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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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A B S T R A C T

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.

Keywords:

- A. Tin
- B. Polarization
- B. Potentiostatic
- C. Passivity
- C. Pitting corrosion

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 ($pH\ 5.6 \pm 0.2$) 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 \times 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 deaerated 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

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:

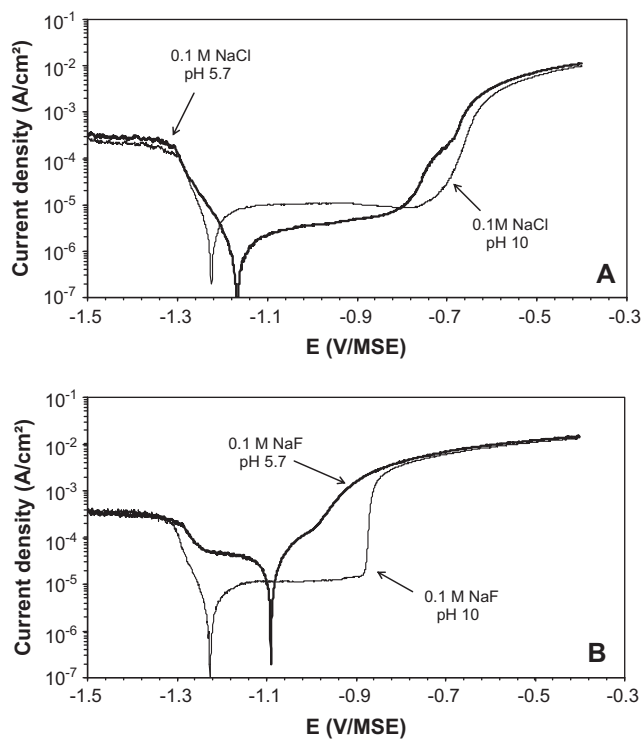
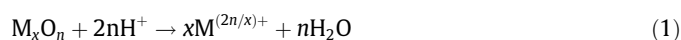


Fig. 1. Semi-logarithmic plots of the current density as a function of the electrode potential in the presence of 0.1 M NaCl solution (A), and in the presence of 0.1 M NaF solution (B), at both pH values.

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

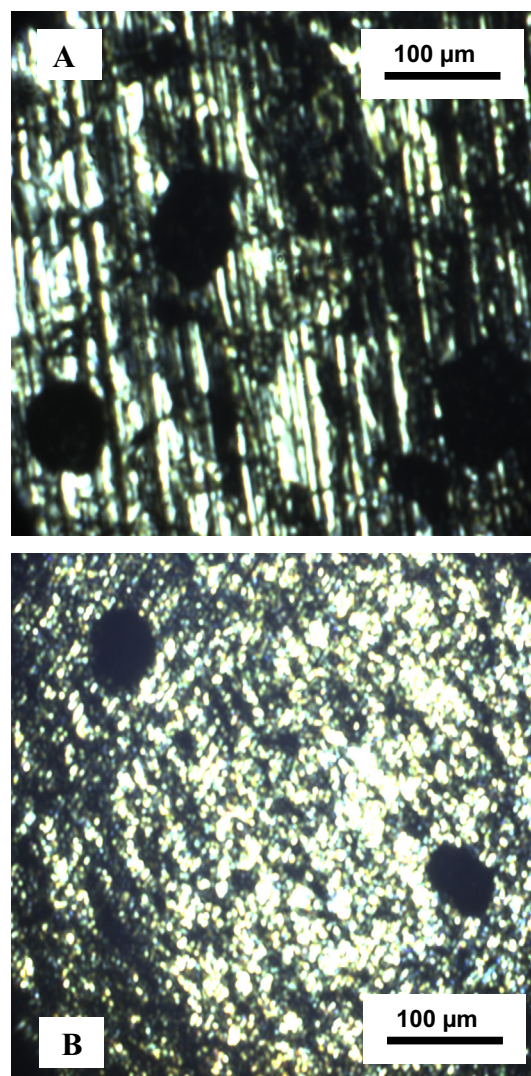


Fig. 2. Photographs of pure tin plate in the presence of 0.1 M NaF at pH 5.7 (A) and in the presence of 0.1 M NaF at pH 10 (B).

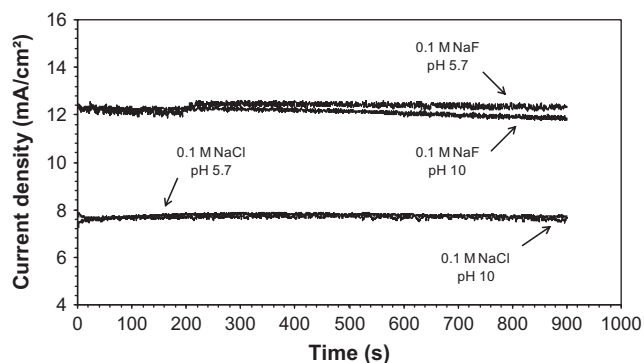


Fig. 3. Chronoamperometric curves at -0.5 V/MSE of pure tin in the presence of 0.1 M NaCl and 0.1 M NaF solutions, at both pH values.

Table 1

Weight loss (Δm), calculated amount of charge (Q), corresponding valence (z) according to Faraday's law, for each electrolyte at both pH values.

Electrolyte	pH	Δm (mg/cm ²)	Q (C/cm ²)	z
NaCl	5.7	4.0	7.01	2.16
NaCl	10	3.8	6.92	2.24
NaF	5.7	6.9	10.92	1.95
NaF	10	6.7	11.12	2.04

valence z of the released cations may be determined according to the Faraday's law:

$$z = \frac{QM_{\text{Sn}}}{F\Delta m} \quad (2)$$

where Q is the amount of charge passed during electrolysis duration, i.e. 900 s (it is calculated by the VoltaMaster 4 software), M_{Sn} is the atomic weight of tin, F is the Faraday constant, Δm is the weight loss of the tin plate. The obtained values are reported in Table 1. Whatever electrolyte and pH, the results give z values around 2 so indicating a corrosion process with formation of tin II species in accordance with the oxidation reaction:



3.2. Passivation of tin in NaOH solution

Numerous studies have been devoted to passivate electrochemically tin electrodes in the presence of various electrolyte solutions, notably in alkaline media owing to its industrial applications [9–11,18,20,35–39]. Although the exact mechanism leading to passivation still offers debate in the literature, a consensus view is that tin passivity results from the formation of a final SnO_2 layer [40–47].

Passivation of tin in the presence of NaOH at 0.1 M concentration has been already reported [11,13,36,47]. The linear voltammogram of tin in the -2 to $+2$ V/MSE potential range is shown in case A of Fig. 4. As expected, two anodic peaks are observed, at -1.29 and -1.08 V/MSE, before the current density decreases abruptly. It remains nearly constant around 150 $\mu\text{A}/\text{cm}^2$ before it increases continuously from 1.7 V/MSE with the onset of oxygen evolution.

Passivation of tin was further performed at 1 V/MSE during 15 min. As an example, the variation of the current density as a function of time is reported in case B of Fig. 4.

3.3. Chronoamperometric measurements with NaF and NaCl solutions

Once the tin plates have been passivated, the NaOH solution was removed (see experimental section). Chronoamperometric

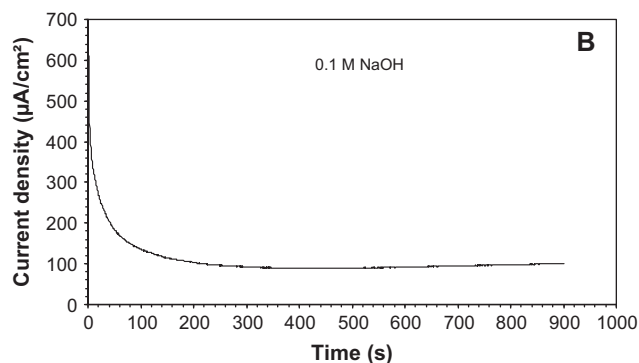
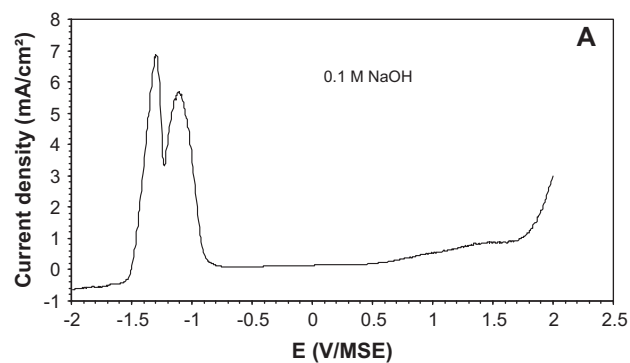


Fig. 4. Polarization curve of pure tin in the presence of 0.1 M NaOH solution (A); anodization of tin at 1 V/MSE during 15 min in the presence of 0.1 M NaOH solution (B).

experiments were performed at -0.5 V/MSE to investigate the comparative aggressiveness of fluoride and chloride at both pH values, i.e. 5.7 and 10 , see Fig. 5 (cases A and B).

Although film dissolution is promoted in more acidic conditions (see Eq. (1)), the aggressiveness of chlorides is quite similar whatever solution pH (the amount of free chlorides in solution is expected to be the same at both pH as NaCl is the sodium salt of the strong acid HCl), see Fig. 5 (case A). At both pH, the current density increases steeply before it rapidly levels off.

In the case of NaF, the effect of pH is much more sensitive (see Fig. 5). As fluoride is the anion of the weak acid HF, with a pK 3.2 (see Table 2), the extent of free fluoride anions is expected to be much greater in aqueous solution at pH 10 than that at pH 5.7 . Nevertheless the obtained results show that the aggressiveness is weaker at pH 10 where the current density increases more slowly when compared to the case at pH 5.7 (see cases A and B in Fig. 5). Moreover the difference in aggressiveness is very pronounced when compared to chloride at the same pH 10 , see Fig. 5. At pH 5.7 , the current density first increases slowly with NaF, when compared to the case with NaCl, before it rises significantly. The experiments were repeated to appreciate the reproducibility, see the corresponding thick curves in cases A and B of Fig. 5 for NaF at both pH values. In the case of NaCl the results were identical.

4. Discussion

4.1. The kosmotrope/chaotrope nature of the halides

This distinction is based on the ability to highly/poorly structure the water molecules in their vicinity. Hydration effects are quite sensitive with the anions since they can form an apparent hydrogen bond with the small hydrogen atom of the surrounding water molecules.

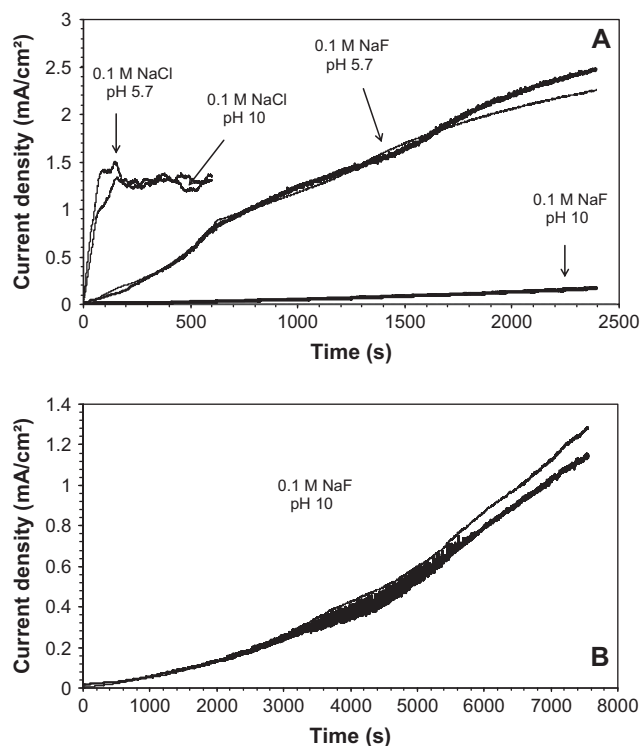


Fig. 5. Chronoamperometric curves at -0.5 V/MSE after anodization in NaOH solution in the presence of 0.1 M NaCl and 0.1 M NaF solutions, at both pH values (A); chronoamperometric curves at -0.5 V/MSE with 0.1 M NaF at pH 10 at longer duration.

Table 2

ionic radius (r), surface charge density (σ), viscosity B coefficient value, pK of the corresponding acid of the halides.

Anion	r (nm) ^a	σ (mC/m ²)	B (L/mol) ^b	pK ^c
F ⁻	0.133	720.2	0.127	3.2
Cl ⁻	0.181	388.8	-0.005	-7
Br ⁻	0.196	331.6	-0.033	-9
I ⁻	0.220	263.2	-0.073	-10

^a From Ref. [48].

^b From Ref. [51].

^c From Ref. [53].

Simple ions in water generate electric fields which are strong enough to orient water dipoles. However the effect is more pronounced, and over longer distances, as the surface charge density σ of the anion is higher [48], see Table 2. As a result, in the case of monovalent species such as the halides, this effect is intimately related to the size of the anion. Small ions with a relatively high surface charge density generate high electric fields at short distances, so binding water molecules around them more strongly than water itself in the aqueous phase. These ionic species are referred as water-structure-making ions or kosmotropes. Those presenting the opposite effect are water structure-breaking ions or chaotropes. They are usually large and generate weak electric fields, so possessing a loose hydration shell which can be easily removed. The well-known Hofmeister lyotropic sequence thus divides the halides between the (sole) kosmotrope fluoride and the chaotropes chloride, bromide and iodide [49].

Although the knowledge of the surface charge density can help to anticipate the presumed affinity of the anions to the water molecules, the distinction between them can be conveniently made according to the sign of the viscosity B coefficient value of the Jones-Dole relationship [50], which is determined from dynamic

conditions (viscosity measurements) when the ions move in solution with their more or less tightly attached hydration shell:

$$\eta = \eta_w(1 + Ac^{1/2} + Bc) \quad (4)$$

where η is the dynamic viscosity of the aqueous electrolyte solution at molar concentration c and η_w is the dynamic viscosity of pure water. The coefficient A , which is positive for all electrolytes, is an electrostatic term due to the interaction between the ions. The coefficient B represents a physical parameter that provides information on the strength of attachment of the surrounding water molecules to the ion. Positive B values are associated with kosmotrope ions where the hydration shell is thick and strongly attached, so that the resistance to flow of these solutions is greater than that of pure water. At the opposite, negative B values refer to chaotrope ions for which the adjacent water molecules are far away and not orientated. Whereas $B > 0$ for the kosmotrope fluoride anion [51], $B < 0$ for the other chaotrope halides, see Table 2.

4.2. Influence of anion properties on solution pH

The origin of such different pH values for NaCl and NaF solutions at 0.1 M concentration, i.e. 5.7 and 10, respectively, is classically ascribed to the possibility of fluoride anion to react with water to give hydroxide anion OH⁻ and hydrofluoric acid HF, which is a weak acid, according to the following reaction scheme:



In contrast, as NaCl is the sodium salt of hydrochloric acid HCl, which is a strong acid that fully dissociates in water, chloride anion will not interact with water and no release of hydroxide anion is expected, so that pH remains practically unchanged.

These differences may be interpreted from the kosmotrope/chaotrope nature of the involved anion. When halide compounds (acids or electrolytes) are added into an aqueous phase, the formation of either free ion pairs or strong ion pairs depends on the 'law of matching affinities' concept [49,52]: oppositely charged ions with equal water affinity tend to come together to form contact ion pairs whereas oppositely charged ions with differing water affinities tend to stay apart. Two well hydrated small ions (kosmotropes) of opposite charge experience a very strong attraction between them. They can come closer to form a direct ion pair by expelling, at least partially, the hydration shells between them. In the case of two weakly hydrated large ions (chaotropes), the electrostatic attraction between them is weak but the hydration shells are so loosely bound that the chaotrope ions can also form direct ion pairs by fully expelling the hydration water between them. When the interaction of one kosmotrope ion with an oppositely charged chaotrope counter-ion is concerned the attraction of the chaotrope counter-ion is not strong enough that the kosmotrope ion can loose its hydration shell. As a consequence, a kosmotrope/chaotrope pair is always separated by water and cannot form strong ion pairs. This explains the reason why HF behaves as a weak acid, i.e. with a positive pK value [53] (see Table 2), so reflecting that the interaction between H⁺ and F⁻ is sufficiently strong enough that HF does not fully dissociate in water (H⁺ being a kosmotrope cation [49]), whereas the corresponding acids of the other chaotrope halides (HCl, HBr, HI) are all strong acids, i.e. with large negative pK values (see Table 2).

Therefore, when a salt such as NaF is added into water, the ions can separate sufficiently from one another so that the kosmotrope fluoride anions will interact more favourably and strongly with the hydronium cations (H₃O⁺) of the aqueous phase that possess a high surface charge density. As a result, there will exist statistically a much greater extent of free hydroxide anions OH⁻ in the aqueous phase with respect to free hydronium cations, so that the whole pH increases.

4.3. Influence of anion properties on the breakdown of passivity of tin

The previous results (see Section 3.3) exhibit a significant difference in the kinetics of attack between fluoride and chloride when a protective passive layer is formed on the surface. These discrepancies in the observed aggressiveness may be interpreted from the kosmotrope and chaotrope nature of the involved anions.

The very slow increase of the current density from the beginning with NaF at pH 10 (see cases A and B in Fig. 5) suggests that free fluoride anions are not engaged in a dominant pitting process but rather in a slower thinning process of the oxide film. Previous studies on passivated metals such as iron and nickel support this mechanism, where the slow and continuous increase of the current density was ascribed to the dissolution of the film through the formation of soluble complexes or salts with metallic cations present in the passive film [54–61]. The enhanced transfer of metallic cations from the oxide to the solution results from a homogeneous attack of the passive layer leading to a decrease of oxide thickness with time. The pronounced ability of fluoride than the other halides to promote film thinning has been classically rationalized to their greater complexing tendency through the comparison of the stability constants of metal-halide complexes [60].

When the well-hydrated kosmotrope fluoride anions become adsorbed at the surface of the passive film on tin substrate, they are not inclined to loose their hydration shell since the energetic contribution is too unfavourable. However they can partially dehydrate if they are susceptible to interact favourably with surface tin cations present in the passive film, that possess also a sufficiently high surface charge density, following the ‘law of matching affinities’ concept (as information, all metallic cations with a valence z greater than one are kosmotrope species with positive B values [51]). The formation of soluble and stable complexes between tin cations and fluoride ligands is then promoted.

Owing to its reduced size, fluoride is the most electronegative atom among the halides (Pauling scale) [62]. For a given number of ligand, the stability constant β of halide tin complexes is effectively the highest in the case of fluoride [63,64]; the comparative β values between fluoride and chloride are reported in Table 3. This justifies why fluoride is prone to form such tin complexes, so contributing to an enhanced thinning process of the passive film which is widespread on the whole surface. As the thickness of the passive film becomes smaller, an increased electric field is generated across the film. This enhances the formation of flaws and cracks within the film so that the breakdown of the passive layer may occur. Pitting of passivated tin may be observed with fluorides once the passive film has been sufficiently weakened. This is the reason why the kinetics of attack is much slower with fluorides.

Table 3

Comparative values of the stability constant (β) of the complex formation between tin cation with fluoride and chloride anions.

Complex formation	$\log \beta^a$
$\text{Sn}^{2+} + \text{F}^- = \text{SnF}^+$	5.25
$\text{Sn}^{2+} + \text{Cl}^- = \text{SnCl}^+$	1.52
$\text{Sn}^{2+} + 2\text{F}^- = \text{SnF}_2$	8.89
$\text{Sn}^{2+} + 2\text{Cl}^- = \text{SnCl}_2$	2.17
$\text{Sn}^{2+} + 3\text{F}^- = \text{SnF}_3^-$	11.5
$\text{Sn}^{2+} + 3\text{Cl}^- = \text{SnCl}_3^-$	2.13
$\text{Sn}^{4+} + 6\text{F}^- = \text{SnF}_6^{2-}$	25
$\text{Sn}^{4+} + 6\text{Cl}^- = \text{SnCl}_6^{2-}$	9.83

The stability constant β for each complex formation corresponding to the reaction: $M + iL = ML_i$ (where M is the metallic cation and L is the halide ligand) is defined as: $\beta = \frac{[ML_i]}{[M][L]^i}$.

^a From Ref. [63].

The faster kinetics of passivity breakdown with fluoride at pH 5.7 than at pH 10 (see Fig. 5) should stem from a greater extent of oxide film dissolution in such acidic conditions, as already mentioned (see Section 3.1).

When the chaotrope chlorides are adsorbed at the surface of the passive film, the formation of the corresponding tin complexes is less favoured than with fluorides, as it can be seen in Table 3. As a result, the thinning process of the oxide film exists but it is less pronounced. However as these anions can loose easily their hydration shell, they may be expected to exert greater stresses on the passive film and/or to be more able to penetrate into the passive layer than the kosmotrope fluorides. This should contribute to weaken more the film structure locally (pit initiation), so enabling the electrolyte solution to infiltrate into the passive layer and to lead faster to a direct contact with the underlying tin surface. Such a rapid attack by chlorides through this dominant pitting process may justify why no great difference is observed at both pH values, see case A in Fig. 5.

Nevertheless, pitting of valve metals by fluoride (aluminum [65], titanium [66]) may be observed but not within the operating conditions that are commonly used with other metals, i.e. greater fluoride concentrations and/or higher electrode potentials are required. The passive films of valve metals have the propensity to regenerate (self-healing) sufficiently quickly and cohesively after an eventual breakdown [67–70]. This is the main difference with metals such as tin or iron and nickel [71]. The slow oxide thinning process, through enhanced formation of soluble salts or complexes between the kosmotrope fluorides and metallic cations from the passive film, is balanced by the concomitant and efficient oxide regeneration so that pitting is not favoured. A characteristic example is that of the controlled building of well-defined porous nanotubes within the passive film on titanium resulting from the extensive formation of $[\text{TiF}_6]^{2-}$ soluble complexes without occurrence of pitting [72]. In contrast, pitting of valve metals is favoured in the presence of the other chaotrope halides since the kinetics of oxide regeneration is challenged and dominated by the ability of these anions to dehydrate so that they can alter locally and irreversibly the passive film structure.

5. Conclusion

It is believed that the electrochemical behavior of pure and passivated tin in the presence of fluorides has not been reported so far.

The results confirm the significant difference in the kinetics of attack of a passivated metal surface between the kosmotrope fluoride and the representative chaotrope chloride. This different aggressiveness originates from the competition between the kinetics of various processes, pitting and/or film thinning versus film regeneration, which may be anticipated according to the ‘law of matching affinities’ concept through the knowledge of the halide-specific hydration properties.

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