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# The comparative breakdown of passivity of tin by fluorides and chlorides interpreted through the 'law of matching affinities' concept

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ABSTRACT

The comparative breakdown of passivity of tin by fluorides and chlorides highlight the significant slower kinetics of attack by the kosmotrope fluoride when compared to the chaotrope chloride at pH 5.7 and 10. The origin of this difference is ascribed to the predominant halide-dependent mechanism of attack, pitting with chlorides and film thinning with fluorides, which is conditioned according to the anion-specific hydration properties.

## 1. Introduction

When studying the breakdown of passivity of various metals in the presence of halide anions ($F^-$, $Cl^-$, $Br^-$, $I^-$), the behavior with fluorides is often observed to be different from the others although the underlying reasons remain unclear. Sometimes the case with fluorides is even not considered. It is notably and surprisingly the case for tin (Sn) [1–8] although its electrochemical behavior, owing to its technological applications, has been extensively studied in the presence of many electrolytes (including the other halide anions) [4,9–31], apart from some polarographic studies of fluoride complexes of tin [32,33].

Among the halides, fluoride possesses the highest surface charge density due to its smaller size. This simple property implies not only important consequences between the behavior of fluoride and the other halides in the aqueous phase but it may be also the cause of significant differences on their mechanism of attack during the breakdown of passivity.

As the electrochemical behavior of tin has been already reported with other halides (chloride, bromide and iodide), the present study is restricted to the comparative aggressiveness of NaF and NaCl solutions at 0.1 M concentration on the breakdown of passivity of tin at pH 5.7 and 10.

## 2. Materials and methods

The chemical compounds: sodium fluoride (NaF), sodium chloride (NaCl), sodium hydroxide (NaOH), were analytical grade products manufactured by Sigma–Aldrich (France). Deionized water (pH 5.6 ± 0.2) was taken as a solvent for preparation of the electrolyte solutions at 0.1 M concentration. NaCl solution (original pH 5.7) with a pH 10 was obtained by adding some droplets of a sodium hydroxide solution at 0.1 M concentration. NaF solution (original pH 10) with a pH 5.7 was obtained by adding few droplets of a hydrofluoric acid (HF) solution at 48 wt.% (Prolabo). The pH of the solution was measured with an electronic pH-meter (Eutech Instruments).

Small tin plates were cut from a commercial Sn foil (99.95%, Goodfellow, UK) with a thickness of 0.1 mm to obtain rectangular shape (1.5 cm × 0.5 cm). Before use, the plates were degreased with acetone.

The electrochemical experiments were performed with a potentiostat (Radiometer Analytical, VoltaLab PGP 201) controlled with a PC running the electrochemical software (VoltaMaster 4). The electrochemical set up was constituted with a tin plate as the working electrode and a large platinum plate as the auxiliary electrode. The tin plates were immersed at 1 cm depth in 50 mL of non deaereted solution. A mercurous sulfate electrode (MSE), $Hg/HgSO_4/K_2SO_4$ saturated solution (658 mV/SHE), served as a reference electrode. All the reported potential values refer to this reference electrode.

Before any electrochemical experiment, the tin plates were cathodically polarized at −2 V/MSE during 4 min to remove the air-formed oxide. Polarization curves were performed in the range −1.5 to −0.4 V/MSE with a 1 mV/s sweep rate under agitation at

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200 rpm (magnetic stirrer) of the studied solutions. The same device was used for chronoamperometric experiments where the current density was recorded as a function of time at a −0.5 V/MSE imposed electrode potential. Tin plates were anodized at 1 V/MSE during 15 min in the presence of a 0.1 M NaOH solution. After anodization, without interrupting the programme, the NaOH solution was removed from the contact with the anodized plate by lowering the height adjustable stage where the beaker containing the NaOH solution was placed, and then the programme was stopped. The tin anodized plates were thoroughly rinsed with water before they were immersed in the studied halide solution for the chronoamperometric measurements.

An optical microscope (Leica Instrument) equipped with a camera (Kaiser optical system Inc.) was used to observe the aspect of the corroded plates.

## 3. Results

### 3.1. Anodic polarization of pure tin in the presence of NaF and NaCl

While pH of NaCl solution at 0.1 M concentration is similar to that of the used deionized water, i.e. pH 5.7, pH of NaF solution at 0.1 M is quite different, i.e. pH 10. However to make reliable comparative measurements according to the influence of the nature of the halide anion, the same pH conditions have to be used. Moreover it is also a requirement as the thickness of a passive film and its eventual dissolution are known to depend on the pH of the contacting aqueous solution [34]. This is particularly the case in acidic media where the dissolution reaction of an oxide film on a metal substrate may be described as:

$$M_xO_n + 2nH^+ \rightarrow xM^{(2n/x)+} + nH_2O \quad (1)$$

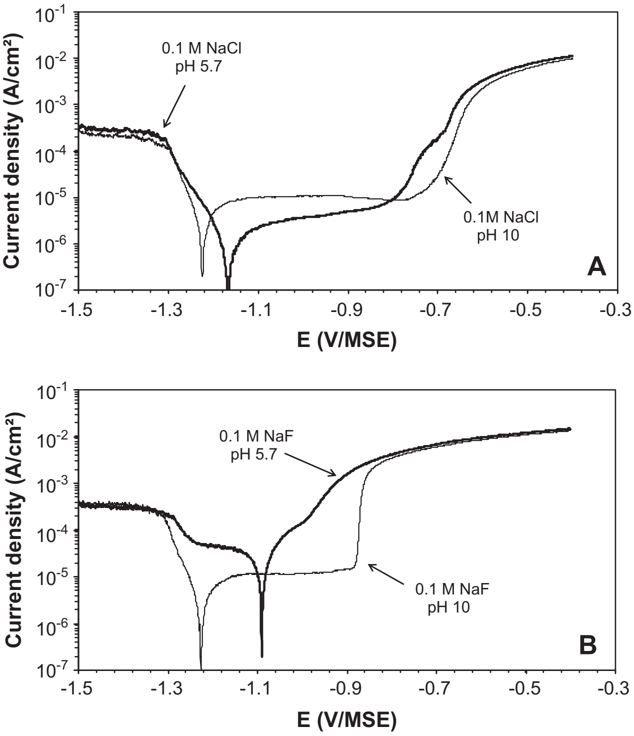

**Fig. 1.** Semi-logarithmic plots of the current density as a function of the electrode potential in the presence of 0.1 M NaCl solution (A), and in the presence of 0.1 M NaF solution (B), at both pH values.

The semi-logarithmic plots of the current density as a function of the electrode potential of pure tin in the presence of both electrolytes at pH 5.7 and 10 (see experimental section) are shown in Fig. 1. Whatever the electrolyte and pH, pitting is observed to occur on tin plates. With NaCl (see case A), the corrosion potential (where the current density passes through zero) corresponds to −1.16 and −1.22 V/MSE, respectively at, pH 5.7 and 10. With NaF (see case B), the corrosion potential corresponds to −1.09 and −1.23 V/MSE, respectively at, pH 5.7 and 10. For both curves at pH 10, the presence of a plateau in the anodic region is indicative of passivation of the surface before breakdown. At pH 5.7, this plateau region is much less pronounced with NaCl and it is almost absent with NaF. With NaCl (see case A), the breakdown potential corresponds to about −0.81 V/MSE at pH 5.7 and −0.76 V/MSE at pH 10. With NaF (see case B), the breakdown potential corresponds to about −0.99 V/MSE at pH 5.7 and −0.88 V/MSE at pH 10. Photographs of tin plates after the onset of pitting are presented in Fig. 2. The aspect was observed to be quite similar with pits of about the same size whatever electrolyte and pH.

Chronoamperometric measurements of pure tin plates with NaCl and NaF at both pH values have been performed at −0.5 V/MSE (a potential greater than the breakdown potential for both electrolytes). The results are reported in Fig. 3. The involved

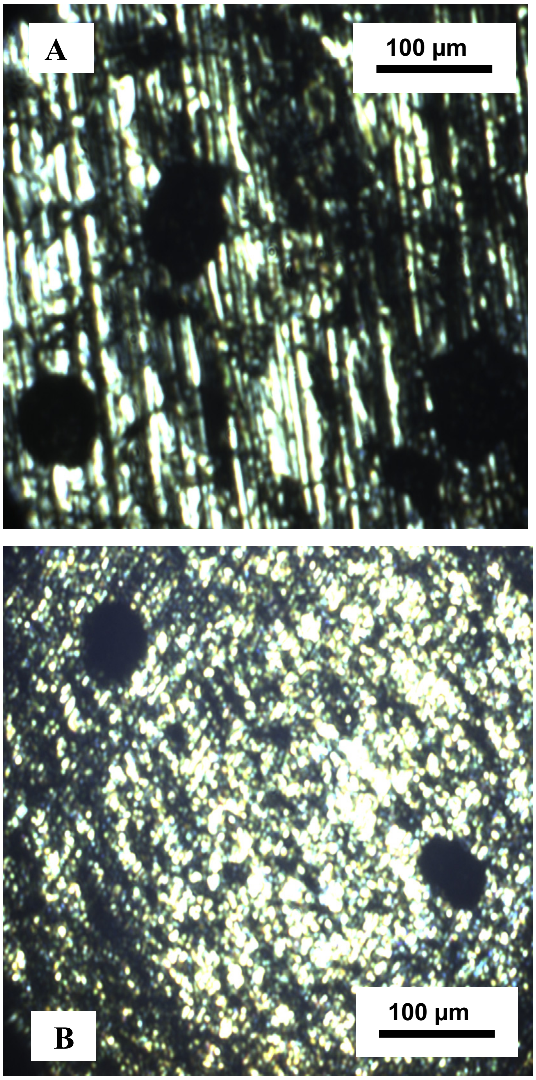

**Fig. 2.** Photographs of pure tin plate in the presence of 0.1 M NaF at pH 5.7 (A) and in the presence of 0.1 M NaF at pH 10 (B).