Study of the influence of phosphoric acid in steel anaerobic corrosion via the hydrogen evolution reaction.

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Although it is well known that the phosphate species are quiet electrochemically inert when considering their calculated redox potential, few studies since the end of 80’s reported electrochemical phenomenon observed in the reduction domain which were linked to the presence of phosphate species. Some authors proposed that phosphate ions and weak acids in general catalysed the electrochemical reduction of water [1-3] following the kind of reactions written above:

Electrochemical reactions

\[
\begin{align*}
\text{H}_2\text{PO}_4^- + e^- & \rightarrow \text{H}_3\text{ad} + \text{HPO}_4^{2-} \quad (1) \\
\text{H}_3\text{ad} + \text{H}_2\text{PO}_4^- + e^- & \rightarrow \text{H}_2 + \text{HPO}_4^{2-} \quad (2) \\
\text{Acido-basic equilibrium} \quad \text{H}_2\text{PO}_4^- + \text{OH}^- & \leftrightarrow \text{H}_2\text{O} + \text{HPO}_4^{2-} \quad (3)
\end{align*}
\]

Combining the reactions, the reduction of water was obtained

\[
2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (4)
\]

Marinovic and Despic [1] assumed that the hydrogen evolution was more likely to occur from species other than water, since the bond between the hydrogen atom and the rest of the molecule is weaker in weak acid compared with the hydrogen-oxygen bond in a water molecule. This was shown on silver electrodes [2] and also on platinum ones [1]. In a previous work [3], we showed that phosphate ions exhibited the same electrochemical behaviour on stainless steel. A theoretical model was proposed according to the experimental data the model showed that a significant quantity of molecular hydrogen was produced by the mechanism presented above.

In the present paper, the influence of phosphoric acid on hydrogen evolution reaction has been studied by voltammetry on platinum and stainless steel rotating disc electrodes. A linear correlation between acid concentration and the absolute value of the current at certain reduction potential has been verified. The effect of the pH value of the solution in the obtained current has demonstrated to be strongly related to the dissociation state of the acid.

In a second part, as the hydrogen evolution reaction is the principal cathodic reaction of metal corrosion in anaerobic aqueous environments, the role that weak acids can play in this process was studied. Corrosion experiments on carbon steel were carried out in phosphoric acid solution under anaerobic conditions. The influence of hydrogen in the solution was also studied. In the absence of oxygen, a substantial increase of corrosion rate was found when carbon steel samples were submerged in low phosphoric acid concentration solution compared to that obtained in distilled water.

References