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Chapter

Phosphonates and Phosphonic Acids: New Promising Corrosion Inhibitors

Nadjib Chafai and Khalissa Benbouguerra

Abstract

In this chapter we present our published research results concerning the use of phosphonates and phosphonic acids synthesized in our laboratory as corrosion inhibitors. Firstly, the corresponding synthetic pathways used to prepare this type of inhibitors have been illustrated. Also, the different experimental methods used to evaluate the inhibition activities of these derivatives have been presented in this chapter such as weight loss measurements, polarization curves, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), atomic force microscopy (AFM), etc. On the other hand, the theoretical approaches such as Density Functional Theory (DFT) and Molecular Dynamic Simulations (MDS) are also implanted in this chapter in order to determine correlations between the experimental efficiencies and some calculated structural and electronic properties.

Keywords: phosphonates, phosphonic acids, synthesis, corrosion inhibitors, mechanism, DFT, MDS, SEM, AFM, adsorption

1. Introduction

The corrosion of metallic materials is one of the most common phenomena that cause problems and losses in billions of dollars annually in the industrial fields. In this context, several methods have been developed and applied to combat this phenomenon such as the use of corrosion inhibitors, cathodic protection, protective coating, and galvanization.

In recent decades, the use of the organic and inorganic corrosion inhibitors takes a great importance in the protection of metals against corrosion in various media. Generally, the mechanism of the action of these inhibitors consists to form an adsorptive protective layer on the metallic surface. Also, the adsorbed inhibitors can be connected to the metallic surface by means of chemical bonds (chemical adsorption) or physical forces (physical adsorption).

Recently, phosphonates and phosphonic acids are largely employed as effective corrosion inhibitors to protect metals against corrosion in various media [1–4]. Based on this, several pathways and procedures have been developed to prepare these derivatives in good yields such as Michaelis–Arbuzov reaction [5, 6], Kabachnik–Fields reaction [7, 8], Pudovik reaction [9], Abramov reaction [10] and Moedritzer-

Irani reaction [11]. In most cases these synthetic reactions require the use of a catalyst or, microwaves or ultrasounds in order to improve their yields and to minimize the reaction time [12–15].

Generally, the inhibition activity of organic and inorganic compounds can be studied experimentally using several chemical, electrochemical and microscopic methods such as weight loss measurements, polarization curves, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), atomic force microscopy (AFM), infrared spectroscopy (IR), ... etc. Moreover, the theoretical methods such as Density Functional Theory (DFT) and Molecular Dynamic Simulations (MDS) are effectively used in the field of corrosion inhibition. Generally, the DFT method can be used to correlate the experimental inhibition efficiencies with some structural and electronic parameters of the investigated inhibitors. On the other hand, the MDS are used to determine the adsorption modes of the inhibitive molecules on the metallic surface and calculating their adsorption energies.

The main objective of this chapter is to present of our published research results concerning the synthesis and the use of phosphonates and phosphonic acids as a new generation of corrosion inhibitors. All inhibitors and their anticorrosion results presented in this chapter are exclusively studied and provided by our research team in the Laboratory of Electrochemistry of Molecular Materials and Complex (LEMMC) at Ferhat ABBAS Setif-1 University, Algeria.

2. Synthetic pathways of phosphonates and phosphonic acids

Many synthetic pathways of phosphonates and phosphonic acids have been developed and presented in the literature. In this context, the most common and important of these pathways are discussed below:

2.1 Michaelis: *Arbuzov* reaction

This reaction is considered as the most used way to synthesize phosphonates derivatives. It consists of adding of a trialkylephosphite to an alkyl halide [5, 6]. **Figure 1** shows the path followed by this reaction.

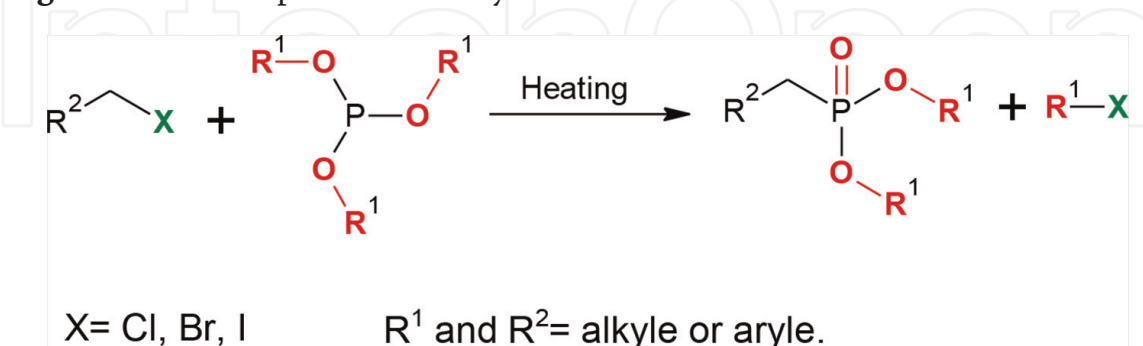
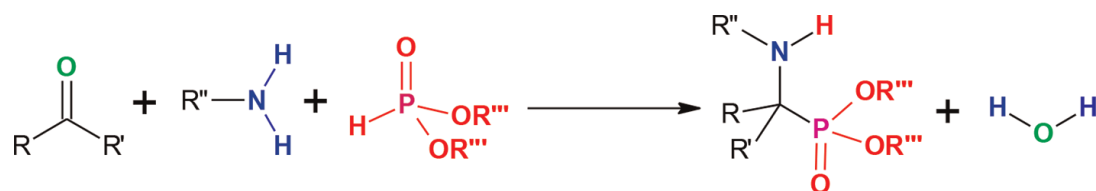


Figure 1.
Michaelis-Arbuzov reaction.

2.2 Kabachnik-Fields reaction (phospha-Mannich)

The Kabachnik-Fields reaction is one of the most important reactions for synthesizing α -aminophosphonates and α -aminophosphonic acids (**Figure 2**). In this



R, R', R'', R''' = H, Alkyle, Aryle

Figure 2.
Kabachnik-Fields reaction.

reaction, we react an amine, a carbonyl derivative and a dialkylphosphite together in one pot (one pot multi-component reaction) [7, 8].

2.3 Pudovik reaction

In this reaction, dialkylphosphites are converted to α -hydroxyphosphonates in the presence of carbonyl derivatives in basic medium [9]. The sequence of this reaction is given in **Figure 3**.

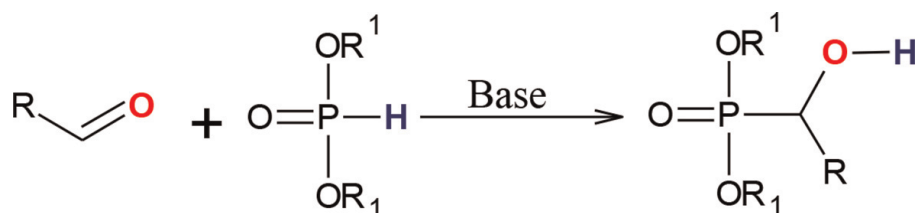


Figure 3.
Pudovik reaction.

2.4 Abramov reaction

Concerning the Abramov reaction, the trialkylphosphite rich in electron can undergo a nucleophilic addition to the carbon atom of the carbonyl compound [10]. The **Figure 4** represents the sequence of this reaction.



Figure 4.
Abramov reaction.

2.5 Moedritzer-Irani reaction

This reaction is developed by Kurt Moedritzer and Riyad R. Irani [11]. It is a new simple and direct procedure to prepare α -aminophosphonic acids basing on the Kabachnik-Fields and Mannich reactions. Generally, the principle of this reaction consists to react the phosphoric acid and formaldehyde with primary or secondary amines (**Figure 5**).



Figure 5.
Moedritzer-Irani reaction.

3. Experimental methods for the evaluation of the inhibition activity of phosphonates and phosphonic acids

Many experimental techniques and theoretical methods have been used to evaluate the corrosion inhibition activity of phosphonates and phosphonic acids. In this context, the most common and important of these techniques and methods are discussed below:

3.1 Weight loss measurements

The weight loss method is simple to implement and does not require significant equipment. Generally, the corrosion rate is determined after 24 h of immersion at a constant temperature equal to 25°C. In general, the operating protocol of this method consists in the first time the preparation of the metallic specimens used in weight loss tests. Then, we weigh the specimens before immersing them in the tested solutions. Also, each specimen was submerged in the tested solutions at constant temperature in absence and in presence of various concentrations of phosphonic inhibitors for a time of 24 h. After the expiration of the immersion time, the specimens have been recuperated from the tested solutions and rinsed with bi-distilled water. Finally, specimens were dried and weighed again.

The corrosion rate, surface coverage and inhibition efficiency are calculated by the following formulas:

$$A_{corr} = \frac{\Delta W}{S \times t} = \frac{W_1 - W_2}{S \times t} \tag{1}$$

$$\theta = \frac{A_{corr}^0 - A_{corr}}{A_{corr}^0} \tag{2}$$

$$E_W(\%) = \frac{A_{corr}^0 - A_{corr}}{A_{corr}^0} \times 100 \tag{3}$$

where:

W_1 : The mass of specimen before immersion in the tested solution.

W_2 : The mass of specimen after immersion in the tested solution.

S : The surface area of the specimen.

t : The immersion time of each test.

A_{corr}^0 : The corrosion rate in the absence of the phosphonate inhibitor.

A_{corr} : The corrosion rate in the presence of the phosphonate inhibitor.

Accordingly, the weight loss method is largely applied to evaluate the corrosion inhibition activity of phosphonates and phosphonic acids. In this context, many our published works on the use of weight loss method indicates that the phosphonates and phosphonic acids are good inhibitors of the corrosion of steel in various aggressive

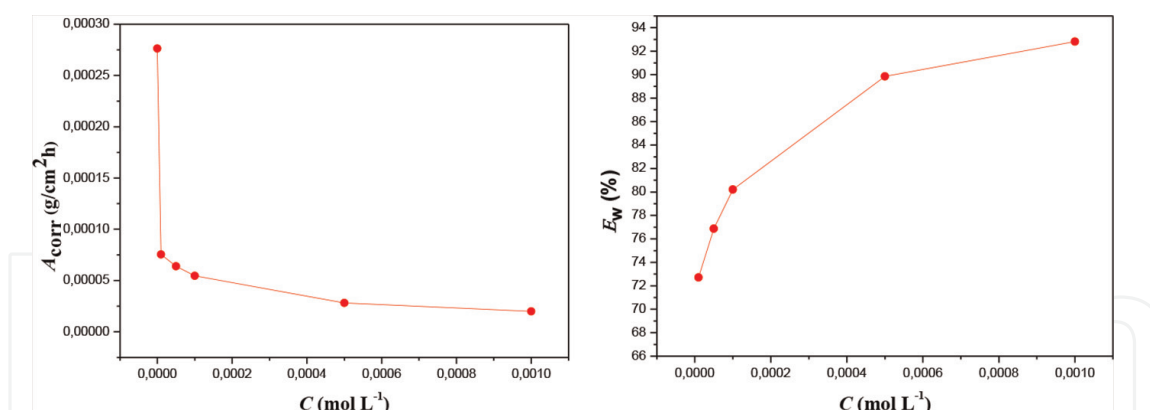


Figure 6.

Weight loss results for the inhibition activity of diethyl ((4-(dimethylamino)phenyl)(phenylamino)methyl)phosphonate obtained for the XC48 carbon steel in 0.5 Mol L⁻¹ H₂SO₄ at 25°C [16].

media. **Figure 6** represents the weight loss results of the inhibition activity of diethyl ((4-(dimethylamino)phenyl)(phenylamino)methyl)phosphonate [16].

3.2 Polarization curves

The polarization curves technique is considered among the most widely used methods to determine the corrosion rate, the corrosion potential and the nature of the influence of the inhibitor on each of the elementary reactions, anodic and cathodic, at the electrode surface. Also, this method makes possible to determine the value of the corrosion current density by extrapolating the Tafel lines to the corrosion potential.

Generally, the following equation may be used to determine the inhibition efficiency obtained from the polarization curves ($E_p(\%)$):

$$E_p(\%) = \frac{i_{\text{corr}}^{\circ} - i_{\text{corr(inh)}}}{i_{\text{corr}}^{\circ}} \times 100 \quad (4)$$

where:

i_{corr}° and $i_{\text{corr(inh)}}$: are the values of the corrosion current density in the absence and in the presence of the inhibitor, respectively.

On the other hand, the values of surface coverage ratio (θ) can be calculated using the following equation:

$$\theta = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \quad (5)$$

Concerning the application of the polarization curves technique in the evaluation of the corrosion inhibition activity of phosphonates and phosphonic acids, we observe from our previously published works that the majority of phosphonates and phosphonic acids derivatives inhibit corrosion by controlling the anodic and cathodic processes (mixed-type inhibitors) without affecting the dissolution of the metal in the anode or the evolution of hydrogen in the cathode [1]. Also, the adsorption of phosphonates and phosphonic acids on the metallic surfaces is responsible for the observed drop in $i_{\text{corr(inh)}}$ and the observed rise in $E_p(\%)$. As an example, **Figure 7**

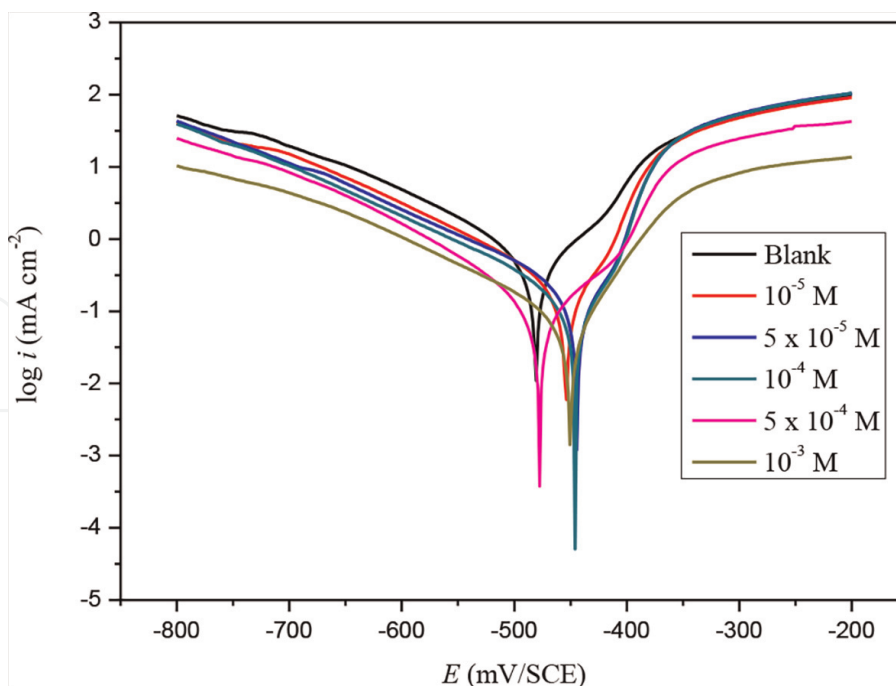


Figure 7. Polarization curves for the inhibition activity of 4-(2-{[ethoxy(hydroxy)phosphonyl](3-nitrophenyl)methyl}hydrazinyl)benzoic acid obtained for the carbon steel in $0.5 \text{ Mol L}^{-1} \text{ H}_2\text{SO}_4$ at 20°C [1].

represents the obtained polarization curves of the inhibition activity of 4-(2-{[ethoxy(hydroxy)phosphonyl](3-nitrophenyl)methyl}hydrazinyl)benzoic acid [1].

3.3 Electrochemical impedance spectroscopy (EIS)

In this technique, we measure the response of an electrode to a sinusoidal modulation of low amplitude of the potential as a function of the frequency. The strength of this technique is that it completely analyzes the mechanism of action of inhibitor on the metallic surface. So, the role of the inhibitor in the different processes occurring at the electrode such as charge transfer, diffusion, adsorption, etc., can be studied in detail, and values such as those of the transfer resistance and the polarization resistance can provide access to the measurement of the corrosion rate even in the case where the metal is covered with a protective layer [17]. Generally, to study the anticorrosion activity of phosphonates and phosphonic acids, the electrochemical impedance (EIS) measurements were performed around in the frequency range from 100 kHz to 10 mHz, with a signal of 5 mV sinusoidal amplitude. In this context, the inhibition efficiency ($E_R(\%)$) can be calculated applying the electrochemical impedance spectroscopy results by using the following equation:

$$\eta_R(\%) = \frac{R_{t(\text{inh})} - R_{t(0)}}{R_{t(\text{inh})}} \times 100 \quad (6)$$

Concerning the application of EIS study for the phosphonate derivatives inhibitors, we take as an example the Nyquist plot of [(2-hydroxy-5-methoxy-1,3-phenylene)bis(methylene)]bis(phosphonic acid) obtained for the carbon steel in $1 \text{ mol L}^{-1} \text{ HCl}$ at 25°C in the absence and in the presence of different concentrations of the inhibitor (Figure 8) [18]. Note that the diameter of the Nyquist diagram increases with the

addition of the inhibitor, suggesting that the corrosion of carbon steel in acidic media is mainly controlled by a charge transfer process [19]. Also, it is clearly observed in **Figure 8** that the Nyquist diagrams of all tested concentrations present similar semi-circle shapes. This means that there is no significant change in the corrosion mechanism due to the addition of the inhibitor [20]. On the other hand, we observe that the obtained diagrams are not perfect semi-circles, because of the frequency dispersion which can be attributed to a surface heterogeneity which generates a frequency distribution. In general, this heterogeneity is due to the roughness of the surface and the chemical composition of carbon steel [21].

Also, the analysis of the results presented in **Figure 8** show that the charge transfer resistance (R_{ct}) values increase and the double layer capacitance (C_{dl}) values decrease with increasing the concentration of the phosphonate derivative. The increase in R_{ct} may be due to the formation of a protective film at the metal/solution interface. On the other hand, the decrease in C_{dl} values is due to the increase in the thickness of the electrical double layer, which indicates that the phosphonate derivative act by adsorption on the metal surface.

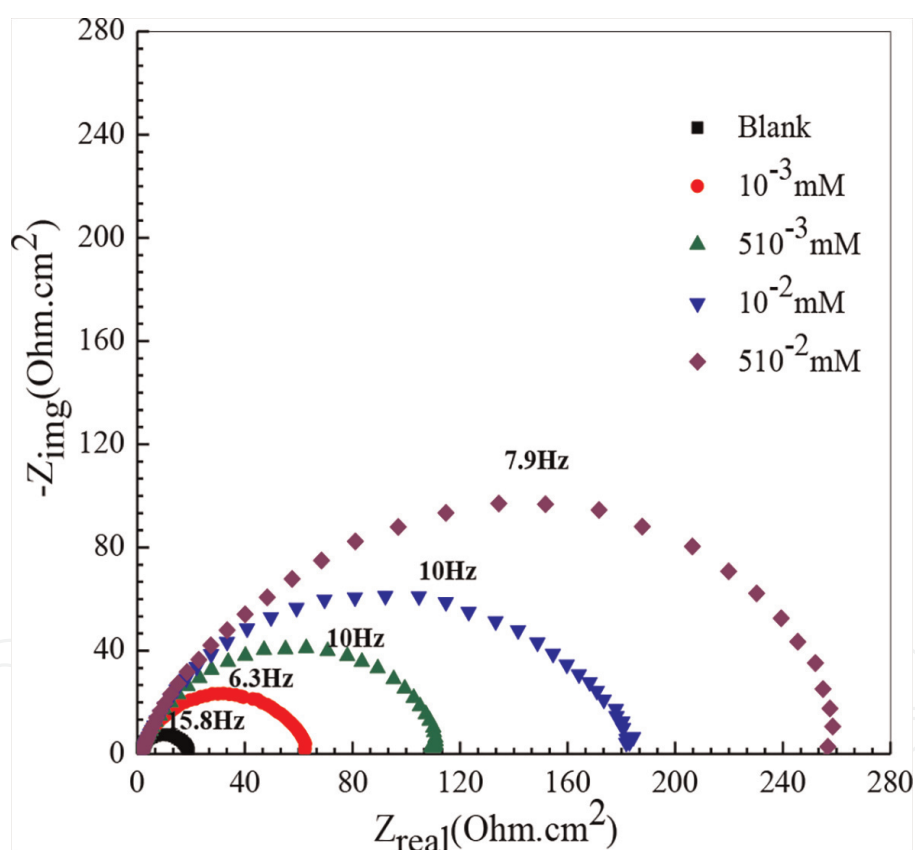


Figure 8. EIS results for the inhibition activity of [(2-hydroxy-5-methoxy-1,3-phenylene)bis(methylene)]bis(phosphonic acid) obtained for the carbon steel in $1 \text{ mol L}^{-1} \text{ HCl}$ at 25°C [18].

3.4 Scanning electron microscopy (SEM)

The Scanning Electron Microscopy (SEM) technique is largely used in the corrosion inhibition field. The main objective of this technique is to visualize the surface morphology of metals in the absence and in the presence of inhibitory molecules. Briefly, a scanning electron microscope uses a very fine beam of electrons which scans, point by point, the surface of the sample to be observed. In this context, this

technique allows researchers to visualize what is happening on the metal surface at the microscopic scale and to know what changes are made on the surface of the metal after the addition of the inhibitor (e.g. the addition of phosphonates and phosphonic acids inhibitors).

Figure 9 represents the SEM image of mild steel specimen in the presence of 10^{-3} mol/L of Ethyl hydrogen [(2-methoxyphenyl)(methylamino) methyl] phosphonate [22]. The examination of the obtained SEM image of the tested phosphonate compound shows an observed reduce in roughness of the surface of mild steel. So, we can say that the metallic surface has been protected against corrosion when the phosphonate derivatives have been added to the corrosive medium. This phenomenon is explained by the formation of an adsorbed layer (thin protective film) of the phosphonate derivative on the metal surface.

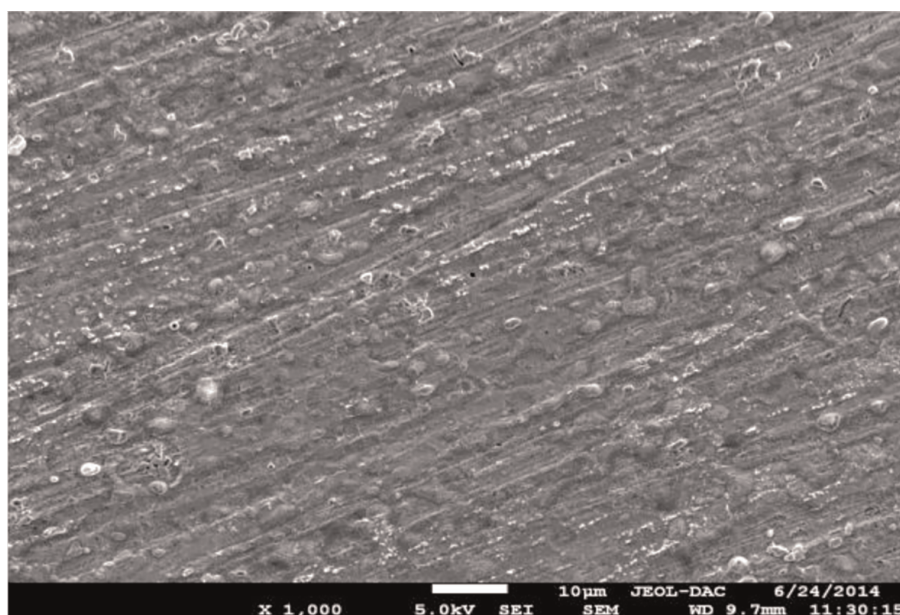


Figure 9. SEM image of mild steel in the presence of 10^{-3} mol/L of ethyl hydrogen [(2-methoxyphenyl)(methylamino) methyl]phosphonate [22].

3.5 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is another useful microscopic technique which is extensively used in corrosion inhibition studies. Especially, this technique makes to determine the formation of a protective layer of the inhibitor on the metal surface by measuring the variation in the roughness values of the metal surface before and after the addition of the inhibitor molecule.

An example of the use of the AFM technique as a useful way to illustrate the formation of adsorbed layers of phosphonic derivatives on the metal surface is demonstrated in **Figure 10**, which shows the obtained AFM images of carbon steel in the presence of diethyl((4-(dimethylamino)phenyl)(phenylamino)methyl)phosphonate and 4-(2-([ethoxy(hydroxy)phosphonyl](3-nitrophenyl)methyl)hydrazinyl)benzoic acid [1, 16].

The analysis of the achieved AFM images indicates that the addition of phosphonates or phosphonic acids makes a significant modification on the surface morphology of the metal indicating the formation of a protective adsorbed layer of

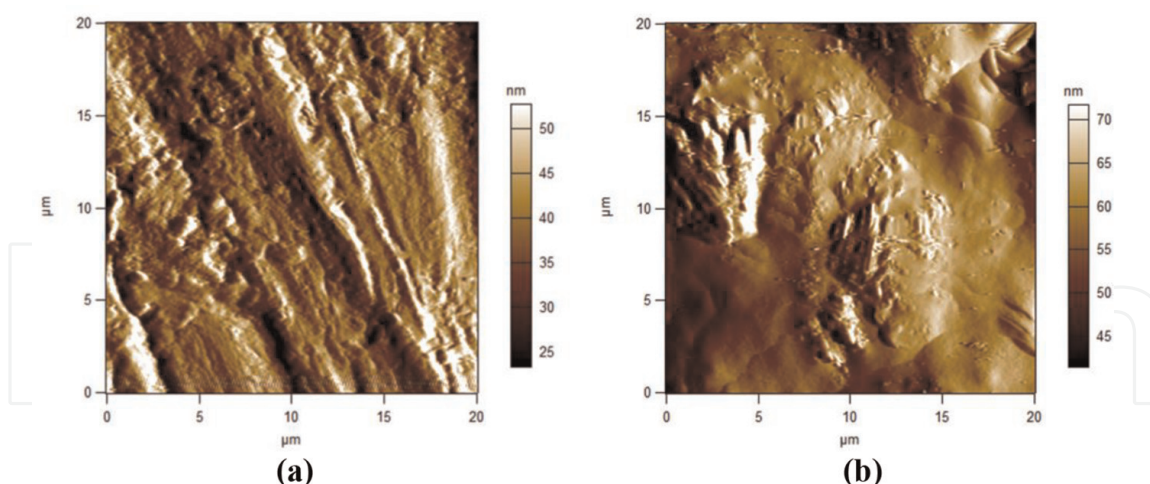
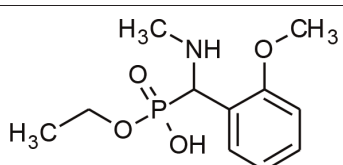
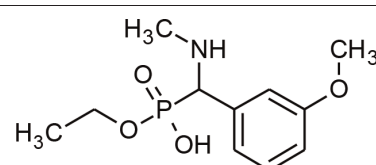


Figure 10. AFM images of mild steel in the presence of 10^{-3} mol/L of diethyl ((4-(dimethylamino) phenyl) (phenylamino) methyl) phosphonate (a) and 4-(2-[[ethoxy(hydroxy)phosphonyl](3-nitrophenyl)methyl]hydrazinyl)benzoic acid (b) [1, 16].

phosphonate molecules. This phenomenon can be explicated by the diminution of the measured values of the roughness of metal after the addition of phosphonates or phosphonic acids to the corrosive media.

3.6 Density functional theory (DFT)

Recently, the quantum chemical calculations by applying DFT method are extensively used to correlate the experimental results of corrosion inhibition efficiencies with some quantum descriptors, electronic and structural proprieties of the inhibitive molecule such as the energy of the Highest Occupied Molecular Orbital (E_{HOMO}), the energy of the Lowest Unoccupied Molecular Orbital (E_{LUMO}), the energy gap (ΔE_{gap}), the absolute electronegativity (χ), the hardness (η), the softness (σ), and the dipole moment (μ). Basing on our previously published works, the DFT results indicated that the high corrosion inhibition activity of phosphonates and phosphonic acids is related to the presence of phosphonate or phosphonic acid functional groups in their molecular structure. Also, DFT calculations on phosphonates and phosphonic acids proved that the active sites responsible for the anticorrosion activity of these derivatives are located on the heteroatoms such as P, O, N and S. On the other hand, the DFT study demonstrates that the most negative sites responsible for the electrophilic attacks are located on the oxygen atoms of the phosphonate groups. The **Table 1** summarized the calculated quantum chemical descriptors of two phosphonate derivatives [22].

| Quantum descriptors |  |  |
|------------------------------|---|--|
| E_{HOMO} (eV) | -6.00039 | 5.99494 |
| E_{LUMO} (eV) | -0.27620 | 0.23402 |
| ΔE_{gap} (eV) | 5.91386 | 5.76092 |
| χ (eV) | 3.13829 | 3.11448 |

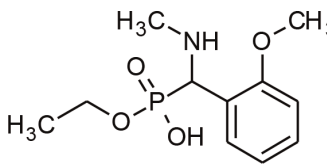
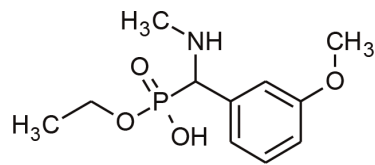
| Quantum descriptors |  |  |
|---------------------|---|--|
| η (eV) | 2.86209 | 2.88046 |
| σ (eV) | 0.34939 | 0.34716 |
| μ (Debye) | 2.9461 | 2.4875 |

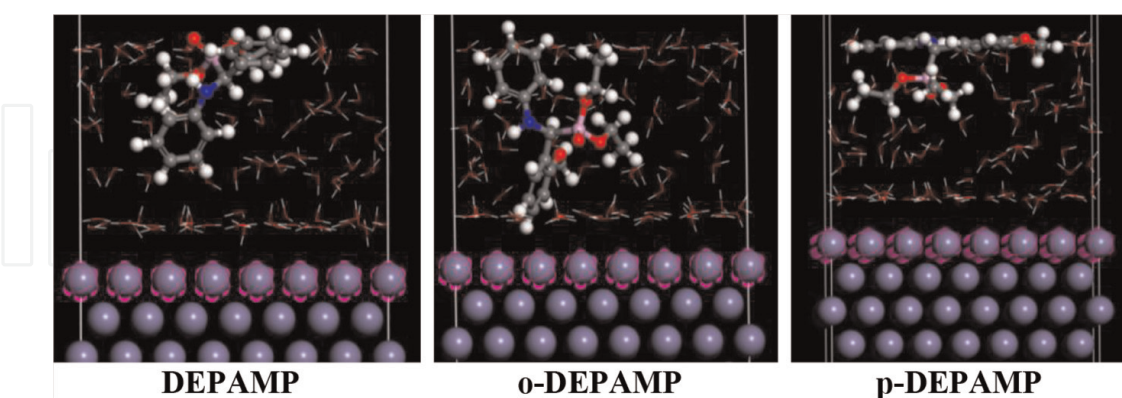
Table 1.

Some calculated quantum chemical descriptors of ethyl hydrogen [(2-methoxyphenyl)(methylamino) methyl]phosphonate and ethyl hydrogen [(3-methoxyphenyl)(methylamino) methyl]phosphonate [22].

3.7 Molecular dynamic simulations (MDS)

Molecular dynamic simulations (MDS) are one of the most effective theoretical methods for elucidates and interprets at the molecular level the mode and configurations of the adsorbed inhibitory molecules on the metal surface. Also, the MDS method is principally used to calculate the adsorption energy of the inhibitive molecules. In this context, MDS are largely applied to analysis the adsorption modes of phosphonates and phosphonic acids on metal surfaces. The adsorption energies of phosphonate derivatives on metal surfaces can be also calculated using MDS.

Concerning the application of MDS to study the mechanism of adsorption of phosphonate molecules on metal surfaces, we can cite the results obtained by Moumeni et al. [23], where she studied the adsorption mode of three phosphonic derivatives on the carbon steel surface (**Figure 11**). Also, the calculated values of the adsorption energy for the investigated inhibitors indicate that adsorption affinity of the substituted phosphonate in *Para* position is higher than these of *Ortho* and *Meta* positions (**Table 2**).

**Figure 11.**

AFM image of mild steel in the presence of 10^{-3} mol/L of ethyl hydrogen [(2-methoxyphenyl)(methylamino) methyl]phosphonate [23].

| Phosphonic inhibitor | DEPAMP | o-DEPAMP | p-DEPAMP |
|----------------------------|---------|----------|----------|
| Adsorption energy (kJ/mol) | -6589.8 | -6614.9 | -6773.9 |

Table 2.

Calculated adsorption energies of DEPAMP, o-DEPAMP and p-DEPAMP using molecular dynamic simulations [23].

Furthermore, the adsorption energy of phosphonates and phosphonic acids increases with the increase in the number of phosphonate groups in the molecule ($\text{O}=\text{P}-(\text{OH})_2$ or $\text{O}=\text{P}-(\text{OR})_2$).

Figure 11 shows the MDS results of Diethyl(phenyl(phenylamino)methyl) phosphonate (DEPAMP), Diethyl(((2-methoxyphenyl)amino)(phenyl)methyl) phosphonate (o-DEPAMP) and Diethyl(((4-methoxyphenyl)amino)(phenyl)methyl) phosphonate (p-DEPAMP) [23].

4. Conclusion

As a conclusion, both experimental and theoretical techniques prove that phosphonates and phosphonic acids are promising corrosion inhibitors and their high inhibitory activity is directly linked to the presence of phosphonic groups ($\text{O}=\text{P}-(\text{OH})_2$ or $\text{O}=\text{P}-(\text{OR})_2$) in their molecular structure. Also, the mechanism of action of this type of inhibitors consists to form an adsorbed layer of the inhibitive molecules on the metal surface. On the other hand, the electrochemical techniques show that phosphonates and phosphonic acids act as mixed type of inhibitor by controlling both anodic and cathodic reactions. Moreover, the microscopic techniques such as SEM and AFM confirm the formation of a protective thin layer of the adsorbed molecules on the metal surface, and this phenomenon is confirmed by the decrease in the values of roughness of metal surface after the addition of inhibitors to aggressive solution. Finally, the theoretical methods such as DFT and MDS demonstrate that the active sites responsible for the adsorption of these molecules are located on the oxygen atoms of the phosphonic functional groups.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

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