



Inhibition of phosphoric acid corrosion of zinc by organic onium compounds and their adsorption characteristics

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Abstract

The inhibiting properties of some organic phosphonium and ammonium compounds were studied with respect to the corrosion of zinc in 1 M H₃PO₄ solution. It was found that onium compounds which have π -electron system(s) are adsorbed following Frumkin's adsorption isotherm and provide better inhibition efficiency than those containing no π -electron system. The adsorption of the latter compounds was found to obey Langmuir's isotherm. Both potentiostatic and electrochemical impedance techniques proved that the studied onium compounds act as primary interface inhibitors without changing the mechanism of either hydrogen evolution reaction or zinc dissolution.

1. Introduction

It is well known that zinc has many practical applications: electrochemical energy generators have a reactive zinc anode, galvanized steels are used in industry [1–3] and zinc metal itself is used in the case of atmospheric corrosion. The use of acid electrolyte in washing and purification of zinc in electrochemical energy generators (to improve efficiency) [4] yields an attack which limits the use of these electrolytes. Thus, it is of great importance to eliminate or minimize this attack [5]. This can be achieved by using of inhibitors.

Although many organic onium compounds have been studied as inhibitors for the corrosion of zinc in HClO₄ [6] and HCl [7] solutions, the effectiveness of these compounds as inhibitors for the corrosion of zinc in phosphoric acid has not yet been studied. Linear polarization resistance (R_p), potentiostatic and electrochemical impedance spectroscopy (EIS) techniques were employed in the present study.

2. Experimental details

The material used in this work was speccure zinc (Johnson Matthey Chemicals Ltd, England). The work-

ing electrode was prepared from zinc rod, (dia. 6 cm), inserted in a Teflon tube and isolated with Araldite so that a circular cross-section (0.2827 cm²) only was exposed. Prior to every experiment, the electrode was polished with successive wet SiC emery papers, degreased with absolute ethanol, washed with doubly distilled water and then transferred wet to the electrochemical cell.

Measurements were carried out in a three-compartment electrochemical cell. The counter electrode was a platinum sheet of large surface area and the reference electrode was a saturated calomel electrode (SCE) to which all potentials are referred. The SCE was connected to the main compartment via a Luggin capillary. The cell was water-jacketed and was connected to an ultrathermostat at 30 °C.

Measurements were performed in 1 M H₃PO₄ solution. This solution was prepared by diluting the concentrated acid (BDH) with bidistilled water. Deaeration of the acid solution was achieved by bubbling highly pure nitrogen for 1 h before use and continued during the course of the measurements. Potentiostatic runs were performed in stirred solutions using B&T reversing magnetic stirrer whereas recording of the impedance spectra was carried out in stagnant solutions because

most of the frequency points were found to be highly scattered and have no meaning (i.e., no definite semi-circle was obtained in the complex plane impedance).

The investigated onium compounds (Aldrich or Merck products) are given in Table 1 and they were used without further purification. They were examined in the concentration range 5×10^{-6} – 1×10^{-3} M except PrTPhPBr and CpTPhPBr where their concentrations varied from 1×10^{-7} to 5×10^{-4} M.

Potentiostatic anodic and cathodic polarization curves were obtained with a scan rate of 0.2 mV s^{-1} in the potential range from -200 to $+150 \text{ mV}$ relative to the corrosion potential (E_{corr}). Values of the corrosion current density (I_{corr}) were obtained by extrapolation of the cathodic branch of the polarization curve back to E_{corr} . Measurements of R_p in the vicinity of E_{corr} ($E = E_{\text{corr}} \pm 20 \text{ mV}$ and scan rate of 1 mV s^{-1}) were also used to determine I_{corr} according to the Stern and Geary [8] equation:

$$R_p = \left(\frac{dE}{dI} \right)_{E=E_{\text{corr}}} \quad (1)$$

$$I_{\text{corr}} = \frac{\beta_a \times \beta_b}{2.303 R_p (\beta_a + \beta_b)} \quad (2)$$

Impedance spectra were recorded at E_{corr} in the frequency range 100 mHz to 50 kHz with 10 points per decade [9]. The ac voltage amplitude was $\pm 5 \text{ mV}$. In the EIS measurements only three concentrations of each inhibitor were tested. All measurements were carried out using EG&G PARC potentiostat model 273 connected to an IBM PS computer. A corrosion software model 352 was employed for R_p and potentiostatic measurements while a PAR lock-in amplifier model 5210 and electrochemical impedance software model 398 were used for EIS measurements. The experimental imped-

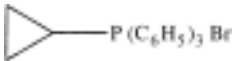
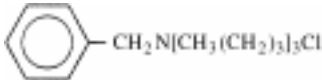
ance spectra were analysed and interpreted on the basis of the equivalent circuit program of Boukamp [10].

3. Results and discussion

3.1. Polarization measurements

Among the investigated onium compounds, CpTPhPBr was chosen as a representative example. Figure 1 shows the anodic and cathodic polarization curves obtained for zinc in $1 \text{ M H}_3\text{PO}_4$ solution without and with 1×10^{-7} – 5×10^{-4} M concentration of CpTPhPBr. It is clearly seen that CpTPhPBr shifts both the anodic and cathodic branches of the polarization curves of the pure acid solution to lower values of current density indicating the inhibition of both the hydrogen evolution (HER) and zinc dissolution reactions. The corrosion kinetic parameters derived from these curves, as well as those obtained in the presence of the investigated onium compounds, are given in Table 2. The data in Table 2 show that values of E_{corr} are shifted to more noble values upon increasing the concentration of CpTPhPBr while values of the anodic (β_a) and cathodic (β_c) Tafel slopes obtained in the absence and the presence of CpTPhPBr are approximately the same. These observations are indicative of mixed-type control and CpTPhPBr in H_3PO_4 acts as a mixed-type inhibitor without changing the mechanism of the hydrogen evolution reaction (HER) or zinc dissolution. It should be mentioned that polarization curves obtained at 5×10^{-5} and 1×10^{-4} M concentration are coincident. Thus, for the sake of clarity only the curve recorded at 5×10^{-5} M is shown in Figure 1. The rest of the onium compounds showed a behaviour similar to that obtained in the presence of CpTPhPBr but the following points must be taken into consideration:

Table 1. Onium compounds investigated

Name	Structure	Abbreviation
Propyltriphenylphosphonium bromide	$\text{CH}_3(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_3\text{Br}$	PrTPhPBr*
Propargyltriphenylphosphonium bromide	$\text{CH}\equiv\text{CCH}_2\text{P}(\text{C}_6\text{H}_5)_3\text{Br}$	PgTPhPBr*
Cyclopropyltriphenylphosphonium bromide		CpTPhPBr [†]
Tetrabutylammonium bromide	$[\text{CH}_3(\text{CH}_2)_3]_4\text{NBr}$	TBuNBr*
Tetrabutylphosphonium bromide	$[\text{CH}_3(\text{CH}_2)_3]_4\text{PBr}$	TBuPBr [†]
Benzyltributylammonium chloride		BTBuNCl [†]

* Aldrich products.

[†] Merck products.

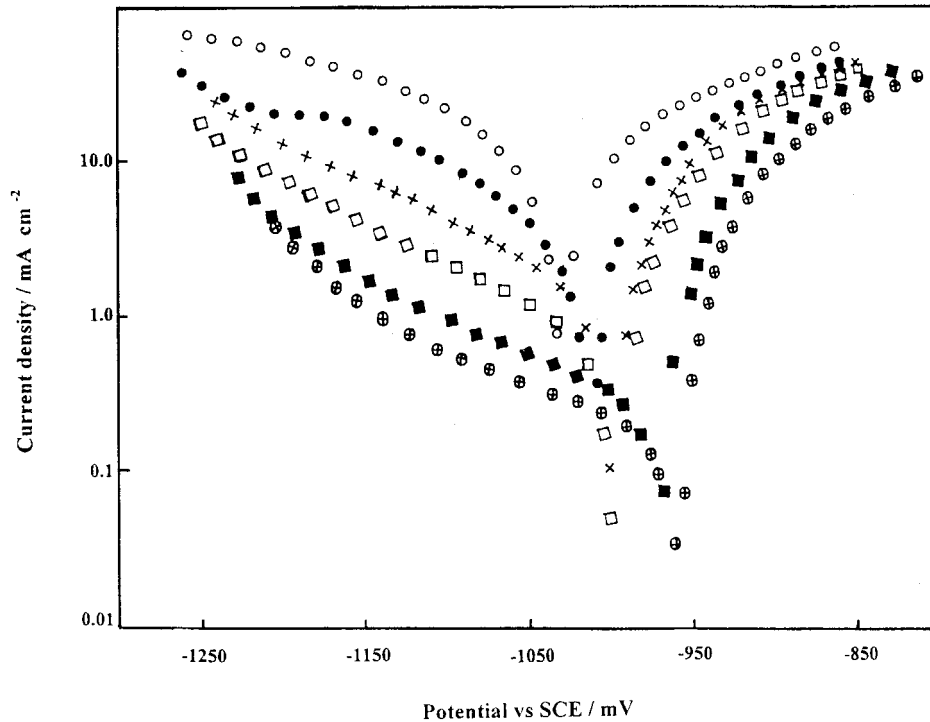


Fig. 1. Potentiostatic polarization curves of Zn in 1 M H_3PO_4 solution without and with CpTPhPBr. Key: (○) 1 M H_3PO_4 ; (●) 1×10^{-7} M CpTPhPBr; (×) 5×10^{-6} ; (□) 1×10^{-5} ; (■) 5×10^{-5} ; (⊕) 5×10^{-4} .

- (i) PgTPhPBr inhibits the anodic dissolution of zinc more than the HER. This observation, along with the large positive shift in values of E_{corr} (Table 2), indicate that this quaternary compound is an inhibitor of mixed type with predominant effect on the anodic reaction.
- (ii) BTBuN⁺, TBuP⁺ and TBuN⁺ inhibit both the zinc dissolution and HER but to a degree lesser than the other onium compounds. From the data given in Table 2, it is seen that BTBuNCl is the most efficient.

Values of the percentage inhibition efficiency (η) obtained from the relation:

$$\eta = \frac{(I_0 - I)}{I_0} \times 100 \quad (3)$$

where I_0 and I are the corrosion current densities (determined from Tafel and R_p methods) obtained in the absence and the presence of the inhibitor, respectively, are included in Table 2. These values indicate that organic onium compounds based on triphenylphosphonium cations offer better inhibition than those based on tributylammonium or phosphonium cations.

3.2. Adsorption isotherms

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics of the inhibitor [11, 12]. The surface coverage (θ) data are very useful while discussing the adsorption characteristics. Assuming no change in the mechanism of HER and zinc dissolution (as previously observed), the surface coverage of each inhibitor at a given concentration can be calculated from

$$\theta = 1 - \frac{I}{I_0} \quad (4)$$

For the onium compounds PrTPhPBr, PgTPhPBr, CpTPhPBr and BTBuNCl, the plot of θ against logarithm of inhibitor concentration (C) gave an S-type curve (Figure 2) characteristic of the Frumkin adsorption isotherm [13] which is given by

$$\frac{\theta}{1 - \theta} \exp(-f\theta) = K_a C \quad (5)$$

where K_a is the equilibrium constant of adsorption and f is another constant.

Table 2. Effect of organic onium compounds on the corrosion parameters of zinc in 1 M H₃PO₄ solution calculated from R_p and Tafel methods at 30 °C

[Inhibitor]/M	$-E_{\text{corr}}$	I_{corr}	β_a	$-\beta_c$	R_p	I_{corr}	$\eta\%$	R_p
	/mV vs SCE	/μA cm ⁻²	/mV dec ⁻¹		/Ω cm ²	/μA cm ⁻²	Tafel	
1 M H ₃ PO ₄	1033	8327	67	190	3.53	6093	–	–
1×10^{-7} PrTPhPBr	1030	6310	66	166	4.03	3730	24.2	38.8
5×10^{-6}	1015	6457	64	170	4.21	3515	22.5	42.3
1×10^{-5}	1005	5754	73	172	4.77	3417	30.9	43.9
5×10^{-5}	979	851	68	182	9.02	1747	89.7	71.3
1×10^{-4}	990	607	62	181	16.74	1198	92.7	80.3
5×10^{-4}	973	94	64	172	31.5	472	98.9	92.2
5×10^{-6} PgTPhPBr	995	3715	61	192	5.43	2713	55.4	55.5
1×10^{-5}	982	3631	73	182	5.71	2904	56.4	52.3
5×10^{-5}	955	2291	66	186	8.06	1924	72.5	68.4
1×10^{-4}	945	2165	75	182	8.87	1906	74.0	68.7
5×10^{-4}	930	832	62	192	20.24	737	90.0	88.0
1×10^{-3}	925	666	63	189	27.29	551	92.0	91.0
1×10^{-7} CpTPhPBr	1010	2754	72	170	5.76	2795	66.9	54.1
5×10^{-6}	1000	1148	68	177	7.38	2119	86.2	65.2
1×10^{-5}	1000	537	68	183	15.31	1031	93.7	83.1
5×10^{-5}	985	229	62	183	20.9	705	97.2	88.4
1×10^{-4}	970	162	60	176	22.08	645	98.0	89.4
5×10^{-4}	960	45	62	177	25.72	568	99.5	90.7
5×10^{-6} TBuPBr	1030	7762	69	185	3.46	4624	6.8	24.1
1×10^{-5}	1030	7586	70	180	3.50	4583	8.9	24.8
5×10^{-5}	1030	7080	73	185	3.97	4196	15.0	31.1
1×10^{-4}	1025	6310	70	185	4.55	3552	24.2	41.7
5×10^{-4}	1005	3388	73	180	7.44	2222	59.3	63.5
1×10^{-3}	1010	2399	63	176	8.2	1801	71.2	70.4
5×10^{-6} BT BuNCl	1032	6026	64	170	3.48	4253	27.6	30.2
1×10^{-5}	1030	5754	69	170	4.0	3905	30.9	35.9
5×10^{-5}	1030	5219	72	172	5.65	2860	37.3	53.1
1×10^{-4}	1023	2884	71	163	6.78	2322	65.4	61.9
5×10^{-4}	1005	1905	71	192	14.42	1144	77.1	81.2
1×10^{-3}	1010	1698	72	190	14.14	1175	79.6	80.7
5×10^{-6} TBuNBr	1035	7943	63	185	3.73	4011	4.6	34.2
1×10^{-5}	1035	7244	68	181	3.56	4419	13.0	27.5
5×10^{-5}	1025	7079	67	183	3.87	4034	15.0	33.8
1×10^{-4}	1025	6310	60	170	4.16	3394	24.2	44.3
5×10^{-4}	1005	3801	66	175	5.48	2785	54.3	54.3
1×10^{-3}	1010	3631	68	174	6.47	2405	56.1	60.5

The constant K_a is related to the standard free energy of adsorption (ΔG_0) by the equation:

$$K_a = \frac{1}{55.5} \exp\left(\frac{-\Delta G_0}{RT}\right) \quad (6)$$

The value of 55.5 is the concentration of water in solution expressed in M. Values of f , K_a and ΔG_0 were calculated and are given in Table 3. The adsorption isotherm of PgTPhPBr shows an S-shaped curve with two inflections (results obtained from Tafel extrapolation and R_p measurements proved the two inflections). This can be explained by adsorption on the zinc surface in two steps: a monolayer of adsorbate is formed on the metal surface and this is followed by the deposition of a second adsorbate layer. Similar behaviour was

obtained for the adsorption of amino acids containing sulphur on mild steel surface in sulphuric acid [14]. On the other hand, adsorption of both TBuPBr and TBuNBr was found to obey Langmuir's adsorption isotherm [15] where θ and C are related via the equation:

$$\theta = \frac{KC}{1 + KC} \quad (7)$$

Rearrangement gives

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (8)$$

Figure 3 shows plots of C/θ against C for the two inhibitors. The data fit straight lines of slopes less than

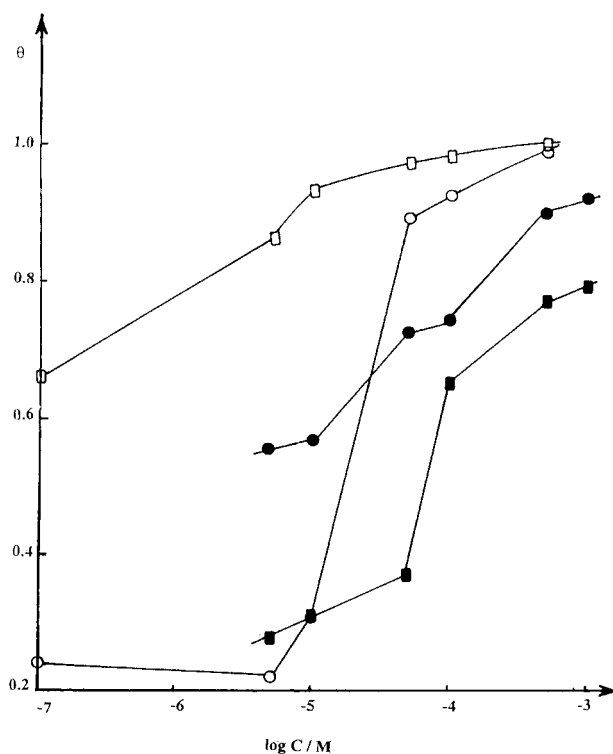


Fig. 2. Frumkin adsorption isotherms for some organic onium compounds on Zn in 1 M H_3PO_4 solution. Key: (○) PrTPhPBr; (●) PgTPhPBr; (□) CpTPhPBr; (■) BTBuNCl.

unity indicating that these inhibitors are adsorbed according to Langmuir's isotherm. Deviation of the slopes of the lines in Figure 3 from unity can be explained in terms of mutual repulsion or attraction of adsorbed species adjacent to each other, a fact which was ignored during the derivation of Langmuir isotherm [16]. Similar results were obtained by many authors [6, 17–21].

Values of K_a and hence those of ΔG_0 , were calculated and are given in Table 3. The large negative values of ΔG_0 indicate the spontaneous adsorption of the inhibitor and are usually characteristic of strong interaction with the metal surface. The results given in Table 3 indicate that values of the equilibrium constant and

Table 3. Adsorption parameters for organic onium compounds tested on zinc in 1 M H_3PO_4 solution at 30 °C

Inhibitor	f	K_a/M^{-1}	$\Delta G_0/\text{kJ mol}^{-1}$
PrTPhPBr	-8.3	1.97×10^8	-58.02
PgTPhPBr	-13.55	7.67×10^5	-44.053
CpTPhPBr	-10.34	2.169×10^{10}	-69.76
BTBuNCl	-5.75	3.622×10^5	-42.176
TBuPBr	-	3.02×10^4	-35.94
TBuNBr	-	2.2387×10^4	-35.19

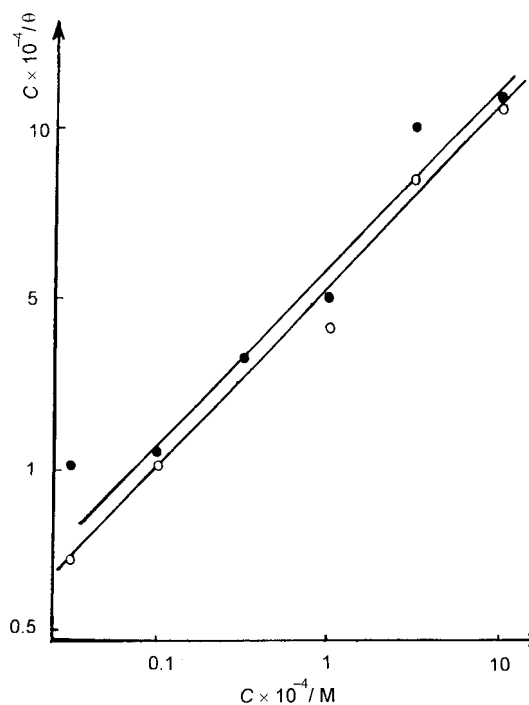


Fig. 3. Langmuir adsorption isotherms for TBuPBr and TBuNBr on Zn in 1 M H_3PO_4 solution. Key: (○) TBuPBr; (●) TBuNBr.

standard free energy of adsorption for CpTPhPBr are the highest and those of TBuNBr are the lowest. This suggests that TBuNBr provides the poorest protection against zinc corrosion and CpTPhPBr is the most effective inhibitor.

3.3. Electrochemical impedance spectroscopy measurements

Impedance measurements on zinc performed at E_{corr} 10 min after the electrode has been immersed in phosphoric acid solution without and with 5×10^{-6} – 1×10^{-3} M PgTPhPBr are presented in the form of Nyquist plots in Figure 4(a) and (b) respectively. Figure 4(a) shows a single depressed capacitive loop indicating that the corrosion of Zn in H_3PO_4 solution is under mixed charge transfer and diffusion control (as predicted from the value of CPE exponent n , $n = 0.75$, in Table 4). The depression, often referred to as frequency dispersion, has been attributed to inhomogeneities of the solid surfaces and mass transfer problem [22]. Fitting of the experimental data suggested the most probable equivalent circuit (Fig. 5) representing the Zn/ H_3PO_4 interface. This model is similar to that usually proposed for the simple metal/electrolyte interface, but with a constant phase element (CPE) which substitutes the capacity of the double layer (C_{dl}) and which takes into

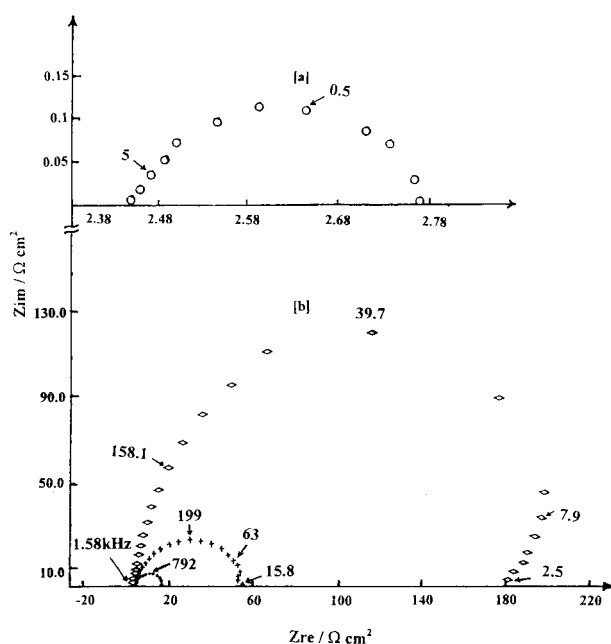


Fig. 4. Complex plane impedance of Zn in 1 M H_3PO_4 solution. (a) No additives and (b) with PgTPhPBr. Values in hertz. Key: (○) 1 M H_3PO_4 in (a); (●) 1×10^{-5} M PgTPhPBr, (+) 1×10^{-4} and (◊) 1×10^{-3} in (b).

account phenomena related to the heterogeneous surface and the diffusion processes [23, 24]. It is observed from Figure 4b that, as the concentration of PgTPhPBr increases, the diameter of the capacitive loop and, consequently, the value of the charge transfer resistance (R_{ct}) increases, which is an indication of the inhibitive

action. All the investigated onium compounds show the same behaviour as that of PgTPhPBr. Thus, Figure 4(b) is representative. Values of EIS parameters corresponding to the impedance spectra recorded in the presence of the investigated compounds are listed in Table 4. It is seen from this table that value of the electrolyte resistance (R_e) obtained in the pure medium increases in the presence of the investigated compounds. This can be attributed to the change in the conductivity of the medium. The change in R_e was observed by Feng et al. [25] and Morad [21]. Recently [26], it was found that the addition of propargyl alcohol to the system:mild steel/ H_3PO_4 resulted in change in R_e . Beside the increase in values of R_{ct} , the value of CPE obtained in the blank solution ($\text{CPE} = 2.06 \Omega^{-1} \text{cm}^{-2} \text{s}^n$) is drastically decreased in the presence of the onium compounds (CPE values range from 1.51×10^{-3} to $1.167 \times 10^{-5} \Omega^{-1} \text{cm}^{-2} \text{s}^n$). This can be correlated to the decrease in the area of Zn surface exposed to corrosive solution (increase in the area covered with the inhibitor) as a result of adsorption. On the other hand, the value of the exponent of CPE, n , can be used as a gauge of the heterogeneity of the surface [27]. The data of Table 4 indicate that the value of n obtained in the pure medium increases in the presence of the onium compounds. This can be attributed to the adsorption of a uniform layer of inhibitor on the surface. The experimentally determined values of the depression angle (φ) from semicircle fitting of the capacitive loops obtained in the absence and the presence of the onium compounds amount to 10–13°. Based on the shape of the Nyquist plot (only one capacitive loop) and the approximate constant values of

Table 4. EIS parameters obtained for zinc corrosion in 1 M H_3PO_4 solution containing some organic onium compounds

[Inhibitor] /M	R_e / Ωcm^2	R_{ct} / Ωcm^2	CPE / $\Omega^{-1} \text{cm}^{-2} \text{s}^n$	n	F_{\max} /Hz
1 M H_3PO_4	2.45	0.33	2.06	0.75	0.5
1×10^{-5} PrTPhPBr	3.53	2.44	1.108×10^{-4}	0.82	3152
1×10^{-4}	3.24	13.07	6.605×10^{-5}	0.89	397
5×10^{-4}	3.70	30.96	2.86×10^{-5}	0.94	251
1×10^{-5} PgTPhPBr	3.52	14.02	1.167×10^{-5}	0.93	792
1×10^{-4}	3.53	52.71	2.66×10^{-5}	0.95	199
1×10^{-3}	3.45	208.74	1.04×10^{-5}	0.98	39.7
1×10^{-5} CpTPhPBr	3.10	1.71	1.51×10^{-3}	0.75	792
5×10^{-5}	3.30	3.56	3.3×10^{-4}	0.91	199
5×10^{-4}	3.50	5.11	4.61×10^{-4}	0.91	126
1×10^{-5} TBuPBr	3.62	1.20	2.55×10^{-4}	0.86	1580
1×10^{-4}	3.84	1.81	4.72×10^{-5}	0.89	2510
1×10^{-3}	3.64	12.63	5.82×10^{-5}	0.87	792
1×10^{-5} BTBuNCl	3.58	1.58	1.01×10^{-4}	0.89	3970
1×10^{-4}	3.82	4.89	7.85×10^{-5}	0.86	1990
1×10^{-3}	3.18	29.0	3.65×10^{-5}	0.95	199
1×10^{-5} TBuNBr	3.25	0.61	4.55×10^{-4}	0.76	7920
1×10^{-4}	3.60	0.90	2.33×10^{-4}	0.87	5000
1×10^{-3}	3.60	9.23	9.91×10^{-5}	0.87	500

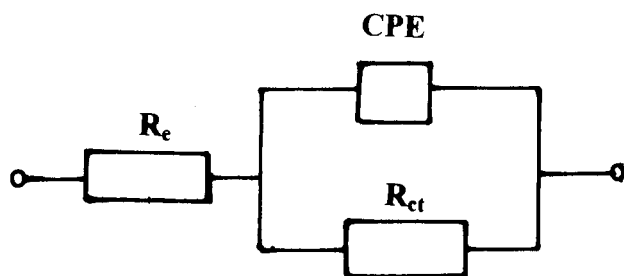


Fig. 5. Equivalent circuit of Zn/1 M H_3PO_4 system without and with organic onium compounds.

ϕ obtained without and with the onium compounds, it can be concluded that the additives are adsorbed on the surface as a two-dimensional layer and act as primary interface inhibitors by geometrical blocking of the electrode surface [28–30]. Similar results were obtained by Reinhard and Rammelt [31] for the inhibition of iron corrosion in de-aerated H_2SO_4 solution by benzyl-*n*-propylsulfide (BPS) and phenyl-*n*-propylsulfide (PPS).

Comparing the values of R_p in Table 2 with those of R_{ct} in Table 4, show that there is a large difference between them. The reason of this discrepancy can be explained as follows:

- (i) According to Gabrielli et al. [32], the I/E polarization curves obtained in the vicinity of E_{corr} do not yield, without ambiguity, the value of R_p since in most cases the electrochemical systems are not purely resistive and also by the fact that the steady state is not always reached.
- (ii) It was reported by Takenouti et al. [33] that zinc kinetics are very sensitive to nonlinear effects and impedance measurements are usually performed with a low amplitude signal (typically 1 r.m.s.). In the present study, the signal amplitude was 5 r.m.s. However, for the Zn/HCl/N-arylpyrrols system, it was found [34] that owing to the nonlinear behaviour of the current–potential curves in the vicinity of E_{corr} , neither R_p nor R_{ct} values could be determined from d.c. and a.c. measurements, respectively.

Remarkable difference between resistance values calculated from d.c. and EIS techniques was found in the literature [35–38].

3.4. Molecular structure–inhibition efficiency relationship

For a given solution, the adsorbability of inhibitors depends on the charge of the metal or approximately on the potential of the metal on the correlative scale (ϕ -scale) of potentials [39]. According to Antropov [40], the value of ϕ -potential of Zn in acidic solutions is -0.23 V, indicating that Zn is negatively charged at the corrosion

potential. Hence, cations are preferentially adsorbed at the Zn surface. Thus, in H_3PO_4 solution, organic onium compounds are readily adsorbed at Zn. Such adsorption is determined by electrostatic forces and is expected to impart high inhibition efficiency. However, the present results show high inhibition efficiencies (percentage η ranges from 92 to 99.5 at the highest examined inhibitor concentrations) for PrTPhPBr, PgTPhPBr and CpTPhPBr compounds.

For these cations it is suggested that the adsorbed cations are oriented with the ring structure parallel to the Zn surface and adsorption occurs via interaction of π -electrons of the benzene rings. Such interaction is expected to increase by participation of π -electrons of the carbon–carbon triple bond of the propargyl group in case of PgTPhPBr. On the other hand, in the case of CpTPhPBr, owing to the strong strain in the cyclopropyl group, the carbon atom has some sp^2 hybrid orbital geometry. Such geometry provides π -electron character on the carbon atom and this compound behaves like those containing a C–C double bond [41, 42]. Therefore, the adsorption of CpTPhP⁺ is enhanced by the interaction of the π -electrons of cyclopropyl group with the Zn surface. The present results show also that according to values of η , at 1×10^{-3} M, the other onium compounds follow the order: BTBuNCl > TBuPBr > TBuNBr. This order can be attributed to the interaction of the π -electrons of the benzyl group present in BTBuNCl with Zn surface. However, the easier polarizability and the lower electronegativity of phosphorous atoms compared to those of nitrogen atoms [43] may explain the higher inhibition efficiency exerted by TBuPBr than TBuNBr. It is observed from the above discussion that the presence of π -electron system in the structure of onium compound results in high inhibition efficiency. Ayer and Hackerman [44] reported that π -interaction is stronger than electrostatic or charge transfer interaction. It was also stated [45] that high adsorption activity of some organic compounds is attributed to the interaction of π -electrons with the surface atoms of the adsorbent. This may also explain the difference in the type of adsorption isotherm of PrTPhPBr, PgTPhPBr, CpTPhPBr, BTBuNCl and that of TBuPBr and TBuNBr (Section 3.2).

4. Conclusions

The following can now be stated:

- (i) Addition of organic onium compounds inhibits the corrosion of Zn in 1 M H_3PO_4 solution without changing the mechanism of HER or Zn dissolution.

- (ii) Organic onium compounds of aromatic nature (having a π -electron system) are adsorbed at the Zn surface following Frumkin's adsorption isotherm and offer better inhibition efficiency than those having no π -electrons. The adsorptive behaviour of the latter compounds obeys the Langmuir isotherm.
- (iii) The studied onium compounds act as primary interface inhibitors and form a two-dimensional layer on Zn surface.

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