An electrochemical study for corrosion inhibition of iron by some organic phosphonium chloride derivatives in acid media

K.F. Khaled*

Chemistry Department, Faculty of Education, Ain Shams University, Cairo 11711, Egypt

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Abstract

The inhibiting action of (chloromethyl) triphenyl phosphonium chloride (CTP), tetraphenyl phosphonum 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 was studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Experimental results revealed 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 increased with increasing concentrations. Equivalent circuits of the investigated systems are suggested.

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Keywords: Iron; Phosphonium chloride; Acid corrosion inhibition; EIS

1. Introduction

Acid solutions are used for the removal of undesirable scale and rust in many industrial processes. The use of inhibitors is one of the most practical methods to protect against excessive corrosion, especially in acidic media. Progress has been made in this field in recent years, as is evident from the output of published literature [1].

Quaternary onium compounds have been described as inhibitors against the acid corrosion of iron and steel [2–6]. Although many organic onium compounds have been studied, apparently no detailed studies of these phosphonium compounds as inhibitors for iron corrosion are available in the literature. In this study, aerated HCl solutions are used as the corrosive medium. The organic phosphinium compounds used consist of (chloromethyl) triphenyl phosphonium chloride (CTP), tetraphenyl phosphonum chloride (TP), triphenyl phosphine oxide (TPO), triphenyl (phenylmethyl) phosphonium chloride (TPM), and triphenyl phosphine (TPP). The corrosion inhibiting behaviour of these compounds is studied using both potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental details

Samples of iron (Puratronic 99.9999%) from Johnson Mattey Ltd., were mounted in a Teflon sheath (exposed surface area 0.28 cm²). Surfaces were prepared by mechanical polishing with emery
papers with different grits 2/0, 3/0, and 4/0, rinsed with double distilled water, degreased with acetone and dried at room temperature. Experiments were carried out in 1 M HCl (Fisher Scientific), with the inhibitors (TCI Co.), which were used without pretreatment in concentration range $10^{-4}$ to $10^{-3}$ M. The electrochemical cell used has been described elsewhere [7]. Experiments were carried out under static conditions at 25 °C on an EG&G Princeton Applied Research potentiostat/galvanostat (PAR model 273) in combination with a Solarton 1250 frequency response analyzer. These were used for polarization and capacitance measurements along with a computer for collecting data. The potentiodynamic current–potential curves were obtained by changing the electrode potential automatically from (-250 to +250 mV SCE) versus open circuit potential with a scan rate of 1 mV s\(^{-1}\).

EIS measurements were carried out in a frequency range of 100 kHz to 30 mHz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. The software used in this study are corrosion software, model 352–252 version 2.23, EIS software model 398. Spectra analysis was performed using Zview impedance analysis software (Scribner Associates Inc., Southern Pines, NC).

3. Results and discussion

The corrosion of iron in 1 M HCl in the presence and absence of phosphonium compounds was initially studied by potentiodynamic polarization. Typical polarization curves obtained for the corrosion of iron in HCl solutions are shown in Figs. 1–4. It is observed that all phosphonium compounds shift the polarization curves to lower current density values without affecting Tafel slopes, except for TPP. It starts with slight inhibition at $10^{-4}$ M, but it is an accelerator at higher concentrations.

Values of all kinetic parameters such as corrosion potential ($E_{corr}$), cathodic and anodic Tafel slopes ($b_c$, $b_a$) and corrosion current density ($i_{corr}$) attained by extrapolation of Tafel lines, as well as inhibitor efficiency are listed in Table 1.

Inhibition efficiency IE%, is reported from Eq. (1)

$$\text{IE\%} = \left( \frac{\rho_{corr}^o - \rho_{corr}^i}{\rho_{corr}^o} \right) \times 100$$

where $\rho_{corr}^o$ and $\rho_{corr}^i$ represent uninhibited and inhibited corrosion current densities, respectively. These results show that except for TPP, all of the examined phosphoniums inhibit the corrosion of iron and the inhibition efficiency increases with concentration.

Fig. 1. Anodic and cathodic Tafel lines for iron in 1 M HCl without and with $10^{-4}$ M of phosphonium compound derivatives: (a) TPP, (b) blank, (c) CTP, (d) TP, (e) TPO, and (f) TPM.
The decrease in corrosion rate is associated with a shift of both cathodic and anodic branches of the polarization curves towards lower current densities, together with a slight positive shift in $E_{\text{corr}}$. This suggests that these compounds act as mixed-type inhibitors.

The values of $b_c$ were changed with increasing inhibitor concentration, which indicates the influence of those compounds on the kinetics of hydrogen evolution reaction. The cathodic current versus potential gave rise to parallel Tafel lines, representing
Fig. 4. Anodic and cathodic Tafel lines for iron in 1 M HCl without and with $10^{-3}$ M of phosphoinum compound derivatives: (a) TPP, (b) blank, (c) CTP, (d) TP, (e) TPO, and (f) TPM.

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activated-controlled reaction of the hydrogen evolution without modifying the mechanism of the proton discharge reaction. The pronounced increase in the anodic Tafel slope $b_a$ at concentrations $3 \times 10^{-4}$ M may be due to changes in the charge transfer coefficient $\alpha_a$ for the anodic dissolution of iron by virtue of the presence of an additional energy barrier due to the presence of the adsorbed inhibitor. Mathematical
treatment of such a dual energy barrier was reported first by Mayer [8] and applied by Conway and Vigh [9]. The rapid attainment of $E_{\text{corr}}$ in the presence of phosphonium compounds suggests that the initial step of adsorption involves the phosphonium cations [10]. It is assumed that the inhibitive effect of phosphonium cations is due to its adsorption with the ring...
structure parallel to the metal surface with subsequent π-electron interaction [11,12]. On the other hand, quaternary phosphonium compounds were found to undergo reduction on various metallic electrodes [13] according to the following reaction:

\[
R_4P^+ + H^+ + 2e^- \rightarrow R_3P + RH
\]

where R is a benzyl or phenyl group. The reduction of the benzyl group was found to be more feasible than either alkyl or phenyl groups [14]. Horner and Ertel [15] ascribed the inhibitive effect of the phosphonium compounds on iron in HCl solutions to their reduction products, R_3P. Lorenz and Fisher [16] found that the inhibitive action of the phosphonium compounds and their reduction products is approximately the same.

The corrosion behavior of iron in this study was investigated by EIS at 25 °C after immersion for 3 h. Nyquist plots of iron in uninhibited and inhibited solutions containing various concentrations of the compounds are shown in Figs. 5–8.

Most of the EIS spectra obtained consists of either one depressed capacitive loop (one time-constant in Bode-phase representation) or two capacitive semicircles (two well-defined time-constants in Bode-phase format). The diameter of the capacitive loop obtained in 1 M HCl solution increases in the presence of phosphonium compounds (except for TPP) indicating inhibition of the corrosion process as shown in Figs. 5–8. Parameters corresponding to the Nyquist plots of the impedance data are calculated from Figs. 5–8 and are shown in Table 2.

When the complex plane impedance (Nyquist plot) contains a ‘‘depressed’’ semicircle with the center under the real axis, such behavior characteristic for solid electrodes and often referred to as frequency

![Fig. 9. Equivalent circuit models used in fitting the experimental impedance data.](image-url)
dispersion, which have been attributed to roughness and inhomogeneities of the surface [17]. The parallel network polarization resistance-double layer capacity (Rp-C_dl) is usually a poor approximation especially for systems where an efficient inhibitor is present.

For TPP, two semicircles are seen in all concentration range, indicating the formation of an incomplete

Fig. 10. (a) Nyquist plots of iron corrosion in 1 M HCl solution at $E_{corr}$. (b) Bode-phase plots of iron corrosion in 1 M HCl solution at $E_{corr}$.
layer on the iron surface. The incompleteness of this layer might be the reason for triphenyl phosphine to act as an accelerator.

Two ways are used in the literature to describe the EIS spectra for the inhomogeneous films on the metal surface or rough and porous electrodes. One is the finite transmission line model [18] and the other is the filmed equivalent circuit model, which is usually proposed to study the degradation of coated metals [19,20]. It has been suggested that the EIS spectra for the metal covered by organic inhibitor films are very similar to the failed coating metals [21]. Therefore, in this work the filmed equivalent circuit model is used to describe the inhibitors-covered metal/solution interface. The circuit model used for failed coating metal/solution interface is shown in Fig. 9(b).

When there is a non-ideal frequency response, it is common practice to employ distributed circuit elements in an equivalent circuit [22]. The most widely used is the constant phase element (CPE), which has a

Fig. 11. (a) Nyquist plots of iron corrosion in 1 M HCl solution with 3 $\times$ 10$^{-4}$ M of TP at $E_{corr}$, (b) Bode-phase plots of iron corrosion in 1 M HCl solution with 3 $\times$ 10$^{-4}$ M of TP at $E_{corr}$.

Fig. 12. (a) Nyquist plots of iron corrosion in 1 M HCl solution with 3 $\times$ 10$^{-4}$ M of TPO at $E_{corr}$, (b) Bode-phase plots of iron corrosion in 1 M HCl solution with 3 $\times$ 10$^{-4}$ M of TPO at $E_{corr}$. 
non-integer power dependence on the frequency. Its impedance is described by the expression

\[ Z_{CPE} = Y^{-1}(i\omega)^{-n} \]  \hspace{1cm} (2)

where \( Y \) is a proportional factor; \( i \) is \( \sqrt{-1} \); \( \omega \) is \( 2\pi f \); and \( n \) is a phase shift [23].

Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system. For example a rough or porous surface can cause a double-layer capacitance to appear as a CPE with an \( n \) value between 0.9 and 1 [22].

For \( n = 0 \), \( Z_{CPE} \) represents a resistance with \( R = Y^{-1} \), for \( n = 1 \) a capacitance with \( C = Y \), for \( n = 0.5 \) a Warburg element and for \( n = -1 \) an inductance with \( L = Y^{-1} \).

Fig. 9 shows the electrical equivalent circuits employed to analyze the impedance plots. \( R_s \) is the electrolyte resistance (\( \Omega \) cm\(^2\)), \( R_{ct} \) is the charge transfer resistance (\( \Omega \) cm\(^2\)). \( Y \left( \Omega^{-1} \text{cm}^{-2} \text{S} \right) \) and \( n \) are parameters used in Eq. (2). Excellent fit with this model was obtained with our experimental data (see Figs. 10–12). It is observed that the fitted data match the experimental, with an average error of about 3% all through.

For the analysis of the impedance spectra containing one capacitive loop the equivalent circuit is given in Fig. 9(a) while the equivalent circuit shown in Fig. 9(b) was used for the spectra exhibiting two capacitive time constants.

Representative examples for the impedance spectra carried out at \( E_{corr} \) on iron exposed to 1 M HCl without and with the investigated phosphonium compounds are shown in Figs. 10–12. The measured and simulated results are shown together in Figs. 10–12. Both simulation and measured results are fit very well. Fig. 10(a) shows Nyquist plots recorded after 3 h immersion in HCl solution without and with phosphonium compounds.

Bode-phase plots (representative example) gave only one capacitive time-constant as in Fig. 10(b). The equivalent circuit, Fig. 9(a) satisfactorily simulates the spectra. Two time constants in Bode plot as in Figs. 11–12(b) suggesting film formation on the electrode surface.

The most probable equivalent circuit which gave good simulation for these results is presented at Fig. 9(b). This model was used for coated metal electrodes [24,25]. It was also used by Bojinov et al. [26] for the corrosion protection of painted steel doped with inhibitors in 5% HCl solution. The high frequency part of the impedance and phase angle describes the behavior of inhomogeneous surface layer, while the low frequency contribution shows the kinetic response for the charge transfer reaction [27].

![Fig. 13. Temkin adsorption plots of iron in 1 M HCl in presence of phosphonium compound derivatives.](image-url)
Assuming no change in the mechanism of both the hydrogen evolution reaction and the anodic dissolution of iron (values of both \( b_a \) and \( b_c \) obtained in the uninhibited system are in good agreement with those previously reported [28]). The degree of coverage \( \theta \) can be obtained using the following Eq. (3):

\[
\theta = \frac{i_{\text{corr}} - i_{\text{corr}}}{i_{\text{corr}}} \tag{3}
\]

Adsorption isotherms for the investigated inhibitors using values of \( \theta \) were found to conform to the Temkin isotherm (Fig. 13), given by Eq. (4)

\[
\theta = \frac{1}{f} \ln BC \tag{4}
\]

where \( f \) is the heterogeneity factor; \( C \), the bulk concentration of the inhibitor; and \( B \) is the adsorption equilibrium constant obtained by Eq. (5)

\[
B = \left( \frac{1}{55.5} \right) \exp \left\{ - \left( \frac{\Delta G_a^0}{RT} \right) \right\} \tag{5}
\]

where \( \Delta G_a^0 \) is the standard free energy of adsorption.

The investigated phosphonium compounds may adsorb through \( \pi \)-electron interactions between the phenyl rings of the molecules and the iron surface. Adsorption can also occur in the cationic form with positively charged part of the molecule (\( P^+ \)) oriented toward negatively charges of ion surface. The adsorption of chloride ions enhanced the adsorption of phosphonium derivatives by acting as bridge in the adsorption process. An interaction of inhibitor molecules with already adsorbed chloride ions was proposed byHackerman and coworkers [29–31].

The corrosion inhibition ability of the five-phosphonium compounds listed has the following order:

\[
\text{CTP} > \text{TP} > \text{TPO} > \text{TPM} > \text{TPP}
\]

This sequence was established from the values of \( R \) and \( i_{\text{corr}} \) given in Tables 1 and 2, respectively.

4. Conclusions

1. The results obtained in this study showed the effectiveness of the investigated phosphonium compounds, except TPP, as inhibitors for the corrosion of iron in aerated 1 M HCl.

2. The organic phosphonium compounds were found to be mixed-type inhibitors affecting both anodic and cathodic sites and their adsorption followed the Temkin isotherm.

3. The charge transfer process controls corrosion of iron in 1 M HCl without and with phosphonium compounds.

Acknowledgements

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References