

Effect of an Alkyl N-aminodimethylphosphonate on the Passivity of Mild Steel as a Function of pH, Studied by EIS and XPS

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The adsorption and the effects on the passivity of a mild steel of an alkyl N-aminodimethylphosphonate, a molecule with two phosphonate groups and a long alkyl chain $-C_n-$ ($12 \leq n \leq 22$), was studied as a function of pH (from 7 to 13), by X-ray Photoelectron Spectroscopy (XPS) and Electrochemical Impedance Spectroscopy (EIS). This molecule is used as a demoulding agent in aqueous phase for steel concrete moulds in the building industry, but it appears to be a poor corrosion inhibitor of steel (E24 steel according to AFNOR, equivalent to an ASTM A283C-A570Gr33 steel) (1). The study was carried out at the corrosion potential E_{cor} .

XPS results show that the surface layer developed on the steel immersed at E_{cor} in the diphosphonate solution ($7 \leq \text{pH} \leq 13$) consists of Fe_2O_3 , covered by a very thin layer of FeOOH . The thickness of the oxide layer measured by XPS is independent of the pH and is equal to 3.2 ± 0.6 nm. XPS analysis also demonstrated the adsorption of the diphosphonate on the outer layer of FeOOH for $\text{pH} \leq 7$ and the absence of adsorption for $\text{pH} \geq 8$ (Fig. 1). Indeed, the zero charge pH of goethite is 7.55 and above this pH, the steel surface and the diphosphonate molecule are both negatively charged, which prevents the adsorption of the diphosphonate.

For $11 \leq \text{pH} \leq 13$, the steel is covered by a protective passive film. For $\text{pH} \leq 10$, the passive film breaks down and pitting is observed. The pits get deeper and more numerous with decreasing pH. This transition of behaviour observed between pH 11 and 10 is explained by the $[\text{Cl}^-] / [\text{OH}^-]$ ratio of the diphosphonate solution that becomes, for $\text{pH} \leq 10$, larger than a threshold value beyond which localized corrosion occurs (2-3).

On the basis of the XPS (Fig. 1) and EIS results (Fig. 2), physical models of the steel / diphosphonate interface at E_{cor} are proposed as a function of pH. For $11 \leq \text{pH} \leq 13$, the electrode impedance roughly equals the passive film impedance (film resistance R_f in parallel with a constant phase element relative to the film CPE_f). For $8 \leq \text{pH} \leq 10$, pitting is translated in the equivalent circuit by a charge transfer at the pits walls (electrolyte resistance through the pits R_{el} , charge transfer resistance R_t and pseudo double-layer capacitance CPE_{dl}) in parallel with the passive film formation / dissolution. Finally, at pH 7, the adsorption of diphosphonate molecules must be taken into account in addition to pitting, which gives rise to a mass transport phenomenon (Z_D), likely of dissolved oxygen towards the pits walls through the adsorbed layer (Fig. 3).

The parameters of these models were fitted. The agreement between experimental and theoretical curves was very good. The fitting procedure provided values for some physical parameters, such as the electrolyte

resistance R_Ω and R_f , from which the film capacitance C_f was calculated (4). Finally, from the C_f value and the film thickness estimated by XPS, the dielectric constant of the oxide layer ϵ was assessed as a function of pH and its values were compared to those found in the literature.

REFERENCES

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FIGURES

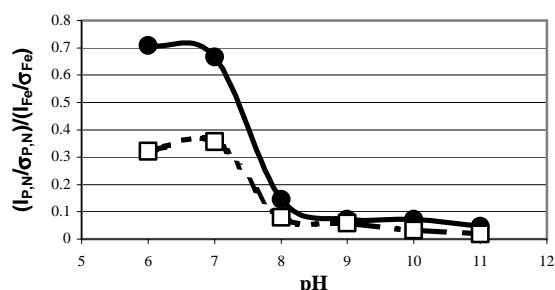


Fig. 1. Adsorption of the diphosphonate on steel as a function of pH: normalized XPS intensity of (●) phosphorus P2p and (□) nitrogen N1s, after 1h of immersion at E_{cor} .

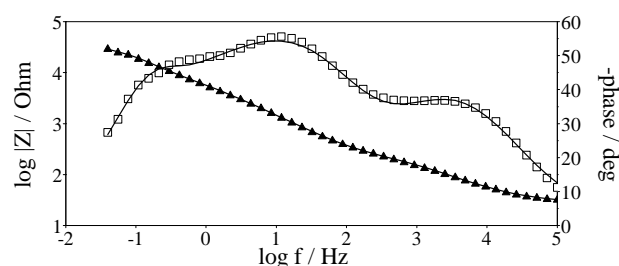


Fig. 2. AC impedance diagrams of the steel electrode, plotted at E_{cor} after 1h of immersion in the diphosphonate solution at pH 7. (▲) Experimental modulus, (□) experimental phase angle and (—) fitted curves.

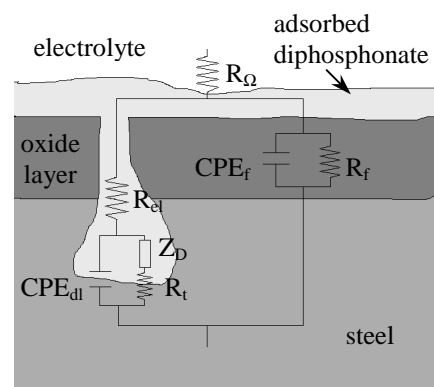


Fig. 3. Physical model of the steel / diphosphonate interface and equivalent circuit for the impedance, at E_{cor} and pH 7.