Corrosion protection of carbon steel by tetraphosphonates of systematically different molecular size

DOI: 10.1016/j.corsci.2018.09.021

Document Version
Accepted author manuscript

Link to publication record in Manchester Research Explorer

Citation for published version (APA):

Published in:
Corrosion Science

Citing this paper
Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher’s definitive version.

General rights
Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy
If you believe that this document breaches copyright please refer to the University of Manchester’s Takedown Procedures [http://man.ac.uk/04Y6Bo] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.
Corrosion protection of carbon steel by tetraphosphonates of systematically different molecular size

Argyri Moschona,1 Nicoleta Plesu,2 Gellert Mezei,3 Andrew G. Thomas,4*
and Konstantinos D. Demadis1*

1 Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete, Voutes Campus, Heraklion, Crete, GR-71003, Greece
2 Institute of Chemistry Timisoara of Romanian Academy, 300223 Timisoara, Romania
3 Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008-5413, U.S.A.
4 School of Materials and Photon Science Institute, The University of Manchester, Manchester, M13 9PL, United Kingdom

KEYWORDS: Mild steel, organic coatings, phosphonates, acid corrosion, inhibition, XPS, thin films.

ABSTRACT: We study the interaction of six systematically varied tetraphosphonate molecules with carbon steel surfaces by XPS at pH 3. All tetraphosphonates [EDTMP (C2), TDTMP (C4), HDTMP (C6), ODTMP (C8) and DDTMP (C12)] belong to the aminomethylene-phosphonate family, and they possess systematically elongated backbone (from two to twelve methylene groups separating the N atoms). XPS studies were performed on powdered samples and also on immersed carbon steel specimens in aqueous solutions. The XPS results also suggest that the tetraphosphonic acid molecules become significantly deprotonated upon interaction with the carbon steel surface and that the surface interaction of the tetraphosphonic acid family leads to additive adsorption on the steel surface via the phosphonate groups. The mode of corrosion inhibition was studied by potentiodynamic polarization and electrochemical impedance spectroscopy. The changes observed in the impedance parameters, like charge transfer resistance (R_	ext{ct}) and constant phase element (CPE) confirm the strong adsorption on the metal surface. The nature of the protective layer formed on the carbon steel surface was examined by Attenuated Total Reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and optical microscopy.

1. Introduction

Corrosion inhibitors are additives that protect metallic surfaces from water-side corrosion. They are either inorganic [1] or organic [2] species and are purposely added into the water system, usually, in ppm quantities. Their principal purpose is to form thin protective films on the metal surface, either by adsorption [3] or by controlled precipitation in synergy with metal ions [4].

Among the plethora of corrosion inhibitors, phosphonates are often used because they possess a number of important attributes: (a) They are resistant to hydrolysis and high temperatures [5]. This is particularly important when oxidizing biocides are used in the water system for microbiological control or when high-temperature metal surfaces are involved in the system operation. (b) They demonstrate high affinity for the metal oxide layer on the metal surface [6]. (c) They can act as both mineral scale and corrosion inhibitors [7]. (d) The acidic phosphonate (-PO₃H₂) moiety may be singly or doubly
deprotonated (depending on pH), thus allowing the phosphonate moiety to be functional in a wide range of pH values [8]. (e) They can act synergistically with metal ions commonly present in the water system (eg. Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, etc.) or other chemical additives, thus offering superior corrosion protection [9-13].

A number of experimental studies are available in the literature on the use of phosphonates as anti-corrosion agents. For example, Laamari et al. studied the efficiency of HDTMP (C6 in this paper), as corrosion inhibitor for carbon steel in 0.5 M HCl [14]. Interactions of the O and N atoms of the inhibitor with the Fe surface were invoked, but no experimental proof was provided. Zhao et al. reported the anticorrosion efficiency of HDTMP on Mg implants by chemical grafting [15]. Al-Khaldi et al. studied the interaction of aminobutylphosphonic acid with carbon steel surfaces [16]. The authors concluded, based on XPS measurements, that the bifunctional phosphonic acid interacts with the iron oxide layer through both phosphonate and protonated amine ends. Paszternák et al. induced steel surface modification with self-assembled alkylphosphonic acid layers [17]. They found that under the experimental conditions studied the alkylphosphonic acids form a protective coating on the metal surface close to a monolayer. Kavipriya et al. evaluated the inhibition of corrosion of carbon steel in sea water by diethylenetriamine-pentamethylenephosphonic acid (DTPMP) and concluded that it functioned as a cathodic inhibitor [18]. Labjar et al. studied amino-tris(methylene phosphonic) acid (ATMP) as corrosion inhibitor of carbon steel in 1 M HCl and discovered that the corrosion inhibition mechanism of ATMP is controlled by a physisorption process [19]. In a similar study, Kar and Singh reported an evaluation of nitrioltriamethylene phosphonic acid (NTMP, it is the same additive as ATMP above) and (for comparison) nitrioltriacetic acid as corrosion inhibitors of carbon steel in sea-water [20]. Based on XPS studies they proposed a Fe-NTMP surface complex, forming a robust thin film. Felhosi and Kalman studied protective layer formation of a,ω-diphosphono-alkane compounds on iron surfaces [21]. Layer formation proved to be a spontaneous process on iron, and was accomplished by multimolecular adsorption. Fang et al. evaluated ATMP, 1–hydroxyethylidenediphosphonic acid (HEDP), N,N–dimethylidene phosphonoglycine (DMPG), 1–ethylphosphonoethylidenediphosphonic acid (EEDP), and ethylenediaminetetramethylene phosphonic acid (EDTMP, C2, in this paper) for protecting mild steel from corrosion [22]. They concluded that ATMP is the most efficient inhibitor and proposed that both N and O atoms in the ATMP molecule were coordinated with Fe$^{2+}$ in the film. A review by Tsirulnikova et al. summarized the chemistry of various formulations as inhibitors of metal corrosion and scaling in water systems [23].

In this paper the interactions of several tetraphosphonate corrosion inhibitors (shown in Figure 1) with carbon steel surfaces are studied by X-ray photoelectron spectroscopy (XPS) at pH 3. The studied tetraphosphonates (C2, C4, C6, C8) contain systematically elongated polymethylene chains linking the N atoms of the amino-bis(methylene phosphonate) termini. These additives demonstrate strong adsorption on the steel surface *via* the phosphonate groups. The potentiodynamic polarization and EIS data reveal that the corrosion protection is induced by the tetraphosphonate additives, while the results confirm that the phosphonate moiety is able to bind to Fe and form a more-or-less dense and compact layer on the metal surface, depending on the structural features of the additives. The tetraphosphonates with 6 or 8 carbon atoms on the chain create a more efficient packing on the carbon steel surface, while the C2 tetraphosphonate appears to form a thin, incomplete and porous layer.

2. Experimental Section

2.1. Synthesis of tetraphosphonic acids. Ethylenediamine, 1,6-diaminohexane, 1,12-diaminododecane, formaldehyde, and phosphorus acid were purchased from commercial sources and used as received. All organophosphonic acid molecules were synthesized via the Mannich-type (Irani-Moedritzer) reaction. In principle, this reaction allows the clean transformation of a primary amine to an amino-
bis(methylene phosphonic acid) moiety. Literature procedures were followed [24-26]. All organophosphonic acids were isolated as high-purity (> 97 %) solids in > 50 % yields, except EDTMP which was kept dissolved in water and used as a 25.4 % w/w stock solution. Schematic structures of all corrosion inhibitors are shown in Figure 1. Single crystals of EDTMP (C2) and HDTMP (C6) were prepared by leaving an aqueous solution of these tetraphosphonic acids to partially evaporate under ambient conditions.

2.2. X-ray crystallography. X-ray diffraction data were collected at room temperature from a single-crystal mounted atop a glass fiber under Paratone-N oil, with a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by employing SHELXTL direct methods and refined by full-matrix least squares on F2, using the APEX2 software package [27]. All non-H atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined using a riding model, except for the water and phosphonic acid O–H hydrogens, which were located from the Fourier difference density maps and refined using a riding model with O–H distance restraints. Crystallographic details are summarized in Table 1.

Table 1. Crystallographic data for compounds C2 and C6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>EDTMP·H₂O (C2)</th>
<th>HDTMP (C6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₆H₂₂N₂O₁₃P₄</td>
<td>C₁₀H₂₈N₂O₁₂P₄</td>
</tr>
<tr>
<td>F.W. (g·mol⁻¹)</td>
<td>454.14</td>
<td>492.22</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/n</td>
<td>p₁</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.105(3)</td>
<td>5.8532(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.898(4)</td>
<td>7.7735(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.168(4)</td>
<td>10.8922(3)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>93.221(2)</td>
</tr>
<tr>
<td>β (°)</td>
<td>95.01(2)</td>
<td>99.503(2)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>96.298(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1674.8(9)</td>
<td>484.445(10)</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.37×0.30×0.25</td>
<td>0.25×0.16×0.08</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>ρcalc (g·cm⁻³)</td>
<td>1.801</td>
<td>1.687</td>
</tr>
<tr>
<td>2θ range (°)</td>
<td>2.28-27.98</td>
<td>1.90-28.61</td>
</tr>
<tr>
<td>Data/Restraints/</td>
<td>3617/0/242</td>
<td>2472/4/136</td>
</tr>
<tr>
<td>Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nº reflections</td>
<td>10227</td>
<td>2472</td>
</tr>
<tr>
<td>Independent reflections [I &gt; 2σ(I)]</td>
<td>3305</td>
<td>2031</td>
</tr>
<tr>
<td>GoF, F²</td>
<td>1.052</td>
<td>1.029</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>R Factor [I &gt; 2σ(I)]</td>
<td>$^aR1 = 0.0341$, $^a_wR2 = 0.0936$</td>
<td>$^aR1 = 0.0339$, $^a_wR2 = 0.0452$</td>
</tr>
<tr>
<td>R Factor (all data)</td>
<td>$^aR1 = 0.0372$, $^a_wR2 = 0.0961$</td>
<td>$^aR1 = 0.0801$, $^a_wR2 = 0.0857$</td>
</tr>
<tr>
<td>CCDC Reference Code</td>
<td>1561765</td>
<td>1561766</td>
</tr>
</tbody>
</table>

$^aR1(F) = \frac{\Sigma|F_o| - |F_c|}{\Sigma|F_o|}; \quad wR2(F^2) = \left[\frac{\Sigma w(F_o^2 - F_c^2)^2}{\Sigma F_o^4}\right]^{1/2}.$

2.3. **XPS studies.** All spectra were recorded using a Kratos Axis Ultra X-ray photoelectron spectrometer, equipped with a monochromatic Al Kα X-ray source ($hν = 1486.6$), hemispherical analyser with magnetic lens system and low energy electron source for charge compensation. Spectra were recorded in normal emission geometry, and all spectra were aligned on the binding energy scale relative to the C 1s peak at 284.8 eV. Binding energies are quoted to ± 0.1 eV. Survey spectra were recorded at a pass energy of 160 eV and narrow scans at a pass energy of 40 eV. Peak fitting was done using the CASA XPS software package [28] with 70:30 Gaussian Lorentzian peak shapes unless stated otherwise.

![Figure 1](image-url)  
**Figure 1.** Schematic structures of all tetraphosphonate corrosion inhibitors.

2.4. **Protocol for carbon steel sample preparation for XPS studies.** Four powder tetraphosphonic acid samples, abbreviated here as C4 (TDTMP), C6 (HDTMP), C8 (ODTMP) and C12 (DDTMP), were analysed in their native state by pressing onto conducting graphite tape. Charge compensation was applied as the powders are insulating. Following this, aqueous solutions of the tetraphosphonic acids were prepared in pH 3 phthalate buffer (Sigma Aldrich) in various concentrations as follows: C2
(EDTMP) 2.00 μL/mL, C4 2.15 mg/mL; C6 1.11 mg/mL; and C8 2.03 mg/mL. C12 would not fully dissolve at pH 3 (most likely due to the long dodecamethylene chain) and was therefore not measured.

Square-shaped mild steel (C1018) specimens of dimensions 1.5 cm × 1.5 cm were prepared by removing any pre-existing oxide or corrosion products by abrading with P240 SiC paper. These were rinsed with deionised water and immersed in the buffer/tetraphosphonic acid solutions for 16 hours. A control sample, containing only phthalate buffer solution was also prepared. After the specimens were removed from solution, they were rinsed with deionized water and dried using N2 gas in a N2-filled glove box attached to the load lock of the XPS instrument. This ensured that the specimens were not exposed to air between the time they were removed from solution and the XPS spectral measurements. This has been shown to be crucial in reducing the oxidation of the steel in air [29]. The mild steel specimens were attached to the sample-mounting bar by means of conducting double sided graphite tape.

2.5. Protocol for carbon steel sample preparation for gravimetric studies. A modified protocol is used based on NACE Standard TM0169-95 (Item No. 21200), National Association of Corrosion Engineers, Houston TX, U.S.A. [30]. Corrosion specimens (pretreated carbon steel, grade C1010) are prepared according to the well-established protocol above. Each specimen is immersed in a control solution (no inhibitor, pH = 3) or in a test solution (containing each of the tetraphosphonic acids at 2 mM concentration, pH = 3) and corrosion progress is monitored by visual inspection for 7 days. Then, the specimens were removed from solution, air-dried, and cleaned by the standard NACE method above to determine corrosion rates from mass loss.

2.6. OCP and Potentiodynamic polarization testing. Potentiodynamic polarization studies were conducted to measure the corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), polarization resistance (R_p) and corrosion rate (R_{corr}), for carbon steel specimens without additives and after their immersion in a test solution containing tetraphosphonates. The electrolyte solution was 3.5 % NaCl. Each electrode (specimen) was immersed in a control solution (no inhibitor, 3.5 % NaCl, with pH adjusted to ~ 3 with HCl) and in a test solution (containing each of the tetraphosphonic acids at 4.9 mM concentration, with pH adjusted to ~ 3, with NaOH). The control solution and test solutions were ultrasonicated for 5 minutes. The experiments were conducted in aerated electrolyte. The experiments were conducted in triplicate.

2.7. Electrochemical Impedance Spectroscopy (EIS) Measurements. Electrochemical impedance spectroscopy (EIS) experiments were also employed to monitor corrosion phenomena. From the evaluation of impedance data, the electrochemical interface behaviour is usually described by simple electrical elements as R, L, and C connected in an adequate equivalent circuit. EIS were performed with an Autolab 302N potentiostat/galvanostat equipped with the FRA2 impedance module. The sinusoidal potential amplitude was 10 mV. All electrochemical measurements were performed at room temperature. All measurements were carried out in a conventional one-compartment three-electrode cell, equipped with two inox counter electrode and Ag/AgCl reference electrode. The exposed surface area of the working electrode used in electrochemical experiments, was 0.785 cm². Electrochemical impedance spectra were recorded at open circuit potentials in 3.5 % NaCl solutions with and without tetraphosphonic acids as the supporting electrolyte. All spectra reported here were measured at the open circuit potential. The tested frequency range was from 0.01 Hz to 100 kHz. The sinusoidal potential amplitude was 10 mV. All electrochemical measurements were performed at room temperature. The experimental data were fitted to the equivalent electrical circuit by a complex non-linear least squares procedure using the ZView- Scribner Associated Inc. software. The EIS and CP tests were performed after one hour immersion time. All the experiments were conducted in triplicate.
2.8. Vibrational Spectroscopy. Attenuated Total Reflectance Infrared (ATR-IR) spectra were recorded with a FT/IR-4200 JASCO Spectrophotometer, equipped with PIKe ATR (MIRacle), DTGS detector, Ge crystal plate. These experiments were set at a resolution of 4 cm\(^{-1}\) in the range of 4000–600 cm\(^{-1}\). All data were analyzed by the Spectral Manager Version 2 software.

3. Results and Discussion

3.1. Structural description

3.1.1. EDTMP (C2). Figure 2 (upper) shows the molecular structure of C2 lattice (the water molecule has been omitted). The molecule as a whole possesses a zwitterionic structure, as expected. Two of the four phosphonic acid moieties are monodeprotonated (-PO\(_3\)H\(^-\), one from each side), whereas the remaining two are fully protonated (-PO\(_3\)H\(_2\)). The two tertiary N atoms are protonated (≡NH\(^+\)) via an intramolecular protonation process. C-C [1.517 (2) Å], C-P [1.818(2) Å – 1.828(2) Å], C-N [1.503(2) Å – 1.518(2) Å], and P-O [1.475(2) Å – 1.558(2) Å] bond lengths are similar to those reported for (NH\(_4\))\(_2\)(EDTMP) \[31\].

However, upon closer examination of the P-O bond lengths it becomes evident that they are separated into two categories, the “short” and the “long” bonds. All “long” bonds are associated with the protonated –P-OH moiety, whereas the “short bonds” are from the non-protonated portion of the -PO\(_3\) moiety. Distinction between the P=O and the P-O\(^-\) bond lengths is not possible because these are of equivalent length, based on the crystallography results. Therefore, this leads to the conclusion that the negative charge is delocalized over the O=P-O\(^-\) moiety. Similar observations have been noted for metal-coordinated (and mono-deprotonated) phosphonates \[34\]. Figure 2 (lower) gives a view of the packing in the structure of C2, including the lattice water molecules (exaggerated green spheres). All hydrogen bonding interactions are given in Table 2. The water molecule interacts through three hydrogen bonds (2.702, 2.716 and 2.467 Å) with phosphonate oxygens (originating from three different C2 molecules. There is a plethora of other hydrogen bonds as well. The two NH\(^+\) moieties from the same C2 molecule form two hydrogen bonds (2.686 and 2.729 Å) with the same phosphonate oxygen from a neighboring C2 molecule. This particular interaction forces the molecule to acquire a “syn” configuration, with the two NH\(^+\) moieties pointing towards the same direction (N-C-C-N torsion angle 86.21°).

3.1.2. HDTMP (C6). C6 crystallizes as the anhydrous form, and is located on an inversion center within the triclinic crystal lattice (Figure 3, upper). As with C2, two phosphonate groups of the zwitterionic molecule are singly protonated (-PO\(_3\)H\(^-\)), whereas the other two are doubly protonated (-PO\(_3\)H\(_2\)). The tertiary N atoms (≡NH\(^+\)) are also protonated. An extended 3D-network is formed by H-bonding between the phosphonate groups and NH\(^+\) moieties (Figure 3, lower). H-bonding parameters are summarized in Table 2. C-C [1.514(2) – 1.523(3) Å], C-P [1.821(2) Å – 1.826(2) Å], C-N [1.496(2) Å – 1.514(2) Å], and P-O [1.478(1) Å – 1.555(1) Å] bond lengths are similar to those reported for (en)(HDTMP) (en = ethylene diammonium dication) \[35,36\]. The NH\(^+\) moiety forms a hydrogen bond (2.739 Å) with a phosphonate oxygen from a neighboring C6 molecule. This N-H···O(P) interaction is augmented with a (P)O-H···O(P) interaction (2.565 Å), thus forming an intermolecular 7-membered ring. The C6 molecule is fully extended with a N-C-C-N torsion angle 180°. All hydrogen bonding interactions are shown in Table 2.

Table 2. Summary of the hydrogen bonding data for C2 and C6.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-H1F···O1W</td>
<td>0.820(2)</td>
<td>1.751(2)</td>
<td>2.467(3)</td>
<td>144.9(1)</td>
<td></td>
</tr>
<tr>
<td>O5-H5C···O2</td>
<td>0.820(2)</td>
<td>1.700(2)</td>
<td>2.512(2)</td>
<td>170.3(1)</td>
<td></td>
</tr>
<tr>
<td>O3-H3C···O7</td>
<td>0.802(2)</td>
<td>1.689(2)</td>
<td>2.500(2)</td>
<td>169.8(1)</td>
<td></td>
</tr>
<tr>
<td>N1-H1E···O4</td>
<td>0.89(3)</td>
<td>1.84(3)</td>
<td>2.686(2)</td>
<td>160(2)</td>
<td></td>
</tr>
<tr>
<td>N2-H2E···O4</td>
<td>0.83(2)</td>
<td>1.93(2)</td>
<td>2.729(2)</td>
<td>161(2)</td>
<td></td>
</tr>
<tr>
<td>O11-H11A···O6</td>
<td>0.820(2)</td>
<td>1.708(2)</td>
<td>2.509(2)</td>
<td>165.5(1)</td>
<td></td>
</tr>
<tr>
<td>O8-H8A···O12</td>
<td>0.819(2)</td>
<td>1.735(2)</td>
<td>2.535(2)</td>
<td>165.0(1)</td>
<td></td>
</tr>
<tr>
<td>O10-H10A···O9</td>
<td>0.829(2)</td>
<td>1.708(2)</td>
<td>2.467(2)</td>
<td>153.0(1)</td>
<td></td>
</tr>
<tr>
<td>O1W-H1D···O7</td>
<td>0.77(4)</td>
<td>2.00(4)</td>
<td>2.716(3)</td>
<td>153(3)</td>
<td></td>
</tr>
<tr>
<td>O1W-H1C···O6</td>
<td>0.75(4)</td>
<td>1.97(4)</td>
<td>2.702(3)</td>
<td>165(4)</td>
<td></td>
</tr>
</tbody>
</table>

**EDTMP (C2)**

| O1-H1···O5#  | 0.785(16) | 1.748(16) | 2.5326(18) | 176(2)   |
| O3-H3···O5#  | 0.810(16) | 1.755(16) | 2.565(2)   | 177(3)   |
| O4-H4···O6#  | 0.789(16) | 1.764(16) | 2.552(2)   | 177(3)   |
| N1-H10···O2# | 0.98      | 1.85      | 2.7390(19) | 150.1    |

**HDTMP (C6)**

![Diagram of compounds with atom coordinates and bond lengths]
3.2. XPS studies

Figure 4 shows survey spectra recorded from the pure tetraphosphonic acid powders (upper panel) and the mild steel specimens which had been immersed for 16 hours in solutions of the tetraphosphonic acids at pH 3 (lower panel). Spectra of the pure powders show only C, O, N and P derived peaks as expected. Spectra of the solution-immersed mild steel specimens show, in addition to the above peaks, additional peaks arising from Fe, the strongest being the Fe 2p peak at a binding energy of around 711
eV. For the pH 3 buffer immersed sample we see no evidence of N or P in the survey scan. C and O 1s peaks are observed for this buffer sample, which may arise from the phthalate. No evidence of K, from the buffer, is seen in any of the survey spectra.

Figure 4. XPS Survey scans of phosphonate powders (upper) and steel coupons immersed in pH 3 solutions of the phosphonates (lower). Spectra are aligned to the C 1s peak at 284.8 eV. EDTMP (C2) is missing from the upper panel, since it was available as a solution.

Detailed core level scans of N 1s, P 2p and Fe 2p recorded from the tetraphosphonic acid pure powders and mild steel specimens are shown in Figure 5. N 1s spectra recorded from the powders (Figure 5a) can be fitted with two peaks at binding energies of 399.8 eV and 401.9 eV, and are assigned to deprotonated and protonated tertiary amine groups, respectively. As can be seen in all cases the protonated form is dominant for all powders, as expected, because of intramolecular protonation of N by an acidic proton from a phosphonic acid group. This is also corroborated by the crystal structures of C2 and C6.

In the equivalent spectra from the steel specimens in Figure 5b the two peaks are almost of equal intensity, suggesting the tetraphosphonic acid molecules become significantly deprotonated. This is perhaps not surprising since they are deposited from solution. The degree of deprotonation appears to increase with the chain length, but, for the reasons discussed below, it is difficult to make any firm
conclusions about why it occurs. The difficulty lies in the fact that the sample immersed in phthalate buffer also shows the presence of N, which we believe is due to traces of nitride from the steel coupons. The N 1s binding energy of this peak at 399.9 eV, the nitride peak overlaps with the deprotonated amine and it is not possible to determine the variation in N content in the steel coupons used. Of some interest is the appearance of a third peak at a binding energy of 403.0 eV in sample C6 and 404.4 eV in sample C4. The origin of these peaks is unclear since N 1s peaks at these binding energies are usually associated with nitrite or nitrate formation, and result from the electronegative oxygen reducing the charge density on the nitrogen.
Figure 5. High resolution XPS scans of (a) N 1s from phosphonate powder (b) N 1s from steel immersed in phosphonate solution, (c) P 2p – powder, (d) P 2p – steel (e) Fe 2p – steel (f) O 1s – powder and (g) O1s – steel. The Fe 2p spectra are fitted with multiplets, color-coded as shown in the legend.

The P 2p spectra shown in Figure 5c for powders C4, C8 and C12 are composed of a single spin-orbit split doublet arising from the 2p$_{3/2}$ (134.5 eV) and 2p$_{1/2}$ (135.4 eV). This is consistent with a singly protonated phosphonate group. There is some evidence that sample C6 has a small proportion of doubly protonated phosphonate in the powder form, shown by the doublet at a binding energy of 135.7/136.6 eV (the green doublet).

For the steel coupons in Figure 5d there is a downward shift of the dominant doublet binding energy to 133.7 eV. This is consistent with deprotonation of the phosphonate group. For phosphates it has been shown that for each proton removed there is a downward shift in binding energy of around 1 eV [37]. We also see evidence of an increase in the amount of doubly protonated phosphonate for the C6 sample. This correlates with the larger relative decrease in the deprotonation of the amine in C6 but it is not likely that these are linked, since the differences in the P 2p spectra of C4 and C8 are not as apparent as the change in degree of deprotonation of the amine. We note that for C4, the region to higher binding energy of the main peak at around 135 eV is not well fitted, suggesting there may also be
some doubly protonated phosphonate groups in this region as well. C8 shows no evidence of a second phosphorus chemical state. The data from the steel coupons – where we see an increase a shift to a doubly deprotonated molecule, would support a binding mechanism of the molecules to the iron via the phosphonate groups [38]. The fact that C6 shows both completely deprotonated and doubly protonated species, may suggest that this molecule binds through two phosphonate groups. It is noted however that the lower concentration of C6 may play a part in this, and further work will be carried out to confirm the effect of concentration on the adsorption mechanism.

The Fe 2p spectra in Figure 5e show evidence of metallic and oxidized Fe for all samples. The relative amounts of each are shown in Table 3. The metallic Fe 2p3/2 peak at a binding energy of 706.6 eV is fitted with an asymmetric Lorentzian peak which accounts for excitation of conduction electrons by the photoelectrons in metallic systems [39]. Oxidized iron is notoriously difficult to fit with a high degree of certainty, mainly due to the multiplet structure of the high spin compounds of iron [40,41]. Each Fe compound gives rise to a distinct set of multiplets with different separations and areas. For the spectra noted here, with the exception of C4, the spectra are well fitted by a combination of FeO, γ-Fe₂O₃ and an averaged FeOOH species. The residual for these fits is around 1.5 - 1.6 which compares well to an electrochemically oxidized Fe sample studied by Biesinger et al. [40] and would seem like a reasonable comparison. It is noted that there is also the possibility of FePO₄ formation at the surface [42], but since detailed multiplet structures have not been determined in the literature for this material peaks for this have not been fitted. The specimen immersed in C4 solution is not well fitted by this combination of peaks. It can be seen that compared to the other solutions, the “oxidized Fe” peak of C4 seems to be weighted more heavily to the higher binding energy side. This might suggest more Fe²⁺ oxidation states, such as carbonates, or possibly Fe(II) phosphate/phosphonate since the Fe²⁺ satellite sits at around 716-718 eV [43,44]. In any case, a satisfactory fit with multiplets from standard compounds could not be achieved for C4. If one adds the multiplet structure of FeCO₃, as a representative Fe(II) compound, then γ-Fe₂O₃ is lost from the fitting. This is the fit shown in Figure 5e for sample C4. The peak areas suggest that C6 results in the largest metallic iron peak in the spectra, followed by C8, which has a similar metallic Fe composition to the sample immersed in pH 3 phthalate buffer. C6 also shows the highest concentration of FeO at the surface, although the ratios for the different oxide/hydroxide species should be regarded with some degree of caution due to the large number of parameters involved [40].

Table 3. Iron composition based on fitting to Fe 2p XPS data. Note the values and actual compositions may vary somewhat from these values.

<table>
<thead>
<tr>
<th></th>
<th>Fe⁰</th>
<th>FeO</th>
<th>γ–Fe₂O₃</th>
<th>FeOOH</th>
<th>“FeCO₃”</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>14.4</td>
<td>43.5</td>
<td>10.86</td>
<td>31.1</td>
<td>-</td>
</tr>
<tr>
<td>C4</td>
<td>29.1</td>
<td>34.9</td>
<td>23.4</td>
<td>12.7</td>
<td>-</td>
</tr>
<tr>
<td>C6</td>
<td>35.0</td>
<td>55.6</td>
<td>5.2</td>
<td>4.2</td>
<td>-</td>
</tr>
<tr>
<td>C8</td>
<td>19.6</td>
<td>30.2</td>
<td>-</td>
<td>30.8</td>
<td>19.4</td>
</tr>
<tr>
<td>Buffer</td>
<td>29.1</td>
<td>33.3</td>
<td>25.5</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

The O 1s spectra shown in Figure 5f and 5g shed some further light on the degree of oxidation of the steel surface. For the powders, two peaks, of similar intensity, are observed at binding energies of 531.7 eV and 532.9 eV, in relatively good agreement with O 1s spectra recorded from phenyl phosphonic acid adsorbed on metal oxide surfaces [38,41]. We note that these binding energies are also consistent with the presence of C=O and C-OH which are likely to be present as contaminants on surfaces exposed to atmospheric pressure [42]. This may also explain the slight variations in the FWHM of the peaks required to adequately fit the O 1s spectra. For the phosphonates on steel placed in phthalate buffer at pH 3 a third peak is observed at a binding energy of 530.0 eV, consistent with the
presence of iron oxide [42]. In addition, we see that the peak at a binding energy of 531.5 eV increases in intensity relative to the peak at 532.9 eV. This can be explained by two phenomena. Firstly, adsorption of the phosphonates on the iron surface involves deprotonation of the phosphate as observed in the P 2p spectra discussed above. In addition, this region is also associated with the presence of metal hydroxides [42]. Comparing the oxide/hydroxide peak intensity in the Fe 2p and O 1s spectra one can see a correlation with the amount of iron oxide for the different powders. Interestingly, the two samples with the lowest oxide content display poor (C2) and good (C4) corrosion inhibition efficiency, as discussed below. Recent XPS measurements performed under nitrogen as is the case in the present work, suggest that a corrosive medium leads to removal of the oxide, with adsorption directly to the metal surface [42,43]. However, other reports suggest that the presence of an oxide/hydroxide layer mediates Cl− adsorption at the steel surface [44,45]. It was shown by Morales-Gil and co-workers [42,43] that exposure to ambient air, even for less than a minute after removal from the corrosive environment, leads to oxidation of the steel surface, whereas transfer to the XPS instrument under N2 gas indicated that imidazolium adsorbed to the bare steel surface – i.e. the oxide was removed by the corrosive medium. Although this work reported here also employed sample transfer to the XPS instrument under N2 gas the acidic medium used a pH 3 buffer, which one might expect to be less corrosive than HCl, as used by Morales-Gil and co-workers. Furthermore, the inhibitors used in the present work are phosphonates, with functional groups known to bind relatively strongly to metal oxides [38,41].

All five tetraphosphonic acids were evaluated for their corrosion inhibition efficiency at pH 3 and concentration 2 mM. Carbon steel specimens were exposed to the same acidic medium (pH = 3) as the XPS measurements. Visual inspection of the “control” specimen (no additive present) after withdrawal from the medium and air-drying, revealed general corrosion throughout the surface of the specimen. In contrast, the presence of tetraphosphonates created a protective coating on the surface. Figure 6 shows all specimens for comparison.

3.3. Corrosion inhibition (mass loss)
In addition to these qualitative observations, general corrosion rates were quantified based on mass loss measurements, and the results are presented in Figure 7. C2 appears to be an ineffective corrosion inhibitor, as it causes metal loss, and most likely facilitates oxide dissolution. This phenomenon could be ascribed to the small size of the molecule, which, in turn, cannot achieve sufficient surface coverage. The corrosion efficiency of the remaining tetraphosphonates (C4, C6, C8 and C12) yield corrosion protection ranging from 28 % to 48 %. It is interesting that the C4 and C6 tetraphosphonates show the lowest corrosion rate and highest surface metallic iron component (see Table 3). This might suggest that the phosphonate binds more strongly to Fe than the oxides and that these “medium” chain lengths lead to more efficient packing on the surface. This is consistent with results reported for 2-mercaptopenizimidazole inhibitors [45].
Figure 6. Unprotected (control) and protected (by the phosphonate additives, as indicated) carbon steel specimens, after exposure for one week to pH = 3.
3.4. OCP and Potentiodynamic polarization testing

The time-dependent variation of OCP potential of carbon steel immersed in 3.5% NaCl solution with different tetraphosphonates is presented in Figure 8.

![Graph showing OCP potential with time for various tetraphosphonates](image)

**Figure 7.** Corrosion rates obtained in the absence (control) and presence of various tetraphosphonates.

**Figure 8.** The variation of OCP potential with immersion time for carbon steel in 3.5% NaCl solution without (control) and with various tetraphosphonates present.

It was observed for all inhibitors that the OCP values decreased in time as a result of dissolution of the passive oxide layer formed at the sample surface (electrodes). This can be explained by the aggressive chloride ions attack. In time, a partial protection of the surface takes place due to formation of corrosion products, capable of blocking the existing pores and cracks on the surface, leading to potential stabilization. In the case of carbon steel immersed in saline solution without additives the OCP reached a constant value after 3000 s. In the presence of tetraphosphonates the OCP reached a constant value more rapidly, after 500 s. In the presence of C12, the OCP values increase immersion, pointing to the formation of a protective barrier. The shorter time needed for OCP stabilization in the presence of
tetraphosphonates, compared to that in their absence suggests the formation of a protecting layer on the metal surface.

The potentiodynamic polarization curves obtained for carbon steel after 60 min immersion in 3.5 % NaCl solution with and without the tetraphosphonate additives are shown in Figure 9.

Figure 9. Potentiodynamic polarization curves for carbon steel after 60 min. immersion in 3.5 % NaCl solutions without (control) and with tetraphosphonates (scan rate = 1 mV/s).

The presence of tetraphosphonic acids in saline solution affects the cathodic and the anodic Tafel slope. The differences observed for the values of cathodic and anodic Tafel slopes suggest that the inhibition corrosion mechanism (adsorption process and protective layer formation) takes place at the active metal surface. It can be observed that the $J_{\text{corr}}$ values for all tetraphosphonates (Table 4) were lower than those for the “control” (no additives), those for C4 and C6 being the lowest. Also, the values of the corrosion rate, $R_{\text{corr}}$, were lower for C4 and C6. The anodic polarization curves were shifted to positive

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{\text{corr}}$, A/cm$^2$</th>
<th>$\beta_c$, V/decade</th>
<th>$\beta_a$, V/decade</th>
<th>$R_p$, Ohm/cm$^2$</th>
<th>$E_{\text{corr}}$, V</th>
<th>$R_{\text{corr}}$, mm/year</th>
<th>IE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>3.25×10^{-5}</td>
<td>0.108</td>
<td>0.135</td>
<td>239</td>
<td>-0.912</td>
<td>0.327</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>8.05×10^{-6}</td>
<td>0.290</td>
<td>0.092</td>
<td>1961</td>
<td>-0.612</td>
<td>0.091</td>
<td>69.85</td>
</tr>
<tr>
<td>C4</td>
<td>4.21×10^{-6}</td>
<td>0.024</td>
<td>0.252</td>
<td>4521</td>
<td>-0.402</td>
<td>0.008</td>
<td>87.05</td>
</tr>
<tr>
<td>C6</td>
<td>4.03×10^{-6}</td>
<td>0.130</td>
<td>0.283</td>
<td>6026</td>
<td>-0.452</td>
<td>0.005</td>
<td>87.99</td>
</tr>
<tr>
<td>C8</td>
<td>7.5×10^{-6}</td>
<td>0.223</td>
<td>0.386</td>
<td>1345</td>
<td>-0.401</td>
<td>0.041</td>
<td>76.92</td>
</tr>
<tr>
<td>C12</td>
<td>9.06×10^{-6}</td>
<td>0.251</td>
<td>0.323</td>
<td>6023</td>
<td>-0.332</td>
<td>0.081</td>
<td>72.12</td>
</tr>
</tbody>
</table>

The values of cathodic ($\beta_c$) and anodic ($\beta_a$) Tafel slope, corrosion potential ($E_{\text{corr}}$), corrosion current density ($J_{\text{corr}}$), polarization resistance ($R_p$), and corrosion rate ($R_{\text{corr}}$) obtained for carbon steel in different solution from the polarization curves shown in Figure 9 are listed in Table 4. The value of $E_{\text{corr}}$ and $J_{\text{corr}}$ were obtained from the extrapolation of anodic and cathodic Tafel lines located next to the linearized current regions and represents the mean value of three determinations.
values for tetraphosphonates of 4 to 12 methylene groups in chain length. The anodic Tafel slope increased with the increase of the chain length of the inhibitor. With the increases of the difference between $\beta_a$ and $\beta_c$, the potential difference between the anodic and cathodic regions decreased and the corrosion rates became lower. In the literature the values reported for the anodic Tafel slope for iron in acidic solution (1.0 N H$_2$SO$_4$ and 1.0 N HCl at 20°C) were around 38-40 mV/decade [46]. The differences observed for the values of Tafel slopes in our case points to a different manner by which the inhibitors are absorbed on the metal surface. The higher Tafel values suggest a slow step in the mechanism of iron dissolution associated with the different adsorption pattern of inhibitor (ligand) present in solution.

Based on the corrosion current density data, the inhibition efficiency was calculated according to Equation 1.

$$IE = \frac{J_{corr} - J_{inh}}{J_{corr}} \times 100 \quad (1)$$

In Equation 1, IE represents the inhibitory efficiency expressed in %, $J_{corr}$ and $J_{inh}$ are the corrosion current density without and with inhibitor, respectively. The best results was obtained for C6 (88%), C4 (87%) and C8 (72%) tetraphosphonic acids.

In all cases a decrease in $E_{corr}$ to less negative values was observed, indicating that carbon steel became passive by simple immersion in aqueous solutions of tetraphosphonic acids. The tetraphosphonic acid can be adsorbed on the carbon steel surface by forming iron-phosphonate complexes capable to provide corrosion protection. The degree of protection is linked with the structure of the newly formed film on the carbon steel surface. In aqueous solution the binding to iron surface is realized by the negatively charged O atoms (resulted from dissociation of the H$^+$ ion from the P–OH group and electron delocalization along the O–P–O segment). Literature reports that layered structures of metal phosphonates formed are predominant with the organic groups being oriented perpendicularly into the interlamellar region [47]. Some differences were observed between the actions of tetraphosphonic acids regarding their ability to bind with the iron surface (mono, bi, tri dentate) and to create a sufficiently compact protective layer (see Figure 10) [48].

The tetraphosphonic acids used herein can form a thin and compact layer on the carbon steel surface as illustrated in Figure 10, lower. They can be deposited on the metal surface by immobilization through surface complexation. The molecules first are anchored covalently on the carbon steel substrate surface via interaction between phosphate groups and metal surface (Figure 10, upper), while the non-coordinated phosphonate group can chelate Fe$^{2+}$ ions released from the substrate by corrosion (Figure 10 lower). Chemical surface immobilization assumes that the molecule is firstly adsorbed onto the iron surface through electrostatic interaction and hydrogen bonds between oxygen atoms from P=O and P–OH groups and hydroxyl groups on the iron substrate forming P–O···H–O–Fe bonds. During the next step the anchored phosphonate molecule via a dehydration reaction is able to link more strongly through P–O–Fe bonds. By this chelating reaction the corrosion products could be retained by the free tetraphosphonic groups, thus remaining in the pores of the newly-formed phosphonate layer. As a result, the pores are sealed and the layer becomes denser and able to provide more effective corrosion protection for prolonged immersion periods. This hypothesis is confirmed by the Fe$^0$ component present in the XPS spectra recorded in the iron specimens which had been immersed for 16 hours in solutions of the tetraphosphonic acids at pH 3 (see Table 3). Formation of similar compact layers was proposed by Chen et al. for magnesium by surface-immobilized of 1-hydroxyethylidene-1,1-diphosphonic acid [49]. The C4 and C6 tetraphosphonic acids show the lowest corrosion rate and highest surface Fe$^0$ component due to the increased capacity of these phosphonate layers to retain iron species present in solution.
Varying the chain length in metal alkylphosphonates can alter the structure considerably. For example the organophosphonic linkers with –CH$_2$– chain lengths of n = 2–4 typically resulted in pillared layered structures [50]. The stable layer formed on the iron surface is capable to protect the surface from aggressive chlorine ions attack, as was reported earlier [51]. Al-Khaldi et al. studied the interaction of aminobutylphosphonic acid with iron surfaces and concluded, based on XPS measurements, that both phosphonate and protonated amine ends of the bifunctional phosphonic acid can interact with the iron oxide layer [16].

ATR-FTIR spectroscopy was used as tool for examination of the layer formed on the carbon steel surface. The spectra are shown in Figure 11, upper. The strong asymmetric phosphonate (-PO$_3^{2-}$) stretch at 1032 cm$^{-1}$ appears in all organophosphonate layers deposited on iron electrodes [34]. The bands at 1240 cm$^{-1}$ and 1030 cm$^{-1}$ was associated with P=O and P-O-C bonds. Scissor deformation and asymmetric deformation bands associated with the methylene group appear at 1450 cm$^{-1}$ and 2845 cm$^{-1}$ and 2914 cm$^{-1}$, respectively. The bands for N-H appear at 1625-1635 cm$^{-1}$ and 3412 cm$^{-1}$. The broad band at ~ 3300 cm$^{-1}$ was attributed to OH stretching vibrations. The absorption peak attributed to OH stretching vibrations (3300 cm$^{-1}$) overlap with the band for N-H, did not disappear in the presence of tetraphosphonic acids but are diminished. This indicates that there are some intermolecular hydrogen bonds between the adsorbed phosphate molecules and iron substrate. The observed bands agree well with those expected, according to literature reports [52-58].

**Figure 10.** Upper: Schematic illustration of surface modification by one phosphonic acids group on oxide surface; R represents the side-group. Lower: Schematic representation of covalent bonding on iron substrate and chelating abilities.
The intensity of the bands observed at 1030 cm\(^{-1}\) (associated with the P-O-C stretch) suggests that in the case of C8, C6 and C12 a thicker and/or more compact layer forms on metal surface. In the case of C4, C6, C8 and C12 the characteristic peak at 1228 cm\(^{-1}\) which corresponds to the P=O stretching mode of free tetraphosphonic disappeared. This suggests further interaction of the P=O moiety and the formation of a new bonds on the iron surface. This observation is corroborated by the higher \(R_{ct}\) value obtained for these tetraphosphonic acids. The lower intensity of this band in the case of C2 indicates its lower capability to anchor to the metal surface via the P=O moiety.

Moreover, the appearance of a new broad band at 2550 cm\(^{-1}\) is an indication for the formation of hydrogen bonds, namely O=P–OH···O associated with the O=P–OH···O interaction [58]. The bands at 2550 cm\(^{-1}\) are higher for C8 followed by those for C6 and C12. From the intensity of these bands it can be concluded that hydrogen bonds are predominant in the layers formed in the presence of C6 and C8. The C6 and C8 additives seem to be the able to form predominantly P—O—H—O—Fe bonds. The absence of the broad band at 2550 cm\(^{-1}\) in the case of C4 points to a binding mode through P—O—Fe bonds.

3.5. Electrochemical Impedance Spectroscopy (EIS) Measurements

Impedance spectra were represented in both complex impedance diagrams (Nyquist plot), and Bode amplitude and phase angle plots. In the Nyquist graph (Figure 12, upper), the imaginary component of
the impedance is plotted as a function of the real component, whereas the Bode representation (Figure 12, lower) shows the logarithm of the impedance modulus $|Z|$ and phase angle as a function of the logarithm of the frequency $f$.

The impedance spectra showed features of an electrode covered with a more-or-less porous layer.

![Nyquist and Bode plots](image-url)

**Figure 12.** Complex plane Nyquist plots (upper) and Bode plots (lower) for iron immersed for 1 hour in 3.5% NaCl solutions in the presence of tetraphosphonic acids.

In the Nyquist plots, Figure 12 upper, the real ($Z_{re}$) and imaginary ($Z_{im}$) components of complex impedance $Z$ are noted. A depressed semicircle appears which has larger diameter than that for saline
solution only (control), as a result of a smaller number of electrons or ions transferred through the interface. The depressed capacitive loop corresponds to surface heterogeneity as a result of surface roughness, dislocation, or adsorption of the phosphonate inhibitor molecules. The variation tendency of impedance value in the Bode modulus plots is consistent with that of semicircle diameter in Nyquist plots.

The Nyquist and Bode phase angle plots presented in Figure 12 show slightly different behavior which could be linked to the structural features of the tetraphosphonic acids. Relaxation phenomena are observed at high, middle and low frequencies (a straight line indicates the existence of diffusion controlled processes). The Bode phase (Figure 12, lower) presents one time constant at middle frequency and an incomplete time constant at low (LF) and frequencies (HF). The loop observed at low frequency is attributed to the mass transfer, at middle frequency is linked to the \( R_t \) and double layer capacitance and at high frequency is due to the response of the porous layer with finite pore length formed on metal surface as was reported by other authors [59]. The capacitive loop observed at high frequency arises from the layer properties and is probably incomplete due to the non-homogenous current distribution on the electrode surface. The simulation of experimental EIS data is sufficiently good for the general shape and characteristic frequencies. At high frequency the experimental diagrams are more poorly resolved than the simulated ones because of electrode roughness and the dispersion phenomena. The time constant for the high frequency curve appears to high frequency due to the dielectric properties of a surface layer.

In the middle frequency region the phase angle presents low phase angle values (\(-40^\circ\)) and high for the tetraphosphonic acid with increased number of methylene groups, the lowest value for phase angle are obtained for C2 and highest for C4, C6 and C8. The high phase angle for tetraphosphonic acids with 4, 6 and 8 methylene groups in structure may be attributed to the decrease in the capacitive behaviour at the metal surface due to decreased metal dissolution rate. The charge transfer resistance (\( R_{ct} \)) increases and the double-layer capacitance (\( C_{dl} \)) decreases usually when on metal surfaces organic molecules are adsorbed [60]. In the presence of tetraphosphonic acids \( R_{ct} \) and electrical double layer at the metal, solution interface increases (decreases of \( C_{dl} \)) due to the adsorption on metal surface and the difference in \( \tau_d \) means difference in the time of adsorption. The adsorption process becomes slow for higher \( \tau_d \) [61]. The results obtained for the time constants (\( \tau_d = C_{dl}.R_{ct} \)) show that the lowest value is obtained for the C2 and highest for C12 and C6. The relaxation time constant (\( \tau_d = 0.23 \) ms for C2, 0.14 ms for C4, 0.15 ms for C6, 0.23 ms for C8 and 0.30 ms for C12). The time constant linked to diffusion controlled process in the low frequency (LF) domain seems to move to lower frequencies indicating an increase in corrosion resistance as the tetraphosphonic acid is anchored to the metal surface and the layer is generated. The position of the peak at low frequencies seems to shift towards lowest value for C4, C8 and C12. The shifts of time constant to lower frequencies in the LF regions is more palpable in the case of C4, C8 and C12 and point to the better hindrances of the corrosion process by these acids and suggest the formation of more compact layer.

The impedance model for the corrosion (Figure 13) was described by the \( R_s \) (electrolyte resistance) in series with a parallel connection of \( C_f \) and \( R_f \) (capacitance and resistance of the layer) which model the layer formed on metal surface, in a series with a parallel connection of elements associated with the double-layer capacitance (\( C_{dl} \)) and charge transfer resistance (\( R_{ct} \)). \( C_d \) was introducing to model some diffusion effects.

In the model presented in Figure 13 due to non-ideal behavior, a constant phase element (CPE) is replaced the pure double-layer capacitor. The used CPE is not an ideal capacitor because of the porosity of the electrode surface and the pores distribution. The CPE is defined by two parameters, CPE-T (\( T \)) and CPE-P (\( \phi \)). If the CPE-P parameter equals 1, then the equation is identical to that of a capacitor. The impedance of constant CPE is given by eq. 2 and the value of perfect capacitor \( C \) can be calculated with eq. 3.
\[ Z_{\text{CPE}} = \frac{1}{T(J,\omega)^\varphi} \]  

(2)

were \(0 < \varphi < 1\) describes the deformation of the circle in the complex plane and \(Q\) is a constant. If \(\varphi = 1\) CPE becomes a perfect capacitor. \(\omega\) is the angular frequencies (in rad·s\(^{-1}\), with \(\omega = 2\pi f\)), \(f\) is the frequency (in Hz).

The \(T\) parameter is proportional to the capacity of the double-layer (eq.3):

\[ T = C_{\text{dl}}^\varphi (R_s^{-1} + A)^{1-\varphi} \]  

(3)

\(C_{\text{dl}}^\varphi\) = capacity of the double-layer, in F
\(R_s\) = solution resistance, in Ω
\(A\) = electrode surface area, in cm²

Figure 13. Schematic representation of the equivalent circuit used for modelling the EIS data for iron immersed in 3.5 % NaCl solutions in the presence of tetraphosphonic acids (upper) and a representative of example simulation of Nyquist and Bode diagrams with suggested model without and with C8 inhibitor (lower).

Figure 13 (lower) reveals a satisfactory correlation for the general shape and frequencies between simulated and experimental curves, except high frequency domain where the reproducibility is less. Possible explanation is the electrode roughness and associated dispersion phenomena. The best fits obtained with the corresponding results are presented in Table 5. In Table 5 are presented the incertitude of parameters \(R_s\), \(R_f\), \(R_{ct}\) and CPE\(_{dl}\)-T. The incertitude of C\(_{dl}\)-T is laying between 0.015 and 12.7\%, for CPE\(_{dl}\)-T between 1.3 and 16.1\% and for CPE\(_{dl}\)-P between 0.07 and 11.1\%.

Table 5. Values of the electric circuit elements for the electrodes after 1 hour of immersion.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Chi-Sqr</th>
<th>Sum-Sqr</th>
<th>$R_f(\Omega \cdot \text{cm}^2)$</th>
<th>$C_f(T(\Omega \cdot \text{cm}^2)$</th>
<th>CPE$_{dl}$ $R(T(\Omega \cdot \text{cm}^2)$</th>
<th>CPE$_{dl}(\Omega \cdot \text{cm}^2)$</th>
<th>$Z_d(T(\Omega \cdot \text{cm}^2)$</th>
<th>$Z_d(P(\Omega \cdot \text{cm}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>7.57x10^{-3}</td>
<td>0.86</td>
<td>9.7±0.92</td>
<td>2.57x10^{-7}</td>
<td>R$_f$</td>
<td>6.83x10^{-3}</td>
<td>0.73</td>
<td>3.56±</td>
</tr>
<tr>
<td>C2</td>
<td>9.69x10^{-3}</td>
<td>1.09</td>
<td>10.1±0.03</td>
<td>1.56x10^{-7}</td>
<td>0.05</td>
<td>1.20x10^{-3}</td>
<td>0.77</td>
<td>4.02</td>
</tr>
<tr>
<td>C4</td>
<td>8.29x10^{-3}</td>
<td>0.94</td>
<td>11.3±0.02</td>
<td>1.38x10^{-7}</td>
<td>0.86</td>
<td>1.00x10^{-3}</td>
<td>0.73</td>
<td>±6.03</td>
</tr>
<tr>
<td>C6</td>
<td>7.94x10^{-3}</td>
<td>0.90</td>
<td>9.8±0.84</td>
<td>1.27x10^{-7}</td>
<td>0.02</td>
<td>1.21x10^{-3}</td>
<td>0.72</td>
<td>188.98</td>
</tr>
<tr>
<td>C8</td>
<td>1.03x10^{-2}</td>
<td>1.17</td>
<td>13.4±0.02</td>
<td>1.57x10^{-7}</td>
<td>0.43</td>
<td>0.0128</td>
<td>0.69</td>
<td>±3.32</td>
</tr>
<tr>
<td>C12</td>
<td>8.69x10^{-3}</td>
<td>0.98</td>
<td>13.4±0.02</td>
<td>1.11x10^{-7}</td>
<td>±0.32</td>
<td>±0.0027</td>
<td>0.48</td>
<td>±6.29</td>
</tr>
</tbody>
</table>

It was considered that the inhibitor layer resistance, $R_f$ is much smaller than the charge transfer resistance, $R_{ct}$. To identify the processes in impedance response the found capacitance is of the $\mu$F/cm$^2$ order. The low values obtained for $C_f$ is consistent with the insulating nature of the layer. In medium and low frequencies typical capacitances are of the order of mF/cm$^2$, diffusion phenomena may appear through the passive layer. $R_s$ refer to the solution resistance and the variation of values arises from the difference in solubility of the compound. The longer chain in tetraphosphonates is more difficult to dissolve (addition of NaOH is required) and then to readjust the pH to the proper value with HCl. The capacitance $C_f$ and $C_{dl}$ are proportional with the surface coverage of metal ($\theta$). The circuit ($C_f$/$R_f$)($C_{ct}$/$R_{ct}$) was simplified into circuit (CR), where $C$ is proportional to the area of the film. The quantitative evaluation of the amounts of inhibitor present on metal surface was evaluated from ATR-FTIR spectra. The $C$ values were obtained using EIS measurement at different immersion time and calculated with the simplified EEC. The intensity of the asymmetric deformation bands associated with the methylene group (at 2914 cm$^{-1}$) increases in time, as the surface coverage increases. The surface coverage $\theta$ was calculated from ATR-FTIR data assuming a 100% surface coverage based on the maximum height of the aforementioned peak recorded for a layer obtained after 120 minute of immersion of electrode in inhibitor solution. A linear relationship between $C$ and surface coverage was obtained for the film ($R = 0.9742$). Figure 14 shows the correlation between $C$ and $\theta$ calculated from ATR-FT-IR data for C6.
The corrosion rate of the iron substrate was considerably reduced by adding phosphonate additives. A variable increase of the capacitive loop diameter was observed in the Nyquist diagrams, depending on the type of the additive used. The tetraphosphonic acids improve the corrosion resistance due to their ability to form P-O···H-O-Fe or P–O–Fe bonds on the iron surface. The robustness of the deposited layer on the metal surface depends on the ability of the tetraphosphonate additive to bind to the metal and create a compact structure. The $R_f$ is a measure of the quality of the layer formed on the metal surface. The corrosion could only occur at the defective sites in the layer. Lower $R_f$ and $R_{ct}$ indicate that the formed layer presents pores or defects. The lowest values for $R_f$ and $R_{ct}$ were obtained for iron immersed in C2.

$R_f$ increases in all tetraphosphonic acids compared to the control solution, indicating the presence of inhibitors on the metal surface. Tetraphosphonic acids with higher chain lengths present higher $R_f$ values (Table 5) and are able to form less porous and thicker layers on the iron surface. This points to a more effective corrosion resistance capability. The highest effect appears in the presence of C12.

The changes in $C_f$ layer capacitances give information about the layer formed. The capacitance of a parallel-plate capacitor is related to the dielectric constant and area of the plate and the distance of separation between plates. Because the area of the electrode surface and the dielectric constant of layers can be assumed to be similar, the change in capacitance should be due to the change in thickness of the layer. Lower $C_f$ values indicate thicker layers and such were observed for C6 and C12. The $R_{ct}$ is high if the layer present on the metal surface is compact, thick and adherent. $R_{ct}$ is less modified through the addition of the C2 to the solution. In contrast, values were obtained for $R_{ct}$ in the presence of C4, C6, C8 and C12 were five times higher. Addition of inhibitors to the solution also modifies the double-layer capacitance $C_{dl}$ (see Table 5). In all cases the values obtained are similar to the typical double-layer capacitance value [62,63]. The low $R_{ct}$ value for C2 is a consequence of its limited ability to link to the metal surface, thus leading to the formation of an incomplete layer. C2 has the “smallest” molecular size of all tetraphosphonates and associated experimental data indicate that it cannot achieve sufficient surface coverage of the carbon steel surface. Thus, C2 seems to stimulate steel corrosion in the corrosive medium as a consequence of its reduced ability to bind to the metal surface, hence leading to the formation of an incomplete layer. From the ATR-IR data it is noted that although C8 has a strong tendency to utilize the P=O and P-O moieties to form a thicker layer on metal surface, the majority of the bonds are of the type P-OH-O-Fe. These bonds are weaker and lead to the formation of a less compact layer, thus offering lower corrosion resistance. Adsorption onto the metal surface causes the...
C_{dl} value to decrease and the R_{ct} value to increase. As a result, a similar trend of surface coverage (θ) values of inhibition efficiencies are observed. Higher R_{ct} and lower C_{dl} values are obtained for C4, C6 and C12, indicating the formation of a thicker layer and strong bonds as P-O-Fe onto the iron surface. The experimental data is in accordance with the gravimetric and potentiodynamic polarization tests. They further suggest that the tetraphosphonates with a chain length of 4 to 12 methylene groups (ie. C4 to C12) are able to bind to the carbon steel surface. The “medium” chain length tetraphosphonates (C4 and C6) bind more strongly and lead to more efficient packing on the surface. The deviation from ideal capacitive behavior observed depends strongly on the state of the surface [64]. The CPE_{dl}-P exponents are in the range 0.48-0.77 and point to a non-homogenous surface. Effects related to surface disorder, adsorption, roughness, pore size and distribution seem to increase with the increase of the number of methylene groups in the tetraphosphonic acid structure.

In the presence of inhibitors a porous layer capable to display opposition to diffusion is formed. The incomplete loop at low-frequency is associated with the diffusion (Z_d) of active species and suggests a decrease of τ time constant in the presence of the inhibitors. This indicates that the relaxation time of the diffusion process through the porous layer is hindered. Diffusion is limited by the relaxation time of bonds established between water molecules and free phosphonic groups and the change in layer conformation on the surface. The exponents Z_d-P reveal a high surface heterogeneity for all the studied tetraphosphonates.

The inhibition efficiency (IE) in % and surface coverage was calculated from the values of charge transfer resistance by equations 4:

\[
IE = \frac{R_{ct}^{inh} - R_{ct}^{control}}{R_{ct}^{inh}} \cdot 100 \quad (4a)
\]

\[
\Theta = \frac{IE}{100} \quad (4b)
\]

In the above equations R_{ct}^{inh} is the charge transfer resistance for electrode in the presence of inhibitor; R_{ct}^{control} is the charge transfer resistance for electrode in solution without inhibitor.

The inhibitory efficiency expressed in %, reveals the following inhibitor ranking: C6 (81.13%), C12 (72.10%), C4 (70.84%) and C8 (67.02%). These values are close to the ones obtained from polarization data. These inhibition efficiencies for C6, C4 and C12 are comparable to values reported for iron in acid media, for example, sodium methyldecylphosphonate (Pho1, IE = 73 %) and sodium methyl (11-methacryloyloxyundecyl)phosphonate (Pho2, IE = 86 %) on mild steel corrosion in sulfuric acid solution [65], benzimidazole (1 mol/L HCl, IE = 36.6–73.8 %) [66], 2-methylbenzimidazole (1 mol/L HCl, IE = 43.9–76.3 %) [66], 2-mercaptobenzimidazole (1 mol/L HCl, IE = 72.6–88.8% [66], 4-methylpiperidine (in HCl, IE = 29.5–60 %) [67]. The inhibiting action of C6 and C12 are also higher than the inhibiting action of (chloromethyl) triphenyl phosphonium chloride (CTP), tetraphenyl phosphonum chloride (TP), triphenyl phosphine oxide (TPO), triphenyl (phenylmethyl) phosphonium chloride (TPM) and triphenyl phosphine (TPP) on the corrosion of iron in 1 M HCl solution [68].

The surface coverage (θ) determined from EIS data can provide additional information about the inhibitors by their adsorption isotherm type. The values of surface coverage θ (equation 4), corresponding to different concentrations of inhibitor were used to get the best linearity isotherms [69]. The Langmuir isotherm (5) was the best fit model for the adsorption of the tetraphosphonic acids.

\[
\frac{C}{\Theta} = \frac{1}{K_{ads}} + C \quad (5)
\]
In Equation 5, $\theta$ is the surface coverage, $C = C_{\text{inhibitor}}$ is the inhibitor concentration, $K_{\text{ads}}$ is the adsorption equilibrium constant. Figure 15 shows the linear plots for $(C/\theta)$ in function of $C_{\text{inhibitor}}$ and the adsorption obeys the Langmuir isotherm.

The values obtained for slopes in the Langmuir model were less than unity and indicate the existence of interactions between the adsorbed inhibitor molecules and metal surface. Based on the value obtained for $K_{\text{ads}}$ the free energy of adsorption ($\Delta G^o_{\text{ads}}$), was calculated using Equation 6.

$$\Delta G^o_{\text{ads}} = -RT\ln(55.5K_{\text{ads}})$$

In Equation 6, $R$ is the universal gas constant (8.314 J·mol$^{-1}$·K$^{-1}$) and $T$ is the absolute temperature in Kelvin, $K_{\text{ads}}$ is the adsorption equilibrium constant, $\Delta G^o_{\text{ads}}$ is the standard free energy of adsorption, 55.5 is the concentration of water in the solution in mol·dm$^{-3}$. The results show that the linear regression coefficients (R) are close to unity, which indicates the existence of molecular adsorption within the adsorbed layer.

Table 6. The parameters $K_{\text{ads}}$, $R_L$ and $\Delta G^o_{\text{ads}}$ for the adsorption of tetraphosphonic acids on carbon steel in 3.5 % NaCl solutions.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C2</th>
<th>C4</th>
<th>C6</th>
<th>C8</th>
<th>C12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{ads}}$, mol$^{-1}$</td>
<td>20408.16</td>
<td>36589.83</td>
<td>46794.57</td>
<td>40535.06</td>
<td>40387.72</td>
</tr>
<tr>
<td>$\Delta G^o_{\text{ads}}$, kJ/mol</td>
<td>-34.54</td>
<td>-35.98</td>
<td>-36.59</td>
<td>-36.24</td>
<td>-36.23</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.329</td>
<td>0.215</td>
<td>0.176</td>
<td>0.198</td>
<td>0.198</td>
</tr>
</tbody>
</table>

$K_{\text{ads}}$ represents the strength of adsorption of the inhibitor onto the metal surface. Higher values of $K_{\text{ads}}$ imply more efficient adsorption. The dimensionless separation factor, $R_L$ [70], described by Equation 7 indicates a highly favorable adsorption process, in the case of a smaller value ($0 < R_L < 1$).

$$R_L = \frac{1}{1 + K_{\text{ads}}C}$$

The calculated values of $R_L$ for the inhibitors at $C = 0.0001$ mol·L$^{-1}$ (Table 6) are all < 1, confirming that the adsorption processes of inhibitors are favorable. These results are consistent with the previously
reported adsorption of phosphonic acids onto a metal surface, which obey the Langmuir adsorption isotherm [14,71,72].

The negative ∆G° ads values and high K ads values obtained in our measurements (Table 6) indicate that the adsorption process is spontaneous with concomitant formation of a stable adsorbed inhibitor layer on the metal surface. Values of ∆G° ads around −20 kJ·mol⁻¹ or more positive indicate physisorption, while values around −40 kJ·mol⁻¹ or more negative point to a chemisorption process [73]. Corrosion inhibition of carbon steel in saline solution at pH ~ 3 by the tetraphosphonates originates from the molecular adsorption on the metal surface. It is known that the first step in corrosion inhibition is adsorption of the inhibitor molecules at the metal/solution interface through electrostatic interactions between the charged additive molecules and charged metal surface, and/or interaction of π-electrons or lone pair(s) of electrons with the metal. These interactions are responsible for the adsorption of organic compounds on the metal and ultimately for their inhibition efficiency [74,75]. The obtained ∆G° ads values (in the -34 to -36 kJ·mol⁻¹ range) suggest combined physisorption/chemisorption processes for the tetraphosphonates [76]. Electrostatic and hydrogen bonding interactions between the O atoms from P=O and P−OH groups and hydroxyl groups on the iron substrate form P−O···H−O−Fe bonds, which are responsible for surface immobilization. The anchored phosphonate molecules can bind more strongly through P−O−Fe bonds, via a dehydration reaction. The resulting corrosion products could be retained by the free tetraphosphonic groups, a hypothesis that is confirmed by the XPS and ATR-FTIR data. Adsorption takes place principally via chemisorption for additives C4, C6, C8, and C12, and via combined physisorption/chemisorption (albeit, mainly physisorption) in the case of C2.

C2 is the smallest molecular size tetraphosphonate. Experimental data indicate that it cannot achieve sufficient surface coverage of the carbon steel surface. Thus, C2 seems to stimulate corrosion, as a consequence of its inefficiency to link to the metal surface, thus resulting in the formation of an incomplete layer. This explanation is also corroborated by the value of ∆G° ads obtained for C2, which shows higher tendency for physisorption compared to the other, longer tetraphosphonates.

The obtained values φφ ∆G° ads are comparable to those for other phosphorus compounds reported in the literature, for example, for mono-n-butyl phosphate ester (BP) -30.40 KJ mol⁻¹, for mono-n-hexyl phosphate ester (HP) -35.78 KJ mol⁻¹ and for mono-n-octyl phosphate ester (OP) -33.43 KJ mol⁻¹ (in 0.5 M H₂SO₄) [77].

4. Conclusions

Immersion of steel coupons in acidic solutions (pH = 3) containing systematically elongated members of the tetraphosphonic acid family C2, C4, C6, C8 (possessing the amino-methylene phosphonate – N+(H)-CH₂-P₂O₂H–zwitterionic moiety), leads to additive adsorption on the steel surface via the phosphonate groups. The XPS results also suggest that the tetraphosphonic acid molecules become significantly deprotonated upon interaction with the carbon steel surface. The Fe 2p spectra show evidence of metallic and oxidized Fe for all samples. The oxidized Fe content for C2-immersed specimens was the highest, compared to the other tetraphosphonate additives, in agreement with the corrosion rate measurements. Except for C2, all other additives achieve corrosion inhibition efficiency 28 % to 48 % (7-day exposure at pH 3 and 2 mM additive concentration). The fact that washing following immersion does not completely remove the phosphonates suggests they are relatively strongly bound.

C2 appears to form a thin, porous and incomplete layer on iron surface resulting in inefficient protection. The layer formed is still porous and allows the corrosive ions to reach the metal surface, resulting in metal loss, and oxide dissolution. This phenomenon could be ascribed to the small size of the C2 molecule, or to insufficient binding which, in turn, cannot achieve sufficient surface coverage. The remaining tetraphosphonates (C4, C6, C8, and C12) present much higher anticorrosion efficiency and render corrosion protection. This might suggest that these tetraphosphonates bind more strongly to the iron surface, and the layer formed is denser and thicker.
The negative $\Delta G_{\text{ads}}^*$ values taken together with the high $K_{\text{ads}}$ values prove that the adsorption process is spontaneous with concurrent formation of a stable adsorbed phosphonate layer on the metal surface. The adsorption takes place mainly via chemisorption for compounds C4, C6, C8, and C12, and mainly via physisorption, in the case of C2.

Further work will focus on the effect of concentration of the phosphonates on the mode of adsorption, via changes to the P 2p spectra. It would also be interesting to monitor the strength of the steel/phosphonate interaction via temperature programmed XPS measurements for varying chain lengths.

**Supplementary Information.** Crystallographic (cif) files for the compounds C2 and C6.

**Corresponding Authors:** * demadis@uoc.gr (KDD), andrew.g.thomas@manchester.ac.uk (AGT).

**Author Contributions.** The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**ACKNOWLEDGMENT.** KDD thanks the University of Crete for financial support through Research Grant KA 3517. GM acknowledges support from the National Science Foundation under Grant No. CHE-1404730. AGT thanks the School of Materials, University of Manchester for access to the XPS instrument. NP thanks the Institute of Chemistry Timisoara of Romanian Academy for financial support through Program No. 2.

**ABBREVIATIONS**
- **EDTMP**, ethylenediamine-N,N,N’,N’-tetakis(methyleneophosphonate)
- **TDTMP**, tetramethylenediamine-N,N,N’,N’-tetakis(methyleneophosphonate)
- **HDTMP**, hexamethylenediamine-N,N,N’,N’-tetakis(methyleneophosphonate)
- **DDTMP**, dodecamethylenediamine-N,N,N’,N’-tetakis(methyleneophosphonate)

**REFERENCES**


(58) R. Yan, X. Gao, D. Lv, H. Ma, A study on the differences in morphology and corrosion resistance performance between two different bis(2-ethylhexyl) phosphate self assembled thin films prepared on an iron substrate in water and ethanol solvents. RSC Adv. 6 (2016) 55936-55945.


(69) M. Bouklah, B. Hammouti, M. Lagrene, F. Bentiss, Thermodynamic properties of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium. Corros. Sci. 48 (2006) 2831-2842.


Table of Contents artwork
Highlights

- A family of systematically elongated tetraphosphonate corrosion inhibitors is studied by XPS.
- The tetraphosphonates strongly interact with the mild steel surfaces at pH 3.
- Shorter chain lengths on the inhibitor backbone cause surface dissolution.
Corrosion protection of carbon steel by tetraphosphonates of systematically different molecular size

Argyri Moschona,¹ Nicoleta Plesu,² Gellert Mezei,³ Andrew G. Thomas,⁴* and Konstantinos D. Demadis¹*

¹ Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete, Voutes Campus, Heraklion, Crete, GR-71003, Greece
² Institute of Chemistry Timisoara of Romanian Academy, 300223 Timisoara, Romania
³ Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008-5413, U.S.A.
⁴ School of Materials and Photon Science Institute, The University of Manchester, Manchester, M13 9PL, United Kingdom

KEYWORDS: Mild steel, organic coatings, phosphonates, acid corrosion, inhibition, XPS, thin films.

ABSTRACT: We study the interaction of six systematically varied tetraphosphonate molecules with carbon steel surfaces by XPS at pH 3. All tetraphosphonates [EDTMP (C2), TDTMP (C4), HDTMP (C6), ODTMP (C8) and DDTMP (C12)] belong to the aminomethylene-phosphonate family, and they possess systematically elongated backbone (from two to twelve methylene groups separating the N atoms). XPS studies were performed on powdered samples and also on immersed carbon steel specimens in aqueous solutions. The XPS results also suggest that the tetraphosphonic acid molecules become significantly deprotonated upon interaction with the carbon steel surface and that the surface interaction of the tetraphosphonic acid family leads to additive adsorption on the steel surface via the phosphonate groups. The mode of corrosion inhibition was studied by potentiodynamic polarization and electrochemical impedance spectroscopy. The changes observed in the impedance parameters, like charge transfer resistance ($R_{ct}$) and constant phase element (CPE) confirm the strong adsorption on the metal surface. The nature of the protective layer formed on the carbon steel surface was examined by Attenuated Total Reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and optical microscopy.

1. Introduction

Corrosion inhibitors are additives that protect metallic surfaces from water-side corrosion. They are either inorganic [1] or organic [2] species and are purposely added into the water system, usually, in ppm quantities. Their principal purpose is to form thin protective films on the metal surface, either by adsorption [3] or by controlled precipitation in synergy with metal ions [4].

Among the plethora of corrosion inhibitors, phosphonates are often used because they possess a number of important attributes: (a) They are resistant to hydrolysis and high temperatures [5]. This is particularly important when oxidizing biocides are used in the water system for microbiological control or when high-temperature metal surfaces are involved in the system operation. (b) They demonstrate high affinity for the metal oxide layer on the metal surface [6]. (c) They can act as both mineral scale and corrosion inhibitors [7]. (d) The acidic phosphonate (-PO$_3$H$_2$) moiety may be singly or doubly
deprotonated (depending on pH), thus allowing the phosphonate moiety to be functional in a wide range of pH values [8]. (e) They can act synergistically with metal ions commonly present in the water system (eg. Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, etc.) or other chemical additives, thus offering superior corrosion protection [9-13].

A number of experimental studies are available in the literature on the use of phosphonates as anti-corrosion agents. For example, Laamari et al. studied the efficiency of HDTMP (C6 in this paper), as corrosion inhibitor for carbon steel in 0.5 M HCl [14]. Interactions of the O and N atoms of the inhibitor with the Fe surface were invoked, but no experimental proof was provided. Zhao et al. reported the anticorrosion efficiency of HDTMP on Mg implants by chemical grafting [15]. Al-Khaldi et al. studied the interaction of aminobutylphosphonic acid with carbon steel surfaces [16]. The authors concluded, based on XPS measurements, that the bifunctional phosphonic acid interacts with the iron oxide layer through both phosphate and protonated amine ends. Paszternák et al. induced steel surface modification with self-assembled phosphonic acid layers [17]. They found that under the experimental conditions studied the phosphonic acids form a protective coating on the metal surface close to a monolayer. Kavipriya et al. evaluated the inhibition of corrosion of carbon steel in sea water by diethylenetriamine-pentamethylenephosphonic acid (DTPMP) and concluded that it functioned as a cathodic inhibitor [18]. Labjar et al. studied amino-tris(methylene phosphonic) acid (ATMP) as corrosion inhibitor of carbon steel in 1 M HCl and discovered that the corrosion inhibition mechanism of ATMP is controlled by a physisorption process [19]. In a similar study, Kar and Singh reported an evaluation of nitrioltrimethylene phosphonic acid (NTMP, it is the same additive as ATMP above) and (for comparison) nitrioltriacetic acid as corrosion inhibitors of carbon steel in sea-water [20]. Based on XPS studies they proposed a Fe-NTMP surface complex, forming a robust thin film. Felhosi and Kalman studied protective layer formation of $\alpha,\omega$-diphosphono-alkane compounds on iron surfaces [21]. Layer formation proved to be a spontaneous process on iron, and was accomplished by multimolecular adsorption. Fang et al. evaluated ATMP, 1-hydroxyethylidenediphosphonic acid (HEDP), N,N-dimethyldenediphosphonoglycine (DMPG), 1-ethylphosphonoethylidenediphosphonic acid (EEDP), and ethylenediaminetetramethylenephosphonic acid (EDTMP, C2, in this paper) for protecting mild steel from corrosion [22]. They concluded that ATMP is the most efficient inhibitor and proposed that both N and O atoms in the ATMP molecule were coordinated with Fe$^{2+}$ in the film. A review by Tsirulnikova et al. summarized the chemistry of various formulations as inhibitors of metal corrosion and scaling in water systems [23].

In this paper the interactions of several tetraphosphonate corrosion inhibitors (shown in Figure 1) with carbon steel surfaces are studied by X-ray photoelectron spectroscopy (XPS) at pH 3. The studied tetraphosphonates (C2, C4, C6, C8) contain systematically elongated polymethylene chains linking the N atoms of the amino-bis(methylene phosphonate) termini. These additives demonstrate strong adsorption on the steel surface via the phosphonate groups. The potentiodynamic polarization and EIS data reveal that the corrosion protection is induced by the tetraphosphonate additives, while the results confirm that the phosphonate moiety is able to bind to Fe and form a more-or-less dense and compact layer on the metal surface, depending on the structural features of the additives. The tetraphosphonates with 6 or 8 carbon atoms on the chain create a more efficient packing on the carbon steel surface, while the C2 tetraphosphonate appears to form a thin, incomplete and porous layer.

2. Experimental Section

2.1. Synthesis of tetraphosphonic acids. Ethylenediamine, 1,6-diaminohexane, 1,12-diaminododecane, formaldehyde, and phosphorus acid were purchased from commercial sources and used as received. All organophosphonic acid molecules were synthesized via the Mannich-type (Irani-Moedritzer) reaction. In principle, this reaction allows the clean transformation of a primary amine to an amino-
bis(methylene phosphonic acid) moiety. Literature procedures were followed [24-26]. All organophosphonic acids were isolated as high-purity (> 97 %) solids in > 50 % yields, except EDTMP which was kept dissolved in water and used as a 25.4 % w/w stock solution. Schematic structures of all corrosion inhibitors are shown in Figure 1. Single crystals of EDTMP (C2) and HDTMP (C6) were prepared by leaving an aqueous solution of these tetraphosphonic acids to partially evaporate under ambient conditions.

2.2. X-ray crystallography. X-ray diffraction data were collected at room temperature from a single-crystal mounted atop a glass fiber under Paratone-N oil, with a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-Kα (\(\lambda = 0.71073 \ \text{Å}\)) radiation. The structures were solved by employing SHELXTL direct methods and refined by full-matrix least squares on F2, using the APEX2 software package [27]. All non-H atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined using a riding model, except for the water and phosphonic acid O−H hydrogens, which were located from the Fourier difference density maps and refined using a riding model with O−H distance restraints. Crystallographic details are summarized in Table 1.

Table 1. Crystallographic data for compounds C2 and C6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>EDTMP·H₂O (C2)</th>
<th>HDTMP (C6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₆H₂₂N₂O₁₃P₄</td>
<td>C₁₀H₂₈N₂O₁₂P₄</td>
</tr>
<tr>
<td>F.W. (g·mol⁻¹)</td>
<td>454.14</td>
<td>492.22</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>p(\bar{1})</td>
</tr>
<tr>
<td>(\lambda) (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.105(3)</td>
<td>5.8532(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.898(4)</td>
<td>7.7735(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.168(4)</td>
<td>10.8922(3)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>93.221(2)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>95.01(2)</td>
<td>99.503(2)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90</td>
<td>96.298(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1674.8(9)</td>
<td>484.445(10)</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.37×0.30×0.25</td>
<td>0.25×0.16×0.08</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (g·cm⁻³)</td>
<td>1.801</td>
<td>1.687</td>
</tr>
<tr>
<td>2(\theta) range (°)</td>
<td>2.28-27.98</td>
<td>1.90-28.61</td>
</tr>
<tr>
<td>Data/Restraints/Parameters</td>
<td>3617/0/242</td>
<td>2472/4/136</td>
</tr>
<tr>
<td>Nº reflections</td>
<td>10227</td>
<td>2472</td>
</tr>
<tr>
<td>Independent reflections [I &gt; 2(\sigma(I))]</td>
<td>3305</td>
<td>2031</td>
</tr>
</tbody>
</table>
2.3. **XPS studies.** All spectra were recorded using a Kratos Axis Ultra X-ray photoelectron spectrometer, equipped with a monochromatic Al Kα X-ray source (hv = 1486.6), hemispherical analyser with magnetic lens system and low energy electron source for charge compensation. Spectra were recorded in normal emission geometry, and all spectra were aligned on the binding energy scale relative to the C 1s peak at 284.8 eV. Binding energies are quoted to ± 0.1 eV. Survey spectra were recorded at a pass energy of 160 eV and narrow scans at a pass energy of 40 eV. Peak fitting was done using the CASA XPS software package [28] with 70:30 Gaussian Lorentzian peak shapes unless stated otherwise.

![Diagram of tetraphosphonate corrosion inhibitors](image)

**Figure 1.** Schematic structures of all tetraphosphonate corrosion inhibitors.

2.4. **Protocol for carbon steel sample preparation for XPS studies.** Four powdered tetraphosphonic acid samples, abbreviated here as C4 (TDTMP), C6 (HDTMP), C8 (ODTMP) and C12 (DDTMP), were analysed in their native state by pressing onto conducting graphite tape. Charge compensation was applied as the powders are insulating. Following this, aqueous solutions of the tetraphosphonic acids were prepared in pH 3 phthalate buffer (Sigma Aldrich) in various concentrations as follows: C2...
(EDTMP) 2.00 µL/mL, C4 2.15 mg/mL; C6 1.11 mg/mL; and C8 2.03 mg/mL. C12 would not fully dissolve at pH 3 (most likely due to the long dodecamethylene chain) and was therefore not measured. Square-shaped mild steel (C1018) specimens of dimensions 1.5 cm × 1.5 cm were prepared by removing any pre-existing oxide or corrosion products by abrading with P240 SiC paper. These were rinsed with deionised water and immersed in the buffer/tetraphosphonic acid solutions for 16 hours. A control sample, containing only phthalate buffer solution was also prepared. After the specimens were removed from solution, they were rinsed with deionized water and dried using N2 gas in a N2-filled glove box attached to the load lock of the XPS instrument. This ensured that the specimens were not exposed to air between the time they were removed from solution and the XPS spectral measurements. This has been shown to be crucial in reducing the oxidation of the steel in air [29]. The mild steel specimens were attached to the sample-mounting bar by means of conducting double sided graphite tape.

2.5. Protocol for carbon steel sample preparation for gravimetric studies. A modified protocol is used based on NACE Standard TM0169-95 (Item No. 21200), National Association of Corrosion Engineers, Houston TX, U.S.A. [30]. Corrosion specimens (pretreated carbon steel, grade C1010) are prepared according to the well-established protocol above. Each specimen is immersed in a control solution (no inhibitor, pH = 3) or in a test solution (containing each of the tetraphosphonic acids at 2 mM concentration, pH = 3) and corrosion progress is monitored by visual inspection for 7 days. Then, the specimens were removed from solution, air-dried, and cleaned by the standard NACE method above to determine corrosion rates from mass loss.

2.6. OCP and Potentiodynamic polarization testing. Potentiodynamic polarization studies were conducted to measure the corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), polarization resistance (R_p) and corrosion rate (R_{corr}), for carbon steel specimens without additives and after their immersion in a test solution containing tetraphosphonates. The electrolyte solution was 3.5 % NaCl. Each electrode (specimen) was immersed in a control solution (no inhibitor, 3.5 % NaCl, with pH adjusted to ~ 3 with HCl) and in a test solution (containing each of the tetraphosphonic acids at 4.9 mM concentration, with pH adjusted to ~ 3, with NaOH). The control solution and test solutions were ultrasonicated for 5 minutes. The experiments were conducted in aerated electrolyte. The experiments were conducted in triplicate.

2.7. Electrochemical Impedance Spectroscopy (EIS) Measurements. Electrochemical impedance spectroscopy (EIS) experiments were also employed to monitor corrosion phenomena. From the evaluation of impedance data, the electrochemical interface behaviour is usually described by simple electrical elements as R, L, and C connected in an adequate equivalent circuit. EIS were performed with an Autolab 302N potentiostat/galvanostat equipped with the FRA2 impedance module. The sinusoidal potential amplitude was 10 mV. All electrochemical measurements were performed at room temperature. All measurements were carried out in a conventional one-compartment three-electrode cell, equipped with two inox counter electrode and Ag/AgCl reference electrode. The exposed surface area of the working electrode used in electrochemical experiments, was 0.785 cm². Electrochemical impedance spectra were recorded at open circuit potentials in 3.5 % NaCl solutions with and without tetraphosphonic acids as the supporting electrolyte. All spectra reported here were measured at the open circuit potential. The tested frequency range was from 0.01 Hz to 100 kHz. The sinusoidal potential amplitude was 10 mV. All electrochemical measurements were performed at room temperature. The experimental data were fitted to the equivalent electrical circuit by a complex non-linear least squares procedure using the ZView- Scribner Associated Inc. software. The EIS and CP tests were performed after one hour immersion time. All the experiments were conducted in triplicate.
2.8. Vibrational Spectroscopy. Attenuated Total Reflectance Infrared (ATR-IR) spectra were recorded with a FT/IR-4200 JASCO Spectrophotometer, equipped with PIKe ATR (MIRacle), DTGS detector, Ge crystal plate. These experiments were set at a resolution of 4 cm$^{-1}$ in the range of 4000–600 cm$^{-1}$. All data were analyzed by the Spectral Manager Version 2 software.

3. Results and Discussion

3.1. Structural description

3.1.1. EDTMP (C2). Figure 2 (upper) shows the molecular structure of C2 lattice (the water molecule has been omitted). The molecule as a whole possesses a zwitterionic structure, as expected. Two of the four phosphonic acid moieties are monodeprotonated (-PO$_3$H, one from each side), whereas the remaining two are fully protonated (-PO$_3$H$_2$). The two tertiary N atoms are protonated (≡NH$^+$) via an intramolecular protonation process. C-C [1.517 (2) Å], C-P [1.818(2) Å – 1.828(2) Å], C-N [1.503(2) Å – 1.518(2) Å], and P-O [1.475(2) Å – 1.558(2) Å] bond lengths are similar to those reported for (NH$_4$)$_2$(EDTMP) [31]. The P-O bond distances are in a typical for organophosphonates [32,33]. However, upon closer examination of the P-O bond lengths it becomes evident that they are separated into two categories, the “short” and the “long” bonds. All “long” bonds are associated with the protonated –P-OH moiety, whereas the “short bonds” are from the non-protonated portion of the -PO$_3$ moiety. Distinction between the P=O and the P-O$^-$ bond lengths is not possible because these are of equivalent length, based on the crystallography results. Therefore, this leads to the conclusion that the negative charge is delocalized over the O=P-O$^-$ moiety. Similar observations have been noted for metal-coordinated (and mono-deprotonated) phosphonates [34]. Figure 2 (lower) gives a view of the packing in the structure of C2, including the lattice water molecules (exaggerated green spheres). All hydrogen bonding interactions are given in Table 2. The water molecule interacts through three hydrogen bonds (2.702, 2.716 and 2.467 Å) with phosphonate oxygens (originating from three different C2 molecules. There is a plethora of other hydrogen bonds as well. The two NH$^+$ moieties from the same C2 molecule form two hydrogen bonds (2.686 and 2.729 Å) with the same phosphonate oxygen from a neighboring C2 molecule. This particular interaction forces the molecule to acquire a “syn” configuration, with the two NH$^+$ moieties pointing towards the same direction (N-C-C-N torsion angle 86.21°).

3.1.2. HDTMP (C6). C6 crystallizes as the anhydrous form, and is located on an inversion center within the triclinic crystal lattice (Figure 3, upper). As with C2, two phosphonate groups of the zwitterionic molecule are singly protonated (-PO$_3$H$^+$), whereas the other two are doubly protonated (-PO$_3$H$_2$). The tertiary N atoms (≡NH$^+$) are also protonated. An extended 3D-network is formed by H-bonding between the phosphonate groups and NH$^+$ moieties (Figure 3, lower). H-bonding parameters are summarized in Table 2. C-C [1.514(2) – 1.523(3) Å], C-P [1.821(2) Å – 1.826(2) Å], C-N [1.496(2) Å – 1.514(2) Å], and P-O [1.478(1) Å – 1.555(1) Å] bond lengths are similar to those reported for (en)$_2$(HDTMP) (en = ethylene diammonium dication) [35,36]. The NH$^+$ moiety forms a hydrogen bond (2.739 Å) with a phosphonate oxygen from a neighboring C6 molecule. This N-H···O(P) interaction is augmented with a (P)O-H···O(P) interaction (2.565 Å), thus forming an intermolecular 7-membered ring. The C6 molecule is fully extended with a N-C-C-N torsion angle 180°. All hydrogen bonding interactions are shown in Table 2.

Table 2. Summary of the hydrogen bonding data for C2 and C6.
<table>
<thead>
<tr>
<th>Compound</th>
<th>D−H⋯A</th>
<th>D−H (Å)</th>
<th>H⋯A (Å)</th>
<th>D⋯A (Å)</th>
<th>D−H−A (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTMP (C2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1−H1F⋯O1W</td>
<td>0.820(2)</td>
<td>1.751(2)</td>
<td>2.467(3)</td>
<td>144.9(1)</td>
<td></td>
</tr>
<tr>
<td>O5−H5C⋯O2</td>
<td>0.820(2)</td>
<td>1.700(2)</td>
<td>2.512(2)</td>
<td>170.3(1)</td>
<td></td>
</tr>
<tr>
<td>O3−H3C⋯O7</td>
<td>0.802(2)</td>
<td>1.689(2)</td>
<td>2.500(2)</td>
<td>169.8(1)</td>
<td></td>
</tr>
<tr>
<td>N1−H1E⋯O4</td>
<td>0.89(3)</td>
<td>1.84(3)</td>
<td>2.686(2)</td>
<td>160(2)</td>
<td></td>
</tr>
<tr>
<td>N2−H2E⋯O4</td>
<td>0.83(2)</td>
<td>1.93(2)</td>
<td>2.729(2)</td>
<td>161(2)</td>
<td></td>
</tr>
<tr>
<td>O11−H11A⋯O6</td>
<td>0.820(2)</td>
<td>1.708(2)</td>
<td>2.509(2)</td>
<td>165.5(1)</td>
<td></td>
</tr>
<tr>
<td>O8−H8A⋯O12</td>
<td>0.819(2)</td>
<td>1.735(2)</td>
<td>2.535(2)</td>
<td>165.0(1)</td>
<td></td>
</tr>
<tr>
<td>O10−H10A⋯O9</td>
<td>0.829(2)</td>
<td>1.708(2)</td>
<td>2.467(2)</td>
<td>153.0(1)</td>
<td></td>
</tr>
<tr>
<td>O1W−H1D⋯O7</td>
<td>0.77(4)</td>
<td>2.00(4)</td>
<td>2.716(3)</td>
<td>153(3)</td>
<td></td>
</tr>
<tr>
<td>O1W−H1C⋯O6</td>
<td>0.75(4)</td>
<td>1.97(4)</td>
<td>2.702(3)</td>
<td>165(4)</td>
<td></td>
</tr>
<tr>
<td>HDTMP (C6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1−H1⋯O5#</td>
<td>0.785(16)</td>
<td>1.748(16)</td>
<td>2.5326(18)</td>
<td>176(2)</td>
<td></td>
</tr>
<tr>
<td>O3−H3⋯O5#</td>
<td>0.810(16)</td>
<td>1.755(16)</td>
<td>2.565(2)</td>
<td>177(3)</td>
<td></td>
</tr>
<tr>
<td>O4−H4⋯O6#</td>
<td>0.789(16)</td>
<td>1.764(16)</td>
<td>2.552(2)</td>
<td>177(3)</td>
<td></td>
</tr>
<tr>
<td>N1−H10⋯O2#</td>
<td>0.98</td>
<td>1.85</td>
<td>2.7390(19)</td>
<td>150.1</td>
<td></td>
</tr>
</tbody>
</table>

![Diagram](image)
Figure 2. Molecular structure of the C2 (EDTMP·H₂O) acid (upper, the lattice water molecule is omitted for clarity) and the packing diagram down the b axis. The lattice water molecule is depicted as an oversized green sphere. Color codes: H white, C black, N blue, P orange, O red.

Figure 3. Molecular structure of the C6 (HDTMP) acid (upper) and a portion of the packing diagram down the a axis. Color codes: H white, C black, N blue, P orange, O red.

3.2. XPS studies

Figure 4 shows survey spectra recorded from the pure tetraphosphonic acid powders (upper panel) and the mild steel specimens which had been immersed for 16 hours in solutions of the tetraphosphonic acids at pH 3 (lower panel). Spectra of the pure powders show only C, O, N and P derived peaks as expected. Spectra of the solution-immersed mild steel specimens show, in addition to the above peaks, additional peaks arising from Fe, the strongest being the Fe 2p peak at a binding energy of around 711
eV. For the pH 3 buffer immersed sample we see no evidence of N or P in the survey scan. C and O 1s peaks are observed for this buffer sample, which may arise from the phthalate. No evidence of K, from the buffer, is seen in any of the survey spectra.

Figure 4. XPS Survey scans of phosphonate powders (upper) and steel coupons immersed in pH 3 solutions of the phosphonates (lower). Spectra are aligned to the C 1s peak at 284.8 eV. EDTMP (C2) is missing from the upper panel, since it was available as a solution.

Detailed core level scans of N 1s, P 2p and Fe 2p recorded from the tetraphosphonic acid pure powders and mild steel specimens are shown in Figure 5. N 1s spectra recorded from the powders (Figure 5a) can be fitted with two peaks at binding energies of 399.8 eV and 401.9 eV, and are assigned to deprotonated and protonated tertiary amine groups, respectively. As can be seen in all cases the protonated form is dominant for all powders, as expected, because of intramolecular protonation of N by an acidic proton from a phosphonic acid group. This is also corroborated by the crystal structures of C2 and C6.

In the equivalent spectra from the steel specimens in Figure 5b the two peaks are almost of equal intensity, suggesting the tetraphosphonic acid molecules become significantly deprotonated. This is perhaps not surprising since they are deposited from solution. The degree of deprotonation appears to increase with the chain length, but, for the reasons discussed below, it is difficult to make any firm
conclusions about why it occurs. The difficulty lies in the fact that the sample immersed in phthalate buffer also shows the presence of N, which we believe is due to traces of nitride from the steel coupons. The N 1s binding energy of this peak at 399.9 eV, the nitride peak overlaps with the deprotonated amine and it is not possible to determine the variation in N content in the steel coupons used. Of some interest is the appearance of a third peak at a binding energy of 403.0 eV in sample C6 and 404.4 eV in sample C4. The origin of these peaks is unclear since N 1s peaks at these binding energies are usually associated with nitrite or nitrate formation, and result from the electronegative oxygen reducing the charge density on the nitrogen.
Figure 5. High resolution XPS scans of (a) N 1s from phosphonate powder (b) N 1s from steel immersed in phosphonate solution, (c) P 2p – powder, (d) P 2p – steel (e) Fe 2p – steel (f) O 1s – powder and (g) O1s – steel. The Fe 2p spectra are fitted with multiplets, color-coded as shown in the legend.

The P 2p spectra shown in Figure 5c for powders C4, C8 and C12 are composed of a single spin-orbit split doublet arising from the 2p<sub>3/2</sub> (134.5 eV) and 2p<sub>1/2</sub> (135.4 eV). This is consistent with a singly protonated phosphonate group. There is some evidence that sample C6 has a small proportion of doubly protonated phosphonate in the powder form, shown by the doublet at a binding energy of 135.7/136.6 eV (the green doublet).

For the steel coupons in Figure 5d there is a downward shift of the dominant doublet binding energy to 133.7 eV. This is consistent with deprotonation of the phosphonate group. For phosphates it has been shown that for each proton removed there is a downward shift in binding energy of around 1 eV [37]. We also see evidence of an increase in the amount of doubly protonated phosphonate for the C6 sample. This correlates with the larger relative decrease in the deprotonation of the amine in C6 but it is not likely that these are linked, since the differences in the P 2p spectra of C4 and C8 are not as apparent as the change in degree of deprotonation of the amine. We note that for C4, the region to higher binding energy of the main peak at around 135 eV is not well fitted, suggesting there may also be
some doubly protonated phosphonate groups in this region as well. C8 shows no evidence of a second phosphorus chemical state. The data from the steel coupons – where we see an increase a shift to a doubly deprotonated molecule, would support a binding mechanism of the molecules to the iron via the phosphonate groups [38]. The fact that C6 shows both completely deprotonated and doubly protonated species, may suggest that this molecule binds through two phosphonate groups. It is noted however that the lower concentration of C6 may play a part in this, and further work will be carried out to confirm the effect of concentration on the adsorption mechanism.

The Fe 2p spectra in Figure 5e show evidence of metallic and oxidized Fe for all samples. The relative amounts of each are shown in Table 3. The metallic Fe 2p_3/2 peak at a binding energy of 706.6 eV is fitted with an asymmetric Lorentzian peak which accounts for excitation of conduction electrons by the photoelectrons in metallic systems [39]. Oxidized iron is notoriously difficult to fit with a high degree of certainty, mainly due to the multiplet structure of the high spin compounds of iron [40,41]. Each Fe compound gives rise to a distinct set of multiplets with different separations and areas. For the spectra noted here, with the exception of C4, the spectra are well fitted by a combination of FeO, γ-Fe_2O_3 and an averaged FeOOH species. The residual for these fits is around 1.5 - 1.6 which compares well to an electrochemically oxidized Fe sample studied by Biesinger et al. [40] and would seem like a reasonable comparison. It is noted that there is also the possibility of FePO_4 formation at the surface [42], but since detailed multiplet structures have not been determined in the literature for this material peaks for this have not been fitted. The specimen immersed in C4 solution is not well fitted by this combination of peaks. It can be seen that compared to the other solutions, the “oxidized Fe” peak of C4 seems to be weighted more heavily to the higher binding energy side. This might suggest more Fe^{2+} oxidation states, such as carbonates, or possibly Fe(II) phosphate/phosphonate since the Fe^{2+} satellite sits at around 716-718 eV [43,44]. In any case, a satisfactory fit with multiplets from standard compounds could not be achieved for C4. If one adds the multiplet structure of FeCO_3, as a representative Fe(II) compound, then γ-Fe_2O_3 is lost from the fitting. This is the fit shown in Figure 5e for sample C4. The peak areas suggest that C6 results in the largest metallic iron peak in the spectra, followed by C8, which has a similar metallic Fe composition to the sample immersed in pH 3 phthalate buffer. C6 also shows the highest concentration of FeO at the surface, although the ratios for the different oxide/hydroxide species should be regarded with some degree of caution due to the large number of parameters involved [40].

### Table 3. Iron composition based on fitting to Fe 2p XPS data. Note the values and actual compositions may vary somewhat from these values.

<table>
<thead>
<tr>
<th></th>
<th>Fe^0 (%)</th>
<th>FeO (%)</th>
<th>γ−Fe_2O_3 (%)</th>
<th>FeOOH (%)</th>
<th>“FeCO_3,” (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>14.4</td>
<td>43.5</td>
<td>10.86</td>
<td>31.1</td>
<td>-</td>
</tr>
<tr>
<td>C4</td>
<td>29.1</td>
<td>34.9</td>
<td>23.4</td>
<td>12.7</td>
<td>-</td>
</tr>
<tr>
<td>C6</td>
<td>35.0</td>
<td>55.6</td>
<td>5.2</td>
<td>4.2</td>
<td>-</td>
</tr>
<tr>
<td>C8</td>
<td>19.6</td>
<td>30.2</td>
<td>-</td>
<td>30.8</td>
<td>19.4</td>
</tr>
<tr>
<td>Buffer</td>
<td>29.1</td>
<td>33.3</td>
<td>25.5</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

The O 1s spectra shown in Figure 5f and 5g shed some further light on the degree of oxidation of the steel surface. For the powders, two peaks, of similar intensity, are observed at binding energies of 531.7 eV and 532.9 eV, in relatively good agreement with O 1s spectra recorded from phenyl phosphonic acid adsorbed on metal oxide surfaces [38,41]. We note that these binding energies are also consistent with the presence of C=O and C-OH which are likely to be present as contaminants on surfaces exposed to atmospheric pressure [42]. This may also explain the slight variations in the FWHM of the peaks required to adequately fit the O 1s spectra. For the phosphonates on steel placed in phthalate buffer at pH 3 a third peak is observed at a binding energy of 530.0 eV, consistent with the
presence of iron oxide [42]. In addition, we see that the peak at a binding energy of 531.5 eV increases in intensity relative to the peak at 532.9 eV. This can be explained by two phenomena. Firstly, adsorption of the phosphonates on the iron surface involves deprotonation of the phosphate as observed in the P 2p spectra discussed above. In addition, this region is also associated with the presence of metal hydroxides [42]. Comparing the oxide/hydroxide peak intensity in the Fe 2p and O 1s spectra one can see a correlation with the amount of iron oxide for the different powders. Interestingly, the two samples with the lowest oxide content display poor (C2) and good (C4) corrosion inhibition efficiency, as discussed below. Recent XPS measurements performed under nitrogen as is the case in the present work, suggest that a corrosive medium leads to removal of the oxide, with adsorption directly to the metal surface [42,43]. However, other reports suggest that the presence of an oxide/hydroxide layer mediates Cl⁻ adsorption at the steel surface [44,45]. It was shown by Morales-Gil and co-workers [42,43] that exposure to ambient air, even for less than a minute after removal from the corrosive environment, leads to oxidation of the steel surface, whereas transfer to the XPS instrument under N₂ gas indicated that imidazolium adsorbed to the bare steel surface – i.e. the oxide was removed by the corrosive medium. Although this work reported here also employed sample transfer to the XPS instrument under N₂ gas the acidic medium used a pH 3 buffer, which one might expect to be less corrosive than HCl, as used by Morales-Gil and co-workers. Furthermore, the inhibitors used in the present work are phosphonates, with functional groups known to bind relatively strongly to metal oxides [38,41].

All five tetraphosphonic acids were evaluated for their corrosion inhibition efficiency at pH 3 and concentration 2 mM. Carbon steel specimens were exposed to the same acidic medium (pH = 3) as the XPS measurements. Visual inspection of the “control” specimen (no additive present) after withdrawal from the medium and air-drying, revealed general corrosion throughout the surface of the specimen. In contrast, the presence of tetraphosphonates created a protective coating on the surface. Figure 6 shows all specimens for comparison.

3.3. Corrosion inhibition (mass loss)

In addition to these qualitative observations, general corrosion rates were quantified based on mass loss measurements, and the results are presented in Figure 7. C2 appears to be an ineffective corrosion inhibitor, as it causes metal loss, and most likely facilitates oxide dissolution. This phenomenon could be ascribed to the small size of the molecule, which, in turn, cannot achieve sufficient surface coverage. The corrosion efficiency of the remaining tetraphosphonates (C4, C6, C8 and C12) yield corrosion protection ranging from 28 % to 48 %. It is interesting that the C4 and C6 tetraphosphonates show the lowest corrosion rate and highest surface metallic iron component (see Table 3). This might suggest that the phosphonate binds more strongly to Fe than the oxides and that these “medium” chain lengths lead to more efficient packing on the surface. This is consistent with results reported for 2-mercaptobenizimidazole inhibitors [45].
Figure 6. Unprotected (control) and protected (by the phosphonate additives, as indicated) carbon steel specimens, after exposure for one week to pH = 3.
3.4. OCP and Potentiodynamic polarization testing

The time-dependent variation of OCP potential of carbon steel immersed in 3.5% NaCl solution with different tetraphosphonates is presented in Figure 8.

It was observed for all inhibitors that the OCP values decreased in time as a result of dissolution of the passive oxide layer formed at the sample surface (electrodes). This can be explained by the aggressive chloride ions attack. In time, a partial protection of the surface takes place due to formation of corrosion products, capable of blocking the existing pores and cracks on the surface, leading to potential stabilization. In the case of carbon steel immersed in saline solution without additives the OCP reached a constant value after 3000 s. In the presence of tetraphosphonates the OCP reached a constant value more rapidly, after 500 s. In the presence of C12, the OCP values increase immersion, pointing to the formation of a protective barrier. The shorter time needed for OCP stabilization in the presence of
tetraphosphonates, compared to that in their absence suggests the formation of a protecting layer on the metal surface.

The potentiodynamic polarization curves obtained for carbon steel after 60 min immersion in 3.5 % NaCl solution with and without the tetraphosphonate additives are shown in Figure 9.

Figure 9. Potentiodynamic polarization curves for carbon steel after 60 min. immersion in 3.5 % NaCl solutions without (control) and with tetraphosphonates (scan rate = 1 mV/s).

The presence of tetraphosphonic acids in saline solution affects the cathodic and the anodic Tafel slope. The differences observed for the values of cathodic and anodic Tafel slopes suggest that the inhibition corrosion mechanism (the adsorption process and protective layer formation) takes place at the active metal surface. It can be observed that the \( J_{\text{corr}} \) values for all tetraphosphonates (Table 4) were lower than those for the “control” (no additives), those for C4 and C6 being the lowest. Also, the values of the corrosion rate, \( R_{\text{corr}} \), were lower for C4 and C6. The anodic polarization curves were shifted to positive

<table>
<thead>
<tr>
<th>Sample</th>
<th>( J_{\text{corr}} ), A/cm(^2)</th>
<th>( \beta_c ), V/decade</th>
<th>( \beta_a ), V/decade</th>
<th>( R_p ), Ohm/cm(^2)</th>
<th>( E_{\text{corr}} ), V</th>
<th>( R_{\text{corr}} ), mm/year</th>
<th>IE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>3.25\times10^{-5}</td>
<td>0.108</td>
<td>0.135</td>
<td>239</td>
<td>-0.912</td>
<td>0.327</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>8.05\times10^{-6}</td>
<td>0.290</td>
<td>0.092</td>
<td>1961</td>
<td>-0.612</td>
<td>0.091</td>
<td>69.85</td>
</tr>
<tr>
<td>C4</td>
<td>4.21\times10^{-6}</td>
<td>0.024</td>
<td>0.252</td>
<td>4521</td>
<td>-0.402</td>
<td>0.008</td>
<td>87.05</td>
</tr>
<tr>
<td>C6</td>
<td>4.03\times10^{-6}</td>
<td>0.130</td>
<td>0.283</td>
<td>6026</td>
<td>-0.452</td>
<td>0.005</td>
<td>87.99</td>
</tr>
<tr>
<td>C8</td>
<td>7.5\times10^{-6}</td>
<td>0.223</td>
<td>0.386</td>
<td>1345</td>
<td>-0.401</td>
<td>0.041</td>
<td>76.92</td>
</tr>
<tr>
<td>C12</td>
<td>9.06\times10^{-6}</td>
<td>0.251</td>
<td>0.323</td>
<td>6023</td>
<td>-0.332</td>
<td>0.081</td>
<td>72.12</td>
</tr>
</tbody>
</table>
values for tetraphosphonates of 4 to 12 methylene groups in chain length. The anodic Tafel slope increased with the increase of the chain length of the inhibitor. With the increases of the difference between $\beta_a$ and $\beta_c$, the potential difference between the anodic and cathodic regions decreased and the corrosion rates became lower. In the literature the values reported for the anodic Tafel slope for iron in acidic solution (1.0 N $\text{H}_2\text{SO}_4$ and 1.0 N $\text{HCl}$ at 20°C) were around 38-40 mV/decade [46]. The differences observed for the values of Tafel slopes in our case points to a different manner by which the inhibitors are absorbed on the metal surface. The higher Tafel values suggest a slow step in the mechanism of iron dissolution associated with the different adsorption pattern of inhibitor (ligand) present in solution.

Based on the corrosion current density data, the inhibition efficiency was calculated according to Equation 1.

$$IE = \frac{J_{corr} - J_{inh}}{J_{corr}} \times 100 \ (1)$$

In Equation 1, $IE$ represents the inhibitory efficiency expressed in %, $J_{corr}$ and $J_{inh}$ are the corrosion current density without and with inhibitor, respectively. The best results was obtained for C6 (88%), C4 (87%) and C8 (72%) tetraphosphonic acids.

In all cases a decrease in $E_{corr}$ to less negative values was observed, indicating that carbon steel became passive by simple immersion in aqueous solutions of tetraphosphonic acids. The tetraphosphonic acid can be adsorbed on the carbon steel surface by forming iron-phosphonate complexes capable to provide corrosion protection. The degree of protection is linked with the structure of the newly formed film on the carbon steel surface. In aqueous solution the binding to iron surface is realized by the negatively charged O atoms (resulted from dissociation of the $\text{H}^+$ ion from the $\text{P}=\text{O}$ group and electron delocalization along the $\text{O}–\text{P}–\text{O}$ segment). Literature reports that layered structures of metal phosphonates formed are predominant with the organic groups being oriented perpendicularly into the interlamellar region [47]. Some differences were observed between the actions of tetraphosphonic acids regarding their ability to bind with the iron surface (mono, bi, tri dentate) and to create a sufficiently compact protective layer (see Figure 10) [48].

The tetraphosphonic acids used herein can form a thin and compact layer on the carbon steel surface as illustrated in Figure 10, lower. They can be deposited on the metal surface by immobilization through surface complexation. The molecules first are anchored covalently on the carbon steel substrate surface via interaction between phosphonate groups and metal surface (Figure 10, upper), while the non-coordinated phosphonate group can chelate $\text{Fe}^{2+}$ ions released from the substrate by corrosion (Figure 10 lower). Chemical surface immobilization assumes that the molecule is firstly adsorbed onto the iron surface through electrostatic interaction and hydrogen bonds between oxygen atoms from P=O and P–OH groups and hydroxyl groups on the iron substrate forming P-O···H-O-Fe bonds. During the next step the anchored phosphonate molecule $\text{via}$ a dehydration reaction is able to link more strongly through P-O-Fe bonds. By this chelating reaction the corrosion products could be retained by the free tetraphosphonic groups, thus remaining in the pores of the newly-formed phosphonate layer. As a result, the pores are sealed and the layer becomes denser and able to provide more effective corrosion protection for prolonged immersion periods. This hypothesis is confirmed by the Fe$^0$ component present in the XPS spectra recorded in the iron specimens which had been immersed for 16 hours in solutions of the tetraphosphonic acids at pH 3 (see Table 3). Formation of similar compact layers was proposed by Chen et al. for magnesium by surface-immobilized of 1-hydroxyethylidene-1,1-diphosphonic acid [49]. The C4 and C6 tetraphosphonic acids show the lowest corrosion rate and highest surface Fe$^0$ component due to the increased capacity of these phosphonate layers to retain iron species present in solution.
Figure 10. Upper: Schematic illustration of surface modification by one phosphonic acids group on oxide surface; R represents the side-group. Lower: Schematic representation of covalent bonding on iron substrate and chelating abilities.

Varying the chain length in metal alkylphosphonates can alter the structure considerably. For example the organophosphonic linkers with –CH$_2$– chain lengths of n = 2–4 typically resulted in pillared layered structures [50]. The stable layer formed on the iron surface is capable to protect the surface from aggressive chlorine ions attack, as was reported earlier [51]. Al-Khaldi et al. studied the interaction of aminobutylphosphonic acid with iron surfaces and concluded, based on XPS measurements, that both phosphonate and protonated amine ends of the bifunctional phosphonic acid can interact with the iron oxide layer [16].

ATR-FTIR spectroscopy was used as tool for examination of the layer formed on the carbon steel surface. The spectra are shown in Figure 11, upper. The strong asymmetric phosphonate (-PO$_3^{2-}$) stretch at 1032 cm$^{-1}$ appears in all organophosphonate layers deposited on iron electrodes [34]. The bands at 1240 cm$^{-1}$ and 1030 cm$^{-1}$ was associated with P=O and P-O-C bonds. Scissor deformation and asymmetric deformation bands associated with the methylene group appear at 1450 cm$^{-1}$ and 2845 cm$^{-1}$ and 2914 cm$^{-1}$, respectively. The bands for N-H appear at 1625–1635 cm$^{-1}$ and 3412 cm$^{-1}$. The broad band at ~ 3300 cm$^{-1}$ was attributed to OH stretching vibrations. The absorption peak attributed to OH stretching vibrations (3300 cm$^{-1}$) overlap with the band for N-H, did not disappear in the presence of tetraphosphonic acids but are diminished. This indicates that there are some intermolecular hydrogen bonds between the adsorbed phosphate molecules and iron substrate. The observed bands agree well with those expected, according to literature reports [52-58].
Figure 11. ATR-FTIR spectra for specimens immersed for 1 hour in 3.5% NaCl solutions in the presence of tetraphosphonic acids in the 4000 – 600 cm\(^{-1}\) region (upper) in the 1250-900 cm\(^{-1}\) region (lower).

The intensity of the bands observed at 1030 cm\(^{-1}\) (associated with the P-O-C stretch) suggests that in the case of C8, C6 and C12 a thicker and/or more compact layer forms on metal surface. In the case of C4, C6, C8 and C12 the characteristic peak at 1228 cm\(^{-1}\) which corresponds to the P=O stretching mode of free tetraphosphonic disappeared. This suggests further interaction of the P=O moiety and the formation of a new bonds on the iron surface. This observation is corroborated by the higher R\(_{ct}\) value obtained for these tetraphosphonic acids. The lower intensity of this band in the case of C2 indicates its lower capability to anchor to the metal surface via the P=O moiety. Moreover, the appearance of a new broad band at 2550 cm\(^{-1}\) is an indication for the formation of hydrogen bonds, namely O=П-OH···O associated with the O=П-OH···O interaction [58]. The bands at 2550 cm\(^{-1}\) are higher for C8 followed by those for C6 and C12. From the intensity of these bands it can be concluded that hydrogen bonds are predominant in the layers formed in the presence of C6 and C8. The C6 and C8 additives seem to be the able to form predominantly P-O···H-O-Fe bonds. The absence of the broad band at 2550 cm\(^{-1}\) in the case of C4 points to a binding mode through P-O-Fe bonds.

3.5. Electrochemical Impedance Spectroscopy (EIS) Measurements
Impedance spectra were represented in both complex impedance diagrams (Nyquist plot), and Bode amplitude and phase angle plots. In the Nyquist graph (Figure 12, upper), the imaginary component of
the impedance is plotted as a function of the real component, whereas the Bode representation (Figure 12, lower) shows the logarithm of the impedance modulus $|Z|$ and phase angle as a function of the logarithm of the frequency $f$.

The impedance spectra showed features of an electrode covered with a more-or-less porous layer.

![Graph showing complex plane Nyquist plots and Bode plots](image)

**Figure 12.** Complex plane Nyquist plots (upper) and Bode plots (lower) for iron immersed for 1 hour in 3.5 % NaCl solutions in the presence of tetraphosphonic acids.

In the Nyquist plots, Figure 12 upper, the real ($Z_{\text{re}}$) and imaginary ($-Z_{\text{im}}$) components of complex impedance $Z$ are noted. A depressed semicircle appears which has larger diameter than that for saline
solution only (control), as a result of a smaller number of electrons or ions transferred through the interface. The depressed capacitive loop corresponds to surface heterogeneity as a result of surface roughness, dislocation, or adsorption of the phosphonate inhibitor molecules. The variation tendency of impedance value in the Bode modulus plots is consistent with that of semicircle diameter in Nyquist plots.

The Nyquist and Bode phase angle plots presented in Figure 12 show slightly different behavior which could be linked to the structural features of the tetraphosphonic acids. Relaxation phenomena are observed at high, middle and low frequencies (a straight line indicates the existence of diffusion controlled processes). The Bode phase (Figure 12, lower) presents one time constant at middle frequency and an incomplete time constant at low (LF) and frequencies (HF). The loop observed at low frequency is attributed to the mass transfer, at middle frequency is linked to the $R_t$ and double layer capacitance and at high frequency is due to the response of the porous layer with finite pore length formed on metal surface as was reported by other authors [59]. The capacitive loop observed at high frequency arises from the layer properties and is probably incomplete due to the non-homogenous current distribution on the electrode surface. The simulation of experimental EIS data is sufficiently good for the general shape and characteristic frequencies. At high frequency the experimental diagrams are more poorly resolved than the simulated ones because of electrode roughness and the dispersion phenomena. The time constant for the high frequency curve appears to high frequency due to the dielectric properties of a surface layer.

In the middle frequency region the phase angle presents low phase angle values (~ -40°) and high for the tetraphosphonic acid with increased number of methylene groups, the lowest value for phase angle are obtained for C2 and highest for C4, C6 and C8. The high phase angle for tetraphosphonic acids with 4, 6 and 8 methylene groups in structure may be attributed to the decrease in the capacitive behaviour at the metal surface due to decreased metal dissolution rate. The charge transfer resistance ($R_{ct}$) increases and the double-layer capacitance ($C_{dl}$) decreases usually when on metal surfaces organic molecules are adsorbed [60]. In the presence of tetraphosphonic acids $R_{ct}$ and electrical double layer at the metal, solution interface increases (decreases of $C_{dl}$) due to the adsorption on metal surface and the difference in $\tau_d$ means difference in the time of adsorption. The adsorption process becomes slow for higher $\tau_d$ [61]. The results obtained for the time constants ($\tau_d = C_{dl} \cdot R_{ct}$) show that the lowest value is obtained for the C2 and highest for C12 and C6. The relaxation time constant ($\tau_d = 0.23$ ms for C2, 0.14 ms for C4, 0.15 ms for C6, 0.23 ms for C8 and 0.30 ms for C12).

The time constant linked to diffusion controlled process in the low frequency (LF) domain seems to move to lower frequencies indicating an increase in corrosion resistance as the tetraphosphonic acid is anchored to the metal surface and the layer is generated. The position of the peak at low frequencies seems to shift towards lowest value for C4, C8 and C12. The shifts of time constant to lower frequencies in the LF regions is more palpable in the case of C4, C8 and C12 and point to the better hindrances of the corrosion process by these acids and suggest the formation of more compact layer.

The impedance model for the corrosion (Figure 13) was described by the $R_s$ (electrolyte resistance) in series with a parallel connection of $C_f$ and $R_f$ (capacitance and resistance of the layer) which model the layer formed on metal surface, in a series with a parallel connection of elements associated with the double-layer capacitance ($C_{dl}$) and charge transfer resistance ($R_{ct}$). $C_d$ was introducing to model some diffusion effects.

In the model presented in Figure 13 due to non-ideal behavior, a constant phase element (CPE) is replaced the pure double-layer capacitor. The used CPE is not an ideal capacitor because of the porosity of the electrode surface and the pores distribution. The CPE is defined by two parameters, CPE-T (T) and CPE-P (φ). If the CPE-P parameter equals 1, then the equation is identical to that of a capacitor. The impedance of constant CPE is given by eq. 2 and the value of perfect capacitor $C$ can be calculated with eq. 3.
were $0 < \phi < 1$ describes the deformation of the circle in the complex plane and $Q$ is a constant. If $\phi = 1$ CPE becomes a perfect capacitor. $\omega$ is the angular frequencies (in rad·s$^{-1}$, with $\omega = 2\pi f$), $f$ is the frequency (in Hz).

The T parameter is proportional to the capacity of the double-layer (eq.3): 

$$T = C_{dl}^\phi \left( R_s^{-1} + A \right)^{1-\phi}$$

$C_{dl}^\phi = \text{capacity of the double-layer, in F}$

$R_s = \text{solution resistance, in } \Omega$

$A = \text{electrode surface area, in cm}^2$

Figure 13. Schematic representation of the equivalent circuit used for modelling the EIS data for iron immersed in 3.5 \% NaCl solutions in the presence of tetraphosphonic acids (upper) and a representative of example simulation of Nyquist and Bode diagrams with suggested model without and with C8 inhibitor (lower).

Figure 13 (lower) reveals a satisfactory correlation for the general shape and frequencies between simulated and experimental curves, except high frequency domain where the reproducibility is less. Possible explanation is the electrode roughness and associated dispersion phenomena. The best fits obtained with the corresponding results are presented in Table 5. In Table 5 are presented the incertitude of parameters $R_s$, $R_f$, $R_{ct}$ and CPE$_{dl}$-T. The incertitude of C$_T$-T is laying between 0.015 and 12.7\%, for CPE$_{dl}$-T between 1.3 and 16.1\% and for CPE$_{dl}$-P between 0.07 and 11.1\%.

Table 5. Values of the electric circuit elements for the electrodes after 1 hour of immersion.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Chi-Sqr</th>
<th>Sum-Sqr</th>
<th>$R_s$, Ω·cm²</th>
<th>$C_{f}$, F/cm²</th>
<th>$R_s$, Ω·cm²</th>
<th>$CPE_{dl}$, F/cm²</th>
<th>$R_{ct}$, Ω·cm²</th>
<th>$Z_{d}$, F/cm²</th>
<th>$Z_{d}$, Ω·cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>7.57x10⁻³</td>
<td>0.86</td>
<td>9.7±0.92</td>
<td>2.57x10⁻⁷</td>
<td>7.90±0.13</td>
<td>6.38x10⁻³</td>
<td>0.73</td>
<td>35.66±0.86</td>
<td>4.19x10⁻²</td>
</tr>
<tr>
<td>C2</td>
<td>9.69x10⁻³</td>
<td>1.09</td>
<td>10.1±0.03</td>
<td>1.56x10⁻⁷</td>
<td>4.16±0.05</td>
<td>6.42x10⁻³</td>
<td>0.77</td>
<td>22.02±0.22</td>
<td>1.59x10⁻²</td>
</tr>
<tr>
<td>C4</td>
<td>8.29x10⁻³</td>
<td>0.94</td>
<td>11.3±0.02</td>
<td>1.38x10⁻⁷</td>
<td>9.00±0.98</td>
<td>1.20x10⁻³</td>
<td>0.73</td>
<td>122.27</td>
<td>3.19x10⁻²</td>
</tr>
<tr>
<td>C6</td>
<td>7.94x10⁻³</td>
<td>0.90</td>
<td>9.8±0.84</td>
<td>1.27x10⁻⁷</td>
<td>8.98±0.86</td>
<td>1.21x10⁻³</td>
<td>0.72</td>
<td>188.98</td>
<td>3.19x10⁻²</td>
</tr>
<tr>
<td>C8</td>
<td>1.03x10⁻²</td>
<td>1.17</td>
<td>13.4±0.02</td>
<td>1.57x10⁻⁷</td>
<td>10.50±0.43</td>
<td>1.53x10⁻³</td>
<td>0.69</td>
<td>±3.32</td>
<td>3.89x10⁻²</td>
</tr>
<tr>
<td>C12</td>
<td>8.69x10⁻³</td>
<td>0.98</td>
<td>13.4±0.02</td>
<td>1.11x10⁻⁷</td>
<td>±0.32±0.02</td>
<td>2.38x10⁻³</td>
<td>0.48</td>
<td>±6.29</td>
<td>7.98x10⁻²</td>
</tr>
</tbody>
</table>

It was considered that the inhibitor layer resistance, $R_f$ is much smaller than the charge transfer resistance, $R_{ct}$. To identify the processes in impedance response the found capacitance is of the µF/cm² order. The low values obtained for $C_f$ is consistent with the insulating nature of the layer. In medium and low frequencies typical capacitances are of the order of mF/cm², diffusion phenomena may appear through the passive layer. $R_s$ refer to the solution resistance and the variation of values arises from the difference in solubility of the compound. The longer chain in tetraphosphonates is more difficult to dissolve (addition of NaOH is required) and then to readjust the pH to the proper value with HCl. The capacitance $C_f$ and $C_{dl}$ are proportional with the surface coverage of metal ($\theta$). The circuit $(C_f R_f)(C_{ct} R_{ct})$ was simplified into circuit $(CR)$, where $C$ is proportional to the area of the film. The quantitative evaluation of the amounts of inhibitor present on metal surface was evaluated from ATR-FTIR spectra. The $C$ values were obtained using EIS measurement at different immersion time and calculated with the simplified EEC. The intensity of the asymmetric deformation bands associated with the methylene group (at 2914 cm⁻¹) increases in time, as the surface coverage increases. The surface coverage $\theta$ was calculated from ATR-FTIR data assuming a 100% surface coverage based on the maximum height of the aforementioned peak recorded for a layer obtained after 120 minute of immersion of electrode in inhibitor solution. A linear relationship between $C$ and surface coverage was obtained for the film ($R = 0.9742$). Figure 14 shows the correlation between $C$ and $\theta$ calculated from ATR-FT-IR data for C6.
Figure 14. ATR-FTIR spectra recorded in the 3000 – 2500 cm\(^{-1}\) region at different surface coverage \(\theta\) (upper) and the correlation between \(C_f\) and \(\theta\) (lower) for specimens immersed in 3.5 % NaCl solutions in the presence of C6.

The corrosion rate of the iron substrate was considerably reduced by adding phosphonate additives. A variable increase of the capacitive loop diameter was observed in the Nyquist diagrams, depending on the type of the additive used. The tetraphosphonic acids improve the corrosion resistance due to their ability to form P-O···H-O-Fe or P–O–Fe bonds on the iron surface. The robustness of the deposited layer on the metal surface depends on the ability of the tetraphosphonate additive to bind to the metal and create a compact structure. The \(R_f\) is a measure of the quality of the layer formed on the metal surface. The corrosion could only occur at the defective sites in the layer. Lower \(R_f\) and \(R_{ct}\) indicate that the formed layer presents pores or defects. The lowest values for \(R_f\) and \(R_{ct}\) were obtained for iron immersed in C2.

\(R_f\) increases in all tetraphosphonic acids compared to the control solution, indicating the presence of inhibitors on the metal surface. Tetraphosphonic acids with higher chain lengths present higher \(R_f\) values (Table 5) and are able to form less porous and thicker layers on the iron surface. This points to a more effective corrosion resistance capability. The highest effect appears in the presence of C12.

The changes in \(C_f\) layer capacitances give information about the layer formed. The capacitance of a parallel-plate capacitor is related to the dielectric constant and area of the plate and the distance of separation between plates. Because the area of the electrode surface and the dielectric constant of layers can be assumed to be similar, the change in capacitance should be due to the change in thickness of the layer. Lower \(C_f\) values indicate thicker layers and such were observed for C6 and C12. The \(R_{ct}\) is high if the layer present on the metal surface is compact, thick and adherent. \(R_{ct}\) is less modified through the addition of the C2 to the solution. In contrast, values were obtained for \(R_{ct}\) in the presence of C4, C6, C8 and C12 were five times higher. Addition of inhibitors to the solution also modifies the double-layer capacitance \(C_{dl}\) (see Table 5). In all cases the values obtained are similar to the typical double-layer capacitance value [62,63]. The low \(R_{ct}\) value for C2 is a consequence of its limited ability to link to the metal surface, thus leading to the formation of an incomplete layer. C2 has the “smallest” molecular size of all tetraphosphonates and associated experimental data indicate that it cannot achieve sufficient surface coverage of the carbon steel surface. Thus, C2 seems to stimulate steel corrosion in the corrosive medium as a consequence of its reduced ability to bind to the metal surface, hence leading to the formation of an incomplete layer. From the ATR-IR data it is noted that although C8 has a strong tendency to utilize the P=O and P-O moieties to form a thicker layer on metal surface, the majority of the bonds are of the type P-OH-O-Fe. These bonds are weaker and lead to the formation of a less compact layer, thus offering lower corrosion resistance. Adsorption onto the metal surface causes the
C\text{dl} value to decrease and the R\text{ct} value to increase. As a result, a similar trend of surface coverage (\(\theta\)) values of inhibition efficiencies are observed. Higher R\text{ct} and lower C\text{dl} values are obtained for C4, C6 and C12, indicating the formation of a thicker layer and strong bonds as P-O-Fe onto the iron surface. The experimental data is in accordance with the gravimetric and potentiodynamic polarization tests. They further suggest that the tetraphosphonates with a chain length of 4 to 12 methylene groups (ie. C4 to C12) are able to bind to the carbon steel surface. The “medium” chain length tetraphosphonates (C4 and C6) bind more strongly and lead to more efficient packing on the surface. The deviation from ideal capacitive behavior observed depends strongly on the state of the surface [64]. The CPE\text{dl}-P exponents are in the range 0.48-0.77 and point to a non-homogenous surface. Effects related to surface disorder, adsorption, roughness, pore size and distribution seem to increase with the increase of the number of methylene groups in the tetraphosphonic acid structure.

In the presence of inhibitors a porous layer capable to display opposition to diffusion is formed. The incomplete loop at low-frequency is associated with the diffusion (Z\text{d}) of active species and suggests a decrease of \(\tau\) time constant in the presence of the inhibitors. This indicates that the relaxation time of the diffusion process through the porous layer is hindered. Diffusion is limited by the relaxation time of bonds established between water molecules and free phosphonic groups and the change in layer conformation on the surface. The exponents Z\text{d}-P reveal a high surface heterogeneity for all the studied tetraphosphonates.

The inhibition efficiency (IE) in % and surface coverage was calculated from the values of charge transfer resistance by equations 4:

\[
IE = \frac{R_{\text{ct}}^{\text{inh}} - R_{\text{ct}}^{\text{control}}}{R_{\text{ct}}^{\text{inh}}} \cdot 100 \quad (4a)
\]

\[
\Theta = \frac{IE}{100} \quad (4b)
\]

In the above equations R\text{ct}^{\text{inh}} is the charge transfer resistance for electrode in the presence of inhibitor; R\text{ct}^{\text{control}} is the charge transfer resistance for electrode in solution without inhibitor.

The inhibitory efficiency expressed in %, reveals the following inhibitor ranking: C6 (81.13%), C12 (72.10%), C4 (70.84%) and C8 (67.02%). These values are close to the ones obtained from polarization data. These inhibition efficiencies for C6, C4 and C12 are comparable to values reported for iron in acid media, for example, sodium methyldecylphosphonate (Pho1, IE = 73 %) and sodium methyl (11-methacryloxyundecyl)phosphonate (Pho2, IE = 86 %) on mild steel corrosion in sulfuric acid solution [65], benzimidazole (1 mol/L HCl, IE = 36.6–73.8 %) [66], 2-methylbenzimidazole (1 mol/L HCl, IE = 43.9–76.3 %) [66], 2-mercaptobenzimidazole (1 mol/L HCl, IE = 72.6–88.8 %) [66], 4-methylpiperidine (in HCl, IE = 29.5–60 %) [67]. The inhibiting action of C6 and C12 are also higher than the inhibiting action of (chloromethyl) triphenyl phosphonium chloride (CTP), tetraphenyl phosphonum chloride (TP), triphenyl phosphate oxide (TPO), triphenyl (phenylmethyl) phosphonum chloride (TPM) and triphenyl phosphine (TPP) on the corrosion of iron in 1 M HCl solution [68].

The surface coverage (\(\theta\)) determined from EIS data can provide additional information about the inhibitors by their adsorption isotherm type. The values of surface coverage \(\theta\) (equation 4), corresponding to different concentrations of inhibitor were used to get the best linearity isotherms [69]. The Langmuir isotherm (5) was the best fit model for the adsorption of the tetraphosphonic acids.

\[
\frac{C}{\Theta} = \frac{1}{K_{\text{ads}}} + C \quad (5)
\]
In Equation 5, θ is the surface coverage, \( C = C_{\text{inhibitor}} \) is the inhibitor concentration, \( K_{\text{ads}} \) is the adsorption equilibrium constant. Figure 15 shows the linear plots for \((C/\theta)\) in function of \( C_{\text{inhibitor}} \) and the adsorption obeys the Langmuir isotherm.

![Graph showing linear plots for (C/θ) in function of C_inhibitor.]

**Figure 15.** Isotherm Langmuir plots for tested inhibitors.

The values obtained for slopes in the Langmuir model were less than unity and indicate the existence of interactions between the adsorbed inhibitor molecules and metal surface. Based on the value obtained for \( K_{\text{ads}} \) the free energy of adsorption \( \Delta G^o_{\text{ads}} \), was calculated using Equation 6.

\[
\Delta G^o_{\text{ads}} = -RT\ln(55.5K_{\text{ads}}) \quad (6)
\]

In Equation 6, \( R \) is the universal gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)) and \( T \) is the absolute temperature in Kelvin, \( K_{\text{ads}} \) is the adsorption equilibrium constant, \( \Delta G^o_{\text{ads}} \) is the standard free energy of adsorption, 55.5 is the concentration of water in the solution in mol·dm\(^{-3}\). The results show that the linear regression coefficients (R) are close to unity, which indicates the existence of molecular adsorption within the adsorbed layer.

**Table 6.** The parameters \( K_{\text{ads}}, R_L \) and \( \Delta G^o_{\text{ads}} \) for the adsorption of tetraphosphonic acids on carbon steel in 3.5 \% NaCl solutions.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C2</th>
<th>C4</th>
<th>C6</th>
<th>C8</th>
<th>C12</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K_{ads}, mol(^{-1})</strong></td>
<td>20408.16</td>
<td>36589.83</td>
<td>46794.57</td>
<td>40535.06</td>
<td>40387.72</td>
</tr>
<tr>
<td><strong>\Delta G^o_{ads}, kJ/mol</strong></td>
<td>-34.54</td>
<td>-35.98</td>
<td>-36.59</td>
<td>-36.24</td>
<td>-36.23</td>
</tr>
<tr>
<td><strong>R_L</strong></td>
<td>0.329</td>
<td>0.215</td>
<td>0.176</td>
<td>0.198</td>
<td>0.198</td>
</tr>
</tbody>
</table>

\( K_{\text{ads}} \) represents the strength of adsorption of the inhibitor onto the metal surface. Higher values of \( K_{\text{ads}} \) imply more efficient adsorption. The dimensionless separation factor, \( R_L \) [70], described by Equation 7 indicates a highly favorable adsorption process, in the case of a smaller value (0 < \( R_L < 1 \)).

\[
R_L = \frac{1}{1 + K_{\text{ads}}C} \quad (7)
\]

The calculated values of \( R_L \) for the inhibitors at \( C = 0.0001 \text{ mol·L}^{-1} \) (Table 6) are all < 1, confirming that the adsorption processes of inhibitors are favorable. These results are consistent with the previously
reported adsorption of phosphonic acids onto a metal surface, which obey the Langmuir adsorption isotherm [14,71,72].

The negative $\Delta G^\circ_{\text{ads}}$ values and high $K_{\text{ads}}$ values obtained in our measurements (Table 6) indicate that the adsorption process is spontaneous with concomitant formation of a stable adsorbed inhibitor layer on the metal surface. Values of $\Delta G^\circ_{\text{ads}}$ around $\pm 20$ kJ·mol$^{-1}$ or more positive indicate physisorption, while values around $\pm 40$ kJ·mol$^{-1}$ or more negative point to a chemisorption process [73]. Corrosion inhibition of carbon steel in saline solution at pH $\sim 3$ by the tetraphosphonates originates from the molecular adsorption on the metal surface. It is known that the first step in corrosion inhibition is adsorption of the inhibitor molecules at the metal/solution interface through electrostatic interactions between the charged additive molecules and charged metal surface, and/or interaction of $\pi$-electrons or lone pair(s) of electrons with the metal. These interactions are responsible for the adsorption of organic compounds on the metal and ultimately for their inhibition efficiency [74,75]. The obtained $\Delta G^\circ_{\text{ads}}$ values (in the -34 to -36 kJ·mol$^{-1}$ range) suggest combined physisorption/chemisorption processes for the tetraphosphonates [76]. Electrostatic and hydrogen bonding interactions between the O atoms from P=O and P–OH groups and hydroxyl groups on the iron substrate form P-O···H-O-Fe bonds, which are responsible for surface immobilization. The anchored phosphate molecules can bind more strongly through P-O-Fe bonds, via a dehydration reaction. The resulting corrosion products could be retained by the free tetraphosphonic groups, a hypothesis that is confirmed by the XPS and ATR-FTIR data. Adsorption takes place principally via chemisorption for additives C4, C6, C8, and C12, and via combined physisorption/chemisorption (albeit, mainly physisorption) in the case of C2.

C2 is the smallest molecular size tetraphosphonate. Experimental data indicate that it cannot achieve sufficient surface coverage of the carbon steel surface. Thus, C2 seems to stimulate corrosion, as a consequence of its inefficiency to link to the metal surface, thus resulting in the formation of an incomplete layer. This explanation is also corroborated by the value of $\Delta G^\circ_{\text{ads}}$ obtained for C2, which shows higher tendency for physisorption compared to the other, longer tetraphosphonates.

The obtained values $\phi_{\text{ph}} \Delta G^\circ_{\text{ads}}$ are comparable to those for other phosphorus compounds reported in the literature, for example, for mono-$n$-butyl phosphate ester (BP) -30.40 KJ mol$^{-1}$, for mono-$n$-hexyl phosphate ester (HP) -35.78 KJ mol$^{-1}$ and for mono-$n$-octyl phosphate ester (OP) -33.43 KJ mol$^{-1}$ (in 0.5 M H$_2$SO$_4$) [77].

4. Conclusions

Immersion of steel coupons in acidic solutions (pH = 3) containing systematically elongated members of the tetraphosphonic acid family C2, C4, C6, C8 (possessing the amino-methyleneephosphonate – N+(H)-CH$_2$PO$_3$H-zwitterionic moiety), leads to additive adsorption on the steel surface via the phosphonate groups. The XPS results also suggest that the tetraphosphonic acid molecules become significantly deprotonated upon interaction with the carbon steel surface. The Fe 2p spectra show evidence of metallic and oxidized Fe for all samples. The oxidized Fe content for C2-immersed specimens was the highest, compared to the other tetraphosphonate additives, in agreement with the corrosion rate measurements. Except for C2, all other additives achieve corrosion inhibition efficiency 28 % to 48 % (7-day exposure at pH 3 and 2 mM additive concentration). The fact that washing following immersion does not completely remove the phosphonates suggests they are relatively strongly bound.

C2 appears to form a thin, porous and incomplete layer on iron surface resulting in inefficient protection. The layer formed is still porous and allows the corrosive ions to reach the metal surface, resulting in metal loss, and oxide dissolution. This phenomenon could be ascribed to the small size of the C2 molecule, or to insufficient binding which, in turn, cannot achieve sufficient surface coverage. The remaining tetraphosphonates (C4, C6, C8, and C12) present much higher anticorrosion efficiency and render corrosion protection. This might suggest that these tetraphosphonates bind more strongly to the iron surface, and the layer formed is denser and thicker.
The negative $\Delta G^{\ast}_{\text{ads}}$ values taken together with the high $K_{\text{ads}}$ values prove that the adsorption process is spontaneous with concurrent formation of a stable adsorbed phosphonate layer on the metal surface. The adsorption takes place mainly via chemisorption for compounds C4, C6, C8, and C12, and mainly via physisorption, in the case of C2.

Further work will focus on the effect of concentration of the phosphonates on the mode of adsorption, via changes to the P 2p spectra. It would also be interesting to monitor the strength of the steel/phosphonate interaction via temperature programmed XPS measurements for varying chain lengths.

**Supplementary Information.** Crystallographic (cif) files for the compounds C2 and C6.

**Corresponding Authors:** * demadis@uoc.gr (KDD), andrew.g.thomas@manchester.ac.uk (AGT).

**Author Contributions.** The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**ACKNOWLEDGMENT.** KDD thanks the University of Crete for financial support through Research Grant KA 3517. GM acknowledges support from the National Science Foundation under Grant No. CHE-1404730. AGT thanks the School of Materials, University of Manchester for access to the XPS instrument. NP thanks the Institute of Chemistry Timisoara of Romanian Academy for financial support through Program No. 2.

**ABBREVIATIONS**

- **EDTMP**, ethylenediamine-N,N,N’,N’-tetrakis(methylene phosphonate)
- **TDTMP**, tetramethylenediamine-N,N,N’,N’-tetrakis(methylene phosphonate)
- **HDTMP**, hexamethylenediamine-N,N,N’,N’-tetrakis(methylene phosphonate)
- **DDTMP**, dodecamethylenediamine-N,N,N’,N’-tetrakis(methylene phosphonate)

**REFERENCES**


29


(58) R. Yan, X. Gao, D. Lv, H. Ma, A study on the differences in morphology and corrosion resistance performance between two different bis(2-ethylhexyl) phosphate self assembled thin films prepared on an iron substrate in water and ethanol solvents. RSC Adv. 6 (2016) 55936-55945.


(69) M. Bouklah, B. Hammouti, M. Lagrene, F. Bentiss, Thermodynamic properties of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium. Corros. Sci. 48 (2006) 2831-2842.


Table of Contents artwork