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# Comparative study of low carbon steel corrosion inhibition in 1M HCl by 1,2,4-triazole-5-thione derivatives

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**Abstract**
The inhibition of carbon steel in 1M HCl by synthesised 3-methyl-1,2,4-triazole-5-thione (MTS) and its derivative surfactant type 1.12-bis(3-méthyl-5(1,12-triazolyl)thiol)dodecane (DTC12) has been studied by electrochemical polarization and electrochemical impedance spectroscopy (EIS). The results obtained reveal that these compounds are efficient inhibitors. The inhibition efficiency increases with the increase of inhibitors concentrations and reached 95% at $10^{-3}$ M for DTC12. Potentiodynamic polarization studies clearly reveal that the presence of compounds studied does not change the mechanism of hydrogen evolution and that they act as mixed type inhibitors. This result was confirmed by the electrochemical impedance spectroscopy measurements. In addition, the impedance diagrams were composed of two capacitive loops. The first loop was attributed to the formation of a protective layer while the second was attributed to the charge transfer resistance. The DTC12 compound was selected as the best inhibitor.

A theoretical study of the corrosion inhibition efficiency of the tested compounds, was carried out using density functional theory (DFT) at the B3LYP/6-31G (d) level of theory. Molecular properties were found to be in good agreement with the inhibition efficiency obtained from electrochemical techniques.

***Key words:*** Corrosion, Inhibition, Surfactant, Carbon steel, 1M HCl, DFT

## 1. INTRODUCTION

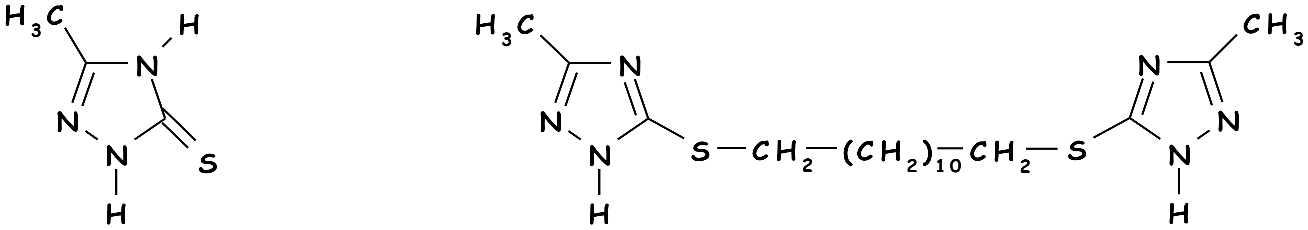
Hydrochloric acid is often used as a pickling acid for iron and its alloys. The main goal is to remove undesirable corrosion products. To make secure from attack of acid, inhibitors are frequently used. The most used inhibitors in acid medium, are those of triazoles compounds containing sulfur atom [1] The current research is moving more and more towards the development of non-toxic organic molecules, such as surfactants [2-5] .The existing data show that most of the organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitors takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. The inhibition efficiency should increase in the order O <N <S <P [6-9].

In this work, the influence of the triazole rings of a synthesized class on inhibition of the corrosion of Carbon steel in 1M HCl was evaluated. The tested molecules were 3-methyl-1,2,4-triazole-5-thione (MTS) and 1.12-bis(3-méthyl-5(1,12-triazolyl)thiol)dodécane (DTC12). The study was made by using potentiodynamic polarization curves and impedance spectroscopy (EIS) methods. In addition to traditional techniques such as electrochemical, a quantum chemical method has been employed in this study. Invaluable quantum chemical parameters such as higher occupied molecular orbital (HOMO), lower unoccupied molecular orbital (LUMO), dipole moment (μ), total energy (E) and energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) were obtained by this method (DFT), and help to understand the adsorption properties by considering the structures of MTS and DTC12 which is the best inhibitor.

## 2. Materials and methods

### *2.1. Inhibitors*

The compounds tested as corrosion inhibitors were synthesized in the laboratory of Materials, Electrochemistry and environment [10]. The products obtained were purified and characterized by $^1$HNMR and $^{13}$CNMR spectroscopies. The structures of the studied compounds are shown in Figure 1.



**3-méthyl-1,2,4-triazole-5-thione (MTS)**

**1,12-bis(3-méthyl-5(1,12-triazolyl)thiol)dodécane (DTC12)**

**Figure 1 :** Molecular structure of compounds studied

### *2.2 Steel samples*

Corrosion tests were performed on a carbon steel which had the following chemical composition (wt%): 0.2 % C; 0.005 % P; 0.O5 % S; 0.07 % N and the remainder iron. Before each essay, the electrode was polished using emery paper until 1200 Grade, rinsed with distilled water, degreased in ethanol, and dried before use.

### *2.3. Corrosive solution*

The aggressive solution of 1M HCl was prepared by dilution of analytical grade 37 % HCl "prolabo" with distilled water.

### *2.4 Potentiodynamic polarization measurement*

Polarization curves were recorded with Biologic Potentiostat PS 200, at a rate of 0,5mv/s using a conventional three-electrode cylindrical glass cell. The working electrode, in the form of a disc cut from carbon steel, had a geometric area of 1 cm$^2$. A saturated calomel electrode (SCE) and a platinum electrode were used as reference and auxiliary electrode, respectively. The temperature was 298 K.

Before recording, the steel electrode was maintained at Ecorr for 30mn. Then the electrode was swept from cathodic potential to anodic potential.

### *2.5 EIS study*

The EIS measurements were carried out with an electrochemical potentiostat suitable for measuring small currents and high impedances (Biologic Potentiostat PS 200). with a small amplitude ac. Signal (10 mV.rms), over a frequency domain from 100 KHz to 10 mHz at 298 K. A circular surface of the carbon steel of 1 cm$^2$ area was exposed to the solution. After the determination of the steady-state, the impedance diagrams are presented in the Nyquist representation.

## 3. Results and discussion

### *3.1 Potentiodynamic polarization studies*

Polarization curves for the steel electrode in 1M HCl with and without various concentrations of MTS and DTC12 at room temperature are shown in Figures 2, and 3.

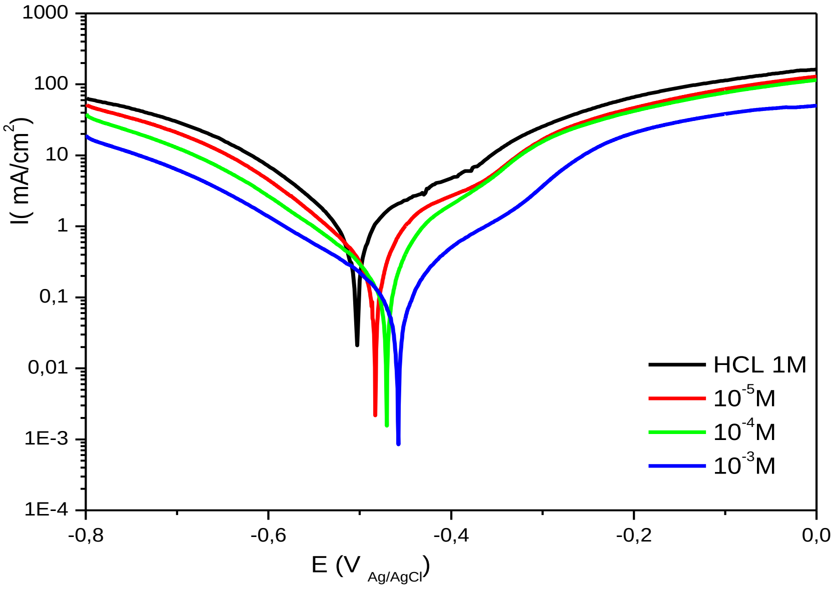


**Figure 2:** Cathodic and anodic curves of carbon steel in 1M HCl with and without different concentrations of MTS at 298 K

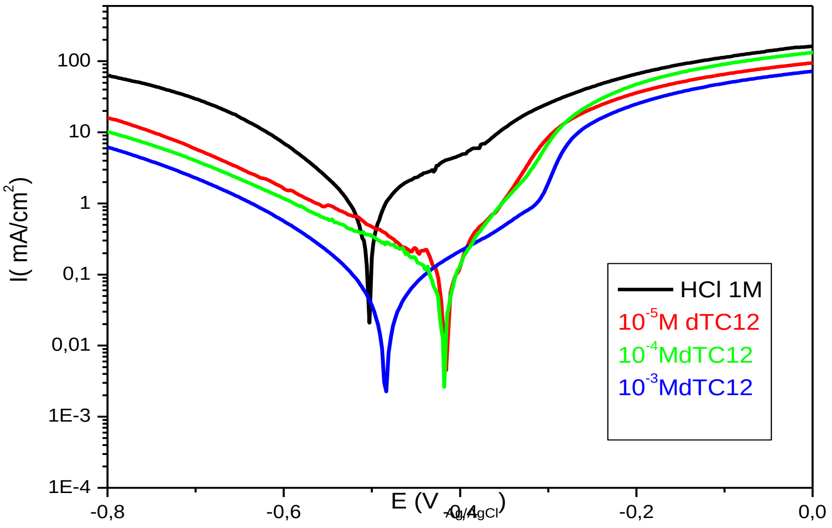


**Figure 3:** Cathodic and anodic curves of carbon steel in 1M HCl with and without different concentrations of DTC12 at 298 K

From electrochemical polarisation measurements, it is clear from results that the addition of MTS and DTC12 caused a decrease of the current density. A hight decrease was observed in the presence of DTC12 compound. Cathodic current–potential curves gave rise to parallel Tafel lines indicating that the hydrogen evolution is activation-controlled. In the presence of inhibitors, the current density tends to a limit value at low potential. It can be assigned to the current limit diffusion of oxygen. The values of corrosion potential (*E*corr) and cathodic

Tafel slope ($\beta$c) changed slightly, when the concentration increase. These results indicated that the reduction of hydrogen ion was inhibited and that the inhibition efficiency increased with inhibitor concentration.

The obtained anodic curves indicate that at over-voltages between -400 and -300 mV, we note a higher decrease of anodic current densities. Probably attributed to an adsorption the inhibitor film on the metal surface clearly marked in the presence of $10^{-3}$M of DTC12 [11].The same results have been reported elswhere [12-16]. At over-voltage higher than-300 mV/SCE, the presence of the inhibitors studied does not change the current versus potential characteristics. This result indicated that the two tested inhibitors acted essentially as cathodic inhibitors. -300 mV can be defined as the desorption potential. The behaviour of MTS and DTC12 at potential higher than -300 mV may be the result of significant steel dissolution leading to desorption of the inhibiting films.

Values of associated electrochemical parameters are given in Tables 1 and 2.

**Table 1:** Electrochemical parameters of carbon steel at various concentrations of MTS in 1M HCl at 298 K

| **Inhibiteurs** | **Concentrations (M)** | **$E_{corr}$ (mV)** | **$I_{corr}$ (µA)** | **βa (mV)** | **-βc (mV)** | **E%** | **θ** |
|---|---|---|---|---|---|---|---|
| | **0** | -487 | 393 | 86 | 98 | | |
| **MTS** | **$10^{-5}$** | -483 | 110 | 42 | 68 | 72 | 0,72 |
| | **$10^{-4}$** | -426 | 66 | 37 | 66 | 82 | 0,82 |
| | **$10^{-3}$** | -458 | 34 | 46 | 60 | 90 | 0,90 |

**Table2:** Electrochemical parameters of carbon steel at various concentrations of DTC12 in 1 M HCl at 298 K

| **Inhibiteurs** | **Concentrations (M)** | **$E_{corr}$ (mV)** | **$I_{cor}$r (µA)** | **βa (mV)** | **-βc (mV)** | **E%** | **θ** |
|---|---|---|---|---|---|---|---|
| | **0** | -487 | 393 | 86 | 98 | | |
| **DTC12** | **$10^{-5}$** | -414 | 47 | 31 | 37 | 88 | 0,88 |
| | **$10^{-4}$** | -421 | 46 | 27 | 39 | 88 | 0,88 |
| | **$10^{-3}$** | -484 | 18 | 59 | 52 | 95 | 0,95 |

The inhibition efficiency were calculated from corrosion current density using the following formula

$$IE\,\% = \frac{I^{\circ}_{Corr} - I_{Corr}}{I^{\circ}_{Corr}} \times 100$$

Where $\mathbf{I}^{0}_{corr}$ and $\mathbf{I}_{corr}$ are the corrosion current densities obtained in the absence and presence of the inhibitor respectively.

It can be noticed that the current densities decrease and the inhibition efficiency values increase by addition of inhibitors. This is due probably that these compounds adsorb on the low carbon steel surface preventing it from corrosion. In addition, the inhibition efficiency follows the following order: DTC12>MTS. This order can be explained by the heteroatoms number on these compounds and the existing hydrocarbon-chain in the surfactant molecule DTC12 (figure 1). The best inhibition efficiency reaches 95% at $10^{-3}$M of DTC12.

### *3.2 Electrochemical impedance spectroscopy*

In order to confirm the obtained results by potentiodynamic polarization measurements and gather some information about the inhibition effect of MTS and DTC12 compounds, the electrochemical impedance spectroscopy was also used. The advantage of this method is that both the polarization resistance values and the double layer capacitance values can be obtained in the same measurement.

Figures 4, 5 and 6 show the Nyquist plots of carbon steel in aerated 1M HCl, with and without inhibitors at various concentrations.

The impedance diagrams do not present a perfect semicircle, generally attributed to the frequency dispersion [16] due to the surface heterogeneity. This heterogeneity results from the roughness, impurities, dislocations, the adsorption of the inhibitor and the formation of porous layers [18, 19].

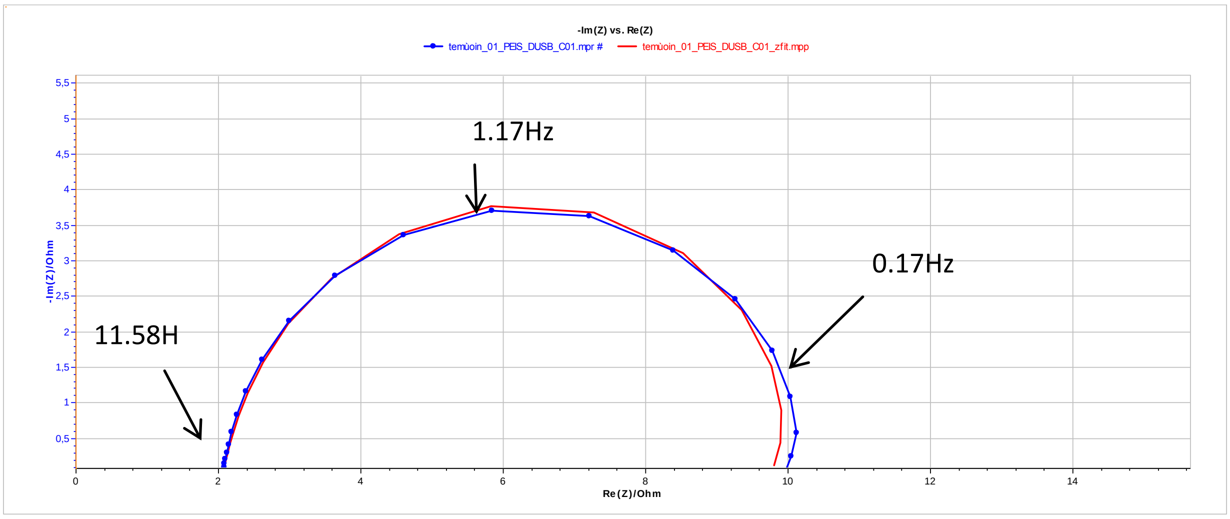


**Figure 4**: Nyquist plots of carbon steel in 1M HCl at 298 K

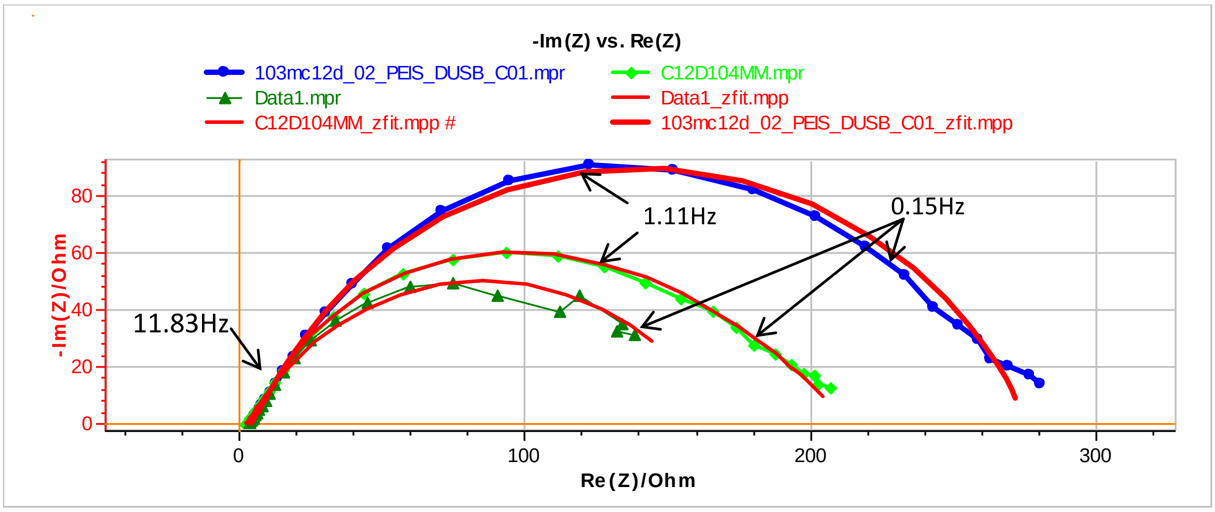


**Figure 5**: Nyquist plots of carbon steel in 1M HCl with different concentrations of DTC12 at 298 K

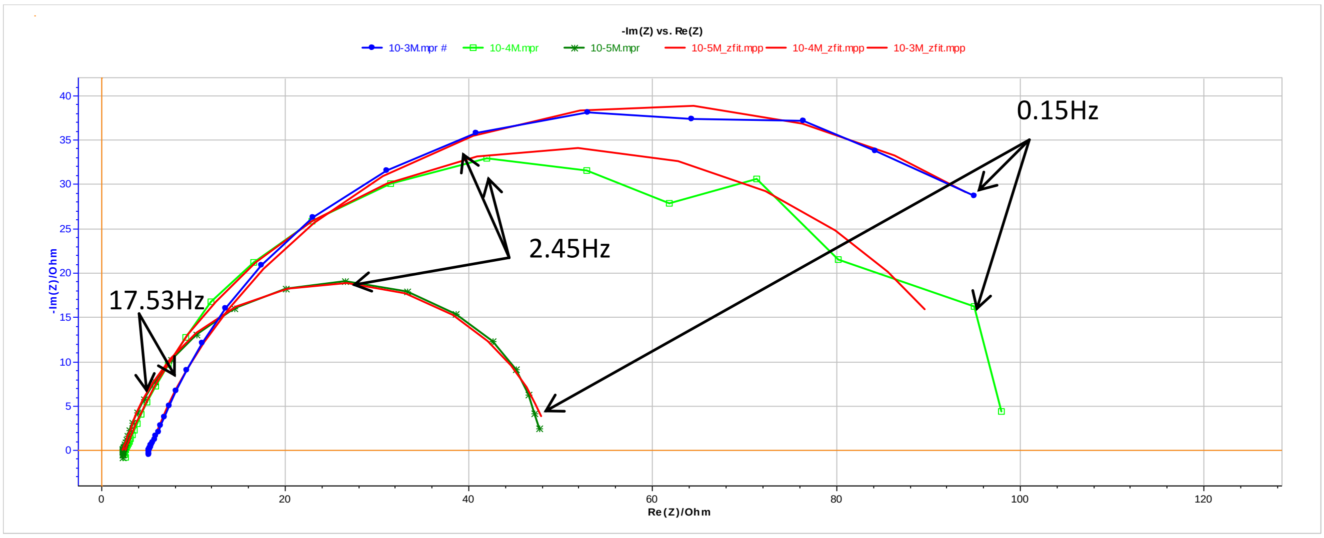


**Figure 6**: Nyquist plots of carbon steel in 1M HCl with diferent concentrations of MTS at298 K

In the absence of inhibitors, the impedance Nyquist diagrams present one capacitive loop with low resistance ($R_e$ = 2.07ohm).

In the presence of inhibitors, the complex plane plots reveal the presence of two capacitive loops. The first at high frequencies with low capacitive values was attributed to the inhibitors films on the metal surface. The second at low frequencies correspond to polarization resistance whose value increases with the addition of inhibitors atributed to the charge transfert. This indicates an improvement in presence of the organic compounds (MTS and DTC12).

The inhibition efficiency is calculated by charge transfert resistance obtained from Nyquist plots, according to the equation:

$$IE\% = \frac{R_t^{-1} - R_{t(inh)}^{-1}}{R_t^{-1}} x100$$

Where $R_{t(inh)}$ and $R_t$ are the charge transfer resistance in the presence and absence of MTS and DTC12, respectively.

The electrochemical parameters extracted from these curves are given in Tables 3 and 4.

**Table 3:** Electrochemical parameters for carbon steel in 1M HCl with and without various concentrations of MTS

| **Concentrations (M)** | **$R_e$ (Ω. cm$^2$)** | **$R_f$ (Ω.cm$^2$)** | **$C_f$ (µF./cm$^2$)** | **$R_t$ (Ω.cm$^2$)** | **$C_d$ (mF /cm$^2$)** | **E%** |
|---|---|---|---|---|---|---|
| 0 | 2.07 | ------ | -------- | 8.2 | 2.632 | ------- |
| $10^{-5}$ | 2.37 | 0.299 | 0.430 | 47 | 1.322 | 82 |
| $10^{-4}$ | 2.65 | 0.26 | 0.298 | 90 | 0.938 | 91 |
| $10^{-3}$ | 5.2 | 0.16 | 0,135 | 120 | 0.863 | 91 |

**Table 4:** Electrochemical parameters for carbon steel in 1M HCl with and without various concentrations of DTC12

| **Concentrations(M)** | **$R_e$ (Ω. cm$^2$)** | **$R_f$ (Ω. cm$^2$)** | **$C_f$ (µF./cm$^2$)** | **$R_t$ (Ω. cm$^2$)** | **$C_d$ (mF /cm$^2$)** | **E%** |
|---|---|---|---|---|---|---|
| 0 | 2.07 | ------ | -------- | 8.2 | 2.63 | -------- |
| $10^{-5}$ | 3.12 | 0.56 | 12.29 | 157 | 0.92 | 94 |
| $10^{-4}$ | 3.67 | 3.34 | 4.67 | 200 | 0.82 | 96 |
| $10^{-3}$ | 3.54 | 1.46 | 4.91 | 277 | 0.73 | 97 |

Tables 3 and 4 gives the values of the charge transfer resistance $R_t$, double-layer capacitance $C_d$, and inhibition efficiency obtained from the above plots. It can be seen that the presence of inhibitors studied enhances the values of $R_t$ and reduces the $C_d$ values. The decrease in $C_d$, which can result from a decrease in local dielectric constant and or an increase in the thickness of the electric double layer [20, 21], suggested that inhibitors molecules function by adsorption at the metal/solution interface. Thus, the decrease in $C_d$ values and the increase in $R_t$ values and consequently of inhibition efficiency may be due to the gradual replacement of water by the adsorption of the MTS and DTC12 molecules on the metal surface, decreasing the extent of dissolution reaction [22, 23].

However, these obtained results confirm those obtained by potentiodynamic polarization curves and the inhibition efficiency follows the following order: DTC12>MTS. Thus the DTC2 was selected as the best inhibitor.

The impedance data for the inhibitors studied can be interpreted using the equivalent electrical circuit of Figure 7, where $C_f$ and $R_f$ represent the coating capacitance, the $C_d$ is the double layer capacitance, and $R_t$ is the charge transfer resistance.

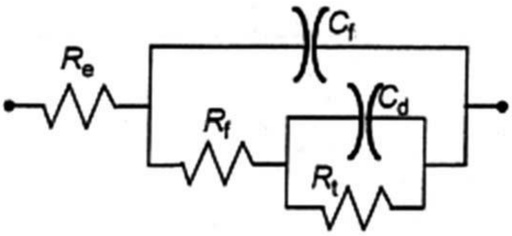


**Figure 7:** Electric equivalent circuit

$R_e$: Electrolyte resistance (Ω.cm$^2$)
$R_f$: Film resistance due to the ionic conduction through inhibitor layer (Ω.cm$^2$)
$C_f$: Film capacitance due to the electronic insulating property (F.cm$^{-2}$)
$R_t$: Charge transfer resistance (Ω.cm$^2$)
$C_d$: Double layer capacitance at the metal electrolyte interface (F.cm$^{-2}$)

### *3.3 Adsorption isotherm*

Organic molecules like inhibitors molecules inhibit the corrosion process via their adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which an inhibitor molecule, $L_{inh.}$, in the aqueous phase substitutes an "x" number of water molecules adsorbed on the metal surface [24].

$$L_{inh\,(aq)} + x\,H_2O_{(sur)} \rightarrow L_{inh\,(sur)} + x\,H_2O_{(aq)}$$

where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface. [25]**.**

To obtain more information about the interaction between the inhibitors studied and the carbon steel surface, different adsorption isotherms were tested. The degree of surface coverage, θ at different concentrations of the MTS and DTC12 in 1 M HCl solutions were determined from the corresponding electrochemical polarization measurements.

The ratio C/θ versus C is plotted linearly, showing that the adsorption of MTS and DTC12 obeys to Langmuir isotherm.

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Where *C, k* and $\theta$ are the concentration of inhibitor, the adsorptive equilibrium constant and the surface coverage, respectively.

The values of linear regressions between $C/\theta$ and *C,* and the parameters of adsorption are determined from Figure 8 and Figure 9.

The obtained slop values indicate that inhibitors adsorption is an ideal one as mentioned by Langmuir hypothesis.

The standard adsorption free energy ($\Delta G^{\circ}_{ads}$) is obtained according to the following equation:

$$\mathbf{K = 1/\,55.5\ exp\ (-\Delta G^{\circ}_{ads}/\ RT)}$$

$$\Delta G^{\circ}_{ads} = -RT\ \ln(55.5 * K)$$

The Langmuir parameters are given in table 5.

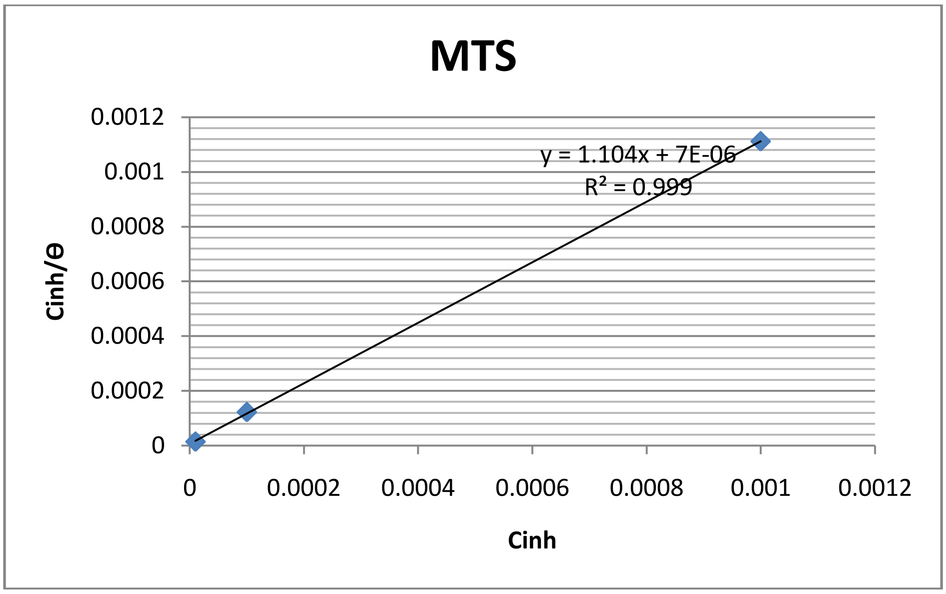


**Figure 8:** Langmuir isotherm adsorption model of MTS on the surface of Carbon steel in 1M HCl

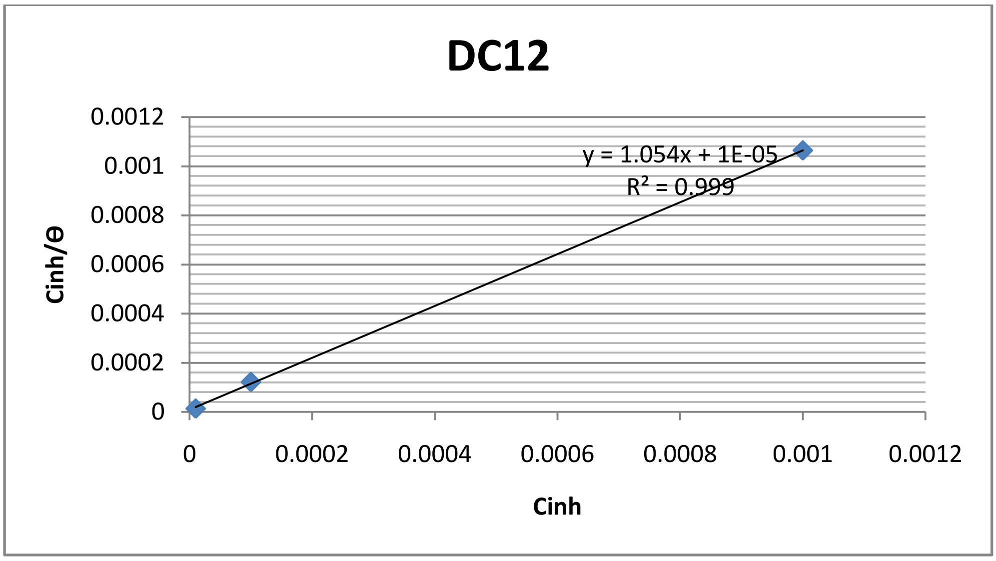


**Figure 9:** Langmuir isotherm adsorption model of DTC12 on the surface of Carbon steel in 1M HCl

**Table 5:** Corresponding values of -ΔG°ads for MTS and DTC12

| **Inhibitor** | **R** | **K** | **- ΔG°ads (KJ/mol)** |
|---|---|---|---|
| **MTS** | 0,999 | 500000 | 42,49 |
| **DTC12** | 0,999 | 140000 | 39,00 |

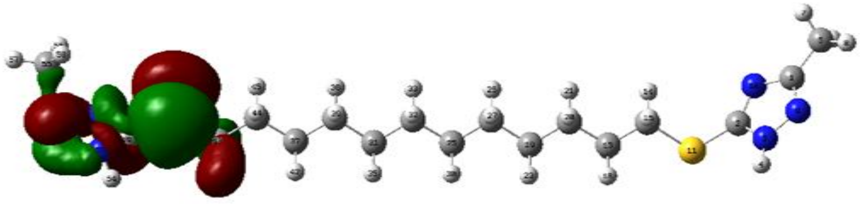
The largest negative value of ΔG°ads indicates that MTS andDTC12 are strongly adsorbed on the steel surface.

### *3.4 Computational procedures*

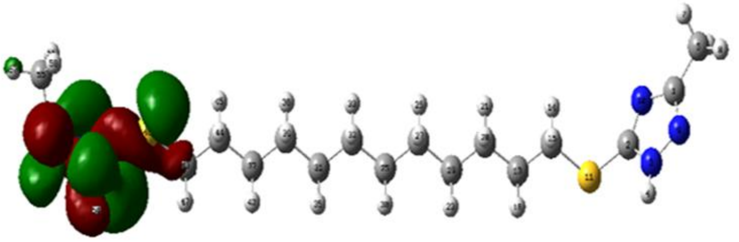
Computational methods have a strong impact toward the design and development of organic corrosion inhibitors. Recently, density function theory (DFT) has been used to analyze the characteristics mechanism of inhibitor adsorption and to describe the structural nature of the inhibitor on the corrosion process. Furthermore, DFT is considered to be a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data [26].

The quantum chemical parameters such as $E_{HOMO}$, $E_{LUMO}$, the energy gap ΔE, and dipole moment (μ) were obtained for the neutral inhibitors used to predict their activity toward metal surface. The low value of ΔE indicates that the compound studied is an efficient inhibitor [27, 28]. Figure 12 shows the HOMO and the LUMO density distribution of MTS and DTC12.

HOMO LUMO



HOMO



**LUMO**

**Figure 10:** Frontier molecular orbital density distributions of MTS and DTC12 (left, HOMO; right, LUMO)
The calculated molecular parameters are listed in Table 6.

**Table 6:** Calculated Quantum Chemical Parameters of MTS and DCT12

| Molécule | $E_{HOMO}$(eV) | $E_{LUMO}$(eV) | ΔE(eV) | μ(Debye) | E(au) |
|---|---|---|---|---|---|
| MTS | -7.507 | -3.617 | 3.889 | 7.1607 | 676.0864 |
| DTC12 | -4.282 | -1.197 | 3.085 | 1.6239 | 1811.9765 |

It can be seen from Figure 10 that inhibitors studied have different HOMO and LUMO distributions. HOMO density distributions were principally localized on triazole ring, which might be due to presence of N and S atoms with π-electrons in the inhibitor molecule. From this table, we see that DTC12 compound have a low energy gap ΔE. This letter is the best inhibitor. In addition, the low dipole moment (μ) causes accumulation of the inhibitor on the surface by increasing the efficiency of inhibition [29]. These results confirm those funded by potentiodynamic and EIS study.

## Conclusion

The synthesized compounds MTS and DTC12 inhibit the corrosion of carbon steel in 1M HCl. The electrochemical study shows that the the inhibition efficiency increase with increasing inhibitors concentrations. The DTC12 was selected as the best inhibitor. Its efficiency reaches 97% at $10^{-3}$M. The EIS measurements indicated that Rt values increase and Cd values decrease with increasing inhibitors concentrations. These inhibitors act by forming a film on the metal surface. These results were confirmed on the basis of the theoretical study. On the other hand the study of the adsorption isotherm shows that the action of the MTS and DTC12 follows the Langmuir adsorption. The negative values of ΔG°ads ensure and confirm the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface and suggest that the adsorption of the inhibitor onto the steel surface is spontaneous process. The free energy values indicate also that the inhibitor interacts on the steel surface by chimisorption effect.

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