Int. J. Electrochem. Sci., 9 **(2014)** 8465 - 8475

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

The Effect of Molybdate Anions on the Corrosion and Passivation of Tinplate in Synthetic Industrial Water

A. Ait Addi[1,*], *E. Ait Addi*[2], I. Bakas[2], *M. Hamdani*[1]

[1]Laboratoire de Chimie Physique, Faculté des Sciences, Université Ibn Zohr, B.P. 8106, Cité Dakhla, Agadir, Maroc.
[2]Equipe de Biotechnologie, Energie et Environnement, Ecole Supérieure de Technologie d'Agadir, B.P: 33/S, Agadir, Maroc.
[*]E-mail: a.aitaddi@uiz.ac.ma

Received: 29 September 2014 / *Accepted:* 19 October 2014 / *Published:* 28 October 2014

Corrosion and passivation behaviour of tinplate in a synthetic medium similar to industrial water containing Cl^-, SO_4^{2-} and HCO_3^- has been studied in the presence and absence of molybdate anions by using electrochemical polarization measurements. The results show that tinplate manifests a passivation phenomenon with a passivation breakdown. The molybdate anions act significantly on the pitting and passivation potentials when their concentration increases in the solution. The analysis of surface using SEM and EDX methods showed that the modification of tinplate surface depends on the components of the aggressive medium. The effect of medium temperature on the tinplate was also studied.

Keywords: Corrosion, Industrial water, Inhibition, Molybdate, Tinplate.

1. INTRODUCTION

The excellent formability, solderability and nontoxicity of tinplate make it the most basic material used in food and electronic industries [1,2]. This material is made from a low carbon mild steel sheet coated on both faces with pure tin. The corrosion behaviour and passivation of tin in different aggressive mediums have been intensively studied [3-9]. I's agreed that solutions containing Cl^-,SO_4^{2-}, NO_3^-, HCO_3^{-} -…are the most aggressive mediums towards all materials such as tinplate.

In our previous work [10], we have studied the corrosion behaviour of tinplate in a synthetic medium similar to industrial water containing sulphates, chlorides and hydrogencarbonate ion. The results obtained by the use of electrochemical and metallographic techniques show that tinplate manifests a passivation phenomenon with rupture of passivation. We have found that tinplate is very sensitive to the variations of anion concentration in solution and the presence of Cl^- and SO_4^{2-} anions stimulate pitting corrosion of tinplate, whereas HCO_3^- ions act as inhibitor for pitting corrosion of this material in the studied medium [10]. On the contrary, many methods have been used to avoid corrosion problems and pitting susceptibility of tinplate. We cite the use of protective lacquers [11] and the addition of inhibitors [12-15]. Among the inhibitors most used, several authors studied the addition of inorganic anions (NO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-} , NO_2^-, ClO_4^-, SO_4^{2-}) to the solutions. They showed that some of these ions inhibit corrosion of tin while others accelerate it [16,17]. Abdel Rehim et al concluded that both $Cr_2O_7^{2-}$ and MoO_4^{2-} inhibit the corrosion of tin and their effectiveness increase with their concentrations [18]. On the other hand , Refaey et al. [19] studied the effect of $Cr_2O_7^{2-}$, MoO_4^{2-} , NO_3^-, and NO_2^- on the pitting corrosion of tin in alkaline and near neutral media. They found that the effectiveness of inhibitors increases in the order: $Cr_2O_7^{2-}$, $> MoO_4^{2-} > NO_3^-$. Despite the demonstrated efficiency of chromate as inhibitor, the known toxicity and carcinogenic properties of Cr(VI) compounds exert a continuous pressure to use green inhibitors with null toxicity [20].

The present work was undertaken to study the effect of adding the molybdate anions MoO_4^{2-} on corrosion and passivation of tinplate in synthetic medium containing Cl^-,SO_4^{2-} and HCO_3^-. We took into account the effects of the inhibitor concentration and the temperature of the medium.

2. EXPERIMENTAL PART

The electrochemical measurements was carried out by using a computerized potentiostatic electrochemical set Voltalab PGP201. Potentiodynamic polarization curves were recorded with a scan rate of 60 mV/min. Before each electrochemical measurement, the working electrode was maintained at free potential for 30 minutes. We used for all electrochemical measurements a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode were used as reference and Auxiliary electrodes, respectively. The working electrode is in the form of disc from tinplate of the surface 0.78 cm^2. Before each experiment, the surface of the working electrode was rinsed with acetone and bidistilled water. The heat treatments were carried out in a programmable continuous pipe still under an inert atmosphere of nitrogen at various temperatures during two hours.

The experiments were carried out in a synthetic medium containing 0.01M NaCl, 0.008M Na_2SO_4 and 0.003M $NaHCO_3$ with the absence and presence of sodium salts molybdate at different concentrations. All aqueous solutions were prepared from bidistilled water and analytical grade chemicals and they were deaerated by bubbling N_2 through the cell unless otherwise stated. Thereafter, a constant flow of N_2 was maintained over the solution. All tests were conducted at 20±1°C in magnetically stirred solutions at pH 8.2 (±0.2). Experiments were repeated three times to ensure the reproducibility.The morphology and composition of the passive layer were performed using scanning electron microscopy (SEM) JEOL JSM-5500 coupled with energy dispersive X-ray (EDX) JEOL-5600.

3. RESULTS AND DISCUSSION

3.1. Effect of molybdate concentration

To better understand the effect of the addition of MoO_4^{2-} anions in synthetic medium to the corrosion and the passivation of tinplate, we propose studying the effect of adding these anions with concentrations between 0.001 and 0.02M.

Figure1 illustrates the polarization curves of tinplate in the synthetic industrial water in the absence and presence of MoO_4^{2-} anions at concentrations 0.001M, 0.01 and 0.02M. These curves indicate that the addition of the molybdates anions at lower concentrations (**<0.01M**) does not have a considerable influence on the shape of the cathodic region of polarization curves. This region is characterized by the cathodic Tafel line indicating that the reduction of water is activation controlled reaction which corresponds to the following reaction (1):

$$2H_2O + 2\,e^- \longrightarrow 4\,OH^- + H_2 \qquad (1)$$

For 0.02M MoO_4^{2-}, there is apparition of an extended current landing for the more cathodic overvoltages. This plateau could be assigned to the reduction of the Sn^{2+} ions following reaction (2):

$$Sn^{2+} + 2\,e^- \longrightarrow Sn \qquad (2)$$

These Sn^{2+} ions are formed previously during the maintenance time of the electrode at its free corrosion potential.

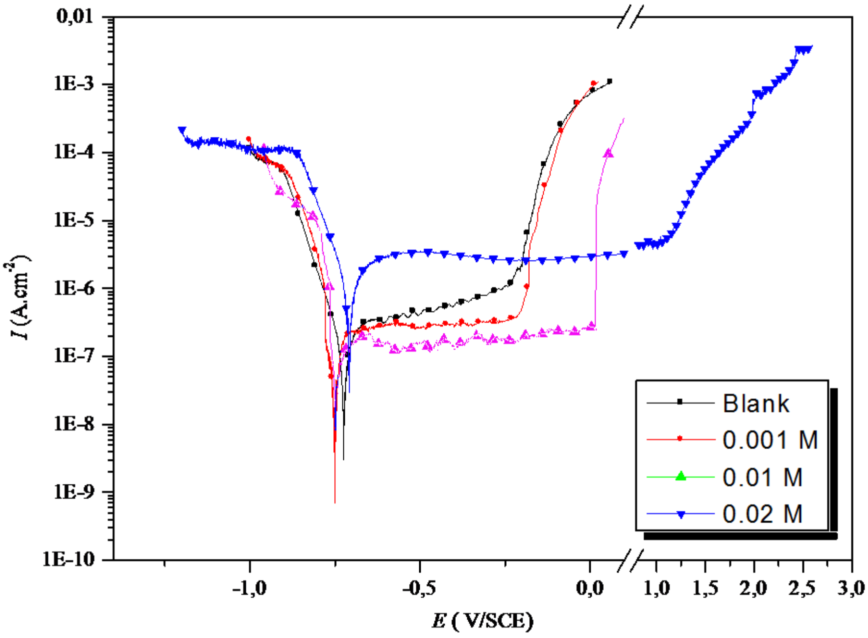

Figure 1. Polarization curves of tinplate in the synthetic medium at different concentrations of molybdate anions.

Nevertheless, the anodic behaviour of tinplate in the presence of MoO_4^{2-} anions is modified. In fact, a displacement of the pitting potential E_{piq} towards more noble values has been observed when the concentration of MoO_4^{2-} increases in solution. The values of the corrosion and passivation current densities decrease when the concentration of the MoO_4^{2-} anions increases until 0.01M. At the concentration of 0.02M, I_{corr} and I_{pass} become more important in comparison with the blank case (Table 1). However, the corrosion potential remains less affected by the molybdates concentration in solution.

We remark that the electrochemical results show that two antagonistic phenomena occur. On the one hand, the tinplate becomes less sensitive to the pitting, which is one advantage in using these anions. On the other hand, the presence of MoO_4^{2-} anions at 0.02M leads to accelerate the uniform corrosion which is considered as a negative action of these anions. This result could be explained by their unfavourable effect on the tinning.

Table 1. Influence of concentration of molybdate on electrochemical parameters of tinplate in the synthetic medium.

$[MoO_4^{2-}]$ (mol.l^{-1})	E_{corr} (mV/SCE)	E_{piq} (mV/SCE)	ΔE (mV/SCE)	I_{corr} (µA.cm^{-2})	I_{pass} (µA.cm^{-2})
Blank	-726	-190	536	0.16	0.4
0.001	-753	-180	573	0.03	0.3
0.01	-750	+350	1100	0.02	0.2
0.02	-710	+1200	1910	1.6	3

3.2. Effect of temperature

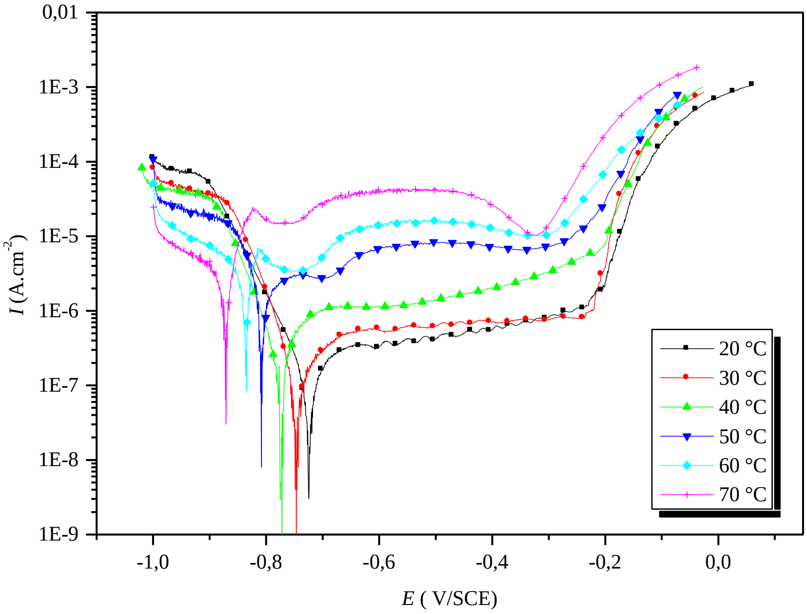

Figure 2. Polarization curves of tinplate in synthetic industrial water at different temperatures.

Temperature is an important factor affecting the corrosion phenomenon. Therefore, we are interested to take into account this factor for two important reasons: firstly, to examine the sensitivity of tinplate to corrosion at high temperatures. Secondly, to verify whether the dissolution/passivation mechanism of tinplate depends on temperature. Figure 2 and 3 present, respectively, the polarization curves of tinplate in synthetic industrial water without and with addition of 0.02M MoO_4^{2-} anions for temperatures from 20 to 70°C. The corresponding electrochemical parameters are given in table 2.

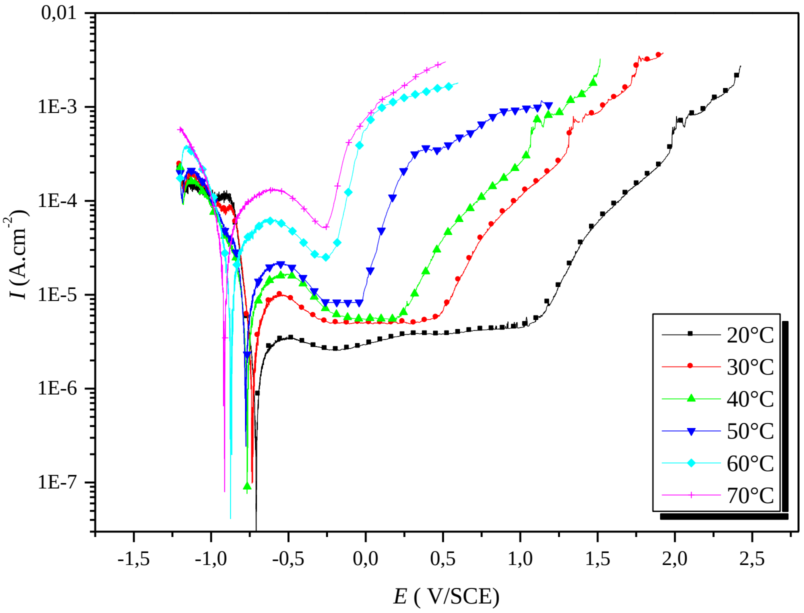

Figure 3. Polarization curves of tinplate in synthetic industrial water with 0.02M MoO_4^{2-} anions at different temperature.

Table 2. Influence of temperature on electrochemical parameters of tin in the synthetic medium with and without 0.02 M molybdate anions.

	T (°C)	E_{corr} (mV/SCE)	E_{piq} (mV/SCE)	I_{pic} (µA.cm^{-2})	I_{corr} (µAcm^{-2})	I_{pass} (µA.cm^{-2})
Blank	20	-726	-190	-	0.16	0.4
	30	-748	-220	-	0.3	0.6
	40	-764	-240	-	0.7	1.5
	50	-810	-250	-	1.5	7
	60	-837	-290	-	2.6	16
	70	-873	-300	-	3.4	41
Blank + 0.02M MoO_4^{2-}	20	-710	1200	3.3	1.6	3
	30	-734	500	10	2.5	5.2
	40	-769	250	16	5.0	6
	50	-778	0	21	7	9.5
	60	-874	-150	63	13.8	26
	70	-914	-250	130	25.1	51

The polarization curves of figure 2 and 3 show that increasing temperature modifies the general shape of the curves. In fact, the corrosion and passivation current densities increase with temperature (Table 2). Thus, the values of corrosion and pitting potentials E_{corr} and E_{piq} are shifted significantly to more active values. The very pronounced dissolution at temperatures higher than 50°C could be interpreted especially by the formation of much more soluble corrosion products as temperature raises [21].

For each temperature, the estimated value of the corrosion current density of the tinplate in the presence of the molybdates anions is more important than that determined in the case of the blank. We also noted during the course of this experiment the apparition of an activity peak in anodic domain. The intensity of this peak increases as the temperature of the medium increases.

Figure 4 shows Arrhenius plots of the corrosion and passivation current densities of tinplate in synthetic industrial water in the absence and presence of 0.02M MoO_4^{2-} anions. The values of apparent activation energy Ea (Blank) and E'a (Blank+ MoO_4^{2-}) are reported in table 4. Ea and E'a are determined by Arrhenius plots according to the following equations:

$$\mathrm{Wcorr} = \mathrm{A} \exp\left(\frac{-\mathrm{Ea}}{\mathrm{RT}}\right) \quad \text{and} \quad \mathrm{W'corr} = \mathrm{A} \exp\left(\frac{-\mathrm{E'a}}{\mathrm{RT}}\right)$$

Ea and E'a are respectively the apparent activation energy for the corrosion with and without inhibitor.

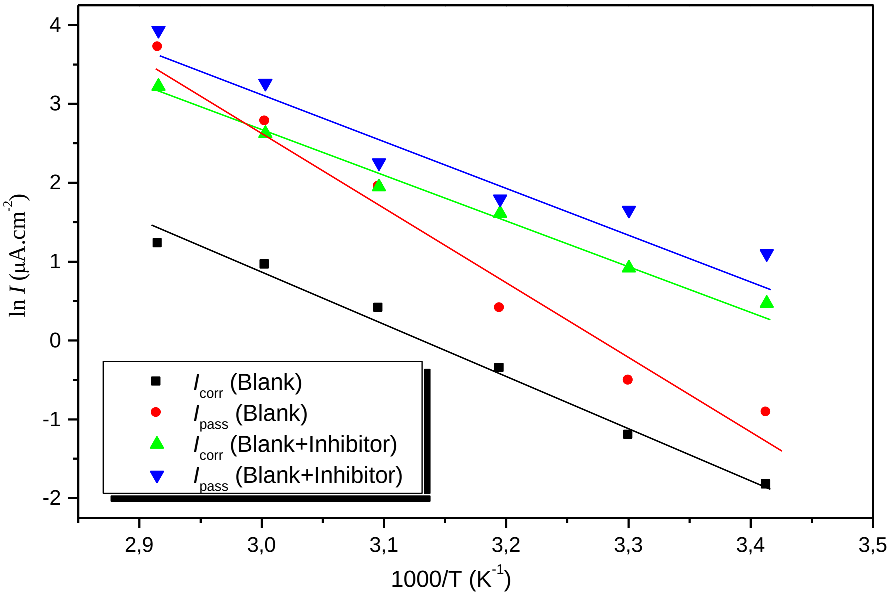

Figure 4. Arrhenius plots for Icorr and Ipass of tinplate in the synthetic medium with and without 0.02M MoO_4^{2-} anions.

It can be seen from the table that, in the blank, Ea related to the variation of I_{corr} is lower than that related to the variation of I_{pass}. Actually, when the material is exposed at its free corrosion potential, there is probably formation of a thin and porous layer on the surface. The corrosion process is done through this layer. When applying an anodic overvoltage in the passivation domain, the passive layer becomes compact and protective probably by a dissolution/precipitation mechanism [22]; this explains the great value of Ea related to the variation of I_{corr} than that related to the variation of I_{pass}.

Table 3. Activation Energy for tin corrosion in the absence and presence of 0.02M MoO_4^{2-}

	Ea (Kj/mol)	E'a (Kj/mol)
I_{corr}	52.1	45.7
I_{pass}	81.6	45.9

In the presence of the molybdate anions, the apparent activation energy (E'a) values are lower than those obtained in the blank case. This confirms that adding molybdate anions will promote the dissolution of tinplate. Previous study reported that the metal has the greatest tendency to corrode for the lowest values of the apparent activation energy [23].

3.3. Long term tests

During the step dedicated to study the effect of adding MoO_4^{2-} anions, we concluded that electrochemical measurement is an efficient and a fast technique to accelerate corrosion and passivation tests. To make an interrelationship between the electrochemical results and the real observed corrosion phenomenon, we achieved tests at long immersion time. The aggressive solutions used are identical to those used during electrochemical tests. The samples are characterized by using the scanning electron microscopy (SEM) coupled to energy dispersive spectroscopy (EDX) before and after the attack. Figures 5 and 7 represent respectively the tinplate surface before and after 15 days immersion.

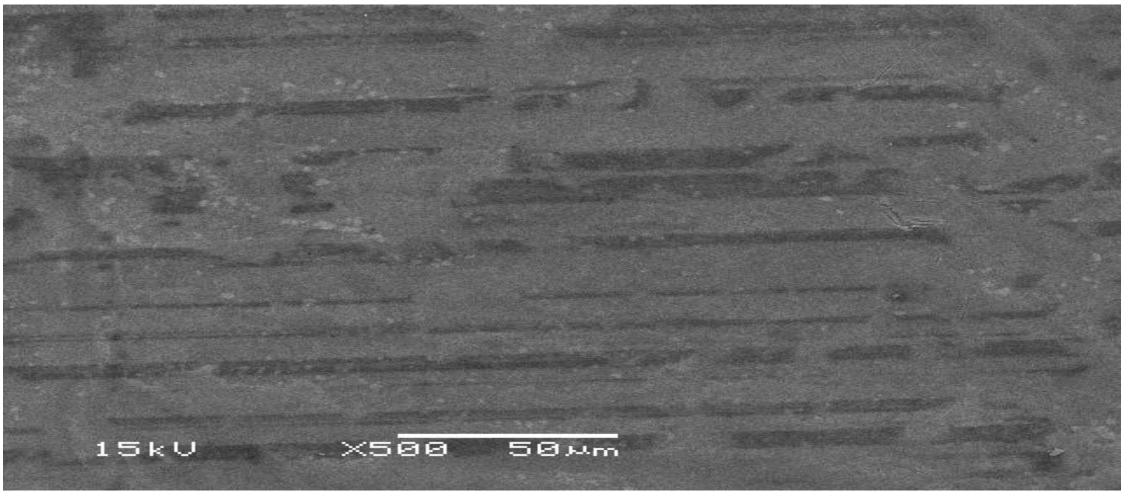

Figure 5. SEM micrograph (x 500) of the tinplate surface before 15 days of immersion in synthetic industrial water.

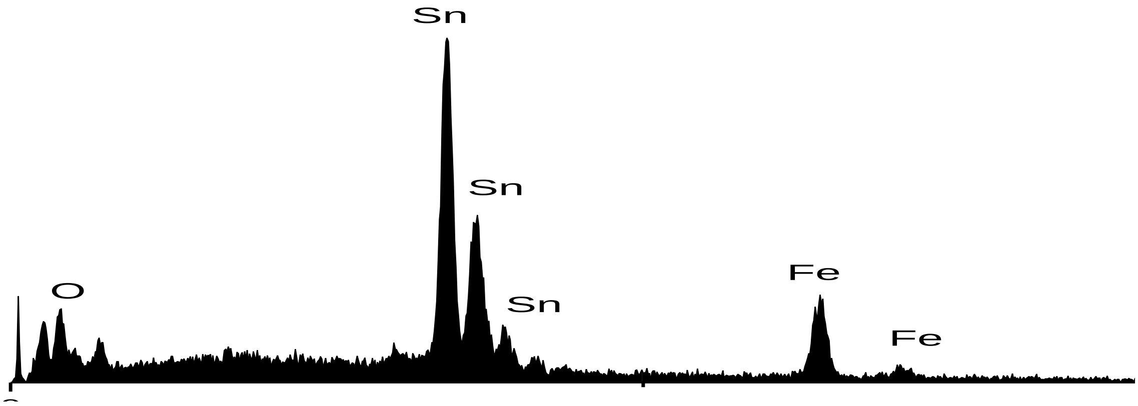

Figure 6. EDX spectral of tinplate before the immersion in synthetic industrial water.

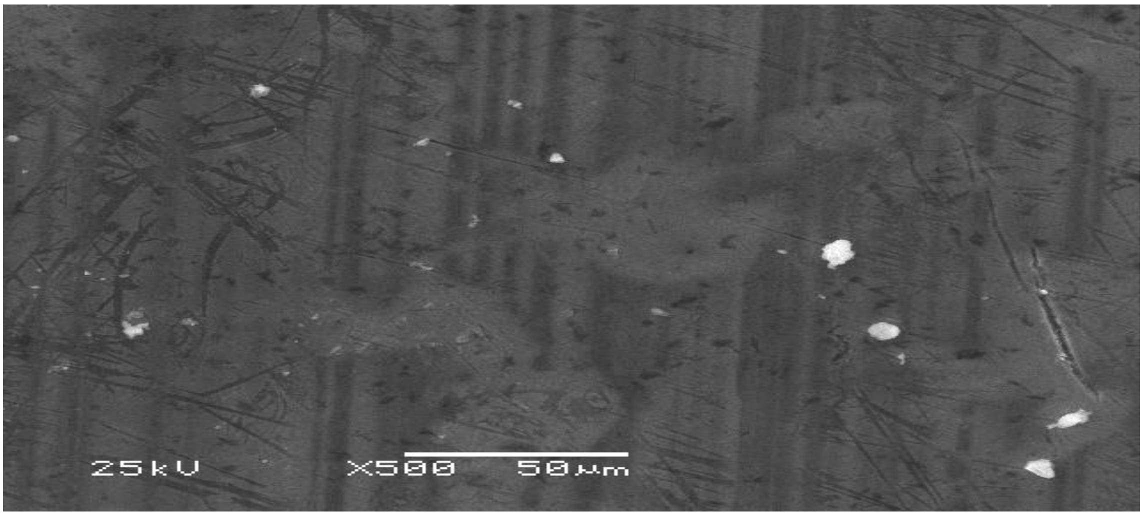

Figure 7. SEM micrograph (x 500) of the tinplate surface after 15 days of immersion in synthetic industrial water.

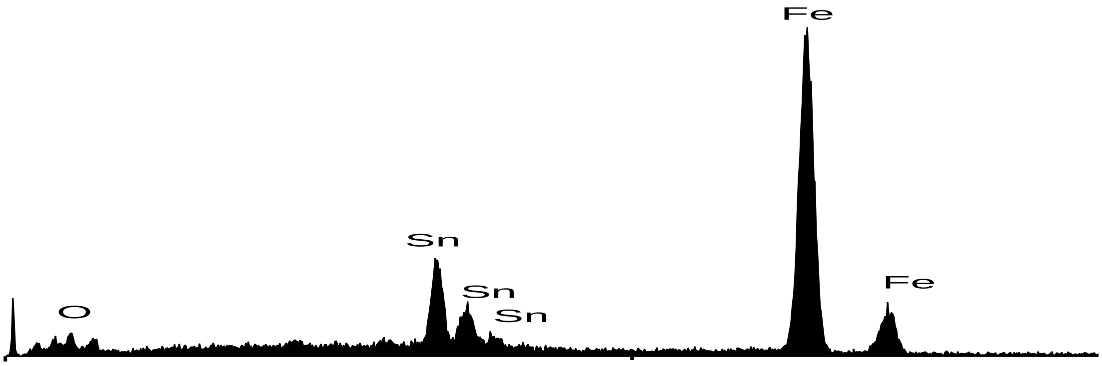

Figure 8. EDX spectral of tinplate after 15 days of immersion in synthetic water.

Figure 5 indicates a homogeneous surface of the tin electrolytically deposited on the surface of mild steel. The spectre represented in figure 6 shows the presence of peaks relative to Oxygen, Sn and Fe elements. The existence of the oxygen peak illustrates the formation of SnO and SnO_2 on the tinplate surface [22-26]. Thus, the intense peak of tin comes from the passive layer and the tin metallic. The weak intensity of the iron peak is probably coming from an analysis in depth (Figure 6).

Figure 7 presents the SEM micrograph of the tinplate surface after 15 days of immersion in the blank solution. We observe the pitting on the tinplate surface.

Figure 9 illustrates the SEM of the tinplate surface after 15 days of immersion in the synthetic medium containing 0.02M of MoO_4^{2-}. We note an untinning that occurs at the tinplate surface. Therefore, EDX spectre does not present any relative peaks corresponding to Mo elements.

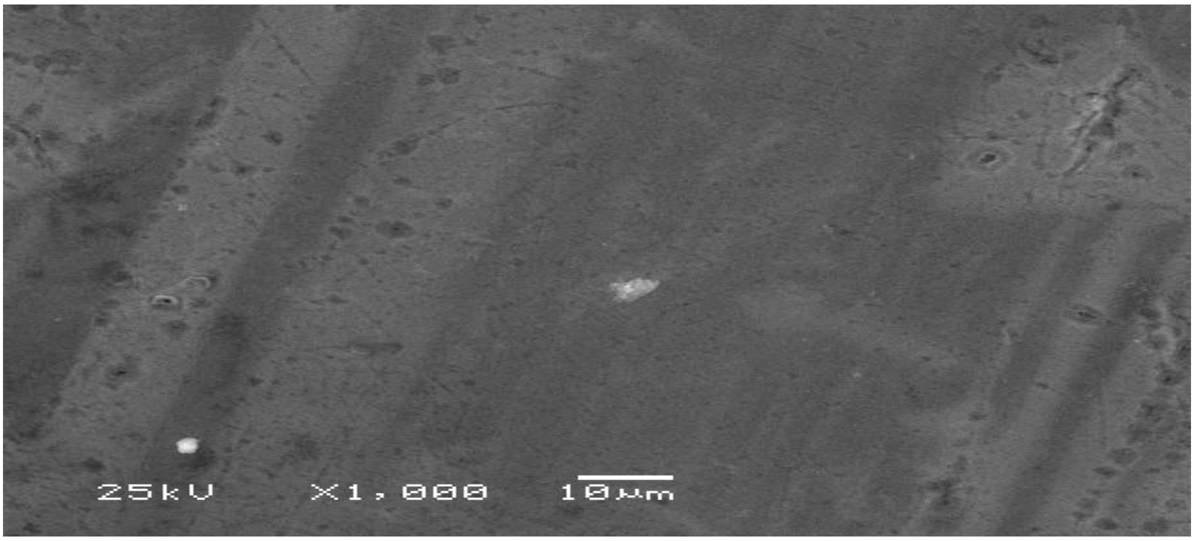

Figure 9. SEM micrograph (x 500) of the tinplate surface after 15 days of immersion in the synthetic medium in the presence of 0.02M MoO_4^{2-}.

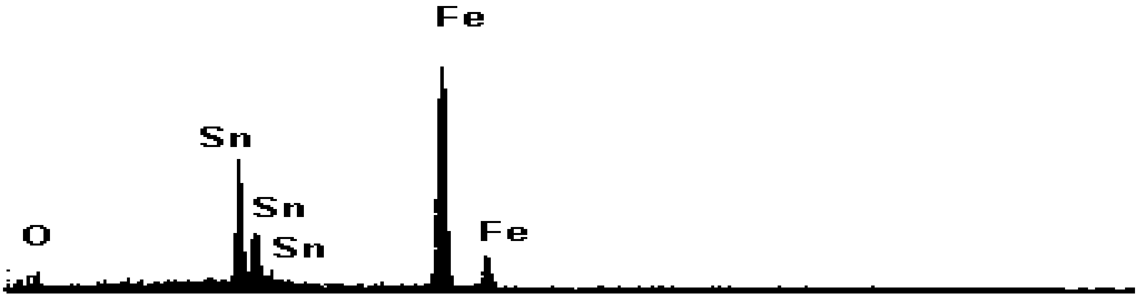

Figure 10. EDX spectral of tinplate after 15 days of immersion in the synthetic medium water in the presence of 0.02M MoO_4^{2-}.

The report of the EDX peaks intensities relative to Sn and to Fe varies with the composition of the medium in which the tinplate was exposed. In the presence of molybdate anions, peaks intensities relative to Fe were significantly reduced compared to those recorded for attacked tinplate but they did not achieve the recorded values in the case of unattacked tinplate. This result does not let any ambiguity on the positive effect of the molybdate anions on the nature of the passive layer formed on the tinplate surface.

4. CONCLUSION

In this work, we have studied the effect of adding molybdate anions on the corrosion and the passivation of the tinplate in the synthetic industrial water. From the overall experimental results the following conclusions can be deduced:

- The molybdates anions present an inhibitory character against the pitting corrosion of tinplate.
- The inhibition effect increases when the concentration of molybdates anions increases in solution.
- The molybdate anions slow down the pitting phenomenon and accelerate at the same time the uniform corrosion by involving the untinning process.
- The increases in temperature can promote the two types of tinplate corrosion.

References

1. D. Yfantis, A. Yfantis, B. Tzalas, D. Schmeisser, *Corrosion*, 56 (2000) 700.
2. J. M. Bastidas, J. M. cabanes, R. J. Catala, *CoatingTechno*l., 67 (1997) 69.
3. E. AitAddi, L. Bazzi, M. Hilali, E. Zine, R. Salghi, S. El Issami, *Can. J. Chem*., 81 (2003) 297.
4. E. Ait addi, L. Bazzi, M. Hilali, B. Hammouti, M. Mihit, *Applied Surface Science*, 253 (2006) 555.
5. Hamdy H. Hassan1, Khalid Fahmy. *Int. J. Electrochem. Sci.*, 3 (2008) 29 .
6. M. S. Morad, A. A. Hermas, *J. Chem. Technol. Biotechnol*., 76 (2001) 401.
7. F. H. Assaf, A. El Sayed, S. S. Abd El Rehim, *Bull. Electrochem.*, 7 (10) (1991) 405.
8. B. F. Giannetti, P.T. Sumodjo, T. Rabockai, M. Souza, J. Barboza, *Electrochim. Acta*, 37(1992) 143.
9. Xiankang Zhong, Guoan Zhang, Yubin Qiu, Zhenyu Chen, Xingpeng Guo, Chaoyang Fu, *Corr. Sci.* 66 (2013) 14.
10. El Habib Ait Addi , Ilham Zaanoun, Abdelaziz Ait Addi, Achemechem Fouad, Lahcen Bazzi, Abdelkader Outzouighit. *Int. J. Electrochem. Sci.*, 8 (2013) 7842.
11. G. G. Do Nascimento, J.L. DOS Santos, I. C. P. Margarit and O.R. Mattos, *Electrochim. Acta.,* 41(1996) 1099.
12. E. E. F. El-Sherbini, S. M. Abd-El-Wahab, M. A. Amin, M. A. Deyab, *Corr. Sci.*, 48 (2006) 1885.
13. S. A. M. Refaey, S. S. Abd El-Rehim, F. Taha, M. B. Saleh, R. A. Ahmed. *Applied Surface Sci.,* 158 (2000) 190.
14. E. E. F. El-Sherbini, *Corr. Sci*., 48 (2006) 1093.
15. AN. Grassino, Z. Grabarić, A. Pezzani, G. Squitieri, K. Berković. *J Sci Food Agric.* 14 (2010) 2419.
16. S. A.M. Refaey, *J. Appl. Electrochem*., 26 (1996) 503.
17. H. H. Hassan, S. S. Abd El Rehim, F.M. Nobl, *Corros. Sci.,* 44 (2002) 37.
18. S. S. Abdel Rehim, S.M. Sayyah, M.M. El Deeb, *Mater. Chem. Phys,* 80 (2003) 696.
19. S. A. M. Refaey, S.S. Abd El Rehim, *Electrochim. Acta* 42 (1997) 667.

20. US Public Health Service Toxicological Profile for Chromium, Agency for Toxic Substances, US Public Health Service, Report no. ATSDR/TP-88/10 (1989).
21. R. S. Alwett, Oxide and Oxide Films, Vol.4, Dekker, New York (1976).
22. L. Brossard, M. Drogowska, H. Ménard, Trends. *Corros. Res.,* 1 (1993) 209.
23. G. K. Gomma, *Materials Chemistry and Physics,* 56 (1998) 27.
24. S. A. M. Refaey , S. S. Abd El Rehim, *Electrochim. Acta*, 42 (1996) 667.
25. M. Drogowska, H. Ménard, L. Brossard, *J. Appl. Electrochem*., 21 (1991) 84.
26. C. A. Gervasi, F.E. Varela, J.R.Vilche, P.E. Alvarez, *Electrochim. Acta*, 42(1997) 537.

© 2014 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).