

## Corrosion Behaviour of Tinplate in Synthetic Industrial Water

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The corrosion behaviour of tinplate in a synthetic medium similar to industrial water containing sulphates, chlorides and  $\text{HCO}_3^-$  ions has been studied. The effect of concentration of anions in solution has been investigated. The results obtained by use of electrochemical and metalographical techniques show that tinplate manifests a passivation phenomenon with rupture of passivity. The examination of the spectra obtained by microanalysis EDAX shows the presence of the chemical elements Sn, Fe and  $\text{O}_2$  on the surface of tinplate but with proportions which depend on the state of material. The results obtained show that tinplate is very sensitive to the anions concentration variation in solution. The presence of anions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  stimulate pitting corrosion of tinplate, whereas  $\text{HCO}_3^-$  ions acted as an inhibitor for pitting corrosion of this material in the studied medium.

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**Keywords:** tinplate, corrosion, passivation, industrial water

### 1. INTRODUCTION

The most widely use of tinplate is in canning industry. It is consumed in enormous quantities for the manufacture of the tin cans in which preserved meat, fish and fruit [1, 2, 3].

As a consequence of this usage, it comes in contact with an innumerable variety of environments.

Indeed, tinplate containers occasionally develop integrity problems which can lead to early failure through corrosion resulting to canned product rejection by the consumer [4].

Can integrity problems reported in the literature include: stress corrosion cracking (SCC), sulfide black corrosion, pitting corrosion involving rapid iron dissolution at fractures or pores in the organic coating, external corrosion involving the formation of rust on the external surface of metal container due to scratch defects and enamel adhesion failure [4,5].

Tinplate corrosion depends on many factors including can material, nature of the organic coating, enamel properties, composition of the contained product and of course nature of the contacting medium [6,7].

Tinplate is a low carbon mild steel sheet coated on both faces with pure tin. In fact, the metal which is initially attacked is tin. The corrosion behaviour of tin has been studied in aqueous solutions by several authors [8-20].

Many investigators reported that pitting corrosion occurs when passivity breaks down at local points of the tin surfaces exposed to aqueous solutions containing aggressive ions as halides; however this form of pitting corrosion may also occur in presence of another anions as perchlorate, sulphate and nitrate [12, 17-19, 21-26].

The present work includes detailed studies on the corrosion and electrochemical behaviour of tinplate in a synthetic medium similar to industrial water used in foodstuff industry in Agadir (southern of Morocco). This medium is characterized by contents of sulphates, chlorides and  $\text{HCO}_3^-$  ions variables from factory to another. We will evoke the effect of concentration of ions  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  in solution. In our knowledge, there have been no literatures to investigate the corrosion behaviour of tinplate in such solution containing the three above mentioned anions simultaneously.

## 2. EXPERIMENTAL PART

Electrochemical measurements were carried out in a conventional three-electrode, cylindrical tempered glass cell. A saturated calomel electrode (SCE) and platinum electrode were used as the reference and auxiliary electrodes, respectively. A tinplate disc with an exposed geometric area of  $0.5 \text{ cm}^2$  mounted in polyester resin was used as working electrode. The tin plate was supplied by Carnaud with reference: 0.19 DR 550 2.8/2.8. Before each experiment, the surface of the working electrode was degreased with acetone and rinsed quickly with bidistilled water. The electrochemical study was carried out using a potentiostat/galvanostat PGP 201 which was controlled by a personal computer using the software (VoltaMaster). Potentiodynamic polarisation curves were recorded at scan rate of  $60 \text{ mV/min}$ . Prior to electrochemical measurements, the working electrode was maintained at free potential during 30 min. Linear polarization resistance ( $R_p$ ) measurements were carried out at  $0.1 \text{ mV/min}$ . Polarization resistance  $R_p$  was defined as the slope of polarization curve at overpotential of  $\pm 10 \text{ mV/SCE}$ .

The morphology and composition of the passive layer were studied using scanning electron microscopy (SEM) JEOL JSM-5500, and energy dispersive X-ray (EDX) JEOL 5600.

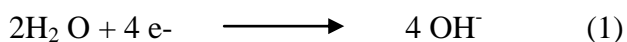
Experiments were carried out in a synthetic medium containing  $0.01 \text{ M Cl}^-$ ,  $0.008 \text{ M SO}_4^{2-}$  and  $0.003 \text{ M HCO}_3^-$ . All aqueous solutions were prepared from bidistilled water and analytical grade chemicals and they were deaerated by bubbling  $\text{N}_2$  through the cell unless otherwise stated. Thereafter,

a constant flow of N<sub>2</sub> was maintained over the solution. Freshly prepared solution and new set of electrodes were used for each run. Runs were carried out at 20 ± 1 °C in magnetically stirred solutions at pH 8.2 (±0.2). Experiments are repeated three times to ensure the reproducibility.

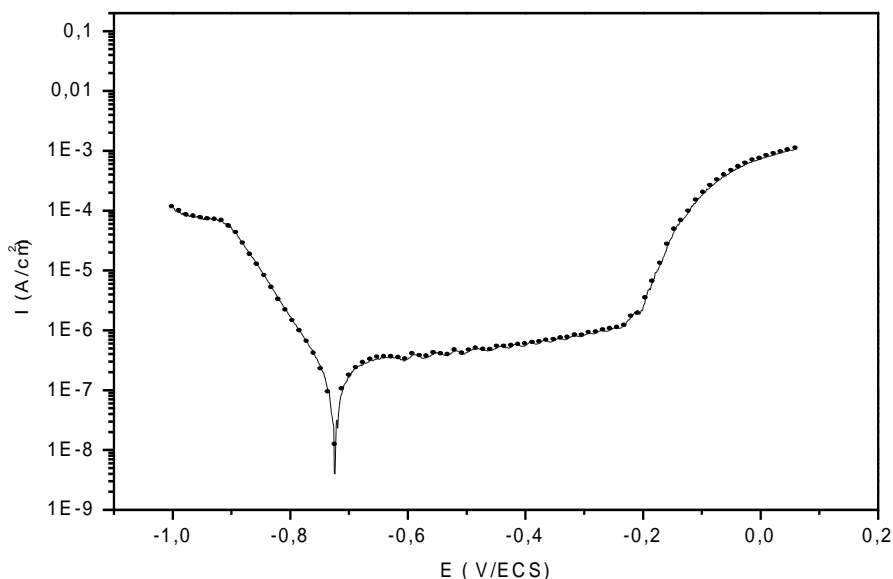
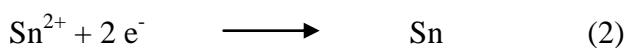
### 3. RESULTS AND DISCUSSION

Figure 1 represents polarization curves for tinplate electrode in the synthetic medium solution.

We observe that the cathodic polarization curve is characterized by parallel Tafel line which indicate that the water evolution reaction is activation controlled [27]



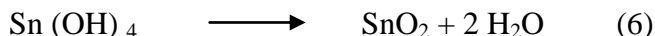
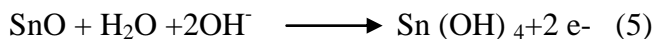
For more cathodic potentials a current plateau appears. It could be attributed to the reduction of Sn<sup>2+</sup> in solution [28].



**Figure 1.** Polarization curves of tinplate in the synthetic medium at 20 °C.

The examination of the anodic branch permits to conclude that tinplate presents a passivation phenomenon with rupture 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 remains constant almost the passive region and then increases abruptly when the pitting potential E<sub>pit</sub> is exceeded denoting film breakdown and pitting corrosion.

According to certain authors [8, 10, 11] in the near neutral medium, the formation of the passive layer could be described by the following scheme:



These results are in agreement with the results obtained in our previous study performed on tin in the same solution [12].

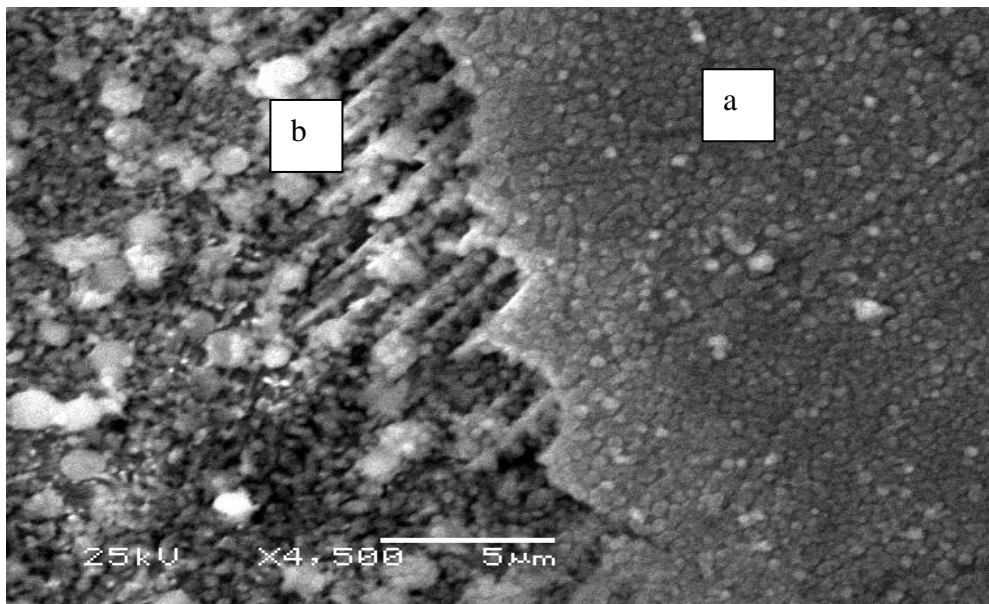
In the other hand, SEM examination of the tinplate electrode surface after polarization scan from -1000 mV/ECS to +1000 mV/ECS in the synthetic medium reveal that the rupture of passivity is due to the local destruction of passive film formed on the surface (figure 2 and figure 3). The SEM data showed the surface to be covered with irregular pits.



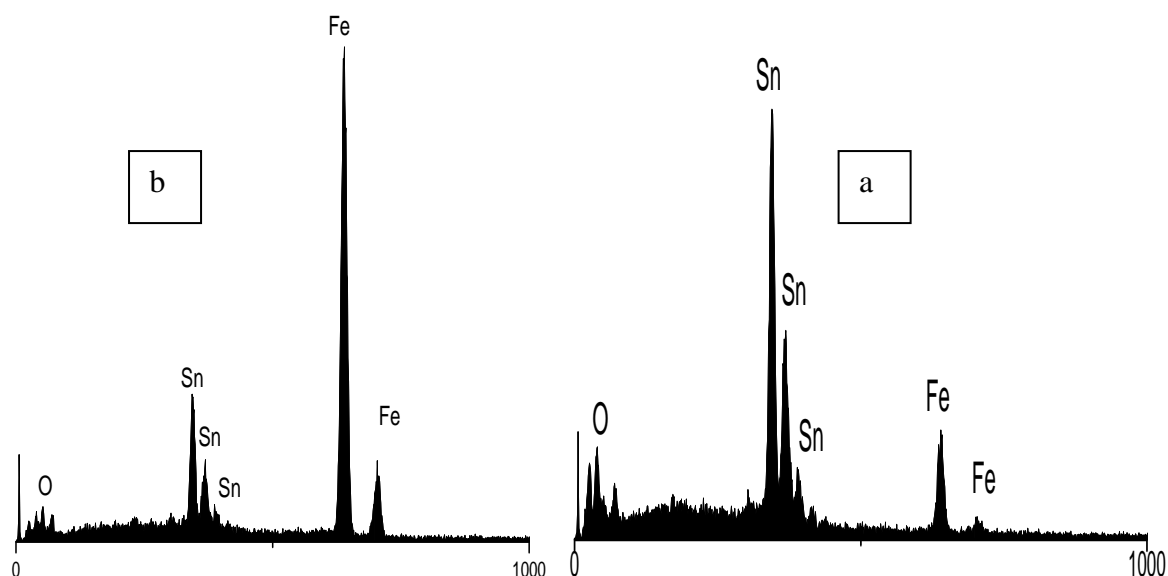
**Figure 2.** SEM micrograph (x 35) of the tinplate electrode surface in a synthetic solution after polarization from -1000 mV to + 1000 mV.

The chemical composition of surface was examined by X-ray diffraction. Examination of spectrum represented in figures (4) shows the presence of peaks relating to Sn, Fe and O<sub>2</sub>. The report/ratio of peaks intensities varies with the nature zone of analyzed surface. In the case of passive zone, peak intensity of Sn is higher than that of iron (figure 4.a). While in the case of an analysis made within the pite, peak intensity of Fe becomes higher than that of Sn (figure 4. b).

Zerfaoui showed that in acid medium, the exposed iron surface does not exceed 8.3% of total tin plate surface [29]. This low value indicates that the contribution of the iron dissolution reaction and the water cathodic reduction on iron in the process of tinplate corrosion is negligible. Thus the retardation of corrosion process observed on tinplate can be related to passivating layer formed on its surface.



**Figure 3.** SEM micrograph (x 4500) of the tinplate electrode surface in a synthetic solution after polarization from -1000 mV to + 1000 mV: a : « passive zone » et b: « within pite ».



**Figure 4.** EDX spectrum of tinplate surface in a synthetic solution after polarization from -1000 mV to + 1000 mV: a : « passive zone » and b: « within pite ».

3.1. Effect of chloride concentration

Figure 5 represents the polarisation curves of tin plate in a synthetic medium with various concentrations of chloride (from 0.0002M to 1M). The electrochemical parameters extracted from these curves are given in table 1. We observed that both the general and localised corrosion resistance of the material was severely deteriorated by the exposure to synthetic solution with 1M chloride.

In the vicinity of  $E_{corr}$ , the cathodic branch presents a linear portion which was characteristic of the reduction of water according to a mechanism of pure activation. The cathodic plateau of current obtained at more negative potentials, is generally attributed to the reduction of  $Sn^{2+}$  in solution.

We remark that the corrosion potential is slightly affected by the concentration of Cl ions between 0.0002M and 0.5M. However, for a higher chloride concentration (1M), a remarkable displacement of  $E_{corr}$  occurs towards nobler values.

In the anodic branch, we note that  $E_{pit}$  shifts towards more active values with increasing chloride concentration indicating that the progressive additions of chloride ions induces pitting corrosion of tinplate.

Moreover, the progressive additions of chloride ions in the solutions enhances  $I_{pass}$  and tends to break down the passive layer at a certain critical pitting potential ( $E_{pit}$ ), at which the passive current rises suddenly indicating initiation and growth of pitting attack. It is observed that the pitting potential  $E_{pit}$  shifts to less noble potentials with increasing the chloride concentration. Figure 6 shows  $E_{pit}$  vs.  $Cl^-$  plots whereby straight lines are obtained satisfying the following equation:

$$E_{pit} = a - b \log Cl^-$$

Where a and b are constants.

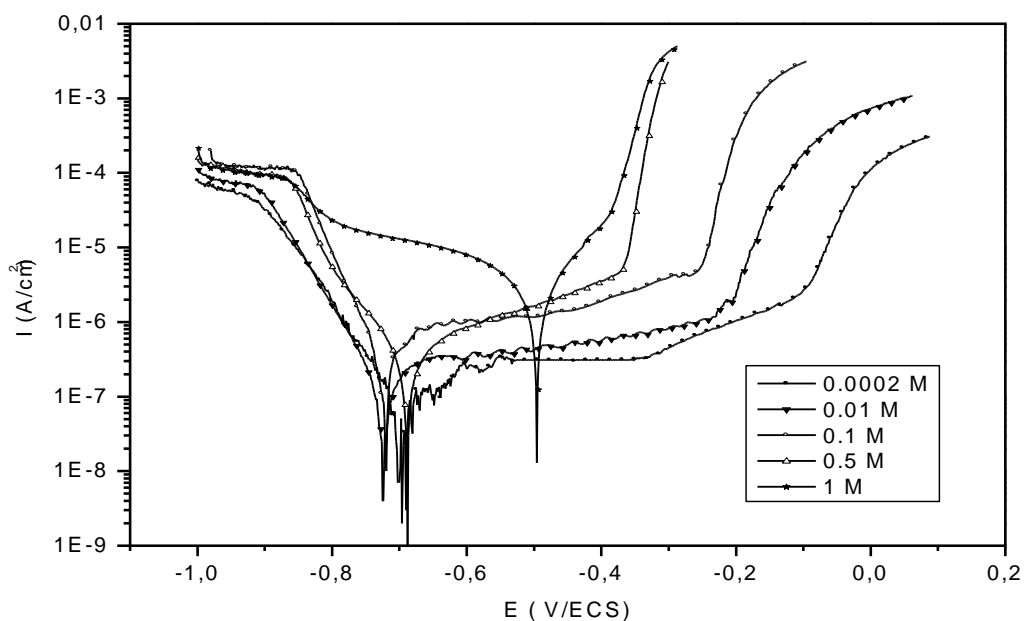
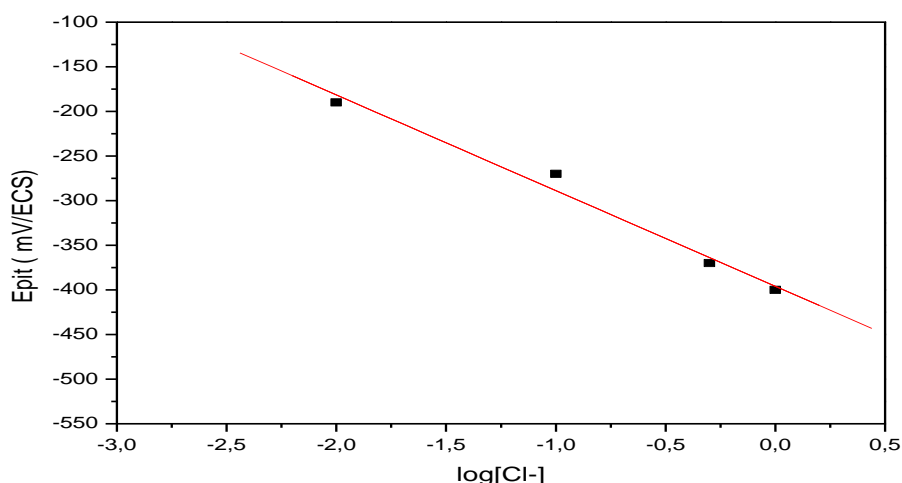


Figure 5. Polarization curves of tinplate in the synthetic medium at different concentrations of chloride.

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

[Cl <sup>-</sup> ] (mole l <sup>-1</sup> )	E <sub>corr</sub> (mV/ECS)	E <sub>pit</sub> (mV/ECS)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	I <sub>pass</sub> (μA/cm <sup>2</sup> )	R <sub>p</sub> (kΩ.cm <sup>2</sup> )
0.0002	-698	-140	0.04	0.7	120.60
0.0100	-726	-190	0.16	1.0	63.40
0.1000	-742	-270	0.50	2.3	22.90
0.5000	-690	-370	0.60	2.4	28.92
1.0000	-498	-400	3.80	-	4.91



**Figure 6.** Dependence of E pit of tinplate in the synthetic medium on chloride concentration.

Aggressiveness of the halide ions as pitting agents may be attributed to their competitive adsorption with the passivating species as OH<sup>-</sup> and H<sub>2</sub>O on the surface of the passive film [17, 30]. When the applied potential reaches E<sub>pit</sub>, the aggressive ions penetrate the film and pitting proceeds. After E<sub>pit</sub>, the halide adsorption is favoured and breakdown of passivity occurs. As both potential and halide ion concentration increase, the protective characteristics of the film decrease. In this case, the aggressiveness of chloride ions on the dissolution of tinplate in solution could be attributed to the formation of soluble complex species, i.e., SnCl<sub>3</sub><sup>-1</sup> and SnCl<sub>6</sub><sup>-2</sup> and to their adsorption on the surface forming active sites of dissolution [11].

### 3.2. Effect of sulphate concentration

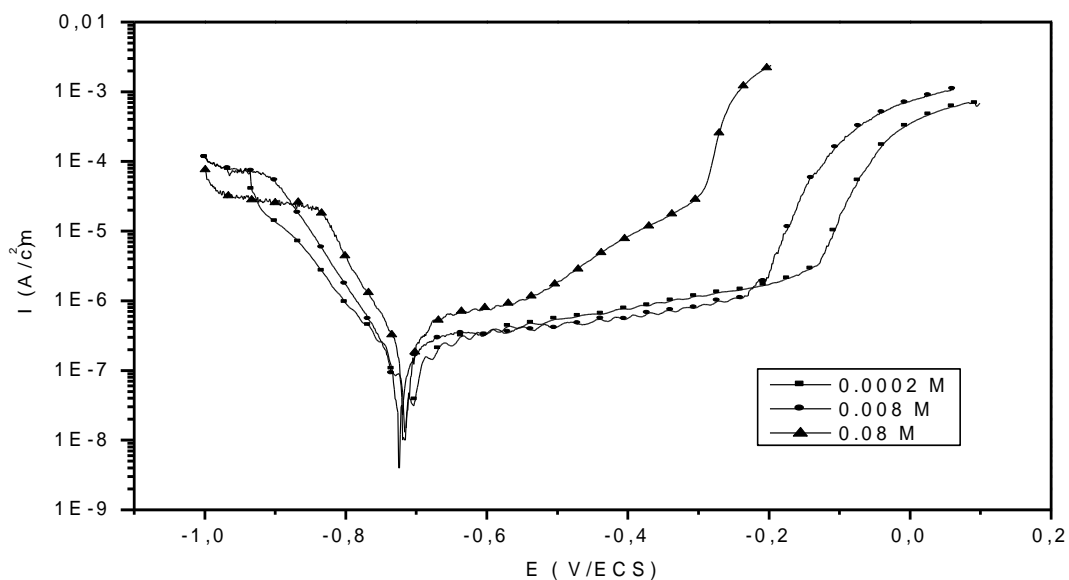
The effect of sulphate concentration on the potentiodynamic polarization curves of tinplate has been studied. Figure 7 presents the polarization data recorded. The corresponding electrochemical parameters deduced from these curves are given in Table2.

Inspection of the data reveals that an increase in  $\text{SO}_4^{2-}$  concentration shifts  $E_{\text{pit}}$  towards more negative (active) direction corresponding to decreased resistance to pitting corrosion. This behaviour is in agree with data reported with Abd El-Rehim and al [25]. They suggested that pitting initiation can be explained through the adsorption competition between sulphate anions and the passivating species on the passivated electrode surface.

In the other hand, Table 2 shows that corrosion current densities (estimated by extrapolation of the cathodic Tafel slopes to  $E_{\text{corr}}$ ) and passive current densities (determined by the minimal level of current plateau) are not affected by the variation of sulphate concentration in solution. Thus, one can said that this variation does not affect significantly the uniform corrosion of tin in the studied medium.

**Table 2.** Influence of sulphate concentration on electrochemical parameters of tinplate in the synthetic medium.

$[\text{SO}_4^{2-}]$ (mole $\text{l}^{-1}$ )	$E_{\text{corr}}$ (mV/ECS)	$E_{\text{pit}}$ (mV/ECS)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$I_{\text{pass}}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_p$ ( $\text{k}\Omega.\text{cm}^2$ )
0.0002	-717	-140	0.13	0.9	87.2
0.0080	-726	-190	0.16	1.0	63.4
0.0800	-718	-340	0.40	2.2	52.5



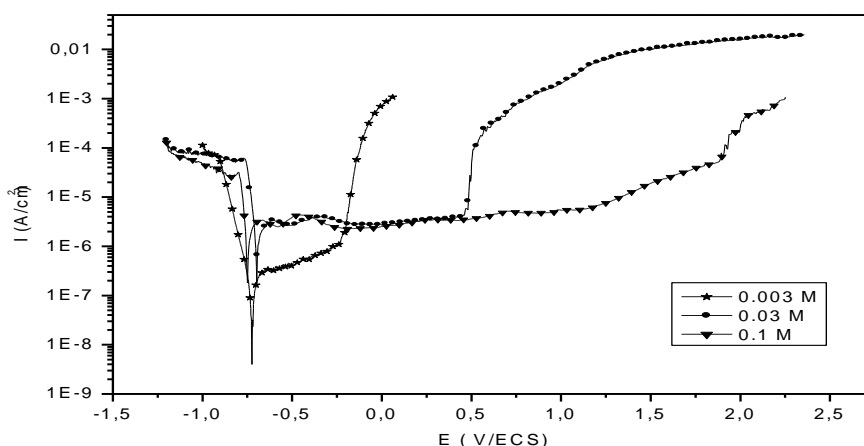
**Figure 7.** Polarization curves of tinplate in the synthetic medium at different concentrations of sulphate.



### 3.3. Effect of $\text{HCO}_3^-$ concentration

The effect of adding increasing amounts of  $\text{HCO}_3^-$  anions to synthetic medium on the anodic and cathodic polarization curves of tinplate was investigated (figure 8). The electrochemical parameters deduced from these curves are given in Table 3. Inspections of these data reveal that both uniform and localized corrosion are affected by adding increasing amounts of  $\text{HCO}_3^-$ . The action of ions  $\text{HCO}_3^-$  is characterized by two antagonistic effects. The first is the deterioration of the general corrosion resistance of the material. Results obtained indicate that increasing of concentration of these anions stimulates general corrosion, increases the corrosion current density  $I_{\text{corr}}$  and passive current density  $I_{\text{pass}}$  and decreases the polarisation resistance value  $R_p$ . The stimulating influence of these anions can be explained on the basis that  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  cations are stabilized by their complexation with  $\text{HCO}_3^-/\text{CO}_3^{2-}$  anions [10].

A second effect is the inhibition of pitting corrosion of tin plate. The data clearly shows that increasing of concentration of these anions in the solution drifts  $E_{\text{pit}}$  towards more anodic potentials (noble direction) and inhibits pitting corrosion of tinplate.



**Figure 8.** Polarization curves of tinplate in the synthetic medium at different concentrations of  $\text{HCO}_3^-$ .

**Table 3.** Influence of  $\text{HCO}_3^-$  concentration on electrochemical parameters of tinplate in the synthetic medium.

$[\text{HCO}_3^-]$ (mole $\text{l}^{-1}$ )	$E_{\text{corr}}$ (mV/ECS)	$E_{\text{pit}}$ (mV/ECS)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$I_{\text{pass}}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_p$ ( $\text{k}\Omega.\text{cm}^2$ )
0.003	-726	-190	0.16	1.0	63.40
0.030	-700	+600	3.1	3.0	3.86
0.100	-751	+1600	3.6	3.1	3.60

#### 4. CONCLUSION

The goal of this work is to study the corrosion behaviour of tinplate in a synthetic medium similar to industrial water containing sulphates, chlorides and  $\text{HCO}_3^-$  ions. The following conclusions can be drawn:

- Tinplate manifests a passivation phenomenon with rupture of passivity.
- The examination of the spectra obtained by microanalysis EDX shows the presence of the chemical elements Sn, Fe and O<sub>2</sub> on the surface of tinplate but with proportions which depend on the state of material.
- The presence of anions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  stimulate pitting corrosion of tinplate,
- $\text{HCO}_3^-$  ions acted as an inhibitor for pitting corrosion of this material in the studied medium.

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