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# Quaternary aryl phosphonium salts as corrosion inhibitors for iron in HCl

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#### Abstract

Cathodic and anodic Tafel extrapolation data for the corrosion inhibition of iron in deaerated 1 M HCl at 22 °C are obtained for five synthesised phosphonium salts, 4-tolyltriphenyl-phosphonium chloride (TTPPC), 4-phenoltriphenylphosphonium chloride (PTPPC), 4-anilinetriphenylphosphonium bromide (ATPPB), 4-benzyl alcoholtriphenylphosphonium chloride (BATPPC), 4-hlorophenyltriphenylphosphonium bromide (CPTPPB), and two commercially available phosphonium salts, tetraphenylphosphonium bromide (TPPB) and methyltriphenylphosphonium bromide (MTPPB). The inhibitor concentrations ranged from 1 ×  $10^{-7}$  to 1 ×  $10^{-3}$  M. The inhibition of iron corrosion in 1 M HCl at 22 °C was found to be in the order TPPB > BATPPC > CPTPPB > PTPPC > MTPPB > TTPPC > ATPPB.

Keywords: polarisation, Tafel region, voltammetry.

(Approx. 8.500 words, 11 tables, 32 figures, 6 reactions/equations and 54 references).

# **1. Introduction**

Corrosion of metals is a serious problem in many industries, including civil services such as water and sewage supplies. Inhibitors are frequently used in order to prevent or minimize the corrosion. Corrosion increases running costs and reduces plant efficiency, availability, and product quality.

Most inhibitors are organic compounds containing polar groups by which the molecule can strongly or specifically adsorbed on the metal surface constitute [1]. Such inhibitors, which include the organic N, P, S, and OH groups, are known to be similar to catalytic poisons, since they decrease the reaction rate at the metal/solution interface without, in general, being involved in the reaction. It is generally accepted that most organic inhibitors act via adsorption at the metal/solution interface [1]. The mechanism by which an inhibitor decreases the corrosion current is achieved by interfering with some of the steps for the electrochemical process.

The inhibition of iron corrosion in aqueous acidic solutions has been widely investigated. In many industries, hydrochloric acid solutions are used to remove scale and salts from steel surfaces, cleaning tanks and pipelines. This treatment may be prerequisite for coating by electroplating, galvanizing or painting techniques. The acid is treated with a soluble inhibitor to prevent extensive dissolution of the underlying metal. Organic inhibitors are normally adsorbed at the metal/solution interface by displacing water molecules and forming a compact barrier film.

Quaternary phosphonium compounds are known to control the bacterial growth in several systems [2]; they are environmentally friendly [3] and can offer relatively low toxicity [4].

Many authors have synthesized and used various phosphorus-containing compounds in their corrosion inhibition investigations. These compounds have included imidazoline double quaternary phosphonium salt [5-12], P,P'-bis (triphenylphosphonio) methyl benzophenone dibromide [13], 4-vinylbenzyl triphenyl phosphonium chloride [14] aromatic phosphonium salts [15], (4-ethoxybenzyl)-triphenylphosphonium bromide [16], tetra butyl phosphonium hydroxide and iodide [17], tetraphenyl phosphonium iodide [18], benzyl triphenyl phosphonium chloride and halide ions [19], butyl triphenyl phosphonium bromide [20], (1,3-dioxolan-2-ylmethyl)-triphenyl phosphonium bromide [21], allyl triphenyl phosphonium bromide [22], phosphonium chloride derivatives [23], tetra-benzyl phosphonium chloride [24], phosphating , salts [25], d-amino acid-derived ionic liquid [26], 1-(4-nitrophenyl)-5-amino-1H-tetrazole [27], and others have used plant extracts as corrosion inhibitors in their investigation [28-32].

In such studies, the phosphorus atom(s) in the compounds were shown to be able to strongly adsorb on the metal surface and form a protective layer which, in turn, increased the corrosion inhibition at higher inhibitor concentration.

In this work, The synthesis, including the preparation of the tris(triphenylphosphine)nickel  $(Ni[P(C_6H_5)_3]_3)$  catalyst and subsequent preparation of the quaternary aryl phosphonium salts, is considered. In most cases, tetraphenylphosphonium chloride was used as a reference for comparison purposes as its structure can be considered the parent of a family of phosphonium salts. Electrochemical techniques are used to determine inhibitor properties of the synthesized phosphonium salts and two commercially available phosphonium salts.

#### 2. Experimental details

# 2.1 Synthesis of quaternary aryl phosphonium salts

The synthesis of quaternary aryl phosphonium compounds involved the use of a nickel (0) complex of triphenylphosphine, tris(triphenylphosphine) nickel, as shown in Figure 1.

As shown in reaction (1) [33], the nickel catalyst (2) undergoes oxidative addition in the presence of aryl halide (1) to form the arylnickel complex (3). Oxidative addition has also been reported for the synthesis of other arylnickel (0, II) complexes [34, 35].

$$R \longrightarrow X + Ni[P(C_6H_5)_3]_3 \longrightarrow R \longrightarrow Ni-X + P(C_6H_5)_3$$

$$(1) \qquad (2) \qquad (3) \qquad (1)$$

The arylnickel complex (3) formed in reaction (1) reacts with triphenylphosphine to give the phosphonium salt (4) and regenerate the nickel catalyst (2) via reaction (2).

$$R \xrightarrow{P(C_{6}H_{5})_{3}}{P(C_{6}H_{5})_{3}} + 2P(C_{6}H_{5})_{3} \xrightarrow{P} \xrightarrow{P} \xrightarrow{P} RX + Ni[P(C_{6}H_{5})_{3}]_{3}$$
(3)
(4)
(2)

The overall reaction can be summarized as:

$$R \longrightarrow X + P(C_6H_5)_3 \longrightarrow Ni[P(C_6H_5)_3]_3 \longrightarrow P \longrightarrow RX$$
(3)

The preparation of tris(triphenylphosphine) nickel has been described in the literature [36] (yield 70%). It was reported to be extremely oxygen sensitive and tends to trap solvent when precipitated from solution. It was also reported that the compound decomposes in solution over several hours; even under rigorous oxygen-free conditions and on standing the deep-red solution darkens and a black precipitate was formed. From the information above, it was decided that isolation of the compound would be impractical and thus preparation of tris(triphenylphosphine)nickel and its subsequent reaction with aryl halides was carried out insitu, under nitrogen inert gas blanket.

# 2.2 Preparation of tris(triphenylphosphine)nickel catalysts

Anhydrous nickel chloride (0.0071 mol, 0.99 g) and triphenylphosphine (0.0304 mol, 8.0 g) were placed into a 1000 mL quickfit conical flask and refluxed in acetonitrile (240 mL) for one hour. The reaction mixture was allowed to cool to room temperature then zinc (0.0117 mol, 0.76 g) was added. The mixture was stirred under nitrogen overnight. A red-brown solid formed and was subsequently used *in-situ* for the preparation of the phosphonium salt.

# 2.3 Preparation of quaternary aryl phosphonium salts [37]

Ethanol (200 mL), triphenylphosphine (0.05 mol, 13.06 g) and p-aryl halides (0.05 mol) were introduced to Ni[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> (0.005 mol, 4.23 g) whilst the apparatus was purged with nitrogen gas. The boiling mixture was stirred for 24 hours. The solution was filtered and the filtrate volume was reduced using a rotary evaporator (under reduced pressure). The remaining solids were then dissolved in water and the solution was filtered to remove any residues. The resulting solution was treated with diethyl ether to remove any non-ionic organics (mainly unreacted triphenylphosphine). The aqueous solution was evaporated to dryness. The crude phosphonium

salts were recrystallized from water (with the exception of 4-anilinetriphenylphosphonium, which was recrystallized from methanol and dried in a vacuum oven at 70 °C overnight). Some of the synthesized inhibitors had restricted solubility in HCl. Table 1 lists the prepared and the commercially available phosphonium salts which were evaluated by electrochemical techniques.

FAB-MS (fast atom bombardment-mass spectroscopy) were obtained on a Joel JMS-DX303 GC/Mass Spectrometer. Using fragmentation patterns, the structure of the organic molecule could be elucidated (Figures 2-6). IR (infra-red) spectra of the synthesized compounds, using a Mattson Instrument Research Series 1 FTIR spectrometer are shown in Figures (7-11). <sup>1</sup>H NMR spectra were obtained on a Joel GSX 270 MHz Fourier transform NMR spectrometer. Proton NMR can reveal information about the protons and the environment they are in, by measurement of the chemical shifts ( $\delta$ ) and coupling constants (*J*) of each synthesized compound (Figures 12-16). Melting points were obtained for each compound and the yields are shown in Table 2.

# 2.4 Working electrode preparation

Iron metal (purity 99.5%) used was obtained, in sheet form, from Goodfellow. The 4 mm diameter working electrode material was punched from sheet material. The working electrode surface was prepared initially with silicon carbide paper, grades 200 to 1200 and followed by polishing with progressively finer grades of alumina slurry (grades 5  $\mu$ m down to 1  $\mu$ m) with absolute alcohol to achieve a reproducible surface finish and rinsed with absolute alcohol before use.

# 2.5 Electrolyte preparation

A 1M HCl stock solution was made up in 2 L volumes from concentrated HCl (Fisons). Inhibited solutions were prepared by dissolution of the phosphonium salts (Table 1) to produce 500 mL of  $1 \times 10^{-3}$  M solutions. Subsequent dilution by a factor of 10 allowed a range of solutions from  $1 \times 10^{-7}$  to  $1 \times 10^{-3}$  M to be prepared. All studies was carried out at a temperature of 22 °C using solutions which had been deoxygenated with a fast stream of nitrogen gas for 25 minutes prior to experiments.

# 2.6 Equipment

Tafel extrapolation data for the inhibition of iron in deaerated 1 M HCl at 22  $^{\circ}$ C are considered for the five synthesised and two commercially available phosphonium salts solutions at concentrations ranging from 1×10<sup>--7</sup> to 1×10<sup>-3</sup> M.

All electrochemical measurements were performed using an EG & G potentiostat / galvanostat, model 273A, interfaced (via the computer's RS232 port) by a National Instruments GPIB-PCII interface board, running NI-488.2 software, to a Viglen PC, model Genie Executive 3SX25 (386SX with a clock speed of 25 MHz and a maths co-processor).

A three electrode cell was used, with a working electrode consisting of an iron disc of circular configuration of 4 mm diameter (geometric surface area 0.1257 cm<sup>2</sup>); a saturated calomel reference electrode (SCE); and a platinum foil counter electrode with a surface area of 3.4 cm<sup>2</sup>. Tafel extrapolation measurements were performed over a polarisation range of  $\pm 200$  mV each side of the corrosion potential,  $E_{cor}$  at a linear potential sweep rate of 0.050 mV s<sup>-1</sup> and an initial delay of 7 minutes preceeded the experiments. Experiments were usually performed in triplicate to ensure reproducibility of the results.

#### 3. Results and discussion

#### 3.1 Tafel extrapolation data for iron in HCl

Tafel extrapolation data for the inhibition of iron in deaerated 1 M HCl at 22 °C were considered for the five synthesized and two commercially available phosphonium salts solutions at concentrations ranging from  $1 \times 10^{-7}$  to  $1 \times 10^{-3}$  M.

Each of the compounds tested by electrochemical techniques will be displayed as a table showing the mean values for corrosion current density  $(j_{cor})$ , inhibitor efficiency (%  $\tau$ ) and corrosion potential ( $E_{cor}$ ) versus the saturated calomel reference electrode (SCE) together with anodic and cathodic Tafel slopes for each of the inhibitor concentrations tested. The percentage inhibition efficiency (%  $\tau$ ) was calculated according to the following equation:

$$\%\tau = \frac{(J_{cor})_{uninh.} - (J_{cor})_{inh.}}{(J_{cor})_{uninh.}} \times 100$$

(4)

where  $\% \tau$  = percentage inhibitor efficiency,  $(J_{cor})_{uninh.}$  = corrosion current density in uninhibited solution, and  $(J_{corr})_{inh.}$  = corrosion current density in inhibited solution.

The effects of each compound are shown in a figure representing a typical Tafel experiment that most closely depicts the mean of the triplicate experimental results. Each figure has an insert showing the values of corrosion current density and inhibitor efficiency for each inhibitor concentration tested.

# 3.2 4-Anilinetriphenylphosphonium bromide (ATPPB)

High inhibition is achieved at the highest inhibitor concentration of  $1 \times 10^{-3}$  M with inhibition at 91.7% (Figure 17), with more extensive data in Table 3. Inhibition dropped rapidly as inhibitor concentration lowered while below  $1 \times 10^{-5}$  M, the corrosion rate is increased compared to the uninhibited iron. The value of corrosion potential moves in a more positive direction as the concentration of inhibitor increases. This is indicative of predominant anodic control. This behaviour at high inhibitor concentrations was explained by Hoar and Holliday [37] and by West [38] for a predominately blocking mode of inhibition. At high surface coverages (near monolayer) any gaps due to irregular packing, will be small and because of the relative size of the hydrated hydrogen and metal ions, anodic inhibition will always predominate. The cathodic Tafel slopes remain near the value of those obtained for uninhibited conditions until the concentration drops below  $1 \times 10^{-5}$  M when an increase is noted. For the anodic Tafel slopes, the values remain near 100 mV per decade with the exception of the highest concentration which is somewhat higher at 136 mV per decade, possibly due to stacking of the adsorbed inhibitor at the metal surface.

The first step in inhibition would be expected to be protonation of the aniline group to form an anilinium ion which can be electrostatically adsorbed at the metal surface. This was considered by Banerjee and Malhotra [39] who studied the corrosion of mild steel in HCl at 30 °C inhibited by aniline. This may help elucidate the reasons for corrosion acceleration at inhibitor concentrations of  $1 \times 10^{-5}$  M and below; the increase in cathodic Tafel slopes could indicate cathodic depolarisation as the protonated anilinium ion may catalyse the cathodic reaction. This is similar to the mechanism suggested by Davolio and Soragni [40] who reported corrosion acceleration of carbon steel in 1 M sulphuric acid at 30 °C in the presence of

phenylmethylsulphoxide. A catalytic effect has been observed for other nitrogen-based inhibitors on the hydrogen evolution reaction for zinc and zinc alloy corrosion in HCl. Similar behaviour has been observed for protonated quinolines [41] and amines [42]. Foroulis [43] observed stimulation of copper corrosion for aniline and *n*-butylamine in 4.2 M sulphuric acid and aniline and pyridine in 2.6 M perchloric acid at 50 °C.

# 3.3 4-Benzyl alcoholtriphenylphosphonium chloride (BATPPC)

At the highest concentrations of  $1 \times 10^{-3}$  and  $1 \times 10^{-4}$  M (Figure 18), this compound exhibits high inhibition with values of 94.7% and 89.5% respectively as shown in Table 4 which summarises the results for this inhibitor. However, inhibition drops rapidly as the inhibitor concentration decreases. Between the concentrations of  $1 \times 10^{-6}$  and  $1 \times 10^{-5}$  M an inflection is observed. The most likely explanation for this effect is a change in the mode or configuration (or both) of adsorption. This has been observed previously by Hackerman et al. [44] who studied homopiperazine adsorption on iron in 6 M HCl at 25 °C. A change in configuration might present itself as the adsorption of a single phenyl ring at high inhibitor concentrations where packing is compacted but, at low inhibitor concentrations, the possibility of a second phenyl ring adsorbing is maybe due to the low covering of inhibitor molecules at the metal surface. This could be initiated through the aliphatic alcohol group via the lone-pair on the oxygen atom or protonation of the alcohol group. The corrosion potential is polarised in the more positive direction compared to uninhibited values. Inhibition is anodic at high inhibitor concentrations indicating a predominately blocking mode of inhibition. The anodic Tafel slopes for iron dissolution as ferrous ions remained close to those obtained for uninhibited conditions until the concentration drops below 1×10<sup>-5</sup> M when deviations are noted. The values of cathodic Tafel slopes for hydrogen evolution remained near -145 mV per decade with the exception of the  $1 \times 10^{-6}$  M solution which gave somewhat higher values of -172 mV per decade.

#### **3.4 4-Chlorophenyltriphenylphosphonium bromide (CPTPPB)**

The results of Tafel analysis are shown in Table 5 and Figure 19 for this inhibitor. At the highest concentrations of  $1 \times 10^{-3}$  and  $1 \times 10^{-4}$  M, this compound exhibited a high inhibition with values of 95.6% and 92.7%, respectively being achieved. However, the degree of inhibition dropped rapidly as the inhibitor concentration decreased. A promotion of corrosion was experienced at 1  $\times 10^{-5}$  M (%  $\tau = -149.4$ %) and  $1 \times 10^{-7}$  M (%  $\tau = -157.8$ %), as previously encountered at low inhibitor concentrations [45-47]. The corrosion potential remained almost constant over the entire range of inhibitor concentration near uninhibited acid values indicating mixed inhibitor. The absence of anodic inhibition at high inhibitor concentrations would suggest that blocking is not the important inhibition mode. The cathodic Tafel slopes exhibited a decrease with inhibitor concentration. However, the anodic Tafel slopes showed the opposite effect, suggesting that the anodic reaction became more difficult. Such complex behaviour is often experienced due to the diversity of adsorption modes, which can involve electrostatic interaction of charged inhibitor, delectrons in the outer metal surface shell, molecular polarizability, inductive and steric effects.

# **3.5** Methyltriphenylphosphonium bromide (MTPPB)

The plot of inhibitor efficiency against inhibitor concentration (Figure 20 and Table 6) showed two steps at  $1 \times 10^{-3}$  to  $1 \times 10^{-4}$  M and at  $1 \times 10^{-5}$  to  $1 \times 10^{-6}$  M. Acceleration of corrosion was achieved at inhibitor concentration of  $1 \times 10^{-7}$  M (signified by a negative inhibitor efficiency, %  $\tau$ 

= -33.7%). The corrosion potential is polarised 20 mV more positive compared to uninhibited values for the highest concentration and shifts to approximately 15 mV basic compared to uninhibited values at concentrations  $< 1 \times 10^{-4}$  M. The anodic Tafel slopes remained near the value of that obtained for uninhibited conditions with the exception of the  $1 \times 10^{-3}$  M concentration which is 50 mV per decade higher. The cathodic Tafel slopes values appear to oscillate around the value obtained for that in uninhibited conditions. The only close literature comparison appears to be due to Allen *et al* [48], who reported an inhibitor efficiency of 98.9% at an inhibitor concentration of  $1 \times 10^{-3}$  M for carbon-steel in 5.7 M HCl at 80 °C using weight loss and solution analysis techniques.

# 3.6 4-Phenoltriphenylphosphonium chloride (PTPPC)

Good inhibition was observed at the two highest concentrations with inhibitor efficiencies of 95.0% and 89.1% as illustrated in Table 7 and Figure 21. Below these concentrations, however, inhibitor efficiency dropped close to zero. The two highest concentrations exhibited corrosion potentials near those obtained for uninhibited solutions to within 1 mV. Concentrations that have inhibitor efficiencies approximately zero are polarised at less than 10 mV more positive compared to the uninhibited value. The anodic and cathodic slopes for all concentrations, except  $1 \times 10^{-3}$  M, showed large deviations compared to uninhibited values, the shift indicating strong adsorption of inhibitor molecules at the metal surface.

Figure 22 shows the possible resonance structures of 4-phenoltriphenylphosphonium chloride and indicates the initiation of electrostatic adsorption or the protonated phenol group, stabilized by similar resonance structures to the above examples that can offer an alternative initiation step. The resonance structures shown in Figure 22 could indicate the loss of inhibition at

concentrations of  $1 \times 10^{-5}$  M and below. Cathodic splitting, as explained by Horner *et al.* [49] in reaction (5), could produce a phosphine containing the phenol ring, Ph<sub>2</sub>Ph(OH)P, by attack of the phosphorus-carbon bond. The subsequent phosphine might accelerate corrosion, nullifying the effect of the phosphonium parent, probably through interaction with the corrosion intermediate. The Tafel slopes have increased significantly above the values for inhibited concentrations. An alternative reason for acceleration of corrosion might arise via an analogy to the 4-aniline system. The phenol group can protonate similar to the aniline group, although much less readily. The resulting protonated phenol ion may then catalyse the cathodic reaction through cathodic depolarisation.

$$\left[ R_{3}PR' \right]^{+} \xrightarrow{e^{-}} \left[ R_{3}PR' \right]^{\bullet} \longrightarrow R_{3}P + R' \xrightarrow{e^{-}, H^{+}} R_{3}P + R' H$$
 (5)

#### **3.7** Tetraphenylphosphonium bromide (TPPB)

Inhibition is achieved over the entire concentration range as shown in Table 8 and Figure 23. The corrosion potential shows little variation throughout the concentration range but all values are approximately 15-20 mV more positive than that in uninhibited solution. The cathodic slopes show only minor variations but remain slightly smaller when compared to the uninhibited solution. However, the anodic slope is 20 mV lower than uninhibited solutions at the lower concentrations and rise rapidly to 201 mV per decade at the highest concentration. The only literature comparison is attributable to Pagetti *et al.* [50] and Troquet and Pagetti [51] who reported an inhibitor efficiency of 75% at an inhibitor concentration of  $1 \times 10^{-3}$  M for Armco iron in 1 M HCl at 20 °C using Tafel analysis. The only secondary inhibitor for TPPB is triphenylphosphine [51-53] due to cathodic splitting.

#### **3.8 4-Tolyltriphenylphosphonium chloride (TTPPC)**

From Table 9 and Figure 24, this compound exhibits a high degree of inhibition with a value of 96.4% being achieved at maximum concentration. However, the degree of inhibition drops rapidly as the inhibitor concentration decreases, until acceleration occurs at  $1\times10^{-6}$  M (% $\tau$  = -193.6%) and  $1\times10^{-7}$  M (% $\tau$  = -150.2%). The two concentrations that exhibited high inhibitions have corrosion potentials near uninhibited ones but the lower concentrations have slightly more positive values. The cathodic Tafel slopes for the three lower concentrations are similar to uninhibited one and show a decrease at higher concentrations. The anodic Tafel slopes remain similar to those for uninhibited conditions, with the exception of the highest concentration which is 84 mV per decade higher. Adsorption of the para-substituted ring is likely to be enhanced due to the hyperconjugation effect (Figure 25) previously proposed by Ayers and Hackerman [54] who studied the effect of methyl substitution on the pyridine ring using 2-, 3-, and 4-picoline inhibition of iron in 6.08 M HCl at 35 °C.

A comparison was made among the seven inhibitors and the results are summarised in Table 10. TPPB gives the best overall inhibition throughout the concentration range tested, as shown in Figure 26 and Table 10, although TTPPC gives the highest individual inhibition of 96.4% at the  $1\times10^{-3}$  M level. BATPPC was the only other inhibitor to function over the entire concentration range studied. The other five inhibitors accelerated the corrosion rate of iron in 1 M HCl at low concentration levels. These five did give some degree of corrosion protection at the two highest concentration levels (%  $\tau$  = 75 - 97%).

ATPPB produces a linear relationship between corrosion inhibition (Figure 26) and current density (Figure 27) vs. inhibitor concentration despite this compound accelerating corrosion at low inhibitor levels. TPPB also shows a similar relationship but in this case inhibition is observed over the entire concentration range. MTPPB exhibits the lowest inhibition at the highest concentrations but shows a lower rate of decrease in inhibition compared to the synthesized phosphonium salts. This would seem to indicate that the 4-substituted phenyl compounds exhibit greater structural effects than replacement of a benzene ring. The two features noted above, namely very good inhibition at high inhibitor concentration and a rapid loss of inhibition, in some cases leading to corrosion acceleration are most prominent for the para-substituted compounds. This infers that surface coverage and molecular packing are important in the nature of these inhibitors at the iron surface. For BATPPC, the percentage inhibition increased, fell and rose once more to give 94% inhibition at 1×10-3 M. This may be due to this compound undergoing a change in molecular configuration as inhibitor concentration varies. At high inhibitor concentrations, where packing is compacted, singularly chemisorbed phenyl ring is the predominant configuration. At low inhibitor concentrations, the possibility of a second phenyl ring adsorbing might due to the low covering of inhibitor molecules at the metal surface. Acceleration might be achieved via a catalytic pathway involving the para-substituted ring or a decomposition product that is repelled by the layer of phosphonium ions at high inhibitor concentrations. ATPPB is the poorest inhibitor of the compounds tested and acceleration of corrosion is achieved at inhibitor concentrations of  $1 \times 10^{-5}$  M and below. The order of inhibition is TPPB > BATPPC > CPTPPB > PTPPC > MTPPB > TTPPC > ATPPB for iron in 1M HCl at 22 °C, by Tafel extrapolation.

Figure 28 shows a Hoar-Holliday plot [37] of corrosion potential against the logarithm of corrosion current density. At corrosion current densities  $< 150 \mu A \text{ cm}^{-2}$ , the inhibitors can be divided into two groups. The first consists of CPTPPB, TTPPC and PTPPC where  $E_{cor.}$  is within 5 mV of the uninhibited value. The second group comprises ATPPB, BATPPC, TPPB and MTPPB which are polarised approximately 20 mV more positive. ATPPB appears to shows a nearly linear relationship between corrosion potential and corrosion current density. The shape and features of the curve show a similarity for this compound with those shown in Figures 24 and 26. For ATPPB, the mode of inhibition and acceleration are due to changes in the electrical double layer. From the inclusion of an aniline group to the phosphonium salt another positive centre is created due to protonation from electrolyte; counter ions must be present to neutralise this charge. At high concentrations, the adsorption of the positive phosphonium ions causes the charge of the double layer to decreases, which will decrease corrosion. At lower concentrations, the majority of the phosphonium ion species is more widely distributed about the metal surface during adsorption. Adsorption of the bromide, counter ion, is more likely as these are smaller and can exert greater influence over surface charge, thus corrosion increases. The linear relationship between potential and corrosion current density indicates that adsorption is mainly through electrostatic adsorption. Chemisorption of a phenyl ring in the phosphonium ion is not indicated to a significant degree. BATPPC shows linearity in Figure 28, despite the reversal in the direction of change in corrosion current density as the inhibitor concentration is change between 1×10<sup>-6</sup> and 1×10<sup>-5</sup> M. MTPPB is only the compound that demonstrates significant cathodic characteristics as the corrosion potential is more basic than in the uninhibited solution.

As general rule, the cathodic Tafel slopes for all the phosphonium salts tested are shown in Figure 29. The dotted line indicates the Tafel slope of uninhibited acid. At high concentrations

the majority of the data points are lower than the dotted line, then move to within 10 mV of the dotted line. A similar trend is shown for the anodic Tafel slopes in Figure 30, with the exception that the data points at the highest concentration are all larger than the dotted line. There are two exceptions in both cases, PTTPC shows values that are significantly higher than any other at the lower concentrations; TPPB shows the opposite effect.

# 3.9 Adsorption isotherms

Table 11 shows the adsorption isotherm data for the Inhibition of iron in 1M HCl at 22 °C by varous phosphonium salts, determined by Tafel extrapolation.

The Langmuir adsorption isotherm can be described by the following equation:

$$\log \frac{\theta}{1-\theta} = \log a + \log c - \frac{q}{2.303RT} \tag{6}$$

where c = inhibitor concentration and  $\theta =$  surface coverage; q and a are constants characteristic of each system.

To show a relationship for the tested Langmuir adsorption isotherm the correlation coefficient of apparent linear fit (determined by Least squares analysis), r, was calculated for each curve and is displayed adjacent to the appropriate legend. A value of r = 1.00 represents an ideal straight line; values close to 1.00 show the degree of linearity. For general purposes,  $\geq 0.99$  indicates a very good correlation and values of  $\geq 0.98$  can be considered to show fair agreement.

An invariable test for Langmuir isotherm adsorption is a rectilinear plot of log  $\theta/1-\theta$  against log c, as illustrated by Figure 31. The correlation is poor; TPPB shows the highest correlation

coefficient, of 0.977. Inhibitor adsorption is complex and rarely shows a close fit to simple adsorption isotherm models.

For electrochemical impedance spectroscopy (EIS) studies, a PC controlled Autolab PGSTAT128N Modular Potentiostat (electrochemical workstation) (supplied by Metrohm) capable of driving currents up to  $\pm$  800 mA with an output potential across the cell of up to  $\pm$  10 V was used. EIS scans were performed at a sinusoidal excitation AC voltage of +10 mV (rms) and the response was determined in the frequency range of 100 kHz–10 mHz with 50 points per decade. A Nyquist plot for iron in 1.0 M HCl in the presence of various concentrations of methyltriphenylphosphonium bromide (MTPPB) at 22 °C is presented in Figure 32.

#### 4. Comments on the techniques used and the mechanism of corrosion inhibition

While a wide range of techniques can be deployed to study the inhibition of corrosion, several comments may be made:

a) Imaging techniques, such as optical microscopy, scanning electron microscopy and atomic force microscopy are useful in examining surface morphology but. In the present case, merely conform that uniform corrosion takes place over the metal surface, inhibitors giving rise to less pronounced etching at a given time. No quantitative information is provided on the rate of corrosion.

b) Surface spectroscopy techniques, including infra-red and Raman spectroscopy can provide useful information on surface adsorbed species, leading to mechanistic clues but only qualitative data tends to be produced.

c) Established, classical techniques provide trusted data yet no mechanistic or rate information.

Weight loss requires multiple replicate samples and becomes insensitive at high levels of corrosion inhibition, hence low degrees of weight loss. Solution analysis can provide a useful means of analysing a wide range of general corrosion rate but gives no information on the electrochemistry or mechanism.

d) Electrochemical techniques are well developed and can provide information on quantitative corrosion rates via the corrosion current density, provided adequate precautions are made in cell design/operation and data analysis. Steady state direct current (dc) polarisation methods are particulary well accepted. Adequate attention must be paid to minimising uncompensated ohmic drop, using well-defined flow conditions and known dissolved oxygen levels, as in the present experiments. Such methods can be used to examine cathodic and anodic (metal dissolution) kinetics and, via Tafel extrapolation, corrosion current. However, Tafel kinetics take place over a limited range of potential, due to the effects of mass transfer control and ohmic drop. Small perturbation techniques, such as linear polarisation resistance, can be convenient and fast but can be subject to application of unchecked software analysis and sometimes lack a preliminary characterisation of the electrode reactions using wider potential range polarisation via voltammetric sweep). In the present studies, we have used both linear dc polarisation and Tefel extrapolation to obtain quantitative data. Small perturbation alternating current (ac) techniques, such as electrochemical impedance spectroscopy have become increasing available, can maintain the electrode potential near its open-circuit value and can be powerful tools for organic, e.g., paint films but are subject to less confidence than dc and classical techniques, due to complex data analysis and the need for software to rationalise behaviour via equivalent circuit models.

The mechanism of corrosion inhibition is complex due to the number of (electronic, structural and steric) chemical interactions between the primary and secondary inhibitor and the surface,

participation of anodic and cathodic reactions and the complex adsorption of organic inhibitor species, which can involve different coverage (rather than a single monolayer, stacking can take place), several molecular layers (rather than one) and all the above being concentration- and time-dependent. Hence, application of a simple adsorption isotherm, such as a Langmuir one, over a wide concentration range is expected to present challenges.

In the case of phosphonium inhibition of transition metals in aqueous acidic electrolytes, we aim to elaborate on the factors considered in this section in a forthcoming review.

#### **5.** Conclusions

The order of inhibition for iron in 1 M HCl at 22 °C is TPPB > BATPPC > CPTPPB > PTPPC > MTPPB > TTPPC > ATPPB. Another noticeable trend is that Tafel extrapolation measurements show that the two highest concentrations impart high inhibition (%  $\tau$  = 75 - 97%), which is followed by a rapid fall at 1×10<sup>-5</sup> M, indicating a different inhibition mechanism or mode of action between high and low inhibitor concentration. CPTPPB, TTPPC and PTPPC showed mixed inhibition, while ATPPB, BATPPC, TPPB and MTPPB primarily exhibited anodic inhibition. ATPPB showed corrosion acceleration at concentrations below 1×10<sup>-5</sup> M, whereas corrosion acceleration occurred at concentrations lower than 1×10<sup>-6</sup> M for both CPTPPB and TTPPC. Langmuir isotherm adsorption studies showed that TPPB exhibits the highest correlation coefficient (0.977) to a simple adsorption isotherm, compared to the other inhibitors.

# List of symbols

Symbol	Meaning		Units
$b_a$	Anodic Tafel slope		mV per decade
$b_c$	Cathodic Tafel slope		mV per decade
С	Molar concentration		$M = mol L^{-1}$
$E_{cor}$	Corrosion potential		v
j	Current density		A cm <sup>-2</sup>
$j_{cor}$	Corrosion current density	Č	A $cm^{-2}$
Ζ	Real component of impedance		ohm
Z'	Imaginary component of impedance	S	ohm

# Greek

$\% \tau$	Percentage Inhibitor efficiency	Dimensionless
θ	Surface coverage	Dimensionless

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# **Figure captions**

- Figure 1. Structure of tris(triphenylphosphine)nickel, Ni[P( $C_6H_5$ )<sub>3</sub>].
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- Figure 4. FAB-MS of 4-chlorophenyltriphenylphosphonium bromide (CPTPPB).
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Table 1. Synthesized and commercially available phosphonium salts evaluated by electrochemical techniques in this paper.

P-	Melting point / °C	Yield		Molar mass / g mol <sup>-1</sup>	
R	Х		/ g	/ %	
CH <sub>3</sub>	Cl	277-8	10.23	52.61	388.88
OH	Cl	296-9	3.47	17.76	390.85
CH <sub>2</sub> OH	Cl	235-6	12.33	60.91	404.88
Cl	Br	265-7	11.74	51.75	453.75
NH <sub>2</sub>	Br	338-40	14.49	66.72	434.32

Table 2. Melting point and yield data for synthesised phosphonium salts.

с / М	$j_{cor}$ / $\mu A \text{ cm}^{-2}$	%τ	E <sub>cor</sub> vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>
$1 \times 10^{-3}$	45	91.7	-0.496	136	<mark>-</mark> 143
$1 \times 10^{-4}$	245	54.7	-0.515	101	<mark>-</mark> 139
$1 \times 10^{-5}$	681	-25.9	-0.519	100	<mark>-</mark> 145
$1 \times 10^{-6}$	1004	-85.7	-0.528	99	<mark>-</mark> 155
$1 \times 10^{-7}$	1558	-188.1	-0.534	101	<mark>-</mark> 177
0	541	-	-0.526	86	<mark>-</mark> 149

Table 3. Tafel extrapolation data for 4-anilinetriphenylphosphonium bromide (ATPPB) for the inhibition of iron in 1 M HCl at 22  $^{\circ}$ C.

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с / <mark>М</mark>	$j_{cor}$ / $\mu A \text{ cm}^{-2}$	% au	E <sub>cor</sub> vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>		
$1 \times 10^{-3}$	28	94.7	-0.497	108	<mark>-</mark> 154		
$1 \times 10^{-4}$	57	89.5	-0.508	98	<mark>-</mark> 151		
$1 \times 10^{-5}$	446	17.6	-0.525	95	<mark>-</mark> 139		
$1 \times 10^{-6}$	319	40.9	-0.523	114	<mark>-</mark> 172		
$1 \times 10^{-7}$	512	3.9	-0.526	70	<mark>-</mark> 142		
0	541	-	-0.526	86	<mark>-</mark> 149		

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Table 4.Tafel extrapolation data for 4-benzylalcoholtriphenylphosphonium chloride<br/>(BATPPC) for the inhibition of iron in 1 M HCl at 22  $^{\circ}$ C.

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с / <mark>М</mark>	$j_{cor}$ / $\mu A \text{ cm}^{-2}$	%   au	E <sub>cor</sub> vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>
$1 \times 10^{-3}$	24	95.6	-0.526	126	<mark>-</mark> 113
$1 \times 10^{-4}$	39	92.7	-0.524	108	<mark>-</mark> 118
$1 \times 10^{-5}$	455	15.8	-0.516	72	<mark>-</mark> 130
$1 \times 10^{-6}$	1349	-149.4	-0.530	112	<mark>-</mark> 151
$1 \times 10^{-7}$	1394	-157.8	-0.531	78	<mark>-</mark> 145
0	541	-	-0.526	86	<mark>-</mark> 149

Table 5.Tafel extrapolation data for 4-chlorophenyltriphenylphosphonium bromide<br/>(CPTPPB) for the inhibition of iron in 1 M HCl at 22 °C.

с / <mark>М</mark>	$j_{cor}$ / $\mu A \text{ cm}^{-2}$	% au	E <sub>cor</sub> vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>
$1 \times 10^{-3}$	111	79.4	-0.503	139	<mark>-</mark> 173
$1 \times 10^{-4}$	130	76.0	-0.542	80	<mark>-</mark> 144
$1 \times 10^{-5}$	449	17.0	-0.542	82	<mark>-</mark> 163
$1 \times 10^{-6}$	518	4.3	-0.540	90	<mark>-</mark> 143
$1 \times 10^{-7}$	723	-33.7	-0.542	90	<mark>-</mark> 153
0	541	-	-0.526	86	<mark>-</mark> 149

Table 6.Tafel extrapolation data for methyltriphenylphosphonium bromide (MTPPB)Inhibition of iron in 1 M HCl at 22  $^{\circ}$ C.

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с / <mark>М</mark>	$j_{cor}$ / $\mu A \text{ cm}^{-2}$	% au	E <sub>cor</sub> vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>	
$1 \times 10^{-3}$	27	95.0	-0.525	70	<mark>-</mark> 141	
$1 \times 10^{-4}$	59	89.1	-0.525	117	<mark>-</mark> 124	
$1 \times 10^{-5}$	535	1.0	-0.512	213	<mark>-</mark> 205	
$1 \times 10^{-6}$	544	-0.7	-0.512	172	<mark>-</mark> 203	
$1 \times 10^{-7}$	532	1.6	-0.516	207	<mark>-</mark> 174	
0	541	-	-0.526	86	<mark>-</mark> 149	

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Table 7.Tafel extrapolation data for 4-phenoltriphenylphosphonium chloride (PTPPC) for the<br/>inhibition of iron in 1 M HCl at 22  $^{\circ}$ C.

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с / <mark>М</mark>	$j_{cor}$ / µA cm <sup>-2</sup>	%   au	$E_{cor}$ vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>
$1 \times 10^{-3}$	43	92.0	-0.499	201	<mark>-</mark> 134
$1 \times 10^{-4}$	86	84.1	-0.511	122	<mark>-</mark> 140
$1 \times 10^{-5}$	102	81.2	-0.508	66	<mark>-</mark> 123
$1 \times 10^{-6}$	129	76.1	-0.503	68	<mark>-</mark> 119
$1 \times 10^{-7}$	195	63.8	-0.504	70	<mark>-</mark> 127
0	541	-	-0.526	86	<mark>-</mark> 149

Table 8.Tafel extrapolation data for tetraphenylphosphonium bromide (TPPB) inhibition of<br/>iron in 1 M HCl at 22  $^{\circ}$ C.

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с / <mark>М</mark>	$j_{cor}$ / $\mu A \text{ cm}^{-2}$	% au	E <sub>cor</sub> vs. SCE / V	$b_a$ mV dec <sup>-1</sup>	$b_c$ mV dec <sup>-1</sup>
$1 \times 10^{-3}$	19	96.4	-0.529	170	<mark>-</mark> 125
$1 \times 10^{-4}$	96	82.2	-0.522	93	<mark>-</mark> 130
$1 \times 10^{-5}$	354	34.4	-0.516	89	<mark>-</mark> 150
$1 \times 10^{-6}$	1588	-193.6	-0.504	101	<mark>-</mark> 143
$1 \times 10^{-7}$	1353	-150.2	-0.518	108	<mark>-</mark> 148
0	541	-	-0.526	86	<mark>-</mark> 149

Table 9.Tafel extrapolation data for 4-tolyltriphenylphosphonium chloride (TTPPC)<br/>inhibition of iron in 1 M HCl at 22  $^{\circ}$ C.

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С	Percentage Inhibitor efficiency, $\%\tau$						
/ <mark>M</mark>	ATPPB	BATPPC	CPTPPB	MTPPB	PTPPC	TPPB	TTPPC
$1 \times 10^{-3}$	91.7	94.7	95.6	79.4	95.0	92.0	96.4
1×10 <sup>-4</sup>	54.7	89.5	92.7	76.0	89.1	84.1	82.2
1×10 <sup>-5</sup>	-25.9	17.6	15.8	17.0	1.0	81.2	34.4
1×10 <sup>-6</sup>	-85.7	40.9	-149.4	4.3	-0.7	76.1	-193.6
1×10 <sup>-7</sup>	-188.1	3.9	-157.8	-33.7	1.6	63.8	-150.2

Table 10. Inhibitor efficiency for iron in 1 M HCl at 22 °C in the presence of various phosphonium salts.

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С	Surface coverage, $\theta$						
/ <mark>M</mark>	BATPPC	MTPPB	PTPPC	TPPB			
$1 \times 10^{-3}$	0.947	0.794	0.950	0.920			
$1 \times 10^{-4}$	0.895	0.760	0.891	0.841			
$1 \times 10^{-5}$	0.176	0.170	0.010	0.812			
$1 \times 10^{-6}$	0.409	0.042	-0.007	0.761			
$1 \times 10^{-7}$	0.039	-0.34	0.016	0.638			

Table 11. Adsorption isotherm data for the inhibition of iron in 1 M HCl at 22 °C by various phosphonium salts, determined by Tafel extrapolation.

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Figure 1. Structure of tris(triphenylphosphine)nickel, Ni[P( $C_6H_5$ )<sub>3</sub>].



Figure 10. Infra-red spectra of 4-phenoltriphenylphosphonium chloride (PTPPC) (KCl Disc).



Figure 11. Infra-red spectra of 4-tolyltriphenylphosphonium chloride (TTPPC) (KCl Disc).



Figure 12. <sup>1</sup>H NMR of 4-anilinetriphenylphosphonium bromide (ATPPB), Expansion of 8.0-6.8 ppm range.



Figure 13. <sup>1</sup>H NMR of 4-benzyl alcoholtriphenyl-phosphonium chloride (BATPPC), Expansion of 8.0-7.5 ppm Range.



Figure 14. <sup>1</sup>H NMR of 4-chlorophenyltriphenyl-phosphonium chloride (CPTPPB), Expansion of 8.0-7.4 ppm range.



Figure 15. <sup>1</sup>H NMR of 4-phenoltriphenylphosphonium chloride (PTPPC), Expansion of 8.0-7.3 ppm range.



Figure 16. <sup>1</sup>H NMR of 4-tolyltriphenylphosphonium chloride (TTPPC), Expansion of 7.4-8.0 ppm range.



Figure 17. Tafel polarisation curves for 4-anilinetriphenylphosphonium bromide (ATPPB) inhibition of iron in 1 M HCl at 22 <sup>o</sup>C.



Figure 18. Tafel polarisation curves for 4-benzylalcoholtriphenylphosphonium chloride (BATPPC) inhibition of iron in 1 M HCl at 22 <sup>o</sup>C.



Figure 19. Tafel polarisation curves for 4-chlorophenyltriphenylphosphonium bromide (CPTPPB) inhibition of iron in 1 M HCl at 22 <sup>o</sup>C.



Figure 2. FAB-MS of 4-anilinetriphenylphosphonium bromide (ATPPB).



Figure 20. Tafel polarisation curves for methyltriphenylphosphonium bromide (MTPPB) inhibition of iron in 1 M HCl at 22 <sup>o</sup>C.



Figure 21. Tafel polarisation curves for 4-phenoltriphenylphosphonium chloride (PTPPC) inhibition of iron in 1 M HCl at 22 °C.







Figure 23. Tafel polarisation curves for tetraphenylphosphonium bromide (TPPB) inhibition of iron in 1 M HCl at 22 <sup>o</sup>C.



Figure 24. Tafel curves for 4-tolyltriphenylphosphonium chloride (TTPPC) inhibition of iron in 1 M HCl at 22 <sup>o</sup>C.



Figure 25. Resonance structures of 4-tolyltriphenylphosphonium chloride (TTPPC).



Figure 26. Variation in inhibitor efficiency with inhibitor concentration determined by Tafel extrapolation for iron in 1 M HCl at 22 <sup>o</sup>C inhibited by various phosphonium salts.



Figure 27. Variation in corrosion current density with inhibitor concentration determined by Tafel extrapolation for iron in 1 M HCl at 22 <sup>o</sup>C inhibited by various phosphonium salts.



Figure 28. Variation in corrosion potential with corrosion current determined by Tafel extrapolation for iron in 1 M HCl at 22 °C in the presence of various phosphonium salts.



Figure 29. Variation in anodic Tafel slope with inhibitor concentration determined by Tafel extrapolation for iron in 1 M HCl at 22 °C inhibited by various phosphonium salts (Uninhibited data are shown by dotted lines).



Figure 3. FAB-MS of 4-benzyl alcoholtriphenylphosphonium chloride (BATPPC).

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Figure 30. Variation in cathodic Tafel slope with inhibitor concentration determined by Tafel extrapolation for iron in 1 M HCl at 22 °C inhibited by various phosphonium salts. (Uninhibited data are shown by dotted lines).



Figure 31. Langmuir isotherm plot for iron in 1 M HCl at 22 °C inhibited by various phosphonium salts, determined by Tafel extrapolation (the number indicates the correlation coefficient of apparent linear fit).



Figure 32. Nyquist plot for iron in 1 M HCl in the presence of various concentrations of methyltriphenylphosphonium bromide (MTPPB) at 22 °C.



Figure 4. FAB-MS of 4-chlorophenyltriphenylphosphonium bromide (CPTPPB).



Figure 5. FAB-MS of 4-phenoltriphenylphosphonium chloride (PTPPC).



Figure 6. FAB-MS of 4-tolyltriphenylphosphonium chloride (TTPPC).



Figure 7. Infra-red spectra of 4-anilinetriphenylphosphonium bromide (ATPPB) (KCl Disc).



Figure 8. Infra-red spectra of 4-benzyl alcoholtriphenylphosphonium chloride (BATPPC) (KCl Disc).



Figure 9. Infra-red spectra of 4-chlorophenyltriphenylphosphonium Bromide (CPTPPB) (KCl Disc).
## Highlights

- The synthesis of a series of quaternary aryl phosphonium salts is described.
- Their efficiency as corrosion inhibitors of iron in 1 M HCl is studied.
- Mechanistic aspects of corrosion inhibition are discussed.
- Tafel extrapolation data are considered against a Langmuir adsorption isotherm.