

## Electrochemical Study on Corrosion Inhibition of Iron by Synthesized Butyl Triphenylphosphonium Chloride in Acid Media

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**Abstract:** The present work is aimed mainly to synthesize a phosphonium salt, butyl triphenylphosphonium chloride, and evaluate inhibitive effect against carbon steel corrosion in aerated 1 M HCl solutions. Thus, 1-butyl triphenylphosphonium chloride was synthesized by the reaction of an equimolar quantity of a solution of 1-butyl chloride and triphenyl phosphine in toluene in 95 yield. We have found that, the use of toluene for this reaction of triphenyl phosphine with aryl or alkyl chloride is a convenient synthesis of many phosphonium salts since the halogen as a leaving group (requires a temperature higher than boiling point of chloroform). The purity of this compound was estimated by TLC technique and microanalysis, while its structure was supported by the usual spectroscopic methods such as UV, infrared, <sup>1</sup>H. NMR and <sup>13</sup>C. NMR.

Exploration of the Corrosion measurements based on polarization resistance (*R<sub>p</sub>*), potentiodynamic polarization curves indicates that 1-butyl triphenylphosphonium chloride, in most cases act as strong inhibitors. This phosphonium inhibitor acts as anodic type inhibitors with predominant effect on the anodic dissolution of iron. Analysis of the polarization curves indicates that charge transfer process mainly controls carbon steel corrosion in HCl solution without and with phosphonium salt.

A Comparative electrochemical study with that reported in the literature revealed that the efficiency of the inhibitors follows the order: 1-butyl triphenylphosphonium chloride > (chloromethyl) triphenyl phosphonium chloride (CTP) > tetraphenylphosphonium chloride (TP) > triphenyl phosphine oxide (TPO) > triphenyl (phenylmethyl) phosphonium chloride (TPM). It was also reported in the literature that the efficiency of halide inhibitors follows the order: I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup>.

**Keywords:** 1-butyl triphenylphosphonium chloride; Iron; corrosion, inhibition; potentiodynamic polarization.

### I. INTRODUCTION

The chemistry of organophosphorus compounds falls into two areas reactions involving the phosphorus atom itself, which form the majority of the chemistry and reactions in which the presence of the phosphorus atom contributes to the reactions of the organic moieties present in the molecule. Phosphonium salts have gained an increasing interest due to their successful applications in different fields of chemistry, such as the corrosion inhibitors. Thus, by definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. To prevent the corrosion of the materials, organic compounds having  $\pi$ -bonds and heteroatom such O, N and S have been widely used [1-4]. The inhibitive performances of a molecule are substantially connected on its adsorption on metal surface. In recent years, many experimental methods are used to determine the corrosion inhibition efficiencies and to understand the inhibition mechanisms of chemical compounds such as potentiodynamic polarization (PDP) [5], weight loss [6], electrochemical impedance spectroscopy (EIS) [7], Fourier transform infrared spectroscopy (FTIR) [8], and scanning electron microscopy (SEM) [9], in spite of the fact that they are in general expensive and time consuming too.

In recent years we have also published many papers about that phosphonium salts derivatives are effective against the corrosion of metals such as mild steel [10, 11]. More recently, we reported that tetraphenylphosphonium iodide acts as anodic type inhibitors with predominant effect on the anodic dissolution of iron [12].

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 1-butyl triphenylphosphonium chloride acting as anodic type inhibitors with predominant effect.

## II. RESULTS AND DISCUSSION

Phosphorus lies in V of the periodic table and forms two series of compounds. In the first series, phosphorus is in the +3 oxidation state and the phosphorus itself carries a lone pair of electrons. This lone pair of electrons enables phosphorus (III) compounds to undergo *Nucleophilic* attack on a wide range of compounds. Phosphorus itself is a relatively electropositive element and so can also act as an *electrophile*; such reactions are particularly important for compounds of phosphorus in its higher oxidation state of +5. Although the valence electrons of phosphorus are two 3s and 3p electrons, there are relatively low-lying empty 3d orbitals which contribute significantly too many aspects of phosphorus electrochemistry. The inhibitive performances of a molecule are substantially connected on its formation of coordination bonds on metal surface.

To support our development of electrochemical study for corrosion inhibition of iron by lists of numerous chemical compounds that exhibit inhibitive properties such as phosphonium halide derivatives in acid media, we required a synthesis of different phosphonium salts such as 1-butyl triphenylphosphonium chloride. Thus, the strategy we have adopted for this project consists of the following steps: (i) synthesis of 1-butyl triphenylphosphonium chloride 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.

### II. I. Synthesis part

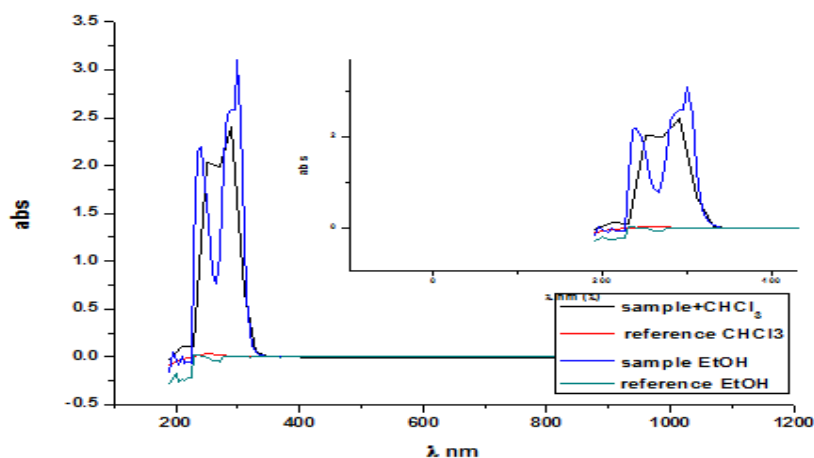
#### II. I. 1. Experimental

##### II.I. 1.1. materials

Triphenylphosphine (98%), 1-chlorobutane (98%), acetone (99.5%), and hexane (99%) were purchased from Alfa Aesar. Magnesium sulfate anhydrous (97%), and ethyl acetate was purchased from Acros Organics. Ethanol and toluene p.a were purchased from Biochem Chemopharma Co (Canada). All other reagents used were of analytical grade.

##### II.I.1.2. Procedure for the Synthesis of tetraphenylphosphonium iodide

1-chlorobutane (1.41g, 15.2619 mmol) was added in small portions to well-stirred solution of Triphenylphosphine (4.00g, 15.26 mmol) in toluene (20 mL). The resulting mixture was then heated under reflux for 1-1.5 hours. It was then allowed to cool to room temperature. The resulting precipitate was separated by filtration and the crude product was recrystallized from toluene to afford 1-butyl triphenylphosphonium chloride (5.15g, 95%) as white crystals, m.p. 98°C;  $\nu_{\max}$ (KBr disc): 491.8, 503, 692.4, 742.5, 995.2, 1024.1, 1068.5, 1075, 1269.1, 1431.1, 1473.5, 2275 and 3000-3075  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  0.9 (t, 3H,  $\text{CH}_3$ ); 1.3 (m, 6H,  $\text{CH}_2\text{CH}_2$ ); 7.3 (d, 6H, ortho  $\text{P}^+\text{-Ph}$ ); 7.45 (d, 9H, Meta and Para  $\text{P}^+\text{-Ph}$ );  $^{13}\text{C}$  NMR:  $\delta$  (-ve DEPT) 13.8 (1C,  $\text{CH}_3$ ); 25.8 (1C,  $\text{CH}_2$ ), 24.4 (1C,  $\text{CH}_2$ ), 22.5 (1C,  $\text{CH}_2$ ), 117.9 (3C,  $\text{P}^+\text{-Ph}$ ); 130.4 (6C, Meta  $\text{P}^+\text{-Ph}$ ); 130.7 (6C, ortho  $\text{P}^+\text{-Ph}$ ); 135.0 (3C, Para  $\text{P}^+\text{-Ph}$ );  $\lambda_{\max}$  (reference  $\text{CHCl}_3$ ; sample +  $\text{CHCl}_3$ ) = 300 nm,  $\lambda_{\max}$  (reference EtOH; sample + EtOH) = 304 nm as shown in (Fig. 1).



**Fig.1:** UV-vis (EtOH); UV-vis ( $\text{CHCl}_3$ ) of compound butyl triphenylphosphonium chloride

##### II.I.1.3. Methods

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). Solvents were purified according to the standard methods [13].

#### II.I.1.4. Physical measurements

$^1H$  NMR spectra were recorded on BRUCKER AC 300 MHz spectrometer at  $0^\circ C$ , 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).

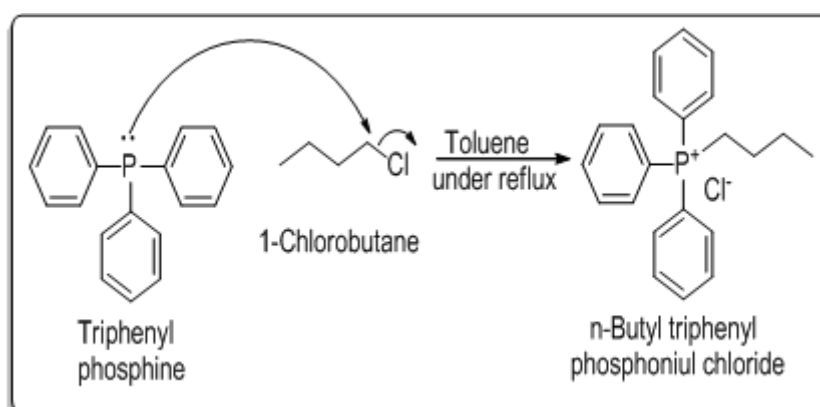
$^{13}C$  NMR and DEPT were recorded on BRUCKER AC 75 MHz spectrometer at  $0^\circ C$  and all are reported in ppm relative to the central line of the triplet for  $CDCl_3$  at 77.16 ppm. The spectra reported are proton decoupled.

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 60F<sub>254</sub> purchased from Merck.

#### II.I.2. Interpretation

We have published several papers describing the general route for the synthesis of aryl or alkyl triphenylphosphonium halide such as 1-butyl triphenylphosphonium chloride by using triphenyl phosphine and aryl or alkyl halide in  $CHCl_3$ [10-12]. Thus, the procedure was adopted for the synthesis of butyl triphenylphosphonium chloride except that toluene was used instead of chloroform as shown in **scheme-1**.



**Scheme-1** : Synthesis of 1-butyl triphenylphosphonium chloride

We have found that, the use of toluene for this reaction of triphenyl phosphine with aryl or alkyl chloride is a convenient synthesis of many phosphonium salts since the halogen as a leaving group (requires a temperature higher than boiling point of chloroform). The general procedure involves dropwise addition of an equimolar quantity of a solution of 1-chlorobutane in toluene to a stirred solution of triphenyl phosphine in toluene at  $0^\circ C$ . After the addition was complete, the reaction mixture was refluxed for 1-1.5 hrs. Work-up of the reaction product gave the corresponding phosphonium salt; 1-butyl triphenylphosphonium chloride. This phosphonium product is either commercially available or prepared from triphenyl phosphine and 1-chlorobutane as described earlier.

butyl triphenylphosphonium chloride 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. A great number of scientific studies have been devoted to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field. Rules, equations, and theories to guide inhibitor development or use are very limited [14]. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. The presence of halogen anion in the molecule of butyl triphenylphosphonium chloride increases the inhibition [15-18]. The comparative study of this butyl triphenylphosphonium chloride with phosphonium chloride salts reported by K.F. Khaled revealed that this phosphonium salt is the convenient inhibitor [19].

## II. II. Corrosion behavior study

### II.II. 1. Experimental details

#### II. II. 1. 1. Chemicals and solutions

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

**Table 1:** chemical composition of carbon steel sheet.

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

This material (XC70) is utilised widely in petroleum and gas industry; they were used without previous purification. Distilled and deionizer water was used for solution preparations. Stock solutions of 1 M HCl were employed as the blank, i.e., butyl triphenylphosphonium chloride-free. For the experiments containing butyl triphenylphosphonium chloride, the appropriate weight was added to blank solutions to reach final concentrations of 5, 10, 20, 40 or 70 ppm.

#### II. II.1. 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<sup>2</sup>. 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.

#### II.II 1. 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 voltmaster 4 version 7.08 soft ware (radiometer analytical SAS).

#### II.II. 1. 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.).

#### II. II. 2. 1. Open-circuit potential and corrosion potential

The variation in the open-circuit potential (OCP) and the corrosion potential ( $E_{\text{corr}}$ ) of the carbon steel electrode in 1M HCl as a function of 1-butyl triphenylphosphonium chloride concentration is shown in **Table 2**. The OCP values were obtained after 30 min immersion of the electrode in the test solutions under non-polarized conditions, while the  $E_{\text{corr}}$  values were determined by extrapolation of the Tafel lines, i.e., with the electrode polarized. Although the nature of the experiments is different, comparisons between the OCP and  $E_{\text{corr}}$  values are important to understanding the primary action of the corrosion inhibitor. The change in the OCP and  $E_{\text{corr}}$  values with the addition of the inhibitor is often a useful indication of which reaction is more affected: cathodic or anodic. The OCPs observed for carbon steel in 1M HCl solutions containing 5, 10, 20, 40 and 70 ppm butyl triphenylphosphonium chloride were slightly more negative than that in the absence of the organic phosphonium inhibitor.

On the other hand,  $E_{\text{corr}}$  was shifted by -20 mV towards more negative potentials under the same conditions. These results suggest that butyl triphenylphosphonium chloride can retard both reactions under open-circuit conditions: the oxidation of the oxide-free iron and the discharge of the hydrogen ions to produce hydrogen gas on the surface steel, since only a slight change in the OCP values was observed. However, when the working electrode is polarized, the data suggest that butyl triphenylphosphonium chloride acts preferentially on the cathodic sites, delaying the hydrogen evolution reaction, and the displacement of the  $E_{\text{corr}}$  was more well-defined [20].

Adsorption is the mechanism generally accepted to explain the inhibitory action of organic corrosion inhibitors [21]. Adsorption of inhibitors can affect the corrosion rate in two ways:

(i) By decreasing the available reaction area; the so-called geometric blocking effect; and (ii) by modifying the activation energy of the cathodic and/or anodic reactions occurring in the inhibitor-free metal in the course of the inhibited corrosion process. It is a difficult task to determine which aspects of the inhibiting effect are connected to the geometric blocking action and which are connected to the energy effect

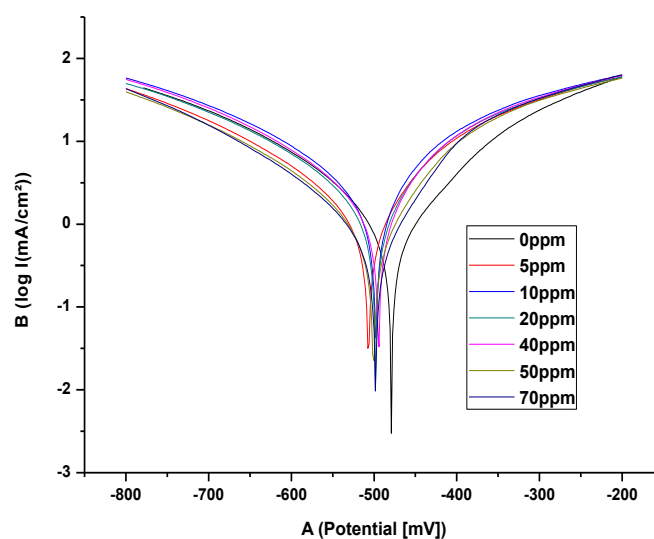
#### II.I. 2. 2. Polarization Measurements

The kinetics of the anodic and cathodic reactions occurring on carbon steel electrodes in 1 M HCl solutions with different butyl triphenylphosphonium chloride concentrations (5–70 ppm) was studied through the polarization measurements. The complete potentiodynamic polarization curves are shown in Fig. 2. The electrochemical parameters, i.e. corrosion current density ( $i_{corr}$ ), anodic ( $b_a$ ) and cathodic ( $b_c$ ) Tafel constants and polarization resistance ( $R_p$ ), shown in Table 2, were collected from Tafel plots and polarization resistance experiments carried out separately.

Regarding the potentiodynamic polarization curves, as previously observed, it can be clearly seen that the  $E_{corr}$  values shifted to more negative potentials with an increase in the 1-butyl triphenylphosphonium chloride concentration. This effect may be related to the adsorption of the organic phosphonium compound at the active sites of the electrode surface, retarding the corrosion reaction. The increase in the butyl triphenylphosphonium chloride concentration caused a clear decrease in the cathodic current density, but did not change significantly the cathodic Tafel slopes (Table 2), indicating that the hydrogen evolution reaction is diminished exclusively by the surface blocking effect of butyl triphenylphosphonium chloride [22].

**Table 2:** Electrochemical parameters for carbon steel in 1 M HCl solutions containing 10-70 ppm of butyl triphenylphosphonium chloride

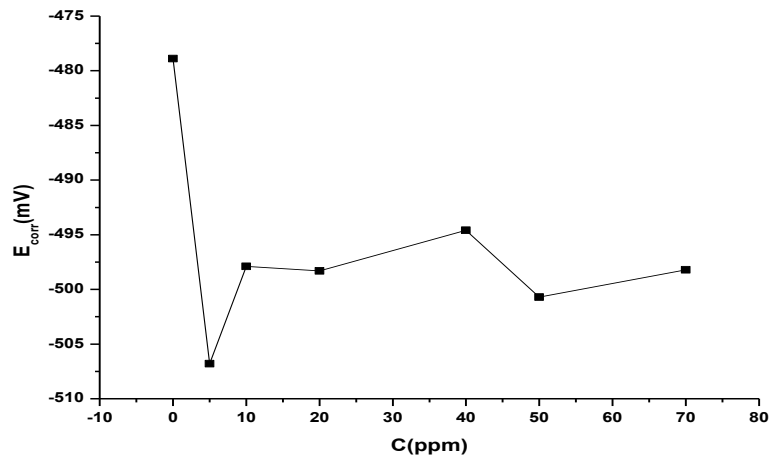
HCl 1M (ppm)	$R_p$ (ohm.cm <sup>2</sup> )	IE% (Rp)	$E_{corr}$ (mV)	$i_{corr}$ (mA/cm <sup>2</sup> )	IE% ( $i_{corr}$ )	$V_{corr}$ (mm/Y)	IE% $V_{corr}$	$\beta_a$ (mV)	$\beta_c$ (mV)
0	13.92	-	-478.9	1.0405	-	12.17	-	122.4	-138.9
5	16.58	16.043	-506.8	0.7344	29.419	8.590	29.417	79.0	-102.8
10	17.51	20.503	-497.9	0.7369	29.178	8.618	29.187	55.5	-68.2
20	22.08	36.957	-498.3	0.5993	42.402	7.010	42.399	57.6	-69.0
40	29	52	-494.6	0.5652	45.610	6.610	45.686	51.3	-62.7
50	30.22	53.938	-500.7	0.3627	65.142	4.242	65.144	58.7	-70.1
70	34.85	60.057	-498.2	0.2923	71.908	3.418	71.915	56.6	-65.6



**Fig.2.** Potentiodynamic polarization curves for carbon steel in 1 M HCl and solutions containing 5-70 ppm of butyl triphenylphosphonium chloride.

Regarding the anodic region of the potentiodynamic polarization curves, there is no evidence of passive film formation on the electrode surface either in the presence or in the absence of the inhibitor. Also, the currents remained almost the same for the blank and the 5, 10, 20, 40, 50 and 70 ppm butyl triphenylphosphonium chloride in the active dissolution region of the metal, but increased for higher concentrations of the organic phosphonium compound. This behavior could be related to a change in the anodic reaction mechanism (iron dissolution), corroborated by a decrease in the anodic Tafel slope with increasing concentration of butyl triphenylphosphonium chloride (Table 2).

This behavior could originate from the adsorption of the inhibitor at low concentrations. In addition to the energy effect, the pronounced lowering of the anodic Tafel slope could be partly due to electrochemical desorption of the inhibitor at higher concentrations from the metal surface during dissolution [23].



**Fig.3.** Variation of the corrosion potential with the concentration of butyl triphenylphosphonium chloride in 1M HCl solution

Summarizing, the lowering of the anodic Tafel slope can be interpreted as being due to (i) the adsorption of butyl triphenylphosphonium chloride at lower concentrations (energy effect), (ii) a change in the mechanism reaction, and (iii) the desorption of butyl triphenylphosphonium chloride at higher concentrations, all in agreement with the mechanism proposed above.

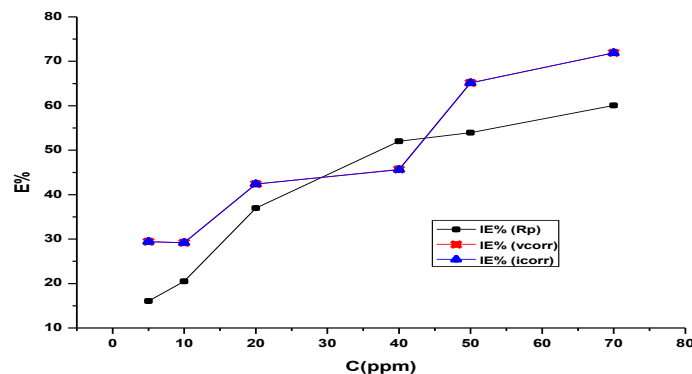
The data shown in **Table 2** clearly show that the  $i_{corr}$  values decreased and the  $R_p$  values, as expected, increased in the presence of butyl triphenylphosphonium chloride, indicating that the corrosion process was suppressed with the increase in inhibitor concentration. The inhibition efficiency (IE%) was computed for carbon steel in 1 M HCl solutions containing 5, 10, 20, 40, 50 and 70 ppm of butyl triphenylphosphonium chloride from the Tafel plots and polarization resistance measurements. The  $R_p$ , IE% values were obtained from  $i_{corr}$  and  $R_p$  data using the equations below:

$$IE\%_{V_{corr}} = \left(1 - \frac{V_{corr}}{V_{corr}^0}\right) * 100 \dots \dots \dots (1)$$

$$IE\%_{i_{corr}} = \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) * 100 \dots \dots \dots (2)$$

$$IE\%_{R_p} = \left(1 - \frac{R_p^0}{R_p}\right) * 100 \dots \dots \dots (3)$$

Where  $i_{corr}^0$  and  $R_p^0$  are the corrosion current density and the polarization resistance, respectively, measured in solutions without inhibitor and  $i_{corr}$  and  $R_p$  are the same parameters determined in solutions containing inhibitor. The results obtained are given in **Table 2**.



**Fig. 4.** Variation of the inhibition efficiency (as calculated from  $R_p, V_{corr}$  and  $i_{corr}$  results) with the concentration of 1-butyl triphenylphosphonium chloride in HCl 1M solution.

As can be seen, the IE% increased with increasing concentration of butyl triphenylphosphonium chloride, but the IE% values obtained from the Tafel experiments ( $i_{corr}$ ) were higher than those obtained through the polarization resistance ( $R_p$ ). At a glance, this behavior suggests that the inhibitor action is dependent on the



potential applied and time of polarization, since in the  $R_p$  experiments only  $\pm 30$  mV around  $E_{corr}$  was applied to the working electrode and the duration of the experiment was shorter. However, the data clearly show that the carbon steel electrochemical corrosion rate decreased in the presence of butyl triphenylphosphonium chloride. The phosphonium salt was effectively adsorbed on the mild steel surface impeding the corrosion process supporting the mechanism discussed, which proposes that butyl triphenylphosphonium chloride acts by blocking the cathodic sites without a change in the mechanism of the hydrogen evolution reaction and by modifying the activation energy of the anodic reaction occurring in the inhibitor-free metal in the course of the inhibited corrosion process.

**II. 3. 3. Adsorption isotherms**

In order to evaluate the adsorption process of butyl triphenylphosphonium chloride on the carbon steel surface, Langmuir, Temkin and Frumkin adsorption isotherms were obtained according to the following equations [23-25].

Langmuir: 
$$\frac{\theta}{(1 - \theta)} = KC$$

Rearrangement gives: 
$$\left(\frac{C}{\theta}\right) = \frac{1}{K} - aC \dots \dots \dots (4)$$

Temkin: 
$$\log\left(\frac{\theta}{C}\right) = \log K - g\theta \dots \dots \dots (5)$$

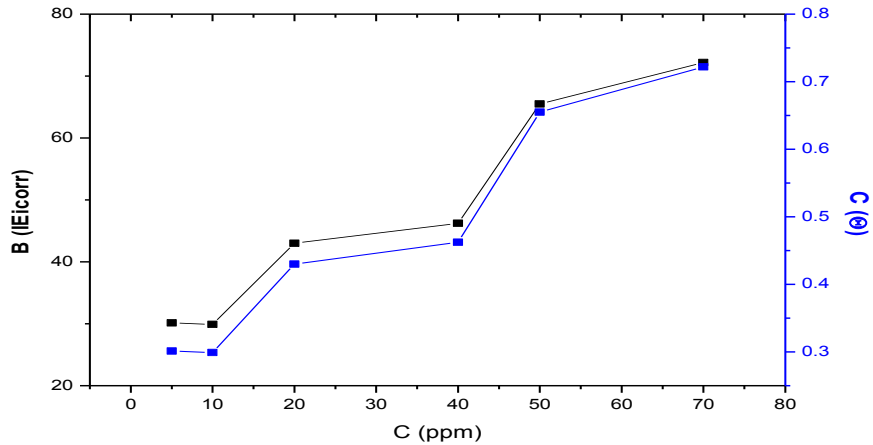
Frumkin: 
$$\frac{\theta}{(1 - \theta)} \exp(-g\theta) = KC$$

Or its linear form: 
$$\log\left(\frac{\theta}{(1 - \theta)C}\right) = \log K + g\theta \dots \dots \dots (6)$$

Where  $\theta$  is the surface coverage, K the adsorption–desorption equilibrium constant, C the inhibitor concentration and g the adsorbate interaction parameter. Considering that the double-layer capacitance is proportional to the surface not covered by the inhibitor, the fraction of the surface covered by adsorbed molecules was determined according to the ratio [26].

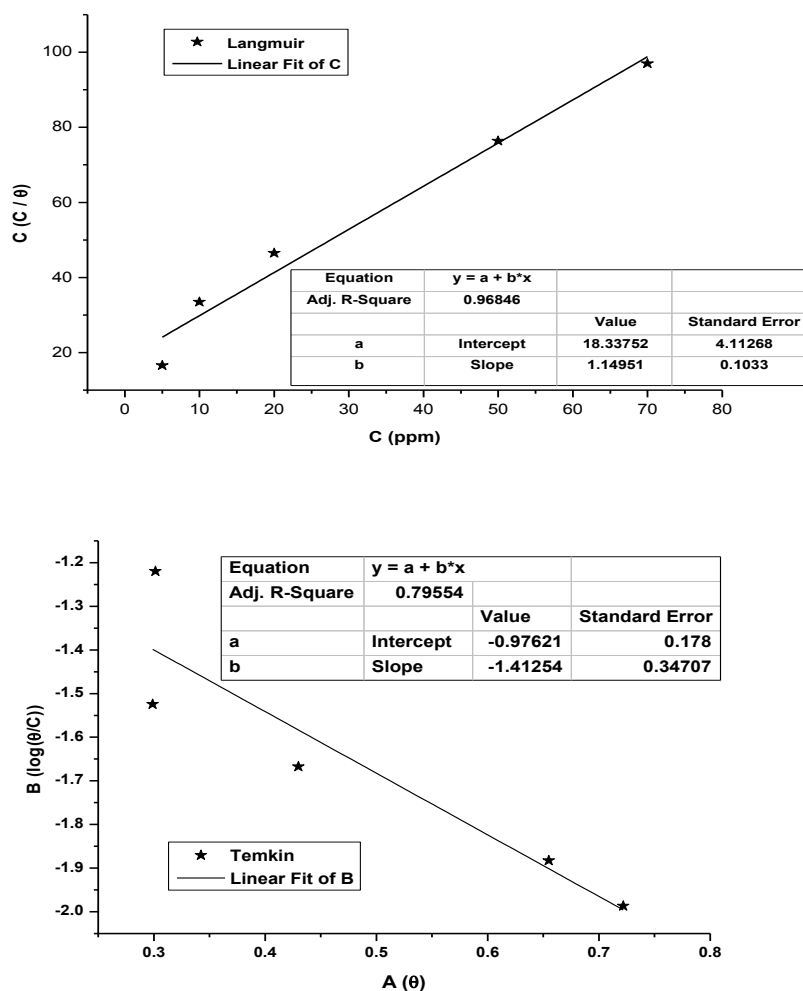
$$\theta_{i_{corr}} = \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) = \frac{E\%(i_{corr})}{100} \dots \dots \dots (7)$$

Where  $i_{corr}$  and  $i_{corr}^0$  are the corrosion current densities in the presence and absence of the inhibitor, respectively



**Fig.5.** Variation of the inhibition efficiency (as calculated from  $i_{corr}$  and  $\theta$  surface coverage results) with the concentration of butyl triphenylphosphonium chloride in HCl 1M solution.

The increasing steel surface coverage as a function of butyl triphenylphosphonium chloride concentration is shown in **Fig. 4**. To determine which adsorption isotherm best fits the surface coverage and to calculate the free-energy of adsorption, the respective plots were obtained. The three isotherms tested fitted well the data obtained, as can be



**Fig.6.** Isotherms for the adsorption of butyl triphenylphosphonium chloride on the surface of carbon steel in 1 M HCl.

The constant K is related to the standard free energy of adsorption ( $\Delta G_{ads}$ ) by the equation:

$$K = (1/55.5) \exp(-\Delta G_{ads}^0/RT) \dots \dots \dots (8)$$

$$\Delta G_{ads}^0 = -RT(\ln 55.5K) \dots \dots \dots (9)$$

The values of the constant K and the standard free energy of Adsorption by different isotherms for butyl triphenylphosphonium chloride molecules are shown in the **table 3**.

**Table 3:** Isotherms for the adsorption of butyl triphenylphosphonium chloride on the surface of carbon steel in 1 M HCl

isotherme	Equation linear	R <sup>2</sup>	K(M <sup>-1</sup> )	g or a	$\Delta G_{ads}$ (kj/mol)
Langmuir	$(C/\theta)=1.15C+18.338$	0.968	308702.044	0.946	-42.481
Temkin	$\text{Log}(\theta/C)=-1.413\theta+0.976$	0.796	3357750.954	0.982	-48.566
Frumkin	$\text{Log}(\theta/(1-\theta)C)=-0.489\theta-1.109$	0.162	-	-	-

Where K is the equilibrium constant of the adsorption process. **Fig. 5** shows plot of C/θ against C where straight lines are obtained. For the inhibitor, the slope of the straight line is equal to unity while the straight line obtained in case of butyl triphenylphosphonium chloride has a slope >1. So, it could be concluded that Phosphonium salt is adsorbed at the steel surface following Langmuir isotherm without interaction between the adsorbed molecules. In case of butyl triphenylphosphonium chloride molecules, deviation of the slope from unity can be explained in terms of repulsion or attraction of the adsorbed molecules adjacent to each other, a fact which was ignored during the derivation of Langmuir isotherm. The interaction between butyl



triphenylphosphonium chloride molecules can be ascribed to the steric hindrance exerted by the tetra phenyl groups. Adsorption of butyl triphenylphosphonium chloride molecules was found to obey Frumkin's model which is given by linear equation:

$$\text{Log } (\theta/(1-\theta) C) = -0.489 \theta - 1.109, R^2=0.162$$

On the light of these results, the characteristic parameters of adsorption of butyl triphenylphosphonium chloride were found to obey Temkin's isotherm:  $g = -1.413$ ,  $\log K = 0.976$ . The negative value of  $g$  indicates the presence of repulsive forces between the adsorbed species of butyl triphenylphosphonium chloride. The values of  $K$  and  $\Delta G_{\text{ads}}$  by different isotherm Langmuir and Temkin were found to be [308702.044 and 3357750.954]  $M^{-1}$  and [-42.481 and -48.566]  $\text{kJ mol}^{-1}$  while the high negative value of  $\Delta G_{\text{ads}}$  indicates that butyl triphenylphosphonium chloride is strongly adsorbed (chemisorptions) on the steel surface.

These results are analogous to those reported by K.F. Khaled which involves inhibiting action of (chloromethyl) triphenyl phosphonium chloride (CTP), tetraphenylphosphonium chloride (TP), triphenyl phosphine oxide (TPO), triphenyl (phenylmethyl) phosphonium chloride (TPM) and triphenyl phosphine (TPP) on the corrosion of iron in 1 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [19]. Moreover, the experimental results provides further evidence that CTP, TP, TPO, and TPM act as inhibitors for iron in acid environments, while TPP is an accelerator. These compounds are mixed-type inhibitors and the inhibition efficiency is due to the presence of chloride ion which increased with increasing concentrations. By comparison our results with those obtained by Khaled, triphenylphosphonium chloride derivative show good cathodic inhibition performance.

A Comparative electrochemical study with that reported in the literature revealed that the efficiency of the inhibitors follows the order: butyl triphenylphosphonium chloride > (chloromethyl) triphenyl phosphonium chloride (CTP) > tetraphenylphosphonium chloride (TP) > triphenyl phosphine oxide (TPO) > triphenyl (phenylmethyl) phosphonium chloride (TPM). It was also reported in the literature [27-30] that the efficiency of halide inhibitors follows the order:  $I^- > Br^- > Cl^- > F^-$ .

### III. CONCLUSION

The phosphonium salt, 1-butyl triphenylphosphonium chloride has been successfully synthesized in high yield (95%). The results obtained from electrochemical studies showed that butyl triphenylphosphonium chloride is an excellent corrosion inhibitor for carbon steel under acidic conditions. The maximum inhibition efficiency was 71.92% for 70 ppm. Excellent agreement between the inhibition efficiencies calculated using polarization techniques was obtained. The adsorption of the phosphonium salt inhibitor onto the carbon steel surface was characterized by the decrease in (i) the cathodic and anodic current densities observed in the potentiodynamic polarization curves carried out in the presence of butyl triphenylphosphonium chloride.

The organic phosphonium molecule acts by blocking the cathodic surface sites and by modifying the activation energy of the anodic reaction. The former effect was demonstrated by the decrease in the cathodic current densities observed in the potentiodynamic polarization curves without changes in the respective Tafel slope, while the later was observed through the changes in the Tafel slopes of the anodic polarization curves.

The chemisorption aspect of the adsorption process was well-established by the value of  $\Delta G_{\text{ads}}^0 = [-42.481 \text{ and } -48.566] \text{ kJ mol}^{-1}$  calculated from the slope of the Langmuir and Temkin isotherms which best fitted the experimental data of the relationship between butyl triphenylphosphonium chloride concentration and surface coverage;  $R^2=0.968$  and  $0.796$ . The lower activation energy of the corrosion process in the presence of the corrosion inhibitor, when compared to that in its absence, also demonstrated the chemisorptive nature of the adsorption.

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