



Swansea University  
Prifysgol Abertawe



## Cronfa - Swansea University Open Access Repository

---

This is an author produced version of a paper published in :  
*Surfaces and Interfaces*

Cronfa URL for this paper:

<http://cronfa.swan.ac.uk/Record/cronfa30873>

---

### Paper:

Nagarajan, P., Jothi, S., Chowhan, L., Bosco, I. & Cole, I. (2016). Corrosion Inhibition on Mild Steel by Phosphonium Salts in 1M HNO<sub>3</sub> Aqueous Medium. *Surfaces and Interfaces*

<http://dx.doi.org/10.1016/j.surfin.2016.10.003>

---

This article is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Authors are personally responsible for adhering to publisher restrictions or conditions. When uploading content they are required to comply with their publisher agreement and the SHERPA RoMEO database to judge whether or not it is copyright safe to add this version of the paper to this repository.

<http://www.swansea.ac.uk/iss/researchsupport/cronfa-support/>

# Corrosion Inhibition on Mild Steel by Phosphonium Salts in 1M HNO<sub>3</sub> Aqueous Medium

N. Palaniappan,<sup>a</sup> L. Raju Chowhan,<sup>a\*</sup> Sathiskumar Jothi,<sup>b</sup> Infant G. Bosco,<sup>c</sup> Ivan S. Cole<sup>d</sup>

<sup>a</sup>School of Chemical Sciences, Central University of Gujarat, Gandhinagar

<sup>b</sup>College of Engineering, Swansea University, Bay Campus, Swansea, UK; s.jothi@swansea.ac.uk

<sup>c</sup>Institute for Frontier Materials, Deakin University, 3125 Victoria, Australia

<sup>d</sup>CSIRO Manufacture Clayton, 3169 Victoria, Australia

## Abstract

The corrosion inhibition on mild steel by phosphonium salts in 1 M HNO<sub>3</sub> medium has been investigated by weight loss and polarization techniques. The result revealed that these derivatives are excellent inhibitors. Potentiostat polarization, impedance, and electrochemical noise studies showed mixed type inhibitors. Ellipsometer, quantum chemical and FTIR results indicated Phosphonium bromide derivatives exhibit excellent corrosion protective thin layer performance.

Key words: Corrosion Inhibitor, Mild steel Electrochemical Studies, Phosphonium Salts; Quantum Chemical.

## 1. Introduction

Prevention of corrosion still remains one of the challenging problems since past several decades. Oil and gas industries, nuclear plants, ship hull, alkaline bridges are most affected by the corrosion. The various methods are employed for inhibition of corrosion [1-2]. As early research work reported that hetero organic compound has good inhibition properties [3]. Although, newly designed organic inhibitors are less toxic and environmentally benign, especially nitrogen containing compounds have shown excellent corrosion inhibition properties [4-5]. Moreover, sulphamide series has been reported as corrosion inhibitor in acidic medium [6]. However, lactone derivatives have been studied on mild steel in strong aggressive medium [7]. Whereas the impedance spectroscopy has significant role in determining electrode kinetic properties [8]. Poly hetero atoms like nitrogen, sulphur, and oxygen are having excellent metal retardation nature [9]. Although, past few years medicinal

plant extracts are used as inhibitor in acidic and alkali medium such as chitosan derivative's [10], Vitamin B [11], chlorophytum borivilianum [12], suhinopsis lorentzil [13], mansoa alliacea [14]. In general nitrogen based compound have remarkable corrosion mitigation activity in acidic medium. In addition, benzyl triphenylphosphonium bromide [15], butyltriphenylphosphonium bromide [16], (2-hydroxyethyl) triphenylphosphonium bromide [17] was studied as corrosion inhibitor in sulphuric acid medium. The present work is mainly focuses on the effect alkyl/aryl chain on corrosion inhibition in nitric acid medium. To our delight the phosphonium salt (**1-4**) are showing effective corrosion inhibition. In addition, 3-amino-1, 2,4-triazole, triazole [18], oxo-triazole, Ochrosia oppositifolia [19-22] are excellent corrosion inhibitors. The present research aim is economically favour Wittig salt based phosphonium bromide derivatives (**1-4**) as a corrosion inhibitor for mild steel.

The following reason the selection of phosphonium derivatives as corrosion inhibitor

- (a) The phosphonium salts have three phenyl rings which is act as centre for adsorption of inhibitor molecules and electron transfer from inhibitor molecule to mild steel surface.
- (b) The phosphonium salts are chemical cheap simple synthesis method and inhibitor stability high is acidic medium. Whereas the plant extraction protective layer stability week in acidic medium. We have examined electrochemical corrosion activity and weight loss method, potentiodynamic polarization, and impedance spectroscopy, electrochemical noise. All the techniques triplicated to confirmation and reproducibility inhibitor efficiency.

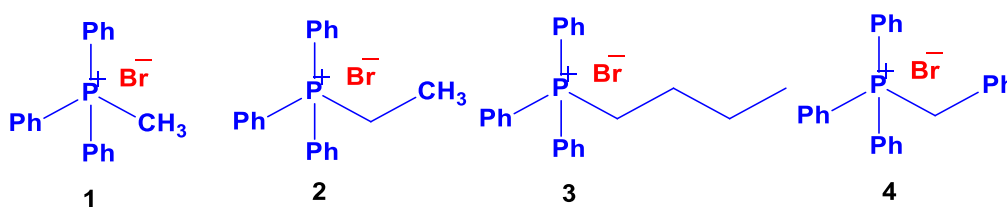


Fig 1. Phosphonium bromide Inhibitors utilised in corrosion study

## 2.1. Experimental

### 2.1.1. Methods and Materials

Methyltriphenylphosphonium bromides (MePh<sub>3</sub>PBr) **1**, Ethyltriphenylphosphonium bromide (EtPh<sub>3</sub>PBr) **2**, Butyltriphenylphosphonium bromide (BuPh<sub>3</sub>PBr) **3**, Benzyltriphenylphosphonium bromide (BnPh<sub>3</sub>PBr) **4**, all AR grade inhibitors were used without any further purification. Electrochemical measurements were carried out with inhibitor and without inhibitor, immersed in 1M of 100 mL HNO<sub>3</sub> for 5 days at 310 ±1 °K and 0.5 mg of inhibitors are used.

### 2.1.2. Electrode preparation

The working electrodes used in this experiment were prepared from mild steel rod with the chemical composition as shown below

Element	C	Si	S	P	Mn	Fe
Weight %	0.15	0.31	0.025	0.025	0.02	99.47

Araldite (Klear brand) was applied over the entire surface. The exposed surface area of 1cm for the studies. The mild steel coupons were polished with different silicon carbide paper (150-1200) rinsed with Millipore water, degreased with acetone and dried at room temperature before the experiments.

## 2.2. Electrochemical study

The electrochemical measurements were performed with CH 920D model Potentiostat in a conventional electrochemical three electrode system. The mild steel as working electrode, platinum foil as counter electrode respectively and saturated Ag/AgCl as a reference electrode were used to carry out electrochemical reaction [23]. All potentials were measured with respect to Ag/AgCl(sat KCl) reference electrode experiments were carried out under non deaerated conditions at 310±1 °K. The polarization curves were recorded as per the ASTM

standard  $\pm 250$  mV w.r.t. OCP, with a scan rate of 0.1 mV/s. The data was collected and analyzed using CH 920D electrochemical software. Electrochemical Impedance Spectroscopy (EIS), Electrochemical Noise (ECN) were carried out with respect open circuit potential (OCP) [24]. All the experiments were performed on three replicates  $310 \pm 1$  °K temperature.

## **2.3 Surface analysis**

### *2.3.1. XRD analysis*

The thin film of inhibitor was carefully scratched and made in the form of fine powder. The sample was analyzed by powder XRD. Bruker Cu,  $k\alpha$  radiation ( $\lambda = 1.54$  Å) at 40 kV, 30 mA, scanning rate 0.01. The range of  $2\theta$  between  $5-80^\circ$ . The peaks were showing phosphonium bromide substrate present in the form of thin protective film.

### *2.3.2. Ellipsometer analysis*

The iron/phosphonium complex film thickness was studied by ellipsometer model fitting method. The amplitude ratio ( $\tan \Psi$ ), phase shift difference ( $\Delta$ ) of the two orthogonally polarized components of the reflected wave ( $r_s$  and  $r_p$ ) were defined through the equation  $\tan(\Psi) \exp(i\Delta) = r_p/r_s$ . Ellipsometer was an indirect model analysis the self-assembled monolayer iron complex on the working electrode. The mild steel samples were continuously immersed in 1M HNO<sub>3</sub> for 5 days with and without inhibitor. The various test electrodes were taken out from solution and dried in inert nitrogen atmosphere. The thin film monolayer was analysed by the Ellipsometer model HORIBA UVI cell2.

### *2.3.3. FTIR analysis*

The thin film was removed from the working electrode surface and mixed with KBr, made into the pellet form for IR analysis using Perkin Elmer FT-IR 1600 spectrometer in the range of  $400-4000$  cm<sup>-1</sup>.

#### 2.3.4. Surface morphology

Scanning Electron Microscope are well-established technique to study the surface morphology. The mild steel coupons were studied on continues immersed for 5 days in 1M HNO<sub>3</sub> in the absence and presence inhibitors. After 5 days interval the metal coupon taken out washed with Millipore water, acetone and dried at room temperature. The microstructure was confirmed by using scanning electron microscope (SEM) Supra 40, Carl Zeiss, Germany.

#### 2.3.5. Quantum chemical study

Theoretical calculations were carried out using Gaussian 09 Programme package software. All quantum chemical calculations of inhibitor molecules were accomplished by the density functional theory (DFT) B3LYP/6-31G method. The DFT has been adopted to precisely calculate the data molecular geometric and electron distribution, inhibitor molecules metal/solution interface. The inhibitor geometries, optimization and frequency calculation were carried out in gas phase.

### 3. Results and Discussion

#### 3.1. Weight Loss Measurements

The corrosion rate values of mild steel were decreased by addition of phosphonium bromide derivative to 1M HNO<sub>3</sub> at 320±1 °K. The corrosion inhibition effect by aryl/alkyl chain of phosphonium bromide derivatives are as shown Fig 2. The results are compiled in Table 1. From table 1 it is learned that the corrosion rates are considerably decreased in presence of inhibitor. The inhibition efficiency increased by increasing the bulkiness of alkyl/aryl group of the triphenylphosphonium bromide derivatives [25]. The inhibition efficiency is in the following order BnPh<sub>3</sub>PPBr > BuPh<sub>3</sub>PBr > EtPh<sub>3</sub>PBr > MePh<sub>3</sub>PBr. Aromatic derivative shows good inhibition effect compared to the corresponding alkyl phosphonium derivatives. This is due to the presence of +M and +I effect, delocalization of π bond electron and the size of the aryl phosphonium derivative [26-27]. The strongly formed thin film inhibitor

molecules on the metal surface acts as a righteous corrosion resistance, decreasing the metal dissolution. The Inhibition efficiency ( $\eta$  %) are calculated from weight loss by the following relationship.

$$\eta \% = \frac{w^0 - w^i}{w^0} \times 100 \text{ ---- } 1$$

$w^0$  = weight before corrosion,  
 $w^i$  = weight after corrosion

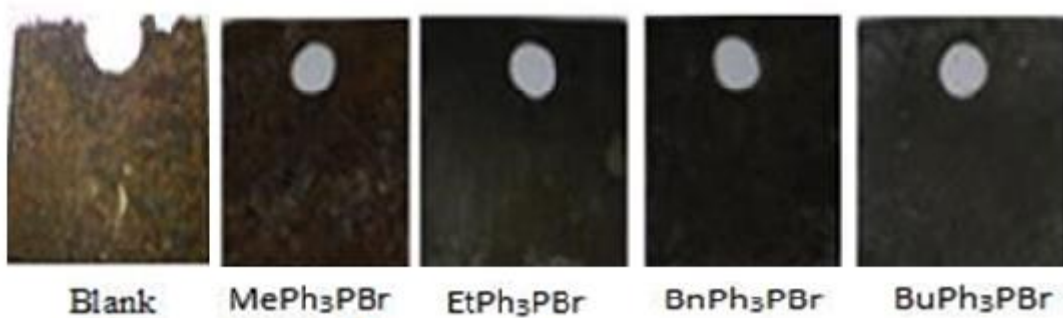


Fig 2. Weight loss measurement 5 days immersion at 310 °K, 0.5 mg concentration inhibitors in 1M  $\text{HNO}_3$  medium mild steel coupons.

S. No.	Inhibitor	Initial weight (g)	Final weight (g)	Weight loss %	Inhibition Efficiency ( $\eta$ %)
1	Blank	4.2687	1.8510	56.63	----
3	MePh <sub>3</sub> PBr	4.0710	3.2656	19.78	65.1
2	EtPh <sub>3</sub> PBr	3.9547	3.0023	24.08	57.4
4	BuPh <sub>3</sub> PBr	4.2710	3.4381	19.50	65.5
5	BnPh <sub>3</sub> PBr	4.1095	3.3263	19.05	66.4

Table 1. Weight loss method mild steel continuously immersion for 5 days at 310 °K in 1M  $\text{HNO}_3$  in different phosphonium bromide derivatives.

### 3.2. Ellipsometer

The ellipsometer study revealed the change in polarization is caused by interaction with self-assembled monolayer thin film. The sample analysed by normal steps at 70° angle of incidence. Ellipsometer has fully automated rotating polarizer compensator suitable model fitted two main layers existing shown in Fig 3. From the figure suggest that corrosion layer model co-inside with experimental studies. The layer thickness is shown in the table 2.  $\chi^2$

values are as per the library search best model fitting. All inhibitor molecules  $\chi^2$  for all inhibitors are having notable less value. [28] In addition, that without inhibitor molecule no significant wave form and  $\chi^2$  value also increased. Thus proves that inhibitor complex is formed on mild steel surface.

S. No.	Inhibitor	$\chi^2$	Thickness ( $\text{\AA}$ )
1	Blank	2.0891	131.491
3	MePh <sub>3</sub> PBr	0.4925	107.225
2	EtPh <sub>3</sub> PBr	0.7019	107.946
4	BuPh <sub>3</sub> PBr	0.2342	114.011
5	BnPh <sub>3</sub> PBr	0.3969	210.124

Table 2. Ellipsometer thin film analysis mild steel continuously immersion for 5 days at 310 °K in 1M HNO<sub>3</sub> With different phosphonium bromide derivatives.

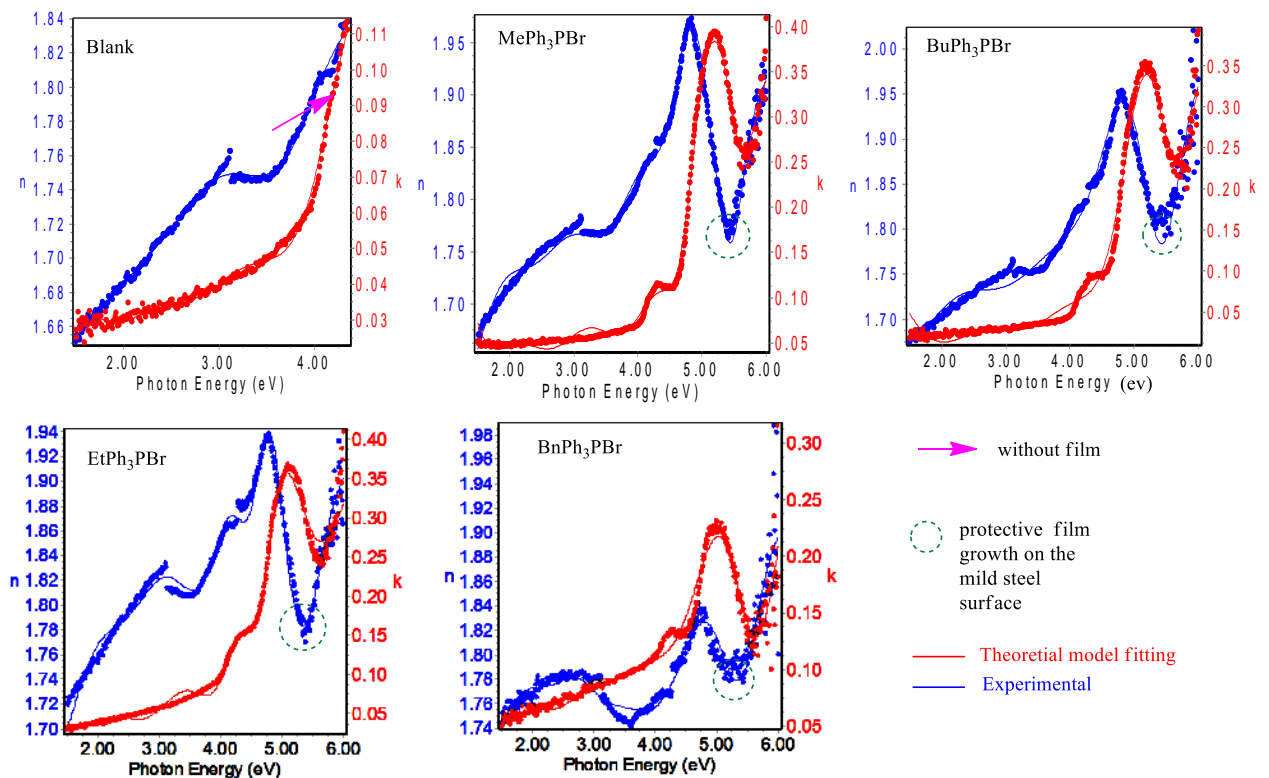


Fig 3. Ellipsometer spectra of mild steel surface immersed 5 days in various environments at 310 °K.

### 3.3. FTIR Analysis of Protective Thin Film \

The FTIR, spectra triphenyl phosphonium bromide derivatives are shown in Fig 3. In addition that the triphenyl phosphonium bromide film deposited on mild steel surface, the film functional group are studied at different environment immersion. Moreover, the observed stretching frequencies are assigned at C-Br 690 cm<sup>-1</sup>. Whereas, the peak indicate that Br<sup>-</sup> ion are co-ordinate with Fe<sup>2+</sup>



complex film formed on the metal surface [29-30]. Furthermore, the peak is assigned C-H  $2930\text{ cm}^{-1}$ , C-C  $1451\text{ cm}^{-1}$  and peak assigned at  $700\text{ cm}^{-1}$   $\text{Fe}_2\text{O}_3$ . Furthermore, the stretching frequency are appear at  $3500\text{ cm}^{-1}$  indicate  $3\text{Fe}(\text{OH})_2$ . Although, the peak appear at  $1620\text{ cm}^{-1}$  P-O-Fe complex film present on the mild steel surface. Moreover, the stretching frequency are appear at  $793\text{ cm}^{-1}$  indicates iron phosphonium complex present in the thin film. However, the bands are more intensive suggest that the phosphonium derivatives barrier film strongly adsorbed on mild steel surface.

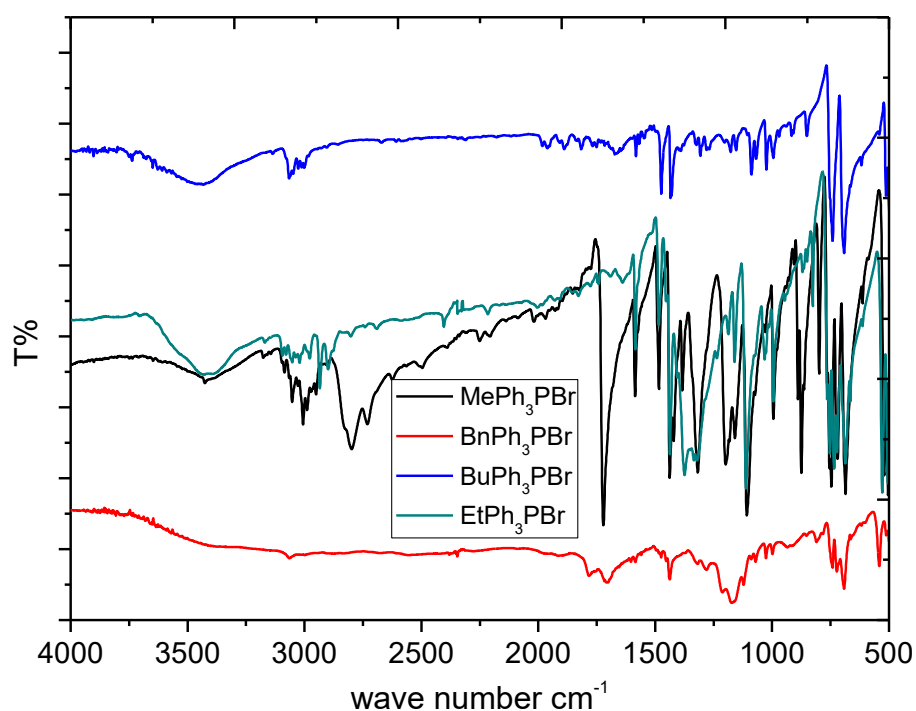


Fig 4. FTIR Spectra of mild steel surface immersed in various environments.

### 3.4. XRD Analysis of Protective Thin Film

The XRD pattern of phosphonium bromide derivatives indicates its crystalline nature. The different environment containing of 0.5 mg of  $\text{MePh}_3\text{PBr}$ ,  $\text{EtPh}_3\text{PBr}$ ,  $\text{BuPh}_3\text{PBr}$  and  $\text{BnPh}_3\text{PBr}$  test solution are shown in Fig 5. The absence of peak at  $2\theta = 43.8^\circ$  is due to iron complex formation. The peak at  $21.6^\circ$  for  $\text{EtPh}_3\text{PBr}$ ,  $22.8^\circ$  for  $\text{MePh}_3\text{PBr}$ ,  $23.2^\circ$  for  $\text{BuPh}_3\text{PBr}$  and  $23.5^\circ$  for  $\text{BnPh}_3\text{PBr}$  can be assigned to oxides of iron [31-34]. Thus it is proving that the surface of the metal immersed in 1M  $\text{HNO}_3$  solution contains iron oxides

and Fe-Br-PPh<sub>3</sub>R (R= Bn, Bu, Et, Me) complex. It indicates that the protective film is free from any oxides of iron.

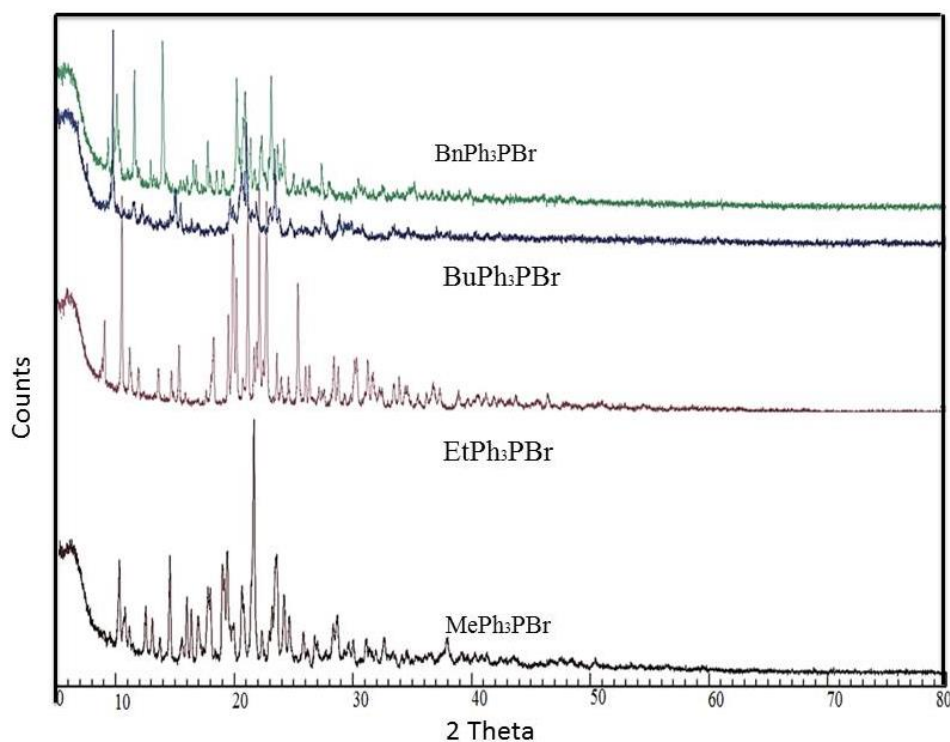


Fig 5. The XRD patterns of mild steel surface immersed in various environments at 310 °K.

### 3.5. SEM Measurements

The surfaces of metal coupons were after exposing in 1M HNO<sub>3</sub> solution in the absence and presence of 0.5 mg of inhibitors molecules evaluated by the SEM [35]. The SEM images of the mild steel surface are shown in fig 6, for Blank, MePh<sub>3</sub>PBr, EtPh<sub>3</sub>PBr, BuPh<sub>3</sub>PBr, and BnPh<sub>3</sub>PBr. Specimen blank, the mild steel surface is strongly damaged due to the excessive metal dissolution in aggressive solution attack. The SEM image of blank clearly shows that the corrosion reaction very high compare to presence of inhibitors. However, the surface is remarkably protected by the phosphonium derivatives inhibitor. Significantly no pits observed in the micrograph after adding BuPh<sub>3</sub>PBr to the corrosive solution. In comparison to all phosphonium bromide derivative BnPh<sub>3</sub>PBr are showing notable free pit on the surface [36-37]. It is clearly indicating that, the inhibitor molecules are adsorbed on the mild steel

surface and forms protective film. The surface films are highly stable and protective against mild steel dissolution.

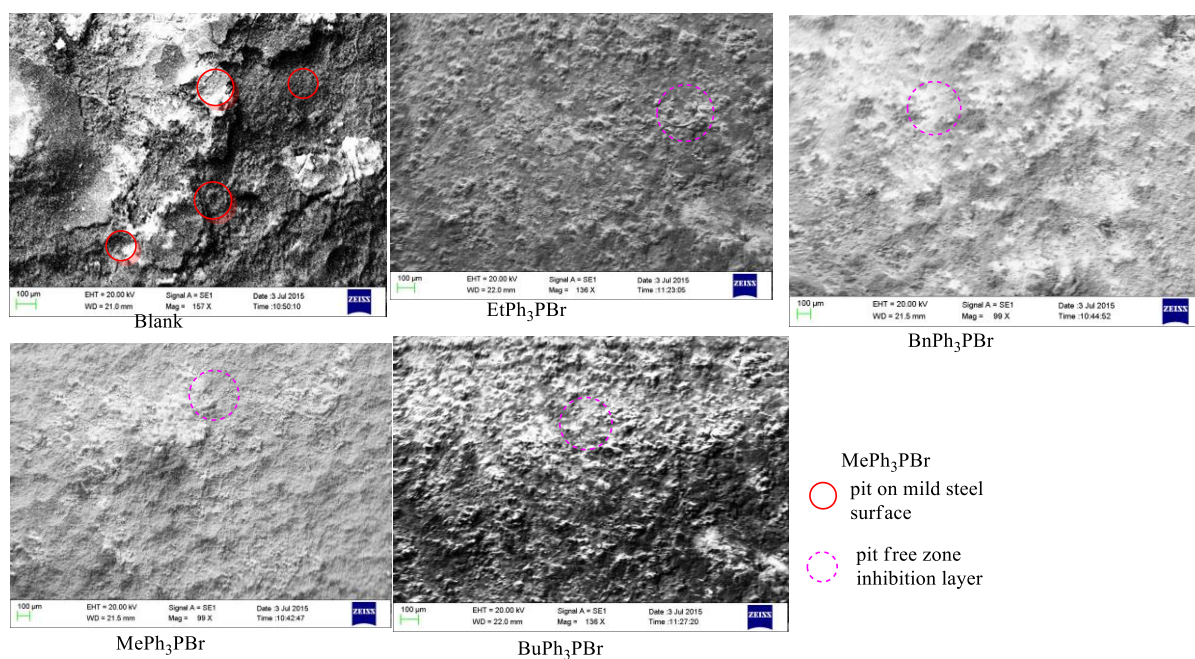


Fig 6. SEM Analysis of the mild steel 5 day immersion with and without inhibitor molecules in 1M HNO<sub>3</sub> medium

### 3.6. Open Circuit Potential

Significant care are taken in stability of the corrosion potential,[38-39] before each analysis of electrochemical study such as polarization, impedance and electrochemical noise technique. The OCP value of bare metal is suddenly increased suggest that mild steel undergoes corrosion and with inhibitors notable steady state potential obtained as shown in Fig 7.] In addition, the OCP measurement suggests that the inhibitor molecules are self-assembled monolayer formed on the mild steel surface [40-41. The inhibitor OCP value is towards the noble direction as well as the potential back towards the active values. The inhibitor molecule BnPh<sub>3</sub>PBr, EtPh<sub>3</sub>PBr, MePh<sub>3</sub>PBr, BuPh<sub>3</sub>PBr has blocked the active region of the metal surface. These results are confirmed from weight loss measurements. The phosphonium bromide derivatives are act as mixed inhibitors.

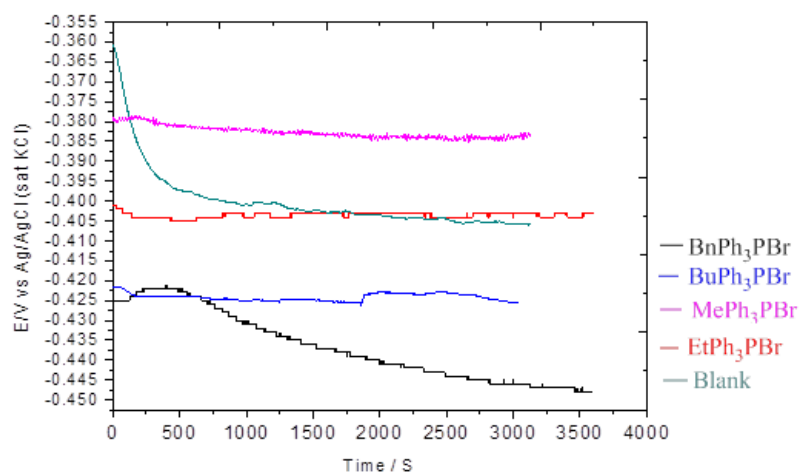


Fig 7. Open circuit potential of the mild steel continuous immersion 5 days in 1M HNO<sub>3</sub> various environments.

### 3.7. Potentiodynamic Polarization

The potentiodynamic studies are shown in Fig 8a. The cathodic reactions as well as anodic reaction are well distinct [37-42] as shown in fig 8a. The anodic and cathodic polarization curves are extrapolated and the point of intersection X axis known as  $E_{\text{corr}}$  value and the anodic and cathodic polarization curves are intersection point at Y axis known as  $I_{\text{corr}}$  value as shown in fig (8b). Although the anodic curve and cathodic curves are controlled by inhibitor molecules. The spectra suggested that self-assembled monolayer was formed on the working electrode surface [43].

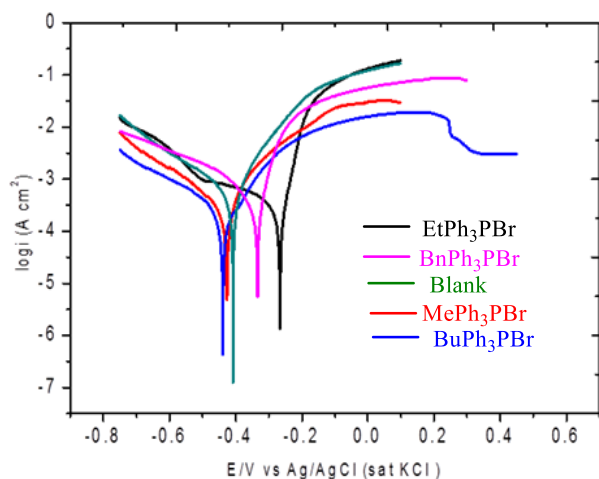


Fig a

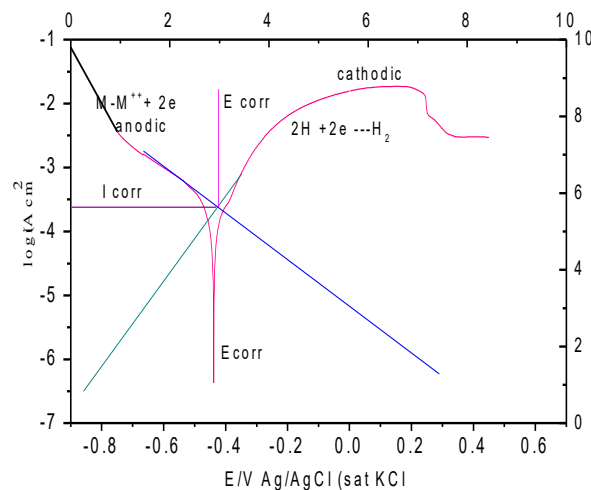


Fig b

Fig 8. Potentiodynamic polarization of the mild steel continues immersion with and without inhibitor 5 days in 1M HNO<sub>3</sub> medium

Moreover, the phosphonium salt have polarized cation and anion part it would be deposited on the cathodic active part of mild steel thus hydrogen evolution suppressed [44-45]. The polarization resistance values shown in the Table 3. It is observed that polarization resistance gradually increases by influence of different aryl/alkyl side chain of phosphonium cation interaction with iron surface, hydrophobic effect also observed. The alkyl/aryl chain plays a significant role in the change inhibition efficiency and electrostatic attraction. The anion plays primary role to adsorb cation on polarized metal surface to make barrier film on metal surface. Finally, the phosphonium bromide derivatives (**1-4**) corrosion inhibition efficiency variation depends on the molecular structure,  $\pi$  electron and alky/aryl group substitution effect. The corrosion potential shifted marginally towards more positive values, even though there is no specific relation between  $E_{corr}$  and  $I_{corr}$ . The percentage of inhibition efficiency (IE %) were calculated using the following relationship.

$$IE(\%) = \frac{I^0 - I}{I^0} \times 100 \quad \text{---2}$$

S. No.	Inhibitors	-E <sub>corr</sub> (mV)	I <sub>corr</sub> (mA)	IE%
1	Blank	400	3.888	
5	MePh <sub>3</sub> PBr	405	1.817	53.26
2	BuPh <sub>3</sub> PBr	410	1.901	51.10
4	EtPh <sub>3</sub> PBr	280	1.933	50.28
3	BnPh <sub>3</sub> PBr	350	1.944	50.00

Table 3. The potentiodynamic polarization of mild steel with and without inhibitor molecules immersion in 1M HNO<sub>3</sub>.

### 3.8. Impedance Spectra

The impedance technique is one the fundamental studies for electrode kinetic as well as homogeneities of working electrode surface [46]. The charge transfer resistance (R<sub>ct</sub>) and double layer capacitance (C<sub>dl</sub>) values were calculated using the following equation.

$$C_{dl} = \frac{1}{2\pi \times f_{mx} \times R_{ct}} \times 100 \text{-----3}$$

$$R_{ct} = (R_s - R_t) \text{-----4}$$

Where R<sub>s</sub> = solution resistance, f<sub>mx</sub> = maximum frequency.

AC impedance spectra are recorded with potential E = 0 V, frequency ranges 1x10<sup>5</sup>-10 mHz, amplitude 0.005 V, and quite time 2 s. The nyquist plot is as shown in Fig 9. The randle circuit is used for curve fitting and this circuit explain about interaction of inhibitor molecules /iron surface. The impedance parameters are shown in the table table 4. Hence, the change in R<sub>ct</sub> and C<sub>dl</sub> were affected by the replacement of water molecules by the inhibitors adsorption on mild steel surface and control metal dissolution.

S. No	Inhibitors	R <sub>s</sub> (Ω cm <sup>2</sup> )	R <sub>ct</sub> (Ω cm <sup>2</sup> )	C <sub>dl</sub> (μFcm <sup>-2</sup> )
1	Blank	4	7	1.1373
3	MePh <sub>3</sub> PBr	2	20	0.2653
2	EtPh <sub>3</sub> PBr	3	27	0.1156
5	BuPh <sub>3</sub> PBr	4	20	0.1592
4	BnPh <sub>3</sub> PBr	3	45	0.0393

Table 4. Impedance spectroscopy study mild steel continuously immersion for 5 days at 310 °K in 1M HNO<sub>3</sub> different phosphonium bromide derivatives.

From the Fig 9a, 9b the bode modulus plots electrode impedance and phase angle increased suggest an high capacitive involved between metal/ inhibitor interaction. Hence the log frequency plots are also showed the phase shift in the low frequency without inhibitors. [51-52]. The presence of inhibitor molecule inhibition increased would be main reason of ionic structure of  $\text{Ph}_3\text{---P}^+ \text{Br}^-$  and alkyl chain effect ,which is one major role to block active site of mild steel surface . [52-53]. The phosphonium bromide derivatives are promote electron transfer from inhibitor donor site to empty d orbital of mild steel and the hydrogen bond and  $\text{Br}^-$  ion interaction with mild steel surface. These are the significant anomalous physicochemical properties phosphonium salt adsorbed on metal surface.

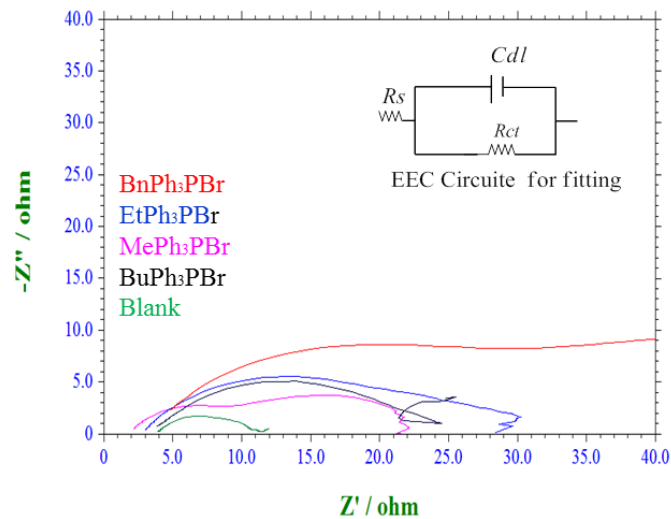


Fig 9. Nyquist diagrams for mild steel in 1M  $\text{HNO}_3$  containing different phosphonium bromide derivatives

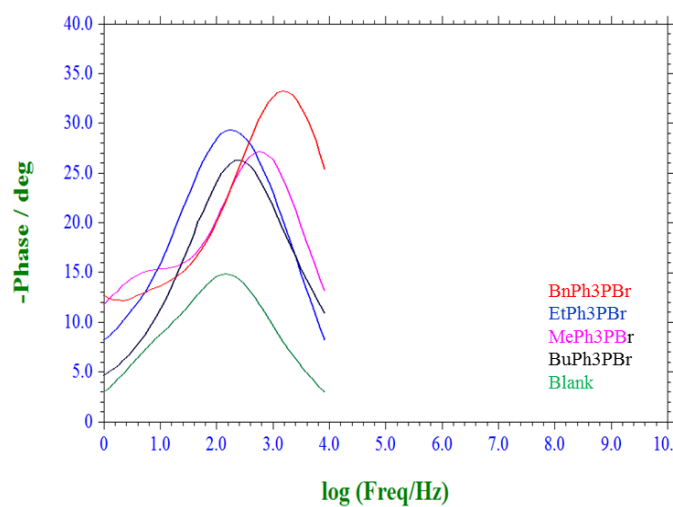


Fig 9a. Phase angle bode spectra of mild steel in 1M HNO<sub>3</sub> in the absence and presence phosphonium derivatives at 310 K

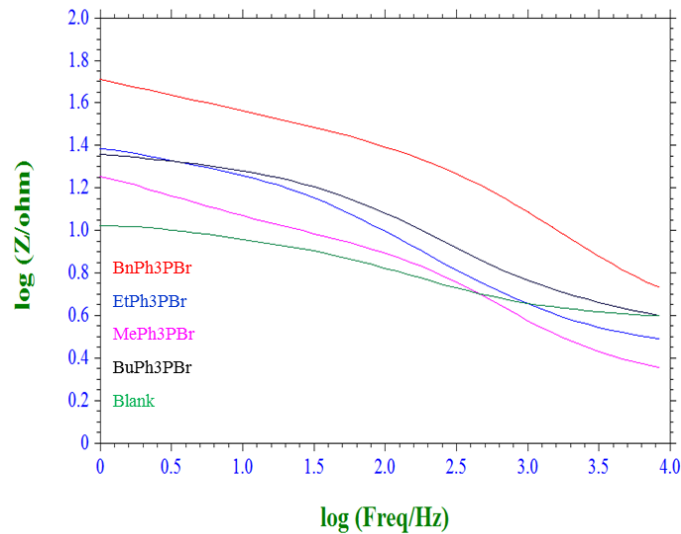


Fig 9b. Bode plot of mild steel in 1M HNO<sub>3</sub> in the absence and presence of phosphonium bromide at 310 K

### 3.9. Electrochemical Noise Measurement (ECN)

The electrochemical noise techniques are carried out potentiostatic or galvanostatic (CH-Model-920D) three cells conventional method. However, the electrochemical noise techniques is primary function of the time and frequency fluctuation as shown in figure .9 According to figure10, the phosphonium bromide derivative are block the active part of mild steel surface and also without inhibitor molecule current burst fluctuation high. Whereas, the fluctuation of the potential and current are directly related to working electrode corrosion behavior and barrier film stability [54-60]. In addition, that frequency doming are significant role for investigate the localized corrosion of mild steel surface. According to Cottis et al [61,62] electrochemical noise technique is similar to impedance, potentiodynamic polarization method . The current burst is attributed to pitting on the mild steel surface. However the alky group effect of the Ph<sub>3</sub>PBr cation enhance hydrophobic properties and reduced pit on the mild steel surface .Furthermore , the electrochemical noise current fluctuation value are shown in table (6). According to the table value mean current fluctuation and standard deviation value are decreased, indicate that the alky chain effect of the [ Ph<sub>3</sub>---P ]<sup>+</sup>Br<sup>-</sup> cation and bromine anion adsorption on the mild steel surface .Over all



the ECN techniques are good agreement with SEM and weight loss ,impedance, polarization technique, the phosphonium bromide act as mixed type inhibitor molecules.

Inhibitors	I Mean (mA)	S.D of R (ohm)
Blank	4.467	9.992
MePh <sub>3</sub> PBr	4.124	9.957
EtPh <sub>3</sub> PBr	4.215	1.009
BuPh <sub>3</sub> PBr	5.318	1.005
BnPh <sub>3</sub> PBr	3.827	1.009

Table 5. Electrochemical noise analysis mild steel continuously immersion for 5 days at 310 °K in 1M HNO<sub>3</sub> different phosphonium bromide derivatives.

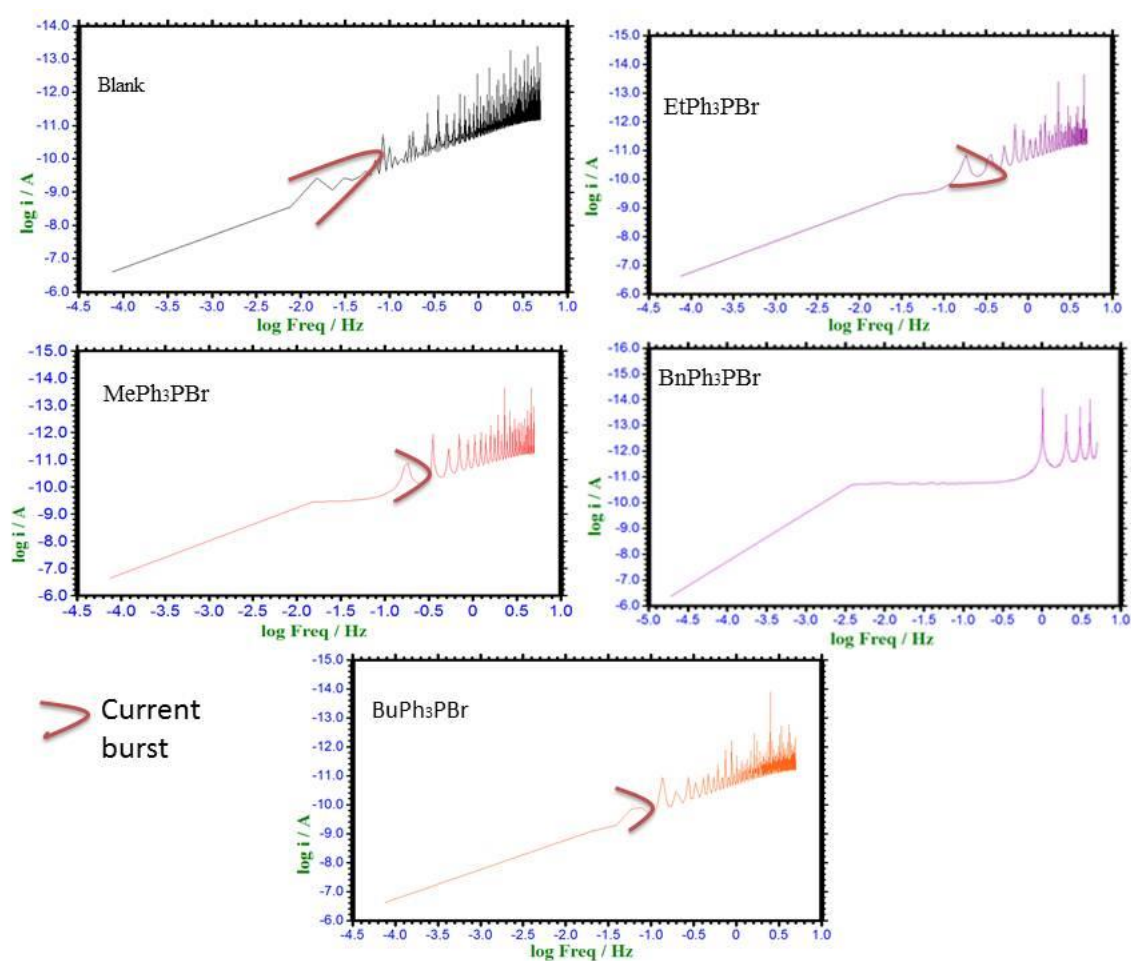


Fig 10. Electrochemical noise power spectra mild steel with and without inhibitor molecules immersed in 5 days 1 HNO<sub>3</sub> solution.

### 3.10. Quantum Chemical Analysis

The theoretical study of the inhibitors molecules, adsorption activity and optimized structure have been explored by the density function theory (DFT).Further ,the DFT Optimized

calculation was standardized, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO). However, the density distribution of HOMO and LUMO are significant roles for the adsorption centers of the inhibitor molecules, it is associated with metal and inhibitor molecule interaction.[63,64]. The ionization potential and electron affinity are directly related to A and I respectively as follows  $A = -E_{LUMO}$ ,  $I = E_{HOMO}$ . Further, the quantum chemical parameters electronegativity ( $\chi$ ), global softness ( $\sigma$ ), hardness ( $\eta$ ), electrophilicity ( $\omega$ ), are calculated using the following equations.

$$\chi = \frac{I + A}{2} - 5$$

$$\eta = \frac{I - A}{2} - 6$$

$$\sigma = \frac{1}{\eta} - 7$$

$$\omega = \frac{\chi^2}{2\eta} - 8$$

S. No.	Parameter	Br <sup>-</sup>	MePh <sub>3</sub> PBr	EtPh <sub>3</sub> PBr	BuPh <sub>3</sub> PBr	BnPh <sub>3</sub> PBr
1	HOMO (ev)	-0.5823	-10.3052	-10.2673	-10.2165	-9.4853
2	LUMO (ev)	-1.3615	-4.3979	-4.4025	-4.3388	-4.3755
3	$\Delta E$ (ev)	0.7792	5.9664	5.8648	5.8777	5.1098
4	$\chi$ (ev)	-0.9716	7.3515	7.3349	7.2776	6.9304
5	$\eta$ (ev)	-0.3896	2.9536	2.9324	2.9388	2.5549
6	$\sigma$ (ev)	0.1948	0.3385	0.3410	0.3402	0.39140
7	$\omega$ (ev)	1.2116	9.1489	9.2151	9.0110	5.1097

Table 6. Quantum Chemical Parameters for Inhibitors Calculated with DFT Method in gas phase Br anion, EtPh<sub>3</sub>PBr, MePh<sub>3</sub>PBr, BuPh<sub>3</sub>PBr, BnPh<sub>3</sub>PBr.

In general, the inhibitor molecules are adsorption on the mild steel surface could be on the basis of donor, acceptor. The HOMO are directly related electron transferred ability of inhibitor molecules. Further, the HOMO, value increase suggest that inhibitor molecule have high tendency to donate electron to empty vacancy of metal d orbital. The LUMO are associated with ability of electron acceptor. In addition, the low E LUMO value of inhibitor molecules are adsorbed on the mild steel surface, which is a mean excellent corrosion inhibition property. Whereas the low  $\Delta E$  value reveal that inhibitor molecules are promote the strength of the barrier film. The quantum chemical parameter are shown in the table 6, the HOMO value in order to decreased  $\text{MePh}_3\text{PBr} > \text{EtPh}_3\text{PBr} > \text{BuPh}_3\text{PBr} > \text{BnPh}_3\text{PBr} > \text{Br}$  and LUMO the following order increase  $\text{Br} < \text{EtPh}_3\text{PBr} < \text{MePh}_3\text{PBr} < \text{BnPh}_3\text{PBr} < \text{BuPh}_3\text{P} < \text{Br}$ . Furthermore, the effect of alkyl chain attached to the  $\text{Ph}^3\text{P}^+$  cation increase energy level of HOMO and decreased the  $\Delta E$  value in order  $\text{BnPh}_3\text{PBr} > \text{MePh}_3\text{PBr} > \text{BuPh}_3\text{PBr} > \text{EtPh}_3\text{PBr} > \text{Br}$ . The quantum chemical parameter such as electronegativity ( $\chi$ ) and global chemical hardness ( $\eta$ ), global softness ( $\sigma$ ) are decrease indicated that inhibitor molecules adsorption on the mild steel surface. This result is good correlate with experimental value, the phosphonium salt act as mixed type inhibitor molecules.

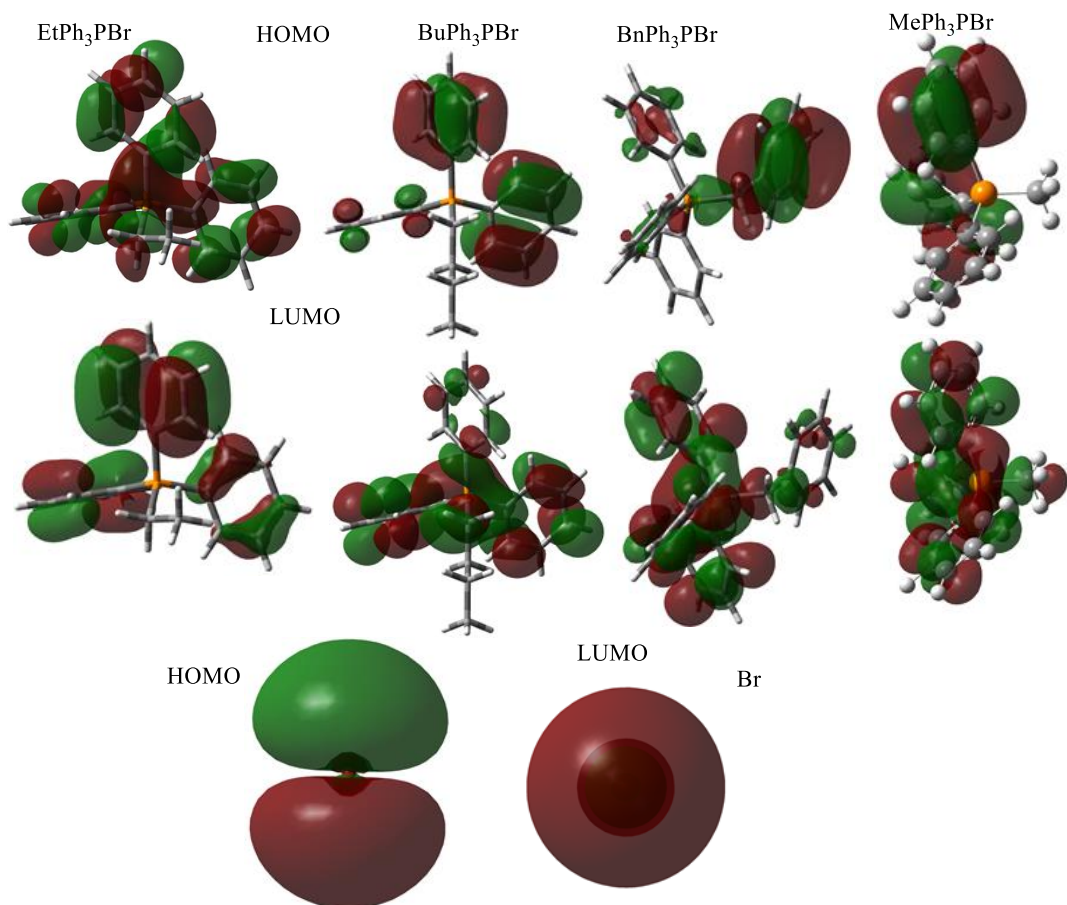


Fig 11. Computational analysis of phosphonium bromide derivatives optimized geometries, HOMO and LUMO B3LYP/6-31G method.

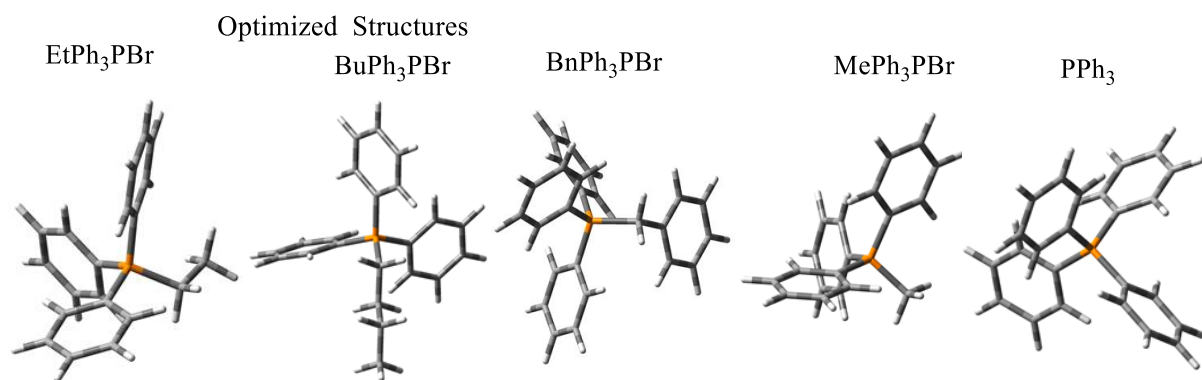


Fig 12. The optimised structure of triphenyl phosphonium bromide derivatives inhibitor molecules

### 3.11. Conclusions

Triphenyl phosphonium bromide series has been evaluated corrosion inhibition for mild steel in 1HNO<sub>3</sub> medium the following conclusions.

- Potentiodynamic study revealed that these compounds are suppressed cathodic and anodic by the phosphonium salt.
- Impedance as well as electrochemical noise technique were depicted excellent adsorption on the mild steel surface, control charge transfer double layer capacitance.
- XRD and FTIR result are the crystallinity and functional group of the inhibitor molecules thin film.
- SEM and Ellipsometer results were depicted the surface roughness of the mild steel and film thickness of the inhibitor molecules.
- There is a good agreement with Theoretical calculation and experimental result.

#### Acknowledgement

The authors would like to express their gratitude to CIF, Central University of Gujarat. The authors would also like to thank Dr. Prakash Chandra Jha for helping quantum chemical calculation. N. P Thanks to UGC for fellowship, RC thanks to DST-SERB (SB/EMEQ-304/2014) for financial support.

#### References

- [1] K.R. Ansari, M.A. Quraishi. *Journal of Industrial and Engineering Chemistry* 20 (2014) 2819–2829.
- [2] I.Ahamad, Rajendra Prasad, M.A. Quraishi. *Corrosion Science* 52 (2010) 933–942.
- [3] A.O.Yuce, B.AkdogruMert, GulfezaKardas, B.Yazici. *Corrosion Science* 83 (2014) 310–316.
- [4] N.A. Odewunmi, S.A. Umoren, Z.M. Gasem. *Journal of Industrial and Engineering Chemistry* 21 (2015) 239–247.
- [5] Ime B. Obot, Eno E. Ebenso, Mwacham M. Kabanda. *Journal of Environmental Chemical Engineering* 1 (2013) 431–439.
- [6] Taner Arslan, Fatma Kandemirli, Eno E. Ebenso, Ian Love, Hailemichael Alemu. *Corrosion Science* 51 (2009) 35–47.
- [7] K. Tebbji, N. Faska, A.Tounsi, H. Oudda, M. Benkaddour , B. Hammouti. *Materials. Chemistry and Physics* 106 (2007) 260–267.

- [8] A. Popova, M. Christov, A. Vasilev. *Corrosion Science* 53 (2011) 1770–1777.
- [9] A. Popova, M. Christov, A. Vasilev. *Corrosion Science* 49 (2007) 3290–3302.
- [10] Y. Sangeetha, S. Meenakshi, C. Sairam Sundaram. *International Journal of Biological Macromolecules* 72 (2015) 1244–1249.
- [11] Ramazan Solmaz. *Corrosion Science* 81 (2014) 75–84.
- [12] Gopal Ji Priyanka Dwivedi, Shanthi Sundaram, and Rajiv Prakash. *Ind. Eng. Chem. Res.* 52 (2013) 10673–10681.
- [13] Husnu Gerengi, and Halil Ibrahim Sahin. *Ind. Eng. Chem. Res.* 51 (2012) 780–787.
- [14] Fabienne Suedile, Florent Robert, Christophe Roos, Mounim Lebrini. *Electrochimica Acta* 133 (2014) 631–638.
- [15] Kalpana Bhrara, Gurmeet Singh. *Applied Surface Science.* 253 (2006) 846–853.
- [16] Kalpana Bhrara, Hansung Kim, Gurmeet Singh. *Corrosion Science* 50 (2008) 2747–2754.
- [17] Hemlata Vashisht, Sudershan Kumar, Indra Bahadur, Gurmeet Singh. *Int. J. Electrochem. Sci.* 8 (2013) 684 – 699.
- [18] Zhihua Tao, Shengtao Zhang, Weihua Li, Baorong Hou. *Corrosion Science* 51 (2009) 2588–2595.
- [19] Pandian Bothi Raja, Mehran Fadaeinasab, Ahmad Kaleem Qureshi, Afidah Abdul Rahim, Hasnah Osman, Marc Litaudon, and Khalijah Awang. *Ind. Eng. Chem. Res.* 2013, 52, 10582–10593
- [20] Maduabuchi A. Chidiebere, Cynthia E. Ogukwe, Kanayo L. Oguzie, Chukwuemeka N. Eneh, and Emeka E. Oguzie. *Ind. Eng. Chem. Res.* 51 (2012) 668–677
- [21] Husnu Gerengi and Halil Ibrahim Sahin. *Ind. Eng. Chem. Res.* 51 (2012) 780–787.
- [22] Emeka E. Oguzie, Kanayo L. Oguzie, Chris O. Akalezi, Irene O. Udeze, Jude N. Ogbulie, Victor O. Njoku. *Sustainable Chem. Eng.* 1 (2013) 214–225.
- [23] Wenjun Kuang, James A. Mathews, Matthew L. Taylor, Digby D. Macdonald. *Electrochimica Acta* 136 (2014) 493–503.
- [24] Ursula Rammelt, Silvio Kohler, Georg Reinhard. *Electrochimica Acta* 53 (2008) 6968–6972.
- [25] H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh. *Electrochimica Acta* 50 (2005) 3446–3452.
- [26] Q. B. Zhang, Y.X. Hua. *Electrochimica Acta* 54 (2009) 1881–1887.
- [27] S. Ramesh, S. Rajeswari. *Electrochimica Acta* 49 (2004) 811–820.
- [28] Simion Jitian. *Romanian Reports in Physics* 65 (2013) 204–212

- [29] Ying Yana, Weihua Li, Lankun Caia, Baorong Houb. *Electrochimica Acta* 53 (2008) 5953–5960.
- [30] U.M. Eduok, S.A. Umoren, A. P. Udoh. *Arabian Journal of Chemistry*. 5 (2012) 325–337.
- [31] 28 Chennappan Kamal and Mathur Gopalakrishnan Sethuraman. *Ind. Eng. Chem. Res.* 51 (2012) 10399–10407.
- [32] Susai Rajendran, B. V. Apparao, N. Palaniswamy. *Electrochimica Acta* 44 (1998) 533-537.
- [33] D. Gopi, El-Sayed M. Sherif, V. Manivannan, D. Rajeswari, M. Surendiran, L. Kavitha. *Ind. Eng. Chem. Res.* 53 (2014) 4286–4294.
- [34] C.B. Pradeep Kumar, K.N. Mohana. *Journal of the Taiwan Institute of Chemical Engineers* 45 (2014) 1031–1042.
- [35] A. Lalitha, S. Ramesh, S. Rajeswari. *Electrochimica Acta* 51 (2005) 47–55.
- [36] E.E. Oguzie, Y. Lia, F.H. Wang. *Electrochimica Acta* 52 (2007) 6988–6996.
- [37] Ayse Ongun Yuce, Gulfeza Kardas. *Corrosion Science* 58 (2012) 86–94.
- [38] Bei Qian, Baorong Hou, Meng Zheng. *Corrosion Science* 72 (2013) 1–9.
- [39] M. Motamedi, A.R. Tehrani-Bagha, M. Mahdavian. *Corrosion Science* 70 (2013) 46-54.
- [40] Shobhana Chongdar, G. Gunasekaran, Pradeep Kumar, *Electrochimica Acta* 50 (2005) 4655–4665.
- [41] Saad Ghareba, Sasha Omanovic. *Electrochimica Acta* 56 (2011) 3890–3898.
- [42] F. Blin, P. Koutsoukos, P. Klepetsianis, M. Forsyth. *Electrochimica Acta* 52 (2007) 6212–6220.
- [43] Mohammed A. Amin, Sayed S. Abd El-Rehim, E.E.F. El-Sherbini, Rady S. Bayoumi. *Electrochimica Acta* 52 (2007) 3588–3600.
- [44] M.G. Hosseini, M. Ehteshamzadeh, T. Shahrabi. *Electrochimica Acta* 52 (2007) 3680–3685.
- [45] Weihua Li, Qiao He, Changling Pei, Baorong Hou. *Electrochimica Acta* 52 (2007) 6386–6394.
- [46] Maxime Saviour A. Umoren, Zuhair M. Gasem, and Ime B. Obot| *Ind. Eng. Chem. Res.* 52 (2013) 14855–14865.(imped)
- [47] J.M. Sanchez-Amaya, M. Bethencourt, L. Gonzalez-Rovira, F.J. Botana. *Electrochimica Acta* 52 (2007) 6569–6583.

- [48] F. Bentiss, M. Lebrini, M. Lagrenee, M. Traisnel, A. Elfarouk, H. Vezin. *Electrochimica Acta* 52 (2007) 6865–6872.
- [49] E. Kowsari, M. Payami, R. Amini, B. Ramezanzadeh, M. Javanbakht. *Applied Surface Science* 289 (2014) 478–486.
- [50] F. Bentiss, M. Traisnel, M. Lagrenee, *Corros. Sci.* 42 (2000) 127–146.
- [51] S. Murlidharan, K.L.N. Phani, S. Pitchumani, S. Ravichandran, S.V.K. Iyer, J. *Electrochem. Soc.* 142 (1995) 1478–1483.
- [52] M.A. Quraishi, J. Rawat, M. Ajmal, *J. Appl. Electrochem.* 30 (2000) 745–751.
- [53] M.P. Desimone, G. Grundmeier, G. Gordillo, S.N. Simison. *Electrochimica Acta* 56 (2011) 2990–2998.
- [54] P. Raja Kumar, D. Kalpana, N.G. Renganathan, S. Pitchumani. *Electrochimica Acta* 54 (2008) 442–447.
- [55] F. Mohammed A. Amin, Sayed S. Abd El-Rehim, E.E.F. El-Sherbini, Rady S. Bayoumi. *Electrochimica Acta* 52 (2007) 3588–3600.
- [56] Mounim Lebrini, Michel Traisnel, Michel Lagrene, Bouchaib Mernari, Fouad Bentiss. *Corrosion Science* 50 (2008) 473–479.
- [57] C. Cuevas-Arteaga, M. Luna Brito, A. Molina-Ocampo, J. Colín, S. Serna-Barquera, A. Torres- Islas. *Int. J. Electrochem. Sci* 8 (2013) 9593 – 9606.
- [58] C. A. Loto. *Int. J. Electrochem. Sci.* 7 (2012) 9248 – 9270.
- [59] YJ. Tan, s. Bailey and b. Kinsella. *Corrosion Science* 38 (1996) 1681-1695.
- [60] Padilla-Viveros, E. Garcia-Ochoa, D. Alazard. *Electrochimica Acta* 51 (2006) 3841–3847
- [61] Rik-Wouter Bosch, Robert A. Cottis, Kinga Csecs, Thomas Dorsch, Lucia Dunbar, Andreas Heyn, Franc Ois Huet, Outi Hyokvirta, Zsolt Kener, Alena Kobzova, Jan Macak, Radek Novotny, Johan Oijerholm, Juha Piippo, Roy Richner, Stefan Rttter, Jose M. Sanchez-Amaya, Andras Somogyi, Saija Vaisanen, Wenzhong Zhanga. *Electrochimica Acta* 120 (2014) 379–389.
- [62] E. H.A.A. Al-Mazeedi, R.A. Cottis. *Electrochimica Acta* 49 (2004) 2787–2793
- [63] A. Padilla-Viveros, E. Garcia-Ochoa, D. Alazard. *Electrochimica Acta* 51 (2006) 3841–3847.
- [64] Sina S. Jamali, Douglas J. Mills. *Progress in Organic Coatings.* 95 (2016) 26–37.
- [65] JiaJun Fu, HaiShan Zang, Ying Wang, SuNing Li, Tao Chen, and XiaoDong Liu. *Ind. Eng. Chem. Res* 51 (2012) 6377–6386.
- [66] K.F. Khaled. *Electrochimica Acta* 53 (2008) 3484–3492.
- [67] Hari Kumar Sappani and Sambantham Karthikeyan. *Ind. Eng. Chem. Res.* 53, (2014) 3415–3425.



- [68] Lutendo C. Murulana, Ashish K. Singh, Sudhish K. Shukla, Mwadham M. Kabanda, and Eno E. Ebenso. *Ind. Eng. Chem. Res.* 51 (2012) 13282–13299.
- [69] I. B. Obot, N. O. Obi-Egbedi, and A. O. Eseola. *Ind. Eng. Chem. Res.* 50 (2011) 2098–2110
- [70] Xingwen Zheng, Shengtao Zhang, Min Gong, and Wenpo Li. *Ind. Eng. Chem. Res.* 53 (2014) 16349–16358.
- [71] Ali Doner, Ramazan Solmaz, Muzaffer Ozcan, Gulfeza Kardas. *Corrosion Science* 53 (2011) 2902–2913.