



## Tin corrosion inhibition by molybdate ions in 0.2 M maleic acid solution: Electrochemical and surface analytical study

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**Abstract:** The inhibition efficiency of molybdate ions ( $\text{MoO}_4^{2-}$ ) against tin corrosion in 0.2 M Malic acid has been studied using electrochemical (DC and AC) and surface analytical methods (SEM and EDX). The electrochemical polarization curves revealed the presence of an active/passive transition of the tin electrode. The electrochemical impedance measurements (EIS) confirmed the benefic effect of increasing  $\text{MoO}_4^{2-}$  concentration on the inhibition efficiency ( $\eta$  %) (reaching  $\eta_{\text{max}} \approx 88\%$  at 0.02 M), whereas  $\eta$  % decreases by increasing temperature. The molybdate ions inhibition mechanism was attributed to the adsorption on the metal surface involving the formation of the adsorbed protective layer.

**Keywords:** Tin corrosion; Inhibition; Molybdate; Polarization curves; Malic acid.

### 1. Introduction

Corrosion is a global problem that continues to be of high relevance in a wide range of industrial applications and products. The electrochemical behavior of tin in aqueous solutions is of interest due to the widespread technological application in soft solders, bronze, and dental amalgam beside its use as tinplate. The presence of the tin coat on the intern surface of cans leads to the protection of the food flavor and its natural appearance through the oxidation of the tin surface in preference to oxidative degradation of the food. During the corrosion process, foodstuff can be contaminated by tin, even though it is not considered as a poisonous metal, a considerable dose produces serious digestive disturbances <sup>1</sup>.

However, the exposition to aggressive environments during long-term service, the material tends to lose their corrosion resistance ability, which leads to the deterioration of their surfaces and affecting their durability causing severe economic losses and pollution of the environment <sup>2,3</sup>.

Dissolution of metallic tin, in the presence of carboxylic acid, especially from the inside of a can body into the food content has a significant influence on the food quality and may cause toxicological effects.

The process of metal corrosion is electrochemical involving anodic and cathodic reactions. The anodic reaction consists of the dissolution of metal, whereas cathodic reaction involves hydrogen and oxygen reduction. The consequences of metallic component failures related to corrosion are many and include the followings injuries, death, material loss, contamination and pollution, loss of time, mechanical and structural damage, etc. <sup>4</sup>.

Corrosion damages can be prevented by using various methods such as upgrading materials, blending of production fluids, process control, and chemical inhibition <sup>5, 6</sup>. Among these methods, the use of corrosion inhibitors <sup>7</sup> is the best to prevent the destruction of metal surfaces in corrosive media.

Among existing carboxylic acids in food packaging, we cite malic acid. According to the systematic nomenclature, it is a hydroxybutane diacid with the molecular formula  $\text{C}_4\text{H}_6\text{O}_5$ . The chemical structure is shown in [Figure 1](#), where it generates two active forms, namely L-malic acid and D-malic acid <sup>8</sup>. The "L" isomer form of malic acid occurs in natural form (in fruit), while the D-form of the acid is synthetically produced <sup>9</sup>.

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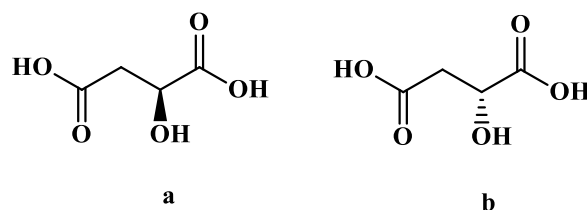
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**Figure 1.** Molecular structure of (a) L- and (b) D-malic acid

Inorganic inhibitors are not so widespread. The cost of these inhibitors is low, but most of them are toxic, for example, chromates, nitrites, and arsenates. It has been reported that molybdate ion ( $\text{MoO}_4^{2-}$ ) has low toxicity and an excellent environmental acceptability<sup>10-11</sup>. Taking these properties into consideration, molybdate ion was tested and reported as the most versatile inhibitor for steel, because of its superb prevention ability in various media, such as neutral aqueous solutions<sup>11-15</sup>, in solutions containing chloride ions<sup>14-17</sup>, and in acidic media<sup>18-21</sup>.

Fujioka *et al.*<sup>22</sup> elucidated the inhibition of pitting corrosion of steel by molybdate ions in a chloride ions borate buffer solution. Refaey *et al.*<sup>23</sup> established that the addition of molybdate ions hinders the localized corrosion of mild steel in chloride solution and that the adsorption of these anions into the metal surface exhibits a vital role in the inhibition process. Deyab *et al.*<sup>24</sup> have revealed that the addition of molybdate ions to alkaline water contributes to the displacement of the corrosion potential towards noble values and the reduction of the corrosion rate of steel. E. Ait Addi *et al.*<sup>25,26</sup> explained the protective influence of molybdate ions and concluded that the presence of these ions inhibits tin pitting corrosion. Furthermore, Mu *et al.*<sup>19</sup> reported decent inhibition efficiencies by molybdate on cold rolling steel in HCl solution in the 0.1–0.5 M concentration range. These findings are indications of the potential of  $\text{MoO}_4^{2-}$  to be a suitable corrosion inhibitor for stainless steel in hydrochloric acid solution<sup>27</sup>.

The present contribution extends our focus on corrosion and passivation behavior of tin in aqueous solutions containing malic acid; being a natural additive in food cans. The control of the corrosion process by the addition of  $\text{MoO}_4^{2-}$  ions as potentially nontoxic corrosion inhibitors was also investigated. Accordingly, conventional electrochemical polarization and electrochemical impedance spectroscopy techniques were applied. Whenever it was necessary, the metal surface was investigated by scanning electron microscopy.

## 2. Experimental

Electrochemical measurements were carried out in a conventional cylindrical three-electrode tempered glass cell. The working electrode was made of a pure tin rod (Aldrich 99.99%) axially embedded in "Araldite" holders to obtain an exposed circular area of 0.785 cm<sup>2</sup>. A saturated calomel electrode (SCE)

and a platinum electrode were used as the reference and auxiliary electrodes, respectively.

Before each experiment, the surface of the working electrode was mechanically polished with different grades of emery papers (down to 1200 grits), degreased with acetone, and rinsed immediately with bi-distilled water. The electrochemical study was carried out using a potentiostat/galvanostat (PGZ 100), which was driven by Volta-Master software.

Potentiodynamic polarization curves were recorded at a scan rate of 60 mV/min. Before the electrochemical measurements, the working electrode was sustained at the open circuit potential (OCP) for 30 minutes. Polarization resistance ( $R_p$ ), is interpreted as the slope of the polarization curve at  $E_{\text{corr}} \pm 10$  mV/SCE.

The tin surface morphology and elementary composition were studied using scanning electron microscopy and dispersive energy X-ray.

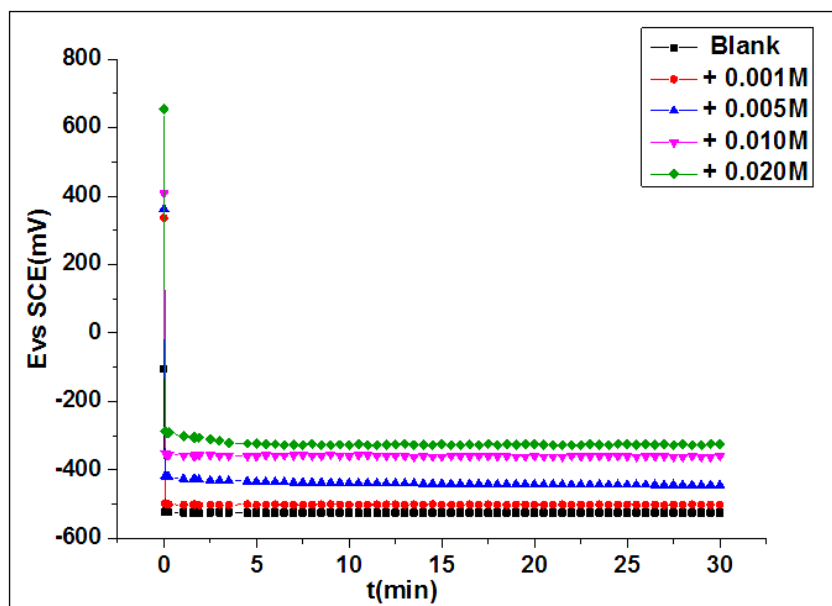
Experiments were carried out in 0.2 M malic acid electrolyte solution (200 ml) without and with the addition of inhibitive molybdate ( $\text{MoO}_4^{2-}$ ). All aqueous solutions were prepared using bi-distilled water and analytical grade chemicals (p.a Merck). Solutions were deaerated by bubbling  $\text{N}_2$  gas through the cell unless otherwise stated. All experiments were performed at 20.1°C and pH of 1.8 and repeated in triplicates to ensure reproducibility.

## 3. Results and discussion

### 3.1. Inhibitor concentration effect

#### 3.1.1. Open circuit potential

Figure 2 displays the variation of tin electrode OCP in time without and with the addition of  $\text{MoO}_4^{2-}$  ions at different concentrations. Upon immersion in the electrolyte, the OCP values shifted to more negative potentials very rapidly, due to the removal of the tin surface oxides formed in the air. The results indicate that the values of OCP shifted to nobler (anodic) upon increasing inhibitor concentration, indicating that the molybdate ions can hinder tin corrosion. On the other hand, we noted that 30 minutes is adequate as immersion time to establish a steady potential of tin electrode. Besides, the results exhibit a definite increase in  $E_{\text{ocp}}$  values with the increase of inhibitor concentrations. It implies that adsorption of molybdate ions on the surface electrode occurs at the defects of the corrosion products, thus reducing the destruction of the passivation film by the acidic medium.



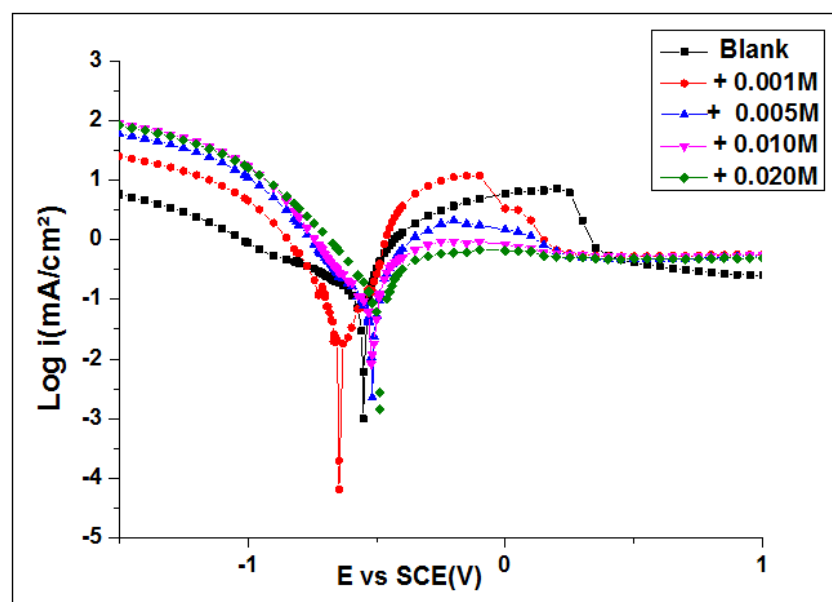
**Figure 2.** Time evolution of the open circuit potential of tin in 0.2 M malic acid without and with the addition of  $\text{MoO}_4^{2-}$  at different concentrations (at 293 K)

### 3.1.2. Potentiodynamic polarization studies

Polarization curves for tin in 0.2M malic acid in the absence and presence of  $\text{MoO}_4^{2-}$  at various concentrations are shown in Figure 3. The important electrochemical parameters, derived from these curves are summarized in Table 1.

As displayed in Figure 3 and Table 1, in the presence of  $\text{MoO}_4^{2-}$  ions, cathodic current–potential curves were characterized by linear domain, indicating that

the hydrogen evolution reaction is under the activation process. From the values of corrosion potential  $E_{\text{corr}}$ , we note that its values are slightly shifted towards noble values in the presence of  $\text{MoO}_4^{2-}$  ions. Additionally, it is suggested that  $\text{MoO}_4^{2-}$  ions acted as a mixed inhibitor based on the fact the displacement in corrosion potential caused by the addition of the inhibitor does not exceed 85 mV<sup>28</sup>.



**Figure 3.** Potentiodynamic polarization curves for tin in 0.2M malic acid-containing different concentrations of  $\text{MoO}_4^{2-}$

The addition of inhibitors ions leads to a decrease in both polarization resistance  $R_p$  and corrosion current density ( $I_{\text{corr}}$ ) which attains the lowest value (i.e.  $18 \mu\text{A} / \text{cm}^2$ ) at  $C = 0.02 \text{ M}$  of  $\text{MoO}_4^{2-}$  ions. Also, at a low molybdate concentration, the inhibition

efficiency is limited, and so the improvement of the corrosion resistance is finite, as shown in Figure 3. To establish a complete, effective, and compact protective film, a suitable molybdate concentration is required.

**Table 1.** Polarization parameters and the corresponding inhibition efficiencies of tin in 0.2 M malic acid-containing different concentrations of MoO<sub>4</sub><sup>2-</sup> at 293 K.

C (M)	E <sub>corr</sub> (mV/SCE)	E <sub>pic</sub> (mV/SCE)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	I <sub>pass</sub> (μA/cm <sup>2</sup> )	I <sub>pic</sub> (mA/cm <sup>2</sup> )	R <sub>p</sub> (Ω/cm <sup>2</sup> )	(η) %
Blank	-558	210	160	193	19.8	17.50	---
1x10 <sup>-3</sup>	-512	-95	91	544	12.02	23.58	43.12
5x10 <sup>-3</sup>	-510	-197	75	548	2.15	111.29	53.12
1x10 <sup>-2</sup>	-512	-225	44	548	0.997	235.8	72.50
2x10 <sup>-2</sup>	-493	-135	18	561	0.480	286.62	88.75

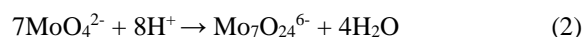
The efficiency of inhibitor in safeguarding or protecting metal surfaces during acid-induced corrosion is dependent on the ability of the molecular inhibitive species of the inhibitor to be adsorbed on the metal surface and the ability of the resulting adsorbed film to disengage the metal surface from the aggressive medium<sup>29</sup>.

The inhibition efficiency (η %) is calculated as follows:

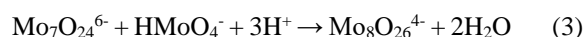
$$\eta\% = \frac{(I_{\text{corr}} - I_{\text{corr-inh}})}{I_{\text{corr}}} \times 100 \quad (1)$$

where I<sub>corr-inh</sub> and I<sub>corr</sub> are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential. The results obtained clearly show that the inhibitory efficiency (η %) increases with the concentration of molybdate ions. The highest inhibition efficiency achieved is 88% at a concentration of 0.02 M of tested inorganic inhibitor.

On the other hand, the addition of the molybdate ions to the medium causes the increase in the cathodic partial current densities sign of activation of the reaction of the evolution of hydrogen. Indeed, the pH of the electrolytic medium affects the behavior of the inhibitory ions. According to Vukasovich *et al.*<sup>30</sup> and Wilcox *et al.*<sup>31</sup>, during high acidity, electrode dissolution is favored by polymerization of molybdates to heptamolybdate. This polymerization generally starts at pH values lower than 6 with the formation of heptamolybdate ions (Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup>) according to the reaction:



However, for even lower pH values down to pH 1.5, octamolybdate ions (Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup>) are obtained according to the reaction:



The formation of heptamolybdate and octamolybdate ions in acidic medium probably leads to the formation of soluble complexes that can stimulate the sensitivity of materials to corrosion<sup>20</sup>. It has been reported that Mo(VI) exists as a cationic poly-nuclear complex in acidic solution with solution pH extending from 0 to 2. Still, several works support that the negative ions

would predominate in solutions at very low pH. However, the distribution diagram of molybdenum species in an acidic medium still generates some controversy in the literature<sup>21</sup>.

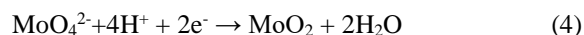
On the other hand, an inspection of anodic branch reveals that tin exhibits a field of activity (activity peaks) in the presence of inhibitors ions, followed by a more or less passivation range breaking by the localized attack. Nevertheless, our results revealed that the addition of MoO<sub>4</sub><sup>2-</sup> ions displace the values of pitting potential E<sub>piq</sub> towards more noble values and peaks potentials E<sub>pic</sub> towards more active values accompanied by a slight decrease of peaks intensities upon increasing of MoO<sub>4</sub><sup>2-</sup> concentration. The most significant displacements are obtained in the case of C = 0.02 M of MoO<sub>4</sub><sup>2-</sup>. This behavior indicates that molybdate ions can hinder tin dissolution and surface damage, furthermore, the inhibition efficiency increases with increasing their concentration in solution.

The inhibition mechanism of molybdate ions can be mostly correlated to the inhibitory species adsorption on the metallic surface initiating regression of the contact surface with aggressive electrolyte beside blocking active sites and consequently reducing the metal dissolution process through the formation of the passive film.

Generally, the first step governing inhibition mechanism in acidic medium is adsorption of inhibitors on the metal surface<sup>13, 32, 33</sup>. Accordingly, molybdate ions significantly reduce the corrosion rate in the aggressive medium by forming a stable passive layer, acting as a physical barrier against aggressive ions. However, the effectiveness of the complexes formed could rely on their stability and solubility in acid solution concerning time, temperature, and concentration. The formation of the layer is linked to the favorable interaction between the molecular inhibitive species and charge on the metal surface<sup>34</sup>.

Additionally, Carrillo *et al.*<sup>35</sup> revealed that molybdate ions are adsorbing on the surface through metal cations and oxides in the anodic sites by electrostatic attraction process. Furthermore, according to Refaey *et al.*<sup>23</sup>, the inhibitory effect of molybdate ions can be based on the strengthening of the passive film by its adsorption on the electrode surface and its reduction

of Mo(VI) (in the form of  $\text{MoO}_4^{2-}$ ) in Mo (IV) (as  $\text{MoO}_2$ ) as follows:



Even if the two species Mo (VI) and Mo (IV) coexist in solution and also with increasing of the molybdate concentration in solution, its solubility limits amount of molybdenum fraction in the form of Mo (IV) in solution. In this case, molybdate ions, which are more stable at high potentials, can adsorb on the surface with sufficient quantity and prevent diffusion of aggressive ions from reaching the metal/film interface by blocking sites through which they enter the film and by the formation of a highly charged film. It has been reported that adsorption of the inhibitor on the metal surface can regulate the rate of dissolution by either reducing the available dissolution area (geometric blocking effect) or by modifying the electrochemical reactions occurring at the metal surface/inhibited solution interface during the inhibition corrosion process <sup>36</sup>.

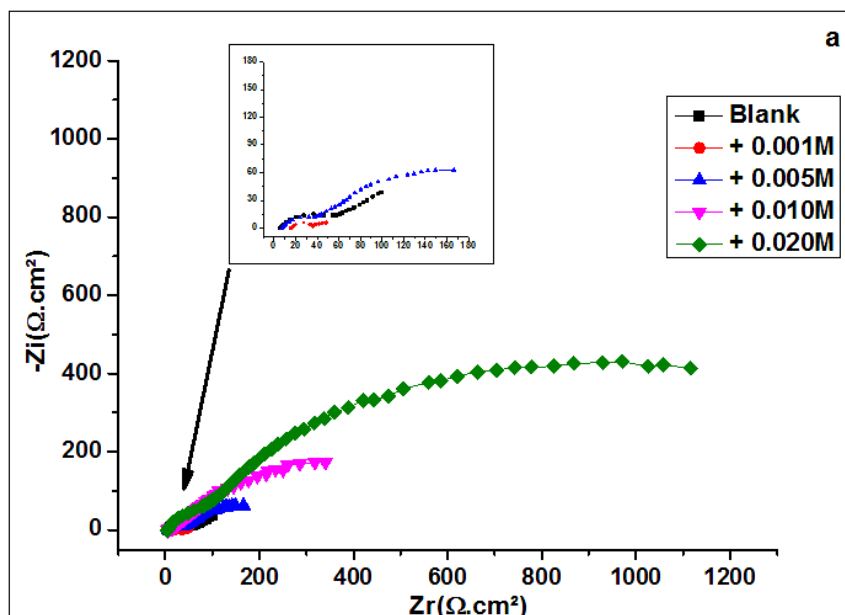
The results obtained in this work are consistent with these proposals that molybdate ions promote the growth of a more protective passive layer that makes the tin metal surface less susceptible to pitting. Besides, according to Ahmed S. Alshamsi et al. while it is generally accepted that relatively high concentrations of  $\text{MoO}_4^{2-}$  inhibit corrosion, there is no widely accepted mechanism on how  $\text{MoO}_4^{2-}$  enhance corrosion resistance <sup>37</sup>.

### 3.2. Electrochemical impedance measurements

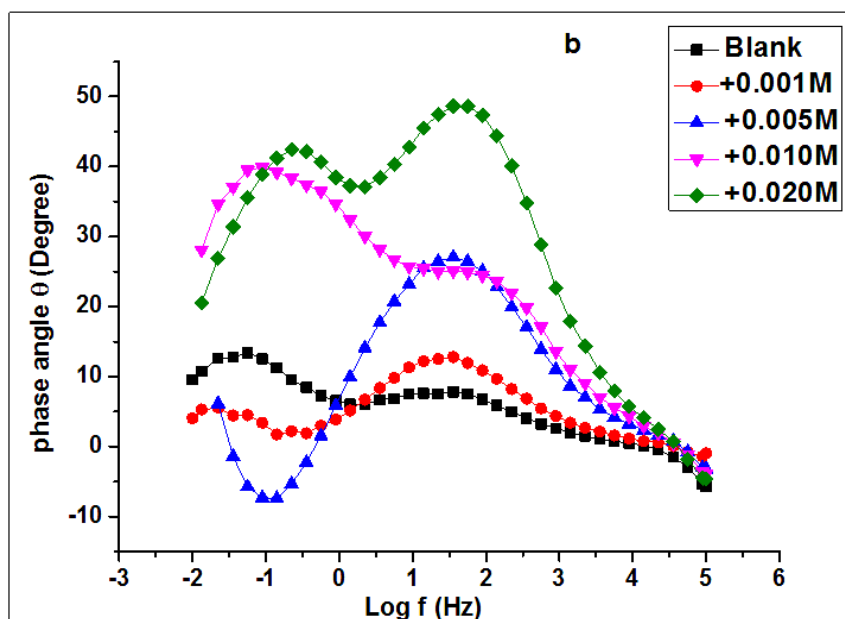
EIS measurements were carried out at OCP ( $E_{\text{corr}}$ ). Figure 4 displays the EIS Nyquist plots (a) obtained in the absence and presence (at different concentrations) of  $\text{MoO}_4^{2-}$ . Frequency scanning was performed from high frequencies (HF) (100,000 Hz) to low frequencies (LF) (0.010 Hz) with a sinusoidal disturbance of 5 mV amplitude at the OCP, where the system is almost static.

The obtained Nyquist plots (Figure 4 (a)) showed imperfect semicircles which is attributed to the frequency dispersion related to the inhomogeneity of the tin electrode surface. In the absence of the inhibitor, the assessment of Nyquist diagrams revealed two distinct relaxation times, one at high frequencies and the other at low frequencies and two-time constants as shown in the Bode diagrams (Figures 4-b) <sup>38-40</sup>.

At the high-frequency range, a semicircle characterizing a capacitive loop is observed, while at low frequencies a linear branch, characteristic of the presence of diffusion Warburg-type layer is displayed in the absence of the inhibitor. On the other hand, in the presence of the inhibitor, the diagrams present two capacitive loops whose size increases with increasing inhibitor concentration to reach a maximum at the concentration of  $10^{-2}$  M. This result demonstrates the inhibitory effect of molybdate ions and their dependence on inhibitor concentration. The HF loop characterizes the charge transfer phenomenon while the LF one describes the oxide film formed on the tin electrode surface.







**Figure 4.** EIS (a) Nyquist and (b) Bode plots obtained for tin in 0.2 M malic acid without and with addition of  $\text{MoO}_4^{2-}$  at various concentrations at 293 K

The main parameters deduced from the impedance diagrams of tin in 0.2 M of malic acid-containing different concentrations of molybdate ions are summarized in Table 2.

The inhibition efficiency ( $\eta$  %) of tin corrosion is calculated from the values of the charge transfer resistance  $R_{tc}$  according to the following relationship:

$$\eta \% = \frac{(R_{tc} - R_{tc-inh})}{R_{tc}} \times 100 \quad (5)$$

where  $R_{tc(inh)}$  and  $R_{tc}$  are respectively the values of the charge transfer resistance of tin in 0.2M of malic acid with and without the inhibitor addition.

**Table 2.** Electrochemical impedance spectroscopy parameters of tin in 0.2M malic acid without and with the addition of  $\text{MoO}_4^{2-}$  at different concentrations (at 293 K).

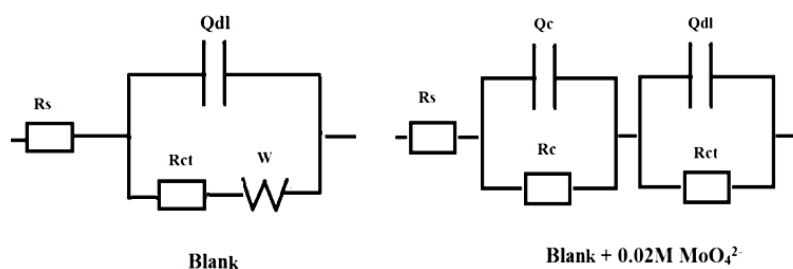
C (M)	$R_s$ ( $\Omega \cdot \text{cm}^2$ )	$R_c$ ( $\Omega \cdot \text{cm}^2$ )	$Q_c$ ( $\Omega^{-1} \text{cm}^{-2} \text{s}^{n1}$ )	$n_1$	W ( $\Omega \cdot \text{cm}^2 \cdot \text{S}^{-1/2}$ )	$R_{tc}$ ( $\Omega \cdot \text{cm}^2$ )	$Q_{dl}$ ( $\Omega^{-1} \text{cm}^{-2} \text{s}^{n2}$ )	$n_2$	$\eta$ (%)
Blank	7.41	---	----	---	0.207	18.43	0.083700	0.5	---
$10^{-3}$	53.8	93.5	0.05120	0.6	---	25.28	0.070850	0.6	27.09
$510^{-3}$	74.3	4.5	0.005562	0.4	---	52.34	0.016330	0.6	64.78
$10^{-2}$	15.9	17.3	0.000696	0.6	---	67.94	0.002812	0.6	72.87
$210^{-2}$	10.3	36.7	0.000224	0.7	---	150.00	0.000595	0.7	87.77

The inspection of results in Table 2 indicates that the value of the charge-transfer-resistance ( $R_{tc}$ ) increases gradually as a function of the inhibitor concentration, which suggests the ability to form a protective film on the tin surface, therefore, improving its resistance against the aggressiveness of malic acid.

On the other hand, the value of the constant ( $Q_{dl}$ ) decreases with the concentration increase of the inhibitor, which corresponds to a firming of the passive film on the tin surface causing a decrease in the rate of corrosion. Additionally, the increase in values recorded for the roughness factor ( $n$ ) as a function of the added concentration can be explained

by a reduction of surface inhomogeneity possibly caused by adsorption of inhibitor ions on the active sites of the tin surface. A comparison may be made between the  $\eta$  values obtained by different methods. It is evident that no significant variations observed in  $\eta$  values obtained from various methods, thus there is an agreement between the two methods applied in this investigation.

Figure 5 shows the equivalent circuits giving the response of the tin electrochemical interface in 0.2 M of malic acid with and without inhibitor using the ZsimpWin (version 3.10) software to evaluate the parameters for all circuit elements.



**Figure 5.** Equivalent circuits chosen to fit experimental EIS data

The results are obtained with acceptable certainty with a correlation factor  $\chi$  of the order of  $2 \cdot 10^{-4}$ . In this case, the use of CPE is essential for the equivalent circuit (Figure 5) and is related to the heterogeneity, roughness, and the porosity of the electrode surface<sup>41</sup>. In the absence of the inhibitor, the corresponding equivalent circuit, in this case, consists of the electrolyte resistance ( $R_s$ ), a constant phase element ( $Q_{dl}$ ) (used in place of the capacity of the double layer ( $C_{dl}$ ) to account for inhomogeneity of the surface) in parallel with the diffusion impedance ( $W$ ) connected in series with the charge transfer resistor,  $R_{ct}$ .

In the presence of the inhibitor, the representative equivalent circuit, in this case, consists on the one hand ( $Q_c$  and  $R_c$ ) corresponding to the film on the tin surface at HF and on the other hand of ( $Q_{dl}$  and  $R_{ct}$ ) corresponding to the charge transfer reaction at LF and recalling that the constant phase element refers to the distribution of relaxation times for microscopic inhomogeneity present at the metal/electrolyte interface<sup>42</sup>. The parameter  $n$  is a constant that can take several values ranging from -1 to 1. When  $n \approx 1$ , the CPE is equivalent to a capacitor,  $n = 0.5$  indicates

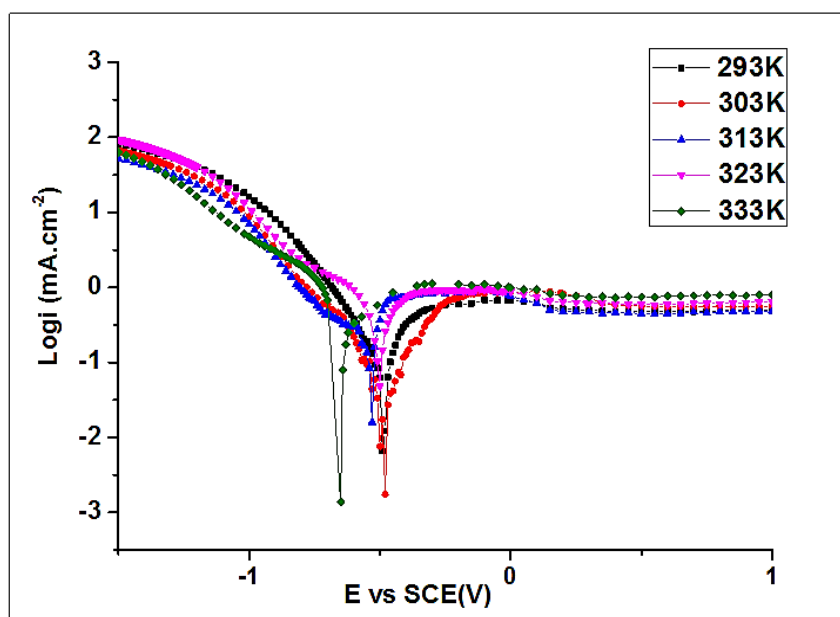
diffusion,  $n = 0$  indicates a resistor and  $n = -1$  represents an inductor.

### 3.3. Temperature effect

#### 3.3.1. Potentiodynamic polarization studies

Raising the temperature of the medium can have a significant impact on the formation of the inhibiting film. Therefore, the stability of a corrosion inhibitor in an aggressive medium at given operating temperatures is substantial for its application. Temperature is indeed one of the factors that can simultaneously modify the behavior of inhibitors and substrates in a given aggressive environment<sup>43</sup>. The increase in temperature thus favors desorption of the inhibitor as well as a rapid dissolution of the organic compounds or complexes formed, consequently weakening the corrosion resistance<sup>44</sup>.

Figure 6 shows the polarization curves of tin in 0.2 M malic acid in the absence and the presence of 0.02M  $\text{MoO}_4^{2-}$  at different temperatures. Table 3 presents the different electrochemical parameters interpreted from the polarization curves.



**Figure 6.** Polarization curves for tin immersed in 0.2 M malic acid in the presence of 0.02 M  $\text{MoO}_4^{2-}$  at different temperatures

**Table 3.** Polarization parameters of tin in 0.2 M malic acid-containing 0.02 M MoO<sub>4</sub><sup>2-</sup> at different temperatures.

T (K)	E <sub>corr</sub> (mV/SCE)	E <sub>piq</sub> (mV/SCE)	E <sub>pic</sub> (mV/SCE)	I <sub>corr</sub> (μA cm <sup>-2</sup> )	I <sub>pass</sub> (μA cm <sup>-2</sup> )	(η) %
293	-493	2578	-17.08	18	561	88.75
303	-533	1986	-123	45	459	72.89
313	-503	1968	-123	102	496	40.35
323	-531	1493	-285	110	714	38.54
333	-651	1482	-284	125	799	33.51

The inspection of polarization curves shows that elevation of temperature strongly affects anodic branches more than cathodic branches. A slight displacement of the values of corrosion potential towards the less noble values is observed (Table 3), which shows the emphasis on the aggressiveness of the medium as a result of raising the temperature. Such behavior is supported, on the one hand, by the increase of corrosion and passivation current densities and on the other hand, by the spectacular regression of the polarization resistance. Besides, the rise in the intensity of the activation peaks as well as the displacement of their potentials towards more negative values confirms that the dissolution of the tin is very affected by the elevation of the temperature even in the presence of the molybdates ions 0.02M. Similarly, the shift of the E<sub>piq</sub> values to the more negative values (from 2578 mV to 2250 mV for the 293 and 333K temperatures, respectively) clearly shows that the increase in temperature weakens the pitting resistance of tin. Such a result corroborates that found by Ait Addi *et al.*<sup>25</sup> in synthesized industrial water. On the other hand, Nwanonyeni *et al.*<sup>4</sup> contributed the high rate of dissolution of carbon steel in 1 M H<sub>2</sub>SO<sub>4</sub> solution observed at elevated temperature to more dissolution energy effect acquired by the corrosive agent within the aggressive

medium. Also, the desorption of adsorbed inhibitor due to enhanced solution agitation by higher rates of hydrogen gas evolution at elevated temperature is possible. It may cause the ability of the inhibitor to be adsorbed on the carbon steel surface to reduce.

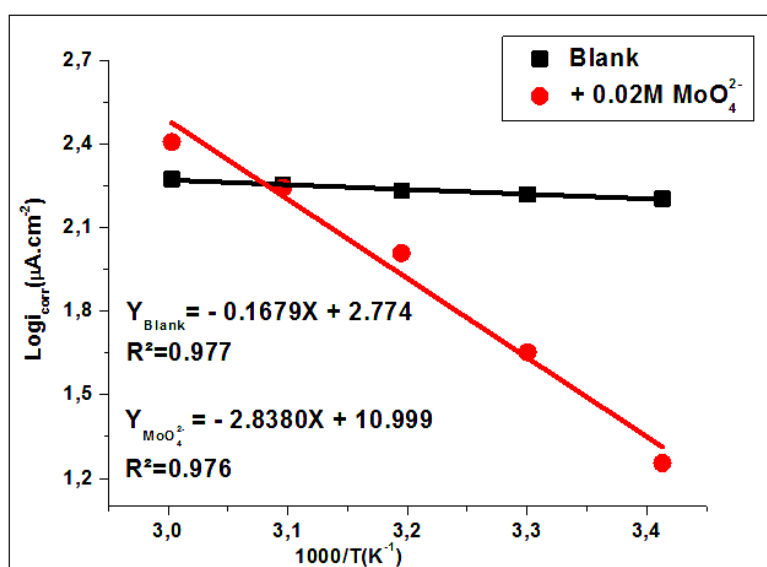
### 3.4. Determination of activation energy

Corrosion degrades the inherent properties of metals by introducing defects in the metal lattice and dislocations resulting in non-homogeneous metal surfaces<sup>45</sup>.

To obtain more information on the corrosion inhibition process, we proceeded to the determination of the activation energy E<sub>a</sub> using the Arrhenius law between the corrosion current and the temperature, in the absence and the presence of the inhibitor, according to the following relationship<sup>46,47</sup>:

$$I_{\text{corr}} = K_{\text{exp}} \left( \frac{-E_a}{RT} \right) \quad (6)$$

where  $i_{\text{corr}}$ : Current density (A cm<sup>-2</sup>), K is pre-exponential constant, E<sub>a</sub> is the activation energy of the corrosion process (kJ mol<sup>-1</sup>), R is the universal gas constant (R = 8.31 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature in K.



**Figure 7.** Arrhenius plots of log ( $i_{\text{corr}}$ ) versus  $1000/T$  for tin in 0.2 M malic acid without and with the addition of 0.02 M MoO<sub>4</sub><sup>2-</sup>



Figure 7 shows the variation of  $\text{Log}(i_{\text{corr}})$  vs. the temperature inverse ( $1/T$ ) for tin in 0.2 M malic acid without and with the addition of inhibitory ions.

The analysis of these curves shows that the variation  $\text{Log}(i_{\text{corr}}) = f(1000/T)$  is linear and respects the Arrhenius law both in the absence and in the presence of the molybdate ions (the determination coefficient  $R^2 = 0.977$ ).

The exploitation of these curves makes it possible to calculate the values of the activation energy from the slope ( $-E_a/R$ ) and the pre-exponential factor from the ordinate at the origin. The value of the activation energy calculated in the presence of the inhibitor is  $E_{a(\text{inh})} = 54.39 \text{ KJ mol}^{-1}$ ; however, the calculated value in its absence is  $E_a = 3.21 \text{ KJ mol}^{-1}$ .

A comparison of the activation energies obtained in the presence ( $E_{a(\text{inh})}$ ) or not ( $E_a$ ) of inhibitor shows that  $E_{a(\text{inh})} > E_a$ , which allows us to conclude that the molybdate ions protect the tin by their adsorption on the surface via electrostatic interactions. However, this type of temperature-sensitive bonding does not

provide adequate protection against corrosion when the temperature increases<sup>48</sup>. Nwanonyi *et al.*<sup>4</sup> concluded that the increase of activation energy is leading to a reduction in the rates of corrosion of carbon steel. Also, it has been reported that adsorption of the inhibitor on the metal surface can regulate the rate of dissolution by either reducing the available dissolution area (geometric blocking effect) or by modifying the electrochemical reactions occurring at the metal surface/inhibited solution interface during the inhibition corrosion process<sup>49</sup>.

### 3.5. Surface analysis

#### 3.5.1. Surface morphology analysis

In the aim to visualize the morphological appearance of the tin surface in the absence and presence of inhibitor after immersion for 24h, we used scanning electron microscopy (SEM). The results obtained by this technique are given in the micrographs of Figure 8-a, b.

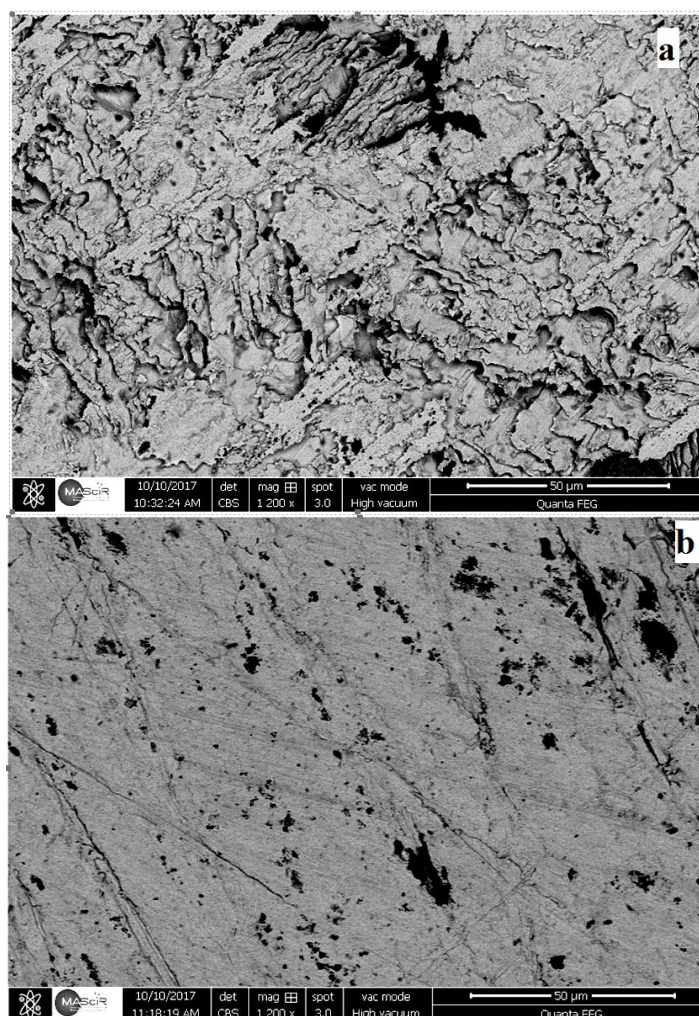
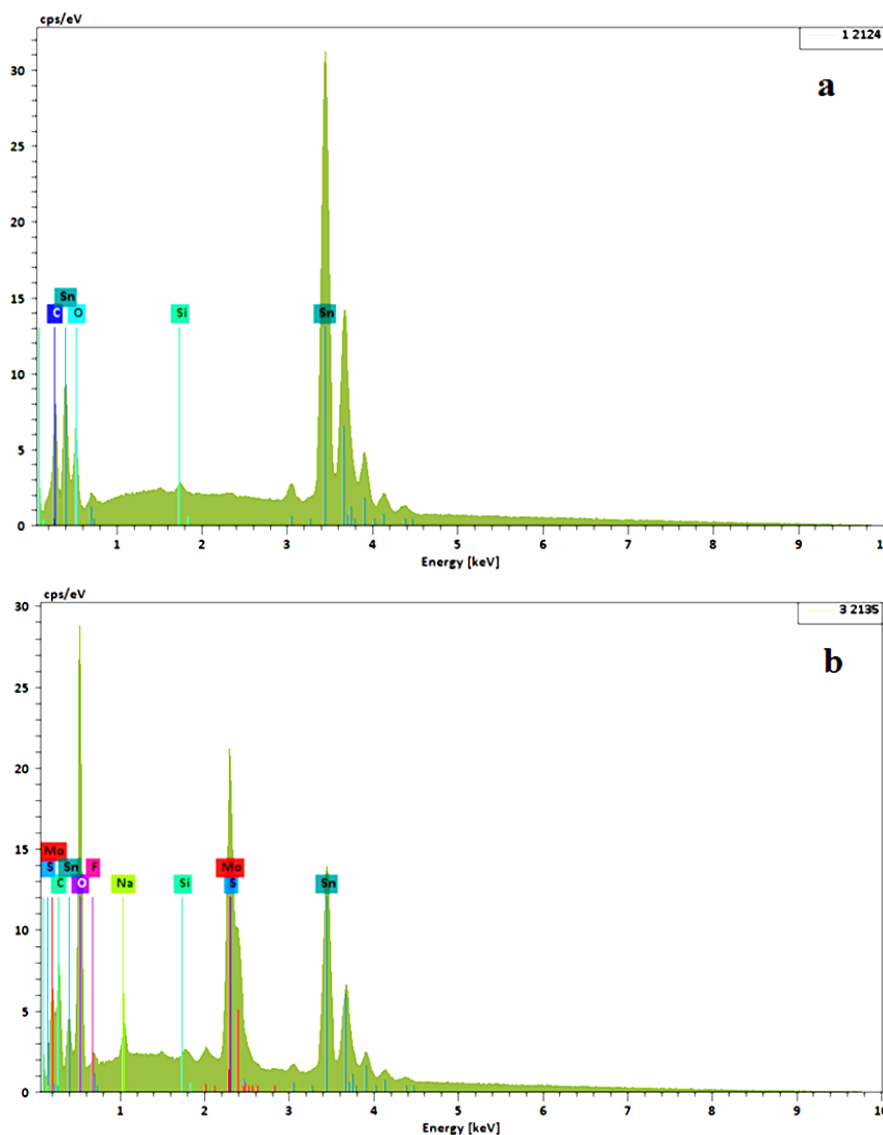


Figure 8. SEM images of tin surface after 24h of immersion in 0.2 M malic acid solution (a) without and (b) with  $0.02 \text{ M MnO}_4^{2-}$  at 293 K

The SEM photographs show that tin surface is highly damaged in the absence of the inhibitor (Figure 8-a) while in its presence (Figure 8-b) is smooth and shows small scratches due to abrasive paper (during the preparation of tin specimen). These observations confirm the protective effect of  $\text{MnO}_4^{2-}$  ions toward tin corrosion. Such protection is due to the formation of inhibitor protective film on the tin surface.

### 3.5.2. Energy dispersive X-ray (EDX) analysis

To identify the different elements, present on the tin surface, we carried out EDX analyzes. Figure 9 illustrates the EDX spectrums of the tin electrode in 0.2M malic acid in the absence and the presence of 0.02M  $\text{MnO}_4^{2-}$  after 24h of immersion at 293 K.



**Figure 9.** EDS spectra of the surface of tin in 0.2 M malic acid in the absence (a) and the presence (b) of 0.02 M  $\text{MoO}_4^{2-}$  at 293K

The analysis of the EDX spectrum of the tin specimen in 0.2 M of malic acid in the absence and the presence of 0.02 M  $\text{MnO}_4^{2-}$  clearly shows the presence of an additional molybdenum peak in the case of inhibited metal. This result confirms that the inhibitory effect of molybdate ions is based on the strengthening of the passive film by its adsorption on the tin surface.

## 5. Conclusion

The ability of  $\text{MnO}_4^{2-}$  ions to reduce the corrosion of tin in 0.2 M malic acid solution is investigated using various electrochemical and surface analysis

techniques. We conclude that the molybdate ions have an interesting inhibitory effect against tin corrosion in the studied medium. The inhibition efficiency of tested anionic inhibitor increases with increasing the inhibitor concentration and reaches 88% at 0.02M. The inhibition mechanism is attributed to the adsorption of molybdate ions on tin surface through electrostatic interactions with it. However, this inhibitory effect is strongly affected by the increase in medium temperature. Surface analysis revealed an initiated surface coverage on the tin surface due to the presence of inhibitor.

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