



Implications of the kosmotrope/chaotrope nature of the anions on the breakdown of passivity of iron by halides



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ABSTRACT

The comparative aggressiveness of NaF and NaCl solutions on the breakdown of passivity of iron has been investigated once the passivating borate buffer solution has been removed. The results highlight the inhibitive action of borate anions towards the less aggressive kosmotrope fluorides. Without borates, the kinetics of attack by fluorides is slower as the prepassivation is longer, and it is considerably retarded when compared to the case with the chaotrope chlorides. The high positive viscosity *B* coefficient value of borate anion argues in favor of its use as an inhibitor or as an efficient electrolyte for anodization baths.

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1. Introduction

The breakdown of passivity of iron has been well documented in the literature [1–26], notably in the presence of halide anions: F^- , Cl^- , Br^- , I^- . Among them, the behavior with fluorides was shown to be different from the others. Whatever the pH, the breakdown of passivity occurs through a pitting corrosion process, i.e. a localized attack, with chlorides, bromides and iodides. In the case of fluorides, a general corrosion process through a uniform dissolution of the film is effective in acidic conditions whereas a pitting corrosion process occurs for pH values greater than 5 [7]. This distinction in the corrosion mechanism was ascribed to the propensity of HF molecules to form in acidic media more stable complexes with surface iron cations, thus leading to a uniform thinning of the passive oxide film on the whole surface [25]. The thinning of the oxide layer was reported to be less pronounced in weakly acid and basic media since the formation and transfer of soluble fluoride complexes was reduced, so that a localized attack was occurring [11,25].

The ability of the halides to cause the breakdown of passivity of iron is classically investigated through chronoamperometric measurements, where a constant electrical potential is applied, and by examining the aspect of the samples together with the results inferred from surface analytical techniques. However, it has to be noted that in these previous studies the halides were either pres-

ent from the beginning in the passivating or buffer solution, or added into the used passivating solution, through a small volume of concentrated solution or as a solid content, once the passive film has been formed [1–20]. Within these conditions, it may be envisaged that the aggressiveness of the halides towards the passive film could be hampered and even altered by the anions coming from the buffer or passivating solution.

In the present work, the comparative aggressiveness of fluorides and chlorides at 0.1 M concentration on the breakdown of passivity of iron has been investigated once the passivating borate buffer solution has been removed. The results were compared with the case where these halide anions were introduced directly into the passivating solution.

2. Material and methods

The chemical compounds: sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), boric acid (H_3BO_3), were analytical grade products manufactured by Sigma–Aldrich (France). Deionized water was taken as a solvent for the preparation of the electrolyte solutions. The pH of the solutions was measured with an electronic pH-meter (Eutech Instruments). NaCl solution at 0.1 M concentration with a pH 10 was prepared by adding some droplets of a sodium hydroxide (NaOH) solution at 0.1 M concentration.

Small iron plates were cut from a commercial Fe foil (99.99%, Goodfellow, UK) with a thickness of 0.25 mm to obtain rectangular shape (1.5 cm × 0.5 cm). Before use, the plates were mechanically polished with 1200 grit SiC. Then they were washed in acetone and rinsed with deionized water.

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The electrochemical experiments were performed 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 (VoltaMaster 2). The electrochemical set up was constituted with an iron plate as the working electrode and a large platinum plate as the auxiliary electrode. The iron plates were immersed at 1 cm depth in 50 mL of the studied solution. A mercurous sulfate electrode (MSE), Hg/HgSO₄/K₂SO₄ 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 iron plates were cathodically polarized at –1.5 V/MSE during 4 min to remove the air-formed oxide. Polarization curves were performed in the range –1.5 to +1 V/MSE with a 5 mV/s sweep rate under agitation at 200 rpm (magnetic stirrer) of the studied solution. The same device was used for chronoamperometric experiments where the current density was recorded as a function of time at an imposed electrical potential.

Iron plates were anodized at 0.4 V/MSE in the presence of a pH 8.4 borate buffer solution, resulting from an equimolar mixture of 0.075 M Na₂B₄O₇·10H₂O and 0.30 M H₃BO₃ [15]. Before passivation, nitrogen was bubbled into the buffer solution during 20 min. In a typical experiment, anodization was programmed by the electrochemical software for a long duration. At the required time (3600 s, 1200 s, 400 s), without interrupting the programme, the borate buffer solution was removed from the contact with the anodized plate by lowering the height adjustable stage where the beaker containing the borate buffer solution was placed, then the programme was stopped. The iron plates were thoroughly rinsed with water before they were immersed in the aggressive halide solutions for the chronoamperometric measurements.

The kinematic viscosity of electrolyte solutions was determined at 25 °C with an Ubbelohde capillary viscosimeter (Schott), equipped with an automatic detection of the time of flowing. The density of the corresponding solutions was measured at 25 °C with an automatic densimeter (DMA 35n, Anton Paar). The stock solution is an aqueous solution of Na₂B₄O₇·10H₂O at 0.1 M concentration from which diluted solutions were prepared. Before the measurements all the solutions were filtered at 0.2 µm.

3. Results and discussion

3.1. The kosmotrope nature of fluoride

It is worth noting that among the halides, fluoride possesses the highest surface charge density σ due to the smaller size of the ionic radius r [28], see Table 1. As a result, when it is associated with cationic species presenting also a high surface charge density strong electrostatic attraction can develop. This is why HF is a weak acid, i.e. with a positive pK value (see Table 1), whereas the other halides give strong acids that fully dissociate in aqueous solution, i.e. with

Table 1
Ionic radius (r), surface charge density (σ), pK of the acid, hydration enthalpy (ΔH_{hyd}) and viscosity B coefficient value of the halides.

Anion	r (nm) ^a	σ (mC/m ²)	pK ^b	ΔH_{hyd} (kJ/mol) ^c	B (L/mol) ^d
F [–]	0.133	720.2	3.2	–510	0.127
Cl [–]	0.181	388.8	–7	–367	–0.005
Br [–]	0.196	331.6	–9	–336	–0.033
I [–]	0.220	263.2	–10	–291	–0.073

^a From Ref. [28].

^b From Ref. [29].

^c From Ref. [30].

^d From Ref. [32].

large negative pK values [29], see Table 1. This contributes to explain the previously mentioned difference in the corrosion mechanism of iron between fluoride and the other halides in acidic conditions since HF is effectively the sole uncharged molecular entity able to form stable complexes with iron cations.

In contrast, when fluoride is associated with cations of much lower surface charge density, as in the case of alkaline metals, the electrostatic attraction is weaker. The formation of free ion pairs is therefore enhanced in aqueous solution and this allows fluoride anions to interact favorably with the surrounding water molecules to create a thick and structured hydration layer, contrarily to the other halides. This property reflecting the affinity for water molecules, which is in close relation with the surface charge density, may be appreciated by the comparison of the exothermic values of the hydration enthalpy (ΔH_{hyd}) of the halides [30], where it is more exothermic in the case of fluoride, see Table 1. This distinction between these anions can be conveniently made according to the sign of the viscosity B coefficient value of the Jones–Dole relationship [31], where $B > 0$ for the kosmotrope fluoride whereas $B < 0$ for the other chaotrope halide anions [32], see Table 1.

3.2. Anodic polarization of pure iron in weakly acid and basic conditions

As pH of NaF and NaCl solutions at 0.1 M concentration is quite different, i.e. pH 10 and 5.5, respectively, and as the thickness of the passive film is known to decrease with decreasing the pH [33], it was necessary to use NaCl solutions at pH 10 (see experimental section) for obtaining reliable comparative results in the following study.

The polarization curves of pure iron in the presence of NaF at pH 10, NaCl at pH 5.5 and NaCl at pH 10 are shown in case A of Fig. 1. The corresponding semi-logarithmic plots of the current density as

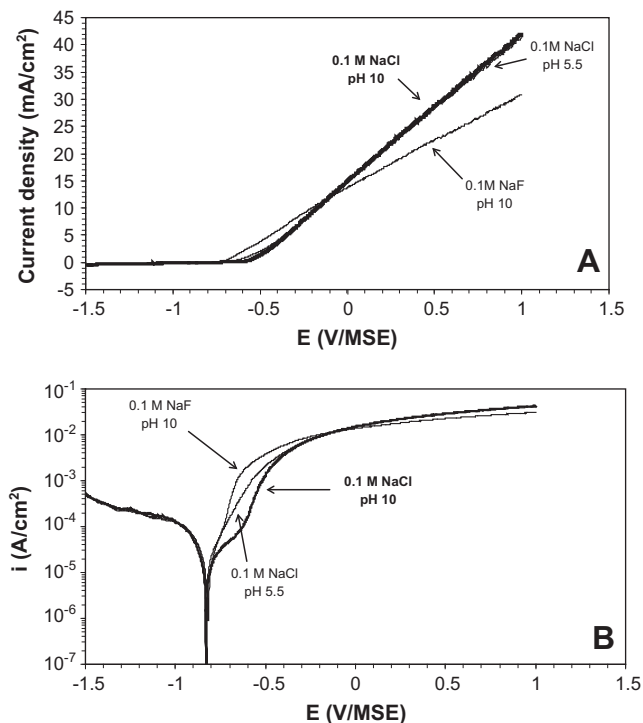


Fig. 1. (A) Polarization curves of pure iron in the presence of 0.1 M NaF at pH 10, in the presence of 0.1 M NaCl at pH 5.5, in the presence of 0.1 M NaCl at pH 10 (thick curve); (B) corresponding semi-logarithmic plots of the current density as a function of the electrical potential.

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