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AN ELECTROCHEMICAL STUDY FOR CORROSION INHIBITION OF IRON BY A DERIVATIVE OF ORGANIC PHOSPHONIUM HALID IN ACID MEDIA

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ABSTRACT

Steel and its alloys have many industrial applications, especially in the chemical, thermal, nuclear and, recently, in the petroleum industry. Therefore, the study of corrosion and corrosion inhibition of this metal is a very important subject. This work describes the study of the corrosion behavior of XC 70 steel in sulfuric acid medium and the evaluation of the protective power of a series of synthesized compounds such as methyltriphenylphosphonium iodide3. The study was carried out using the Tafel straight line method and electrochemical impedance spectroscopy. The results obtained show that methyltriphenylphosphonium iodide (8) is a very effective mixed inhibitor and reaches a maximum of 83.71% at C = 30 M and for the rotational state of 1500 rpm. The inhibitory efficacy of this compound reaches a maximum of 97.80 at C = 60 M and the results indicate that adsorption is chemisorption following Langmur.

Keywords: Iron, Phosphonium salt, sulfuric acid, corrosion, inhibitor, electrochemical methods.

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1. INTRODUCTION

In recent yearswe have published many papers about application of phosphonium salts and phosphonium oxides in electrochemical field on corrosion inhibition of iron in acid media [1, 2]. More recently we have also reported that phosphonium salts derivatives are effective against the corrosion of metals such as mild steel [3]. In 2019, we reported that the phosphonium salts are the convenient inhibitors and their efficienciesfollow the order: phosphonium halids (PH) > phosphonium oxides (PO) [4].

Phosphonium salts appear to have a wide range of potential applications as corrosion inhibitors. As is known, iron is one of the metals used widely used in industry and this metal may be exposed to corrosion due environmental factors. For this reason, the synthesis and design of new corrosion inhibitors to prevent the corrosion of iron are quite important. Thus, in this opportunity we report here the synthesis and characterization of methyl triphenylphosphonuim iodide acting as anodic type inhibitors with predominant effect.

2. EXPERIMENTAL

To support our development of electrochemical study for corrosion inhibition of iron by lists of numerous chemical compounds that exhibit inhibitive properties such as phosphonuim halide derivatives in acid media, we required a synthesis of different phosphonium salts such as methyl triphenylphosphonuim iodide. Thus, the strategy we have adopted for this project consists of the following steps: (i) synthesis of phosphonium salt, methyl triphenylphosphonuim iodide with taking considerations of cost, toxicity, availability, and environmental friendliness. (ii) Employing this product as a chemical inhibitor to decrease the rate of corrosion processes.

2.1. Synthesis part

2.1.1. Materials

Triphenylphosphine (98%), methyl iodide (98%), acetone (99.5%), and hexane (99%) were purchased from Alfa Aesar; magnesium sulfate anhydrous (97%), and acetate ethyl was purchased from Acros Organics; Ethanol, chloroform and toluene p.a were purchased from Biochem Chemopharma Co (Canada).Solvents were purified according to standard methods.Merck 60 silica gel (230-400 mesh) was used for flash chromatography. All reactions were carried out under atmospheric air conditions. Solutions were dried over anhydrous magnesium sulphate $MgSO_4$ and evaporated under reduced pressure using a rotary evaporator (rotary evaporator (IKA Evaporator RV 06-ML).

All the products reported here are known compounds and their identity were determined using authentic samples and also melting or boiling points from the literature including Merck index.

2.1.2. Physical measurements

^1H NMR spectra were recorded on BRUCKER AC 300 MHz spectrometer at 0°C, and the chemical shifts are reported in ppm relative to the central line of the singlet for $CDCl_3$ at 7.26 ppm. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

^{13}C NMR and DEPT were recorded on BRUCKER AC 75 MHz spectrometer at 0°C and all are reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77.16 ppm. The spectra reported are proton decoupled.

IR spectra were recorded on SHIMADZU 830-FTIR spectrometer using KBr pellets. Melting points were recorded on a Gallenkamp melting point apparatus, and are uncorrected.

Thin layer chromatography (TLC) was performed on precooked 0.25 mm silica gel plates 60F254purchased from Merck.

2.1.3 Procedure for theSynthesis of phosphonuim salt 3

Phosphonium salt, methyl triphenylphosphonuim iodide**3**, was prepared from methyl iodide (26.7g, 12 mL, 188 mmol), triphenyl phosphine (40g, 153 mmol) in toluene or chloroform (200 mL) in similar way to those phosphonium salts prepared by Sekhri [5]. The resulting precipitate was separated by filtration and the crude product was recrystallized from toluene to afford methyl triphenylphosphonuim iodide (88%) as white crystals, m.p. 180-182°C.

The phosphonium salt was identified by comparison its spectroscopic data with those of an authentic sample:

ν_{max} (KBr disc): 696.3, 742.5, 954.7, 1068.5, 1110 (P=O), 1434.9, 1558.4, 2341.4and 2350 cm^{-1};^1H NMR: 3.1 (3H, d, J_{PH} = 13.0, CH_3), 7.7 (15 H, m, aromatic) **(Figure 3.1.3a)**; ^{13}C

NMR: δ 117.9(-ve DEPT): 11.50 (d, J_{PC}=57.3 Hz, CH_3); 117.78 (C); 118.96 (C); 130.59 (d, J_{PC}=12.1 Hz, CH); 132.94 (d, J_{PC}=10.56Hz, CH); 134.68 (CH)**(Figure 2.1.3b)**; m/z (FAB) 403 [(M+H),$^+$4], 278 [(M+H-1,11),$^+$ 4], [(M-1,$^+$ 100)], 276 (17), 225 (6), 200 (8), 182 (10), 183 (28), 108 (8) **(Figure 2.1.3c)**; EA**:** requires: C, 56.4%; H, 4.5%; P, 7.7%; found: C, 56.0%; H, 4.5%; P, 7.5%.

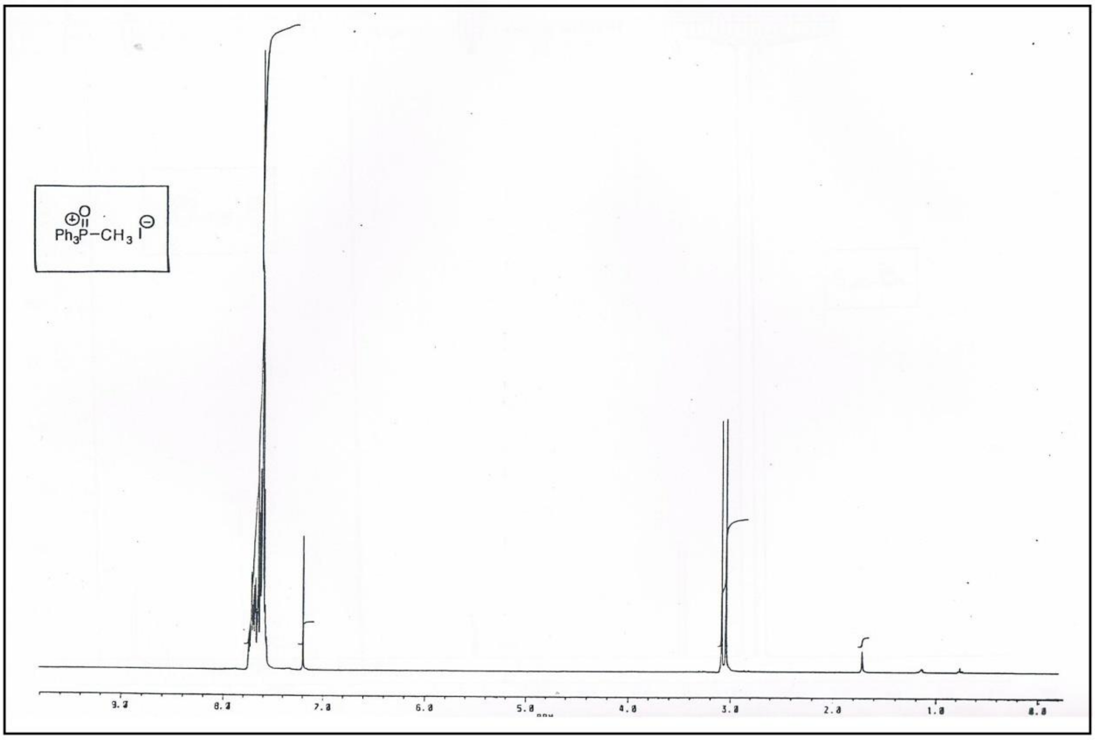


Fig.2.1.3a. ^{1}H NMR spectrum of phosphonium salt **3**

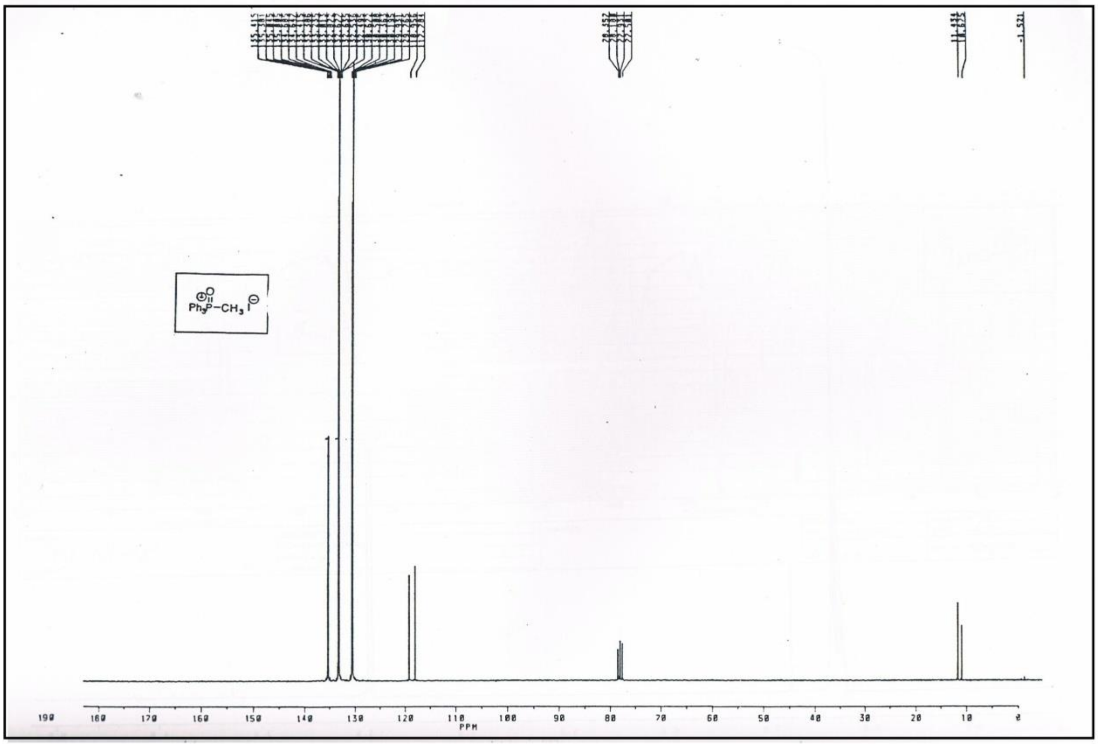


Fig.2.1.3b. ^{13}C NMR spectrum of phosphonium salt **3**

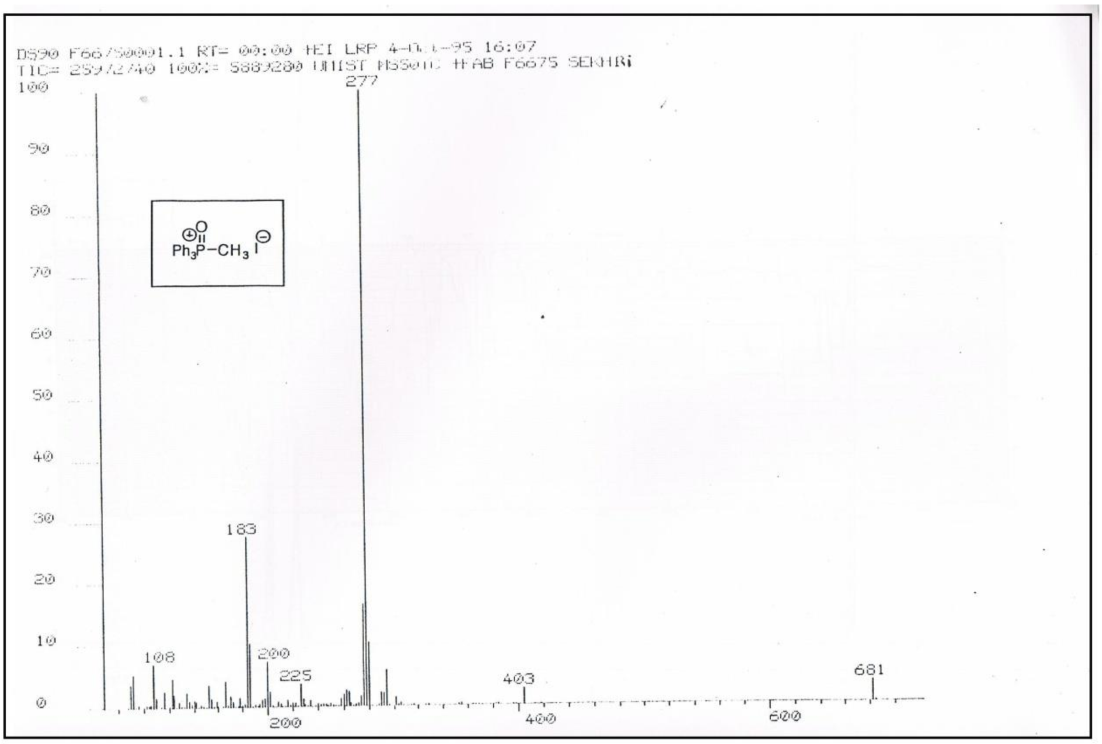


Fig.2.1.3c. Mass spectrum of phosphonium salt **3**

2.2. Corrosion behaviour study

2.2.1. Materials

Working electrodes were cut from a carbon steel sheet, sample of the following chemicalcomposition (as percentage):

Table 2.2.1: chemicalcomposition of carbon steel sheet

Element	**C**	**P**	**S**	**Si**	**Mn**	**Cr**	**Ni**	**Cu**	**Al**	**Nb**	**V**	**Ti**	**Mo**	***Fe***
Value (×10^{-3})	*65*	*2*	*1*	*245*	*1685*	*42*	*26*	*10*	*42*	*67*	*14*	*19*	*5*	*Rest*

This material (XC70) is utilised widely in petroleum and gas industry. Distilled and deionizer water was used for solution preparations. Stock solutions of 0.1 M H_2SO_4 were employed as the blank, i.e., methyl triphenylphosphonuim iodide -free. For the experiments containing methyl triphenylphosphonuim iodide, the appropriate weight was added to blank solutions to reach final concentrations of 5, 10,15, 20, 30,40, 60, 70, 80, 90, or 100 ppm.

2.2.2. Cell, electrodes and coupons

A double-walled glass three-electrode cell was used to carry out the corrosion tests. The working electrode was a disc of carbon steel with a geometric area of 1 cm^2. Prior to each polarization experiment, the electrode surface was polished with 1200-4000 emery paper, degreased with acetone, rinsed with deionizer water and air-dried. The auxiliary electrode was a platinum rod and the reference electrode was a saturated calomel electrode (SCE) connected to the cell by a bridge. All potentials in the text are quoted versus this reference electrode.

2.2.3. Apparatus

Experiments were carried out under static condition at 30°C on a potentiostat/ galvanostat applied research, potentiodynamic polarization curves were obtained using a PGZ301 with voltamaster 4 version 7.08 soft ware (radiometer analytical SAS).

2.2.4. Procedures

The open-circuit potential (OCP) versus time and potentiodynamic polarization curves were measured for 0.5 h before starting the potentiodynamic polarization experiments. The initial potential sweep was always negative to the OCP previously measured. The initial and final potentials were fixed according to the technique employed (Tafel, polarization resistance, etc.).

3. RESULTS AND DISCUSSION

3.1. Synthesis part:

Phosphonium salts are prepared from alkyl or arylhalide and triphenyl phosphine in toluene or chloroform. The procedure was adopted for the synthesis of methyl triphenyl phosphonium iodide except that toluene was used instead of chloroform as shown in **Figure 3.1.**

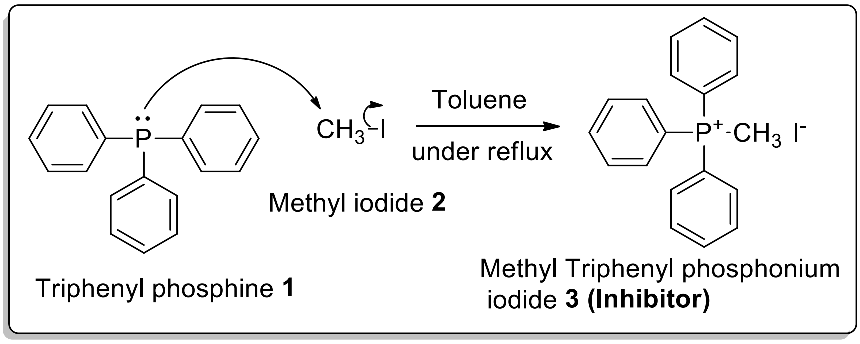


Fig.3.1. Synthesis of phosphonium salt **3**

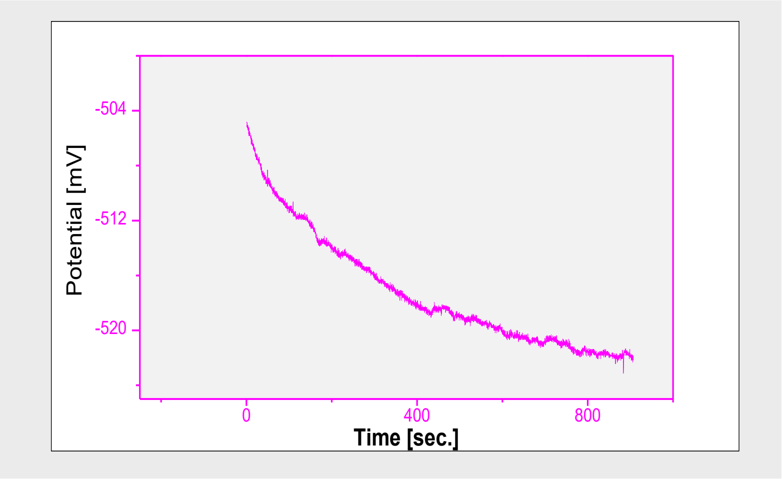
In the present work we found that, the same transformation can be achieved using toluene for this reaction. Therefore, triphenyl phosphine with aryl or alkyl iodide is a convenient synthesis of many phosphonium salts since the halogen as a leaving group (requires a temperature higher than boiling point of chloroform). Work-up of the reaction product gave the corresponding phosphonium salt, methyl triphenyl phosphonium iodide**3**which was either commercially available or prepared from triphenyl phosphine and methyl iodide as described earlier.

Methyl triphenyl phosphonium iodide**3** will be served as a chemical inhibitor to decrease the rate of corrosion processes. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. The comparative study of this phosphonium salt, with phosphonium chloride salts reported by K.F. Khaled revealed that this phosphonium salt is the convenient inhibitor [6].

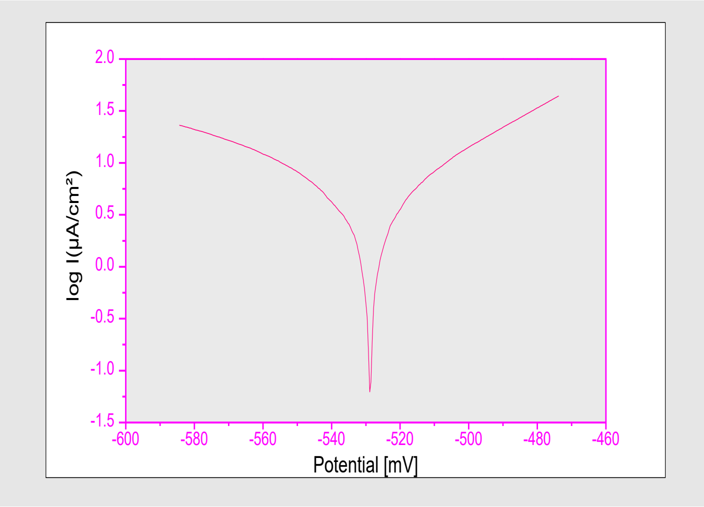
3. 2. Corrosion behaviour study

3.2.1The effect of sulfuric acid H_2SO_4 0.1 M on the corrosion of steel XC 70 by an electrochemical method.

At the beginning of the electrochemical study carried out, it is necessary to establish the stabilization curve of the steel X70 in the corrosive medium H_2SO_4 0.1M and the polarization curve of the steel X70.After several tests, we obtained the following curve, i = f (E) as shown in **Figure 3.2.1.**



(a)



(b)

Fig.3.2.1. Curve of: (a) Open-circuit potential monitoring of X70 steel in a 0.1 M H_2SO_4 solution(b) Tfel corrosion of XC70 steel in a 0.1 M H_2SO_4 solution

We observe that the abandonment potential (Eabd) tends to stabilize after 15 min. of immersion.

3.2.2 Study of corrosion of XC 70 steel in sulfuric acid medium H_2S0_4 in the presence of non-rotating inhibitors

3.2.3. Electrochemical methods

3.2. 3.1. The polarization curves

Plots of the polarization curves made from the most commonly used techniques in electrochemistry to determine the polarization resistance and the rate of corrosion. The Tafel plots allow us direct access to current density values, as can be deduced from the Stern and Geary equation [7]:

$$I_0 = \frac{1}{2.3\ R_p} \frac{B_a\ .B_c}{(B_a + B_c)} \text{.................. (III. 1)}$$

Polarization curves are determined by applying a potential between an XC 70 steel working electrode and a reference electrode (ECS). A stationary current is established after a certain time. It is measured between the working electrode and a counter electrode (or auxiliary electrode) [7]. The plots of the polarization curves were made on the steel working electrode XC 70 in the absence and in the presence of the inhibitors at different concentrations in a sulfuric acid medium H_2SO_4 0.1 M.

3.2.3.2. The effect of the concentration of compound 1 on the corrosion of XC 70 steel in H_2SO_4 medium (0.1M).

In this part we studied the effect of inhibitor, phosphonium salt **3** on the corrosion of XC70 steel in H_2SO_4 sulfuric acid medium (0.1M). For this we have studied the influence of its concentration on the corrosion of steel. The following figure shows the polarization curves of the corrosion of XC 70 steel in 0.1 M H_2SO_4 at different concentrations.

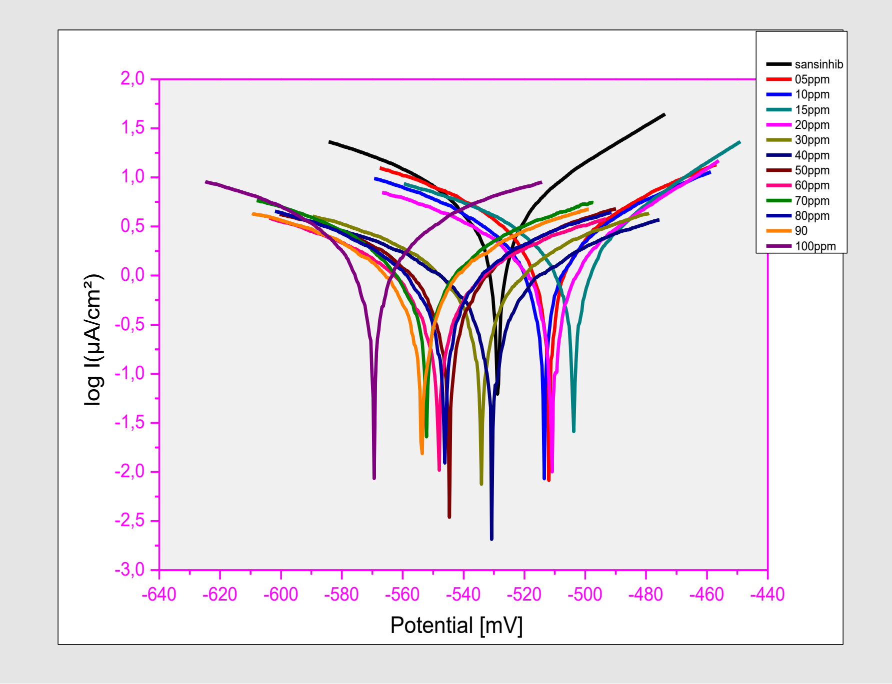


Fig.3.2.3.2a. Polarization curves of XC 70 steel in 0.1M H_2SO_4 without and with addition of different concentrations of phosphonium salt **3**

On the log I = f (E) representations, two parts are distinguished for each curve. A cathodic part which corresponds to the proton reduction reaction on the surface of the XC 70 steel, and an anode part which represents the oxidation of the XC 70 steel. In the cathodic domain, the addition of the inhibitor 1 induces a significant decrease in the cathodic partial current. This decrease is proportional to the inhibitor content. While in the anode domain, the addition of the inhibitor causes a less significant decrease in the anodic partial flow. Based on this result, it can be said that the compound 1 is a mixed inhibitor, with a cathodic predominance.

Electrochemical parameters: corrosion current density (Icorr), corrosion potential (Ecorr), cathodic and anodic Tafel slopes (bc and ba) and inhibition efficiency E (%) for different concentrations of compound1 in H_2SO_4 0.1M medium are reported in **Table 3.2.3.2.**

The effectiveness of the inhibitor (R%) is defined as follows:

$$R\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100$$

Where I^0_{corr} and I_{corr} are respectively the corrosion current density values of XC 70 steel in the absence and in the presence of the inhibitor at different concentrations.

Table 3.2.3.2. Electrochemical Parameters and Corrosion Inhibitory Efficacy of XC 70 Steel in 0.1M H_2SO_4 Before and After Addition of Different Concentrations of Compound1 at Room Temperature

C (ppm)	***Ba*** ***(mV/dec)***	***Bc*** ***(mV/dec)***	***Icorr*** ***(µA/cm²)***	***Ecorr*** ***(mV/ECS)***	***R_p*** ***(KOhm.cm²)***	***Vcorr*** (µm/Y)	***R (%)***	θ
00	65.3	-96.9	6.2568	-528.8	2.47	73.18	-	-
05	84.0	-87.7	3.0187	-511.8	5.25	35.30	51.76	0.52
10	86.3	-96.7	2.6369	-513.6	6.36	30.73	58.01	0.58
15	58.4	-108.6	2.6369	-503.8	6.04	30.84	57.86	0.58
20	60.7	-85.6	1.6641	-510.9	13.13	19.46	73.41	0.73
30	**86.2**	**-88.4**	**1.0195**	**-534.0**	**14.52**	**11.92**	**83.71**	**0.84**
40	99.8	-113.3	1.0479	-530.7	20.88	12.25	83.26	0.83
50	113.6	-130.2	1.5854	-544.7	13.76	18.54	74.66	0.75
60	109.8	-110.1	1.1983	-548.1	16.16	14.01	80.86	0.81
70	95.3	-91.0	1.5039	-552.1	9.27	17.59	75.96	0.76
80	111.7	-111.5	1.4264	-546.1	13.01	16.68	77.21	0.77
90	127.0	-142.5	1.7541	-553.5	13.70	20.51	71.97	0.72
100	104.2	-104.5	2.7156	-569.4	6.81	31.76	56.60	0.57

The analysis of the data shown in Table II.2.3.2, clearly shows that the corrosion current densities (Icorr) decrease as the concentration of inhibitor 1 increases (6.2568 µA / cm² - 1.0195 µA / cm²), while the polarization resistance RP increases with the increase of the concentration of the inhibitor1, and reaches a maximum value of 14520 Ω.cm2 and a better inhibitory efficiency value (R% = 83.71%) at an inhibitory concentration of 30 ppm.

Addition of phosphonium salt **3** to the corrosive medium of 0.1 M H_2SO_4 sulfuric acid results in a change in Tafel slope values, indicating that both anodic and cathodic reactions are affected. In the presence of phosphonium salt 3, the corrosion potential Ecorr increases to more positive values (-528.8 mV to -503.8 mV). Then, the value increases until reaching the value -569.4 mV. These results show that there is formation of a passive protective film on the anode. This result is in accordance with the literature [8]; and according to Ferreira et al. [FER 2004] and Li et al. [LI 2008], if the corrosion potential in the presence of the inhibitor moves by more than 85 mV compared to the white, the inhibitor can be considered as anodic or cathodic inhibitor. In our case, the potential variation does not exceed 40.6 mV. This result leads us to say that phosphonium salt 3 is a mixed type inhibitor.

The intensity-potential curve evolves from the cathodic domain where a decrease of the current to a minimum value corresponding to the corrosion potential (Ecorr) is observed. After this value, the anode zone appears with a strong increase in current relative to the cathode part, which reflects the oxidation of iron. The polarization curves show two potential domains:

An anodic activation domain due to oxidation of the Fe:

$$Fe \leftrightarrow Fe^{2+} + 2e^- \text{ ……………………..(III. 2)}$$

A cathodic activation domain, where the acid reduction reaction controls the cathodic process:

$$2H^+ + 2e^- \leftrightarrow H_2 \text{………………………(III. 3)}$$

The results in **Table 3.2.3.2**, clearly shows that the corrosion rate decreases with the increase in concentration of phosphonium salt **3** as shown in **Figure 2.2.3.2b** below:

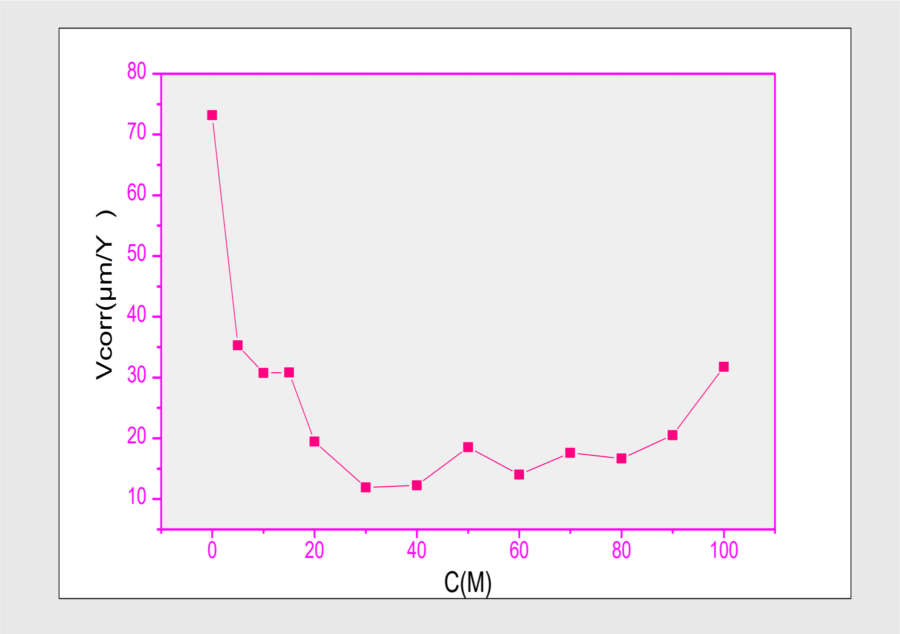


Fig.3.2.3.2b: The variation of the corrosion rate of steel XC 70 in sulfuric acid medium H_2SO_4 0.1 M according to the concentration of phosphonium salt **3**

It is noted that the corrosion rate decreases with the addition of the inhibitor **3**. **Figure 3.2.3.2c** represents the values of the inhibitor1 yields according to its different concentrations.

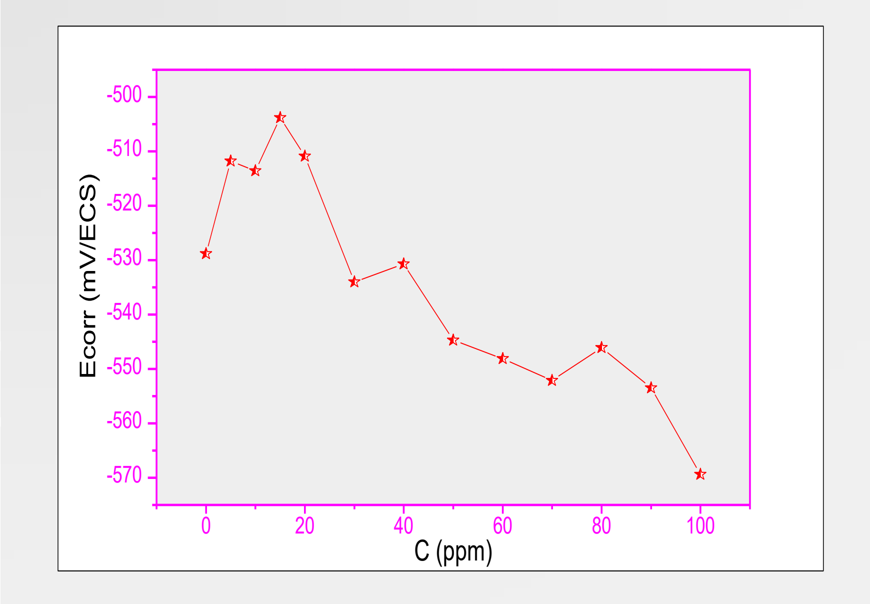


Fig.3.2.3.2c. The variation of the corrosion rate of steel XC 70 in sulfuric acid medium H_2SO_4 0.1 M according to the concentration of phosphonium salt **3**

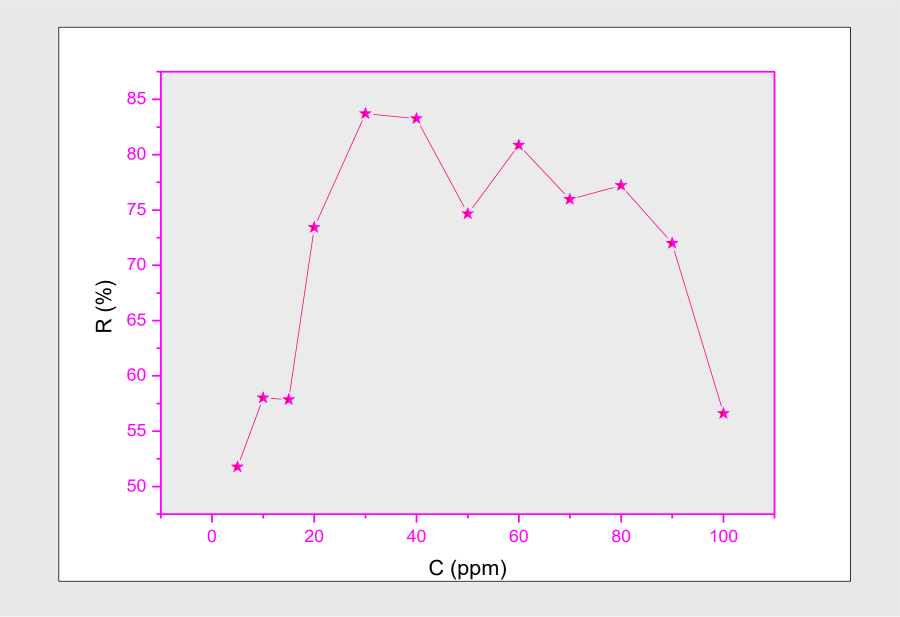


Figure 3.2.3.2d. The variation of the efficiency of the inhibitory efficiency as a function of the different concentrations of compound 1 on the corrosion of steel XC 70 in sulfuric acid medium H_2SO_4 0.1 M

It should be noted that the yield increases with the increase of the concentrations up to the concentration 30 ppm where attains a better inhibitory efficiency R% is 83.71%, then its value decreases.

3.2.3.3. Recovery rate

From the following relation:

$$\theta = \frac{i_0 - i}{i_0} \times 100 \text{……………………..(III. 4)}$$

where:

θ: The weight recovery, given as a function of rate decrease of vcoor.

C: The concentration in M.

K: Equilibrium constant of the formation reaction of the protective layer

i: The current intensity in [µA / $cm2$].

i_0: The maximum current intensity in [µA / $cm2$].

The results are sumarrized in the following table.

Table 3.2.3.3. The values of the recovery variation (C / recovery Θ) calculated for different concentrations of phosphonium salt **3**at room temperature

Concentration (ppm)	**Recoveryθ**	**Concentrations/Recovery**
00	-	-
05	0.52	9.62
10	0.58	17.24
15	0.58	25.86
20	0.73	27.40
30	**0.84**	35.71
40	0.83	48.19
50	0.75	66.66
60	0.81	74.07
70	0.76	92.11
80	0.77	103.90
90	0.72	125
100	0.57	175.44

The results of the **table 3.2.3.3** are explained in the following curve:

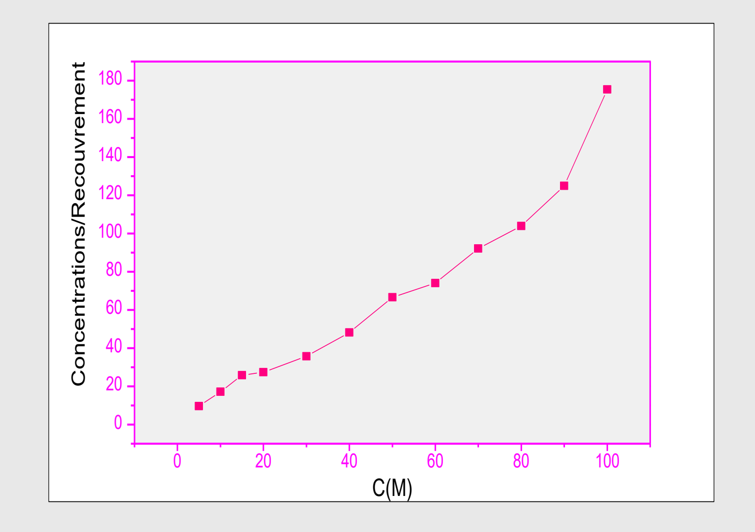


Fig.3.2.3.3. The variation of (C / corrosion recovery Θ) of XC 70 steel in sulfuric acid H_2SO_4 0.1 M as a function of the concentration of phosphonium salt **3**

3.2.3.4. Electrochemical impedance spectroscopy

The study of electrochemical impedance diagrams at the corrosion potential (abandonment potential) for different concentrations was studied in order to complete the understanding of the mechanisms of corrosion and inhibition of XC 70 steel in H_2SO_4 0.1 medium. M at room temperature. The tests were carried out in the frequency range 100 KHz - 10mHz and a disturbance amplitude 10 mV.

3.2.3.5. Electrochemical impedance spectroscopy for phosphonium salt 3 without rotation

The results obtained using this technique in 0.1M H_2SO_4 medium before and after the addition of different concentrations of compound 1 are represented in the form of Nyquist diagrams **(Figure.3.2.3.5).**

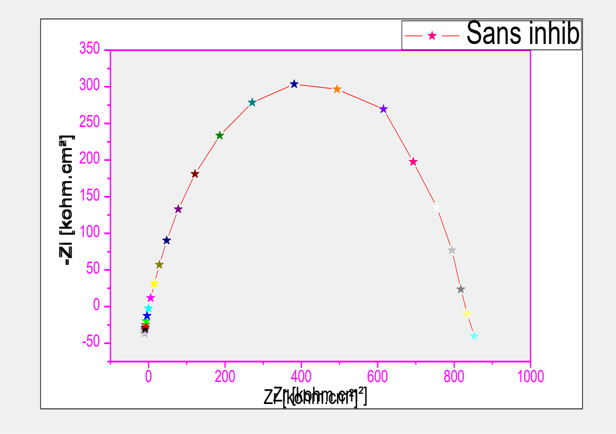


Fig.3.2.3.5. Nyquist electrochemical impedance diagrams of XC 70 steel in sulfuric acid medium H_2S0_4 0.1 M

3.2.3.6 Randles equivalent circuit

The Randles equivalent circuit of the electrochemical system studied includes a double layer capacitance Cdc in parallel with a charge transfer resistanceRtc, both of which are in series with a solution resistance Rs.

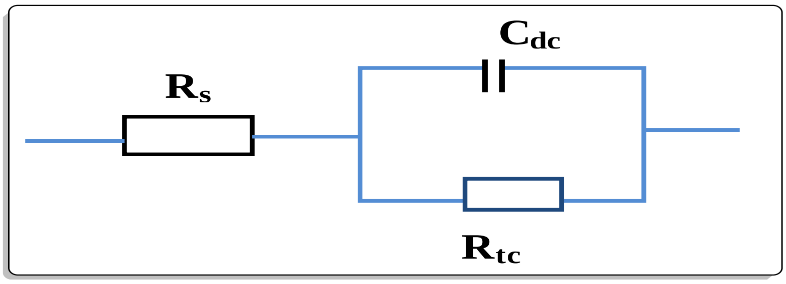


Fig.3.2.3. 6a. Equivalent electrical diagram of the metal / solution interface

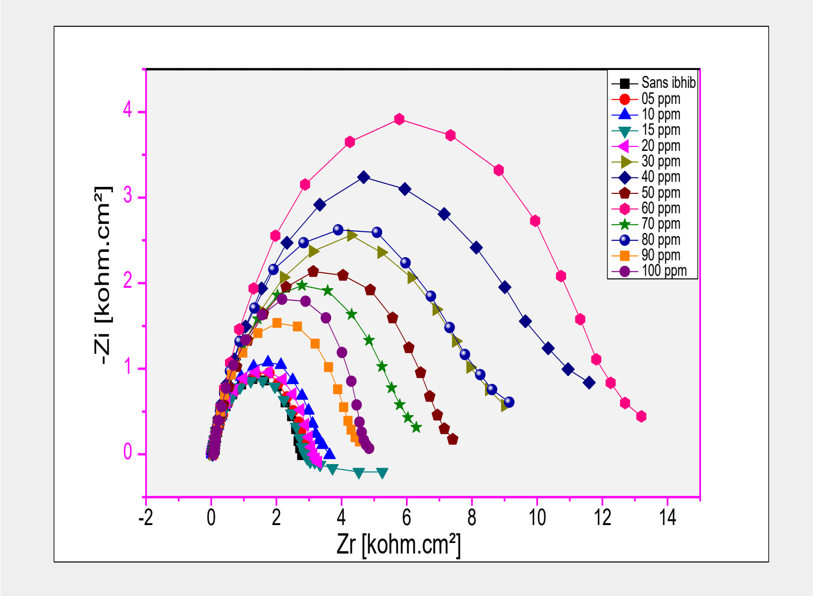


Fig.3.2.3.6b. Nyquist electrochemical impedance diagrams of XC 70 steel in 0.1 M sulfuric acid medium H_2S0_4 without and with addition of compound1 at different concentrations

The impedance diagrams obtained consist of a single capacitive loop which is not a perfect semicircle, and this is attributed to the dispersion of the frequency of the inter-facial impedance [9,10], generally due the heterogeneity of the surface of the electrode. This heterogeneity may result from roughness, impurities, dislocations, adsorption of the inhibitor and formation of porous layers [11,12]. This type of diagram is generally interpreted as a mechanism of charge transfer over a heterogeneous and irregular surface [8,13]. The diameters of the capacitive semicircles increase with increasing inhibitor concentration.

The values of the charge transfer resistance are calculated from the impedance difference at high and low frequencies on the real axis, as suggested by Haruyama and Tsuuru [14]. The capacity of the double layer Cd1 is determined at the frequency for which the imaginary part of the impedance is maximal (max " - Z) from equation [15]:

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_t} \quad \text{……………………..(III. 5)}$$

The corrosion inhibitory efficiency of steel is calculated from the charge transfer resistance according to the relation:

$$E\ (\%) = \left(1 - \frac{R_t}{R'_t}\right) \times 100 \text{……………………..(III. 6)}$$

where R'and Rt respectively represent the values of the charge transfer resistance in the presence and absence of the inhibitor. The analysis of these results reveals that:

(i) The values of the charge transfer resistance Rt become larger with increasing concentration of phosphonium **3**(ii)The capacity of the double layer Cdl decreases. this decrease can be attributed to the adsorption of organic molecules on the surface of the steel in an acid medium.

The following table groups together some electrochemical parameters taken from electrochemical impedance spectra of the previous figure 2**.2.3.6b.**

Table 3.2.3.6a. Electrochemical parameters and corrosion inhibitory efficacy of XC70 steel in 0.1M H_2SO_4 without and with addition of different concentrations of phosphonium salt **3**

C(ppm)	E $_{eq}$[mV]	R_s(ohm.cm^2)	R_{tc} (kohm.cm^2)	C (µF/cm^2)	E(%)
00	-490	31.77	0 .3383	11.75	-
05	-463	21.63	0.9227	6.899	63.34
10	-465	25.62	1.124	5.664	69.90
15	-452	28.68	1.095	5.810	69.11
20	-464	28.18	1.683	3.781	79.90
30	-490	26.29	**3.760**	1.693	**91.00**
40	-477	45.57	2.054	1.937	83.53
50	-482	28.16	2.475	2.571	86.33
60	-471	54.44	2.521	1.577	86.58

70	-495	16.67	3.514	1.132	90.37
80	-468	49.58	1.053	3.775	67.87
90	-470	58.18	2.278	2.794	85.15

The value of the charge transfer resistance (Rt) obtained in the absence of inhibitor shows the dissolution of the steel from the first hours of immersion and the value of the capacity of the double layer is of the order of 11.75 μF.cm^{-2}, this is generally attributed to a conductive layer of corrosion products [16]. The increase in charge transfer resistance (Rt) with the decrease in the capacity of the double layer (Cdl) which is in perfect agreement with the protective power which proved very satisfactory at a concentration of 30 ppm. This is quite consistent with the results of stationary techniques (polarization curves). Indeed, we have already shown that the best behavior was observed for the steel XC 70 in sulfuric acid medium of 0.1 M of compound 1 at the concentration 30 ppm by a yield of 91%, this is also shown by the results of the frequential techniques (impedance diagrams) which is confirmed by the increase of the resistance of the protective film Rtc (0.3383-3.760 kohm.cm^2) and obtained the best result at the concentration 30 ppm Rtc = 3.760 kohm.cm^2.

The decrease in Q may be related to the decrease in the dielectric constant and / or the increase in the thickness of the double layer [17-19]. In other words, in the presence of inhibitors, the thickness of the surface oxide layer decreases and by changing the oxide layer, the influence of the electrode method on the kinetics, as well. The improvement of the properties of the film is characterized, on the impedance diagram, by an increase in the size of the loops.

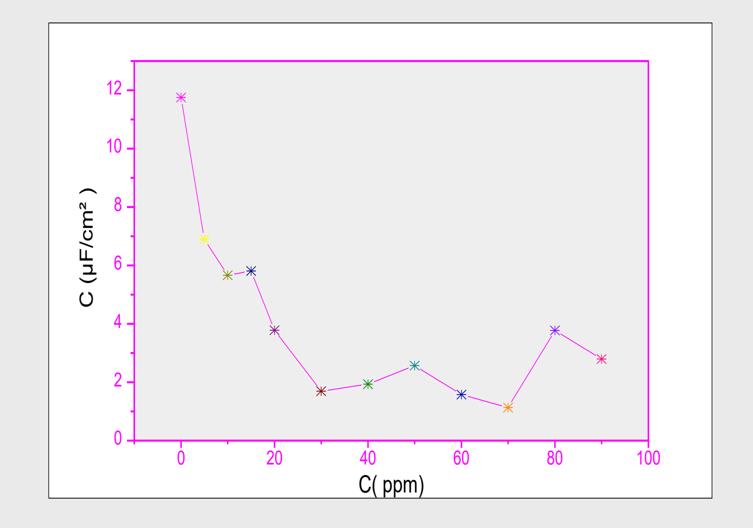


Fig.3.2.3.6c. The variation of the electric double layer capacity as a function of concentration of compound 1 in sulfuric acid medium at 0.1 M

The electric double layer capacity decreases with the increase in concentration. This is quite consistent with the results of stationary techniques (polarization curves).

we have already shown in the table preceding III.8 that the best inhibition takes a value of R = 91.00% was observed for the steel XC 70 in sulfuric acid medium of 0.1 M of compound 1 at the concentration 30 ppm,

The following figure shows the Nyquist coordinate curves obtained for XC 70 steel in 0.1 M sulfuric acidwithout and with the addition of different concentrations of inhibitor **3**.

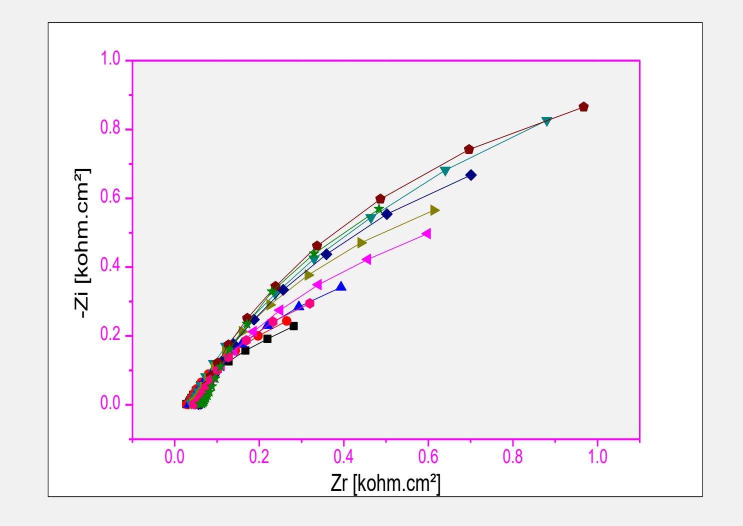


Fig.3.2.3.6d. Zoom on the Nyquist electrochemical impedance curves in the high frequency part for phosphonium salt in 0.1 M H_2SO_4

All the curves are close to each other, they do not give real information on the role of the parameters studied. The value of the total equivalent capacity C can therefore be extracted from the fitting of the following curve:

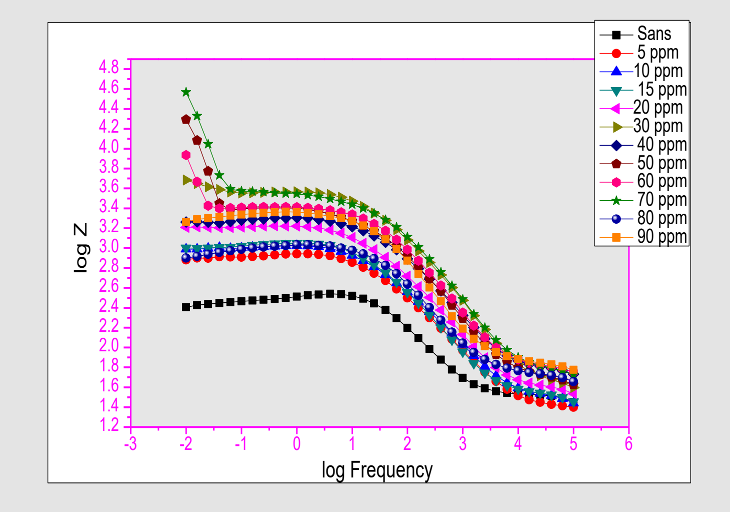


Fig.3.2.3.6e. Fitting the imaginary Z-curve as a function of frequency (logarithmic scale)

The values of the electrical parameters obtained by simulation of the experimental diagrams are presented in **Table 3.2.3.6b**. The thickness of the layer of the precipitate formed can be estimated. The relation connecting the thickness and the capacity as indicated in the following relation is called:

So

$$C = \frac{\varepsilon\varepsilon^{\circ} S}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(III. 7)}$$

$$d = \frac{\varepsilon\varepsilon^{\circ} S}{C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(III. 8)}$$

$$\frac{d}{\varepsilon} = \frac{\varepsilon^{\circ} S}{C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(III .9)}$$

$$d = \varepsilon\varepsilon^{\circ}\, S\,.\frac{1}{C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(III. 10)}$$

$$\frac{d}{\varepsilon} = \varepsilon^{\circ} S \,.\, \frac{1}{C} = 6.25 \,.\, 10^{-15} \frac{1}{C}$$

Table 3.2.3.6b. Electrochemical parameters of the $logZim = (logf)$ curves of corrosion of XC70 steel in 0.1M H_2SO_4 without and with addition of different concentrations of phosphonium salt**.**

C ppm	Equation	R^2	C(F)	d / (nm)
00	y = 2,39101 - 0,18011*x	0,79596	0.014575984	$4.2878752.10^{-13}$
05	y = 2,79225 - 0,26132*x	0,85417	0.009758466	$6.4118171.10^{-13}$
10	y = 2,87393 - 0,26582*x	0,86554	0.008993079	$6.9497888.10^{-13}$
15	y = 2,88351 - 0,27316*x	0,85962	0.008907336	$7.0166882.10^{-13}$
20	y = 3,06218 - 0,28888*x	0,87326	0.007449934	$8.389336.10^{-13}$
30	y = 3,43217 -0,32999*x	0,87113	0.005145977	**$1.2145409.10^{-12}$**
40	y = 3,1581 - 0,26362*x	0,84881	0.006768539	$9.233898.10^{-13}$
50	y = 3,36478 - 0,34394*x	0,92568	0.005504716	$1.13539.10^{-12}$
60	y = 3,32168 - 0,30316*x	**0,89154**	0.005747157	**$1.0874942.10^{-12}$**
70	y = 3,55763 - 0,36011*x	0,92681	0.00453922	$1.3768885.10^{-12}$
80	y = 2,8751 -0,23086*x	0,82134	0.008982563	$6.957925.10^{-13}$
90	y = 3,18692 - 0,27581*x	0,84968	0.006576254	$9.5038908.10^{-13}$

In a general way we note: The increase in the thickness with the increase of the concentration of the inhibitor1, which corresponds to the increase of the values of d / ε from 4.2878752.10-13 (nm) to 1.0874942 .10-12 (nm). The correlation coefficient (R2) is close to 1 (> 0.89154), confirming the validity of the chosen model.

3.2.4 Interpretation of results

The scientific and technical literature on corrosion contains descriptions and lists of many chemical compounds with inhibitory properties. Of these, very few are actually used. The presence of iodide anion in the methylphosphonium iodide **3**molecule increases the inhibition because it contains four free electron pairs and a coordination site, as shown in **Figure (3.2.4)**.

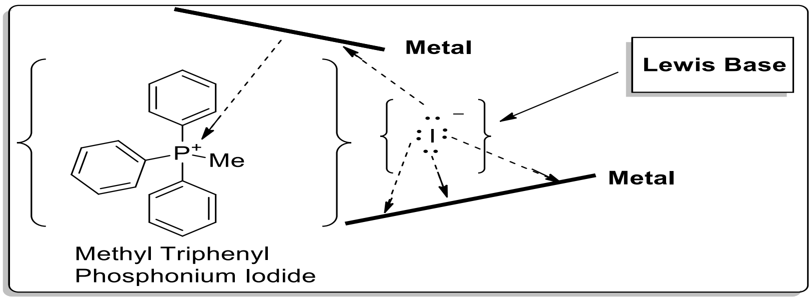


Fig.3.2.4. Formation of the layer on the surface of the metal by the phosphonium salt**3**

4. CONCLUSION

Phosphonium salt **3** has been successfully synthesized in high yield and identified by comparison its spectroscopic data with those of an authentic sample. Exploration of electrochemical studies showed that (i) The corrosion rate of steel XC 70 in sulfuric acid medium H_2S0_4 to O.1 M; without rotation and with 1500 rpm rotation; decreases with increasing concentration of phosphonium salt **3** (ii) the inhibitory efficiency against the corrosion of steel XC 70 in H_2SO_4 at 0.1 M without rotation; is proportional to the concentration of phosphonium salt and reaches a maximum of 83.71% at C = 30 M; The inhibitory efficiency reaches a maximum of 97.80 at C = 60 M. (iii) phosphonium salt **3** is a very effective inhibitor in cases without rotation and with 1500 rpm rotation (iii) The polarization curves show that the inhibitor is a mixed inhibitor (iv) the plot of (C/θ) as a function of the concentration (C) indicating that the adsorption of this salt on the surface of the steel XC 70 in H_2SO_4 0.1M medium is done according to the isothermal model of Langmuir adsorption.

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