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# Influence of the anion specificity on the electrochemical corrosion of anodized aluminum substrates

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## A B S T R A C T

The electrochemical corrosion of anodized aluminum substrates in the presence of various electrolyte solutions at 0.01 mol L<sup>-1</sup> concentration has been investigated. The comparative results were found to exhibit a correlation between the aggressiveness of the anions and their cosmotrope/chaotrope nature. The origin of the observed behavior was assumed to result from a variable resistance against dehydration during the pitting process.

### Keywords:

Electrochemical corrosion

Anodized aluminum

Hofmeister sequence

Chaotrope/cosmotrope anion

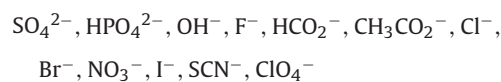
## 1. Introduction

Although the peculiar influence of ion nature has been reported for the first time at the end of the 19th century by Hofmeister, the topic of ion specificity has gained an increasingly interest from very recent years in colloidal and biochemical domains [1]. Indeed, at small separation distance, the interaction between charged bodies immersed in aqueous electrolyte solutions was found to be modulated according to the nature of the ion, even though the ion valence was the same; so contradicting the prevision of the cornerstone DLVO theory (Derjaguin, Landau, Verwey, Overbeek) where ions were considered only as point charges [2]. These ion specific effects play a significant role in numerous domains in which the interfacial behavior of ions is essential, such as (non exhaustive): stability and viscosity of particle dispersions [3,4], denaturation and aggregation of proteins [5], swelling of lipid bilayers [6], polymer conformation and adsorption to surfaces [7], sphere to rod transition of surfactant micelles [8], synthesis of mesoporous materials [9], surface tension of electrolyte solutions [10], inhibition of bubble coalescence [11], characteristics of seawater aerosols [12], behavior of formulations [13], efficiency of effluent purification processes [14].

One of the arguments that were invoked to interpret some of the observed results is ascribed to the cosmotrope/chaotrope nature of the ions which is related to their ability to highly/poorly

structure the water molecules in their vicinity. 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. These ionic species (exhibiting salting-out of neutral solutes) are referred as water-structure-making ions, say cosmotropes. Those presenting the opposite effect are water-structure-breaking ions (exhibiting salting-in), say chaotropes. They are usually large and generate weak electric fields, so possessing a loose hydration shell which can be easily removed. As such, for instance, when colloidal entities approach from one another during an aggregation process, the confined cosmotrope ions can generate higher repulsive dehydration forces than chaotrope ones and this may lead to significant differences in the macroscopic behavior of the system. Hydration effects are known to be more sensitive with the anions than with the cations since the anions can form an apparent hydrogen bond with the small H atom of the water molecules while the cations interact with the O atom of water molecules.

The Hofmeister lyotropic sequence divides therefore the anions and the cations into two broad classes. As often reported in the literature, the ranking for the anions is as follows [9]:



where ions on the left of Cl<sup>-</sup> are cosmotropes and ions on the right (Cl<sup>-</sup> comprised) are chaotropes.

In the field of electrochemical corrosion, numerous studies have been devoted to investigate the corrosive power exhibited by dif-

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ferent ionic species, either on native valve metal surfaces (Al, Ti, Ta, Nb, W) or on protective passive films build-up on these surfaces. In this sense the case of aluminum corrosion is highly representative [15–18].

Owing to its important characteristics (good electrical and thermal conductivity allied with a low density), aluminum is used in a lot of industrial applications such as aeronautic, electronics, architecture, packaging, containers. The resistance against corrosion of aluminum arises from the presence of a natural passive oxide film, usually considered as alumina ( $\text{Al}_2\text{O}_3$ ), with a thickness of a few nanometers, which is formed spontaneously when it is exposed to oxidizing media (air, water). This passive film can be rapidly dissolved in strong acidic or alkaline solutions. When the solution pH is between 4 and 9, this layer is stable but aggressive anions such as the halides, especially the chloride ions, can induce the breakdown of the protective film by a localized attack (pitting) which may result in catastrophic failure of the material.

Nevertheless, the corrosion resistance can be significantly increased by building a thicker oxide layer through anodizing processes where the aluminum sample is anodically polarized in an appropriate electrolyte which is often an inorganic acid. Depending on several factors, two types of anodic films can be produced: barrier-type or porous-type films [19–22]. The experimental conditions (pH, applied voltage, electrolyte type) are chosen so that the rate of oxide formation is higher than the rate of its dissolution. Almost all anodic films are usually composed with an inner oxide layer and an outer hydroxide layer whose thickness can be modulated according to experimental parameters. For these reasons, studies of the corrosion and the protection of aluminum and its alloys are of considerable interest for many years [23–31].

Electrochemical experiments are a rapid and convenient technique to evaluate the resistance properties of different surface treatments against the corrosiveness of aggressive media. It has been generally accepted that electrochemical corrosion is ascribed to the rupture and the penetration of the passive film by aggressive anionic species under the application of a high electric field. The migration of the anions in the oxide layer is expected to result from the interplay between their sizes and charges, and the local structuring of the oxide around them and the released  $\text{Al}^{3+}$  cations [32–34].

In this study, the electrochemical corrosion of two types of anodized aluminum samples, a porous-type and a barrier-type, has been investigated in the presence of electrolyte solutions at  $0.01 \text{ mol L}^{-1}$  concentration. The anions were chosen so as to correspond to a range of typical cosmotope and chaotrope ions, thus allowing some general characteristics to be drawn.

## 2. Experimental

All the salts used: sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), sodium nitrate ( $\text{NaNO}_3$ ), sodium thiocyanate (NaSCN), sodium perchlorate ( $\text{NaClO}_4$ ), sodium formate ( $\text{NaHCO}_2$ ), sodium acetate ( $\text{NaCH}_3\text{CO}_2$ ), sodium hydrogenophosphate ( $\text{Na}_2\text{HPO}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium chromate ( $\text{K}_2\text{CrO}_4$ ), were from Prolabo (France) or Sigma–Aldrich (France). Sulfuric acid  $\text{H}_2\text{SO}_4$  (98%, w/w), nitric acid  $\text{HNO}_3$  (52.5%, w/w) and boric acid  $\text{H}_3\text{BO}_3$  were provided by Prolabo (France). Deionized water was taken as a solvent to prepare the electrolyte solutions at  $0.01 \text{ mol L}^{-1}$  concentration for all the electrochemical experiments.

Small aluminum plates were cut from a commercial sheet (A-U4G, Aluminum alloy 2017 containing 4%, w/w, of Cu) to obtain a rectangular shape ( $2 \text{ cm} \times 3 \text{ cm} \times 0.2 \text{ cm}$ ).

The electrochemical experiments were performed at ambient temperature either with a potentiostat (Radiometer Analytical S.A. Copenhagen, Tacussel DEA 332, potential range 0–8 V) coupled with a digital converter (Radiometer Analytical, IMT 102) and controlled by a PC running the electrochemical software (Radiometer Analytical, VoltaMaster 2), or by using a DC power supply (Convergie Fontaine, potential range 0–400 V). The imposed current was checked to be constant with the use of an amperemeter (Metrix MX 55C). The used electrodes were maintained at fixed positions. All the experiments were repeated twice.

The aluminum plates were anodized according to two methods:

To obtain porous-type films, anodization was performed with a sulfuric acid solution. The aluminum plates (plates I) were first thoroughly polished with emery paper and then immersed in acetone. They were further rinsed with deionized water before soaking into an aqueous NaOH solution at  $1 \text{ mol L}^{-1}$  during 1 min. Then they were rinsed with deionized water before soaking into an aqueous  $\text{HNO}_3$  solution at  $0.83 \text{ mol L}^{-1}$  during 1 min. They were finally rinsed with deionized water and dried. Anodization experiments were carried-out at ambient temperature by immersion of these plates (2.5 cm depth) in an aqueous  $\text{H}_2\text{SO}_4$  solution at  $1.5 \text{ mol L}^{-1}$  where a current intensity of  $0.35 \text{ A}$  was applied during 30 min; a platinum plate was taken as a cathode.

To obtain barrier-type films, anodization was performed with a boric acid solution. The aluminum plates (plates II) were first degreased with ethanol before soaking 5 min into an aqueous  $\text{Na}_3\text{PO}_4 + \text{Na}_2\text{CO}_3$  ( $12.5$  and  $6.2 \text{ g L}^{-1}$ , respectively) solution at  $93^\circ\text{C}$ . Then, they were rinsed with deionized water before soaking into an aqueous  $\text{HNO}_3$  solution (50%, v/v) for 3 min at room temperature. Anodization experiments were carried-out at  $65^\circ\text{C}$  by immersion of these plates in an aqueous  $\text{H}_3\text{BO}_3$  solution at  $2.32 \text{ mol L}^{-1}$  where an electric tension of 50 V was applied during 10 min; a lead plate was taken as a cathode.

Linear voltammograms were performed in the range  $-1000$  to  $5000 \text{ mV}$  versus a mercury sulfate reference electrode (MSE) with a  $10 \text{ mV s}^{-1}$  sweep rate and under agitation at 400 rpm (magnetic stirrer) of the electrolyte solution.

To investigate the electrochemical corrosion of the anodized aluminum plates, two procedures were applied:

A first electrochemical set up was constituted with an anodized aluminum plate as the anode (working electrode), a flat platinum plate as the auxiliary electrode and a mercury sulfate reference electrode. The electrical current was recorded during 10 min under application of an imposed voltage of 8 V/MSE.

For the second electrochemical set up, an anodized aluminum plate was taken as the anode and a flat platinum plate as the cathode. A DC power supply was used to measure the required value of the cell tension to impose a  $0.1 \text{ A}$  current intensity during 10 min.

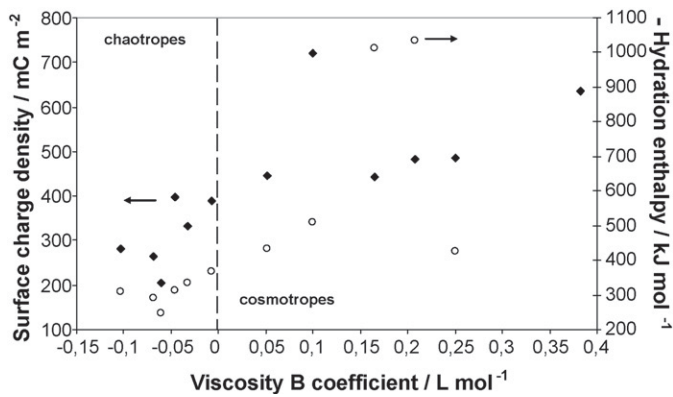
In both procedures, the anodized plates were immersed at 2.5 cm depth in 100 mL of aqueous electrolyte solutions at  $0.01 \text{ mol L}^{-1}$  concentration under agitation at 400 rpm (magnetic stirrer).

The pH and the conductivity of the electrolyte solutions were measured respectively with an electronic pH-meter (Hanna Instrument) and a Tacussel electrode (Tacussel Instrument).

A 3CCD digital video camera, Panasonic NV-GS 120 (Crystal Engine), was used to take photographs of the aluminum plates.

An Axiothech optical microscope (Zeiss Instrument) equipped with a camera (Evolution VF Monochrome, MediaCybernetics Canada) was used to observe the qualitative aspect of the corroded anodized plates. The images were analyzed with the software Image ProPlus 5.1.

Field Emission Gun Scanning Electron Microscope (FEG-SEM JEOL JSM 6700F) was used to analyze the microstructure of the anodic film obtained on plates I and II.



**Fig. 1.** Positioning of the surface charge density ( $\blacklozenge$ , scale on the left axis) and the hydration enthalpy ( $\circ$ , scale on the right axis) as a function of the viscosity  $B$  coefficient of the anions.

### 3. Results and discussion

#### 3.1. Classification of anions

As mentioned previously, anions can be classified according to the Hofmeister lyotropic sequence reflecting their ability to structure the water molecules in their vicinity. The cosmotrope or chaotrope nature of the ions can be conveniently distinguished according to the sign of the viscosity  $B$  coefficient appearing in the well-known Jones–Dole empirical relationship [35,36]:

$$\frac{\eta}{\eta_w} = 1 + A \times \sqrt{c} + B \times c \quad (1)$$

where  $\eta$  is the viscosity of aqueous salt solution at molar concentration  $c$  and  $\eta_w$  is the viscosity of pure water. The coefficients  $A$  and  $B$  were fitted to the experimental data.

The coefficient  $A$ , which was found to be positive for all salts investigated, corresponds to an electrostatic term originating from the interaction between the ions; it is about 1 for moderate salt concentrations. The value of  $B$ , which was found to be either positive or negative, relates how the viscosity changes with the electrolyte concentration.  $B$  is a direct measure of the strength of ion–water interactions normalized to the strength of the water–water interactions in bulk solution. With structure-maker ions, the hydration shell around the ions is thick and it is held strongly, so that the resistance to flow of these aqueous electrolyte solutions is higher than that of pure water. Positive values of  $B$  are thus associated to cosmotrope ions whereas values less than zero correspond to chaotrope ions for which the immediately adjacent water molecules are far away and not oriented.

According to literature sources [36–39], the ionic radius ( $r$ ), the hydrated radius (sum of the ionic radius plus the width of the hydration shell), the surface charge density (corresponding to  $ze/4\pi r^2$  where  $z$  is the ion valence and  $e = 1.6 \times 10^{-19}$  C is the elementary charge), the hydration enthalpy and the Jones–Dole viscosity  $B$  coefficient at 25 °C of the studied anions are listed in Table 1. To get further insight in the demarcation between strong and weak hydration, the positioning of the surface charge density and the hydration enthalpy as a function of  $B$  values is shown in Fig. 1.

As expected, anions with a surface charge density lower than 400 mC m<sup>-2</sup> and with a hydration enthalpy greater (less exothermic) than -400 kJ mol<sup>-1</sup>, i.e. Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, all exhibit negative  $B$  values, so corresponding to chaotrope anions. On the contrary, the cosmotrope anions with higher surface charge densities and more exothermic hydration enthalpies, i.e. F<sup>-</sup>, HCO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, possess positive  $B$

values. Although the general tendency shows that the  $B$  values increase as the surface charge density is higher and the hydration enthalpy is more exothermic, Fig. 1 indicates that there is not a direct proportionality between these parameters. Whereas the knowledge of the surface charge density can help to anticipate the presumed affinity of the ion to the water molecules, the hydration enthalpy (corresponding thermodynamically to the transfer of the ion from the gas state to the aqueous state) give information about the extent of this interaction but in static conditions. The  $B$  value represents a physical characteristic that provides information on the strength of attachment of the surrounding water molecules to the ion since it is determined from dynamic conditions (viscosity measurements) when the ion moves in solution with its tightly attached hydration shell. For this reason, the  $B$  value will be preferred in the following as a better representative parameter of the cosmotrope/chaotrope nature of the ions; moreover the difference in sign of the  $B$  values makes the distinction evident.

It has to be noted that according to the previously described anion sequence [9], the case of the cosmotrope OH<sup>-</sup> ion was not investigated until now. This comes from pH restrictions to avoid dissolution of the alumina passive layer during the following corrosion experiments. Nevertheless, it was replaced by the study of the CrO<sub>4</sub><sup>2-</sup> ion which represents a practical interest since it is often used in anodization treatments.

#### 3.2. Anodized aluminum substrates and SEM characterization

According to the anodization electrolyte, especially its pH value, the anodic films can present, or not, a porosity. Barrier-type films can be formed in (almost) neutral electrolytes such as boric acid, ammonium borate, tartrate, and ammonium tetraborate in ethylene glycol. On the contrary, porous-type films are obtained with strong acidic or alkaline electrolytes including usually sulfuric, phosphoric, chromic and oxalic acids. The most hydrophilic anodic aluminum oxide films contain no more than 6% (w/w) of water. The thickness of the anodic films is mainly determined by the applied voltage; however the nature of electrolytes and the temperature may have an influence (the anodizing ratio is defined as the oxide thickness formed per volt). Moreover the thickness of the anodic film is also time-dependent, in agreement with the Faraday's law. Usually, the barrier-type anodic films are thin (<1 μm), while the thickness obtained in porous anodizing conditions varies from 1 to 300 μm [40].

The barrier-type films consist of an inner oxide (adjacent to oxide/metal interface) of high purity alumina and an outer oxide layer (adjacent to the electrolyte/oxide interface) which may contain incorporated anions from the electrolyte. The growth of the oxide occurs mainly at the metal/oxide interface due to inward migration of O<sup>2-</sup> ions across the barrier layer. Simultaneously, Al<sup>3+</sup> ions migrate outward to the electrolyte [41,42].

The microstructure of the porous anodic films is made up of a relative thin barrier layer at the interface with the metal and an outer porous layer with ideally cylindrical pores [43]. The thickness of the barrier layer and the diameter of the pores correlate with the anodizing voltage, with typical ratios of the order 1 nm V<sup>-1</sup>, and they depend upon parameters such as current density and composition of the electrolyte [44,45]. On the other hand, the porous layer thickens in proportion to the charge passed during anodizing at a particular current density. However, despite plenty of previous studies, the pores growth mechanism is still open to discussion; the most used model being based on a thermally-assisted, field-accelerated dissolution of anodic alumina at the base of each pore [41,42].

As described in Section 2, aluminum plates were anodized to prepare a porous-type (plate I) and a barrier-type (plate II) anodic

**Table 1**

Values of the ionic radius, the hydrated radius, the surface charge density, the hydration enthalpy and the viscosity *B* coefficient at 25 °C of the studied anions.

Anion	Ionic radius <sup>a</sup> (nm)	Hydrated radius <sup>a</sup> (nm)	Surface charge density (mC m <sup>-2</sup> )	Hydration enthalpy <sup>b</sup> (kJ mol <sup>-1</sup> )	Viscosity <i>B</i> coefficient at 25 °C (L mol <sup>-1</sup> )
F <sup>-</sup>	0.133	0.212	720.16	-510	+0.1 <sup>c</sup>
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	0.162	0.217	485.40	-425	+0.25 <sup>c</sup>
HCO <sub>2</sub> <sup>-</sup>	0.169	0.219	446.02	-432	+0.052 <sup>c</sup>
NO <sub>3</sub> <sup>-</sup>	0.179	0.223	397.58	-312	-0.046 <sup>c</sup>
Cl <sup>-</sup>	0.181	0.224	388.84	-367	-0.007 <sup>c</sup>
Br <sup>-</sup>	0.196	0.231	331.60	-336	-0.032 <sup>c</sup>
HPO <sub>4</sub> <sup>2-</sup>	0.200	0.260	636.94	Unknown	+0.382 <sup>b</sup>
SCN <sup>-</sup>	0.213	0.242	280.78	-311	-0.103 <sup>c</sup>
I <sup>-</sup>	0.220	0.246	263.20	-291	-0.068 <sup>c</sup>
SO <sub>4</sub> <sup>2-</sup>	0.230	0.273	481.62	-1035	+0.208 <sup>c</sup>
CrO <sub>4</sub> <sup>2-</sup>	0.240	0.279	442.32	-1012	+0.165 <sup>b</sup>
ClO <sub>4</sub> <sup>-</sup>	0.250	0.261	203.82	-246	-0.061 <sup>c</sup>

<sup>a</sup> From ref. [37].

<sup>b</sup> From ref. [38].

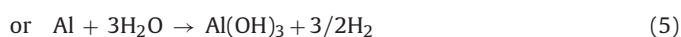
<sup>c</sup> From ref. [36].

film. The FEG-SEM cross-section view of plate I in Fig. 2A shows that the thickness is about 4.5 μm in average and the anodic film is sponge-like with a quite tortuous porosity, see Fig. 2B and C corresponding respectively to the plan view and the enlargement of the cross-section view. In the case of plate II, the thickness lies between 100 and 150 nm, see Fig. 3A, and the anodic film is compact where no porosity is observed, see the plan view in Fig. 3B.

### 3.3. First trends about the electrochemical corrosion of anodized samples

The electrochemical mechanisms of pitting corrosion are complex and remain not fully understood in spite of numerous studies on the subject [18]. Three main mechanisms have been proposed to explain the processes leading to passivity breakdown. These are the penetration mechanism [46], the electrostriction mechanism [47] and the adsorption mechanism [48]. However it was recognized that according to varying experimental conditions and environmental specificities each of them could be predominant [49]. Nevertheless it is generally considered that when the electric field reaches a critical value corresponding to the pitting potential,  $E_{pit}$ , aggressive ions can rupture and penetrate the passive layer at its defects by the digging of a cavity, say a pit, up to the base metal surface where aluminum is oxidized [19,26]. The increasing migration of anions towards the bottom of the pit is enhanced owing to the accumulation of electrogenerated Al<sup>3+</sup> cations. Among the anions, chlorides are assumed to have a high propensity to be incorporated since they are small and thus quite mobile. As a result, soluble aluminum salts may be formed and some of the Al<sup>3+</sup> ions that are locally concentrated at the bottom will diffuse towards the opening of the pit into the water where they will form Al(OH)<sub>3</sub> precipitates.

The corrosion of aluminum in aqueous media results from the sum of two electrochemical reactions, i.e. aluminum oxidation at the anode and proton reduction at the cathode:



To appreciate the corrosive power of the anions, linear voltamograms were performed on plates I that were placed in contact

with some aqueous sodium salt solutions at 0.01 mol L<sup>-1</sup> concentration. The results are presented in Fig. 4. Within the investigated potential range, -1000 to 5000 mV/MSE, no signal was detected in the presence of anions such as CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>. The pitting potential, i.e. the potential for which an anodic current is measured and that increases further with the applied potential, corresponds approximately to 80, 110, 90, 980, 3100 and 3800 mV/MSE for Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SCN<sup>-</sup>, respectively, which all are chaotrope ions.

These preliminary experiments indicate that the anodizing treatment has conferred a sufficient protective alumina layer on the surface to inhibit the action of the least aggressive ions. Moreover it suggests that the ability for corrosion might depend on the nature of the ions and that apparently the copper content (4%, w/w), which is known to enhance pitting, has no influence on the presumed categorization of the studied anions.

### 3.4. Comparative electrochemical corrosion at constant working potential

The electrochemical corrosion of the anodic film on plates I in the presence of the electrolyte solutions was studied by recording the variation of the electrical current when an imposed working electrode potential of 8 V/MSE was applied during 10 min. The pH and the conductivity values of the salt solutions are reported in Table 2. As the pH is comprised between 5.7 and 8.6, the alumina passive layer is expected to remain stable against dissolution. The results were complemented by the qualitative aspect of the plates.

**Table 2**

Values of the pH and the conductivity at 25 °C of the studied aqueous electrolyte solutions at 0.01 mol L<sup>-1</sup> concentration.

Electrolyte solution at 0.01 mol L <sup>-1</sup>	pH	Conductivity at 25 °C (mS cm <sup>-1</sup> )
NaF	8.1	0.92
NaCH <sub>3</sub> CO <sub>2</sub>	6.9	0.81
NaHCO <sub>2</sub>	6.4	0.97
NaNO <sub>3</sub>	6.8	1.06
NaCl	6.6	1.02
NaBr	6.0	1.19
Na <sub>2</sub> HPO <sub>4</sub>	8.6	1.40
NaSCN	6.6	0.90
NaI	5.8	1.07
Na <sub>2</sub> SO <sub>4</sub>	6.4	1.87
K <sub>2</sub> CrO <sub>4</sub>	8.3	2.22
NaClO <sub>4</sub>	6.0	1.08

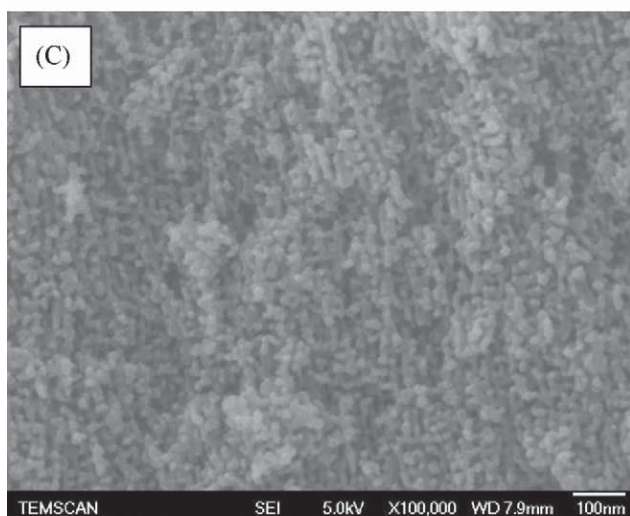
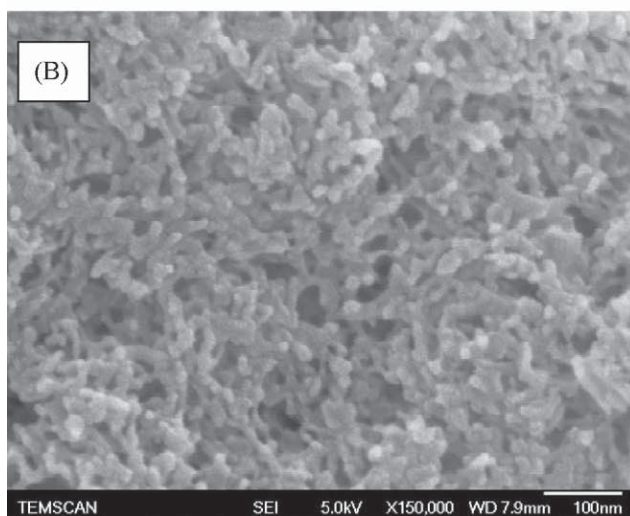
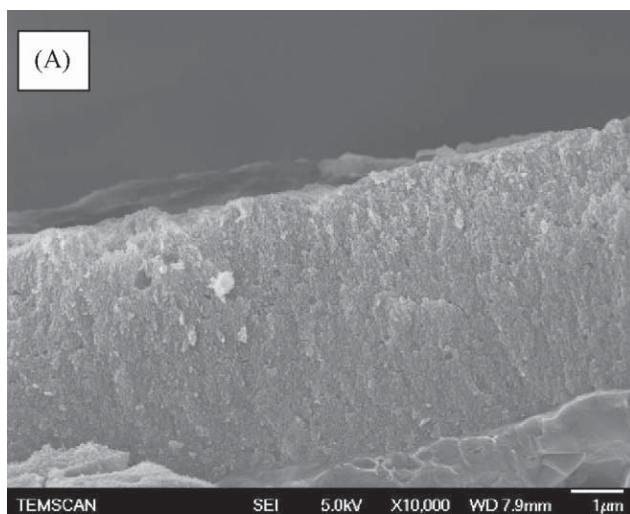


Fig. 2. FEG-SEM micrographs of plate I (anodization with sulfuric acid): cross-section view (A), plan view (B), enlargement of cross-section view (C).

In the case of the investigated chaotrope anions, as shown in Fig. 5A, the curves are characterized by a short latency period of about 20 s (see Fig. 5B) corresponding to a leakage current during which poor gas evolution is observed at the electrodes. Then, the current intensity increases more or less sharply according to the studied anion. The sudden increase of the anodic current indicates

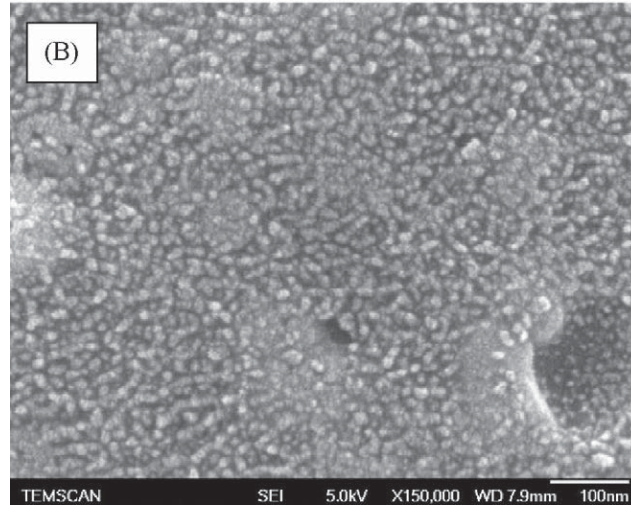
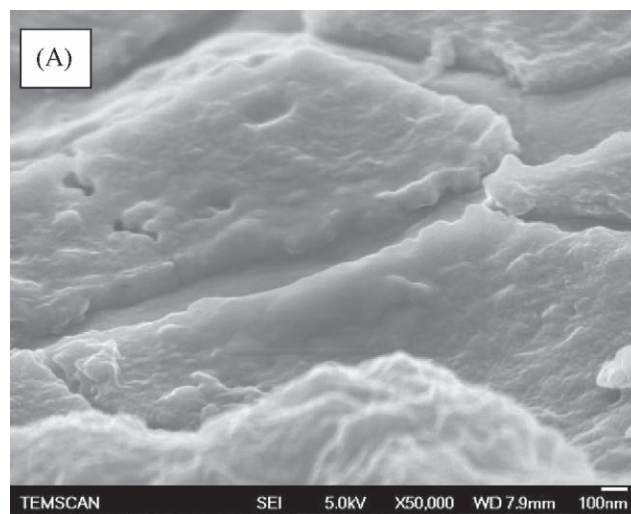


Fig. 3. FEG-SEM micrographs of plate II (anodization with boric acid): cross-section view (A), plan view (B).

the breakdown of passivity and the initiation of a pitting process. During this step, gas bubbling is observed and the characteristic aluminum hydroxide precipitate  $\text{Al}(\text{OH})_3$  forms in solution, so confirming that corrosion is effective. For longer times the current intensity remains definitively constant.

Corrosion pits are found to be present for all the corresponding anodized plates; however the number and the size of the pits are somewhat different. In the case of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  anions,

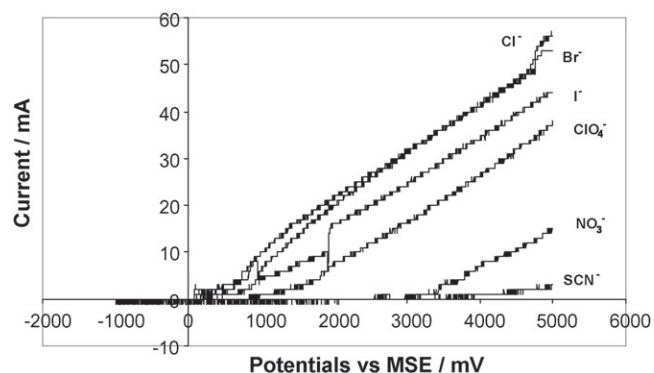
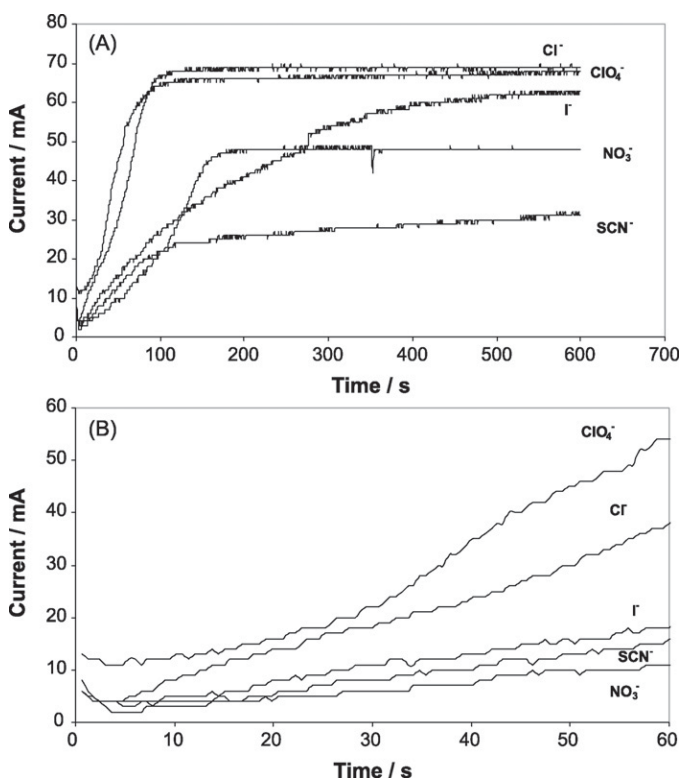


Fig. 4. Linear voltammograms obtained on plates I in the presence of some chaotrope ions.



**Fig. 5.** Variation of the current intensity as a function of time during application of a 8 V/MSE working potential on plates I in the presence of chaotrope anions at 0.01 mol L<sup>-1</sup> concentration, in the whole time interval (A) and in the prime instants (B).

a great number of small pits covering the surface are observed, see the representative photographs in Fig. 6; whereas for I<sup>-</sup> and SCN<sup>-</sup> ions fewer pits are present but they are larger in size. Closer inspection reveals that the aspect of the pit is not the same, see the corresponding micrographs (magnification  $\times 50$ ) at the right side in Fig. 6. For Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, the crater at the centre is surrounded by a dense deposit (it is of reduced width with NO<sub>3</sub><sup>-</sup> ion) coming from the digging of the alumina layer. For I<sup>-</sup>, an extensive and more open deposit is present at the periphery of the central crater; whereas in the case of SCN<sup>-</sup> a relatively small crater is embedded in a compact deposit.

In the case of the cosmotope ions (HCO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>), the behavior is radically different, see Fig. 7. All the curves are nearly superimposed showing that the current intensity drops steeply in the prime instants before it remains equal to zero until the end. This is in agreement with the absence of significant gas evolution at the electrodes during run time and without the presence of any pit on the surface. As it can be seen on the representative photograph for SO<sub>4</sub><sup>2-</sup> (see Fig. 8), the anodized plate is unaltered and it looks like the plate entitled AA corresponding to the aluminum plate after the anodization treatment. Although no pitting occurred in the case of F<sup>-</sup>, the presence of a precipitate was observed on the surface when the anodized plate was removed from the solution (see Fig. 8). This may be ascribed to the formation of sodium cryolite, Na<sub>3</sub>AlF<sub>6</sub>, which is known to have a very poor solubility in water (2 mmol L<sup>-1</sup> at 20 °C) [50,51].

Generally, the corrosiveness of the ions is assumed to depend on their size: the ions of smaller size with a greater mobility being the most aggressive. This is verified in some cases for ions of the same chemical nature such as the halide sequence Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, although the case of F<sup>-</sup> remains unclear [15,29,34]. However, according to the obtained results and when comparing in Table 1 some ions

such as HCO<sub>2</sub><sup>-</sup> or HPO<sub>4</sub><sup>2-</sup> with bigger anions like I<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>, this hypothesis does not hold. Although ion bare sizes are usually considered for comparison, it is often neglected that the ions come to the oxide-solution interface with their surrounding hydration shell. The results rather indicate that the corrosiveness of the anions is intimately related to their chaotrope nature, say their proneness to loose their hydration shell. This emphasizes an important nuance at the phenomenological level. The criterion represented by the negative sign of the viscosity *B* coefficient seems more pertinent than that based on the comparison of ionic radius for which some confusing results can be found in the literature. Indeed, care must be taken in the definition of the ionic size and its accurate estimation from diverse techniques (electron diffraction, lattice energy calculation, thermochemical measurement), notably in the case of polyatomic anions due to their asymmetrical nature [38,52]. As an example, the ionic size of formate and acetate ions corresponds respectively to 2.04 and 2.32 Å when estimated from the fitting of thermodynamic data [38], which is in the reverse order of that given in Table 1 [37,39].

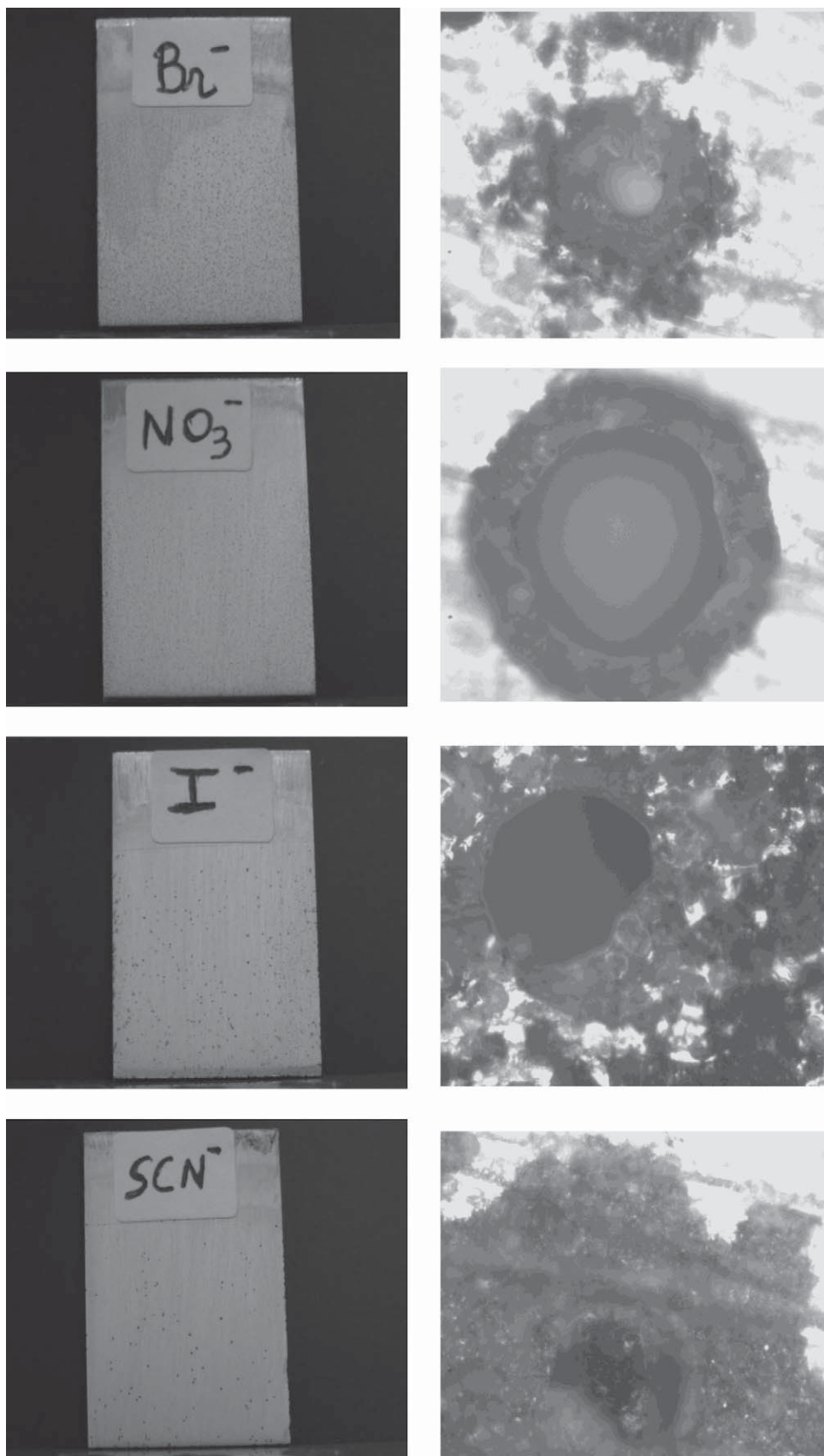
### 3.5. Comparative electrochemical corrosion at fixed current intensity

To confirm the previous trends with the same kind of anodized plates (plates I) and to intent to force the cosmotope ions to initiate pitting, a DC power supply was used to measure the required cell tension to impose a constant current intensity of 0.1 A (i.e. greater than the highest current that was recorded in the previous experiment) passing through the system in the presence of the electrolyte solutions. The measured values were found to stabilize after 2 min, except in the case of HPO<sub>4</sub><sup>2-</sup> ion. The obtained results, reported in Fig. 9, reflect the pronounced influence of the ion nature.

In the case of the chaotrope anions (corresponding to negative *B* values), the cell tension is approximately the same between 21 and 24 V. Within such imposed conditions, a lot of small corrosion pits are now observed in the case of I<sup>-</sup> and SCN<sup>-</sup>, see Fig. 10.

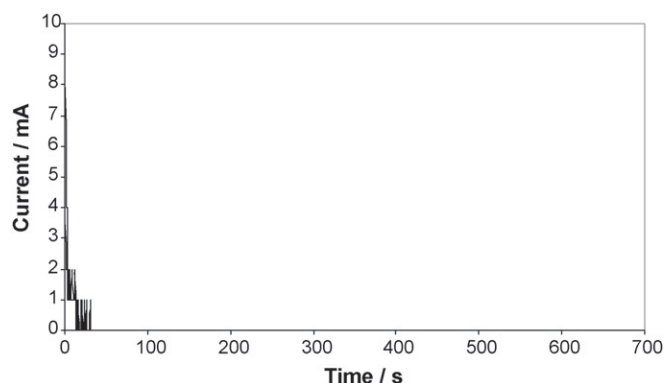
In the case of the cosmotope ions, the magnitude of the cell tension is higher. The minimum value corresponds to about 60 V; this confirms that much severe conditions need to be applied for an effective corrosion with these anions. In the case of HPO<sub>4</sub><sup>2-</sup> ion, which possesses the highest *B* value in Table 1, no definite constant potential could be obtained since it increased continuously up the above limit, say 400 V. The qualitative aspect of the plates is instructive since the anodized surfaces have been now subjected to corrosion, see the corresponding photographs in Fig. 10. This reveals that upon application of a greater electrical tension the cosmotope ions have been forced to attack the alumina layer, as an indication the formation of aluminum hydroxide precipitate was effectively noted in solution. For CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, as with HCO<sub>2</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> (not shown), some small corrosion pits are present; for SO<sub>4</sub><sup>2-</sup>, there are fewer pits but much larger; for CrO<sub>4</sub><sup>2-</sup>, corrosion craters are observed; in the case of F<sup>-</sup>, corrosion pits of medium size are surrounded by dendritic filaments that may be attributed to incipient cryolite precipitates. These observations are in accordance with the expected behavior since the electrochemical corrosiveness of a surface is enhanced as the difference between the pitting potential and the applied anodic potential increases.

Similar experiments were performed by using aluminum plates that were anodized in boric acid bath (plates II) in order to obtain a compact barrier-type alumina layer, see Fig. 11. Whatever the chaotrope ion considered, the required cell tension is about the same around 22 V. It is at least 46 V for the cosmotope anions and the general tendency indicates that the required cell tension increases with the *B* value, although the obtained value for F<sup>-</sup> has



**Fig. 6.** Photographs (on the left side) and micrographs (on the right side, magnification  $\times 50$ ) of plates I after corrosion experiments in the presence of some electrolyte solutions at  $0.01 \text{ mol L}^{-1}$  concentration.



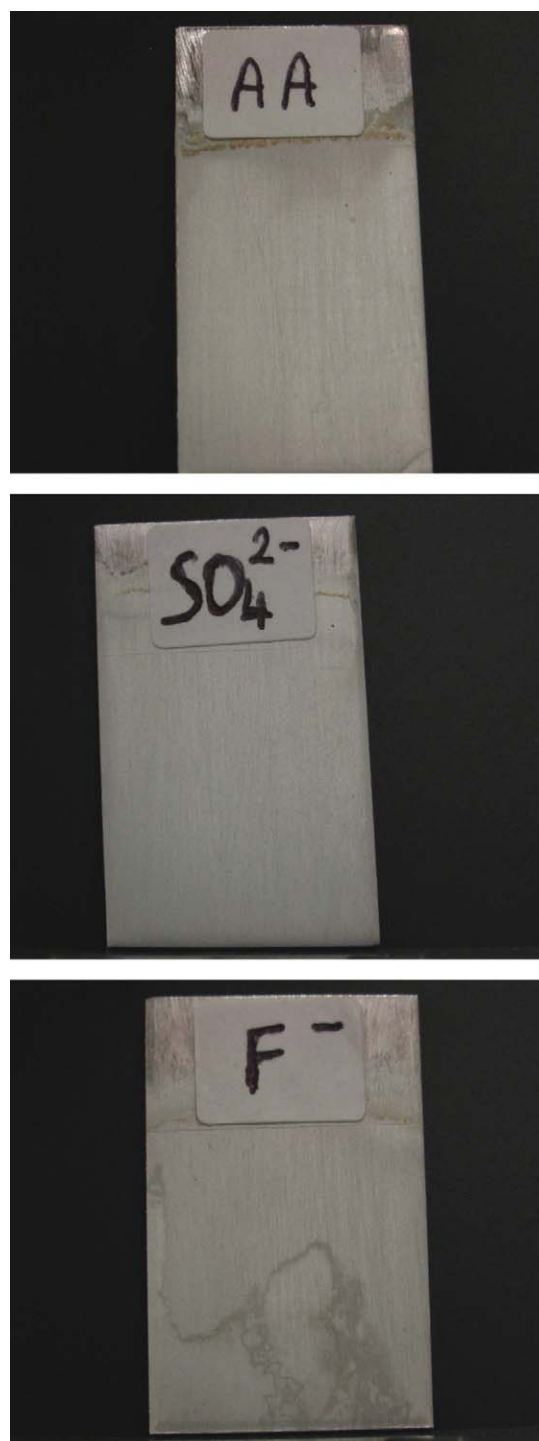


**Fig. 7.** Variation of the current intensity as a function of time during application of a 8 V/MSE working potential on plates I in the presence of cosmotope anions at 0.01 mol L<sup>-1</sup> concentration.

been confirmed to be repeatedly lower than that for HCO<sub>2</sub><sup>-</sup>. These results reflect that the conditions become harder for the corrosion to be effective as the anion is more cosmotope. The presence of a thick and cohesive hydration shell around the ion implies that greater electrical energy has to be supplied to allow the pitting process.

These complementary results give evidence of a distinct response whatever the type of anodic film. This strengthens the assumption that the specific interaction of the anions with the water molecules is probably implicated during the corrosion process. When an electric field is generated between the electrodes, it may be assumed that there is for the anions a competition between two concomitant effects. Once the electrodes become polarized, the anions are attracted towards the anode where the oxidation of aluminum is expected to occur, and consequently the anions can adsorb onto the alumina layer. It has to be indicated that as the solution pH values are lower than the isoelectric point of alumina, which is equal typically to 9–9.5 [53], the anions are naturally attracted at the positively charged alumina surface. However the eventual penetration of the insulate oxide layer is balanced by an energetic dehydration contribution since the anions have to migrate across the confined alumina barrier layer where very few constitutive water molecules are entrapped [54,55]. As a consequence, there exists for the anions a marked difference between the hydration state inside the passive layer and outside at the contact of the electrolyte solution. In the case of the cosmotope anions, this energetic dehydration contribution may be quite repulsive. In such conditions and as long as the magnitude of the attractive electric field is not sufficiently high to compensate their dehydration (at least partially), the cosmotope ions remain adsorbed so as to preserve their hydration state and the pitting process is precluded. On the contrary, the chaotrope anions exhibit a much weaker resistance to dehydration, so that they can favorably initiate pitting through the passive layer. In this sense, this may explain the nearly identical results (cell tension values) observed whatever the chaotrope anion.

These considerations allow to interpret some of the literature results where anions such as SO<sub>4</sub><sup>2-</sup> were found to remain adsorbed while others like NO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> were observed to be incorporated into the oxide film and initiated pitting [25,26,30,56]. They contribute also to confirm that Cl<sup>-</sup> ions are the most aggressive anions since these are the smallest among the chaotropes anions which are prone to loose their hydration shell. In the same way, it may be expected that during corrosion the release of Al<sup>3+</sup> ions towards the electrolyte solution is highly promoted since as a quite cosmotope cation ( $r = 0.5 \text{ \AA}$ ;  $B = +0.67 \text{ L mol}^{-1}$  [38]) much better conditions are encountered for its hydration. From a mechanistic point of view,



**Fig. 8.** Photographs of aluminum plates after the anodization treatment (AA) and after corrosion experiments in the presence of some electrolyte solutions at 0.01 mol L<sup>-1</sup> concentration.

the cosmotope nature of sulfate, chromate or phosphate ions provides a justification why the corresponding inorganic acids are preferentially used during anodization treatments for porous-type films. These anions can be entrapped in, or adsorbed on, the outer porous layer of the anodic film, but the alumina barrier layer which develops on the base aluminum surface is not subjected to pitting corrosion and remains thus preserved when moderate voltage is applied during anodization.

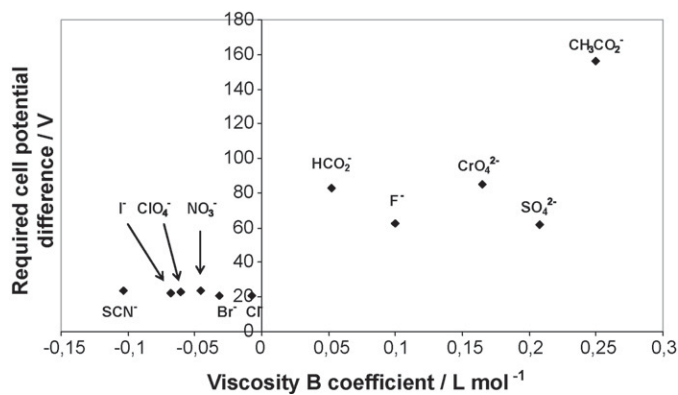


Fig. 9. Variation of the required cell potential difference to obtain a 0.1 A current intensity as a function of the viscosity *B* coefficient in the case of plates I.

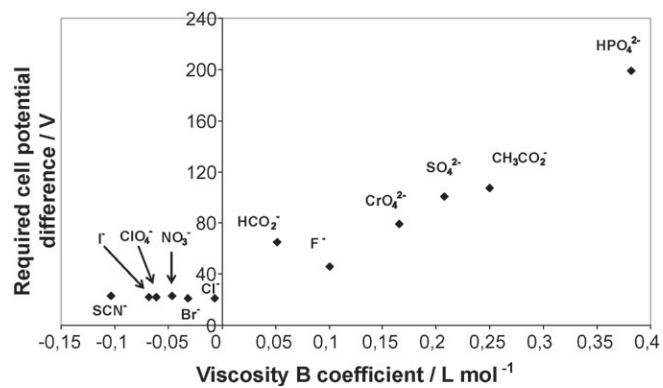


Fig. 11. Variation of the required cell potential difference to obtain a 0.1 A current intensity as a function of the viscosity *B* coefficient in the case of plates II.

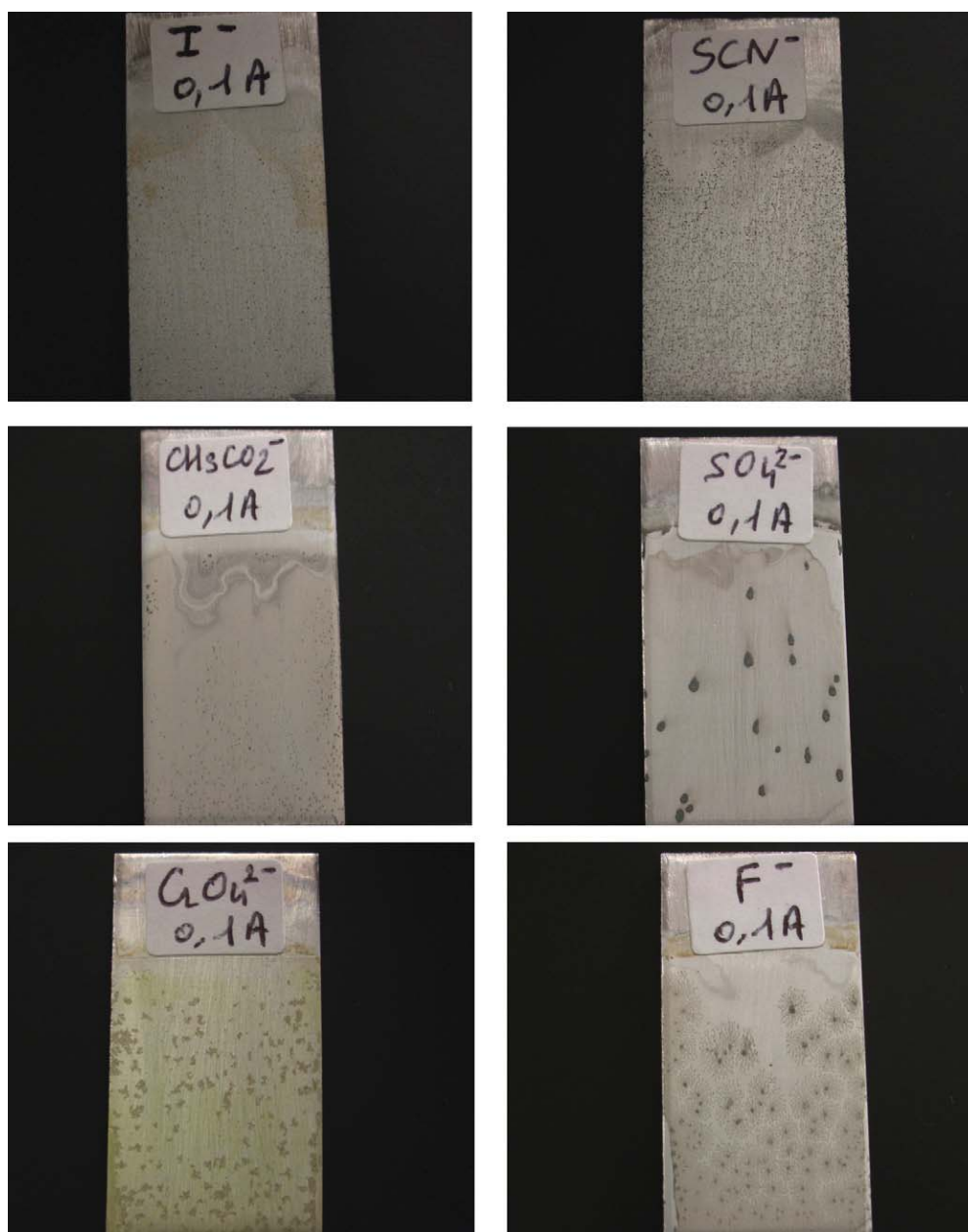


Fig. 10. Photographs of plates I after application of the required cell tension to obtain a 0.1 A current intensity in the presence of some electrolytes.

## 4. Conclusions

The obtained results shed more light on the electrochemical corrosion process of anodized aluminum substrates. The variable resistance of the anions against dehydration when penetrating the passive oxide film upon application of the electric field is expected to contribute to some extent in the observed ion corrosiveness. The pronounced discrepancy between the cosmotrope/chaotrope character of the investigated ions advocates in this sense.

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