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Corrosion monitoring of mild steel in sulphuric acid solutions in presence of some thiazole derivatives – Molecular dynamics, chemical and electrochemical studies

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The physical behavior of three selected thiazole derivatives, namely 2-Amino-4-(p-tolyl)thiazole (APT), 2-Methoxy-1,3-thiazole (MTT) and Thiazole-4-carboxaldehyde (TCA) at iron (1 1 0) surface dissolved in aqueous solution were studied via molecular dynamics (MD) simulations. From the calculated binding energies, APT showed preferred adsorption on the steel surface among the three tested thiazole derivatives. The inhibition performance of the three thiazoles on the corrosion of mild steel in 0.5 M H₂SO₄ solutions was investigated at 25 °C. Measurements were conducted under various experimental conditions using weight loss, Tafel polarization and electrochemical impedance spectroscopy. Electrochemical frequency modulation (EFM) technique was also employed here to make accurate determination of the corrosion rates and test validation of the Tafel extrapolation method for measuring corrosion rates. Polarization curves showed that the three thiazole derivatives were of mixed-type inhibitors for mild steel corrosion in 0.5 M H₂SO₄ solution. EFM results were in agreement with other traditional chemical and electrochemical techniques used in corrosion rate measurements. Chemical and electrochemical measurements are consistent with computational study that APT is the most effective inhibitor among the tested thiazoles.

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1. Introduction

Despite the experimental work in corrosion inhibition studies, an understanding of the atomic level interactions at the inhibitor/metal interface is still needed. Although various experimental and theoretical techniques [1–4] have been developed to elucidate the structural properties of molecules at interfaces little is known about the interactions that occur between adsorbed molecules and solid surfaces [5]. A practical route in order to study these very complex processes is computer simulations [6–12] of suitable models. Interactions at metal surfaces and interfaces are critical to understand the corrosion inhibition phenomena. Properties of interest to corrosion scientists include the structure of the interface or interphase, how it differs from the bulk and the interaction of inhibitor molecules with metal surface. Due to the relatively large number of molecules (atoms) involved in adsorption on metal surface, a molecular dynamics method using a proper force field is the best choice. Contrary, quantum chemistry computing methods, such as ab initio and semi-empirical methods, are computational expensive and are usually only applied to systems containing no more than 100 atoms or small molecules. Recently, molecular dynamics (MD) simulations are performed to study the interaction of several corrosion inhibitors with metal surfaces [6,11,12–14]. From these studies, molecular dynamics simulations provide insights into the design of inhibitor systems with superior properties.

In general, most of the effective and efficient inhibitors in usage are organic compounds having π bonds in their structures. The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface. 4-acetyl pyridine [15], aliphatic amines [16] such as dimethylaniline, ethylamine, diethylamine, butylamine, butyldiethylamine and other derivatives of octylamine inhibit the corrosion of steel in acid solution by donating the unshared pair of electrons from the N atom and form a surface complex. Alkylene pyridinium compounds inhibit mild steel corrosion in 0.5 M H₂SO₄ due to inter-molecular synergism by the introduction of substituents in the pyridine ring [17]. The inhibitive effect of aniline and alkylamine [18], p-substituted anilines [19] and N-substituted anilines [20] are attributed to the interaction of π-electron cloud of aromatic ring on iron and steel surface through vacant’d’ orbital of iron leading to the formation of co-ordination bond between Fe–N. The corrosion inhibition property of low molecular weight straight chain amines for steel corrosion has also been studied [21]. Ortho-substituted anilines [22] and polyanilines [23–24] were also studied.
In this paper, the inhibition effect of three selected thiazole derivatives, namely, 2-Amino-4-(p-tolyl)thiazole (APT), 2-Methoxy-1,3-thiazole (MTT) and Thiazole-4-carboxaldehyde (TCA) on the corrosion of mild steel in 0.5 M H₂SO₄ was discussed. The inhibitive properties of these three thiazoles were investigated experimentally, using measurements based on weight loss, Tafel polarization, impedance and electrochemical frequency modulation techniques. Corrosion rates (in μm y⁻¹) determined from the EFM technique were compared with those recorded from the Tafel extrapolation method. It was also the purpose of the present work to study the adsorption of these compounds on iron (1 1 0) surface, using molecular dynamics simulations. The objective of this theoretical study is to explain the mechanism of adsorption, and therefore offer theoretical information regarding designing and synthesizing novel corrosion inhibitors.

2. Theoretical models and methods

Accurate simulation of atomic and molecular systems generally involves the application of quantum mechanical theory. However, quantum mechanical techniques are computationally expensive and are usually only applied to small systems containing between 10 and 100 atoms, or small molecules. It is not practical to model large systems such as corrosion systems containing many thousands of molecules in this way. Even if such a simulation were possible, in many cases much of the information generated would be discarded. This is because in simulating large systems, the goal is often to extract bulk (statistical) properties, such as diffusion coefficients or Young’s modulus, which depend on the location of the atomic nuclei or, more often, an average over a set of atomic nuclei configurations. Under these circumstances the details of electronic motion are lost in the averaging processes [25].

The Discover molecular dynamics module in Materials Studio 4.3 software from Accelrys Inc. [26] allows selecting a thermodynamic ensemble and the associated parameters, defining simulation time, temperature and pressureing and initiating a dynamics calculation. The first step to calculate the interaction energy between the inhibitor molecule and the metal surface is to build the iron (1 1 0) surface by importing the iron crystal and then cleave its surface through the cleavage plane (1 1 0). To get an accurate result, the thickness of the surface must be more than the non-bond cut-off distances in the force field. After building the iron (1 1 0) surface, the surface must be relaxed by minimizing its energy using molecular mechanics. The next step is to increase the surface area of the iron (1 1 0) and changing its periodicity by the same procedure was also used in case of gravimetric experiments.

The interaction energy E_{Fe–inhibitor} of the Fe surface with the thiazole derivatives was calculated according to the following Equation:

$$ E_{Fe–inhibitor} = E_{complex} - (E_{Fe} + E_{inhibitor}) $$

with $E_{complex}$ the total energy of the Fe crystal together with the adsorbed inhibitor molecule, $E_{Fe}$ and $E_{inhibitor}$ are the total energy of the Fe crystal and free inhibitor molecular, respectively. The binding energy of the inhibitor molecule is the negative value of the interaction energy, $E_{binding} = -E_{Fe–inhibitor}$ [6].

For the whole simulation procedure, COMPASS (Condensed-phase Optimized Molecular Potentials for Atomicistic Simulation Studies) forcefield [29] which used to optimize the structures of all components of the system of interest (Fe/solvent/thiazoles derivatives) and represents a technology break-through in forcefield method. COMPASS is the first ab initio forcefield that enables accurate and simultaneous prediction of chemical properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of chemical systems. It is also the first high quality forcefield to consolidate parameters of organic and inorganic materials.

3. Experimental procedures

Experiments were carried out using mild steel rods (C = 0.12%; Mn = 0.85%; S = 0.055%; P = 0.05%; Si = 0.09% and the remainder iron), as the electrode material. Steel rods were mounted in Teflon with surface area of 0.28 cm². The surface was abraded using emery papers of (180, 120, 0, 4/0) grit size, polished with Al₂O₃ (0.5 μm particle size), cleaned in 18 MΩ water in an ultrasonic bath, and subsequently rinsed with acetone and bidestilled water, the same procedure was also used in case of gravimetric experiments.

Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser. The solution volume was 100 ml. The steel specimens used have a rectangular form (length = 2 cm, width = 1 cm, thickness = 0.06 cm). The duration of tests was 6 hours at 25 °C. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in (mg cm⁻² h⁻¹).

A conventional electrolytic cell, as described elsewhere [30], was used for all of the experiments with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All reported potential values are on the SCE scale. Electrochemical experiments were carried out under stagnant conditions at 25 °C in aerated solutions, with a fine Luggin capillary closely placed to minimize ohmic resistance.

The structures of the studied thiazole derivatives are presented below:

![Thiazole derivatives](image-url)

All compounds investigated were obtained from Sigma–Aldrich Chemical Co. They were put in the 0.5 M H₂SO₄ (Fisher Scientific) without pretreatment at concentration of 10⁻⁴ M, 10⁻³ M, 5.0 × 10⁻³ M and 10⁻² M. The electrode was immersed in these solutions for one hour before starting measurements.
Fig. 1. Energy fluctuation curves performed for the three thiazole derivatives on Fe (1 1 0) surface obtained by molecular dynamic simulations.
Potentiodynamic cathodic and anodic polarization curves were obtained by changing the electrode potential automatically from $(-250 + 250 \text{ mV}_{\text{SCE}})$ versus open circuit potential with a scan rate of 1.0 mV s$^{-1}$. EIS measurements were carried out in a frequency range of 100 kHz–30 mHz with an amplitude of 5.0 mV peak-to-peak using ac signals at open circuit potential. EFM measurements carried out using two frequencies of 2.0 and 5.0 Hz. The base frequency was 1.0 Hz.

Electrochemical measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400, Gamry applications that include DC105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy measurements along with a computer for collecting data. Echem Analyst 4.0 Software was used for plotting, graphing and fitting data.

### 4. Results and discussion

#### 4.1. Computational study

The molecular dynamics simulations are performed to study the adsorption behavior of some thiazole derivatives (APT, MTT and TCA) on Fe (1 1 0) surface. The studied system reaches equilibrium only if both of the temperature and energy reach balance. The geometry optimization of the studied system is carried out using an iterative process, in which the atomic coordinates are adjusted until a local minimum in the potential energy surface. Fig. 1 shows the energy fluctuation curves. It can be seen from Fig. 1 that the system tends to equilibrium, by the end of the simulation process. The values of the interaction energy and the binding energy of the three thiazole derivatives on iron (1 1 0) surface are listed in Table 1.

As can be seen from Table 1, the binding energy, in all cases, has a positive value. As the value of the binding energy increases, the more easily the inhibitor adsorbs on the metal surface, the higher the interaction energy [6]. It follows from the data presented in Table 1 that, during the simulation process, APT possesses the maximum binding energy to the iron (1 1 0) surface among the three tested inhibitors. High values of binding energy indicate that APT molecule will give the highest inhibition energy from the theoretical point of view. From the structure of iron surface, it is evident that the presence of unoccupied d-orbital exhibits a tendency to obtain electrons from the adsorbed molecules. Thiazole derivatives studied in this work have a number of lone pair of electrons on the S, N and O atoms as well as the $\pi$-electron clouds on the aromatic rings. This will make it possible to provide electrons to the unoccupied orbitals of iron surface to form a stable co-ordination bonds.

Therefore the studied thiazole derivatives are likely to chemisorb on the iron surface, protecting it from corrosion. In addition, based on the equilibrium configuration of the three thiazole derivatives adsorbed on Fe (1 1 0) surface, presented in Fig. 2, we can draw a conclusion that the studied thiazole derivatives can be absorbed on the Fe surface through the thiazole ring and heteroatoms. In this way, the exposed part of Fe surface can be reduced by the covering of the thiazole ring and heteroatoms, consequently preventing the surface from the acid.

#### 4.2. Weight loss measurements

Table 2 presents the values of the corrosion rates (in g cm$^{-2}$ h$^{-1}$) and the inhibition efficiency, $\zeta_w (\%)$, derived from weight loss measurements for mild steel in 0.5 M H$_2$SO$_4$ solutions without and with various concentrations of thiazole derivatives at 25°C.

### Table 1

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$E_{\text{binding}}$ (kJ mol$^{-1}$)</th>
<th>$E_{\text{interaction}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APT</td>
<td>-398.1</td>
<td>398.1</td>
</tr>
<tr>
<td>MTT</td>
<td>-327.6</td>
<td>327.6</td>
</tr>
<tr>
<td>TCA</td>
<td>-261.7</td>
<td>261.7</td>
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</table>

### Table 2

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (M)</th>
<th>Corrosion rate (mg cm$^{-2}$ h$^{-1}$)</th>
<th>$\zeta_w (%)$</th>
</tr>
</thead>
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</tr>
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<td>2.89</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>10$^{-6}$</td>
<td>2.69</td>
<td>48.2</td>
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<td></td>
<td>5 × 10$^{-4}$</td>
<td>2.46</td>
<td>52.6</td>
</tr>
<tr>
<td></td>
<td>10$^{-4}$</td>
<td>1.84</td>
<td>64.6</td>
</tr>
<tr>
<td></td>
<td>5 × 10$^{-3}$</td>
<td>1.11</td>
<td>78.63</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>4.01</td>
<td>92.3</td>
</tr>
<tr>
<td>MTT</td>
<td>10$^{-5}$</td>
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<td>51.2</td>
</tr>
<tr>
<td></td>
<td>10$^{-4}$</td>
<td>2.28</td>
<td>56.3</td>
</tr>
<tr>
<td></td>
<td>5 × 10$^{-4}$</td>
<td>2.09</td>
<td>59.8</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>1.59</td>
<td>69.4</td>
</tr>
<tr>
<td></td>
<td>5 × 10$^{-3}$</td>
<td>0.80</td>
<td>84.6</td>
</tr>
<tr>
<td></td>
<td>10$^{-2}$</td>
<td>0.34</td>
<td>93.4</td>
</tr>
<tr>
<td>APT</td>
<td>10$^{-5}$</td>
<td>1.96</td>
<td>62.3</td>
</tr>
<tr>
<td></td>
<td>10$^{-4}$</td>
<td>0.93</td>
<td>82.1</td>
</tr>
<tr>
<td></td>
<td>5 × 10$^{-4}$</td>
<td>0.54</td>
<td>80.7</td>
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<td>5 × 10$^{-3}$</td>
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<td>94.4</td>
</tr>
<tr>
<td></td>
<td>10$^{-2}$</td>
<td>0.01</td>
<td>98.1</td>
</tr>
</tbody>
</table>

Fig. 2. Equilibrium configuration performed for the three thiazole derivatives on Fe (1 1 0) surface obtained by molecular dynamic simulations.
inhibition efficiency values for the three tested thiazole derivatives increase with increase in their concentrations, and this increase in the inhibition efficiency, at a given inhibitor concentration, enhances, as will be discussed later, following the order: APT > MTT > TCA. Thus, weight loss measurements, in accordance with theoretical study, demonstrate that all studied thiazoles exhibit inhibition properties, and the most effective one is the APT derivative. Indeed, we see that the skeleton of the three tested thiazole derivatives is approximately similar (except for the presence of a substituted phenyl group in the APT structure). The high inhibition performance recorded for APT, therefore can be explained on the basis of the larger steric size of APT caused by the phenyl ring. This larger steric body of APT in comparison to MTT and TCA may result in a higher surface coverage area during the chemical adsorption process. The phenyl ring in APT molecule may also support electron donation to the vacant d-orbital of the Fe atoms, and consequently chemical adsorption of this molecule is favored.

4.3. Tafel Polarization measurements

Tafel polarization curves recorded for mild steel electrode in 0.5 M H2SO4 solutions without and with various concentrations of APT, MTT or TCA are shown in Fig. 3. It is clear from Fig. 3 that both cathodic and anodic reactions of mild steel electrode corrosion were inhibited with the increase of thiazole derivatives concentrations in 0.5 M H2SO4. It is obvious that the polarization plots display a cathodic region of Tafel behavior, see later.

On the other hand, the anodic polarization curves do not display an extensive Tafel region, may be due to the deposition of the corrosion products or impurities on the steel (e.g., Fe3C) to form a non-passive surface film [31]. The deposition of corrosion products and the existence of such impurities do not result in a well-defined experimental anodic Tafel region. The cathodic curves are, therefore preferred, as will be seen, over the anodic ones for determining corrosion currents using the Tafel extrapolation method.

It also follows from the polarization plots presented in this figure that the shapes of the polarization plots for inhibited electrodes are not substantially different from those of uninhibited electrodes. The presence of these compounds decreases the corrosion rate but does not change other aspects of the behavior. This means that these inhibitors do not alter the electrochemical reactions responsible for corrosion. In addition, as will be seen, the absence of significant changes in the cathodic Tafel slope in the presence of inhibitor indicates that the hydrogen evolution reaction is activation controlled. This reaction is, therefore slowed down by the surface blocking effect of the three inhibitors. This indicates that the inhibitive action of these three thiazole derivatives may be related to their adsorption and formation of a barrier film on the electrode surface.

Based on E. McCafferty, who presented a valuable study concerning validity of the Tafel extrapolation method for measuring corrosion rates [32], the use of both the anodic and cathodic Tafel regions is undoubtedly preferred over the use of only one Tafel region for corrosion rates determination by this method. However, McCafferty pointed out that the corrosion rate can also be determined by Tafel extrapolation of either the cathodic or anodic polarization curve alone. If only one polarization curve alone is used, it is generally the cathodic curve which usually produces a longer and better defined Tafel region. Anodic polarization may sometimes produce concentration effects, due to passivation and dissolution, as noted above, as well as roughening of the surface which can lead to deviations from Tafel behavior.

Due to the absence of linearity in our anodic branches, accurate evaluation of the anodic Tafel slope by Tafel extrapolation of the anodic branch is impossible [33–37]. There is, therefore an uncertainty and source error in the numerical values of the anodic Tafel slope (βa), and may be in values of jcorr too, calculated by the software; the reason why we did not introduce here jcorr as well as βa values recorded by the software. On the same basis, we cannot determine jcorr from impedance plots, since these require accurate Tafel slopes. For these reasons we used, as will be seen later, the electrochemical frequency modulation, EFM, technique (featuring
of obtaining the Tafel slopes directly, small polarization and short measuring time, offers a novel way for electrochemical corrosion monitoring) to evaluate accurate values of the corrosion rates and compare them with those obtained from the Tafel extrapolation method. The aim here is to test validation of corrosion rates measured by Tafel extrapolation method; see details in Section 4.5.

We believe that the existence of the anodic Tafel region, together with the cathodic Tafel region, in the polarization plots is essential for accurate evaluation of the corrosion rates. For this reason we adopted here McCafferty method for evaluation of corrosion rates using Tafel extrapolation method [32]. This method was successfully applied in our previous study [38]. Based on this method, the cathodic Tafel region is extrapolated back to zero overvoltage to give the net rate of the cathodic reaction at the corrosion potential; this is also the net rate of the anodic reaction at the corrosion potential. Consequently, it is possible to calculate the anodic Tafel line from the experimental data, as shown in Fig. 4, as a representative example. The Tafel line of the cathodic polarization curve is first extended, since it exhibits a linear Tafel region, to electrode potentials below the corrosion potential, and then the anodic current density \( j_a \) is calculated from:

\[
\frac{j_a}{j_a \text{ (net experimental)}} = j_a - j_c
\]

where the subscripts \( a \) and \( c \) refer to the anodic and cathodic direction, respectively. Thus, \( j_a \text{ (net)} \) and \( j_c \text{ (net)} \) refer, respectively, to the rates of the anodic dissolution of Fe and the cathodic hydrogen evolution reactions; see more details in Ref. [32]. \( j_a \text{ (net)} \) and \( j_c \text{ (net)} \) are the cathodic current density. Thus, the anodic current density \( j_a \) is the sum of the experimentally observed anodic current density and the extrapolated cathodic current density. The result from Fig. 4 is that \( j_a \text{ (net)} \) = 4.4 \( \times \) 10\(^{-4}\) A cm\(^{-2}\). This \( j_a \text{ (net)} \) value is converted into the corrosion rate in \( \mu \text{m y}^{-1} \), see later, using Eq. (5) [39].

\[
\text{Corrosion rate (} \mu \text{m y}^{-1} \text{)} = 3290 \times j_a \text{ (net)} \times (M/nd)
\]

where \( M \) is the atomic weight of Fe (55.85 g), \( n \) the number of electrons transferred in the corrosion reaction (\( n = 2 \)) and \( d \) the density of Fe (7.88 g cm\(^{-3}\)).

It was well known that Tafel slopes have units of Volts per current-density-decade, where a decade is one order of magnitude current density, such as from 0.10 to 1.0 A cm\(^{-2}\). Fig. 4 also illustrates how to estimate the anodic and cathodic Tafel slopes for inhibitor-free sulphuric acid solutions. In this example, the Tafel slopes were estimated to be \( \beta_a = 34 \text{ mV dec}^{-1} \) and \( \beta_c = -170 \text{ mV dec}^{-1} \). The rest values for \( j_{corr}, \beta_a \) and \( \beta_c \) (together with the corrosion potential, \( E_{corr} \)) were also recorded for various concentrations of the three inhibitors, Table 3, using the respective polarization curves based on the same calculations presented in Fig. 4. Inhibition efficiency values, \( \xi_{Tafel} \% \), calculated from Eq. (6), are also presented in Table 3.

\[
\xi_{Tafel} \% = \left( \frac{j_{corr} - j_{corr}}{j_{corr}} \right) \times 100
\]

As it can be seen from these polarization results, the \( j_{corr} \) values, in all cases, decrease in the presence of the three thiazoles, and this decrease enhances with increasing inhibitor concentration. It is obvious that, under the same conditions, the corrosion current decreases in the order: TCA > MTT > APT. This sequence again reflects the increased ability of APT to inhibit steel corrosion in sulphuric acid solutions as compared to MTT and TCA. No definite trend was observed in the shift of \( E_{corr} \) values, in the presence of various concentrations of these inhibitors in 0.5 M H\(_2\)SO\(_4\) solutions. Based on these results, thiazole derivatives are considered as mixed-type inhibitors. Meaning that the addition of thiazole derivatives to 0.5 M H\(_2\)SO\(_4\) solutions reduces the anodic dissolution of mild steel and also retards the cathodic hydrogen evolution reaction. Further inspection of Table 3 reveals that the inhibition efficiency for the three thiazoles enhances with increase in their concentrations. The highest efficiency was also recorded for APT. These findings confirm theoretical study and weight loss measurements that APT is the most effective inhibitor among the three thiazoles used.

It is well known that the spontaneous dissolution of steel in acid medium give Fe\(^{2+}\) ions, this reaction accompanied by hydrogen evolution reaction which is a cathodic reaction. The corrosion of iron in uninhibited acidic solutions is controlled by the hydrogen evolution reaction [40–42]. In presence of an adsorbed inhibitor molecules, hydrogen ionization as well as the proceeding of electrochemical reactions can be neglected on the surface sites covered by the inhibitor molecules. Besides, it is accepted that the presence of Fe\(^{2+}\) (due to metal dissolution) on the uncovered surface has almost no effect [41]. The studied thiazole derivatives affect the rate of the corrosion process mainly through the variation of the degree of surface coverage, i.e., by blocking effect they exert, as previously mentioned. This is in turn results in a decrease of the concentration of the hydrogen ions in the surface layer and a corresponding increase in the hydrogen evolution overpotential.

### Table 3: Electrochemical parameters, together with the inhibition efficiencies, \( \xi_{Tafel} \% \), calculated from polarization measurements on the steel electrode in 0.5 M H\(_2\)SO\(_4\) solutions without and with various concentrations of the three thiazole derivatives at 25 °C.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>[Inhib.]/M</th>
<th>(-E_{corr}/\text{mV SCE})</th>
<th>(-b_a/\text{mV dec}^{-1})</th>
<th>(-b_c/\text{mV dec}^{-1})</th>
<th>(j_{corr}/\mu\text{A cm}^{-2})</th>
<th>(\xi_{Tafel} %/)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCA</td>
<td>10(^{-5})</td>
<td>497</td>
<td>172</td>
<td>36</td>
<td>283</td>
<td>35.69</td>
</tr>
<tr>
<td></td>
<td>10(^{-4})</td>
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<td>168</td>
<td>35</td>
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<td>38.09</td>
</tr>
<tr>
<td></td>
<td>10(^{-3})</td>
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<td>169</td>
<td>37</td>
<td>252</td>
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<td>37</td>
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<tr>
<td></td>
<td>10(^{-1})</td>
<td>512</td>
<td>168</td>
<td>34</td>
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Fig. 4. Determining corrosion current and Tafel slopes from Tafel plots using Tafel extrapolation method for the cathodic and anodic polarization curves recorded for mild steel electrode in 0.5 M H\(_2\)SO\(_4\) solutions at a scan rate of 1.0 mV s\(^{-1}\) and 25 °C.
Fig. 5. Complex-plane impedance plots recorded for mild steel electrode in 0.5 M H₂SO₄ solutions without and with various concentrations of the three thiazole derivatives at 25 °C.
4.4. Impedance measurements

It is evident that the more efficient the inhibitor, the lower the corresponding corrosion rate and the higher the charge-transfer resistance, \( R_{ct} \). EIS technique was used to evaluate the efficiency of the three tested thiazoles against the sulphuric acid corrosion of steel. In most cases either the values of the corrosion rates or inhibition efficiencies obtained from \( R_{ct} \) values were compared with those obtained using other techniques.

The results of the EIS measurements were presented in Fig. 5 as Nyquist plots. Impedance measurements were conducted in 0.5 M \( \text{H}_2\text{SO}_4 \) solutions without and with different concentrations of the three thiazoles at the respective corrosion potentials at 25 °C. Complex-plane impedance plots presented in Fig. 5 showed a capacitive loop in the high frequency (HF) range and an inductive loop in the low frequency (LF) range. The capacitive loop was related to charge-transfer in corrosion process [43]. The depressed form of the higher frequency loop reflects the surface inhomogeneity of structural or interfacial origin, such as those found in adsorption processes [44]. The presence of the LF inductive \( R_L \)-\( L \) loop may be attributed to the relaxation process obtained by adsorption species like \( \text{H}_2\text{SO}_4^+ \) on the electrode surface. It may also attribute to the re-dissolution of the passivated surface at low frequencies [45].

The two equivalent circuits, depicted in Fig. 6, were used to fit the EIS data. In these two circuits, the solution resistance, \( R_s \), the charge-transfer resistance, \( R_{ct} \), the constant phase element, CPE, and the inductive arrangement, \( R_L \) and \( L \), were fitted and their values were listed in Table 4. The \( R_{ct} \) values increase with the increase in concentration of thiazole derivatives, indicating the formation of an insulating adsorption layer. Indeed, the inhibition efficiencies of these inhibitors, as will be seen, were evaluated by \( R_s \) and \( C_{dl} \) values of the impedance. The more densely packed the monolayer of the inhibitor, the larger the diameter of the semicircle, which results in higher \( R_s \) and lower \( C_{dl} \) values. Data presented in Table 4 showed that, in all cases, the values of \( R_{ct} \) increase in inhibitor concentration, while those of \( C_{dl} \) (derived, as will be discussed from CPE) tend to decrease.

The \( R_{ct} \) values were used to calculate the inhibition efficiency, \( \zeta_z \) (%), as a function of the concentration of the three tested thiazoles, using Eq. (7):

\[
\zeta_z(\%) = \left(1 - \frac{R_{ct}}{R_{ct,0}}\right) \times 100
\]

where \( R_{ct} \) and \( R_{ct,0} \) are the charge-transfer resistance values in the absence and presence of the inhibitor, respectively. It is apparent that, in all cases, the inhibition efficiency increases with inhibitor concentration. A maximum inhibition efficiency of about 97% was recorded for APT at a concentration of 0.01 M. These results again confirm previous findings that APT was better inhibitor than MTT and TCA under these conditions.

CPE is used as a substitute for capacitor to fit more accurately the impedance behavior of the electric double layer. The impedance of the CPE is expressed as:

\[
Z_{\text{CPE}} = \frac{1}{\nu Y_0(j\omega)^n}
\]

where \( Y_0 \) is the magnitude of the CPE, \(-1 \leq n \leq 1\). The higher frequency range loops have depressed semicircular appearance, \( 0.5 \leq n \leq 1 \), which is often referred to as frequency dispersion as a result of the non-homogeneity or the roughness of the solid surface [44,46]. The HF capacitive loop, \( R_{ct,0}\)-CPE, can be attributed to the charge-transfer reaction.

The capacitance values can be calculated from CPE parameter values \( Y \) and \( n \) using the expression [47].

\[
C_a = \frac{Y_0}{\sin(\pi n/2)}
\]

According to the expression of the layer capacitance presented in the Helmholtz model [48].

\[
C_a = \frac{\varepsilon_0 \varepsilon A}{d}
\]

where \( d \) is the thickness of the film, \( A \) is the surface area of the electrode, \( \varepsilon_0 \) is the permittivity of the air and \( \varepsilon \) is the local dielectric constant. The decrease in \( C_{dl} \) is due to the gradual replacement of water molecules by the adsorption of the thiazole derivatives at mild steel/0.5 M \( \text{H}_2\text{SO}_4 \) solution interface, leading to a protective film on the steel surface, then decreasing the extent of dissolution reaction [49]. Also, the increase of \( n \) values, Table 4, with concentration of the three thiazoles could be explained by decreasing in

<table>
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<tr>
<th>Inhibitor</th>
<th>[Inhib.]/ M</th>
<th>( R_s ) ( \Omega \text{cm}^2 )</th>
<th>CPE/( \nu )</th>
<th>( n )</th>
<th>( R_{ct} ) ( \Omega \text{cm}^2 )</th>
<th>( R_L ) ( \Omega \text{cm}^2 )</th>
<th>( L ) ( \text{Hcm}^2 )</th>
<th>( \zeta_z ) (%)</th>
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<td>2.1</td>
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<td>369.4</td>
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surface heterogeneity, due to the adsorption of the inhibitor on the most active adsorption sites [50].

4.5. Electrochemical frequency modulation, EFM measurements

The corrosion rate and Tafel parameters can be obtained with one measurement by analyzing the harmonic frequencies. Because current is a non-linear function of potential, the system responds in a non-linear way to the potential excitation. The current response contains the input frequencies, frequency components which are the sum, difference, and multiples of the two input frequencies.

In corrosion research, it is known that the corrosion process is non-linear in nature, a potential distortion by one or more sine waves will generate responses at more frequencies than the frequencies of the applied signal. Virtually no attention has been given to the intermodulation or electrochemical frequency modulation. However, EFM showed that this non-linear response contains enough information about the corroding system so that the corrosion current can be calculated directly. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [51]. With the causality factors the experimental EFM data can be verified.

The results of EFM experiments are a spectrum of current response as a function of frequency. The spectrum is called the intermodulation spectrum and examples for corrosion of mild steel in absence and presence of thiazole derivatives in 0.5 M H₂SO₄ are

![Representative examples for intermodulation spectra recorded for mild steel electrode in 0.5 M H₂SO₄ solutions in the absence and presence of various concentrations of the three thiazole derivatives at 25 °C.](image)
shown in Fig. 7. The spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density $i_{corr}$, the Tafel slopes ($\beta_c$ and $\beta_h$) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined by Gamry EFM140 software, and listed in Table 5.

As can be seen from Table 5, the corrosion current densities decrease by increasing the concentrations of the studied inhibitors. The inhibition efficiencies, $\eta_{EFM}$ (%), calculated from Eq. (11), increase by increasing the studied inhibitor concentrations.

$$\eta_{EFM} (%) = \left( \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \right) \times 100$$

where $i_{corr}^0$ and $i_{corr}$ are corrosion current densities in the absence and presence of inhibitors, respectively. The causality factors in Table 5 indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively [51]. Here again, the values of $i_{corr}$ recorded by the EFM technique were converted into corrosion rates (in $\mu$m y$^{-1}$) following Eq. (5). Table 6 presents values of corrosion rates monitored for mild steel in 0.5 M H$_2$SO$_4$ solutions without and with various concentrations of the three thiazole derivatives at 25 °C.

In the present work, molecular dynamics simulations method using a COMPASS forcefield is used to calculate the interaction energy, and hence the binding energy of some thiazole derivatives on mild steel Chemical (weight loss) and electrochemical (Tafel extrapolation) methods were used to study the capability of these thiazole derivatives to inhibit the corrosion of mild steel in aerated stagnant 0.5 M H$_2$SO$_4$ solutions at 25 °C. The calculated inhibition efficiencies obtained are in good agreement with that obtained from EFM. The corrosion rates calculated by EFM were higher, but still of the same order of magnitude as those obtained using other traditional techniques. These results are in consistence with our previous study [13,38,52–56]. Based on these results, the electrochemical frequency modulation (EFM) technique appears capable of monitoring the corrosion inhibition of mild steel in 0.5 M H$_2$SO$_4$ solutions with different concentrations of thiazole derivatives at 25 °C.

### 5. Conclusion

In the present work, molecular dynamics simulations method using a COMPASS forcefield is used to calculate the interaction energy, and hence the binding energy of some thiazole derivatives on mild steel Chemical (weight loss) and electrochemical (Tafel polarization, electrochemical impedance spectroscopy and electrochemical frequency modulation) methods were used to study the capability of these thiazole derivatives to inhibit the corrosion of mild steel in aerated stagnant 0.5 M H$_2$SO$_4$ solutions at 25 °C.

The following are the main conclusions of this study:

- Molecular dynamics simulation results show that the three thiazole derivatives can adsorb on the iron (1 1 0) surface through the thiazole ring and the heteroatoms as well as $\pi$-electrons in the aromatic structure. Addition of thiazole derivatives reduced significantly the corrosion of mild steel in 0.5 M H$_2$SO$_4$. The highest inhibition efficiency achieved with APT. Polarization curves demonstrated that the thiazole derivatives were of mixed-type inhibitors for mild steel corrosion in these solutions. EIS plots indicated that the addition of inhibitors increases the charge-transfer resistance of the corrosion process, and this increase in the
charge–transfer resistance, and hence the inhibition performance, enhances with inhibitor concentration and depends on the type of the adsorbed molecule. EFM results were in good agreement with other traditional chemical and electrochemical techniques used. Corrosion rate monitored using the EFM technique was consistency with those obtained from the Tafel extrapolation method.

References