tbody>
</table>

3.4. Temperature effect

The effect of temperature on the corrosion rate of steel in 1M HCl containing the tested ,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ was studied in the temperature range 30-60°C using weight loss measurements at 60 minute.

The corrosion rate increased both in the presence and absence of the inhibitors by increasing the temperature of the system (Figure 4).

Hence we notice that the inhibitive efficiency of ,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ decreases with the rise of temperature and becomes 31.7% for ,7− bis (2- hydroxy benzamido)-4-azaheptane H₄L³ at 10⁻³M at 60°C (Table 5).
Table 5. Effect of temperature on the corrosion of steel in 1M HCl and in presence of 7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃ at 10⁻³M.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1M HCl W₀ (mg.cm⁻²h⁻¹)</th>
<th>H₄L₃ W'(mg.cm⁻²h⁻¹)</th>
<th>E%</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.4272</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>35</td>
<td>0.6111</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>0.5270</td>
<td>0.0132</td>
<td>97,50</td>
</tr>
<tr>
<td>45</td>
<td>0.5751</td>
<td>0.1715</td>
<td>70,17</td>
</tr>
<tr>
<td>50</td>
<td>0.6851</td>
<td>0.4288</td>
<td>50,29</td>
</tr>
<tr>
<td>55</td>
<td>0.8627</td>
<td>0.3836</td>
<td>44</td>
</tr>
<tr>
<td>60</td>
<td>1.2015</td>
<td>0.8211</td>
<td>31,75</td>
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</tbody>
</table>

Figure 4. Arrhenius plots for steel dissolution in presence and absence of 10⁻³M 7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃ in 1 M HCl

Figure 4 shows Arrhenius plots of the corrosion rate for both the blank and the solution of inhibitor. The relation can determine the apparent activation energies [3, 14, 15]:

\[ W' = K \exp \left( \frac{-E_a}{RT} \right) \]

\[ W = K \exp \left( \frac{-E_a'}{RT} \right) \]

\[ E_a = -112.12 \text{ kJ.mol}^{-1} \text{ and } E_a' = -18.748 \text{ kJ.mol}^{-1} \] are the apparent activation energies in the absence and presence of 7− bis (2-hydroxy benzamido)-4-azaheptane H₄L₃, respectively. The presence of inhibitor causes a change in the values of apparent activation energy. We remark the slight increase of activation energy in presence of inhibitors as compared to that obtained in the blank.
It is clear that the inhibitive efficiency of the tested 7− bis (2- hydroxy benzamido)-4-azaheptane $H_4L_3$ decreases with the rise of temperature. This indicates that the compounds are physically adsorbed. Metals and alloys react with hydrochloric acid by giving hydrogen and the metal. The evolved hydrogen is used in reducing hydrochloric acid to various products [2, 3, 47]. Inhibitors protect the metal by adsorbing on to the surface. Hoar showed that inhibitor molecules are adsorbed to a different extent at different types of surface sites and influence the anodic and cathodic reactions unequally [44, 60-63]. Hoar has further concluded that the adsorption of inhibitor molecules reduces the number of electrode reaction sites and thus inhibition becomes more predominant when the surface is covered with nearly a monolayer of the inhibitor.

In 7− bis (2- hydroxy benzamido)-4-azaheptane $H_4L_3$ molecules, N atom acts as reaction centre leading to the formation of the complex film on the surface of the alloy. 7− bis (2- hydroxy benzamido)-4-azaheptane $H_4L_3$ is an excellent inhibitor it has two polar atoms N and O. The cyclic provides a high electron density and it has found that inhibitor efficiency increases with the electron density.

### 3.5. Adsorption isotherm

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor, which obeys to:

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh} \tag{8}$$

$$b = \frac{1}{55.5} \exp(-\frac{\Delta G^o_{ads}}{R.T}) \tag{9}$$

$C_{inh}$ is the inhibitor concentration; $\theta$ is the fraction of the surface covered, $b$ is the adsorption coefficient and $\Delta G^o_{ads}$ is standard free energy of adsorption.

The adsorption isotherm can be determined if the inhibitor effect is due mainly to the adsorption on the metal surface (i.e., to its blocking). The type of the adsorption isotherms provides information about the interaction among the adsorbed molecules themselves and also their interactions with the electrode surface. Figure. 5 show the dependence of the ratio of the surface covered $C/\theta$ as function of the concentration (C) of 7− bis (2- hydroxy benzamido)-4-azaheptane $H_4L_3$. The degree of surface coverage $\theta$ for different concentrations of the inhibition in acidic media has been evaluated from weight loss using the equation [17, 18]:

$$\theta = \frac{W_{(\theta=0)} - W_\theta}{W_{(\theta=0)} - W_{(\theta=1)}} \tag{10}$$
Figure 5. Langmuir isotherm adsorption model of 7− bis (2- hydroxy benzamido)-4-azaheptane on the surface of steel in 1M HCl

Figure 5 illustrates the dependence of the fraction of the concentration and the surface covered C/θ as function of the concentration of the 7− bis (2- hydroxy benzamido)-4-azaheptane . The obtained plot of inhibitor is linear with a slope 1.03668 to close to unity. The regression coefficient is $R = 0.99996$ the intercept permit the calculation of the equilibrium constant $b$ which is 362971.136 M$^{-1}$ which leads to evaluate $\Delta G_{ads}^{o} = -43.067$ kJ/mol. The large negative values of $\Delta G_{ads}^{o}$ ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface as well as a strong interaction between the 7− bis (2- hydroxy benzamido)-4-azaheptane molecules and the metal surface [47, 48, 56, 59].this value indicates also that inhibitor interacts on the steel surface by electrostatic effect. These results indicate that the presence of 7− bis (2- hydroxy benzamido)-4-azaheptane increases the inhibition efficiency without change in adsorption mechanism. The results suggest that the experimental data are well described by Langmuir isotherm.

3.6 Theoretical calculations

Improving the effectiveness of inhibition caused by the increase of the interaction of between heteroatom’s and ring benzenes. The efficiencies inhibition are explicated by adsorption oxygen atoms and nitrogen in the structure of 7− bis (2- hydroxy benzamido)-4-azaheptane $H_4L^3$ on the metal surface. View that the nitrogen atoms are steric crowded by methyl groups and that the oxygen atoms are steric free. The oxygen atoms are essentially strongly adsorbed which prove more by increasing the electron density in the molecules.
In order to confirm these results, we have performed molecular modelling in order to understand if any structural differences induced by an oxygen atom in a $7 - \text{bis}(2\text{-hydroxy benzamido})-4$-azaheptane $\text{H}_4\text{L}_3$ molecule can be reliable to the observed differences in corrosion efficiency values. Relationships between electronic structure and efficiency of $7 - \text{bis}(2\text{-hydroxy benzamido})-4$-azaheptane $\text{H}_4\text{L}_3$ is deduced from quantum mechanical calculations. We performed molecular modeling to understand whether the structural steric crowding induced by oxygen atoms in the molecule can be reliably observed differences in the values of corrosion performance. The electronic structure and efficiency of P is deduced from quantum mechanical calculations [45, 64-66].

In this way, the calculated quantum chemical indices, Total charge density, EHOMO and $E_{\text{LUMO}}$ are calculated and shown in Table 6 and Figure 6-8. The calculated HOMO and LUMO energies are respectively $-6.393667\text{eV}$ and $-2.539514\text{eV}$ for $7 - \text{bis}(2\text{-hydroxy benzamido})-4$-azaheptane $\text{H}_4\text{L}_3$ molecule. This result indicates that $\text{H}_4\text{L}_3$ molecule can easily transfer an electron from Homo to Lumo level. Thus, inhibition efficiency increases with increasing values of $E_{\text{HOMO}}$ and of the decreasing values of $E_{\text{LUMO}}$. The results seem to indicate, that charge transfer from the inhibitor takes place during the adsorption to the metal surface. Increasing values of the $E_{\text{HOMO}}$ may facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [16-19, 25, 43, 44, 60-63]. Moreover we can also see that the Homo is located at the oxygen heteroatom’s atom site whereas for the $\text{H}_4\text{L}_3$ molecule the Homo is distributed along the entire cycle site (Figure 7 and 8).

Table 6. Quantum chemical indices of $\text{H}_4\text{L}_3$

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>EHOMO (eV)</th>
<th>ELUMO (eV)</th>
<th>(debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_4\text{L}_3$</td>
<td>$-6.393667$</td>
<td>$-2.539514\text{eV}$</td>
<td>4.411</td>
</tr>
</tbody>
</table>

Total charge density calculated by extended Huckel

C(2) -0.072, C(3) -0.099, C(4) -0.018, C(5) -0.016, C(6) -0.077, C(7) -0.015, C(8) -0.077, C(9) -0.101, C(10) -0.018, C(12) -0.070, N(17) -0.205, N(18) -0.185, O(20) -0.765, O(22) -0.477, O(24) -0.246, O(26) -0.765, C(29) -0.285, C(31) -0.285

Figure 6. Total charge density calculated by extended Huckel
4. CONCLUSION

- The principal finding of the present work can be summarised as follows:
- The 7− bis (2- hydroxy benzamido)-4-azaheptane H4L3 inhibit the corrosion of steel in 1M HCl
- Steady state electrochemical measurements have shown that the 7− bis (2- hydroxy benzamido)-4-azaheptane H4L3 act a mixed inhibitor for the corrosion of steel in 1M HCl without modifying the mechanism of hydrogen evolution reaction.
- The polarization resistance of the system increases when the 7− bis (2- hydroxy benzamido)-4-azaheptane H4L3 is added to the solution
- The adsorption of the H4L3 on the steel surface in molar hydrochloric acid obeys to the Langmuir adsorption isotherm model.
- The inhibition efficiency of H4L3 is temperature dependent and the addition of H4L3.
- Computational chemistry results revealed that the better inhibition efficiency obtained by H4L3 can be explained in terms of electronic densities and therefore to the possibility for this molecule to accept, thought the oxygen orbital a charge transfer from the metal surface.
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References