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Role of pH and calcium ions in the adsorption of an alkyl *N*-aminodimethylphosphonate on steel: An XPS study

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Abstract

The role of pH and calcium ions in the adsorption of an alkyl *N*-aminodimethylphosphonate on mild steel (E24) surfaces was investigated by XPS. Fe $2p_{3/2}$ and O 1s spectra show that the oxide/hydroxide layer developed on the steel surface, immersed in the diphosphonate solution ($7 \leq pH \leq 13$, without Ca^{2+}) or in a filtered cement solution (pH 13, 15.38 mmol l^{-1} of Ca^{2+}), consists of Fe_2O_3, covered by a very thin layer of FeOOH (goethite). The total thickness of the oxide/hydroxide layer is ~3 nm and is independent of the pH and the presence/absence of Ca^{2+}. In the absence of Ca^{2+} ions, the N 1s and P 2p spectra reveal that the adsorption of the diphosphonate on the outer layer of FeOOH takes place only for pH lower than the zero charge pH of goethite (7.55). At pH 7, the adsorbed diphosphonate layer is continuous and its equivalent thickness is ~24 Å (monolayer). In the presence of Ca^{2+} ions, the C 1s and Ca 2p signals indicate that calcium is present on the steel surface as calcium phosphonate (and $Ca(OH)_2$, in very small amount). The adsorption of the diphosphonate molecules on the steel surface is promoted in alkaline solution ($pH > 7.55$) by the doubly charged Ca^{2+} ions that bridge the O^- of goethite and the P–O^- groups of the diphosphonate molecules. The measured values for the Ca/P intensity ratio are in the range 0.75–1, which suggests that the diphosphonate molecules are adsorbed on steel forming a polymer cross-linked by calcium ions through their phosphono groups. In the presence of Ca^{2+} ions in alkaline solution, the adsorbed diphosphonate layer is discontinuous and the surface coverage is found to be ~34%.

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1. Introduction

Phosphonates are known to be environmentally friendly corrosion inhibitors, which form adsorbed layers on oxide- or hydroxide-covered metal surfaces.

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Many works can be found in the literature about the interactions between phosphonates and iron or steels. In particular, Ochoa et al. studied the interaction between phosphonocarboxylic acid salts (monophosphonates) and a carbon steel [1,2]. Kálmán et al. investigated the corrosion inhibition of carbon steel by 1-hydroxy-ethane-1,1-diphosphonic acid (HEDP) in neutral solutions [3]. Alkane-mono- and diphosphonates were successfully applied to form self-assembled surface layers on iron [4]. Surface modification of metals by self-assembled molecules is a potential method of corrosion protection. Another example is the work of Rohwerder et al. who studied the protective properties of self-assembled phosphonate films on aluminium oxides [5].

Phosphonates are also used in herbicides. Their fate in the environment is of significant interest and the nature of their adsorption on mineral surfaces plays a significant role in their degradation. Thus, Sheals et al. studied the adsorption of *N*-(phosphonomethyl)glycine (a monophosphonate called glyphosate) on goethite [6].

The effect of bivalent cations on the adsorption of phosphonates on mild steels has also been investigated by some authors. In particular, the presence of Ca^{2+} ions in neutral aqueous media containing HEDP was found to increase considerably the amount of phosphonate adsorbed on carbon steel surfaces [7]. Moreover, addition of both Ca^{2+} and Zn^{2+} ions to HEDP solution increased further the corrosion inhibition efficiency [8]. Another example is the work of Nakayama who studied the inhibitory effects of nitrilotris(methylenephosphonic acid) (NTMP) on cathodic reactions of steels used for reinforced concrete and city gas pipes, in saturated $Ca(OH)_2$ solutions [9]. His results suggested that NTMP was probably adsorbed on the cathodic portions of steel surfaces, mainly forming a polymer cross-linked by calcium ions through its three phosphono groups.

The alkyl *N*-aminodimethylphosphonate, a molecule with two phosphono groups and a long alkyl chain with 14 carbon atoms, is used in the building industry as an agent in aqueous phase to reduce the adhesion of concrete to steel moulds [10,11]. This chemical agent, called Aquadem®, is sprayed on the mould surfaces prior to pouring the concrete. Therefore, the surface pH of steel can vary between 7 (initial pH of the diphosphonate solution) and 13 (pH of concrete).

For a better understanding of the interaction between the diphosphonate molecules and the steel surface in contact with concrete, the behaviour of E24 mild steel, the constituent steel of most moulds, was studied in an aqueous solution of diphosphonate ($7 \leq pH \leq 13$) and in a filtered cement solution (pH 13), with or without diphosphonate previously sprayed on the steel surface. The filtered cement solution is an electrolyte representative of the liquid phase of concretes. The role of pH and calcium ions (present in concrete) on the adsorption of the diphosphonate was investigated. For this purpose, X-ray photoelectron spectroscopy (XPS) was used.

2. Experimental

2.1. Material and electrolytes

The material was a mild steel of composition 0.18 wt.% C, 0.06 wt.% P, 0.05 wt.% S, and iron (balance), denoted E24 according to the NF A 35-501 French standard, equivalent to a S235JR steel according to the EN 10025 European standard and to a A283C–A570Gr33 steel using the ASTM American standards.

The samples consisted of cross-sections of cylindrical steel rods (0.785 cm^2 surface area), obtained by machining a piece of an industrial mould. The side walls of the rods were covered with cataphoretic paint. Before each experiment, the samples were mechanically polished with diamond paste down to 1 μm.

The two following electrolytes were used:

(i) a filtered cement solution, i.e. the aqueous phase collected by filtration of a cement from Saint-Pierre-la-Cour® (CEM I cement with a water/cement mass ratio equal to 0.5), 90 min after mixing. This electrolyte was chosen because it was considered as representative of the liquid phase of concrete. The concentrations of the main species contained in this solution are reported in Table 1. The pH of this solution was ~13. It contained no chloride ion (no $CaCl_2$ was added to the cement) and

(ii) an aqueous solution of an alkyl *N*-aminodimethylphosphonate i.e., a molecule with two phosphono groups and a long alkyl chain R ($R = C_{14}$ with 14 carbon atoms) [10]; this molecule, denoted in this