Corrosion inhibition of carbon steel by new enaminonitrile derivatives in HCl Solution

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In the present investigation new corrosion inhibitors, enaminonitrile derivatives (1-3) were synthesized characterized and tested as corrosion inhibitors for carbon steel in 1 M HCl using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation techniques. The corrosion inhibition efficiency measured by the above three techniques were in good agreement with each other. Electrochemical polarization data revealed the mixed mode of inhibition. The inhibition efficiency increases with increasing inhibitor concentration. Adsorption of enaminonitrile derivatives 1-3 was found to follow the Temkin adsorption isotherm. The mechanism of inhibition process was discussed in the light of the chemical structure and quantum-chemical calculations of the investigated inhibitors.

Keywords: Corrosion inhibition, HCl, enaminonitrile derivatives, carbon steel, quantum chemical calculations.

Introduction
Carbon steel is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal-processing equipment. Enaminonitriles are important intermediates for the preparation of heterocyclic compounds possessing diverse biological activities. They are of particular interest as very promising reagents for cascade heterocyclization, which will undoubtedly become one of the main approaches to the targeted synthesis of heterocycles in the near future, in the rapidly-rising field of combinatorial chemistry1-5. The use of inhibitors is one of the most practical methods for protection against corrosion. The concentration of a given inhibitor needed to protect a metal will depends on a number of factors such as composition of the environment, temperature, velocity of the liquid etc. Several works have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acidic media5-17. These inhibitors are adsorbed on the metal surface and protect the metal surface from the corrosive medium. Adsorption of these compounds on metal surface depends on nature and charge of the metal, the type of electrolyte, and the chemical structure of the inhibitor. Quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the reaction mechanism of the inhibitor molecule and the metal surface. The structural and electronic parameters of the inhibitor molecules can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry18. The present work was designed to study the corrosion inhibition of carbon steel in 1 M HCl solutions by some new enaminonitrile derivatives as corrosion inhibitors using different electrochemical techniques, also, to compare the experimental results with the theoretical ones.

Experimental procedure
Carbon steel specimens (C = 0.2, Mn = 0.91, P = 0.007, Si = 0.002 % and the rest Fe) of rectangular design having an area of 1 cm² were used in this study. The electrode surface was abraded with emery paper (200-1000grit size) and degreased with acetone. Analytical Reagent grade (Merck) and double distilled water were used for preparing test solution of 1 M HCl (37 %) for all experiments. The concentration of the acid was checked by titration with standard solution of sodium carbonate. The inhibitors were synthesized in the laboratory according to a previously described experimental procedure19 purified and characterized by

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elemental analysis, melting point and spectral data (IR, NMR and mass spectroscopy). All chemicals used are of analytical grades. Stock solutions (100 mL, \(10^{-3}\) M) of the organic compounds were prepared by dissolving an accurately quantity of each material in DMF and ethanol (1:9), then the required concentrations (\(5 \times 10^{-6} - 21 \times 10^{-6}\)) were prepared by dilution with double distilled water.

Methods

Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques have been employed for studying the corrosion inhibition of carbon steel by the investigated compounds. All electrochemical experiments were carried out using Gamry PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 corrosion software, EIS300 Electrochemical impedance software, EFM140 Electrochemical frequency modulation software and Echem Analyst 5.2.1 for results plotting, graphing, data fitting and calculating.

A three-electrode glass cell assembly, consisting of carbon steel electrode with an exposed area of 1cm² as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a platinum sheet (1 cm²) as counter electrode were used for electrochemical studies. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -1500 to +500 mV with scanning rate 5mVs⁻¹. The EIS spectra were recorded at open circuit potential (OCP) after immersion the electrode for 20 minutes. The AC signal was 5 mV peak to peak and the frequency range studied was between 10 mHz-100 kHz. Experiments were carried out in EFM measurements using potential amplitude 10 mV for both frequencies 2 and 5 Hz. The electrode potential was allowed to stabilize 30 min before starting the measurements. All the experiments were conducted at 25 ± 1°C.

Quantum Study

Molecular orbital calculations (MOC) are based on the semi-empirical self consistent methods (SCF). A full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles) without any symmetry constraint was performed at the restricted Hartree-Fock level (RHF). We used MNDO semi-empirical SCF-MO methods in the MATERIALS STUDIO V.4.4.0 program, implemented on an Intel Pentium IV, 3.6 GHz computer.

Results and Discussion

Potentiodynamic Polarization Measurements

Anodic and cathodic polarization curves for carbon steel in 1 M HCl in the absence and presence of various concentrations of the inhibitor (3) at 25 °C are given in Fig. 1. Similar curves were obtained for other inhibitors (not shown). The degree of surface coverage (θ) and inhibition efficiency (% IE) of various inhibitors were calculated from the following equation:

\[
%\text{IE} = \theta \times 100 = [1 - (i'_{\text{corr}}/i_{\text{corr}})] \times 100 \quad ... (1)
\]

where \(i'_{\text{corr}}\) and \(i_{\text{corr}}\) are the corrosion current densities in the presence and absence of the inhibitor, respectively. The electrochemical parameters are given in Table (1). The results in Table 1 indicate that:

![Image of potentiodynamic polarization curves](image-url)
1- The cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of enaminonitrile derivatives increased both cathodic and anodic overvoltage and caused mainly parallel displacement to the more negative and positive values, respectively. This indicates that there is no change in the mechanism of the process.

2- The corrosion current density ($i_{\text{corr.}}$) decreases with increasing the concentration of enaminonitrile derivatives, which indicates that the presence of these compounds retards the dissolution of carbon steel in 1 M HCl solution and the degree of inhibition depends on the concentration and type of the inhibitor used.

3- The investigated compounds appeared to act as mixed type inhibitors, as it is shown from Fig. 1, where both cathodic and anodic polarization curves are influenced by the presence of investigated compounds in the corrosive media. This indicates that the hydrogen evolution and metal dissolution reactions were activation controlled and the addition of inhibitors did not modify the mechanism of these processes\textsuperscript{20,21}. The inhibitive action of these investigated compounds occurs by blocking of active site on the electrode surface and consequently decreasing the surface area available for the electrochemical reactions.

4- The corrosion potential ($E_{\text{corr.}}$) does not remarkably shift in presence of these investigated compounds, therefore these compounds can be described as mixed type inhibitors for carbon steel in 1M HCl solution\textsuperscript{22}.

5- The order of decreased inhibition efficiency of the investigated additives is: 3 > 2 > 1.

### Electrochemical Impedance Spectroscopy (EIS)

The corrosion behavior of carbon steel in 1 M HCl solution in the absence and presence of different concentrations of enaminonitrile derivatives was investigated by the EIS technique at 25°C. Fig. 2 shows the Nyquist plots for carbon steel in 1M HCl solution in the absence and presence of different concentrations of investigated enaminonitrile derivatives at 25°C. The obtained Nyquist impedance diagrams in most cases does not show perfect semicircle, generally attributed to the frequency dispersion\textsuperscript{23} as a result of roughness and inhomogeneity of the electrode surface. The data revealed that, each impedance diagram consists of a large capacitive loop with low frequencies dispersion (inductive arc). This inductive arc is generally attributed to anodic adsorbed intermediates controlling the anodic processes\textsuperscript{24,25}. The impedance spectra of the different Nyquist plots (Fig. 2) were analyzed by fitting the experimental data to a simple equivalent circuit model as given in Fig. 3, which includes the solution resistance $R_s$ and the double layer capacitance $C_{\text{dl}}$ which is placed in parallel to the charge transfer resistance $R_{\text{ct}}$.\textsuperscript{26} The capacity of double layer ($C_{\text{dl}}$) can be calculated from the following equation:

$$C_{\text{dl}}=1/(2\pi f_{\text{max}} R_{\text{ct}}) \quad \cdots (2)$$

### Table 1 - Effect of concentrations of inhibitors 1-3 on the corrosion potential ($E_{\text{corr.}}$), corrosion current density ($i_{\text{corr.}}$), Tafel slopes ($\beta_a$ and $\beta_c$), corrosion rate (CR), polarization resistance ($R_p$), degree of surface coverage ($\theta$) and inhibition efficiency (% IE) of carbon steel in 1 M HCl at 25 °C.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Conc. M</th>
<th>$E_{\text{corr.}}$ (mV)</th>
<th>$i_{\text{corr.}}$ mA cm$^{-2}$</th>
<th>$\beta_a$ mV dec$^{-1}$</th>
<th>$\beta_c$ mV dec$^{-1}$</th>
<th>CR mm y$^{-1}$</th>
<th>$R_p$ ohm cm$^2$</th>
<th>$\theta$ % IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1M HCl</td>
<td>477.0</td>
<td>224</td>
<td>109</td>
<td>165</td>
<td>102.4</td>
<td>0.130</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>5x10$^{-6}$</td>
<td>473.0</td>
<td>160</td>
<td>93</td>
<td>138</td>
<td>73.82</td>
<td>0.151</td>
<td>0.286</td>
</tr>
<tr>
<td></td>
<td>9x10$^{-6}$</td>
<td>476.0</td>
<td>149</td>
<td>92</td>
<td>142</td>
<td>67.89</td>
<td>0.160</td>
<td>0.335</td>
</tr>
<tr>
<td></td>
<td>13x10$^{-6}$</td>
<td>476.0</td>
<td>135</td>
<td>93</td>
<td>144</td>
<td>61.63</td>
<td>0.182</td>
<td>0.397</td>
</tr>
<tr>
<td></td>
<td>17x10$^{-6}$</td>
<td>479.0</td>
<td>129</td>
<td>94</td>
<td>141</td>
<td>58.78</td>
<td>0.190</td>
<td>0.421</td>
</tr>
<tr>
<td></td>
<td>21x10$^{-6}$</td>
<td>475.0</td>
<td>121</td>
<td>86</td>
<td>132</td>
<td>55.47</td>
<td>0.191</td>
<td>0.460</td>
</tr>
<tr>
<td>2</td>
<td>5x10$^{-6}$</td>
<td>474.0</td>
<td>149</td>
<td>83</td>
<td>146</td>
<td>68.21</td>
<td>0.154</td>
<td>0.312</td>
</tr>
<tr>
<td></td>
<td>9x10$^{-6}$</td>
<td>473.0</td>
<td>146</td>
<td>92</td>
<td>134</td>
<td>66.60</td>
<td>0.162</td>
<td>0.348</td>
</tr>
<tr>
<td></td>
<td>13x10$^{-6}$</td>
<td>478.0</td>
<td>140</td>
<td>82</td>
<td>147</td>
<td>64.09</td>
<td>0.163</td>
<td>0.345</td>
</tr>
<tr>
<td></td>
<td>17x10$^{-6}$</td>
<td>475.0</td>
<td>127</td>
<td>80</td>
<td>146</td>
<td>58.21</td>
<td>0.180</td>
<td>0.375</td>
</tr>
<tr>
<td></td>
<td>21x10$^{-6}$</td>
<td>477.0</td>
<td>105</td>
<td>86</td>
<td>121</td>
<td>48.03</td>
<td>0.210</td>
<td>0.531</td>
</tr>
<tr>
<td>3</td>
<td>5x10$^{-6}$</td>
<td>478.0</td>
<td>133</td>
<td>88</td>
<td>144</td>
<td>60.77</td>
<td>0.180</td>
<td>0.406</td>
</tr>
<tr>
<td></td>
<td>9x10$^{-6}$</td>
<td>480.0</td>
<td>123</td>
<td>85</td>
<td>139</td>
<td>56.20</td>
<td>0.190</td>
<td>0.459</td>
</tr>
<tr>
<td></td>
<td>13x10$^{-6}$</td>
<td>482.0</td>
<td>116</td>
<td>85</td>
<td>139</td>
<td>53.04</td>
<td>0.200</td>
<td>0.482</td>
</tr>
<tr>
<td></td>
<td>17x10$^{-6}$</td>
<td>486.0</td>
<td>114</td>
<td>87</td>
<td>133</td>
<td>52.25</td>
<td>0.210</td>
<td>0.491</td>
</tr>
<tr>
<td></td>
<td>21x10$^{-6}$</td>
<td>483.0</td>
<td>70</td>
<td>88</td>
<td>139</td>
<td>31.98</td>
<td>0.330</td>
<td>0.690</td>
</tr>
</tbody>
</table>
where \( f_{\text{max}} \) is the maximum frequency.

The inhibition efficiencies and the surface coverage \((\theta)\) obtained from the impedance measurements are defined by the following relation:

\[
\% \text{IE} = \theta \times 100 = [1 - (R_{ct}^{o}/R_{ct}^{i})] \times 100 \quad \text{...(3)}
\]

where \( R_{ct}^{o} \) and \( R_{ct}^{i} \) are the charge transfer resistance in the absence and presence of inhibitor, respectively.

It can see from Table 2 that the values of charge transfer resistance increase with inhibitor concentration also, the \% IE increases as the phase angle increases. It is also noted that the \((C_{dl})\) values tend to decrease when the concentration of these compounds increases. This decrease in \((C_{dl})\), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that these compound molecules function by adsorption at the metal/solution interface. In the case of impedance studies, \% IE increases with inhibitor concentration in the presence of enaminonitrile derivatives and the \% IE of these investigated inhibitors is as follows: 3 > 2 > 1. The impedance study confirms the inhibiting characters of these compounds obtained with weight loss and potentiodynamic polarization methods.

**Electrochemical Frequency Modulation Technique (EFM)**

Results of EFM experiments are a spectrum of current response as function of frequency. The spectrum is called

![Nyquist plots](image-url)
the “inter modulation spectrum”. Figs. 4 and 5 represent the EFM intermodulation spectra of carbon steel in 1 M HCl in the absence and presence of different concentrations 21x10^{-6} M of compound 3 as an example at 25 °C.

Fig. 3 - Equivalent circuit model used to fit the impedance spectra

Fig. 4 - Intermodulation spectrum for carbon steel in 1 M HCl of blank at 25 °C.

Fig. 5 - Intermodulation spectrum for carbon steel in 1 M HCl in presence of 21x10^{-6} M of inhibitor (3) at 25 °C.
The corrosion parameters such as inhibition efficiency (\% IE), corrosion current density (\(i_{\text{corr}}\)), Tafel constants (\(\beta_a\) and \(\beta_c\)) and causality factors; CF-2, CF-3, at different concentrations of enaminonitrile derivatives compounds in 1 M HCl at 25 °C are presented in Table 3. It is observed from this Table that the corrosion current densities decreased by increasing the concentrations of the different inhibitors.

The great strength of the EFM is the causality factor, which serves as an internal check on the validity of the EFM measurement. The values of causality factors obtained under different experimental conditions are approximately equal the theoretical values (2 and 3) indicating that the measured data are of good quality.

The values of corrosion current density (\(i_{\text{corr}}\)) decreased by increasing the different concentrations of the investigated compounds at 25 °C, indicating the compounds inhibit the corrosion of carbon steel in HCl solution through adsorption on carbon steel surface. The inhibition efficiency, % IE, calculated from equation (4), is clear that the increase of % IE with increasing the studied enaminonitrile derivatives concentrations.

\[
% \text{IE}_{\text{EFM}} = \left[ 1 - \left( \frac{i'_{\text{corr}}}{i_{\text{corr}}} \right) \right] \times 100 \quad \ldots(4)
\]

where \(i'_{\text{corr}}\) and \(i_{\text{corr}}\) are corrosion current densities in the presence and absence of inhibitors, respectively. The % IE obtained from EFM measurements is the same as those obtained from EIS measurements and polarization. The order of decreasing % IE of these compounds is: 3 > 2 > 1.

**Adsorption Considerations**

The enaminonitrile derivatives inhibit corrosion of carbon steel by adsorbing onto the metal surface in acid solution. Basic information on the interaction between the inhibitor and the metal can be provided by the adsorption isotherm. The values of surface coverage (\(\theta\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc.M</th>
<th>(i_{\text{corr}}) mA cm(^{-2})</th>
<th>(\beta_{\text{anV dec}}^{-1})</th>
<th>(\beta_{\text{anV dec}}^{-1})</th>
<th>CF-2</th>
<th>CF-3</th>
<th>CRmpy</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1M HCl</td>
<td>454.8</td>
<td>68</td>
<td>68</td>
<td>1.0</td>
<td>1.162</td>
<td>167.4</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>5x10(^{-6})</td>
<td>299.1</td>
<td>94</td>
<td>105</td>
<td>2.01</td>
<td>3.74</td>
<td>136.7</td>
<td>0.342</td>
</tr>
<tr>
<td>2</td>
<td>5x10(^{-6})</td>
<td>287.1</td>
<td>88</td>
<td>117</td>
<td>2.04</td>
<td>2.99</td>
<td>131.2</td>
<td>0.370</td>
</tr>
<tr>
<td>3</td>
<td>5x10(^{-6})</td>
<td>262.5</td>
<td>92</td>
<td>99</td>
<td>2.45</td>
<td>120.0</td>
<td>0.423</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td>9x10(^{-6})</td>
<td>252.2</td>
<td>88</td>
<td>100</td>
<td>3.17</td>
<td>115.2</td>
<td>0.445</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>13x10(^{-6})</td>
<td>214.0</td>
<td>71</td>
<td>98</td>
<td>4.16</td>
<td>84.49</td>
<td>0.529</td>
<td>52.9</td>
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<tr>
<td></td>
<td>17x10(^{-6})</td>
<td>285.2</td>
<td>86</td>
<td>105</td>
<td>3.49</td>
<td>130.3</td>
<td>0.373</td>
<td>37.3</td>
</tr>
<tr>
<td></td>
<td>21x10(^{-6})</td>
<td>269.8</td>
<td>91</td>
<td>120</td>
<td>2.27</td>
<td>123.3</td>
<td>0.410</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>9x10(^{-6})</td>
<td>267.3</td>
<td>91</td>
<td>105</td>
<td>2.10</td>
<td>122.1</td>
<td>0.412</td>
<td>41.2</td>
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<tr>
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<td>158.9</td>
<td>63</td>
<td>73</td>
<td>5.36</td>
<td>72.60</td>
<td>0.651</td>
<td>65.1</td>
</tr>
<tr>
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<td>98</td>
<td>104</td>
<td>5.14</td>
<td>71.44</td>
<td>0.752</td>
<td>75.2</td>
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<tr>
<td></td>
<td>21x10(^{-6})</td>
<td>91.78</td>
<td>65</td>
<td>68</td>
<td>5.65</td>
<td>41.94</td>
<td>0.798</td>
<td>79.8</td>
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<tr>
<td></td>
<td>9x10(^{-6})</td>
<td>83.28</td>
<td>73</td>
<td>76</td>
<td>8.72</td>
<td>38.05</td>
<td>0.817</td>
<td>81.7</td>
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<tr>
<td></td>
<td>13x10(^{-6})</td>
<td>79.19</td>
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<td>91</td>
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<td>36.19</td>
<td>0.826</td>
<td>82.6</td>
</tr>
<tr>
<td></td>
<td>17x10(^{-6})</td>
<td>78.05</td>
<td>74</td>
<td>80</td>
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<td>82.8</td>
</tr>
<tr>
<td></td>
<td>21x10(^{-6})</td>
<td>71.47</td>
<td>58</td>
<td>62</td>
<td>7.45</td>
<td>32.66</td>
<td>0.872</td>
<td>87.2</td>
</tr>
</tbody>
</table>

![Fig. 6 - Temkin adsorption isotherms for the investigated compounds on carbon steel surface in 1 M HCl at 25 °C](image-url)
corresponding to different concentrations of the inhibitor have been used to determine the adsorption isotherm. The adsorption Temkin has been tested for the description of adsorption behavior of the inhibitor.

It could therefore be concluded that in addition to protonated species, investigated compounds can also be present as molecular species and that both protonated and molecular species can be adsorbed on carbon steel surface and influence the corrosion process differently.

The calculated values of molecular interaction a, equilibrium constant of adsorption process, K and free energy (\( \Delta G_{ads}^{\circ} \)) obtained from Temkin plot are shown in Table 4. The values of a are positive showing that attraction exist in adsorption layer[31]. The values of K decrease in the order: 3 > 2 > 1 which parallel to the % IE. The negative values of \( \Delta G_{ads}^{\circ} \) indicate spontaneous adsorption of investigated compounds onto the carbon steel surface[32] and strong interactions between inhibitor molecules and the metal surface[33]. In general, the standard free energy values of -20 kJ mol\(^{-1}\) or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, resulting in physisorption, and those of -40 kJ mol\(^{-1}\) or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form coordinate covalent bond, resulting in chemisorption[34]. The\( \Delta G_{ads}^{\circ} \) values obtained for the studied compounds on carbon steel surface in 1 M HCl range from -38.6 to -35.1 kJ mol\(^{-1}\), indicating both physical and chemical adsorption[35].

**Quantum Chemical Study**

Quantum chemical calculations are useful approach to investigate the reaction mechanism of the inhibitor molecule and the metal surface. The structural and electronic parameters of the inhibitor molecules can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry[36].

Geometric and electronic structures of the inhibitors were calculated by optimization of their bond lengths and bond angles. The optimized molecular structures of the inhibitors are given in Fig. 7. It clear from this Figure
that the value of electron negativity charges of O, N, and C, which connect to the donating electrons, were irrelevant to the inhibition efficiency. Also, from this Figure, we can see that the electron density of the frontier orbital is well proportioned. This kind of structure is difficult to form chemical bond active center, which the probability of the physical adsorption between the interaction sites. High value of $E_{HOMO}$ indicates a tendency of the molecule to donate electrons to act with acceptor molecules with low- energy, empty molecular orbital ($E_{LUMO}$) for $3 > E_{LUMO}$ for $2 > E_{LUMO}$ for 1). Similarly, the $E_{LUMO}$ represents the ability of the molecule to accept electrons. The lower value of $E_{LUMO}$ suggests the molecule accepts electrons more probable ($E_{LUMO}$, for $1 > E_{LUMO}$ for $2 > E_{LUMO}$ for $3$)$^{37,38}$. Table 5 shows a higher dipole moment ($\mu$) for compound 3 in comparison to compounds 2 and 1. Authors are not unanimous about the influence of the dipole moment on corrosion inhibition. Some authors showed that an increase of the dipole moment leads to decrease of inhibition and vice versa, suggesting that lower values of the dipole moment will favor accumulation of the inhibitor in the surface layer$^{10,41}$. In contrast, the increase of the dipole moment can lead to increase of inhibition and vice versa$^{42,43}$, which could be related to the dipole-dipole interaction of molecules and metal surface. The higher value of $\mu$ obtained for compound 3 is coherent with the second explanation indicating strong dipole-dipole interactions of compound 3 molecules and metallic surface in comparison to that of compound 2 and 1.

**Mechanism of corrosion inhibition**

These complexes might get adsorbed onto steel surface by van der Waals force to form protective film which covers both anodic and cathodic reactive sites on the steel surface, and inhibits both reactions at the same time. The inhibition efficiency of those compounds is as follows: $3 > 2 > 1$. Since the basicity of N, O and C atoms decrease in the order: $N > O > C$. So, we observe that compound (3) more efficient than compound (2) than compound (1).

**Conclusions**

From the results of the study, the following conclusions were drawn:

i) The investigated enaminonitrile derivatives are efficient inhibitors for carbon steel in HCl solution and % IE increases with increase in concentration of these derivatives

ii) Polarization data indicate that the inhibitors are mixed type ones

iii) The inhibitors function through adsorption following Temkin adsorption isotherm.

iv) The results indicate physical adsorption of the inhibitors on metal surface

v) The values of $\delta_{ads}$ suggest that the inhibitor molecules may be strongly adsorbed on the metal surface.

vi) The inhibiting efficiencies determined by polarization and EIS were in good agreement with that from EFM measurements

**References**


4. Azab ME (2008), Utility of the enaminonitrile moiety in the synthesis of some biologically active thiopyrimidine derivatives, **Phosphorus Sulfur and Silicon 183** (2008) 1766

5. Dyachenko VD, Dyachenko AD, Synthesis of 4-alkyl(aryl, heteryl)-2-thioxo-5,6,7,8-tetrahydroquinoline-3-carbonitriles and their derivatives by cross-recyclization of 4-alkyl(aryl, heteryl)-2,6-diamino-4H-thiopyran-3,5-dicarbonitriles with 4-(cyclohex-1-en-1-yl)-morpholine, alkyh halides, and cyclohexanone, **Russ J Org Chem, 44** (2008) 412


8. Merari B, Elattar H, Traisnel M, Bentiss F & Lagrene M, Inhibiting effects of 3,5-bis(n-pyridyl)-4-amino-1,2,4-triazoles on the corrosion for mild steel in 1 M HCl medium, **Corros Sci, 40** (1998) 391

10 Elkadi L, Mernari B, Traisnel M, Bentiss F & Lagrenee M, The inhibition action of 3,6-bis(2-methoxyphenyl)-1,2-dihydro-1,2,4,5-tetrazine on the corrosion of mild steel in acidic media, Corros Sci, 42 (2000) 703


12 Bentiss F, Traisnel M, Vezin H, Hildebrand HF, Lagrenee M, 2,5-Bis(4-dimethylaminophenyl)-1,3,4-oxadiazole and 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole as corrosion inhibitors for mild steel in acidic media, Corros Sci, 46 (2004) 2781


16 Al-Sarawy AA, Fouda AS, Shehab WA, Some thiazole derivatives as corrosion inhibitors of C-steel in acidic medium, Desalination, 229 (2008) 279


20 Kerte S, Hammouti B, Corrosion inhibition of iron in 1M HCl by 1-phenyl-5-mercapto-1,2,3,4-tetrazole, Appl Surf Sci, 93 (1996) 59


22 Fouda AS, El-Sherbiny M F, Motawea M M, Corrosion inhibition of Al alloy in HPO₄ solution using para-thiazolidinone derivatives, Desalination and Water Treatment, 30 (2011) 207


24 Caprani A, Epelboin I, Morel Ph, Takenouti H proceedings of the 4th Eur sym on Corros Inhibitors, Ferrara, Italy, (1975) 571


28 Lagrenee M, Mernari B, Bouanis B, Traisnel M, Bentiss F, Study of the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on mild steel corrosion in acidic media, Corros Sci, 44 (2002) 573

29 Bosch RW, Hubrecht J, Bogaerts WF, Syratt BC, Electrochemical frequency modulation: A new electrochemical technique for online corrosion monitoring Corrosion, 57 (2001) 60


38 Ozcan M, Dehari I, Electrochemical and quantum chemical studies of some sulphur-containing organic compounds as inhibitors for the acid corrosion of mild steel Prog Org Coat, 51 (2004) 181

39 El-Naggar M M., Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds, Corros Sci, 49 (2007) 2226


45 Singh AK, Quaisri MA, Inhibitive effect of diethylcarbamazine on the corrosion of mild steel in hydrochloric acid, Corros Sci, 52 (2010)