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# Synthesis of ethylene bis [(2-hydroxy-5,1,3-phenylene) bis methylene] tetraphosphonic acid and their anticorrosive effect on carbon steel in 3% NaCl solution



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# ABSTRACT

The inhibition performance of the newly synthesized Ethylene bis [(2-hydroxy-5,1,3-phenylene) bis methylene] tetraphosphonic acid (ETPA) toward carbon steel in 3% NaCl was investigated at different concentrations using potentiodynamic polarization (PDP) and impedance spectroscopy (EIS) methods. It was found that the inhibition capability was increased with increasing inhibitor dose and reach 92% at  $10^{-3}$  mol/L. Also, Polarization curves showed that ETPA acts as a mixed type inhibitor with predominantly control of anodic reaction. The new inhibitor was investigated by different spectroscopic methods such as <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>PNMR. The quantum parameters such as absolute electronegativity ( $\chi$ ), energy gap  $\Delta E$  (E<sub>HOMO</sub>-E<sub>LUMO</sub>), global softness ( $\sigma$ ), global hardness ( $\eta$ ), electrophilicity index ( $\omega$ ) and the number of transfer electrons ( $\Delta N$ ) are calculated by density functional theory (DFT). The experimental also correlated with density functional theory results. The calculations show that ETPA has high density of negative charge located on the oxygen atoms of the phosphonate group facilitating the adsorption of ETPA on the surface of carbon steel. The inhibition efficiency of ETPA was discussed in terms of blocking of electrode surface by adsorption of ETPA molecules through active centers. The adsorption of ETPA on the surface of carbon steel loeyed the Langmuir isotherm paradigm.

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# 1. Introduction

Corrosion of carbon steel (CS) in acidic, saline, neutral media is highlighted in the research and industry [1].

Various organic compounds containing P, N, O, S donor centers and – C = N– linkage can adsorb on the metal surface and works as inhibitors to protect the steel form dissolution [2–4]. The inhibitor usually blocks the active sites and decreases the corrosion rate [5–9]. Nowadays, due to new restrictive environmental laws, the inhibitors must be non-toxic and biodegradable [10]. Phosphonates have considerable attributes; they are chemically stable, hydrosoluble, flexible, non-toxic [11–14] and wide spread as corrosion inhibitors in cooling water system and sea water [15–17]. Especially their action as inhibitors for metals in neutral chloride media have been reported in many articles [18–20]. For example, Amar et al. [21,22] have examined the impact of two phosphonic acid as inhibitors for the corrosion of iron in sodium chloride

\* Corresponding author. *E-mail address:* nabila\_aliouane@yahoo.fr (N. Aliouane). solutions. The results indicate that phosphonate can be adsorb very well on the metal surface and enhance inhibition efficiency (IE).

Recently, Moschona et al. [23] studied the inhibitory effect of six phosphonates compounds, namely EDTMP, TDTMP, HDTMP, ODTMP and DDTMP on a carbon steel surface in 3,5% NaCl using the XPS method. They found that the thickness of the protective film adsorbed on the steel surface which is formed by this negatively charged inhibitors improve their effective corrosion inhibition. In a previous work [24] we studied the inhibitory effect of the phosphonate namely 2hydroxy-5-[4-hydroxy-3,5-bis (phosphonomethyl) benzyl]-3-(phosphonomethyl) benzylphosphonic acid (TPA) on carbon steel in 3% NaCl. We found that TPA acts as anodic inhibitor and the inhibitory efficiency is increased with increasing the concentration. Also, it's adsorption on the surface of the carbon steel follows the Langmuir adsorption isotherm. Also, phosphonates have a large number of binding sites and can efficiently act as a barrier to chlorides ions [25] resulting in reduce of the local corrosion of steel [26], whereas the increase of chain length will improve the corrosion inhibition [27].

Phosphonates are also, investigated in acidic media, Chafai et al. [28] studied the inhibitory action of  $\alpha$  -aminophosphonic derivative namely

4-(2-{[ethoxy (hydroxy) phosphonyl] (3-nitrophenyl) methyl} hydrazinyl) benzoic acid on the corrosion of carbon steel. They found that the inhibitory adsorption of this phosphonate followed Langmuir isotherm.

Metal surface modification with self-assembled phosphonic acid layers has also investigated [29,30]. It is found that the protective layer was spontaneously formed on metal surface and efficiently prevents the metal from corrosion in sodium chloride solution. However, X.T. Le [31] found that, the self-assembled benzylphosphonic acid layers are instable in sulfuric acid due to excess of protons.

Table 1 shows the results of previous studies [24,32–35]. Optimal inhibition efficiency greater than 90% can be achieved with phosphonate in aggressive environments. Furthermore, inhibitory action is due to the existence of heteroatoms (N, P and O), conjugate bonds and aromatic rings in molecular structure which are served as centers of interaction between phosphonates and metallic surfaces.

In the present work, the corrosion inhibition efficiency of new phosphonic acid, ethylene bis [(2-hydroxy-5,1,3-phenylene) bis methylene] tetraphosphonic acid (ETPA), which have four phosphonic acid functions and many binding molecules on the corrosion of carbon steel in 3% NaCl solution was studied using potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). Some thermodynamic values were deduced from adsorption isotherms. Finally DFT was employed to find the quantum parameters to estimate the adsorption behavior and describes the mechanism of corrosion inhibition.

## 2. Experimental and theoretical calculation

NMR spectra were recorded with a JeolGX. Purification of the phosphonate derivative was performed with a Hewlett-Packard 1100 HPLC system using  $C_{18}$  column.

#### 2.1. Synthesis of ETPA

The novel polyphosphonate (ETPA) was synthesized through a multi-step process as shown in Scheme 1 (Section 3.1).

## 2.1.1. Synthesis of 4-methoxybenzyl chlorate 2

2 mol of SiO<sub>2</sub>, 0.18 mol of trimethylsilyl chloride (TMSCI)) and 1.25 mL of CCl<sub>4</sub> were added to 100 mL round-bottom flask. The mixture was stirred at room temperature for a few minutes and 92.5 mmol of 4-methoxybenzyl alcohol (2.88 mL) was added drop wise. The mixture was stirred for 2 h at room temperature. The solvent was evaporated at 117–118 °C and under 10 mmHg with hexamethyl disiloxane to give the expected chloride **2** with excellent purity and a 50% yield. Compound **2** can be stabilized by addition anhydrous potassium carbonate and stored under nitrogen. <sup>1</sup>HNMR (CDCl<sub>3</sub>,  $\delta$  ppm): 3.19 (s, OCH<sub>3</sub>, 3H), 3.98 (s, 2H), 6.32 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H). <sup>13</sup>CNMR (67.5 MHz, CD<sub>3</sub>Cl):  $\delta$  = 46.3 (CH<sub>2</sub>-Cl), 55.23 (O-CH<sub>3</sub>), 114.1 (2 × CH), 129.85(2 × CH), 134.1 (C-CH<sub>2</sub>Cl), 152.8 (C-OCH<sub>3</sub>).

# 2.1.2. Synthesis of diethyl4-methoxybenzylphosphonate 3

(2.1 g, 0.21 mol) of 4-methoxybenzyl chloride **2** and (0.26 mol, 1.91 mL) of triethylphosphite were added into a two-neck 100 mL

round-bottom flask, equipped with a reflux condenser. The mixture was heated at 150 °C for 6 h. The excess of triethylphosphite was evaporated under reduced pressure with diethyl ether. The diethyl 4-methoxybenzyl phosphonate **3** was then analyzed by <sup>1</sup>HNMR. Yield: (1,5 g, 50%). <sup>1</sup>HNMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1,29 (t, 14,2 Hz, 2 × CH<sub>3</sub>, 6H), 3.05 (d, J = 20.9 Hz, 2H), 3.83 (s, OCH<sub>3</sub>, 3H), 4.01(q, J = 10.6 Hz,2 × CH<sub>2</sub>,4H), 6.80 (d, J = 8.1 Hz, arom-H, 2H), 7.17 (d, J = 10.6 Hz, arom-H, 2H).

#### 2.1.3. Synthesis of 1-(1'-methoxy-4'-phenylvinyl)-4-methoxybenzene 4

Compound **4** was prepared according to a published procedure [36] with some modification as follow: 250 mL reaction vessel equipped with a magnetic stirrer and reflux condenser. The flask was charged with (0.100 g, 2.1 mol) of diethyl 4-methoxybenzyl phosphonate and (0.100 g, 2.1 mol) 4-methoxybenzaldehyde. After stirring for 1 h, (0.035 g, 2.5 mol) of sodium ethylate in dry DMF (600 mL) was added. The mixture was stirred for 1 h at 0 °C then at room temperature for 24 h. The yellow precipitate which was formed was recrystallized by ice water (yield 80%). <sup>1</sup>HNMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 4.21 (s, 6H, O-CH<sub>3</sub>), 7.34(d, *J* = 8.85 Hz, 4H, arom-H), 7.44 (s, 2H, HC=CH), 7.91 (d, *J* = 10.1 Hz, 4H, arom-H).

## 2.1.4. Synthesis of 1,2-Bis (4-methoxyphenyl) ethane 5

The reaction vessel is a stainless-steel Parr-Hydrogenator (Parr-4842) that can stand pressures up to 10 bar. The reaction mixture which was prepared by adding 0.100 g of **4** and 0.050 g of Pd/C and 4 mL of methanol was stirred for 3 h under H<sub>2</sub> atmosphere. The mixture was diluted with 10 mL EtOH then filtered through celite. The filtrate was evaporated under vacuum and the remaining residue was washed with chloroform and dried under vacuum to give 0.098 g (98% yields). <sup>1</sup>HNMR (CDCl<sub>3</sub>,  $\delta$  ppm): 2.83 (s, 4H, H<sub>2</sub>C-CH<sub>2</sub>), 3.79 (s, 6H, O-CH<sub>3</sub>), 6.83 (d, 4H, arom-H), 7.09 (s, 4H, arom-H).

## 2.1.5. Synthesis of Bis (4-hydroxyphenyl)ethane) 6

Compound 6 was prepared according to the literature [37] with some modification as follow: (0.1 g, 0.037 mol) of bis-(4-methoxyphenyl)-ethane was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (1.7 mL) and under nitrogen in a 150 mL Erlenmeyer flask, fitted with a septum. The solution was cooled to -70 °C in dry ice/2-propanol bath. Boron tribromide (0.9 mL, 0.078 mol) was added through the septum. The reaction mixture was stirred at room temperature overnight and then poured into ice-cold water. After neutralization with an excess of so-dium acetate (10 mol/L), the resulting suspension was filtered. The precipitate was washed twice with H<sub>2</sub>O (20 mL) and air-dried overnight to give a white crude product. Finally, (0.095 g, 0.035 mol) of white solid was taken up in methanol (100 mL), filtered and evaporated (yield: 95%). <sup>1</sup>HNMR (CD<sub>3</sub>OD,  $\delta$  ppm): 2.70 (s, 2 × CH<sub>2</sub>), 6.65 (d, J = 8.2 Hz, 4 × arom-H), 6.90 (d, J = 8.2 Hz, 4 x arom-H).

# 2.1.6. Synthesis of 4,4-ethylenebis[2,6-bis(hydroxymethyl)phenol] 7

Compound **7** was synthesized according to published procedure [38], the product **7** is obtained with a yield of (1,4 g, 70%). <sup>1</sup>HNMR (CD<sub>3</sub>OD,  $\delta$  ppm): 3.78 (s, 4H, 2 × CH<sub>2</sub>), 4.65 (s, 8H, 4 × CH<sub>2</sub>-OH), 6.98 (s, 4H, arom-H).

#### Table 1

Studies of phosphonates as inhibitors for metals in different corrosive environments.

Compounds	Metal	Aggressive environment	IE (%)	Optimum concentration	Ref
Diethyl(phenyl(phenylamino)methyl)phosphonate (DEPAMP)	CS	1 M HCl	92	10 <sup>-3</sup> mol/L <sup>-</sup>	[32]
[hydroxy(phenyl)methyl] phosphonate Acid (HPMPA)	CS	1 M HCl	91	0.4 mM	[33]
Phosphatidylcholine	Cu	1 M HCl	96	10%	[34]
$\alpha$ -aminophosphonates	CS	250 g/m <sup>3</sup> CO <sub>2</sub> and 200 g/m <sup>3</sup> H <sub>2</sub> S	94.3	50 mg/ml	[35]
2-hydroxy-5-[4-hydroxy-3,5-bis(phosphonomethyl) benzyl]-3-(phosphonomethyl) benzylphosphonic acid,	CS	3% NaCl	88	10 <sup>-3</sup> M	[24]



Scheme 1. Synthesis of the inhibitor ETPA (9).

2.1.7. Synthesis of {ethylene bis [(2-hydroxy-5,1,3-phenylene) bismethylene]} tetraphosphonic acid (ETPA, 9)

The product **9** was obtained with a yield of (1,4 g, 76%) according to the published procedure [38–40]. <sup>1</sup>HNMR (D<sub>2</sub>O,  $\delta$ ) 3.04 (d, 2 x CH<sub>2</sub>, 4H), 3.68 (d, J<sub>PH</sub> = 20.7 Hz, 4 x CH<sub>2</sub>-P, 8H), 6.93 (s, arom-H, 4H).<sup>13</sup>CNMR (D<sub>2</sub>O,  $\delta$ ):30.3 (d, J<sub>PC</sub> = 132.0 Hz, CH<sub>2</sub>-P), 40.0 (s, Ph-CH<sub>2</sub>-CH<sub>2</sub>-Ph), 122.6 (m, C-CH<sub>2</sub>-P), 131.2 (s, CH), 135.4 (t, J<sub>PC</sub> = 2.5 Hz, C-CH<sub>2</sub>), 151.0 (t, J<sub>PC</sub> = 6.0 Hz, C-OH). <sup>31</sup>PNMR (D<sub>2</sub>O,  $\delta$ ) 25.9. MS-ESI: [M-H]<sup>-</sup> at *m*/*z* 588.9.

# 2.2. Density functional theory calculations (DFT)

Full geometry optimization of ETPA and quantum chemical calculations were performed using the Gauss View [41] and standard Gaussian-03 software package [42]. Geometry optimization of the ETPA in the gas phase was carried out using density functional theory (DFT) level with the non-local hybrid density functional B3LYP [43], combining with Becke's three-parameter hybrid exchange correlated with Lee et al. functional [44] at 6-31G(d,p) basis set [45].

The values of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  have been used to calculate energy gap  $\Delta E$ , global hardness ( $\eta$ ), global softness ( $\sigma$ ), absolute electronegativity ( $\chi$ ), electrophilicity index ( $\omega$ ) and number of transfer electrons ( $\Delta N$ ) as shown in the Eqs. (1)–(5) [45–50].

$$\Delta E = E_{\rm HOMO} - E_{\rm LUMO} \tag{1}$$

$$\sigma = \frac{1}{\eta} \tag{2}$$

$$\chi = \frac{-(E_{\text{LUMO}} - E_{\text{HUMO}})}{2} \tag{3}$$

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$$\omega = \frac{\chi^2}{2\eta} \tag{4}$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{[2(\eta_{Fe} + \eta_{inh})]}$$
(5)

where is  $\chi_{Fe} = 7.0$  eV and  $\eta_{Fe} = 0$  for Fe bulk.

## 2.3. Electrochemical measurements and solution

Both electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements (PDP) were carried out using Autolab PGSTAT30 potentiostat/galvanostat. A 250 mL cylindrical glass cell with three electrodes system was used. A platinum sheet and a saturated calomel electrode (SCE) were used as auxiliary (AE) and reference electrodes (RE), respectively. A disc of carbon steel (CS) with an area of 0.196 cm<sup>2</sup> and composition (wt%): 0.11C, 0.45Mn, 0.04P, 0.05S, 0.25Si and the remainder is Fe was used as working electrode. According to literature [51], the shear stress induced by the hydrodynamic flow causes the desorption of inhibitory molecules from the surface so the study is conducted in stagnant condition. Tafel curves were obtained with the scan rate of 1 mV s<sup>-1</sup> between potential ranges from +250 to -250 mV versus open circuit potential (OCP). The inhibition efficiency *IE* (%) was calculated using Eq. (6):

$$IE(\%) = \frac{\mathbf{i}_{corr^{\circ}} - \mathbf{i}_{corr}}{\mathbf{i}_{corr^{\circ}}} \times 100$$
(6)

where:  $i_{\rm corr^o}$  and  $i_{\rm corr}$  are the corrosion current density values without and with inhibitor.

The EIS measurements were carried out using AC signal (10 mV) peak to peak at the open circuit potential (OCP) in the frequency range of 100 kHz to 10mHz. The inhibition efficiencies *IE* (%) of the tested inhibitor were calculated from the  $R_p$  values at  $1 \times 10^{-4}$ ;  $5 \times 10^{-4}$  and  $1 \times 10^{-3}$  mol/L at 298 K using the following equation:

$$IE(\%) = \left[\frac{R_p - R_p^\circ}{R_p}\right] \times 100 \tag{7}$$

where,  $R_p$  and  $R_p^{\circ}$  are the values of total polarization resistance in presence and absence of the ETPA.  $R_p$ , which signifies different resistances established at the metal-electrolyte interface and its value, was obtained experimentally by fitting the Nyquist plots employing suitable equivalent electrical circuit.

#### 3. Results and discussion

#### 3.1. Synthesis of the inhibitor ETPA

Polyphosponic acids are compounds which have significant binding affinity toward heavy metals and lanthanides [52,53]. The new inhibitor ETPA (**9**) have four phosphonic acids which was prepared by heating the crude ester **8** with a water/methanol solution at 90 °C in a sealed tube for 30 h (Scheme 1). The ester **8** was prepared by many steps reactions from benzyl halide with trialkyl phosphites according to the Michaelis–Arbuzov reaction [38–40].

The ETPA inhibitor is characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>PNMR spectroscopy. The <sup>1</sup>HNMR spectrum of **9** (Fig. 1a) shows a doublet at 3.68 ppm for eight protons which is assigned to CH<sub>2</sub>-PO<sub>3</sub>H<sub>2</sub>. These splitting for CH<sub>2</sub>-PO<sub>3</sub>H<sub>2</sub> are due to the coupling of the benzylic proton and the phosphorus atom with  $J_{PH}$  is equal to 20.2 Hz. The doublet around 3.04 is assigned to the two-bridging benzylic proton. In the <sup>13</sup>CNMR spectrum (Fig. 1b), the doublet appears at 30.3 ppm with a coupling constant  $J_{PC}$  is equal to 132.0 Hz is assigned to CH<sub>2</sub>-P. The singlet peak at 25.88 ppm in the phosphorus NMR spectrum (Fig. 1c) is assigned to the four equivalent phosphors atoms. Mass spectroscopy was used to identify and verify the purity of compound **9**. In ESI-MS negative ionization mode, the molecular ion at m/z = 588.9 is assigned to [M-H] – ion.

#### 3.2. Quantum chemical calculations

Frontier molecular orbital (HOMO and LUMO) and molecular electrostatic potential (MEP) for the inhibitor ETPA are shown in Fig. 2. The electronic distribution of HOMO is located mainly on the phenol rings. Also, both HOMO and LUMO of the entire ETPA molecule participates in the charge sharing. From the MEP image (Fig. 2), we note that the active sites of the molecule are presented by the different colors, knowing that the region from red to green is associated with an electrophilic attack while the region from green to blue corresponds to the nucleophilic attack. These colors are observed throughout the molecule (aromatic rings, oxygens, methyl carbons and two phosphonate groups).

The quantum chemical parameters (Table 2) such as: E<sub>HOMO</sub>, E<sub>LUMO</sub>,  $\Delta$ E,  $\mu$ ,  $\chi$ ,  $\eta$ ,  $\sigma$ ,  $\omega$  and  $\Delta$ N are used to estimate the efficiency of the inhibitor [54]. It has been established that a small  $\Delta$ E, low value of  $\eta$  and a high value of  $\chi$  and  $\mu$  are an indication of a high inhibition performance of the inhibitor. The dipole moment of ETPA  $\mu_{inh}$  is 6.75D which is largely higher than the dipole moment for water  $\mu_{H2O}$  (1.88D) which means that there is a strong dipole–dipole interaction between ETPA molecules and metallic surface.

Electrophilicity ( $\omega$ ) was used by Parr as a measurement for the tendency of inhibitor to gain electron [55–57]. A more reactive nucleophilic has low-value of  $\omega$ . The low value of the electrophilicity index  $\omega$  (1.94) for ETPA means a good inhibitory efficiency. Furthermore, the inhibition efficiency (%IE) is increased with increasing  $\Delta$ N values [58]. If  $\Delta$ N < 3.6 this means that ETPA is electron donors and that the surface of steel is an acceptor [55]. The electronegativity value ( $\chi$ ) of the inhibitor molecule (3.27 eV) is lower than that of iron (7.0 eV), suggesting an electron transfer from the HOMO of the inhibitor to the empty 3d orbital of Fe.

Table 3 shows the Mulliken charges of the inhibitor atoms. Generally, Mulliken population analysis is used to full fill the adsorption unshared electron pairs of the inhibitor on the iron surface orbitals. The more negatively charged of the heteroatom in the inhibiting species the strongly adsorbed inhibitor on the surface of steel by donoracceptor reaction type [59]. Table 3 shows that the more negative charges of ETPA are localized in all O atoms and the two carbon atoms of the two aromatic rings which make them a good adsorption sites [60]. According to similar compound in the literature [61], ETPA can form a thin, compact layer on the surface of carbon steel oriented perpendicularly into the interlamellar region. It can be chelated to metal surface by the phosphonate groups (PO(OH)<sub>2</sub>. The tetraphosphonic acid can be adsorbed on the carbon steel surface by forming ironphosphonate complexes capable to provide corrosion protection.

# 3.3. Open circuit potential (OCP) experiments

The open circuit potential of the working electrode was recorded before EIS and PDP experiments during 1 h to reach a steady state condition. The OCP experiments of CS substrate immersed in 3% NaCl were performed in the absence and the presence of the varying concentrations of the ETPA inhibitor (Fig. 3). Generally, straight OCP versus time curves suggest the dissolution of surface metal oxide and adsorption of the inhibitor [62]. From the results shown in Fig. 3, it is clear that the addition of the varying concentrations of the ETPA inhibitor to the corrosive solution produced a shift in the OCP curves to negative values without causing any modification in the general characteristic features of the curves [63]. Also, the OCP curves for CSI with ETPA are shifted to more positives compared to the OCP curve of carbon steel. This result suggests that the formation of a stable film of ETPA on the CS, and the shift in the OCP can be explained by the presence of a thin film of inhibitor at the metal/electrolyte interface.





Fig. 1. <sup>1</sup>HNMR (a), <sup>13</sup>CNMR (b), <sup>31</sup>PNMR (c) Spectrum of compound 9.



Fig. 1 (continued).

#### 3.4. Potentiodynamic polarization

ETPA was added to the 3% NaCl blank solution to give the final concentrations of ETPA 1  $\times$  10  $^{-4}$ ; 5  $\times$  10  $^{-4}$  and 1  $\times$  10  $^{-3}$  mol/L, respectively. All the test solutions were adjusted to pH = 7 using NaOH solution. Fig. 4 shows the Tafel polarization curves for the dissolution of CS in 3% NaCl solution, at 25 °C, in the absence and presence of different concentrations of ETPA. The Tafel parameters such as corrosion potential ( $E_{corr}$ ), rate of corrosion ( $i_{corr}$ ), cathodic slope ( $b_c$ ), surface coverage ( $\theta$ ) and inhibition efficiency (%*IE*) are computed and tabulated in Table 4. As expected, with addition of ETPA to the corrosive solution both anodic dissolution of CS and cathodic oxygen evolution reaction are reduced. This result can be explained by a barrier effect [64] by which the adsorbed inhibitor molecules form a thick electric double layer and decrease the cathodic transfer coefficient [65]. According to DFT results, the thick layer is due to the adsorption of the negatively charged oxygen atoms of the phosphonate group of ETPA molecules with the surface metal atoms. The presence of ETPA moves  $E_{\rm corr}$  in the positive direction relative to the blank curve. These results suggest that the ETPA can be classified as a mixed type corrosion inhibitor with predominantly control of anodic reaction for carbon steel in 3% NaCl. Table 4 shows that the values of  $b_a$  and  $b_c$ change significantly in the presence of ETPA, therefore inhibitory molecules can be adsorbed to anodic and cathodic sites. The parallel Tafel lines (Fig. 4) indicate that the inhibiting process is a charge-transfer mechanism [66] and the inhibition rate reaches 92% at  $10^{-3}$  mol/L. DFT results supported very well the experimental results, higher value of  $E_{\rm HOMO}$  (6.33 eV),  $\mu$  (6.75) and lower values of  $E_{\rm LUMO}$ (0.50 eV) and  $\Delta E$  (5.53 eV) for ETPA indicated that ETPA has more potency to get adsorbed on the carbon steel surface resulting in greater inhibition efficiency [67].

## 3.5. Adsorption isotherm

To search for the adsorption isotherm type of ETPA on the surface of carbon steel in a 3% NaCl, several isotherms models were used namely Langmuir, Frumkin and Temkin. These models are given by the following equations:

Langmuir : 
$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$
 (8)

Frumkin: 
$$\frac{\theta}{1-\theta} \exp\left(-2f\theta\right) = K_{ads}C$$
 (9)

Temkin : 
$$\exp(f\theta) = K_{ads}C$$
 (10)

where C is the inhibitor concentration (mol/L),  $K_{ads}$  the equilibrium constant of adsorption process,  $\theta$  the degree of coverage of a metal surface by inhibitor and f is the factor of energetic inhomogeneity.

The Langmuir, Temkin and Frumkin plots are given in Fig. 5. It is found that the Langmuir model fits perfectly with  $R^2 = 0.999$  and a slope value = 1.04 (Fig. 5a). These values are close to unity while for the Temkin and Frumkin isotherms, the slope values are 0.21 and 7.67 respectively (Fig. 5b-5c). The deviation of slope values from the unity is attributed because of the intermolecular interactions of the adsorbed species that cause repulsion or mutual attraction [68]. The Langmuir model implies a fixed adsorption centers number on the surface and the adsorption of one species by each center [69]. The  $K_{ads}$  constant may be determined from the intercept in Fig. 5a and its value is found to be  $K_{ads} = 10^5$  L/mol. This high value of  $K_{ads}$  means a strong adsorption of the inhibitor on carbon steel surface [61,70,71]. The adsorption free energy ( $\Delta G_{ads}$ ) can be calculated using Eq. (11).



Fig. 2. HOMO, LUMO and MEP view of ETPA given by the B3LYP/6-31(d.p).

 Table 2

 The calculated quantum chemical parameters for the studied ETPA in the gas and aqueous phase obtained using the DFT method at the B3LYP/6-31G(d,p) basis set.

Paramètres quantiques	$E_{tot}\left(eV\right)$	$E_{HOMO}\left(eV ight)$	$E_{LUMO} \left( eV \right)$	$\Delta E_{GAP}\left( eV\right)$	μ Debye	η (eV)	$\sigma(\text{eV}^{-1})$	χ (eV)	ω (eV)	$\Delta N$
Phase gazeuse	-84,913.2	-6.33	-0.68	-5.65	3.72	2.82	0.36	3.5	2.17	0.62
Phase aqueuse	-84,914.5	-6.04	-0.50	-5.53	6.75	2.76	0.36	3.27	1.94	0.67

#### Table 3

Obtained Mullikan atomic charges of the ETPA inhibitor.

Atom	Mulliken Charges	Atom	Mulliken Charges	Atom	Mulliken Charges	Atom	Mulliken Charges
C <sub>1</sub>	-0.166314	C <sub>16</sub>	-0.153239	0 <sub>31</sub>	-0.595735	047	-0.544169
$C_2$	-0.226807	C <sub>17</sub>	-0.153535	H <sub>32</sub>	0.310182	048	-0.534984
C <sub>3</sub>	0.128772	C <sub>18</sub>	0.036327	O <sub>33</sub>	-0.596999	049	-0.500524
$C_4$	-0.177059	H <sub>19</sub>	0.076529	H <sub>34</sub>	0.314702	0 <sub>50</sub>	-0.544499
C <sub>5</sub>	0.114367	C <sub>20</sub>	0.037693	<b>O</b> <sub>35</sub>	-0.607026	C <sub>51</sub>	-0.426489
C <sub>6</sub>	0.366958	H <sub>21</sub>	0.080766	H <sub>36</sub>	0.339431	H <sub>52</sub>	0.191430
H <sub>7</sub>	0.227475	C <sub>22</sub>	0.288680	<b>O</b> <sub>37</sub>	-0.560743	H <sub>53</sub>	0.170886
H <sub>8</sub>	0.075029	P <sub>23</sub>	0.941770	H <sub>38</sub>	0.325096	C <sub>54</sub>	-0.460088
C <sub>9</sub>	-0.218395	P <sub>24</sub>	1.108849	<b>O</b> <sub>39</sub>	-0.587042	H55	0.184222
H <sub>10</sub>	0.123727	P <sub>25</sub>	1.109448	H40	0.350540	H56	0.143983
H11	0.112594	P <sub>26</sub>	1.055609	<b>O</b> <sub>41</sub>	-0.546839	C <sub>57</sub>	-0.484729
C <sub>12</sub>	-0.267761	<b>0</b> <sub>27</sub>	-0.442469	H42	0.309066	H <sub>58</sub>	0.235788
H <sub>13</sub>	0.104484	H <sub>28</sub>	0.322491	0 <sub>43</sub>	-0.538418	H59	0.225664
$H_{14}$	0.090532	<b>O</b> <sub>29</sub>	-0.585809	H44	0.287679	C <sub>60</sub>	-0.384291
C <sub>15</sub>	0.102097	H <sub>30</sub>	0.317967	<b>O</b> <sub>45</sub>	-0.597402	H <sub>61</sub>	0.204536
				H46	0.342007	H <sub>62</sub>	0.143989

Bold signifies negatively charged atoms.



Fig. 3. Evolution of OCP with time measured for carbon steel in 3% NaCl without and with various concentrations of ETPA at room temperature.

$$K_{ads} = \frac{1}{55, 5} \exp \frac{-\Delta G^{\circ}_{ads}}{RT}$$
(11)

where,  $K_{ads}$  is adsorptive equilibrium constant, R is the universal gas constant, T is the temperature (K) and 55.5 is the water concentration in the solution (mol/L).  $\Delta G_{ads}$  is calculated from the adsorption isotherm and found to be -38 kJ/mol at 298 K. This negative value of  $\Delta G_{ads}$  indicates that the adsorption of ETPA on the CS surface is spontaneous. The value of  $\Delta G_{ads} \leq -40$  kJ/mol means that the interaction of ETPA molecule onto the carbon steel surface is strong and the adsorption is chemisorption [72,73].

# 3.6. EIS measurements

Impedance spectra (Fig. 6) were represented the Nyquist and Bode plots for the CS interface in 3% NaCl at different concentrations of ETPA. The Nyquist curve (Fig. 6a) shows that there is a depressed semi circles (loop capacitive) in the presence of inhibitor suggesting the non-homogeneity and roughness of the carbon steel surface. It is also observed that the size of the semi circles is increased with increasing the concentration of the inhibitor which increases the charge transfer resistance due to adsorption of ETPA on the surface of the carbon steel.



Fig. 4. Polarization plots of carbon steel in 3% NaCl at various concentrations of ETPA.

Fig. 6b shows the plot of Z-module and phase angle values versus frequency (|Z| and  $\theta$ ). The observed small values for  $\theta$  (20°) is due to the attack of the metal surface by chloride ions (blank) and  $\theta$  is increased to  $65^{\circ}$  as the concentration of ETPA is increased to  $10^{-3}$  M. The increasing of  $\theta$  is probably due to the formation of a protective film from phosphonate on carbon steel surface. It is also observed that |Z| value is increased with increasing the concentration of ETPA and reach a value of 545  $\Omega$ .cm<sup>2</sup> which is greater than the value obtained for the blanck (100  $\Omega$ .cm<sup>2</sup>) due to the resistivity of the medium in the presence of ETPA [74]. The equivalent circuit (EC) presented in Fig. 7 was used to analyze the EIS results. In this model, R<sub>s</sub> represents the solution resistance and R<sub>ct</sub> represents the resistance of charge transfer. Electrical circuits were used to model the steel/NaCl interface in the absence and presence of inhibitor using the Zview software (Fig. 7). In the absence of ETPA, the Nyquist plot is equivalent to an electrical circuit (Fig. 7a) consisting of a charge transfer resistor ( $R_{ct}$ ) parallel to a constant phase element (CPE) and both in series with the resistance of the electrolyte ( $R_c$ ). While in the presence of ETPA it is equivalent to the electrical circuit in Fig. 7b. The same electrical circuit is found for all concentrations of ETPA. Fig. 8 is an example of fitting of Nyquist and Bode diagrams of carbon steel in 3% NaCl solution without and with  $10^{-3}$  mol/L of ETPA. The fitting is in good agreement with the models which was obtained for all experimental data and the impedance plots are consistent with those calculated using different equivalent circuit models. From the Nyquist plots,  $R_{ct}$ ,  $C_{dl}$ , n,  $Y_{o}$  and  $E_{EIS}$  could be derived by Zview impedance fitting software and listed in Table 5.

The polarization resistance  $R_p$ , which is equivalent to charge transfer resistance  $R_{ct}$  is calculated by the summation of  $R_1$  and  $R_2$  at different inhibitor concentrations and the resultant  $R_{ct}$  is used to calculate the percentage of inhibition efficiency *IE* (%).

The results in Table 5 show that the value of  $R_p$  ( $R_1 + R_2$ ) increases with the concentration of ETPA. In addition, the admittance  $Y_{01}$  and  $Y_{02}$  values proportional to CPE<sub>1</sub> and CPE<sub>2</sub> decrease with increasing ETPA concentration. The variation of the  $R_p$  and  $Y_{01}$  and  $Y_{02}$  values can be related to the gradual elimination of the water molecules (active sites for the reaction of corrosion) by the ETPA molecules on the surface of the electrode [75–77]. The increase in the value of  $R_p$  is attributed to the formation of a protective film at the metal / solution interface. The values of *n* in this study ranged from 0.8 to 0.9 and it decrease to 0.7 in the presence of  $10^{-3}$  M inhibitor compared to pure 3% NaCl (0.8) suggesting there is an increase in heterogeneity due to the adsorption of ETPA on CS/ electrolyte interface [78]. This low value of n is also sign of a non homogeneous nature of the ETPA protective film [24,79]. However, the difference between n values is not large indicating that the dissolution mechanism of CS is controlled by charge transfer in the absence

#### Table 4

Electrochemical parameters of steel at various concentrations of ETPA studied in 3% NaCl at 298 K with corresponding corrosion inhibition efficiencies.

[ETPA] (10 <sup>-4</sup> mol/L)	E <sub>corr</sub> (mV/SCE)	i <sub>corr</sub> (mA/cm <sup>2</sup> )	b <sub>a</sub> (mV/dec)	b <sub>c</sub> (mV/dec)	IE (%)	θ
0	-555	0.965	175.9	495.36	/	
1	-501	0.280	138.75	399.63	70.0	0.70
5	-494	0.153	161.57	305.64	84.0	0.84
10	-485	0.0770	119.58	359.69	92.0	0.92



**Fig. 5.** Langmuir (a), Temkin (b) and Frumkin (c) adsorption isotherm plots for the adsorption of ETPA on carbone steel surface in 3% NaCl.

and presence of ETPA. We also note that the inhibition efficiency increases with the increase in the concentration of ETPA to reach a



Fig. 6. Nyquist (a) and Bode (b) plots of carbon steel at different concentrations of ETPA.

maximum value of 91% at  $10^{-3}$  mol/L. This result is due also to the low values of  $\Delta E$ ,  $E_{LUMO}$ ,  $\omega$ ,  $\eta$  and high values of  $E_{HOMO}$ ,  $\mu$ ,  $\sigma$ ,  $\Delta N$  in aqueous medium. This indicates that the ETPA molecules are adsorbed at the metal/solution interface, which slows down the corrosion process. These results confirm that ETPA presents an excellent inhibitory performance of carbon steel in 3% NaCl medium.

## 3.7. Potential of zero charge (pzc)

The surface charge of metal can be determined by the position of open circuit potential in respect to the respective pzc [80]. The EIS offers a good method to determine the potential of zero charge (pzc) of metals. For this purpose, the EIS technique was used to define the pzc of the CS in the inhibited 3% NaCl solution with the addition of  $10^{-3}$  mol/L ETPA. The  $E_{\text{OCP}}$  value of CS in 3% NaCl solution containing  $10^{-3}$  mol/L ETPA and  $E_{pzc}$  values are plotted in the same diagram. The surface charge of CS is indicated by comparing the corrosion potential with the  $E_{pzc}$  (the maximum  $R_P$  value corresponds to minimum  $C_{dl}$ value) [81]. The plot of the R<sub>P</sub> versus the applied potentials after 1 h of immersion time is given in Fig. 9. It can be seen that the obtained arc appears to be parabolic and has a pzc at -0.493 (V/SCE). The open circuit potential of the CS in the same condition is found to be -0,485 V/SCE. The difference,  $E_r = E_{OCP} - E_{PZC} = 0.008$  V, where  $E_r$  is the Antropov's "rational" corrosion potential [82]. Er is positive, which means that the metal surface is positively charged at the open circuit potential after 1 h of exposure time.



Fig. 7. Equivalent circuits used to fit experimental EIS data for the corrosion of the carbon steel specimen in 3% NaCl in the absence (a) and presence of ETPA (b).

## 3.8. Adsorption mechanism research

According to DFT calculation, there is a correlation between the molecular structure of the ETPA molecules and their inhibitory power. The electron-rich HOMO orbital is localized mainly on the phenol rings. ETPA can exert its inhibition action by adsorption on the carbon steel surface through the  $\pi$ -electrons of the two phenyl rings and the (P, O) unpaired electrons of the  $PO(OH)_2$  with the vacant d orbital of iron. This hypothesis is supported by the negatives Mulliken charges of the ETPA inhibitor which are localized on the oxygen atoms. These results are in agreement with that of Abdallah et al. [83–85] where the inhibitors with electron donating increase the percentage of inhibition efficiency as the concentration increases. In addition, the PDP, EIS and pzc experiments support that the corrosion inhibition is depend on the



Fig. 8. Fitted Nyquist and Bode plots at  $10^{-3}$  mol/L of ETPA (a, b).

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Fig. 9. The plot of  $R_{\rm p}$  versus applied potential obtained in 3% NaCl containing  $10^{-3}$  mol/L ETPA.

concentration and nature of the inhibitor. Furthermore, isotherm adsorption model conforms that the adsorption of ETPA on the carbon steel surface obeys Langmuir monolayer adsorption. In addition, the negative value of  $\Delta G_{ads} \leq -40$  kJ/mol support that there is a strong interaction of ETPA molecule onto the carbon steel surface.

## 4. Conclusions

In this study, a new inhibitor, ethylene bis [(2-hydroxy-5,1,3phenylene) bis methylene] tetraphosphonic acid (ETPA), was synthesized and characterized using various spectroscopic methods. DFT calculations showed that ETPA is a good corrosion inhibitor due to its  $\Delta E$ ,  $E_{LUMO}$ ,  $\omega$ ,  $\eta$  low values and  $E_{HOMO}$ ,  $\mu$ ,  $\sigma$  and  $\Delta N$  high values in aqueous medium. Polarization curves revealed that this compound is a mixed-type inhibitor with predominantly control of anodic reaction. Its inhibition efficiency IE(%) increased with its concentration and reach a maximum value of 92% at  $10^{-3}$  mol/L. The results of the EIS indicate that the values that  $R_p$  and IE(%) tend to increase with increasing inhibitor concentrations. This result can be attributed to an increase in the thickness of the protective film formed on the surface of the carbon steel. The adsorption of ETPA on carbon steel in 3% NaCl solution obeyed Langmuir adsorption isotherm. Finally, the quantum chemical calculations support the experimental electrochemical study.

## **Credit author statement**

**N. Sait:** Conceptualization, Data curation, Formal analysis, Investigation\_ Methodology, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, review & editing. **N. Aliouane:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, review & editing. **L. Toukal:** Conceptualization, Data curation, Formal analysis, Investigation\_Methodology, Resources, Software, Supervision, Validation, Visualization, Writing - original draft. review & editing. **H. Hammache:** Data curation, Formal analysis, Investigation\_ Methodology, Project administration, Resources, Software, Validation, Visualization, Writing - original draft., review & editing. **M. Al-Noaimi:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, review & editing. **J. J. Helesbeux:** Data curation, Formal analysis, Investigation\_Methodology, Resources, Software, Validation, Visualization, Writing - original draft, review & editing. **O. Duval:** Data curation, Formal analysis, Investigation\_Methodology, Resources, Software, Validation, Visualization, Writing - original draft, review & editing. **O. Duval:** Data curation, Formal analysis, Investigation\_Methodology, Resources, Software, Validation, Visualization, Writing - original draft, review & editing. **O. Duval:** Data curation, Formal analysis, Investigation\_Methodology, Resources, Software, Validation, Visualization, Writing - original draft, review & editing.

## **Declaration of Competing Interest**

None.

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