Comparative study of the action of oxo-anions on the corrosion and passivation of tin and tinplate in synthetic industrial water

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Abstract

The synthetic industrial water (Cl^-, SO_4^{2-} and HCO_3^-), similar to industrial water used in fish canning industry in Agadir (southern of Morocco), was tested as an aggressive medium towards tin and tinplate at room temperature (20±1°C). The corrosion and passivation behaviours of these materials are studied in the presence of the oxo-anions (molybdate, silicate and phosphate) at various concentrations. The technique used in this study is the electrochemical measurement. The results obtained show that both tin and tinplate manifest a comparable electrochemical behaviour in synthetic industrial water. Tinplate presents always a resistance against the two types of corrosion as well as the tin. As for the presence of the oxo-anions in solution, they accelerate the uniform corrosion (untinning) and prevent the pitting corrosion of tinplate and their action is more pronounced in the case of tinplate than the tin electrode.

Keywords: Corrosion, Industrial water, Tin, Tinplate, Oxo-anions.

1. Introduction

The examination of potential-pH diagram [1] shows that tin can be existed in an active or passive state. Tin reacts in acid and basic media, and it is relatively stable and resistant in the neutral mediums. Its dissolution is minimum at pH = 8.5. For these reasons, tin is widely used as a protective coating material for iron in contact with aggressive solutions. Tinplate is a low carbon mild steel sheet coated on both faces with pure tin by different methods such as dipping in a molten tin or electrodeposition. This material is generally used for containers for a wide variety of products in the canning food industry [2,3].

Numerous works focused on the electrochemical behaviour of tin and tinplate in various aggressive mediums [4-13]. The corrosion process of an ideal continuous Sn coating is similar to what occurs in pure tin. However, the protective properties are conditioned by the presence of defects or discontinuities in the outer layer.

The Sn behaves as an anode regarding to the intermediate alloyed layer of the $FeSn_2$ is exposed to the corrosive media launching the attack in the less noble areas [14].

Tin presents in several solutions the passivation phenomenon attributed, generally, to the formation of the passive layer of oxides and/or hydroxides of tin [15,16]. Therefore, the presence of some inorganic compounds such as CrO_4^{2-}, $Cr_2O_7^{2-}$ or HCO_3^- inhibited the pitting process of the metals [17,18]. Alvarez and all [19] suggested that, in the presence of HCO_3^- / CO_3^{2-} or $B_4O_7^{2-}$ in an aggressive solution, the successive oxidation of Sn to Sn(II) and Sn(II) to Sn(IV) stabilized the passive film by dehydratation processes. On the other hand, the addition of Cl^-, Br^-, SO_4^{2-}, NO_3^- … stimulate the localized corrosion leaving the alloyed layer of Sn-Fe of tinplate [20,21].

Among the studies that are realized on tinplate, Zerfaoui et al. [22] showed that the organic compounds such as Arginine and methionene-ethyl-ester are good corrosion inhibitors of tinplate in de-aerated citric acid. Arenas et al. [23] also studied the inhibition of tinplate in a 3.56% NaCl solution by cerium. They found that the addition of cerium prevents corrosion. The results of the study carried out by Bouya [24] showed that the presence of ascorbic, gallic and benzoic acid in solution reinforces the protection of naked tinplate in citric medium by the simultaneous inhibition of iron and tin. In the opponent side, Echcherki [25] examined the effect of gallic acid on the corrosion of naked and varnished tinplate. They found that the complexes of gallic acid with the citrates ions are adsorbed on the surface of the metal. The incorporation of this product in epoxy varnishes shows a good dispersion in the matrix of these varnishes causing the increase of the inhibition of corrosion of tinplate.

In our laboratory, we have effectively focused on the application of organic and inorganic compounds as corrosion inhibitors for different metals in various aggressive solutions [26-32]. The present work includes comparative study of the action of oxo-anions such as MoO_4^{2-}, SiO_4^{2-} and PHO_4^{2-} on the corrosion and electrochemical behavior of tin and tinplate in a synthetic medium similar to industrial water used in fish canning industry in Agadir (southern of Morocco). This medium is characterized by contents of sulphates, chlorides and HCO3- ions variables from factory to another.

2. Methods and materials

The electrochemical study was carried out by the use of a potentiostat/galvanostat PGP 201, piloted by ordinate. Potentiodynamic polarisation curves were recorded at scan rate of 60 mV/min. Before each electrochemical measurement, the working electrode was maintained at free potential during 30 min. Linear polarization resistance (R_P) measurements were carried out at 0.1 mV/min. Polarization resistance R_P was defined as the slope of polarization curve at over potential of -10 mV/SCE. We used for all electrochemical measurements a cell with three electrodes thermostats with double wall (Tacussel Standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode are used as reference and Auxiliary electrodes, respectively. The working electrode is in form of disc from tinplate or tin of the surfaces 0.78 and 0.5 cm^2, respectively. Tinplate is composed of a thin sheet of carbon steel, laminated and coated by a layer of pure tin on both faces. Between the tin layer and the carbon steel, there is the formation of Fe-Sn alloys. This material was supplied by Carnaud with reference: 0.19 DR 550 2.8/2.8, the tinned rate is 2.8 g /m^2 on both faces.

Prior each experiment, the surface of the working electrode was rinsed with acetone and bidistilled water. The heat treatments are carried out in a programmable continuous pipe still under inert atmosphere of going nitrogen at various temperatures during two hours.

The experiments were carried out in a synthetic industrial water containing 0.01M Cl^-, 0.008M SO_4^{2-} and 0.003M HCO_3^- with the absence and presence of the molybdate (MoO_4^{2-}), silicate (SiO_4^{2-}) or phosphate

(PHO_4^{2-}) anions at different concentrations. All aqueous solutions were prepared from bidistilled water and analytical grade chemicals. The solution test is also de-aerated with pure nitrogen. Gas bubbling is maintained prior and through the experiments. All tests were conducted at 20°C (±1°C) in magnetically stirred solutions at pH 8.2 (±0.2). Experiments are repeated three times to ensure the reproducibility.

3. Results and discussions

3.1. Comparative study

3.1.1. Effect of the presence of molybdate anions in synthetic industrial water

The effect of the addition of molybdate anions in a de-aerated synthetic medium similar to industrial water on the corrosion and passivation of tin and tinplate has been studied. Figure 1 illustrates the polarization curves of both tin and tinplate in the presence of MoO_4^{2-} at various concentrations. The corresponding electrochemical parameters are reported in table 1.

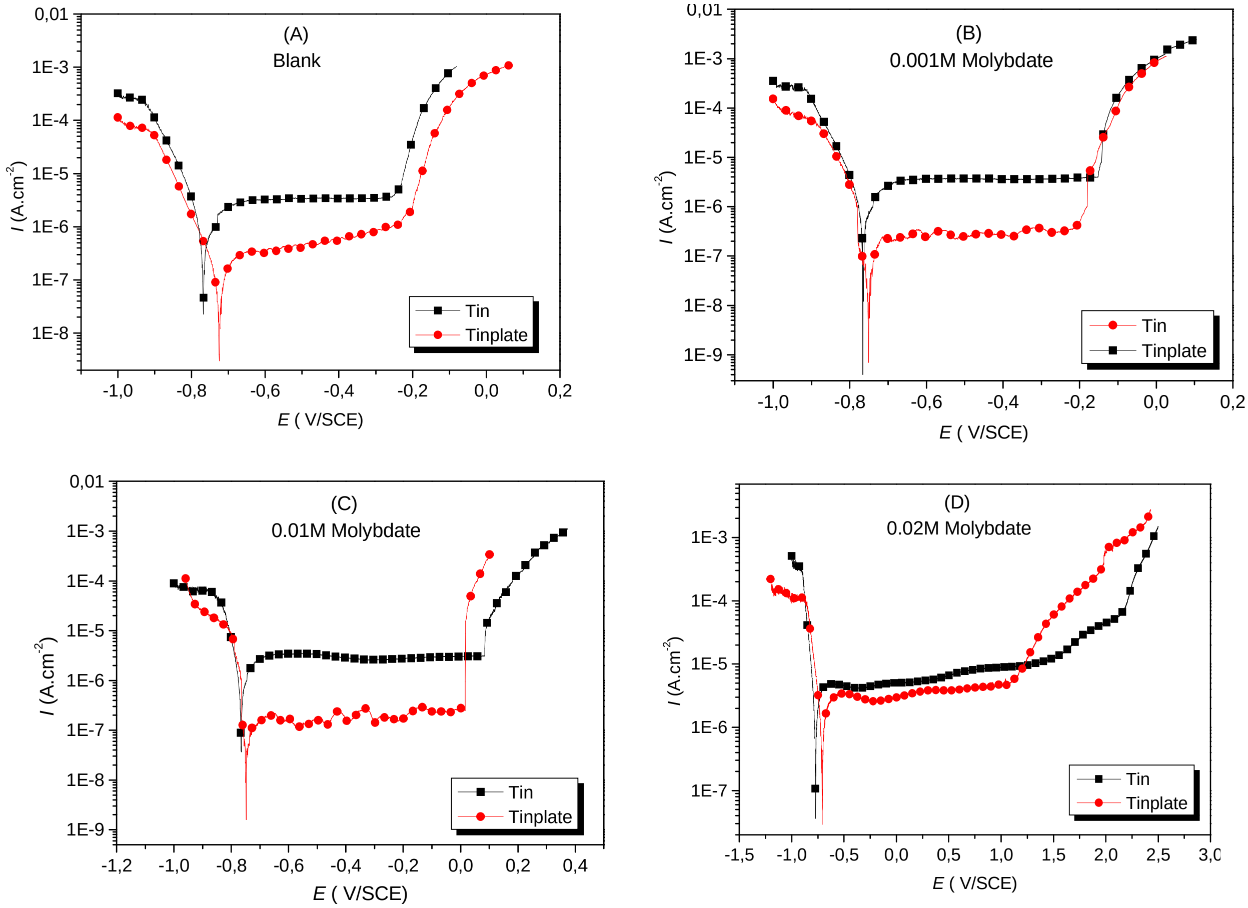

Figure 1. Polarization curves of tin and tinplate in solution : (A) Blank, (B) Blank + 0.001M MoO_4^{2-}, (C) Blank + 0.01M MoO_4^{2-}, (D) Blank + 0.02M MoO_4^{2-}, at T=20°C.

Table 1. Electrochemical parameters derived from Figure 1.

[MoO_4^{2-}] ($mol.l^{-1}$)	Metal	E_{corr}	E_{pit}	ΔE	I_{corr}	I_{pass}	Rp ($K\Omega.cm^2$)
		(mV/SCE)			($\mu A.cm^{-2}$)		
Blank	Tin	-769	-234	535	1.40	3.1	16.94
	Tinplate	-726	-190	536	0.16	0.4	63.40
0.001M	Tin	-735	-170	565	2.40	3.4	13.80
	Tinplate	-753	-180	573	0.03	0.3	95.00
0.01M	Tin	-767	+100	867	3.00	2.6	7.22
	Tinplate	-750	+350	1100	0.02	0.2	80.50
0.02M	Tin	-774	+2000	2774	3.40	4.0	6.51
	Tinplate	-710	+1200	1910	1.60	3.0	8.29

3.1.2. Effect of addition of silicate anions in synthetic industrial water

Figure 2 illustrate polarization curves of both tin and tinplate in a de-aerated synthetic medium similar to industrial water with and without addition of various concentrations of silicate anions. The corresponding electrochemical parameters are reported in tables 2.

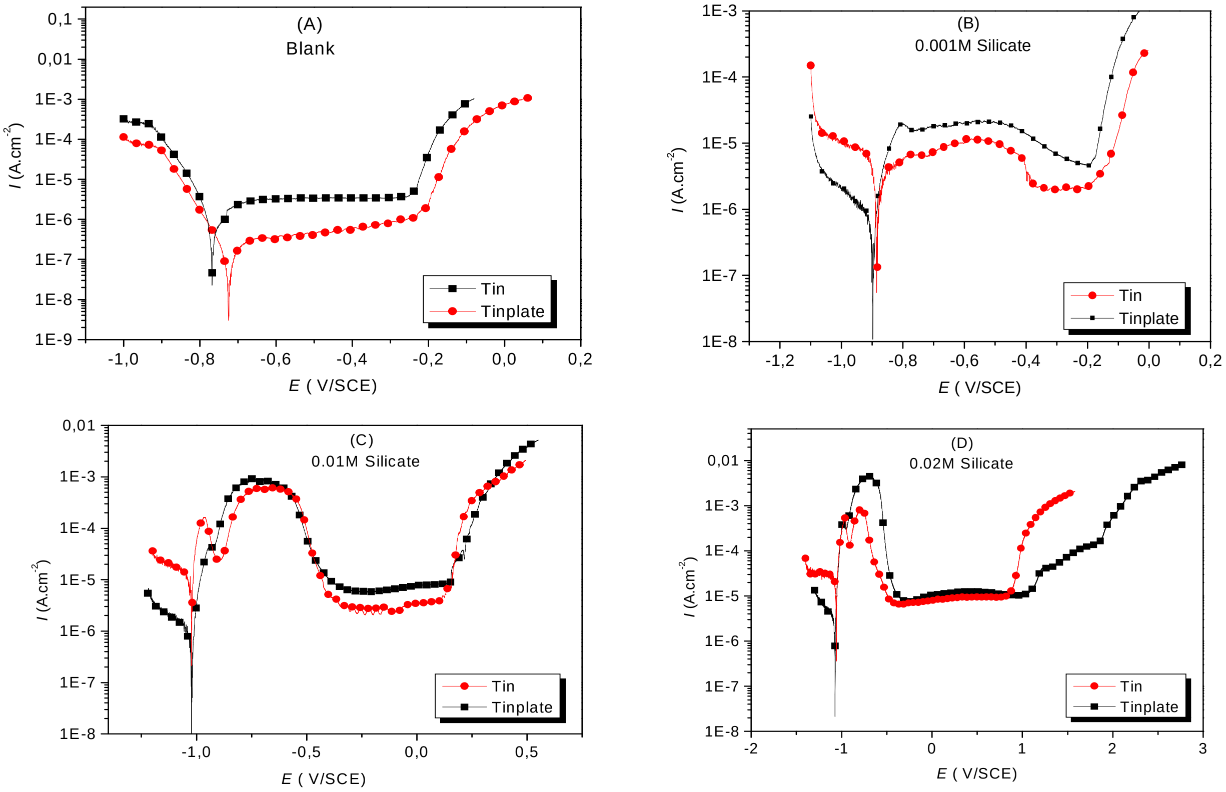

Figure 2. Polarization curves of tin and tinplate in solution : (A) Blank, (B) Blank + 0.001M SiO_4^{2-}, (C) Blank + 0.01M SiO_4^{2-}, (D) Blank + 0.02M SiO_4^{2-}, at T=20°C

Table 2. Electrochemical parameters derived from figure 2.

$[SiO_4^{2-}]$ (mol.l^{-1})	**Metal**	E_{corr}	E_{pit}	ΔE	I_{corr}	I_{pass}	$I_{pic\ 1}$	$I_{pic\ 2}$	**Rp (KΩ.cm^2)**
		(mV/SCE)			**(µA.cm^{-2})**				
Blank	Tin	-769	-234	535	1.40	3.1	-	-	16.94
	Tinplate	-726	-190	536	0.16	0.4	-	-	63.40
0.001M	Tin	-899	-200	699	1.58	4.6	-	21	16.02
	Tinplate	-886	-180	706	2.70	2.1	-	12	8.34
0.01M	Tin	-1003	400	1403	1.90	6.0	43	900	12.43
	Tinplate	-1020	+190	1210	23.0	2.9	170	620	0.68
0.02M	Tin	-1074	1500	2574	4.80	7.5	360	4500	4.39
	Tinplate	-1060	+860	1920	39.08	7.0	510	850	0.36

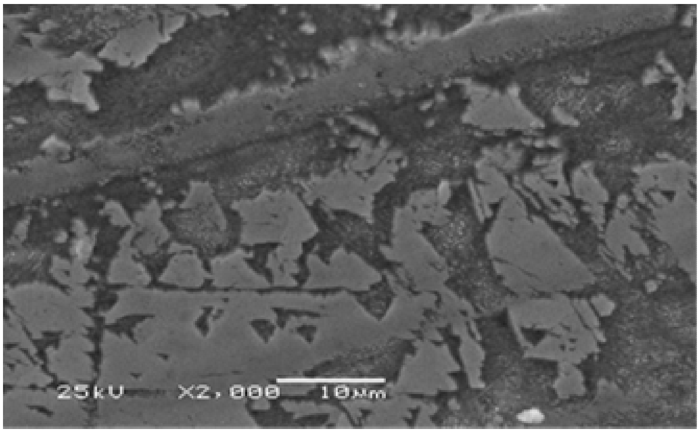

Figure 3. SEM micrograph (x 2000) of the tinplate electrode surface in a synthetic solution containing 0.02M of ion silicates after polarization from -1000 mV to + 1000 mV.

3.1.3. Effect of addition of phosphate anions in synthetic industrial water

The corrosion and passivation behaviour of tin and tinplate in a de-aerated synthetic medium similar to industrial water was studied also in the presence of the phosphate anions. Figure 3 presents the polarization curves of both tin and tinplate in the presence of HPO_4^{2-} at various concentrations and table 3 gathered the corresponding electrochemical parameters.

3.2. Discussion

The corrosion current densities I_{corr} are determined by Tafel Extrapolation Method. They are estimated by extrapolation of the cathodic Tafel slopes to E_{corr}. The passive current densities I_{pass} are determined by the minimal level of current plateau.

The examination of the anodic branch indicates that tin and tinplate present a passivation phenomenon with breakdown of passivity in the synthetic medium. Indeed, the anode current density increases with the electrode potential to reach a current plateau called passivation plateau. The passive current density I_{pass} remains almost constant and then increases abruptly when the pitting potential Epit is exceeded denoting film breakdown and pitting corrosion phenomenon.

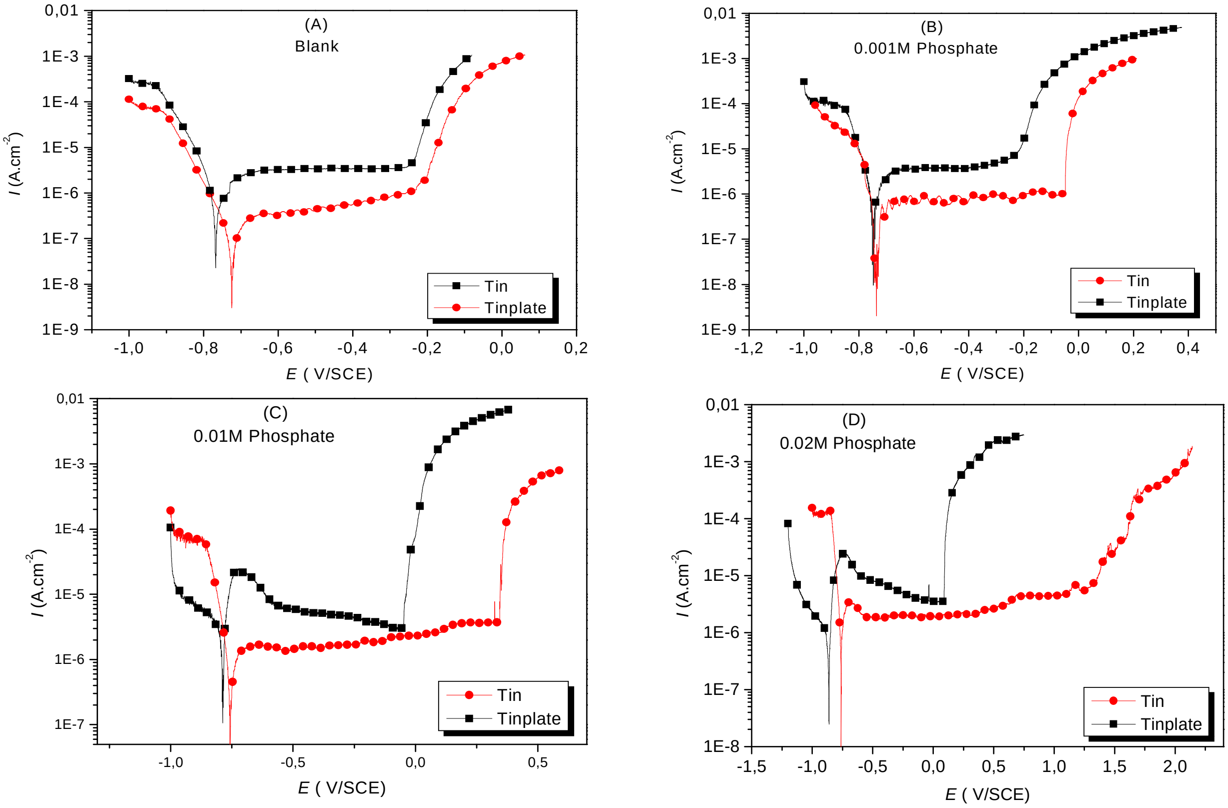

Figure 4. Polarization curves of tin and tinplate in solution : (A) Blank, (B) Blank + 0.001M HPO_4^{2-}, (C) Blank + 0.01M HPO_4^{2-}, (D) Blank + 0.02M HPO_4^{2-}, at T=20°C.

Table 3. Electrochemical parameters derived from figure 3.

[HPO_4^{2-}] **(mol.l^{-1})**	**Metal**	***E*$_{corr}$**	***E*$_{pit}$**	**Δ*E***	***I*$_{corr}$**	***I*$_{pass}$**	***I*$_{pic}$**
		(mV/SCE)			**(µA.cm^{-2})**		
Blank	Tin	-769	-234	535	1.4	3.1	-
	Tinplate	-726	-190	536	0.16	0.4	-
0.001M	Tin	-749	-230	519	1.5	3.2	-
	Tinplate	-736	-50	686	0.1	0.8	-
0.01M	Tin	-789	-10	779	3.6	3.2	22
	Tinplate	-758	+390	1148	1.4	1.5	-
0.02M	Tin	-864	+100	964	3.8	4	25
	Tinplate	-763	+1700	2463	2.5	2.1	4

To achieve the comparative study between the two materials studied, we respected the same electrochemical conditions of the tests. The comparison has been made according to the concentration of the oxo-anions added in solution. Sub-figures. (A), (B), (C) and (D) correspond, respectively, to the inhibitors concentrations 0, 0.001, 0.01 and 0.02M. The analysis of these polarization curves and the exam of the results obtained allowed us to note:

3.2.1. Case of molybdate anions

The general shape of the polarization curves of both tin and tinplate is not affected by the addition of the molybdate anions to the synthetic industrial water (Figure 1). In comparison with the tin electrode, the uniform corrosion resistance of tinplate is more improved when the concentration of the molybdate increases in solution. These results demonstrate the fact that the values of corrosion and passivation current density of tinplate decrease when the molybdate concentration increases in solution from 0 to 0.01 M and they are lower than those recorded for tin. The measurement of the polarisation resistance corroborates these results (Table 1).

As to the pitting corrosion, both tin and tinplate present the same sensitivity to the pitting. An exception is observed at the concentration 0.02M of molybdate anions where this latter’s action becomes more important towards tin.

3-2.2. Case of silicate anions

The addition of the silicates anions provokes an important modification of the shape of the polarization curves corresponding to both tin and tinplate (Figure 2). At each silicate concentration, the value of the corrosion current density of tinplate is more important than that of tin (Table 2). We remark that increase of silicate concentration from 0 to 0.02 M is accompanied by both increase of I_{corr} and I_{pas}. R_p additionally decreases with the rise of silicates concentration in solution (Table 2). After polarisation, the surface state of sample has been examined by SEM in order to see the effect of the attack. Figure 3 shows destruction and a corroded surface. These results show that silicate anions encourage the uniform corrosion of tinplate. The variation of the corrosion potential according to the silicate concentration for the two materials studied is similar. Therefore, the anodic branch related to both tin and tinplate presents two peaks of activity; the current intensities of these peaks tend to grow while the concentration of the silicate anions increases in solution. We observe also that the passivation current density of tinplate is lower than that obtained in the case of tin, and this is observed at all silicate concentrations explored.

3-2.3. Case of phosphate anions

The presence of phosphate anions in synthetic industrial water is not affects the general shape of the polarization curves of tinplate. However, we noted the appearance of a dissolution peak when the concentration of these anions reached 0.02M. On the other hand, in the case of tin, the appearance of this peak is observed as from the concentration 0.01M (Figure 4). The comparison of the values of the corrosion and passivation current densities and the corrosion potential shows that the tinplate resists against the uniform corrosion better than the tin. Thus, an important displacement of the pitting potential towards nobler potentials is observed in the case of tinplate. This result shows that the phosphates anions inhibit the pitting corrosion as much as for tinplate than tin electrode.

4. Conclusion

The comparative study of the corrosion and the passivation of tin and tinplate reveals that both samples have the comparable electrochemical behaviour in synthetic industrial water. However, over our studies, tinplate presents always a resistance against the two types of corrosion as well as the tin. These results reveal that the tinning of the steel prevents the formation of the pitting and consequently the iron doesn't contribute to the corrosion process. On the other hand the presence of an initial passivation layer on the surface improves the protection of the tinplate.

The results obtained by electrochemical technique reveal that the oxo-anions MoO_4^{2-}, SiO_4^{2-} and HPO_4^{2-} present two antagonistic effects:

* They contribute efficiently to inhibit the pitting corrosion of tinplate and they have a best action in comparison with the tin.

* They tend to accelerate the uniform corrosion process for the tinplate. This phenomenon has been interpreted by an activation of the phenomenon of un-tinning that occurs in presence of these oxo-anions.

References

1. Pourbaix, M. Atlas of Electrochemichal Equilibria Pergamon. Oxford (1966) 475.
2. Mahadeviah, M. *Indian Food Packer.* 9 (1976) 30.
3. Bastidas, J. M., Cabanes, J.M., Catala, R. *J. Coating Technol.* 67 (1997) 69.
4. Ait Addi, E., Bazzi, L., Hilali, M., Zine, E., Salghi, R., El Issami, S. *Can. J. Chem.* 81 (2003) 297.
5. Ait Addi, E., Bazzi, L., Hilali, M., Hammouti, B., Mihit, M. *Applied Surface Science.* 253 (2006) 555.
6. Bammou, L., Chebli, B., Salghi, R., Bazzi, L., Hammouti, B., Mihit, M., El Idrissi, H. *Green Chemistry Letters and Reviews.* 3 (2010) 173.
7. El-Sayed, A., Mohran, H.S., Abd El-Lateef, H.M. *Corros. Sci.* 52, (2010) 1976.
8. Radojčić, I., Berković, K., Kovač, S., Vorkapić-Furač, J. *Corros. Sci.* 50 (2008) 1498.
9. Mora, N., Cano, E., Polo, J.L., Puente, J.M., Bastidas, J.M. *Corros. Sci.* 46(2004) 563.
10. Morad, M.S., Hermas, A.A. *J. Chem. Technol. Biotechnol.* 76 (2001) 401.
11. Assaf, F.H., El Sayed, A., Abd El Rehim, S.S. *Bull. Electrochem.* 7-10 (1991) 405.
12. Giannetti, B.F., Sumodjo, P.T., Rabockai, T., Souza, M.J. Barboza. *Electrochim. Acta,* 37 (1992) 143.
13. El Sayed, A., Assaf, F.H., Abd El Rehim, S.S. Hung. *J. Ind. Chem.* 19 (1991) 207.
14. Arenas, M.A., Conde, A., Damborenea. J.J. *Corros. Sci.* 44 (2002) 511.
15. Drogowska, M., Ménard, H., Brossard, L. *J. Appl. Electrochem.* 21 (1991) 84.
16. Brossard, L., Drogowska, M., Ménard, H. *Trends in corros. Research.* 1 (1993) 209.
17. Hassan, H.H., Abd El Rehim, S.S., Nobl, F.M. *Corros. Sci.* 44 (2002) 37.
18. Bazzi, L. Kertit, S., Hamdani, M. *J. Chim. Phys.* 92 (1995) 1612.
19. Alvarez, P.E., Ribota, S.B., Folquer, M.E., Gervasi, C.A., Vilche. J.R. *Corros. Sci.,* 44 (2002) 49.
20. Refaey, S.A.M., Abd El Rehim, S.S. *Electrochim. Acta*, 42 (1997) 667.
21. Refaey, S.A.M., *Electrochim. Acta,* 41 (1996) 2545.
22. Zerfaoui, M. Thèse Nationale, Université Mohammed 1^er^, Oujda, Maroc (2001)
23. Arenas, M.A., Conde, A. J. de Damborenea, *Corros. Sci.* 44 (2002) 511.
24. Bouya, A. Thèse Nationale, École Mohammadia d'Ingénieurs, Maroc (2000).
25. Echcherki, K. Thèse d'état, École Mohammadia d'Ingénieurs, Maroc (1996).
26. Belkhaouda, M., Bazzi, L., Belhachemi, A., Salghi, R., Hammouti, B., Kertit, S. *Appl. Surf. Sci.* 252 (2006) 7921.
27. Salghi, R., Hammouti, B., Aouinti, A., Berrabah, M., Kertit, S. *Ind. J. Electrochem Soc.* 49 (2000) 40.
28. El Issami, S., Bazzi, L., Hilali, M., Salghi, R., Kertit, S. *Ann. Chim. Sci. Mat.* 27 (2002) 63.
29. Mihit, M., El Issami, S., Bouklah, M., Bazzi, L., Hammouti, B., Ait Addi, E., Salghi, R., Kertit, S. *Applied Surface Sci.* 252 (2006) 2389.
30. Mihit, M., Salghi, R., El Issami, S., Bazzi, L., Hammouti, B., Ait Addi, E., Kertit, S. *Pigment and Resin Technology,* 35 (2006) 151.
31. Belkhaouda. M., Bazzi, L., Salghi, R., Jbara, O., Hammouti, B., Benlhachmi, A., Douglad, J. *J. Mater. Environ. Sci.* 1 (2010) 25.
32. Mihit, M., Salghi, R., Bazzi, L., Belkhaouda, M. *J. Physical Chemistry*, 2 (2007) 84.