

Voltammetric Study of Iron in Sodium Borate/Perchlorate Solutions

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Foi investigado o comportamento eletroquímico do ferro em soluções diluídas de borato puro, numa solução tampão de ácido bórico-borato de sódio e em soluções de perclorato contendo ou não borato. Foram usados voltametria cíclica com varredura triangular de potencial e um eletrodo rotatório de disco. O pH das soluções variou de 8,6 a 9,1, dependendo da concentração de borato. Os voltamogramas foram obtidos na faixa de potencial entre -1,30 e +1,20 V (SCE) e apresentaram influência da concentração de borato, velocidade de varredura do potencial, tempo de ciclagem e velocidade de rotação do eletrodo. Foi observado que, para o mesmo pH, na presença de borato, as densidades de corrente anódica foram mais baixas. Este efeito aumenta quando a concentração de borato aumenta e quando a velocidade de varredura do potencial diminui. O perfil voltamétrico é também influenciado pela velocidade de rotação do disco, mas menos marcantemente nas soluções contendo borato do que na solução de perclorato puro.

The electrochemical behavior of iron in diluted solutions of pure borate, in a buffer solution of boric acid-sodium borate and in solutions of perchlorate with and without borate was investigated. Cyclic voltammetry with a triangular potential scan and a rotating disk electrode were used. The pH of the solutions varied between 8.6 and 9.1, depending on the borate concentration. The voltammograms were obtained in the potential range of -1.30 to +1.20 V (SCE) and showed the influence of the borate concentration, potential scan rate, cycling time and rotation speed. It was observed that for the same pH in the presence of borate the anodic current densities were lower. This effect increased as the borate concentration increased and as the potential scan rate decrease. The voltammetric curve profile was also influenced by the rotating disk rate, much less markedly in the solutions containing borate than in the solution of pure perchlorate.

Keywords: *iron, passivity, borate*

Introduction

The electrochemical behavior of iron and steel in alkaline solutions has been studied by many authors; however there is no general agreement about the nature of the oxide or hydroxide phases formed under different conditions and the sequence in which they appear along a potential scan. Some authors¹ attribute the anodic peaks to iron dissolution as Fe(II) species, followed by a discontinuous film formation of Fe₃O₄ as the anodic potential becomes more positive by the oxidation of metallic iron, together with Fe₃O₄ to γ -Fe₂O₃, and from this to an oxide structure containing vacancies with Fe at a higher valence state. This last species should be responsible for passivation.

MacDonald *et al.*² identified three anodic peaks and two cathodic peaks working with steel in NaOH solutions using cyclic voltammetry with low potential scan rate values. They attributed the first two anodic peaks to Fe(OH)₂ formation, the third one to an FeOOH formation, and the

two cathodic peaks to the FeOOH reduction to Fe(OH)₂ and from this to metallic iron, respectively. These authors² do not believe in a sequential oxidation mechanism, but rather in sequential reactions with parallel steps.

Guzmán *et al.*³, studying the potentiodynamic behavior of iron in alkaline solutions, also identified three anodic peaks and two cathodic peaks. They attributed the first anodic peak either to the oxidation of adsorbed hydrogen or to the first steps of iron oxidation to Fe(OH)₂ completed in the second peak. The third anodic peak they attributed to Fe(OH)₂ oxidation to Fe₂O₃.H₂O. The cathodic peaks should correspond to the reduction of Fe₂O₃.H₂O and Fe(OH)₂, respectively. Sodium borate has been considered an anodic inhibitor because it acts as a buffer and keeps the solution alkaline which promotes passivation^{4,5,6,7,8}. Some authors^{4,5,6} believe that the borate anion participates in iron passivation, from the early steps, forming complexes that confer an inhibitive character to the film. Normally borate is used only as a support electrolyte, and very few studies

of iron in diluted solutions of this anion have been conducted. In the present work voltammetric experiments in borate and/or perchlorate solutions were performed with the aim of contributing to the understanding of iron behavior in slightly alkaline solutions and the effect of borate ions.

Experimental

Cyclic voltammograms were obtained with a Pine Model AFRDE 4 Bipotentiostat. A Pine Analytical Rotor and a BBC XY Model Se 780 recorder made up the rest of the equipment. The working electrode was a pure iron disk (Gallard-Schlesinger 99.999%) embedded in PTFE with a diameter of 4.9 mm the surface of which was polished with emery paper from grit 400 to 1000, and then with 0.1 μm alumina, washed with double-distilled water and alcohol, and then dried. The solutions used were 0.1 M $\text{NaClO}_4 + x$ ppm borax ($0 < x < 3000$), diluted solutions of pure borax (from 500 to 3000 ppm) and a borate buffer solution which was prepared by mixing 38.6 ml of 0.1 M H_3BO_3 with 20 ml of 0.25 M borax until the volume reached 100 ml. Before each experiment the working electrode was electroreduced at -1.3 V(SCE) for five minutes, and pure N_2 bubbling was used to remove oxygen from the solution. The recorded data, unless otherwise stated, were obtained from the first cycle of the potential scan. Potentials were measured against a saturated calomel electrode, and all values in the text are referred to it. The auxiliary electrode was a platinum wire with a sufficient area. The electrochemical cell was a traditional 250 ml Pyrex flask with three entrances.

Results

Figure 1 presents the cyclic voltammograms obtained for iron in a borate buffer solution. As v increases, anodic peaks I and II shift to more positive potentials, and peak III to more negative potentials.

Figure 2 shows the cyclic voltammograms of iron in the same buffer solution, but with different anodic reversal potentials. Independently if potential reversal occurs before peak I, after peak I, between peaks I and II or before peak II potential, no reduction peak was observed although in all cases a hysteresis was clearly visible. Cathodic peak III only appears when the reversal potential far exceeds the peak II potential. This indicates that the products formed at peak II are reduced at peak III in the reverse scan, and those formed at peak I, if they are reduced at all, are reduced at more negative potentials in the region of the HER potential.

For diluted solutions containing only borax, the cyclic voltammograms show a profile similar to that obtained in Fig. 1, but anodic peak I is greater, peak II is smaller (more like a shoulder), and cathodic peak III is present as a shoulder. Figure 3 presents the results for a solution of 1000 ppm borax, obtained with $w = 3000$ rpm and v varying

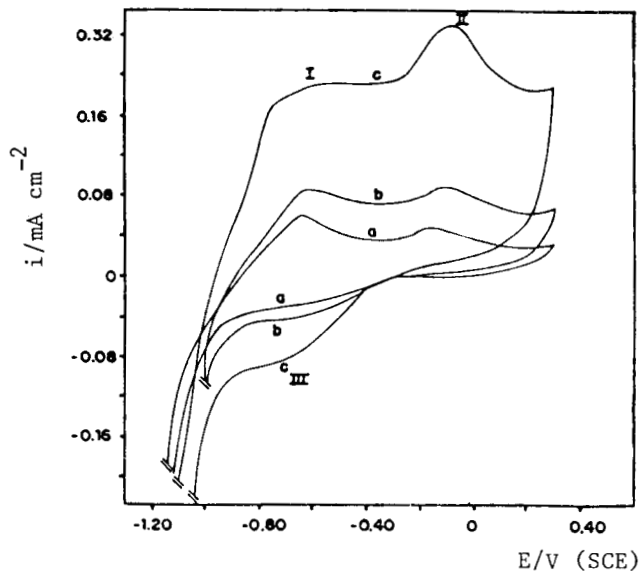


Figure 1. Cyclic voltammograms of iron in $\text{H}_3\text{BO}_3\text{-Na}_2\text{B}_4\text{O}_7$ solution, $\text{pH} = 8.4$, $w = 2000$ rpm. Influence of the potential scan rates: $v = 0.01$ (a), 0.02 (b), and 0.05 (c) V s^{-1} .

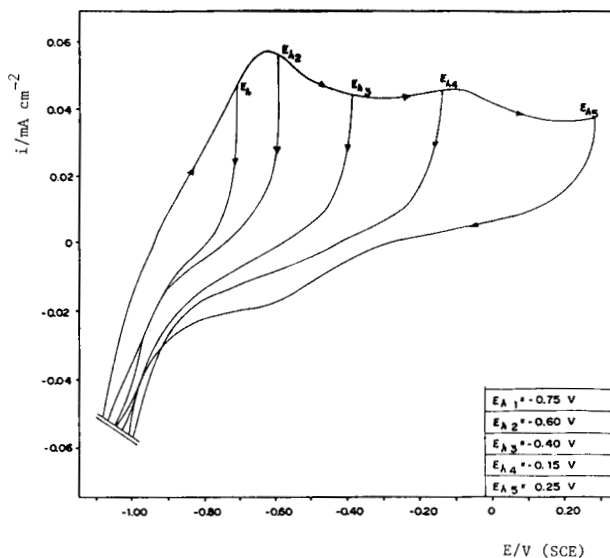


Figure 2. Cyclic voltammograms of iron in $\text{H}_3\text{BO}_3\text{-Na}_2\text{B}_4\text{O}_7$ solution, $\text{pH} = 8.4$, $w = 1000$ rpm, $v = 0.01$ V s^{-1} . Influence of the anodic reversal potentials.

between 0.01 and 0.10 V s^{-1} . A ratio between the total anodic charge (Q_a) and total cathodic charge (Q_c) greater than 1 was found. If anodic peaks I and II are considered symmetrical, it is possible to carry out the deconvolution and the result show that at peak potentials (E_{pI} and E_{pII}) with low v values, the anodic curves are not superimposed. A linear relationship between i_p and $v^{1/2}$ was obtained for peak I. Peak potential E_{pI} shifts to more positive values with the increase of v , following a linear relationship with $v^{1/2}$. For peak II a linear relationship between $\log i_p$ and $\log v$, and between E_p and $\log v$, was observed. All the previously mentioned linear relationship were followed with a correlation coefficient higher than 0.99. Observing the voltam-

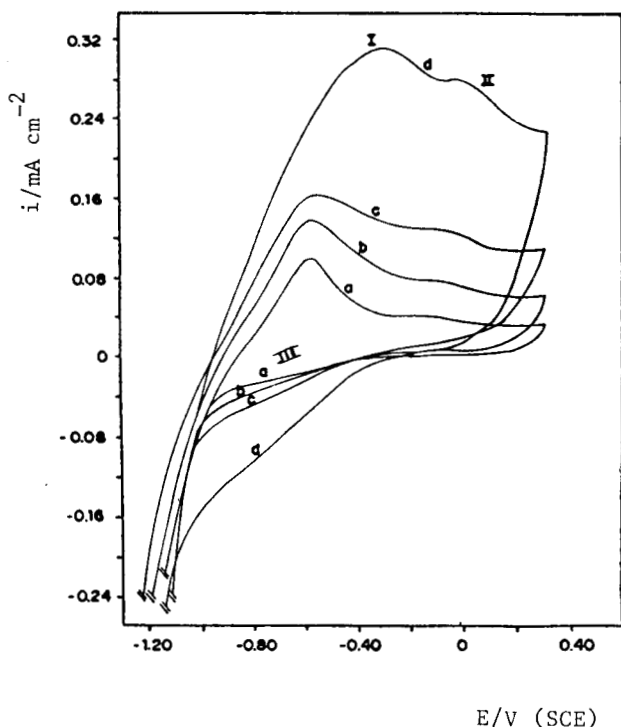


Figure 3. Cyclic voltammograms of iron in 1000 ppm borax solution, pH = 8.4, $w = 3000$ rpm. Influence of the potential scan rates: $v = 0.01$ (a), 0.02 (b), 0.05 (c), and 0.10 (d) $V s^{-1}$.

mograms it can be seen that peak I shifts more quickly to more positive potentials than peak II as v increases. As a consequence, for high potential scan rates ($v > 0.10 V s^{-1}$) the voltammetric profile modifies and just one anodic peak can be observed, because peaks I and II are superimposed. Therefore, only low potential scan rates ($v < 10 V s^{-1}$) were analyzed.

Figure 4 presents three cyclic voltammograms of iron, obtained in a $0.1 M NaClO_4$ solution with pH = 6.5, in a similar solution but with the pH adjusted to 9.1, and in a $0.1 M NaClO_4 + 2000$ ppm borax solution. In the first voltammogram just one anodic peak (peak A) was observed with a peak current density of $8 mA cm^{-2}$ at $-0.10 V$, and one cathodic peak (peak C) was observed at a potential near the HER. In the second voltammogram the peak A current density decreases and the peak potential shifts to more negative values. The cathodic peak appears at the same potential as in the first voltammogram, but the cathodic charge is greater than in the first case. In the solution containing borax anodic peak A disappears, and the anodic current density along the whole potential range is not greater than $0.4 mA cm^{-2}$. Cathodic peak C appears at potentials less negative than before.

If repetitive scans are done in $0.1 M NaClO_4 + 3000$ ppm borax solution and if the profile is recorded on a more expanded scale, it can be seen that the first scan is quite different from the other ones (see Fig. 5): three anodic shoulders (I', I and II) and one cathodic shoulder (III) can

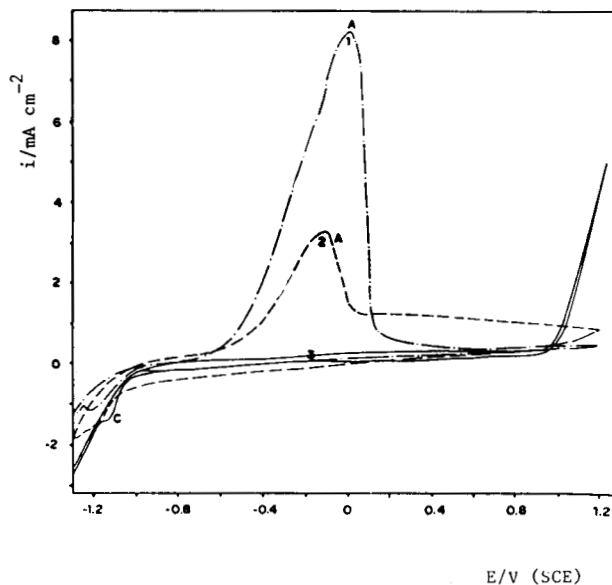


Figure 4. Cyclic voltammograms of iron obtained with $v = 0.02 V s^{-1}$ and $w = 1000$ rpm: 1) $0.1 M NaClO_4$ solution, pH = 6.5; 2) $0.1 M NaClO_4$ solution, pH = 9.1; and 3) $0.1 M NaClO_4 + 2000$ ppm borax solution, pH = 6.5.

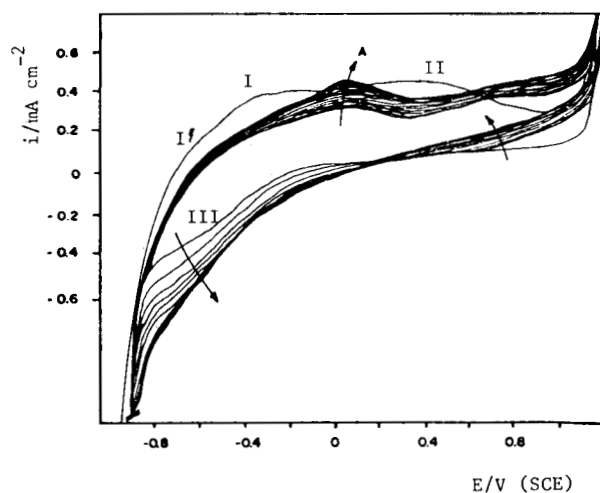


Figure 5. Cyclic voltammograms of iron in $0.1 M NaClO_4 + 3000$ ppm borax solution, pH = 9.1, $w = 1000$ rpm, $v = 0.04 V s^{-1}$. Influence of the cycling time.

be observed. In the second scan, the anodic current decreases considerably if compared to the first scan, after which it increases with the successive scans, presenting one anodic peak like that observed in the Fig. 4, for borax-free solutions, but with much smaller current densities. The cathodic current density also increases continuously with successive scans.

Figure 6 shows the influence of v on the first cycle in $0.1 M NaClO_4 + 2000$ ppm borax solution. As v increases, the anodic peak current densities as well as the cathodic peak current density increase. It can be seen that for high v , even for the first cycle, the profile of the voltammogram seem to tend towards those obtained for borax-free solu-

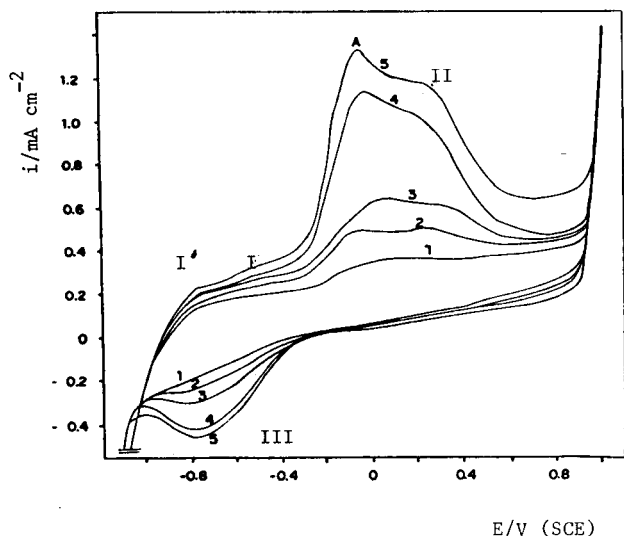


Figure 6. Cyclic voltammograms of iron in 0.1 M NaClO₄ + 2000 ppm Borax solution, pH = 9.1, w = 1000 rpm. Influence of the potential scan rates: v = 0.04 (1), 0.05 (2), 0.06 (3), 0.08 (4) and 0.10 (5) V s⁻¹.

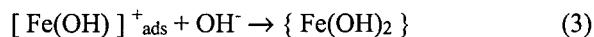
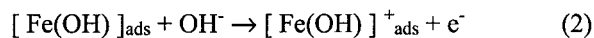
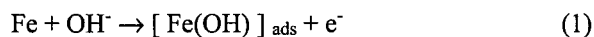
tions (Fig. 4). Figure 6 shows that at v = 0.10 V s⁻¹ anodic peak A (indicated in Fig. 4 in a borate-free perchlorate solution) and anodic peak II (indicated in Fig. 5 in a perchlorate with borate solution, first cycle) were evident. Anodic peak A, in the perchlorate with borate solution, presents a lower current density when compared to the borate-free perchlorate solution, but with the same pH.

Discussion

Borax buffer solutions and diluted borax perchlorate-free solutions

Anodic peak I in the present work appears in the same potential range as that observed by MacDonald *et al.* and Guzmán *et al.* as cited in the introduction, and can thus be attributed to Fe(OH)₂ formation.

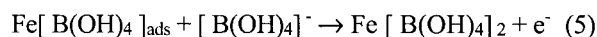
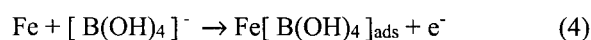
Guzmán *et al.*³ suggested the following sequential reactions:



The first and the second steps are responsible for a monolayer formation on the metallic surface, whereas the third step produces a new phase, {Fe(OH)₂}. The brackets represent the formation of monolayer and the keys represent the formation of tridimensional phases. The transformation from [Fe(OH)]_{ads}⁺ either to soluble Fe(II) species or to a Fe(OH)₂ film depends on the Fe(II) hydrolysis constant and on the H⁺ ion activity at the metal/solution interface. The charge involved in the formation of anodic peak I in the present work, calculated from Fig. 2, is approximately 2 mC cm⁻². The monolayer charge of

Me(OH)₂, where Me = Fe, Ni or Co, is estimated to be approximately 0.70 mC cm⁻². Even if a roughness factor of 1 is assumed, it can be expected that no more than three monolayers will be formed. In the presence of borate ion, its buffering capacity promotes a decrease in H⁺ ion activity, which makes the Fe(OH)₂ film formation easier than the Fe(II) species dissolution. In the presence of borate it can be observed that the current densities in this potential range are smaller than in the solutions containing other anions, such as CO₃²⁻/HCO₃⁻, at the same pH^{9,10,11,12}.

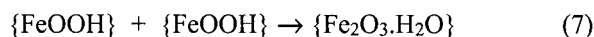
Fischer *et al.*⁵ proposed that this is due to the adsorption of hydrolyzed borate ions on the metallic surface, where they complex the iron ions, inhibiting their dissolution. The proposed mechanism is:



Reactions 4 and 5 probably occur in parallel with Reactions 1, 2 and 3.

The linear variation of both i_p and E_p with v^{1/2} for anodic peak I in both solutions (buffer and diluted borax solution) suggests that the oxidation process at this potential is kinetically controlled by ohmic resistance^{13,14}.

The anodic peak II potential range in this work is more positive than the values found by the authors already mentioned^{2,3}, but it is still higher than the equilibrium potential for the formation of Fe(III) species from metallic iron or from Fe(OH)₂, thus this peak can still be associated with the formation of Fe(III) species. According to Guzmán *et al.*³, in alkaline solutions, the reactions in this potential range are:



The Fe₂O₃·H₂O formed should be responsible for the passivation. The keys represent species related to the formation of new phases.

In the work of Markovac and Cohen¹⁵, in solutions containing borate this anion was not detected in the inner part of the film. According to these authors, if any Fe(II) ion is present in solution, whether free or complexed with borate, it oxidizes at the oxide/solution interface and precipitates on the film as g-Fe₂O₃, or as a complex such as Fe[B(OH)₄]₃, Fe(OH)[B(OH)₄]₂, or Fe(OH)₂[B(OH)₄], thus explaining the presence of borate anions in the outer part of the film found by these authors¹⁵.

The linear relationships log i_p vs. log v and E_p vs. log v obtained for peak II suggest that the film is formed by an irreversible process through a mechanism controlled by the diffusion of reactants across an oxide layer¹⁴.

In the reverse scan just one cathodic peak is observed in the unstirred borate buffer solution, becoming less defined in stirred solutions. In the works already men-

tioned^{2,3}, the two cathodic peaks attributed to FeOOH and Fe(OH)₂ reduction were obtained at more negative potentials because these authors worked in slightly more alkaline media. In solutions containing only borate, these peaks are not observed, and only a large cathodic shoulder can be seen which is not dependent on the electrode rotation rate. Perhaps the reduction reaction occurs via solid state, promoting dissolution of the film formed during the anodic scan, and this reduction continues at HER potential range and is probably not complete. According to MacDonald² the Fe(OH)₂ film needs large overpotentials for its reduction because it is still detected after reduction peaks.

Perchlorate containing solutions

The anodic peak (A) observed in 0.1 M NaClO₄ solution with pH = 6.5 (Fig. 4) may be associated with a non-protective film formation which allows some iron dissolution. In fact, the peak current density increased with the rotation rate, and after the test the solution became yellowish. Cathodic peak (C) must be associated with the reduction of iron ions present in the solution near the electrode surface, and with the reduction of the film formed in the anodic scan, since a small increase in the cathodic peak current density with w was observed. The reduction of the anodic peak current density, and the peak potential shift to negative values when the pH is adjusted to 9.1, demonstrate that, at this pH value, iron passivity is favored. The charge increase observed for the cathodic reduction in this medium points to a larger amount of film formed in the anodic scan. The voltammogram change when a small quantity of borate is added to the perchlorate solution shows the great inhibitive character of this anion. An easy explanation for the ability of borate to promote passivation, according to MacDougall^{7,8}, is its capacity to buffer the pH near the electrode, preventing any acidification due to iron ion hydrolysis. Borate also acts as an inhibitor by adsorption^{7,8}, participating directly in the oxidation reaction on the metallic surface.

These results may also indicate that the difficulty of iron passivation in solutions containing only perchlorate is not due to this anion being aggressive to iron oxides, but rather that it does not interact with the iron surface and does not have an important buffer capacity. This explains why it does not facilitate the iron passivation.

The fact that the successive scans change the voltammetric profile (Fig. 5) may be due to an electrostrictional phenomenon. At each scan the oxide formed undergoes a partial rupture when the potential scan reverts, as a result of the high electrostrictional pressure¹⁶. This rupture, together with the electrode rotation allows direct contact, between the perchlorate-containing solution and the bare electrode surface, promoting dissolution. It is possible that the metal dissolution across the film formed on the electrode surface in a borate/perchlorate solution also occurs.

At more anodic potentials passivation occurs again, explaining why a reactivation peak in the reverse scan is not observed. In fact, the anodic peak is similar to the Fig. 4 anodic peak A in solutions without borate, in spite of a smaller anodic current density. The borate and perchlorate anions seem to compete in metal passivation and dissolution processes, respectively.

During a voltammetric film formation, the current increases due to metal/film interface polarization and decreases due to the aging of the film, which probably dehydrates and becomes more resistive. As v increases (Fig. 6), film aging is not favored¹⁶ because the electrode stays less time at each potential. Then, the anodic peak current increases and the passivation occurs at more positive potentials. The competition between passivation by formation of an amorphous^{7,8} protective film containing borate and the metal dissolution stimulated by the perchlorate anions is clearer at these high potential scan rates. The curve then resembles that in Fig. 4 obtained in perchlorate medium without the addition of borax, although the anodic peak current density is smaller and the anodic peak potential is shifted to more noble potential values. The peak II splitting (namely peak A and peak II in Fig. 6) demonstrates that the electrochemical processes were separate: anodic peak A seems to be related to dissolution and film formation in perchlorate solutions (see Figs. 4 and 5), and anodic peak II seems to be related to some electrochemical transformation of this film, perhaps caused by borate.

Conclusions

1 - The electrochemical behavior of iron in slightly alkaline solutions depends on the anion present in the solution. In the presence of perchlorate, one anodic peak (peak A) and one cathodic peak (peak C) are observed. In the presence of borate, two anodic peaks (peaks I and II) and one cathodic peak (peak III) are observed with smaller current densities than in the perchlorate medium. These two anodic peaks in the medium containing only borate may be related to film formation reactions with different kinetic controls. Small amounts of borate added to the perchlorate solution change the voltammetric profile, which tends towards that obtained in perchlorate-free borate solution for the the first cycle with low v .

2 - The film formed in borate solutions is more resistant than the one formed in perchlorate, mainly at slow v . Borate, even in small quantities, inhibits iron dissolution. This property is due to both its buffering capacity which maintains the alkaline pH close to the electrode, and to the formation of complexes between borate and iron which are adsorbed on the metallic surface, inhibiting dissolution^{5,7,8}.

3 - Perchlorate apparently does not act as an aggressive anion, since pitting was not observed in the studied poten-

tial range. Perhaps this anion does not interact with the metallic surface and does not facilitate its passivation.

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