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Behaviour of sodium silicate and sodium phosphate (tribasic) as corrosion inhibitors for iron

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The effectiveness of sodium silicate (Na_2SiO_3) and trisodium phosphate (Na_3PO_4) as corrosion inhibitors for iron in 0.1 M $NaClO_4$, in both aerated and deaerated solutions has been investigated. Both sodium silicate and trisodium phosphate are effective inhibitors in unbuffered solutions as a result of inhibiting the rate of the anodic iron dissolution reaction. However, the inhibition of the corrosion rate in the (final) pH range 9.6–11.6 is entirely due to the change in pH which the addition of Na_2SiO_3 and Na_3PO_4 to unbuffered solutions causes, and not to the presence of silicate/phosphate species. Where the final pH was in the range 5–7 addition of 1 mM sodium silicate to acidified aerated unbuffered solutions caused slight inhibition of the iron dissolution reaction when compared with a solution of the same pH. Lower concentrations of Na_2SiO_3 at the same final pH did not cause inhibition. Silicic acid has an approximate solubility of 1 mM and it is likely that the inhibitive behaviour in this pH range is due to the precipitation of H_2SiO_3 at the electrode surface. An aerated phosphate buffer of pH 7.0 inhibited both the anodic and cathodic reactions when compared with a 0.1 M sodium perchlorate solution at the same pH. This was due to the presence of phosphate species at the electrode surface. In carbonate and acetate buffers neither Na_2SiO_3 nor Na_3PO_4 caused corrosion inhibition.

1. Introduction

Sodium silicate has been used for the inhibition of the corrosion of steel for more than 70 years [1–10]. In 1922 Speller suggested the addition of silicate to domestic water supplies would control the corrosion of steel pipework. A number of authors have discussed the mechanism of formation and the nature of the protective layers on steel in solutions of sodium silicate [2–10]. In 1952 Pryor and Cohen [2] showed that a film of γ-Fe_2O_3 formed on iron in contact with aerated solutions of sodium silicate. Katsanis *et al.* [7] suggested that a thin film of silica forms on metal water pipes as dissolved silicate is fed through them. Chen *et al.* [10] postulated that a layered structure of $Fe_2O_3/FeO/Fe$ is responsible for the lowering of the corrosion rate of iron in contact with both aerated and deaerated silicate solutions.

It is well known that whilst the corrosion rate of iron in aerated solutions is independent of pH between pH 4 and pH 10, at a pH > 10 the corrosion rate decreases rapidly with increasing pH [11]. The use of solutions of sodium silicate to inhibit the corrosion of steel is complicated [12] by the fact that the dissolution of Na_2SiO_3 in water generally increases the pH since silicic acid, H_2SiO_3 is a weak acid with $pK_1 = 9.5$ and $pK_2 = 12.7$. This means that when Na_2SiO_3 is dissolved in water the following reaction occurs:

$$SiO_3^{2-} + H_2O = HSiO_3^- + OH^-$$

For example a solution which is nominally 0.1 M Na_2SiO_3 solution actually contains the following species:

$[SiO_3^{2-}]$ 0.05 M
$[HSiO_3^-]$ 0.05 M
$[OH^-]$ 0.05 M giving a pH of 12.7.

However if Na_2SiO_3 is dissolved in a buffer the pH is determined by the buffer at low Na_2SiO_3 concentrations. For a buffer of pH < 8 the SiO_3^{2-} ions are present largely as H_2SiO_3.

In 1981 Lahodny-Sarc and Kastelan [6] investigated the role of pH in the inhibition of corrosion of iron by sodium silicate. They concluded that a protective effect due to soluble silicate species could be distinguished from that due to the pH change. In this present paper we have examined the relative importance of pH changes and the concentration of silicate species in the inhibition of iron corrosion.

Dissolution of trisodium phosphate (Na_3PO_4) or disodium phosphate (Na_2HPO_4) in unbuffered solutions will also result in an increase in alkalinity. It is therefore necessary to distinguish between inhibition simply caused by an increase in pH and inhibition due to phosphate species.

Na_3PO_4 and Na_2HPO_4 were investigate by Pryor and Cohen [3] as corrosion inhibitors for iron in aerated solutions. They found at a concentration $>\sim 3 \times 10^{-3}$ M in unbuffered solutions Na_3PO_4 was an effective corrosion inhibitor. However the pH of such a solution is close to 11 [12], so the question arises as to whether the inhibition is other than that due to the alkaline media. For Na_2HPO_4 effective

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inhibition was only found at a salt concentration above 10^{-2} M. The most important recent work on the behaviour of Na_3PO_4 and Na_2HPO_4 as inhibitors for iron is that by Melendres *et al.* [13] who report that in 0.1 M Na_3PO_4 (pH 11.9) and 0.1 M Na_2HPO_4 (pH 8.7) 'the behaviour is that predicted by the Pourbaix diagram for the Fe–H_2O system', which presumably implies that it can be attributed to the effect of OH^- alone. Melendres *et al.* also reported that the composition of the passive films formed on iron in phosphate containing solutions where the pH was 6.4 or greater was largely Fe_3O_4 with PO_4^{3-} incorporated into the lattice structure of the film.

2. Experimental details

Rotating disc electrodes (area 0.13 cm^2) were made from iron rods (99.99% purity, Goodfellow Metals, Cambridge) which were embedded in Teflon holders. The rotation rate was 480 rpm throughout. The electrodes were prepared by abrading with γ-alumina then washing with deionised water. Measurements were made in a three electrode electrochemical cell. A separate reference electrode compartment with a three way tap was connected to the main compartment via a ball and socket joint and a fine Luggin capillary. This allowed the working and counter electrodes to be immersed in buffer solutions while the reference electrode was filled with sodium hydroxide solution. Mercury/mercuric oxide reference electrodes in 0.1 M NaOH were used throughout and all potentials are quoted relative to them. The three electrolytes investigated were (a) 0.1 M sodium acetate + 0.1 M acetic acid, pH 4.6, (b) 0.1 M sodium carbonate + 0.1 M sodium hydrogen carbonate, pH 9.6 and (c) 0.1 M $NaClO_4$. They were prepared from AnalaR grade reagents and high purity deionised water (Purity *Stillplus* HP). Sodium metasilicate pentahydrate (BDH technical grade) and trisodium phosphate, dodecahydrate (98 + %) were added in various quantities to the base electrolytes. Disodium phosphate (AnalaR) and monosodium phosphate (AnalaR) were used to give a phosphate buffer of pH 7.0. To bring the pH of unbuffered sodium silicate solutions into the range 5–7, 0.1 M perchloric acid was added dropwise. All measurements were made at room temperature (23 ± 2 °C).

The polarisation diagrams of iron in each electrolyte were determined by slow linear sweep (1 mV s^{-1}). These measurements were made for each electrolyte in the presence and absence of the inhibitor. The solutions were saturated during each experiment either with nitrogen or oxygen gas. All linear and cyclic sweep measurements were carried out on an OxSys electrochemical interface controlled by an Atari ST^E microcomputer. They were initiated at −1.2 V and proceeded in a positive direction. Prior to every electrochemical measurement the working electrodes were exposed to the aqueous solution for 2 h, in order to allow a steady state condition to be achieved. Electrochemical impedance spectroscopy was performed using an ACM AutoAC 127 rig. A sinusoidal signal of RMS amplitude 10 mV was applied at the rest potential developed by the system after 1 h on open circuit. The frequency was swept between 10 kHz and 1 mHz.

Fourier transform infra-red spectroscopy (FTIR) was employed in an attempt to compare the surface films formed on iron immersed in various phosphate solutions. Iron coupons were degreased with acetone and immersed in the test solution to which air was freely admitted. After a period of 72 h the coupons were removed, washed with distilled water and dried under a stream of nitrogen. Spectra were obtained from a Biorad FTS 70 spectrometer coupled to a variable angular specular reflectance unit. This permitted the use of specular reflectance spectroscopy at an angle of incidence of 45°.

In the potentiostatic determination of passivation currents a fixed potential was applied to a rotating iron disc in the deaerated test solution. The current was determined at this fixed potential as a function of time. The applied potential was that which developed when iron was contacted with the aerated test solution at open circuit for 1 h.

3. Results and discussion

3.1. *Corrosion of iron in the presence of sodium silicate in buffered solutions*

Typical *i*/*E* curves are shown in Figs 1 and 2. Figure 1 compares results for iron in aerated acetate buffer for (a) no sodium silicate, (b) 1 mM sodium silicate and (c) 10 mM sodium silicate. Within experimental error the corrosion rate of the iron was unaffected by the presence of sodium silicate up to a level of 10 mM. Figure 2 compares results for iron in deaerated carbonate/bicarbonate buffer for (a) no sodium silicate, (b) 0.1 mM sodium silicate, (c) 1 mM sodium silicate and (d) 10 mM sodium silicate. At a sodium silicate concentration of 10 mM a decrease in the rate of the anodic reaction and the critical current

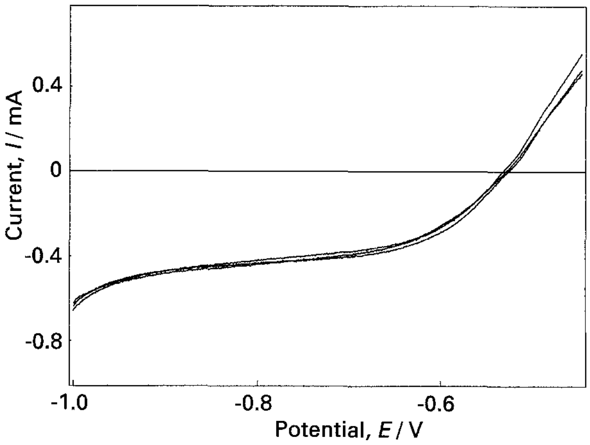

Fig. 1. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in aerated acetate buffers with (a) no silicate, (b) 1 mM sodium silicate and (c) 10 mM sodium silicate. In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

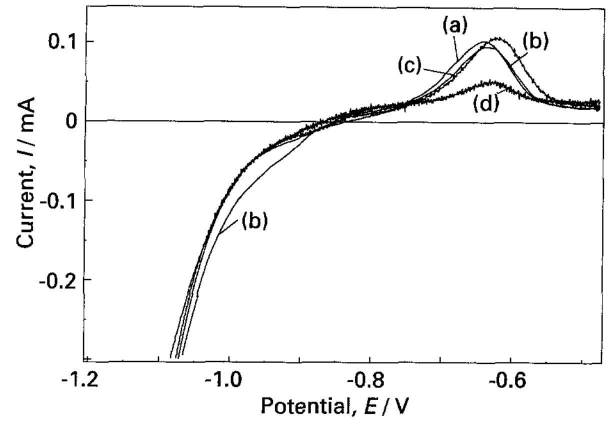

Fig. 2. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in deaerated carbonate/bicarbonate buffers with (a) no silicate, (b) 0.1 mM sodium silicate, (c) 1 mM sodium silicate and (d) 10 mM sodium silicate. In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

required for passivation was observed. A white precipitate, thought to be silicic acid, slowly develops in the carbonate buffer at this silicate level. It is probable that the corrosion inhibition is associated with the precipitation of silicic acid at the electrode surface.

Therefore it is clear that in well buffered solutions sodium silicate is ineffective as a corrosion inhibitor for iron, except when the silicate level is so high that silicic acid is precipitated on the electrode surface.

3.2. *Corrosion of iron in the presence of sodium silicate in unbuffered solutions in the pH range 9.6–11.6*

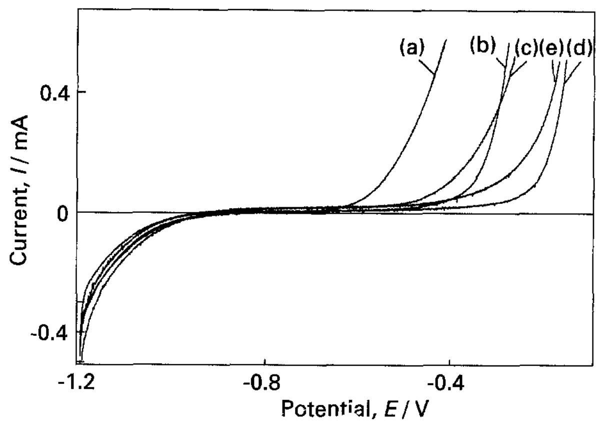

Fig. 4. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in deaerated sodium perchlorate solutions with (a) no sodium silicate, (b) 0.1 mM sodium silicate (pH 9.6), (c) NaOH (pH 9.6), (d) 1 mM sodium silicate (pH 10.6), (e) NaOH (pH 10.6). In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

Typical *i*/*E* curves are shown in Figs 3 to 5. Figure 3 compares results for iron in aerated 0.1 M sodium perchlorate solution for (a) no sodium silicate, (b) 0.1 mM sodium silicate (pH 9.6), (c) NaOH (pH 9.6), (d) 1 mM sodium silicate (pH 10.6), (e) NaOH (pH 10.6), (f) 10 mM sodium silicate (pH 11.6) and (g) NaOH (pH 11.6). At high negative applied potentials the cathodic current is due to a combination of the reduction of water to hydrogen and the reduction of oxygen to hydrogen ions. Nearer the corrosion potential oxygen reduction predominates, however there is no consistent effect on the cathodic region due to the presence of dissolved silicate and/or hydroxide ions. A cyclic voltammogram of solution (a) indicates the anodic region is due to true active dissolution. Additions of silicate and/or hydroxide promote passivity at the surface. Application of increasingly positive applied potentials leads to pitting corrosion, again this is strongly indicated in cyclic voltammograms of iron in silicate and hydroxide solutions. A direct relationship is observed between the amount of dissolved silicate and/or hydroxide and the positive applied potential required for the onset of pitting corrosion.

Figure 4 compares results for iron in deaerated 0.1 M sodium perchlorate solution for (a) no sodium silicate, (b) 0.1 mM sodium silicate (pH 9.6), (c) NaOH (pH 9.6), (d) 1 mM sodium silicate (pH 10.6) and (e) NaOH (pH 10.6). The cathodic region is independent of both pH and silicate concentration. It is therefore thought to be due to the reduction of water to hydrogen. As in the unbuffered, aerated example, the addition of silicate and/or hydroxide promotes

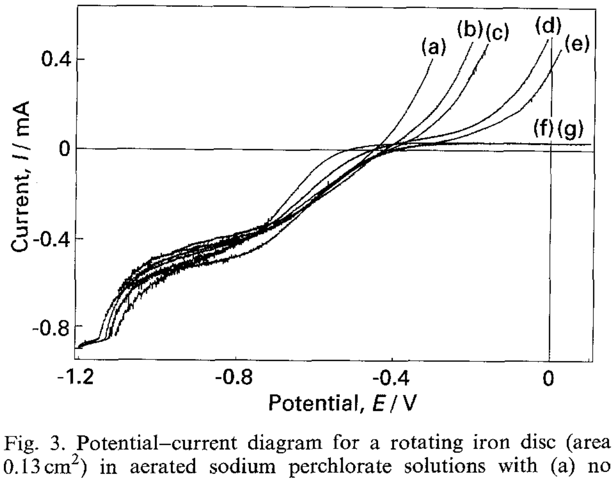

Fig. 3. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in aerated sodium perchlorate solutions with (a) no sodium silicate, (b) 0.1 mM sodium silicate (pH 9.6), (c) NaOH (pH 9.6), (d) 1 mM sodium silicate (pH 10.6) (e) NaOH (pH 10.6), (f) 10 mM sodium silicate (pH 11.6) and (g) NaOH (pH 11.6). In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

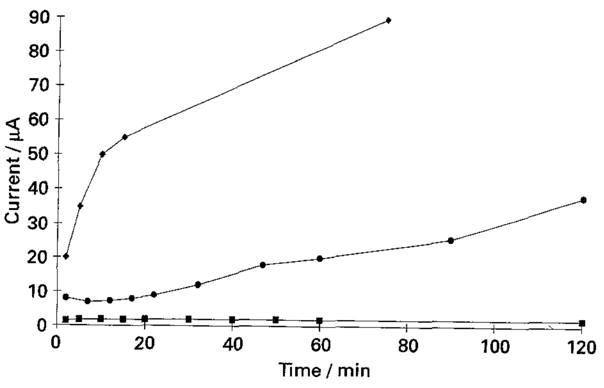

Fig. 5. Current as a function of time for a rotating iron disc in deaerated 0.1 M sodium perchlorate solutions with (◆) 0.1 mM sodium silicate, (●) 1 mM sodium silicate and (■) 10 mM sodium silicate. In all cases the iron was rotated at 8 rps on open circuit for 1 h in the aerated solution and the final rest potential was noted. The system was subsequently deaerated and after a period of 10 min had elapsed the determined rest potential was potentiostatically applied and the current noted at various time intervals.

passivity. Again, a direct relationship is found between the level of silicate/hydroxide and the positive applied potential required for the onset of the pitting corrosion.

Figure 5 shows current as a function of time for an iron electrode held potentiostatically in deaerated unbuffered silicate solutions. This current gives an estimate of the passivation current for iron in those solutions in the presence of oxygen. The plot displays results for 0.1 M sodium perchlorate with 0.1 mM sodium silicate, 1 mM sodium silicate and 10 mM sodium silicate. The results show that both the 1 and 10 mM silicate solutions exhibit relatively stable passivation currents (16–80 μA cm^{-2}) up to a period of 1 h. The 0.1 mM silicate solution initially displays a small current which rapidly increases, indicating the system is on the verge of passivation. Further experiments substituting sodium hydroxide for sodium silicate, in the above solutions, at equivalent pH values gave the same results within experimental error.

Therefore it is clear that in unbuffered solutions sodium silicate is effective as a corrosion inhibitor for iron by inhibiting the anodic dissolution of the metal. However the reduction of the corrosion rate in the pH range 9.6–11.6 can be entirely accounted for by the change in pH caused by the addition of the sodium silicate.

3.3. *Corrosion of iron in the presence of trisodium phosphate in buffered solutions*

Experiments performed in both aerated and deaerated carbonate and acetate buffers showed no effect on the corrosion of iron up to a concentration of 10 mM sodium phosphate.

3.4. *Corrosion of iron in the presence of trisodium phosphate in unbuffered solutions in the pH range 9.7–11.7*

All the experiments performed on sodium silicate were repeated for trisodium phosphate and all showed striking similarity. An example of the correlation between phosphate and silicate at these high pH values is given in Fig. 6 which compares results for iron in deaerated 0.1 M sodium perchlorate solution for (a) no sodium phosphate, (b) 0.1 mM trisodium phosphate (pH 9.7), (c) 1 mM trisodium phosphate (pH 10.7), (d) NaOH (pH 9.7) and (e) NaOH (pH 10.7). There is a very good agreement between Fig. 6 and Fig. 4.

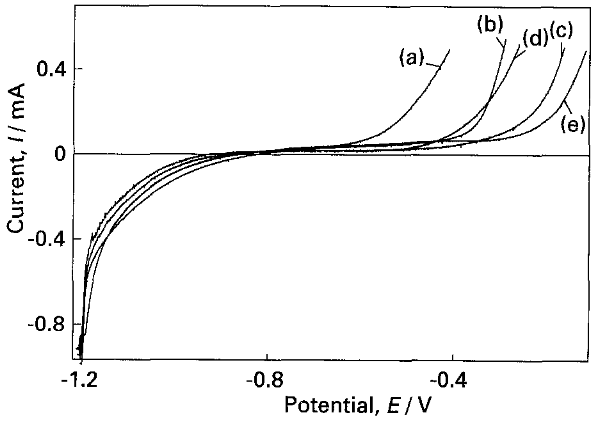

Fig. 6. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in deaerated sodium perchlorate solutions with (a) no sodium triphosphate, (b) 0.1 mM sodium triphosphate (pH 9.7), (c) 1 mM sodium triphosphate (pH 10.7), (d) NaOH (pH 9.7) and (e) NaOH (pH 10.7). In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

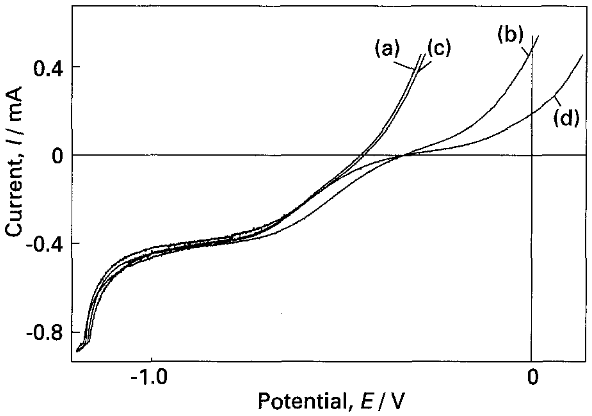

Fig. 7. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in aerated sodium perchlorate solutions at (a) pH 5.0, (b) pH 5.0 + 1 mM sodium silicate, (c) pH 7.0 and (d) pH 5.0 + 1 mM sodium silicate. In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

Therefore, as with sodium silicate in unbuffered solutions, trisodium phosphate (Na_3PO_4) is effective as a corrosion inhibitor for iron by inhibiting the anodic dissolution of the metal. However the reduction of the corrosion rate in the pH range 9.7–11.7 can be entirely accounted for by the change in pH caused by the addition of the trisodium phosphate.

3.5. *Corrosion of iron in the presence of sodium silicate in unbuffered solutions in the pH range 5–7*

Figure 7 compares results for iron in aerated 0.1 M sodium perchlorate solution for the conditions (a) pH 5, (b) pH 5 + 1 mM sodium silicate, (c) pH 7 and (d) pH 7 + 1 mM sodium silicate. The presence of 1 mM sodium silicate at pH 5 and 7 in unbuffered

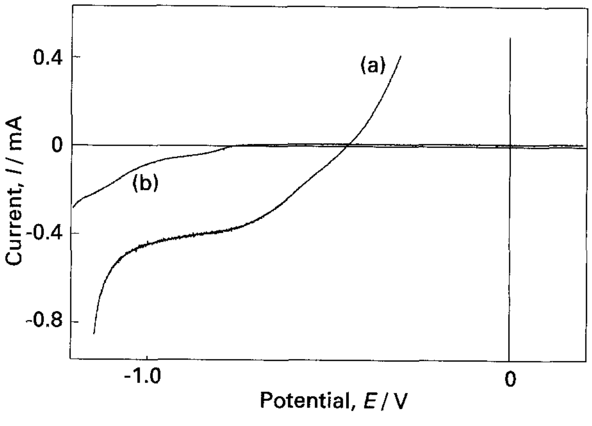

Fig. 8. Potential–current diagram for a rotating iron disc (area 0.13 cm^2) in aerated (a) 0.1 M sodium perchlorate (pH 7.0) and (b) pH 7.0 buffer consisting of 0.065 M Na_2HPO_4 and 0.042 M NaH_2PO_4. In all cases the iron was rotated at 8 rps on open circuit for 2 h prior to measurements.

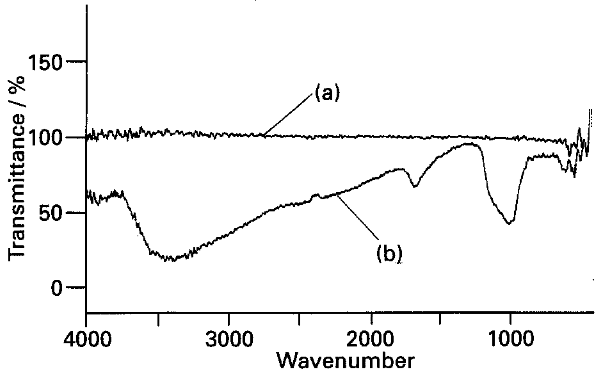

Fig. 9. *Ex situ* reflectance FTIR analysis of iron coupons immersed for 72 h in (a) 10 mM trisodium phosphate (pH 11.7) and (b) pH 7.0 buffer consisting of 0.065 M Na_2HPO_4 and 0.042 M NaH_2PO_4.

environments produces considerable retardation of the anodic reaction. Electrochemical impedance spectroscopy performed on an iron electrode immersed in aerated 0.1 M sodium perchlorate (pH 5 and 7) solutions indicated that a film was present on the surface at the rest potential obtained in the presence of 1 mM sodium silicate. However, the analogous polarization experiments conducted at a dissolved silicate level of 0.1 mM showed no anodic inhibition at either pH 5 or 7. Silicic acid has a solubility limit of approximately 1 mM and thus it is concluded that solid H_2SiO_3 is precipitated at anodic sites at the electrode surface thus inhibiting the iron dissolution reaction.

3.6. *Corrosion of iron in a phosphate buffer of pH 7.0*

Figure 8 compares the results for iron in aerated (a) 0.1 M sodium perchlorate and (b) pH 7.0 buffer consisting of 0.065 M Na_2HPO_4 and 0.042 M NaH_2PO_4. At pH 7 in the presence of oxygen and phosphate species the rates of both the anodic and cathodic reactions are retarded when compared to those obtained for 0.1 M sodium perchlorate (pH 7.0). This experiment coupled with the work on phosphate in high pH solutions demonstrates that at relatively high concentrations and in aerated solutions below pH 9.6 phosphate species act as both anodic and cathodic inhibitors.

Figure 9 compares *ex situ* reflectance FTIR analysis of iron immersed for three days in (a) 10 mM trisodium phosphate and (b) the pH 7.0 phosphate buffer. The band on spectra (b) at 1000 wavenumbers is assigned to a phosphorus–oxygen stretch. No such peak is observed on (a) and thus the spectra illustrate the difference in inhibitive behaviour of phosphate at pH 7 and pH 11.7.

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