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Influence of the anion specificity on the anodic polarization of titanium

J.L. Trompette [a,*], L. Massot [a], L. Arurault [b], S. Fontorbes [b]

[a] Laboratoire de Génie Chimique (LGC), UMR 5503, 4 allée Emile Monso, 31432 Toulouse Cedex 4, France
[b] Université de Toulouse, CIRIMAT, UPS/INPT/CNRS, LCMIE, Bât. 2R1, 118 route de Narbonne, 31062 Toulouse Cedex 9, France

ABSTRACT

The anodic polarization of titanium in the presence of selected electrolytes at 0.1 mol/L concentration has been investigated. The results were interpreted according to the categorization of anions based on their cosmotrope/chaotrope character. The aggressiveness of the anions is found to be related for a part to their proneness to loose their hydration shell during the penetration of the passive film, provided they can access sufficiently to the passive surface.

1. Introduction

When studying the electrochemical corrosion of different passive substrates some ions are observed to cause localized corrosion much more favorably than others and it is even rarely the case for some of them, however, the underlying reasons remain unclear. Owing to the economical impact of corrosion problems in the failure of materials a lot of studies have been carried out for many years to elucidate the mechanisms of localized corrosion [1–20] and some of the different ways to prevent its occurrence [21–28]. At the present time, four main mechanisms have been proposed to explain the processes leading to the breakdown of the passive films [29–32]. These films are usually assumed to be composed with an inner oxide layer, being the barrier layer against cation transfer, and an outer hydroxide being an exchange layer with the electrolyte. In the penetration mechanism [33], the dissolution of the metal is expected to occur once the aggressive ions have reached its surface after their migration through the passive film, without destroying it, with the assistance of the electrostatic field. In the film breaking mechanism [34,35], the dissolution of the metal is proposed to occur once the passive film has been mechanically fractured with the apparition of flaws and cracks within its structure due to the exerted electrostatic stress and the combined reduction of the surface tension at the passive film–solution interface. In the adsorption mechanism [36,37], the dissolution of the metal is assumed to occur once the bare surface has been discovered through the continuous thinning of the passive film due to the formation of soluble complexes or salts of the metallic cations at the passive film–solution interface. In the point defect model [38,39], the anions are supposed to remain adsorbed into oxygen vacancies at the passive film–solution interface, so generating cation vacancies that migrates to the metal–passive film interface. When reaching the metal surface, the collapse of the film may occur if the rate of accumulation of the cation vacancies is not counterbalanced by the rate of the oxidation reaction releasing the metallic cations towards the film.

Nevertheless, the whole process of the breakdown of passive films has been recognized to be not fully understood. Moreover, according to varying experimental conditions and environmental specificities, each of these mechanisms could be predominant; sometimes the distinction between them is also quite tenuous [32].

In a previous study [40], the electrochemical corrosion of anodized aluminum alloy 2017 samples (4%, w/w, of Cu) has been investigated in the presence of various electrolytes. The results were found to indicate the role of the specific interaction of the anions with the water molecules. As it is well documented in the literature [41,42], the ions may be categorized into two classes according to the properties of their surrounding hydration shell. The ionic species referred as water-structure-making ions, say cosmotrope ions, exhibit a relatively high surface charge density. They thus generate high electric fields at short distances, so binding water molecules in their vicinity more strongly than water itself. Those presenting the opposite effect are referred as water-structure-breaking ions, say chaotrope ions. They are usually large and generate weak electric fields around them, so possessing a loose hydration shell that can be easily removed.

Whereas all the tested chaotrope anions were able to initiate pitting, no breakdown of passivity was found to occur in the presence of the cosmotrope anions unless much higher voltages were

* Corresponding author. Tel.: +33 05 34 32 36 34; fax: +33 05 34 32 36 97.
  E-mail address: jeanluc.trompette@ensiacet.fr (J.L. Trompette).

Anion	Ionic radius[a] (nm)	Hydrated radius[a] (nm)	Viscosity B coefficient at 25 °C (L/mol)	Conductivity of the salt solution at 0.1 mol/L (mS/cm)
F^-	0.133	0.212	+0.1[c]	8.57
$CH_3CO_2^-$	0.162	0.217	+0.25[c]	6.96
HCO_2^-	0.169	0.219	+0.052[c]	8.51
NO_3^-	0.179	0.223	−0.046[c]	9.94
Cl^-	0.181	0.224	−0.007[c]	10.54
Br^-	0.196	0.231	−0.032[c]	10.66
HPO_4^{2-}	0.200	0.260	+0.382[b]	13.37
SCN^-	0.213	0.242	−0.103[c]	9.25
I^-	0.220	0.246	−0.068[c]	9.96
SO_4^{2-}	0.230	0.273	+0.208[b]	16.29
CrO_4^{2-}	0.240	0.279	+0.165[b]	20.98
ClO_4^-	0.250	0.261	−0.061[c]	9.20

[a] From Ref. [45].
[b] From Ref. [46].
[c] From Ref. [44].

applied. These results reflected there was probably a correlation between the aggressiveness of the anions and their ability to dehydrate, even if other factors can contribute to the breakdown of metal passivity. This suggests it would be interesting to investigate whether the previous trends could be extended to other cases.

In this study, the increasing anodic polarization of titanium plates in the presence of various electrolytes at 0.1 mol/L concentration has been reported; the corresponding anions were selected so as to correspond to a range of typical cosmotrope and chaotrope ions. These experiments were complemented by photographs and SEM pictures of the treated surfaces to appreciate the anion-dependant breakdown of passivity of titanium.

2. Material and methods

All the salts used: sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), sodium nitrate (NaNO₃), sodium thiocyanate (NaSCN), sodium perchlorate (NaClO₄), sodium formate (NaHCO₂), sodium acetate (NaCH₃CO₂), sodium hydrogenophosphate (Na₂HPO₄), sodium sulfate (Na₂SO₄), potassium chromate (K₂CrO₄), were analytical grade products manufactured by Prolabo (France) or Sigma–Aldrich (France). Deionized water was taken as a solvent to prepare the electrolyte solutions at 0.1 mol/L concentration.

Small titanium plates were cut from a commercial Ti foil (99.6%, Goodfellow, UK) with a thickness of 0.1 cm to obtain rectangular shape (1 cm × 2.5 cm). Before the experiments, the titanium plates were washed in acetone and rinsed with deionized water before etching 25 s into a HF 2%, v/v, + HNO₃ 4%, v/v, aqueous solution. Then they were rinsed with deionized water and dried in air.

The electrochemical set up was constituted with the titanium plate as the anode and a flat platinum plate as the cathode. The anodic polarization of titanium plates was performed in the range 0–120 V with a 20 mV/s sweep rate by using a DC power supply (Convergie Fontaine, 400 V – 1 A). The potential of the working electrode (titanium) versus the mercury sulfate reference electrode (MSE) was recorded by the use of an automatic multimeter Metrix MX 55C that was placed in parallel.

The plates were immersed at 1.5 cm depth in 100 mL of aqueous electrolyte solutions at 0.1 mol/L concentration under agitation at 200 rpm (magnetic stirrer). All the electrochemical experiments were performed at ambient temperature and repeated twice. The used electrodes were maintained at fixed positions.

A spectrophotometer (Varian, Cary 1E) was used to measure the UV absorbance of aqueous solutions in the 200–400 nm range of wavelength; quartz cells (1 cm length) were used.

After anodic polarization, a 3CCD digital video camera, Panasonic NV-GS 120 (Crystal Engine), was used to take photographs of the plates; they were examined by scanning electron microscopy (SEM) with a LEO 435 VP electron microscope using various magnifications to observe the aspect of the surfaces.

3. Results and discussion

3.1. Categorization of anions

The same characteristic anions as those studied previously were used [40], say for the cosmotrope ions: SO_4^{2-}, HPO_4^{2-}, CrO_4^{2-}, F^-, HCO_2^-, $CH_3SO_2^-$ and for the chaotrope ions: Cl^-, Br^-, I^-, ClO_4^-, NO_3^- SCN^-. The sign of the viscosity B coefficient appearing in the Jones–Dole relationship [43,44] is taken as the criterion allowing the convenient distinction between the cosmotrope and the chaotrope anions:

$$\frac{\eta}{\eta_w} = 1 + A \cdot \sqrt{c} + B \cdot c \tag{1}$$

where η is the viscosity of aqueous salt solution at molar concentration c and η_w is the viscosity of pure water. The coefficient A, which is positive for all electrolytes, is an electrostatic term originating from 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 cosmotrope ions where the hydration shell is thick and tightly attached, so that the resistance to flow of
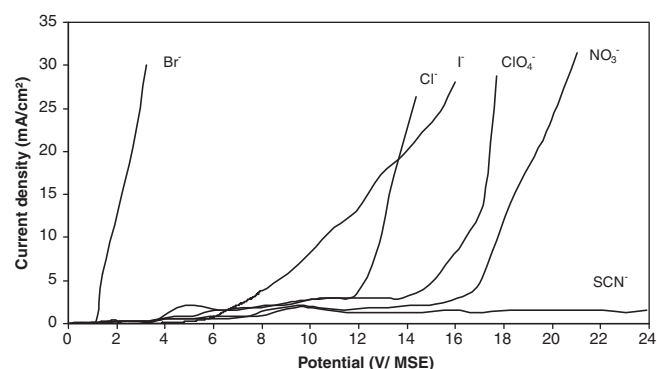
Fig. 1. Variation of the current density as a function of the potential (versus MSE) in the presence of the chaotrope anions.

these solutions is higher than that of pure water. At the opposite, negative B values correspond to chaotrope ions for which the adjacent water molecules are far away and not oriented.

The ionic radius [45], the hydrated radius [45], the Jones–Dole viscosity B coefficient at 25 °C of the anions [44,46] and the conductivity of the corresponding salt solutions at 0.1 mol/L are listed in Table 1.

3.2. Anodic polarization of titanium

The resistance against corrosion of a valve metal such as titanium is known to result from the existence of a natural and cohesive passive film, with a thickness of a few nanometers (about 5 nm typically), which is formed spontaneously when it is exposed to oxidizing media (air, water). The reasons why valve metals become irreversibly corroded depend on the ability of the passive film to reform (self-healing) sufficiently after its eventual breakdown. Following the classical procedure of increasing anodic polarization, the electrochemical corrosion of titanium plates was appreciated by recording the current density as a function of the electrical potential of the titanium plate (versus MSE) in the presence of the electrolyte solutions.

For the chaotrope anions, see Fig. 1, the curves exhibit a sharp increase of the current density, except for the thiocyanate ion (SCN^-) where it remains lower than 5 mA/cm^2, even for potentials above 110 V/MSE. The corresponding average potential values for which the steep rise of the current density occurs are, respectively, 1.3, 6.2, 11.9, 13.8 and 16 V/MSE for Br^-, I^-, Cl^-, ClO_4^-, and NO_3^-. Photographs and SEM pictures of the plates after anodic polarization are presented, respectively, in Figs. 2 and 3. In the presence of Br^- and ClO_4^-, the plates have been significantly damaged on the edges and in the center where impressive holes are obtained. In the case of Cl^-, the edges of the plate are essentially attacked whereas many pits are observed in the center of the plate with I^-. In the case of NO_3^-, the whole surface has been damaged (craters of small depth and fractured corrosion grooves) with the presence of an adhering yellowish precipitate. With SCN^-, the plate remains non-attacked with a smooth and grey coverage on the surface and, as an indication, no precipitate (resulting from the destruction of the passive film) was formed in solution whereas it was the case for the other chaotrope anions.
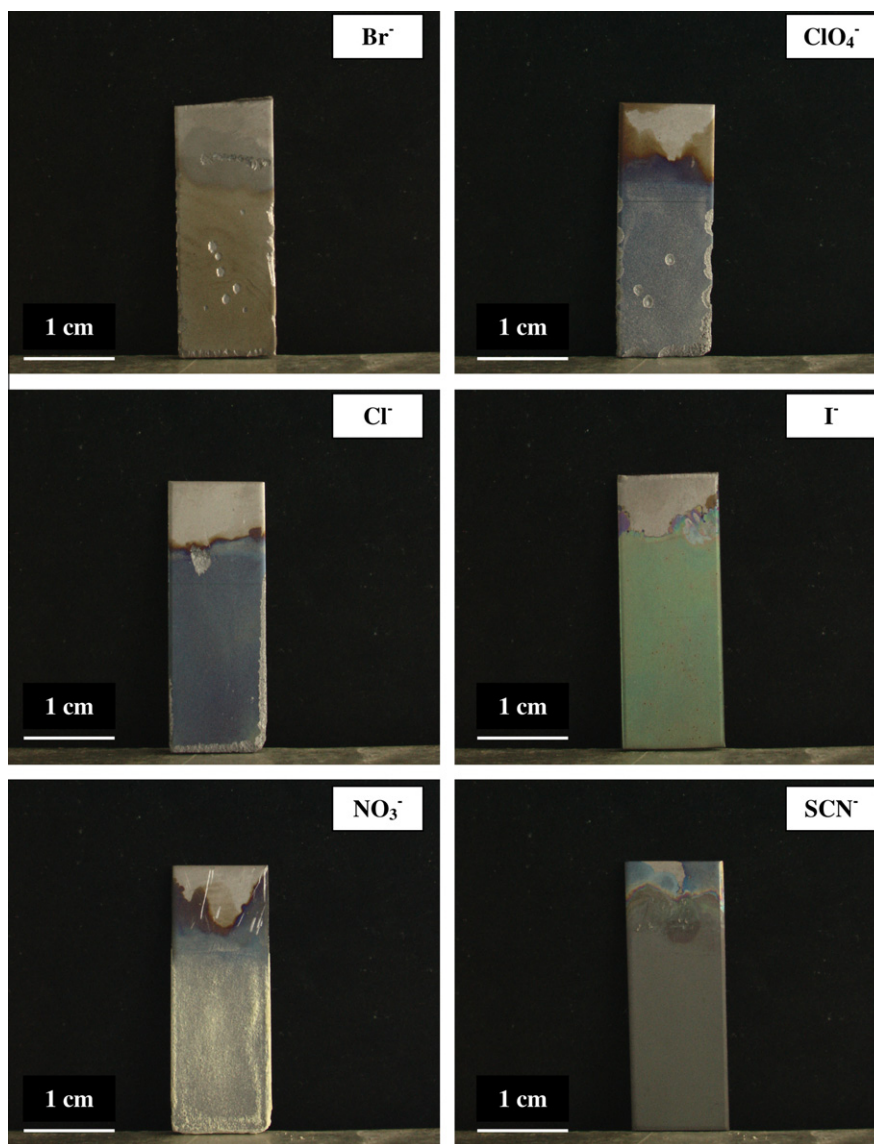

Fig. 2. Photographs of titanium plates after the anodic polarization in the presence of the chaotrope anions.
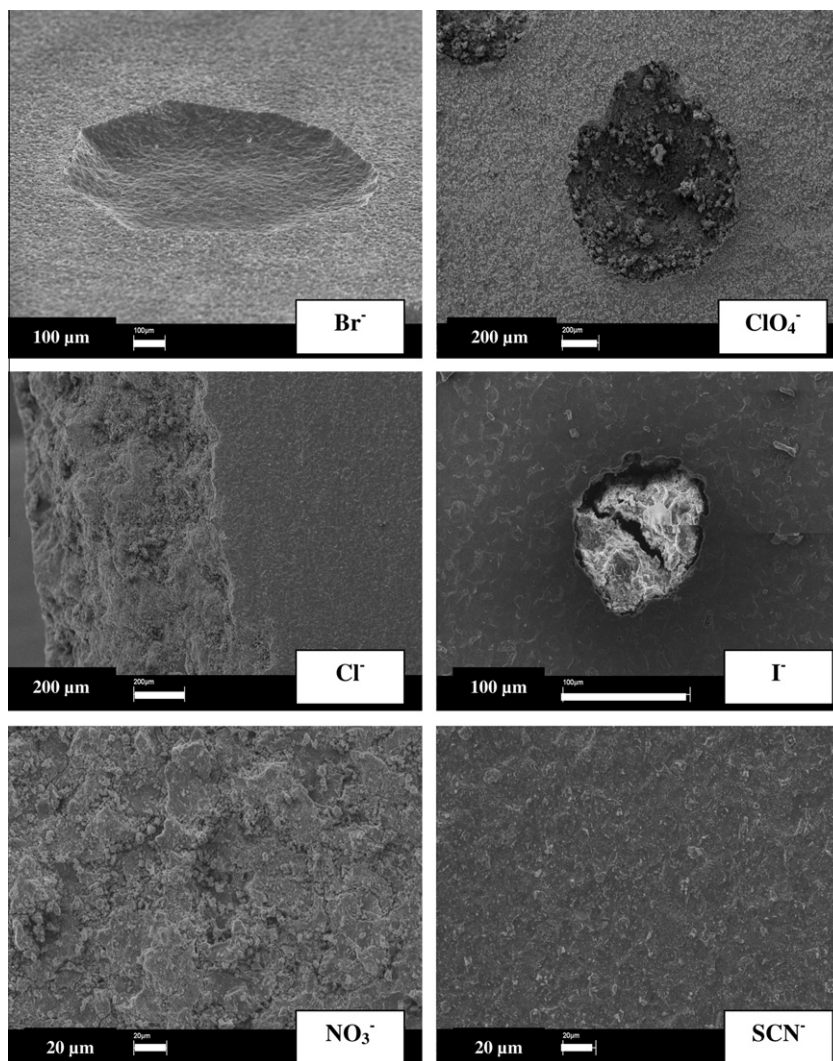
Fig. 3. SEM pictures of titanium plates after the anodic polarization in the presence of the chaotrope anions.

For the cosmotrope anions, see Fig. 4, the current density was found to remain lower than 20 mA/cm² in a large range of the potential scanning. However, in each case for potentials greater than 60 V/MSE, except for acetate ions ($CH_3CO_2^-$), the current density is observed to increase more or less strongly before an unreliable signal is recorded that was found to correspond to the occurrence of sparking at the water-line. This characteristic behavior has been ascribed to the dielectric breakdown of anodized surfaces [47]. Photographs of the plates after the anodic polarization are presented in Fig. 5. The aspect of the titanium plates corroborates the obtained results since none of these plates were damaged, so indicating the absence of the breakdown of passivity (with no precipitate in solution). In the case of F^-, the whole plate is uniform and grey. The plate with HCO_2^- is similar to that obtained with thiocyanate (SCN^-). For $CH_3CO_2^-$, SO_4^{2-}, CrO_4^{2-} and HPO_4^{2-}, the plates are smooth with variable color properties. The coloration of titanium plates during anodization has been interpreted according to light interference effects on the anodic film [48,49]. The SEM pictures of these plates (not shown) were quite similar to that obtained with SCN^-.

During increasing anodic polarization of titanium several processes may take place simultaneously [50–52], such as: the formation and repair of an anodic film of TiO_2 according to the reaction: $Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$, water oxidation leading to electrogenerated oxygen bubbles, gas evolution coming from the

oxidation reaction of some entities (like, for instance, Br_2 production through: $2Br^- \rightarrow Br_2 + 2e^-$) and the onset of the breakdown at a critical potential. This is evidenced in Fig. 1 by the complex succession of intensity waves that reflects principally the balance between the decrease of the current density due to the self-healing of the passive film and the oxidation of the underlying metal [53]. Nevertheless, the irreversible breakdown of the passive film is clearly identified by the abrupt increase of the current density [12,52].
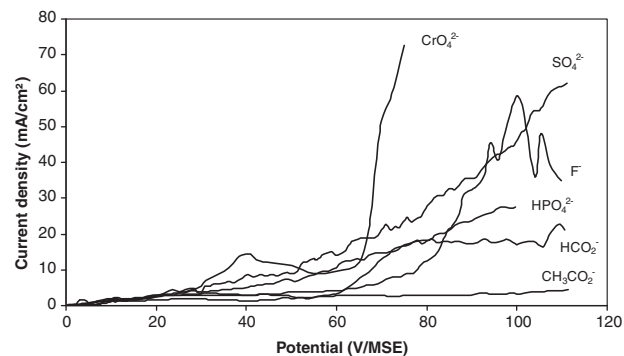

Fig. 4. Variation of the current density as a function of the potential (versus MSE) in the presence of the cosmotrope anions.
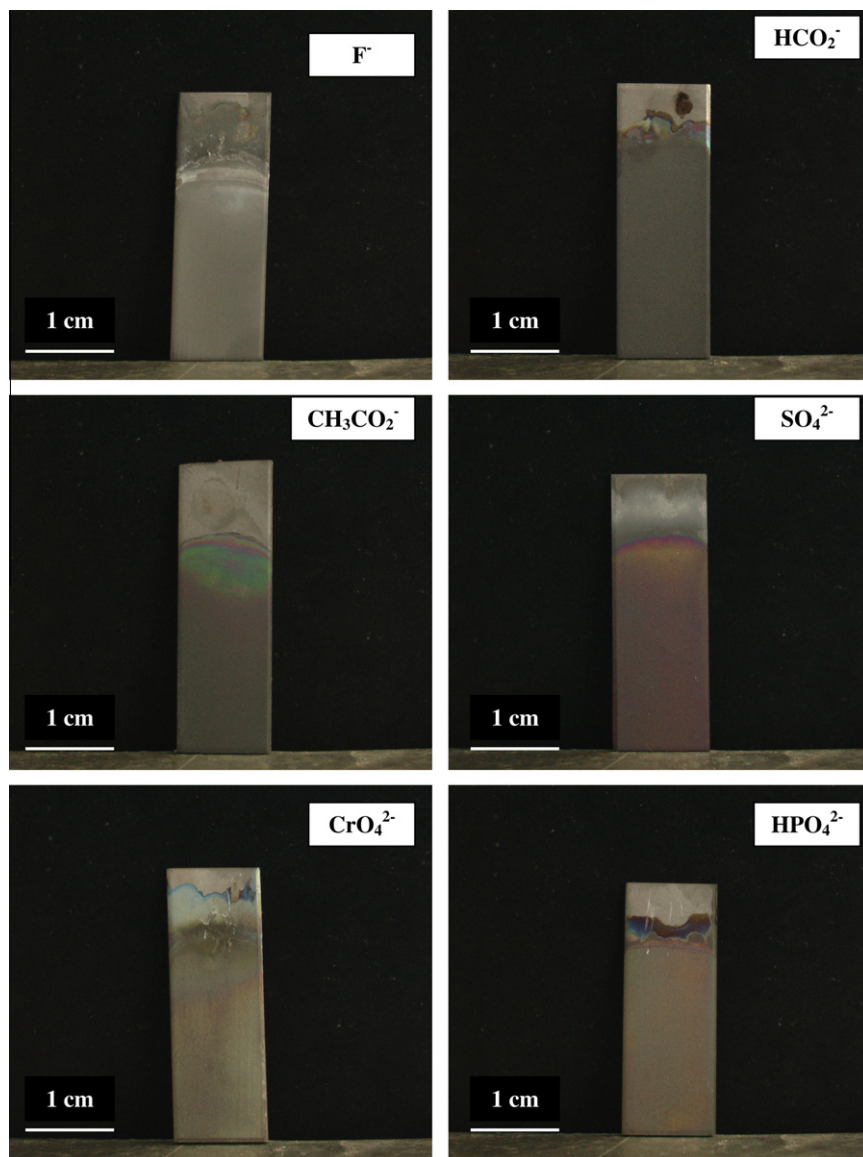
Fig. 5. Photographs of titanium plates after the anodic polarization in the presence of the cosmotrope anions.

Earlier studies were devoted to the growth of anodic TiO_2 films under galvanostatic or (less frequently) potentiostatic steady-state conditions of anodization, in the presence of non-aggressive salts or acids. It was assumed that the breakdown of these films was caused by the occurrence of crystallization at relatively low potentials, typically 5 V [11,54–57], allowing then oxygen evolution and finally breakdown of the anodic film. But the promoting phenomena of the crystallization still remain under debate: internal compressive stresses [11], localized high temperatures or difference of growth rate [55]; cause and effect could not be often distinguished [11]. However, it was unanimously noticed that the incorporation of some exogenous species (coming from the substrate or from the electrolyte) into the anodic amorphous film oxide slowed the crystallization, so modifying the breakdown behavior [57]. Even though the experimental conditions in the present study are quite different, say anodic polarization performed with increasing voltages, it may be assumed that the penetration of aggressive anions into the oxide film delay to some extent the potential at which the breakdown is observed.

The obtained results confirm those of the previous study with aluminum substrates [40], so strengthening the assumption that the categorization of anions contributes to explain, among several other factors, the conditions for the breakdown of passivity of valve metals. They indicate that the chaotrope anions, except, however, the case of SCN^- (see Section 3.3), allow the breakdown of passivity to be effective at relatively low or moderate potentials whereas it is very hard or even not possible for the cosmotrope anions. This clear distinction is assumed to originate from a variable resistance against dehydration when penetrating the passive film [40]. Upon voltage application, the anions are attracted towards the anode. They thus come to the passive film–solution interface with their surrounding hydration shell and they can adsorb onto the passive film. There, they may be involved with some surface metallic cations in the formation of more or less soluble salts or complexes, so participating through an eroding process to the thinning of the passive film [58]. However, the chaotrope anions that exhibit a weaker resistance to dehydration can also penetrate more easily into the passive film at its defects up to the base metal surface where titanium can be oxidized. As a result, they initiate localized corrosion more favorably. For the cosmotrope anions there exists a marked difference between the hydration state inside the confined passive film (where few water molecules may be entrapped) and

outside at the contact of the electrolyte solution where they can preserve their hydration state. As a consequence, the energetic dehydration contribution is quite repulsive and it is difficult to overcome, allowing the growth of a thicker oxide film, i.e. the start of the anodization.

For the halides, the potential values at which the breakdown of the passive film occurs are in accordance with those reported in the literature [47,52,59–61]. It has been already indicated that Br^- and I^- were found to be more efficient than Cl^- (requiring a greater potential) for the breakdown of the passive film on titanium. As expected, owing to the cosmotrope character of F^- (contrarily to the other tested halides), a much higher potential needs to be applied, say around 90 V/MSE, to observe an apparent breakdown before sparking [47]. The results indicate that the chaotrope anions ClO_4^- and NO_3^- are also able to cause the rupture of the passive film on titanium at moderate potentials. This strengthens the assumption that the aggressiveness of the ions is related to their ability to dehydrate. Moreover, as it has been reported in the literature, no breakdown of the passive film on titanium was observed with SO_4^{2-} [47,52] and with the two redox anions hexacyanoferrate III $\left[Fe(CN)_6\right]^{3-}$ and hexacyanoferrate II $\left[Fe(CN)_6\right]^{4-}$ [52,62]. This may be interpreted in light of the categorization of anions since the corresponding values of the viscosity B coefficient are, respectively, +0.208 L/mol for SO_4^{2-} (see Table 1), +0.138 L/mol for $\left[Fe(CN)_6\right]^{3-}$ [46] and +0.4 L/mol for $\left[Fe(CN)_6\right]^{4-}$ [46], so emphasizing the cosmotrope nature of these anions.

Interestingly, the categorization of anions is compatible with the observed inhibiting effects of divalent anions, such as SO_4^{2-}, HPO_4^{2-} and CrO_4^{2-}, on the breakdown of passivity of certain valve metals in the presence of halide anions such as Cl^-, Br^-, I^- [47,63] but also with other chaotrope anions like NO_3^- [63] or ClO_4^- [64]. It is generally accepted that the origin of this behavior results from a competition between the anions for adsorption sites at the passive film–solution interface [64,65]. The double negatively charged anions are more attracted and are thus preferentially adsorbed [15,65]. It may be assumed that due to their cosmotrope nature these anions do not penetrate the passive film and thus remain adsorbed to preserve their hydration state, so preventing the aggressive ions to access sufficiently to the surface of the passive film. As a result, the inhibition becomes more efficient when their concentration increases with respect to that of the chaotrope ions, as it was effectively shown [61,63–65].

3.3. The peculiar case of thiocyanate anions

A question remains: why, among the studied chaotrope anions, no breakdown of passivity is found to occur on titanium in the presence of thiocyanate anions?

Contrarily to the other chaotrope anions, thiocyanate does not form neutral salts or complexes with titanium IV species, such as: $TiCl_4$ (colorless liquid, mp: $-24.8\ ^\circ C$), $TiBr_4$ (brown crystals, mp: $39\ ^\circ C$), TiI_4 (red-brown crystals, mp: $150\ ^\circ C$), $Ti(NO_3)_4$ (crystalline salt, mp: $58\ ^\circ C$) which is a commercial compound used as a CVD precursor to obtain titanium dioxide films [66], $Ti(ClO_4)_4$ is a complex that sublimes at $T < 60\ ^\circ C$ and whose crystal structure has been solved by X-ray diffraction and IR/Raman studies [67,68]. In the literature, the formation and the stability constant of complexes of thiocyanate ions with many metallic cations have been reported [69]. In aqueous solutions, the existence of complexes engaging only one thiocyanate group with titanium IV species has been variously reported as $[Ti(OH)(NCS)]^{2+}$ or $[Ti(H_2O)(NCS)]^{3+}$ or $[TiO(NCS)]^+$ [70,71]. The corresponding stability constant β_1 (L/mol) was found to be in the range 2.3–3.2 at $25\ ^\circ C$ [69]. As an indication, the UV-spectrophotometric study of samples taken at different potentials during anodic polarization of a titanium plate is shown in Fig. 6. The increase of the maximum
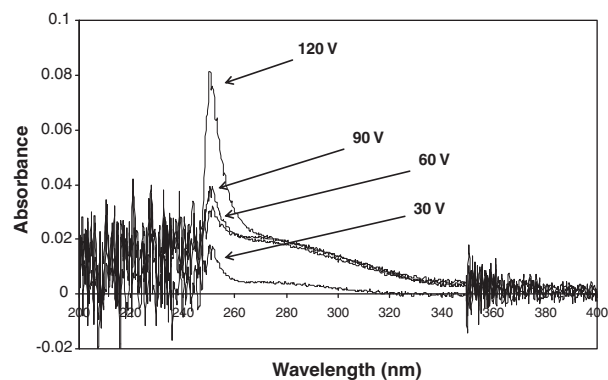
Fig. 6. Variation of the UV absorbance at different potentials during the anodic polarization of a titanium plate in the presence of the NaSCN solution.

absorbance at about 250 nm is ascribed to the presence of the resulting complexes between thiocyanate anions and titanium IV species; the NaSCN aqueous solution at 0.1 mol/L concentration was taken as the blank (reference cell) in the spectrophotometer.

Whatever their exact nature, this indicates that cationic complexes are involved between thiocyanate and titanium. After the SCN^- ions have been adsorbed at the passive film–solution interface it may be assumed that the penetration of these anions is significantly hindered due to their consumption through a 1:1 reaction with the titanium ions to form such complexes which, owing to their positive charge, tend to escape definitively from the anodic environment and are attracted towards the cathode. This suggests that the eroding process due to complex formation is probably not efficient enough to overcompensate the continuous repassivation of the passive film on titanium [30,53], so that the irreversible breakdown of passivity does not occur; thus the concomitant penetration of the passive film by dehydrated anions should appear as a requirement.

4. Conclusions

According to the reported results, the categorization of anions helps to rationalize the influence of ions nature in the breakdown of passivity of titanium. The aggressiveness of the anions is expected to depend for a part on their ability to dehydrate during the penetration of the passive film, provided, however, these ions are not hindered to access sufficiently to the surface of the passive film (strong competitive adsorption, release of cationic corrosion products).

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