A NEW EPOXY RESIN BASED ORGANIC MOLECULE
AS AN EFFECTIVE INHIBITOR OF MILD STEEL CORROSION
IN A SULFURIC ACID MEDIUM

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ABSTRACT

The effect of an epoxy resin based organic molecule, octaglycidylether tetra-aniline para methylene dianiline (OGTAPMDA), on the inhibition of mild steel corrosion in 0.5 M H₂SO₄ is studied at different temperature values using polarization, EIS and computational methods. The polarization curves recorded indicate that OGTAPMDA is a mixed inhibitor. The EIS measurements show an increase of the transfer resistance with the inhibitor concentration increase. The temperature effect on the inhibitor adsorption is followed. The free adsorption energy is determined. Quantum chemical calculations are applied to elucidate further the adsorption pattern of the inhibitor molecule. It is found that the proceeding chemical adsorption is well described by the Langmuir adsorption isotherm.

Keywords: mild steel, H₂SO₄, OGTAPMDA, corrosion inhibition, electrochemical techniques, DFT.

INTRODUCTION

Acid solutions are often used in drilling operations in oil and gas exploration, as well as for cleaning, descaling, and pickling of steel structures. These processes are normally accompanied by considerable dissolution of the metal. A useful method to protect metals and alloys deployed in such aggressive environments refers to the addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction or decrease the corrosion rate. Most of the acid corrosion inhibitors are organic compounds containing electronegative atoms (such as N, S, P and O), unsaturated bonds (such as double or triple bonds), and plane conjugated systems including various aromatic cycles [1 - 14].

The inhibitory action of these compounds is usually attributed to their adsorption interaction with the metal surface [15 - 18]. A bond may be formed between electron pairs and/or electron cloud of the donor atoms of the inhibitors and the metal surface, thereby reducing the corrosive attack in an acidic medium [19]. The stability of the adsorbed inhibitor film on the metal surface depends on some physico-chemical properties of the molecule related to its functional groups, aromaticity, possible steric effects, pi-orbital character of the donating electrons and their density, as well as on the type of the corrosive environment [20 - 22].

Theoretical chemistry, including quantum chemical calculation is proved to be a very powerful tool for studying the mechanism of corrosion inhibition [23]. It is widely used to investigate the correlation between the molecule structure and the inhibition efficiency of an organic compound [24, 25]. Therefore, it is essential to evaluate the the highest occupied molecular orbital energy (E_HOMO), the lowest unoccupied molecular orbital energy (E_LUMO), the dipole moment (μ), etc.

This work reports an investigation on the inhibitor behavior of an epoxy resin based organic compound -
octaglycidylether tetra-aniline para methylene dianiline (OGTAPMDA) or bis [3 (N-glycidyl phenyl) amino 2-glycidyl ether]-N, N (propyl) para methylene dianiline [26] in case of mild steel corrosion in H\textsubscript{2}SO\textsubscript{4} solution. Electrochemical methods including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are employed to investigate the effect of the concentration and the temperature on the inhibitive behavior of this compound. A quantum chemical method is also used to identify the adsorption type and to model the corrosion inhibition.

**EXPERIMENTAL**

**Materials**

The corrosion tests were performed on mild steel of the following composition: 0.21 % C; 0.38 % Si; 0.09 % P; 0.01 % Al; 0.05 % Mn; 0.05 % S and the remainder iron. The pre-treatment of the specimen's surface was carried out by polishing with emery paper of 120-1200 grit, rinsing with bidistilled water, degreasing in ethanol, and drying at room temperature.

The aggressive solution of 0.5 M H\textsubscript{2}SO\textsubscript{4} was prepared by dilution of 98% H\textsubscript{2}SO\textsubscript{4} (pa) with distilled water. The inhibitor solution was prepared by dissolving the amount required in 0.5 M H\textsubscript{2}SO\textsubscript{4}. The concentration range studied was from 10\textsuperscript{-6} M to 10\textsuperscript{-3} M.

**Electrochemical measurements**

The electrochemical measurements were carried out under static conditions using Volta lab (Tacussel-Radiometer PGZ 100) potentiostat controlled by Tacussel corrosion analysis software (VoltaMaster 4). The corrosion cell used had three electrodes. The reference electrode was a (Ag/AgCl) (3M KCl). A platinum electrode was used as an auxiliary electrode of a surface area of 1 cm\textsuperscript{2}. The working electrode was mild steel. All potentials given in this study were referred to the reference electrode pointed above. The working electrode was immersed in the test solution for 30 min to establish steady state open circuit potential (E\textsubscript{ocp}). The electrochemical measurements started after measuring its value. All electrochemical tests were performed in aerated solutions at 298 K. The EIS experiments were conducted at 10 points per decade in the frequency range from 0.1 Hz to 100 kHz by applying 10 mV ac voltage peak-to-peak. The corresponding Nyquist plots were then recorded.

The potentiodynamic polarization measurements were carried out in inhibited and uninhibited solutions scanning from cathodic to the anodic direction (E = E\textsubscript{corr} ± 200 mV) with a scan rate of 1 mV s\textsuperscript{-1}. The potentiodynamic data were analysed using the polarization VoltaMaster 4 software. The linear Tafel segments of the anodic and the cathodic curves were extrapolated to the corrosion potential to obtain the corrosion current density value (I\textsubscript{corr}). The evaluation of the latter was done on the ground of:

\[
I = I_{corr} \left[ \exp \left( \frac{2.3 \Delta E}{\beta_a} \right) - \exp \left( \frac{2.3 \Delta E}{\beta_c} \right) \right]
\]

(1)

The inhibition efficiency was evaluated on the ground of I\textsubscript{corr} values using the following relationship:

\[
\eta_{\text{Tafel}}(\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100
\]

(2)

where I\textsubscript{corr} and I\textsubscript{corr(i)} were the corrosion current densities recorded in the uninhibited and inhibited solution, respectively.

**Computational procedures**

Density functional theory (DFT) is recently used [27 - 30] to describe the interaction between the inhibitor molecule and the surface as well as the properties of these inhibitors concerning their reactivity. The molecular band gap refers to the first vertical electronic excitation energy from the ground state calculated with the application of the time-dependent density functional theory (TD-DFT) approach implemented in Gaussian 03. Some molecular descriptors, such as the HOMO and LUMO energy values, the frontier orbital energy gap, and the molecular dipole moment are required.

**RESULTS AND DISCUSSION**

**Potentiodynamic polarization studies**

**Effect of the inhibitor concentration**

Fig. 1 shows the polarization curves of mild steel in 0.5 M H\textsubscript{2}SO\textsubscript{4} in absence and presence of OGTAPMDA. It is evident that the addition of the latter causes a remarkable decrease in the corrosion rate, shifting both the anodic and cathodic Tafel curves to lower current densities. This phenomenon indicates that reactions are suppressed, while the effect becomes more pronounced with OGTAPMDA concentration increase. The values...
of the electrochemical parameters such as the corrosion potential ($E_{\text{corr}}$), the cathodic Tafel slope ($\beta_c$), the anodic Tafel slope ($\beta_a$), and the corrosion current density ($I_{\text{corr}}$) obtained by extrapolating the Tafel lines are given in Table 1. The corrosion inhibition efficiency ($\eta_{\text{Tafel}}$) of the compound studied is calculated using Eq. (2).

The almost parallel cathodic current-potential curves suggest that the addition of the inhibitor does not modify the activation-controlled hydrogen evolution reaction. An inhibitor can be treated as a cathodic or an anodic one if the corrosion potential displacement is greater than 85 mV (vs. Ag/AgCl) with respect to the corrosion potential obtained in the blank solution [31]. The present study shows that the greatest displacement exhibited by OGTAPMDA is 49 mV. This provides to conclude that OGTAPMDA acts as an inhibitor of a mixed type. The values of $\beta_c$ change significantly with OGTAPMDA concentration increase, which is indicative of the compound effect on hydrogen evolution kinetics [32]. The data in Table 4 reveals that the inhibition efficiency increases with the inhibitor concentration increase, while the corrosion current density decreases sharply. This may be due to the formation of an inhibitor adsorption layer on the metal surface.

**Temperature effect**

The temperature effect on the inhibited acid-metal reaction is very complex because many changes occur on the metal surface such as rapid etching, inhibitor desorption and decomposition [33]. The effect of the temperature on the inhibition performance of OGTAPMDA ($1 \times 10^{-3}$ M) in case of mild steel corrosion in 0.5 M H$_2$SO$_4$ solution at temperature values ranging from 298K to 328K is determined in the course of the potentiodynamic polarization measurements carried out (Figs. 2 and 3). The results are given in Table 2. The inhibition efficiency decreases with solution temperature increase from 298K to 328K. This behaviour can be interpreted as resulting from inhibitor molecules desorption. Table 2 shows that the corrosion rate increases with temperature increase in inhibited solutions.

**Thermodynamic activation parameters**

The evaluation of the activation energy of the corrosion process and the kinetic parameters of OGTAPMDA adsorption presents definite interest. This can be done by investigating the temperature dependence of the corrosion current using the Tafel extrapolation method. The corrosion reaction can be regarded as an Arrhenius-type

Table 1. Corrosion parameters of mild steel in 0.5 M H$_2$SO$_4$ at 298 K.

<table>
<thead>
<tr>
<th>$C_{\text{inh}}$ (REO) (M)</th>
<th>$E_{\text{corr}}$ (mV/Ag/AgCl)</th>
<th>$\alpha_a$ (mV dec$^{-1}$)</th>
<th>$-\beta_c$ (mV dec$^{-1}$)</th>
<th>$I_{\text{corr}}$ (mA cm$^{-2}$)</th>
<th>$\eta_{\text{Tafel}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>–455</td>
<td>64</td>
<td>167</td>
<td>3008</td>
<td>—</td>
</tr>
<tr>
<td>$1 \times 10^{-6}$</td>
<td>–429</td>
<td>63</td>
<td>111</td>
<td>640</td>
<td>79</td>
</tr>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>–447</td>
<td>62</td>
<td>108</td>
<td>370</td>
<td>88</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>–406</td>
<td>40</td>
<td>203</td>
<td>140</td>
<td>95</td>
</tr>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>–439</td>
<td>66</td>
<td>115</td>
<td>34</td>
<td>98</td>
</tr>
</tbody>
</table>
process, whose rate is given by:

\[ I_{\text{corr}} = k \exp \left( -\frac{E_a}{RT} \right) \]  

where \( E_a \) is the apparent activation corrosion energy, \( T \) is the absolute temperature, \( A \) is the Arrhenius pre-exponential constant, while \( R \) is the universal gas constant. This equation can be used to calculate \( E_a \) values of the corrosion reaction in absence and presence of OGTAPMDA. The logarithm of the corrosion current density versus \( 1000/T \) provides the estimation of \( E_a \) on the ground of the corresponding slope value (Fig. 4). The values obtained in absence and presence of OGTAPMDA are listed in Table 3.

OGTAPMDA addition to 0.5 M \( \text{H}_2\text{SO}_4 \) increases the activation energy from 24.54 to 73.88 kJ/mol. This corrosion rate decreases can be due to the formation of a complex layer on the metal surface [34]. Szauer and Brand explain the activation energy increase with the appreciable decrease of the inhibitor adsorption on the carbon steel surface with temperature increase. Adsorption decrease results in desorption increase as these two processes are in an equilibrium. Because of the inhibitor desorption enhancement at higher temperatures, a greater part of the steel surface is in contact with the aggressive environment. This in turn results in higher corrosion.
rate with temperature increase [35].

An alternative formulation of the Arrhenius equation is [36]:

\[
I_{\text{corr}} = \frac{RT}{Nh} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( \frac{\Delta H_a}{RT} \right)
\]

(4)

where \( T \) is the absolute temperature, \( h \) is the Planck’s constant, \( N \) is the Avogadro’s number, \( \Delta S_a \) is the entropy of activation, \( \Delta H_a \) is the enthalpy of activation, while \( I_{\text{corr}} \) is the corrosion rate.

The plots of \( \ln \left( \frac{I_{\text{corr}}}{T} \right) \) versus \( 1000/T \) (Fig. 5) show almost straight lines of regression coefficients close to 1. The values of \( \Delta H_a \) and \( \Delta S_a \) calculated on the ground of the lines slopes and intercepts are listed in Table 3.

Fig. 5 shows a plot of \( \ln \left( \frac{I_{\text{corr}}}{T} \right) \) against 1/T. Straight lines are obtained with a slope of \(-\Delta H_a / R\) and an intercept of \( \ln(R/Nh) + (\Delta S_a / R)\) providing the estimation of the values of \( \Delta H_a \) and \( \Delta S_a \). They are listed in Table 3.

Table 2. Electrochemical characteristics of mild steel in 0.5 M \( \text{H}_2\text{SO}_4 \) at different temperature values. \( C_{\text{OGTAPMDA}} = 1 \times 10^{-3} \text{M} \).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Temperature K</th>
<th>(-E_{\text{corr}} ) vs. Ag/AgCl(mV)</th>
<th>( I_{\text{corr}} ) (µA cm(^{-2}))</th>
<th>( \eta_{\text{Tafel}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>298</td>
<td>-455</td>
<td>3008</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-453</td>
<td>4250</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-449</td>
<td>5650</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-442</td>
<td>7480</td>
<td>—</td>
</tr>
<tr>
<td>OGTAPMDA</td>
<td>298</td>
<td>-473</td>
<td>34</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-413</td>
<td>98</td>
<td>97.7</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-420</td>
<td>212</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-412</td>
<td>544</td>
<td>92.7</td>
</tr>
</tbody>
</table>

Table 3. Values of the activation parameters referring to carbon steel in 0.5 M \( \text{H}_2\text{SO}_4 \) in absence and presence of \( 10^{-3} \text{M OGTAPMDA} \).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Linear regression coefficient (r)</th>
<th>( E_a ) (kJ/mol)</th>
<th>( \Delta H_a ) (kJ/mol)</th>
<th>( \Delta S_a ) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.99964</td>
<td>24.54</td>
<td>21.94</td>
<td>-104.60</td>
</tr>
<tr>
<td>OGTAPMDA</td>
<td>0.99877</td>
<td>73.88</td>
<td>71.28</td>
<td>23.81</td>
</tr>
</tbody>
</table>

Fig. 4. Arrhenius plots of carbon steel in 0.5 M \( \text{H}_2\text{SO}_4 \) in absence and presence of \( 1.0 \times 10^{-3} \text{M OGTAPMDA} \).

Fig. 5. Transition state plots of mild steel in 0.5 M \( \text{H}_2\text{SO}_4 \) + 1.0 mM OGTAPMDA.
It is evident that the thermodynamic parameters ($\Delta H^a$ and $\Delta S^a$) of steel dissolution reaction in presence of OGTAPMDA are higher than those in inhibitor absence (blank). The positive sign of $\Delta H^a$ is indicative of the endothermic nature of the dissolution process [37]. The increase of $\Delta S^a$ in presence of OGTAPMDA shows that the activated complex formation is accompanied by greater disorder [38].

**Electrochemical impedance spectroscopy**

**Inhibitor concentration effect**

Nyquist plots of mild steel in 0.5 M H$_2$SO$_4$ in absence and presence of an inhibitor of a different concentration are shown in Fig. 6. A depressed capacitive loop is seen, which suggests that the corrosion of mild steel in the test solution is mainly controlled by a charge transfer process [39, 40].

The capacitive loop is not a perfect semi-circle in the acid solution which is often referred to frequency dispersion as a result of the roughness and inhomogeneity of electrode surface [39, 41-44]. The equivalent circuit model given in Fig. 7 is used to determine the impedance parameter fitting the data. $R_s$ in Fig. 7 is the solution resistance, $R_{ct}$ is the charge transfer resistance, while CPE is the constant phase element. The impedance of the CPE is expressed as follows [41, 45 - 47]:

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n}$$

where $Y_0$ is the CPE constant, $n$ is the phase shift which can be explained as a degree of surface inhomogeneity [45 - 47], $j$ is the imaginary unit, while $\omega$ is the angular frequency. Depending on the values of $n$, CPE can represent resistance ($n = 0$), capacitance ($n = 1$), inductance ($n = -1$) and Warburg impedance ($n = 0.5$) [41, 45, 48]. So, CPE is often used instead of double layer capacitance ($C_{dl}$) to provide more accurate fit to the impedance data [41, 42, 45].

The impedance parameters such as the charge transfer resistance ($R_{ct}$), the double layer capacitance ($C_{dl}$), and the inhibition efficiency are listed in Table 4. It is seen that $R_{ct}$ value increases, while $C_{dl}$ value decreases with inhibitor addition. The decrease of $C_{dl}$ values is attributed to the

![Fig. 6. Nyquist diagrams of a mild steel electrode in absence and presence of OGTAPMDA at a different concentration after 30 min of immersion.](image)

![Fig. 7. The electrochemical equivalent circuit used to fit the impedance spectra obtained.](image)

<table>
<thead>
<tr>
<th>REO</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
<th>$\eta_z$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.0</td>
<td>7.0</td>
<td>650</td>
<td>-</td>
</tr>
<tr>
<td>10$^{-3}$ M</td>
<td>8.12</td>
<td>554.4</td>
<td>89</td>
<td>98</td>
</tr>
<tr>
<td>10$^{-4}$ M</td>
<td>3.96</td>
<td>224.8</td>
<td>164</td>
<td>96</td>
</tr>
<tr>
<td>10$^{-5}$ M</td>
<td>2.73</td>
<td>73.0</td>
<td>284</td>
<td>91</td>
</tr>
<tr>
<td>10$^{-6}$ M</td>
<td>2.42</td>
<td>41.6</td>
<td>394</td>
<td>83</td>
</tr>
</tbody>
</table>
adsorption of OGTAPMDA on the metal surface [49]. The Nyquist diagrams show that the charge-transfer resistance value of mild steel in uninhibited 0.5 M H₂SO₄ solution changes significantly after inhibitor addition. Furthermore, Cₜₙ decreases with the inhibitor concentration increase. This phenomenon is generally related to the adsorption of organic molecules on the metal surface leading thus to a decrease of the local dielectric constant and/or an increase of the thickness of the electrical double layer [50]:

\[ C_{dl} = \frac{\varepsilon_o \varepsilon}{\delta} S \]  

(6)

where \( \delta \) is the thickness of the protective layer, S is the electrode area, \( \varepsilon_o \) the vacuum permittivity of vide, while \( \varepsilon \) is the dielectric constant of the medium.

A low capacitance may result if the water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption [51]. The larger inhibitor molecules reduce additionally the capacitance through increase of the double layer thickness [52]. The inhibiting effectiveness increases with the inhibitor concentration increase to reach a maximum value of 98 % in 10⁻³ M OGTAPMDA.

The inhibition efficiency of the inhibitor is calculated from the charge transfer resistance values using the following equation:

\[ \eta_z \% = \frac{R_{ct}^i - R_{ct}^\circ}{R_{ct}^\circ} \times 100 \]  

(7)

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

**Effect of the immersion time**

In order to check whether the inhibitive properties of OGTAPMDA are preserved in the course of long-term experiments, ac impedance experiments are performed at the highest concentration of OGTAPMDA studied. The analysis of the Nyquist impedance diagrams obtained at different times of immersion (Fig. 8) shows a single capacitive loop at high frequencies (HF) with one capacitive time constant. The equivalent circuit employed to fit the experimental data is presented in Fig. 7. The main fitted parameters are given in Table 5. After few hours of immersion, significant protection can be achieved because of OGTAPMDA fast adsorption on bare steel.

A continuous increase of the adsorbed layer resistance is thus observed with immersion time increase. The layer resistance is supposed to coincide with the charge-transfer resistance (\( R_{ct} \)) of iron dissolution taking place at pores and defects within the film. Interfacial capacitance (\( C_{dl} \)) decrease can be observed during the adsorption. It is related to the replacement of the hydrated double layer by OGTAPMDA molecules [53]. It is also found that \( R_{ct} \) value increases with immersion time increase. This suggests the formation of a protective film which grows

![Fig. 8. Electrochemical impedance spectra obtained on immersion time variation in 0.5 M H₂SO₄ containing 10⁻³ M of OGTAPMDA.](image)

**Table 5.** Electrochemical impedance parameters referring to immersion time variation in case of mild steel corrosion in 0.5 M H₂SO₄ containing 1.10⁻³ M OGTAPMDA.

<table>
<thead>
<tr>
<th>Immersion period</th>
<th>( R_s ) (Ω cm²)</th>
<th>( C_{dl} ) (µF/cm²)</th>
<th>( R_{ct} ) (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>8.1</td>
<td>284</td>
<td>554</td>
</tr>
<tr>
<td>2 h</td>
<td>5.0</td>
<td>204</td>
<td>592</td>
</tr>
<tr>
<td>4 h</td>
<td>3.6</td>
<td>122</td>
<td>782</td>
</tr>
<tr>
<td>6 h</td>
<td>3.0</td>
<td>95</td>
<td>860</td>
</tr>
<tr>
<td>8 h</td>
<td>2.8</td>
<td>291</td>
<td>480</td>
</tr>
<tr>
<td>10 h</td>
<td>2.1</td>
<td>312</td>
<td>264</td>
</tr>
</tbody>
</table>
with increasing of the exposure time. This observation is also indicative of improvement of the film quality taking place with immersion time increase. A slight decrease of $R_{ct}$ accompanied with $C_{dl}$ values increase is observed (Table 5) in case the immersion time is longer than 8 h. This behavior can be due to the decrease of the protective layer stability as result of OGTAPMDA desorption (only physisorbed species) and/or a diffusion process through the protective layer/electrolyte interface [53]. The impedance studies results illustrate the excellent inhibitive properties of OGTAPMDA at 298K even within 10 h of immersion suggesting that the inhibitor adsorption on the mild steel surface involves two types of interactions, a predominant chemisorption (molecular) and a weak physisorption (ionic). Therefore thermodynamic study is carried out and discussed below providing to choose the most suitable hypothesis.

**Adsorption isotherm**

The action of an inhibitor in aggressive acid media is assumed to be due to its adsorption at the metal/solution interface. The adsorption process depends on the electronic characteristics of the inhibitor, the nature of metal surface, the temperature, the steric effects and the varying degrees of surface-site activity [54]. The determination of the isotherm describing the adsorption behavior of a corrosion inhibitor is important as it provides important clues about the nature of metal-inhibitor interaction. Values of degree of surface coverage ($\theta$) corresponding to different OGTAPMDA concentrations are used to determine which isotherm describes best the adsorption process. The values of $\theta$ are calculated in this study using the impedance results in accordance with the following equation:

$$\theta = \frac{R_{ct} - R_{ct}^i}{R_{ct}}$$  \hspace{1cm} (8)

where $R_{ct}$ and $R_{ct}^i$ are the charge transfer resistance values in inhibitor absence and presence, respectively. The results obtained fit well the Langmuir adsorption isotherm given by Eq. (9):

$$\frac{\theta}{1 - \theta} = K_{ads}C_{inh}$$  \hspace{1cm} (9)

The rearrangement of this equation gives:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$  \hspace{1cm} (10)

where $\theta$ is the surface coverage degree, $C_{inh}$ is the inhibitor concentration in the electrolyte, while $K_{ads}$ is the equilibrium constant of the adsorption process. $K_{ads}$ values may be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface [55]. To calculate the adsorption parameters, straight lines are drawn. The experimental points and the calculated isotherms are plotted in Fig. 9. The corresponding values are presented in Table 6. A very good fit is observed with a regression coefficient ($R^2$) of up to 1.0. The linear dependences obtained have slopes very close to unity, which suggests that the experimental data are well described by Langmuir isotherm exhibiting single-layer adsorption characteristics [7]. This kind of isotherm involves the assumption of no interaction between the adsorbed species and the electrode surface. $K_{ads}$ values

![Fig. 9. Langmuir adsorption of OGTAPMDA on the mild steel surface in 0.5 M H$_2$SO$_4$ solution.](image)
are estimated on the ground of the intercepts of $C_{\text{inh}}$ vs. $q$. They are listed in Table 6. The high values of $K_{ads}$ are indicative of the adsorption process spontaneity. They are also characteristic of strong interaction on the metal surface and stability of the resulting adsorbed layer. $K_{ads}$ is related to the standard free energy of adsorption, $\Delta G_{ads}^\circ$:

$$K_{ads} = \frac{1}{55.55} \exp \left( \frac{-\Delta G_{ads}^i}{RT} \right)$$  

where $R$ is the universal gas constant, $T$ is the thermodynamic temperature, while the value of 55.55 stands for the water concentration in the solution in mol/L.

The high value of $\Delta G_{ads}^i$ and its negative sign are usually an indication of a strong interaction and a high efficient adsorption [56]. Generally, values of $\Delta G_{ads}^i$ around -20 kJ mol$^{-1}$ or lower are consistent with electrostatic interaction between the charged molecules and the charged metal (physisorption). Whereas, values more negative than -40 kJ mol$^{-1}$ involve charge sharing or transfer from the inhibitor molecules to the metal surface forming a coordinate type of bond (chemisorptions) [9].

The value of $\Delta G_{ads}^i$ is equal to -44.11 kJ mol$^{-1}$. It shows that OGTAPMDA chemisorption may occur on mild steel in 0.5 M $\text{H}_2\text{SO}_4$. Possible mechanisms can be attributed to the donation of $\pi$-electron in the aromatic rings and the presence of oxygen and nitrogen atoms in the inhibitor molecule acting as reactive centers.

### Quantum Chemical Studies

The structure and the electronic parameters are obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The optimized molecular structures and frontier molecular orbital density distribution of the studied molecule are shown in Fig. 10. The calculated quantum chemical parameters such as $E_{HOMO}$, $E_{LUMO}$, $\Delta E_{LUMO-HOMO}$, dipole moments ($\mu$) are listed in Table 7. The molecular structure of cimetidine shows that the molecules most probably adsorb on the steel surface by sharing electrons of the nitrogen and oxygen atoms with iron to form coordinated bonds and $\pi$-electron interactions of the aromatic rings.

The value of highest occupied molecular orbital, $E_{HOMO}$, indicates the tendency of the molecule to donate electrons through nitrogen and oxygen atoms to the acceptor molecule with empty and low energy orbitals. $E_{LUMO}$ indicates the tendency of the molecule to accept electrons. Besides, the lower $E_{LUMO}$ is, the greater is the ability of that molecule to accept electrons [57]. The energy gap $\Delta E$ is an important parameter that is related to the reactivity of the inhibitor molecule towards the metal surface. A high $E_{H-L}$ is associated with a less tendency towards reactivity, while a low $E_{H-L}$ is an indication of a great tendency towards reactivity [58]. In this case, cimetidine shows a strong tendency towards reactivity. The polarity of the covalent bond (the dipole moment $\mu$) is determined by the electrons distribution in the molecule. Moreover, the high value of the dipole moment $\mu$ favors the inhibitor adsorption.

### CONCLUSIONS

EIS experiments results reveal that the charge transfer resistance of the mild steel electrode increases greatly, while the double layer capacitance decreases with increase of the inhibitor concentration, implying that OGTAPMDA inhibits the corrosion process taking place.
through an adsorption mechanism. The polarization curves indicate that the inhibitor studied acts as a mixed-type one inhibiting both the anodic and the cathodic reactions. The thermodynamic calculations indicate that the chemisorption of OGTAPMDA involving an interaction between the inhibitor and the mild steel surface is well described by the Langmuir isotherm. The data obtained by quantum chemical calculations using DFT at B3LYP/6-31G(d) level of the theory correlate to the inhibitive effect of OGTAPMDA. All measurements results obtained demonstrate that the inhibitor studied has excellent inhibitive properties in respect to mild steel corrosion in a sulfuric acid solution.

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