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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.

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 \times 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 equivolume 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

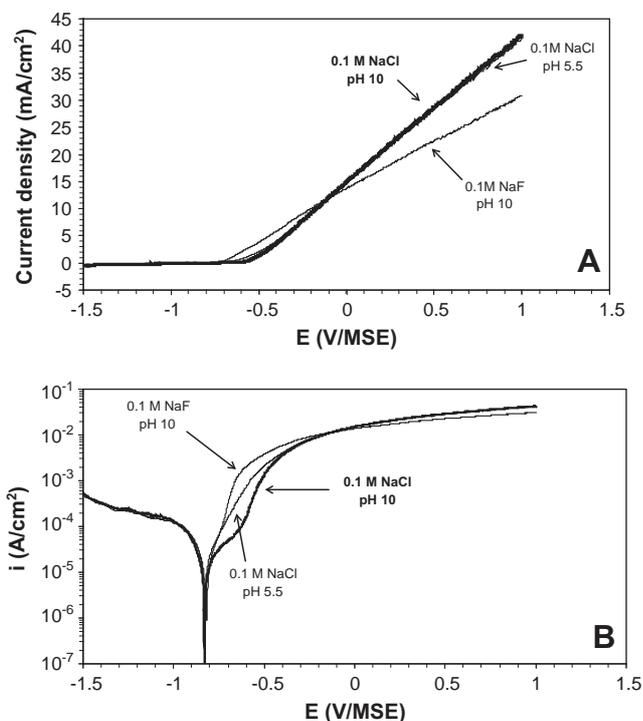


Fig. 1. (A) Polarization curves of pure iron in the presence of 0.1 M NaF at pH 10, in the presence of 0.1 M NaCl at pH 5.5, in the presence of 0.1 M NaCl at pH 10 (thick curve); (B) corresponding semi-logarithmic plots of the current density as a function of the electrical potential.

a function of the electrical potential are presented in case B of Fig. 1. Whatever the electrolyte solution, the qualitative behavior is the same and it is in accordance with the occurrence of pitting on the iron plates. The current density increases definitively when the electrical potential has reached a critical value, i.e. the pitting potential. It corresponds to about -0.68 V/MSE for NaF at pH 10, -0.63 V/MSE for NaCl at pH 5.5 and -0.53 V/MSE for NaCl at pH 10. The curves with NaCl at both pH values are superimposed at high potentials.

3.3. Passivation of iron

The passivation and the growth of passive films on iron have been extensively studied [27,33–45]. The choice of a pH 8.4 borate buffer solution has been found to allow the formation of a ‘true’ passive film [16,45]. It was shown that if passivation is carried out with this electrolyte at an electrical potential located into the passive region, the resulting surface oxide film is formed with a current efficiency of about 100%. The beneficial use of borate buffer as the ideal solution for passivating iron was assumed to be due to its ability to facilitate the nucleation of surface oxide as well as controlling the surface pH. The possible direct participation of borate buffer anions species in iron oxidation was also hypothesized [41]. The consensus view of the passive film is that of the bilayer model with an outer γ - Fe_2O_3 layer and an inner layer of Fe_3O_4 [45,46].

The polarization curve of iron in the presence of pH 8.4 borate buffer solution is shown in case A of Fig. 2. As expected, the current density remains constant at a low level, around 0.06 mA/cm², during a wide range of potential before it increases continuously from -0.6 V/MSE with the onset of oxygen evolution. Passivation of iron plates was further performed with pH 8.4 borate buffer solution at 0.4 V/MSE at different durations: 3600, 1200 and 400 s (see experimental section). As an example, the variation of the current density for anodization during 60 min is reported in case B of Fig. 2.

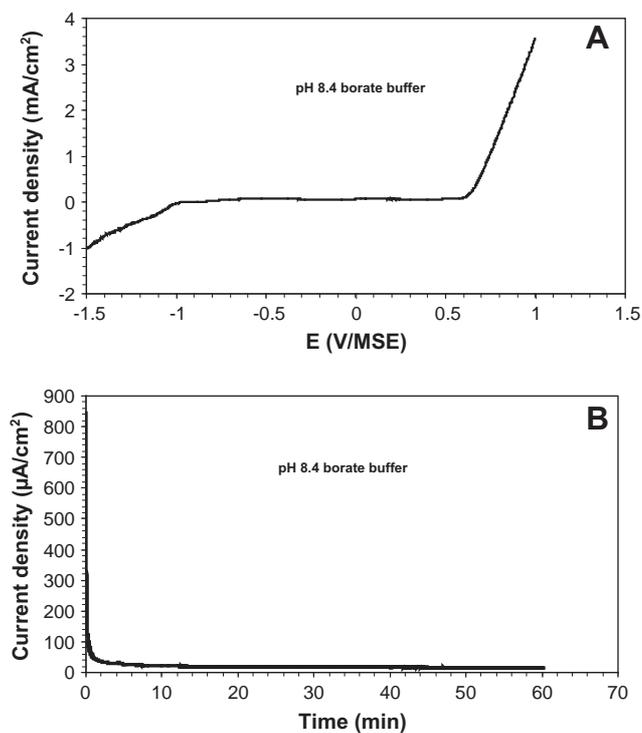


Fig. 2. (A) Polarization curve of pure iron in the presence of pH 8.4 borate buffer solution; (B) anodization at 0.4 V/MSE during 1 h in the presence pH 8.4 borate buffer solution.

3.4. Chronoamperometric measurements after the removal of borate buffer solution

Once the iron plates have been passivated, the borate buffer solution was removed. Chronoamperometric measurements were then performed at 0 V/MSE (at a potential greater than the pitting potential of pure iron, see Fig. 1) to investigate the comparative aggressiveness of NaF (see Fig. 3) and NaCl (see Fig. 4), at 0.1 M concentration and at the same pH 10, with iron plates that were prepassivated at different durations.

Except for curves d corresponding to no prepassivation, the comparative results exhibit a significant difference in the kinetics of attack between fluoride and chloride. With NaF, see case A of Fig. 3, the current density remains at a very low level at the beginning, typically lower than 0.01 mA/cm², see case B of Fig. 3, before it starts to increase with the characteristic development of a yellow color in solution. Then, it rises significantly with the appearance of pits on the surface, above about 1 mA/cm², together with intense hydrogen bubbling at the platinum cathode, to finally level off more or less slowly when the major part of the surface has been severely pitted and with the formation of orange flocs in solution. The time interval prior to the occurrence of pitting increases with longer prepassivation time, so reflecting the effect of the film thickness: the breakdown of passivity is delayed as the passive film is thicker [45]. The same trends were obtained when these experiments were repeated again to test the reproducibility. As an example, the experiment after prepassivation during 3600 s is shown, see thick curve e in case A of Fig. 3 and in case B of Fig. 3. Although there is some variation between curves a and e when the current density increases to high values during the pitting phase, see case A of Fig. 3, the behavior is similar in the initial part and the onset of the increase of the current density is fairly the same, see case B of Fig. 3. In the case of NaCl at pH 10, see Fig. 4, whatever the duration of prepassivation the current density increases steeply with the concomitant occurrence of pits.

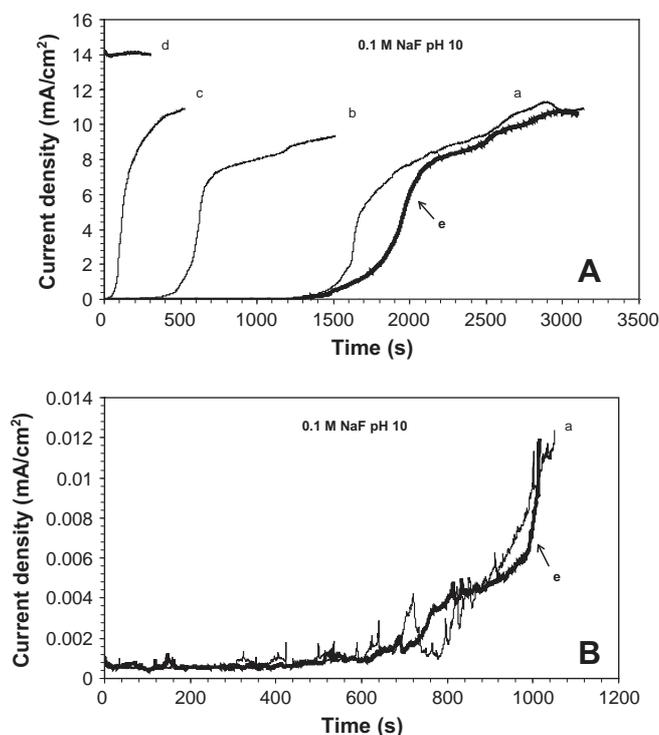


Fig. 3. (A) Chronoamperometric curves at 0 V/MSE in the presence of 0.1 M NaF solution (pH 10) after different prepassivation durations in borate buffer solution: a and e (thick curve), 3600 s; b, 1200 s; c, 400 s; d, 0 s; (B) initial part of comparative curves a and e (thick curve).

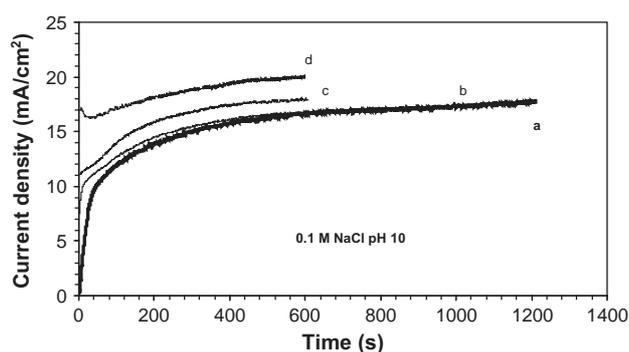


Fig. 4. Chronoamperometric curves at 0 V/MSE in the presence of 0.1 M NaCl solution (pH 10) after different prepassivation durations in borate buffer solution: a, 3600 s; b, 1200 s; c, 400 s; d, 0 s.

Various mechanisms have been proposed to lead to the breakdown of passivity (the penetration mechanism, the film breaking mechanism, the adsorption mechanism, the point defect model) [25] but the whole process of the breakdown of passive films is not fully understood. Moreover according to varying experimental conditions and environmental specificities each of these mechanisms may be predominant, sometimes the distinction between them is quite tenuous and probably mutual aspects of each of them have to be considered. The observed discrepancy in the aggressiveness between fluoride and chloride may be interpreted as originating from the kosmotrope or chaotrope nature of the involved anions [47–50]. Once the fluoride and chloride anions are adsorbed on the surface of the oxide film, they participate to a thinning process of the passive film through the formation of soluble salts or complexes with surface iron cations [14,25]. As the thickness of the passive film becomes smaller, an increased electrical 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. However, owing to their chaotrope character, the chlorides can also lose easily their hydration shell contrarily to the kosmotrope fluoride anions that tend to preserve their hydration state since the energetic dehydration contribution is too unfavorable [47]. The chlorides 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 fluorides. This should contribute to weaken more the film structure, so enabling the electrolyte solution to infiltrate into the passive layer and to lead faster to a direct contact of the electrolyte solution with the underlying metal surface.

Owing to their nature, the kosmotrope fluoride anions are involved in the thinning process of the passive film [14] which is longer as the thickness of the prepassivated film is wider [45]; the slow and continuous increase of the current density is ascribed to the dissolution of the film [11]. The breakdown of the passive film by fluorides occurs when the structure of the film has been sufficiently thinned and weakened [25]. This may explain the reasons why pitting is so retarded when it is compared to the case of chlorides within the same pH conditions. As information, the same trends as those with chlorides were obtained with other chaotrope halides (bromide and iodide).

3.5. Chronoamperometric measurements in the presence of borate buffer solution

For this purpose, a required amount of solid NaF or NaCl was incorporated, so that it corresponded to 0.1 M concentration, into the borate buffer solution when the iron plates were already anodized at 0.4 V/MSE during 3600 and 400 s. The results after passivation during 3600 s are shown in Fig. 5 (the same results were obtained for 400 s). Although the electrical potential is maintained

at 0.4 V/MSE, there is no effect in the case of NaF addition: the passive state is preserved indefinitely; whereas when NaCl is added pitting occurs rapidly, the current density rises sharply after some seconds.

The results with NaF are in accordance with those of Löchel and Strehblow [11] and Cakir [13] where no increase of the passive current density and no thinning of the passive layer were found after the addition of fluorides into the borate buffer solution. This constitutes an important difference with the results obtained in Section 3.4 where borate anions were absent. It indicates that although the use of borate buffer solution is recommended as an efficient electrolyte for passivation and to allow the control of the pH, the borate anions may also exert an inhibiting effect towards some anions that are present in solution. As it is evidenced in curve a, see case A of Fig. 6, the polarization curve of pure iron with pH 8.4 borate buffer solution containing NaF at 0.1 M concentration is qualitatively the same as that without NaF, see case A in Fig. 2. In the presence of pH 8.4 borate buffer solution containing NaCl at 0.1 M concentration, see curve b in case A of Fig. 6, the polarization curve is comparable to that with NaCl, see case A in Fig. 1, although the pitting potential is slightly higher at -0.46 V/MSE. The corresponding semi-logarithmic plots of curves a and b are shown in case B of Fig. 6. These results highlight that the borate anions prevent to study the attack of the less aggressive kosmotrope fluorides towards the passive film and that the borate anions hardly prevent pitting of iron by chlorides.

Many studies have been devoted to the inhibitive action of various species on different metal substrates [51–58]. These inhibitors are effective above a given ratio of non-aggressive to aggressive ions and they cause a shift of the pitting potential in the positive direction. The reported dependence of the pitting potential of iron on chloride concentration in pH 8 borate buffer illustrates this [5]: it increases as the chloride concentration decreases. It is generally considered that the inhibitive behavior originates from a competition between the anions for adsorption sites at the passive film-solution interface. In a previous study [48], the kosmotrope nature of divalent oxyanions such as SO_4^{2-} , HPO_4^{2-} , and CrO_4^{2-} , i.e. with a positive viscosity B coefficient value (see next section), was observed to be compatible with their inhibiting effect on the breakdown of passivity of certain valve metals in the presence of halide anions such as Cl^- , Br^- , I^- . It is assumed that these double negatively charged anions are more attracted at the film surface. Owing to their kosmotrope character these anions remain preferentially adsorbed to preserve their hydration state, so preventing the aggressive anions to access sufficiently to the surface of the passive film. As a consequence, the inhibition becomes more efficient when their concentration increases with respect to that of the aggressive anions. Once adsorbed, the inhibitors have been

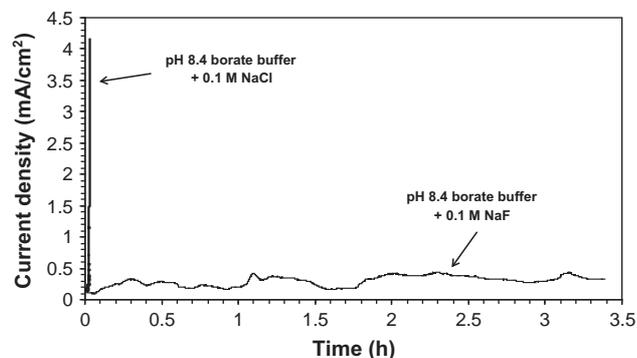


Fig. 5. Chronoamperometric curves at 0.4 V/MSE with addition of 0.1 M NaF into pH 8.4 borate buffer solution and with addition of 0.1 M NaCl into pH 8.4 borate buffer solution, after prepassivation during one hour in the pH 8.4 borate buffer solution at the same potential.

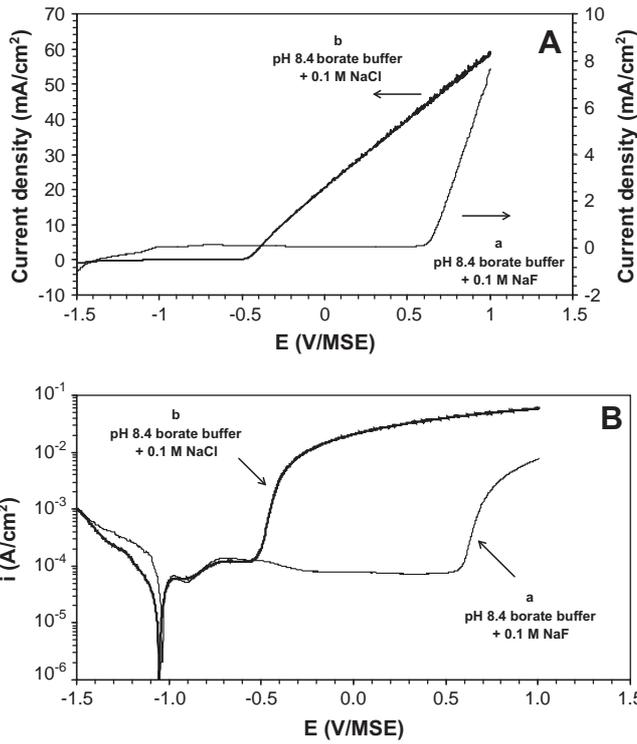


Fig. 6. (A) Polarization curves of pure iron in the presence of pH 8.4 borate buffer solution containing 0.1 M NaF (curve a) and in the presence of pH 8.4 borate buffer solution containing 0.1 M NaCl (curve b) and (B) corresponding semi-logarithmic plots of the current density as a function of the electrical potential.

assumed to participate also to the blockage of reactive sites and/or to assist in the repassivation process (self-healing) of the passive film [55,56].

3.6. The kosmotrope nature of borate anion

Surprisingly, the viscosity B coefficient value of borate ($B_4O_7^{2-}$) anion has not been reported in the literature. It can be determined from the Jones–Dole relationship [31]:

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

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 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 tightly attached, so that the resistance to flow of 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 B value is identified as the slope of the linear variation of the term $(\eta - \eta_w)/(\eta_w c^{1/2})$ as a function of $c^{1/2}$. The dynamic viscosity of each solution was calculated according to:

$$\eta = \nu\rho = Kt\rho \quad (2)$$

where ν and ρ are, respectively, the kinematic viscosity and the density of the electrolyte solution at 25 °C. K and t are, respectively, the constant of the capillary viscometer ($4.8 \times 10^{-9} \text{ m}^2/\text{s}^2$) and the average time of flowing of the electrolyte solution at 25 °C.

The measurements are reported in Table 2 and the corresponding curve is presented in Fig. 7. The B value for $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ electrolyte is found to be $0.840 \pm 0.015 \text{ L/mol}$. As an indication

Table 2

Molar concentration (c), density (ρ), average time of flowing (t), kinematic viscosity (ν) and dynamic viscosity (η) of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ solutions at 25 °C.

c (mol/L)	ρ (kg/m ³)	t (s)	ν (mm ² /s)	η (mPa s)
0	996.8	185.57	0.8907	0.8879
0.0125	999.2	187.32	0.8992	0.8984
0.025	1001.5	188.85	0.9065	0.9078
0.05	1006.3	191.89	0.9211	0.9269
0.1	1015.5	198.14	0.9511	0.9658

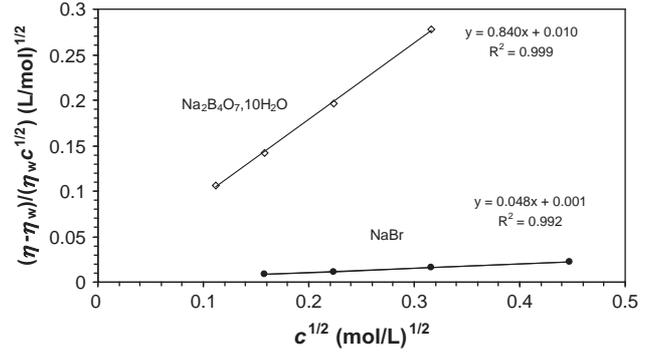


Fig. 7. Determination of the viscosity B coefficient value of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (\diamond) and NaBr (\bullet) electrolytes according to the Jones–Dole relationship.

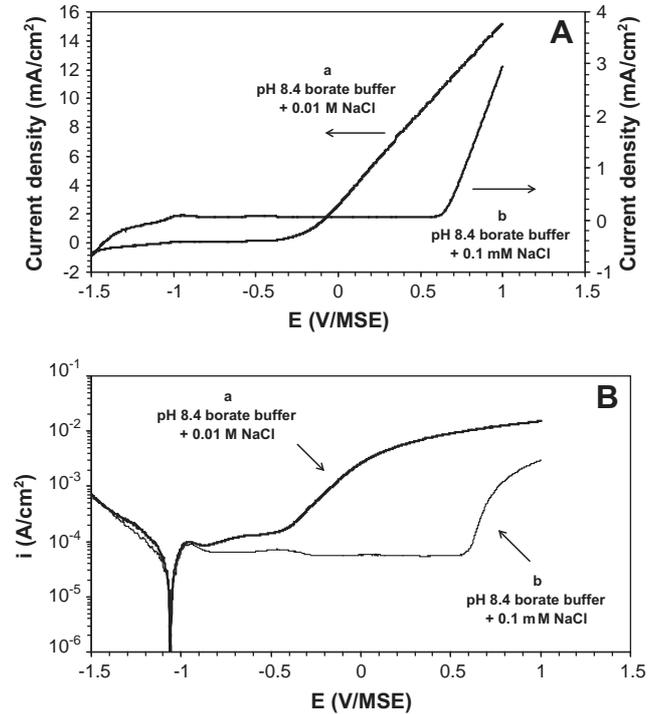


Fig. 8. (A) Polarization curves of pure iron in the presence of pH 8.4 borate buffer solution containing 0.01 M NaCl (curve a) and in the presence of pH 8.4 borate buffer solution containing 0.1 mM NaCl (curve b) and (B) corresponding semi-logarithmic plots of the current density as a function of the electrical potential.

the measurements for NaBr have been also plotted in Fig. 7. The obtained value for NaBr is $0.048 \pm 0.003 \text{ L/mol}$, it is in accordance with the expected value of 0.052 L/mol [32]. Knowing from the literature that $B(\text{Na}^+) = 0.085 \text{ L/mol}$ [32], and following the postulate of Cox–Wolfenden [31]: $B_{\text{electrolyte}} = \sum(\nu_i B_i)$ where ν_i and B_i are, respectively, the stoichiometric coefficient and the viscosity coefficient value of ion i of the electrolyte, it is found that

$B(\text{B}_4\text{O}_7^{2-}) = 0.670 \pm 0.017$ L/mol. When this value is compared with that of other anions, it corresponds to the highest positive value in the literature [32,59], so emphasizing the kosmotrope character of borate anion. Other inorganic divalent oxyanions of the same kosmotrope nature have been recognized as efficient inhibitors of many metal substrates [51,54–58], such as chromate (CrO_4^{2-} , $B = 0.169$ L/mol [32]), molybdate (MoO_4^{2-} , $B = 0.22$ L/mol [32]), tungstate (WO_4^{2-} , $B = 0.099$ L/mol [32]), dichromate ($\text{Cr}_2\text{O}_7^{2-}$, $B = 0.084$ L/mol [32]) or hydrogen phosphate (HPO_4^{2-} , $B = 0.382$ L/mol [32]).

The results reported in Fig. 6 indicate that the inhibitive action of borate anions is much more accentuated towards the less aggressive kosmotrope fluoride ions when compared to the chaotrope chlorides. Indeed chloride is very aggressive since it is one of the smallest anion (as its hydration layer can be easily removed). Nevertheless, iron can be protected against chlorides when the molar ratio [borate]/[chloride] is sufficient enough. To illustrate this, polarization curves of pure iron were performed with pH 8.4 borate buffer solution containing NaCl at 0.01 M concentration, see curve a in case A of Fig. 8, and with pH 8.4 borate buffer solution containing NaCl at 0.1 mM concentration, see curve b in case A of Fig. 8. With 0.01 M NaCl pitting is still obtained from about -0.4 V/MSE (it was -0.46 V/MSE at 0.1 M NaCl). With 0.1 mM NaCl no pitting is observed: curve b in case A of Fig. 8 is qualitatively similar to that of borate buffer, see case A in Fig. 2. The corresponding semi-logarithmic plots of curves a and b are shown in case B of Fig. 8.

At this level, it is interesting to note that the corresponding anions of the acid or neutral baths that are commonly used in anodizing treatments of various metals [45,60] are also kosmotrope ions, such as for instance sulfate (SO_4^{2-} , $B = 0.208$ L/mol [32]), oxalate ($\text{C}_2\text{O}_4^{2-}$, $B = 0.174$ L/mol [32]), carbonate (CO_3^{2-} , $B = 0.278$ L/mol [32]), phosphate (PO_4^{3-} , $B = 0.59$ L/mol [32]). Although these anions are attracted to the metal electrode (i.e. the anode), it may be expected that owing to their property they will remain adsorb at the surface of the growing anodic film, notably during the building of the inner layer, rather than being entrapped in the film. This should strengthen the cohesiveness of the anodic film. Owing to their nature such anions ensure that pitting will not occur during anodization. In this sense, the high positive B value of borate anion may provide a justification for its choice as an efficient electrolyte to obtain 'true' passive films.

4. Conclusion

What makes the originality of the present work is that the aggressiveness of the halides is investigated once the passivating solution has been removed, contrarily to previous studies on the same subject. The results indicate that the kinetics of attack by the kosmotrope fluoride is much slower than that of the chaotrope chloride. The presence of the borate buffer solution prevents the study of the less aggressive kosmotrope fluoride anion on the breakdown of passivity of iron. The high positive B value of borate anion may be taken as a pertinent criterion to justify it can act as an inhibitor or to be used in anodization baths.

More generally, the obtained results confirm again the role played by ion-specific hydration effects in the whole understanding of the corrosion or passivation behavior of metals.

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