Int. J. Electrochem. Sci., 9 **(2014)** 2896 - 2911

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Evaluation of Benzyl Triphenyl Phosphonium Chloride as Corrosion Inhibitor for Mild Steel in Phosphoric Acid

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Received: 30 December 2013 / *Accepted:* 19 February 2014 / *Published:* 23 March 2014

The effect of Benzyl triphenyl phosphonium chloride (BTPPC) on the corrosion of mild steel in a solution of 0.3 M phosphoric acid has been investigated at various inhibitor concentrations and temperatures by Potentiodynamic Polarization Studies, Potentiostatic Polarization Studies, Electrochemical Impedance Spectroscopy Studies (EIS), Temperature Kinetic Studies and Scanning Electron Microscopy (SEM). Results obtained from Potentiodynamic polarization studies reveal that BTPPC is a mixed type inhibitor for mild steel in 0.3 M phosphoric acid. Potentiostatic polarization studies show that BTPPC is a non-passivating type of inhibitor. The corrosion behavior of steel in 0.3 M H_3PO_4 with and without the inhibitor at various concentrations was studied in the temperature range from (298.15 to 338.15) K. The inhibition efficiency increases with an increase in concentration at all temperatures. The inhibition efficiencies decrease with an increase in temperature for lower concentrations of BTPPC, but for the higher concentration such as 1×10^{-3}M, inhibition efficiencies decrease with an increase in temperature up to 318.15 K and then increase with a further increase in temperature up to 338.15 K. The adsorption of BTPPC accords to the El-Awady adsorption isotherm. Kinetic and thermodynamic parameters such as effective activation energy (E_a), Gibbs free energy of adsorption (ΔG^o_{ads}) and heat of adsorption (ΔH^o_{ads}) indicate that adsorption of BTPPC on the mild steel surface is primarily physical in nature. The results of scanning electron microscopy are in agreement with the electrochemical analysis results.

Keywords: Benzyltriphenylphosphonium chloride; Potentiodynamic polarization studies; Potentiostatic polarization Studies; Electrochemical impedance spectroscopy (EIS); Scanning electron microscopy (SEM)

1. INTRODUCTION

Prevention of corrosion of metals and non-metals in various environments is of great importance in industry. The use of inhibitors is one of the most practical methods to protect metal against acid corrosion. Most of the well-known acid inhibitors are organic compounds with an aromatic character and with π bonds. They generally exhibit good inhibitor properties due to interaction of the π orbital with the metal surface. Electron donating groups containing N [1-11], S [12-18], O [19-21] and P [22-24] attached to organic compounds also increase inhibition efficiency. Quaternary onium compounds are found to be excellent inhibitors for the acid corrosion of metals like Fe, steel [25-28], zinc [29, 30] and aluminium and Al-alloys [31]. Phosphonium compounds show biocidal properties against macro and micro-organisms e.g., bacteria, algae, and mollusks etc. Phosphonium compounds [32] can also be used for the protection of technical materials, water systems, lubricants and other materials.

Phosphoric acid is a major chemical product which has many important uses especially in the production of fertilizers. Most of the acid is produced from phosphate rocks. Crude H_3PO_4 from the attack stage is filtered and concentrated in evaporation units [33]. There is a need to protect steel material used in the phosphoric acid industry from corrosion. Little work appears to have been done on the inhibition of steel in H_3PO_4 solutions [34-39]. Fouda et al. [34] studied some quaternary ammonium compounds as corrosion inhibitors for mild steel in 50% H_3PO_4. It was found that the mechanism of corrosion of mild steel in H_3PO_4 did not change with increasing acid concentration.

In this study H_3PO_4 is used instead of HCl and H_2SO_4 because H_3PO_4 is a mineral acid and it is very useful in industries and medicines. Most commonly, it is used in removing dust from metal surfaces. It is also used as a rust converter by bringing it in direct contact with a rusted iron, or steel tools and other surfaces that are rusted. It converts the ferric oxide which is reddish-brown in color to black colored ferric phosphate. When this ferric phosphate is scrubbed off, it will give a new look to the surface of the metal.

Therefore, in this investigation, the inhibition effect of BTPPC for the corrosion of mild steel in 0.3 M H_3PO_4 solution have been studied by potentiodynamic polarization, potentiostatic polarization, electrochemical impedance spectroscopy, temperature kinetic studies and scanning electron microscopy.

2. EXPERIMENTAL

2.1. Materials

The employed working electrodes were prepared from a mild steel rod with the chemical compositions of (wt %): C (0.15), Si (0.31), S (0.025), P (0.025), Mn (1.02) and Fe (balance).

2.2. Solutions

All solutions were prepared from doubly distilled water with conductivity of 5.5×10^{-6} $S \cdot m^{-1}$ and AR grade with ≥ 98 % purity of H_3PO_4 was used. The concentration range of inhibitor employed was 1×10^{-3}M, 1×10^{-5} M and 1×10^{-7}M in 0.3 M phosphoric acid.

2.3. Electrochemical measurements

The working electrode (WE) for the potentiodynamic studies was cut from a mild steel rod and was soldered on one end with an insulated copper wire and it was then embedded in chemical epoxy resin (ARALDITE) leaving an exposed surface area of 1 cm^2 for the studies. The counter electrode was platinum and the reference electrode was saturated calomel electrode (SCE) coupled to a luggin capillary. The potential of the metal electrode versus reference electrode was measured with the help of a Galvanostat. A steady state potential was achieved in 4-5 hours. The electrode system used for potentiostatic polarization studies and electrochemical impedance spectroscopy were the same as the one used for potentiodynamic polarization studies. Potentiodynamic polarization and potentiostatic polarization measurements were performed using an electrochemical analyzer CHI 6021B under aerated conditions. Potentiodynamic anodic and cathodic polarization curves were obtained with a scan rate of 0.001 Vs^{-1} in the potential range from -1.2 V to 0.2 V relative to the corrosion potential (E_{corr}). Potentiostatic polarization curves were obtained with a scan rate of 0.01 Vs^{-1} in the potential range from open circuit potential (OCP) to 2 V. Electrochemical impedance spectroscopy was performed using an electrochemical analyzer CHI760C under aerated conditions. Impedance spectra were recorded at E_{corr} in the frequency range of 10000 Hz to 1 Hz. The ac voltage amplitude was 0.005 V.

Properly grinded and polished samples of mild steel (1cm × 1cm × 1cm) were used for SEM. After being immersed in 0.3 M H_3PO_4, 1×10^{-3} M BTPPC and 1×10^{-7} M BTPPC of the inhibitor in 0.3 M H_3PO_4 for 24 hours at room temperature, the sample was taken out of the solutions and dried in a desicator for 24 hours and then these samples were used for SEM. SEM measurements were performed using LEO 435 VP in high vacuum mode and equipped with digital imaging and 35mm photography system. SEM images were obtained by applying operative voltage of (15-30) kV.

2.4. The structure of BTPPC

The organic additive Benzyltriphenylphosphonium Chloride, $C_6H_5P(C_6H_5)_3.Cl$ used as an inhibitor in this work is shown in Figure 1. This compound has the following physical properties such as M.W. = 388.88g, Assay = 97% and M.P = 325-330 ^{O}C.

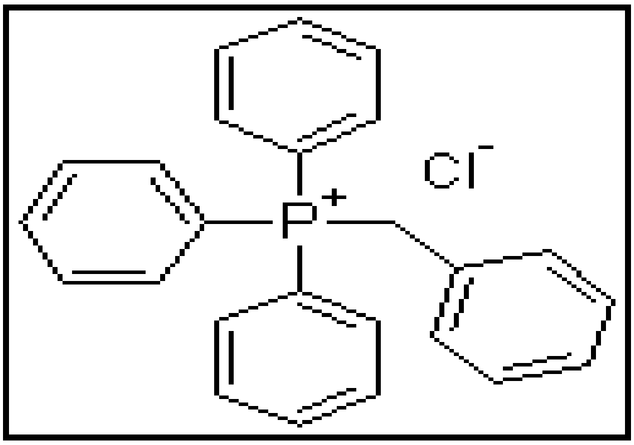

Figure 1. Molecular structure of BTPPC.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization Studies

In the present study, 0.3 M H_3PO_4 was used for the polarization of mild steel at different temperaturas, namely (298.15, 308.15, 318.15, 328.15 and 338.15) K. The potential values are plotted in Figure 2 against the logarithm of current densities. The various parameters are calculated from the graphs and are reported in Table 1.

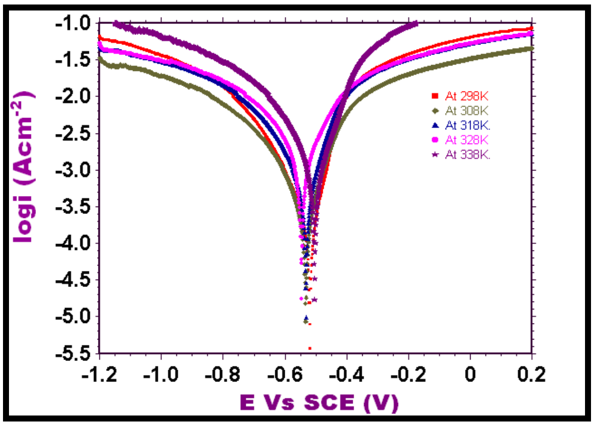

Figure 2. Tafel polarization curves of mild steel in 0.3 M H_3PO_4 at different temperatures.

Table 1. Corrosion Parameters such as corrosion potential (E_{corr}), cathodic and anodic tafel slopes (b_c and b_a), and corrosion current (i_{corr}) of mild steel in 0.3 M H_3PO_4.

T/(K)	$-E_{corr}$ (V)	b_c(mV/dec)	b_a (mV/dec)	i_{corr} (A.cm^{-2}) x 10^4
298.15	0.519	2.395	2.568	8.09
308.15	0.533	2.316	2.455	10.85
318.15	0.532	3.157	3.077	16.11
328.15	0.545	2.252	2.280	27.20
338.15	0.505	1.838	2.911	36.96

An increase in corrosion current values for 0.3 M H_3PO_4 is observed with an increase in temperature, thereby indicating that the extent of corrosion increases with an increase in temperature. An increase in temperature increases the diffusion rate and both over-voltage and viscosity decreases. Increased diffusion enables more dissolved oxygen to reach the cathodic surface, depolarizing corrosion mechanism as it favours solution of atmospheric oxygen and enhances hydrogen evolution.

E_{corr} almost remains constant with an increase in temperature. Anodic and cathodic tafel slopes remain almost constant with temperature and $b_c \approx b_a$.

Solutions of various concentrations of BTPPC were prepared in 0.3 M H_3PO_4 namely 1×10^{-3}M, 1×10^{-5}M and 1×10^{-7}M which were then used for the polarization studies. Potential values were plotted against the logarithm of current densities and various parameters were calculated which are given in Table 2. Figure 3 gives the cathodic and anodic polarization curves for these solutions at 298.15 K.

Table 2. Corrosion parameters such as corrosion potential (E_{corr}), cathodic and anodic tafel slopes (b_c and b_a), corrosion current (i_{corr}) and inhibition efficiency (I %) of mild steel in 0.3 M H_3PO_4 in the presence of BTPPC at different temperatures.

T/(K)	Conc.(M)	$-E_{corr}$ (V)	b_c(mV/dec)	b_a(mV/dec)	i_{corr}(A/cm^2) x 10^5	I%
298.15	1×10^{-3}	0.493	2.628	3.150	4.67	94.23
	1×10^{-5}	0.530	2.750	3.147	10.55	86.96
	1×10^{-7}	0.517	2.130	4.956	39.42	51.28
	H_3PO_4	0.519	2.395	2.568	80.92	-
308.15	1×10^{-3}	0.515	3.384	4.813	12.97	88.05
	1×10^{-5}	0.512	3.036	3.968	38.47	64.54
	1×10^{-7}	0.517	3.156	3.426	64.03	40.98
	H_3PO_4	0.533	2.316	2.455	108.50	-
318.15	1×10^{-3}	0.522	2.484	3.855	61.76	61.66
	1×10^{-5}	0.505	3.154	3.290	110.80	31.22
	1×10^{-7}	0.514	2.944	2.994	114.10	29.17
	H_3PO_4	0.532	3.157	3.077	161.10	-
328.15	1×10^{-3}	0.486	2.620	4.022	44.06	83.88
	1×10^{-5}	0.508	2.220	2.498	199.00	26.38
	1×10^{-7}	0.537	3.401	3.740	224.30	17.53
	H_3PO_4	0.545	2.252	2.820	272.00	-
338.15	1×10^{-3}	0.497	1.946	2.729	54.97	85.13
	1×10^{-5}	0.505	2.106	2.199	331.4	10.33
	1×10^{-7}	0.530	2.035	2.344	348.90	5.64
	H_3PO_4	0.505	1.838	2.911	369.60	-

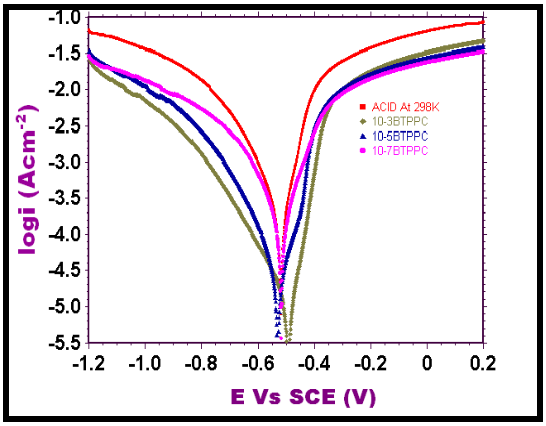

Figure 3. Tafel polarization curves of mild steel in 0.3 M H_3PO_4 and in the presence of different concentrations of BTPPC at 298.15 K.

The inhibition efficiency was calculated using equation (1):

$$I\% = \left(\frac{i_o - i}{i_o}\right) \times 100 \quad (1)$$

where i_o is the corrosion current in the uninhibited solution and i is the corrosion current in the inhibited solution.

The corrosion current values are much lower in the presence of the inhibitor than in pure acid and are lowest for the highest concentration of the BTPPC which is 1×10^{-3}M. The inhibition efficiency increases with an increase in concentration of BTPPC. This shows that the inhibition is due to the adsorption of the additive on the mild steel surface. The inhibition efficiency decreases with an increase in temperature for 1×10^{-5}M and 1×10^{-7}M BTPPC. But the same trend is not observed for the highest concentration i.e. 1×10^{-3}M. With an increase in temperature from (298.15 to 318.15) K the inhibition efficiency decreases. The decrease in I% with increasing temperature may be due to the fact that most of the effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of inhibitor to be adsorbed on the mild steel surface. This can also be explained by Le-Chatelier's principle. According to this, when an adsorbate adsorbs on the adsorbent the heat is released which means that adsorption is exothermic in nature. Therefore, when the heat is supplied externally, the reaction will move in the opposite direction leading to desorption and hence, higher rate of corrosion. Therefore, BTPPC belongs to first category of classification of inhibitors given by Putilova [40] as inhibitive action of the additive diminishes with the increase in temperature of the system. Other possible explanations for the decreased percentage of inhibition in the presence of this inhibitor as the temperature increased is that physical adsorption was the predominant inhibition mechanism, because the quantity of adsorbed inhibitor decreases with increasing temperature [41].

But as the temperature is further increased to 338.15 K the inhibition efficiency increases. This may be because BTPPC is not a linear molecule. The phenyl rings of BTPPC molecule are not in one plane, therefore it is not a perfect donor of electrons and also, the surface coverage can not be as uniform as is observed for planar molecules. However, at higher temperatures, 328.15 K and 338.15 K the phenyl rings of the BTPPC molecule undergoes change in orientation. At high temperature, they may be in the same plane, therefore enhancing the adsorption on the metal surface to retard the corrosion rate.

The values of b_c and b_a show an irregular trend indicating the involvement of other species/anions present in the solution in the adsorption process. E_{corr} remains constant indicating that BTPPC is a mixed type of inhibitor i.e. blocks both cathodic and anodic reactions to an equal extent.

3.2. Potentiostatic Polarizations Studies

The steady state potentiostatic behavior of the anodic dissolution of mild steel in 0.3 M phosphoric acid in the absence and in the presence of BTPPC was studied and is given Figure 4.

From the typical potentiostatic polarization curves, the various parameters (i_c and i_p) were determined and are reported in Table 3.

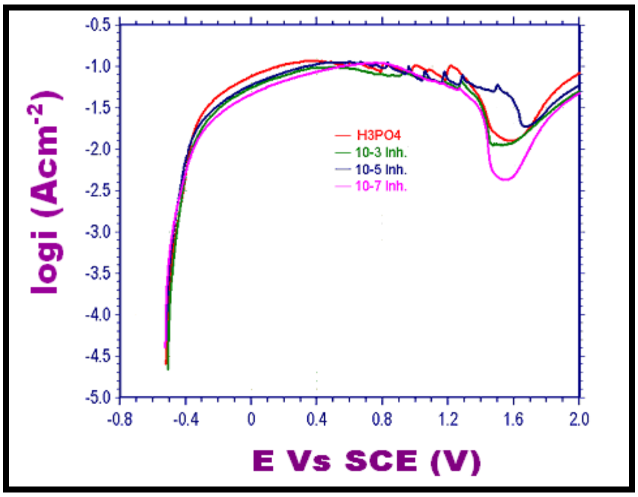

Figure 4. Potentiostatic polarization curves of mild steel in 0.3 M H_3PO_4 and in the presence of different concentrations of BTPPC at 298.15 K.

Table 3. Electrochemical parameters (i_c and i_p) for anodic dissolution of mild steel in 0.3 M H_3PO_4 in the presence of BTPPC.

Solutions	Conc.(M)	i_c(A/cm^2)	i_p(A/cm^2)
H_3PO_4	0.3	0.1165	0.0164
BTPPC	1×10^{-3}	0.0957	0.0120
	1×10^{-5}	0.1114	0.0200
	1×10^{-7}	0.1100	0.0053

When mild steel is exposed to 0.3 M H_3PO_4, there is no formation of a passive layer and the same trend is obtained with different concentrations of inhibitor. i_c values (Table 3) were found to be lower in the presence of different concentrations of BTPPC (1×10^{-3}, 1×10^{-5} and 1×10^{-7}) M as compared to H_3PO_4, which suggest that BTPPC is getting adsorbed on the surface of metal, thereby lowering the maximum current. Therefore, BTPPC acts as a good corrosion inhibitor. But no passivation range is observed for all concentrations of BTPPC. Therefore, BTPPC acts as a non-passivating type of inhibitor for mild steel in 0.3 M H_3PO_4. This is because, corrosion products are either soluble or the film formed is not adherent.

3.3. Adsorption isotherm

Inhibition of corrosion of mild steel in acidic solutions by inhibitors can be explained on the basis of molecular adsorption. Thus, the application of an adsorption isotherm is very useful to study the mechanism of corrosion inhibition. The value of surface coverage (θ) is obtained by using equation (2)

$$\theta = I\%/100 \qquad (2)$$

Various isotherms were studied for the adsorption of BTPPC on mild steel. On comparing the R^2 values of various isotherms it is concluded that adsorption of BTPPC on the mild steel in 0.3 M H_3PO_4 follows the El-Awady isotherm ($R^2 = 0.8950$). The El-Awady adsorption isotherm [42-44] is given by equation (3):

$$\log (\theta/1-\theta) = \log K + y \log c \qquad (3)$$

where c is the concentration of inhibitor and K is the equlibrium constant.

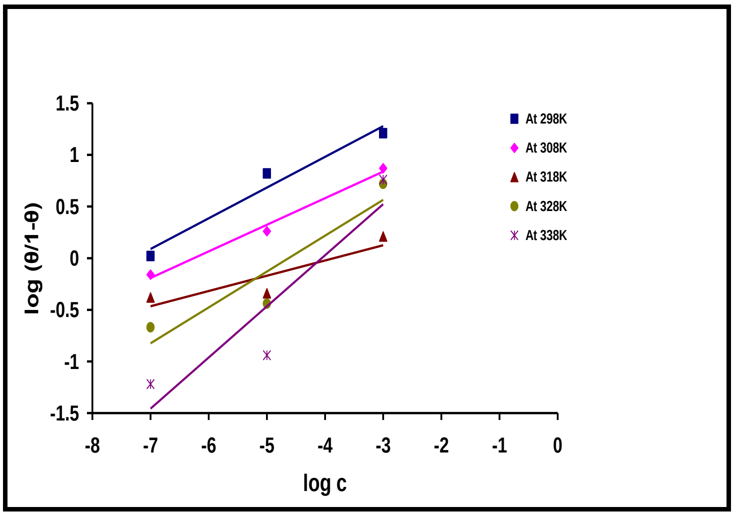

Figure 5. The plot of log (θ/1- θ) against log c for the El-Awady isotherm in the case of BTPPC.

The log (θ/1-θ) is plotted against log c in Figure 5 and log K and y are obtained as intercept and slope respectively and are given in Table 4. X = (1/y) is the number of inhibitor molecules occupying one active site (or the number of water molecules replaced by one molecule of the inhibitor).

Table 4. Slope (x), intercept (c) and correlation coefficient (R^2) values of the curve between log (θ/1-θ) versus log c for BTPPC.

T/(K)	Slope(x)	Intercept (c)	R^2	X=1/y
298.15	0.2975	2.1708	0.9619	3.36
308.15	0.2575	1.6108	0.9888	3.88
318.15	0.1475	0.5675	0.8006	6.78
328.15	0.3475	1.6075	0.8702	2.88
338.15	0.4950	2.0083	0.8536	2.02

3.4. Kinetic studies

Effective activation energy is calculated using equation (4)

$$\log i_{corr} = B - E_a / 2.303RT \qquad (4)$$

Figure 6 shows the graph between log i_{corr} versus 1/T. Effective activation energy values are calculated from the slope of these curves and are given in Table 5. The effective activation energy for corrosion of mid steel in 0.3 M H_3PO_4 was found to be 33.07 kJ/mol. In the presence of BTPPC, the average E_a = 57.13 kJ/mol, which is higher compared to pure acid. Hence, BTPPC induces higher energy barrier and therefore the rate of corrosion decreases.

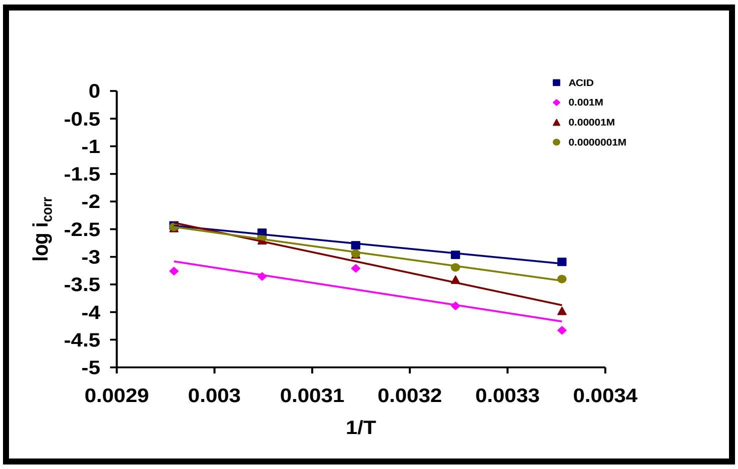

Figure 6. The plot of log i_{corr} against 1/T for mild steel in 0.3 M H_3PO_4 in the presence of BTPPC at different concentrations.

Table 5. Calculated values of effective activation energy (E_a) for the corrosion of mild steel in 0.3 M H_3PO_4 in the presence of BTPPC at different concentration.

Conc.(M)	Slope	E_a (kJ/mol)	R^2
H_3PO_4	-1727.2	33.07	0.9872
1×10^{-3}	-2738.2	52.43	0.7831
1×10^{-5}	-3759.9	71.99	0.9730
1×10^{-7}	-2453.3	46.97	0.9945

In the present case E_a in the presence of inhibitor was found to be lower than 80 kJ/mol, therefore the adsorption of BTPPC occurs via physiosorption [45].

Table 6. Equilibrium constant (K) and Gibbs free energy (ΔG^o_{ads}) values for BTPPC calculated from the El-Awady isotherm.

T/(K)	Slope (x)	Intercept (c)	K	- ΔG^o_{ads} (kJ/mol)
298.15	0.2975	2.1708	148.18	22.34
308.15	0.2575	1.6108	40.81	19.78
318.15	0.1475	0.5675	3.69	14.07
328.15	0.3475	1.6075	40.50	21.05
338.15	0.4950	2.0083	101.93	24.28

Table 6 gives the values of equilibrium constant K and the ΔG^o_{ads} values using the El-Awady isotherm. The negative value of ΔG^o_{ads} [46-48] reveals the spontaneity of the adsorption process. The mean value of ΔG^o_{ads} is -20.30 kJ/mol. A ΔG^o_{ads} value above 50 kJ/mol is indicative of chemisorption. The low value of ΔG^o_{ads} in the present study further confirms physisorption.

Figure 7 displays the variation of log (θ/1-θ) vs. 1/T.

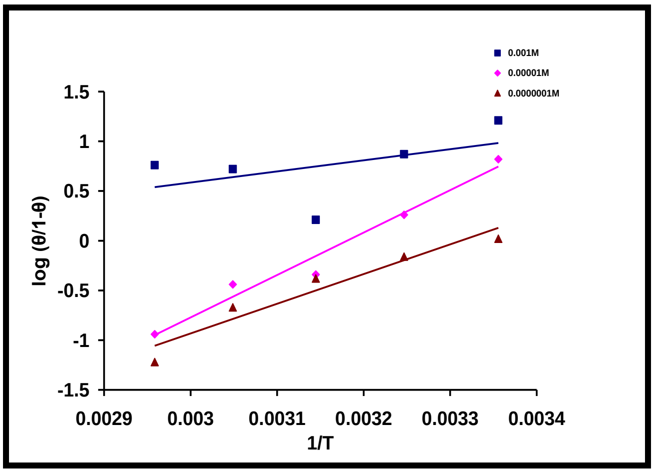

Figure 7. The plot of log (θ/1-θ) against 1/T for BTPPC.

The heat of adsorption has been calculated using equation (5)

$$\log \theta/(1-\theta) = \log (K.c) - Q/2.303RT \qquad (5)$$

where Q is the heat of adsorption. The average value of heats of adsorption at 1×10^{-3}M, 1×10^{-5}M and 1×10^{-7}M concentrations is 53.41 kJ/mol are given in Table 7 are found to be much lower than 80 kJ/mol, further confirming the fact that the adsorption is physical in nature. The negative value of heat of adsorption also indicates that the adsorption of the inhibitor is an exothermic process [49].

This physical adsorption may be due to interaction between the BTPPC molecules through their partially delocalized π- electrons and the vacant d-orbitals of metal surface.

Table 7. Calculated values of heat of adsorption (Q) for the corrosion of mild steel in 0.3 M H_3PO_4 in presence of BTPPC.

Conc.(M)	Slope (x)	-Q(kJ/mol)
$1x10^{-3}$	1118.1	21.41
$1x10^{-5}$	4267.2	81.70
$1x10^{-7}$	2983.9	57.13

3.5. Electrochemical Impedance Spectroscopy (EIS)

The corrosion of mild steel in an acidic solution in the presence of BTPPC was investigated by EIS at 298.15 K after immersion for 5 h. Double layer capacitance values (C_{dl}) and charge transfer resistance values (R_{ct}) were obtained from impedance measurements. The value of charge transfer resistance was obtained measuring the diameter of the semicircle and the double layer capacitance was calculated using the following relation:

$$C_{dl} = (2\pi f R_{ct})^{-1}$$

The inhibition efficiency is also calculated using equation (6):

$$I\% = \left(\frac{R_{ct(i)} - R_{ct(a)}}{R_{ct(i)}}\right) \times 100 \qquad (6)$$

where $R_{ct(a)}$ and $R_{ct\ (i)}$ are charge transfer resistance values with and without inhibitor for mild steel in 0.3 M H_3PO_4, respectively.

Nyquist plots of mild steel in uninhibited solution (0.3 M H_3PO_4) displayed two capacitive loops and the same was obtained for the lower concentration of inhibitor (1×10^{-7} M BTPPC). The high frequency (HF) loop, the smaller one, can be attributed to the film formation at the steel surface while the low frequency (LF) loop, larger one, can be attributed to the charge transfer reaction. The HF capacitive loop is so small, that it can not be seen clearly. The HF loop indicates the existence of Warburg impedance [50] which is characteristic of the diffusion process (diffusion layer of finite thickness) [51]. The high frequency part of the impedance describes the behavior of inhomogeneous surface layer while the low frequency contribution shows the kinetic response for the charge transfer reaction. Other inhibited acidic solutions containing 1×10^{-3}M and 1×10^{-5}M concentrations of BTPPC displayed one capacitive arc as shown in Figure 8.

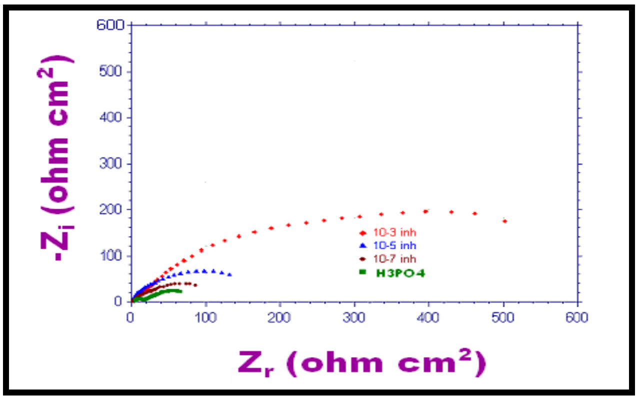

Figure 8. Nyquist plot of mild steel in 0.3 M H_3PO_4 and in presence of different concentrations of BTPPC at 298.15 K.

It is apparent from figure 8 that the impedance capacitive loop for mild steel in 0.3 M H_3PO_4 solutions changes significantly with increasing inhibitor concentrations. The diameter of the capacitor loop increases tremendously in the presence of inhibitor as compared to that of acid which indicates a high inhibition of corrosion. The largest capacitive loop was obtained for highest concentration (1×10^{-3}M) of inhibitor (BTPPC). Approximately semi-circular [52] appearance shown by the impedance diagrams indicates that corrosion of mild steel is mainly controlled by charge transfer process.

Parameters obtained from EIS and calculated inhibition efficiency (I%) are given in Table 8.

Table 8. Impedance parameters (R_{ct}, f and C_{dl}) and inhibition efficiency (*IE*) for the corrosion of mild steel in 0.5 M H_2SO_4 without and with addition of various concentrations of BTPPC at 298.15 K.

Compound	Conc.(M)	$R_{ct}(\Omega cm^2)$	f (Hz)	$C_{dl}(F/cm^2)$	IE (%)
H_3PO_4	0.3	24.449	1.738	$3.74X10^{-3}$	-
BTPPC	1×10^{-3}	747.900	3.090	$5.33X10^{-4}$	96.73
	1×10^{-5}	193.650	1.434	$1.27X10^{-4}$	87.37
	1×10^{-7}	64.350	5.486	$4.68\ X10^{-4}$	62.00

The R_{ct} value obtained for highest concentration of 1×10^{-3}M BTPPC was 747.9 Ωcm^2. The value of R_{ct} increases in the presence of inhibitor which in turn leads to a decrease in the corrosion current for mild steel in 0.3 M H_3PO_4. Among all the concentrations of BTPPC, 1×10^{-3} M of BTPPC performs best in 0.3 M H_3PO_4 by enhancing the value of R_{ct} and lowering the C_{dl} value. Higher values of R_{ct} which arise with a higher concentration of BTPPC, is indicative of greater inhibition efficiency.

The double layer capacitance at the Fe/H_3PO_4 interface decreases with an increase in inhibitor concentration. A decrease in $C_{dl,}$ which can result from a decrease in local dielectric constant or an increase in the thickness of the electrical double layer, indicates that the inhibitor was adsorbed on the surface at both cathodic and anodic sites [53, 54]. The results obtained by the impedance studies correlate very well with the potentiodynamic results for all the three concentrations of inhibitor at 298.15 K. The inhibition efficiencies show an extremely good quantitative correlation.

3.6. Scanning electron microscopy

Figures 9 (a) and (b) show the scanning electron micrographs of unexposed specimen of mild steel and mild steel exposed to 0.3 M phosphoric acid.

Figures 10 (a) and (b) show the scanning electron micrographs of mild steel specimens exposed to 0.3 M phosphoric acid containing 1×10^{-3} M and 1×10^{-7} M BTPPC.

Figure 9 (a) shows that the surface of the mild steel metal is completely free from any pits and cracks. Polishing scratches are also visible. Flakes can be seen Figure 9 (b) on the whole of the mild steel surface when dipped in 0.3 M H_3PO_4 which shows uniform corrosion. It can be seen from Figure 10 (a) that at higher concentration of inhibitor, i.e. 1×10^{-3} M BTPPC, the metal surface is fully covered with the inhibitor molecules giving it a high degree of protection against corrosion.

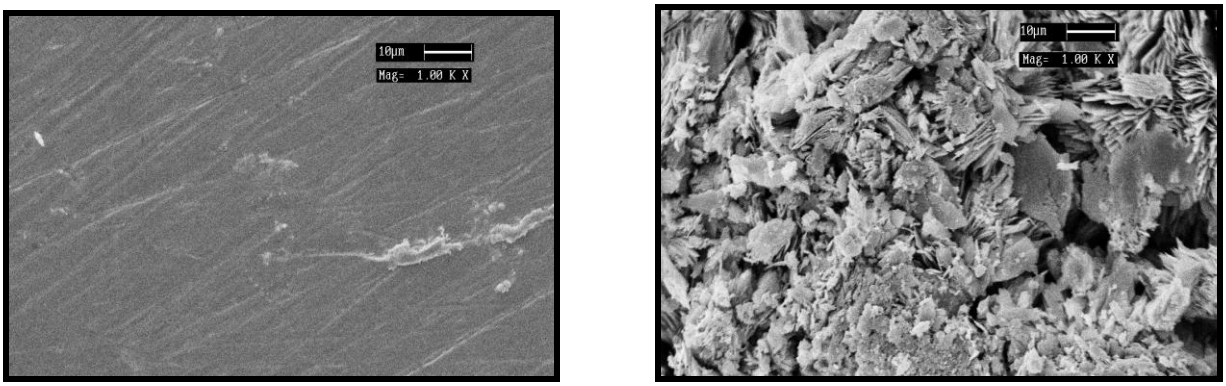

Figure 9. Shows scanning electron micrograph of: (a) Plain mild steel surface and (b) Mild steel exposed to 0.3 M H_3PO_4.

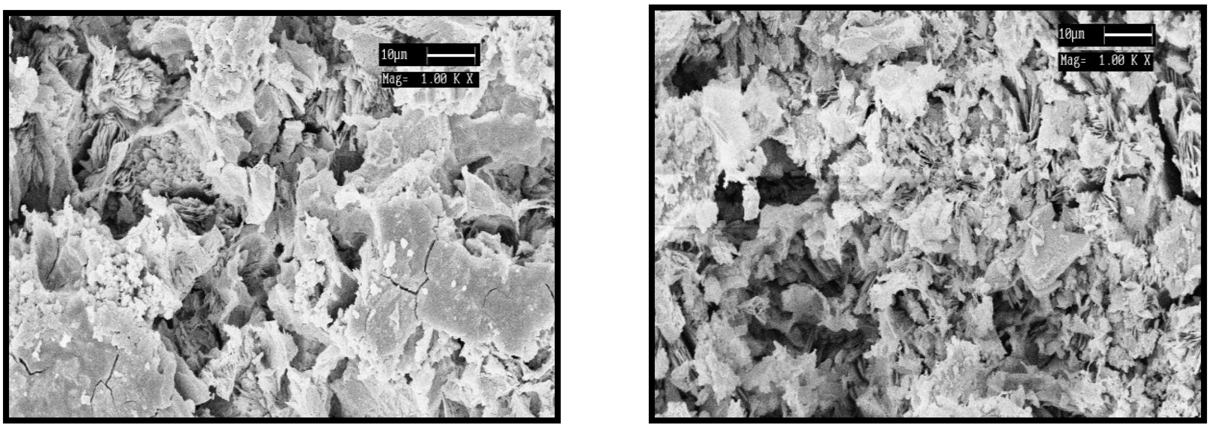

Figure 10. Show scanning electron micrograph of mild steel exposed to 0.3 M H_3PO_4 in the presence of: (a) 10^{-3} M BTPPC and (b) 10^{-7} M BTPPC.

Figure 10 (b) shows that at the lowest concentration of inhibitor, i.e. 1×10^{-7}M, the metal surface is covered with corrosion products.

However, the extent of corrosion in the presence of inhibitor is much less compared to specimens exposed to 0.3 M phosphoric acid, Figure 9 (b).

4. CONCLUSIONS

The goal of this research is to investigate the inhibition action of BTPCC on the corrosion of mild steel in 0.3 M H_3PO_4 at (298.15 to 338.15) K. The results show that BTPCC is an excellent inhibitor for mild steel in 0.3 M H_3PO_4. The inhibition efficiencies increase with an increase in concentration but decrease with an increase in temperature for BTPPC. The E_{corr} values remains constant indicating that BTPPC is mixed type of inhibitor in 0.3 M H_3PO_4 i.e., blocking both cathodic and anodic reactions to an equal extent. Adsorption of BTPPC may have the involvement of other species/anions present in the solution as indicated by the irregular trends of b_c and b_a. Adsorption of BTPPC on the mild steel follows the El-Awady isotherm. The negative values of ΔG^o_{ads} indicate the spontaneity of the adsorption process. ΔG^o_{ads} almost remains constant with temperature in case of BTPPC. The values of E_a and Q in the presence of BTPPC are are found to be lower than 80 kJ/mol and indicates adsorption occurs via physiosorption. Although there is decrease in the i_c value compared to acid, no passivation range is observed. This indicates that BTPPC acts as non-passivating type of inhibitor for mild steel in 0.3 M H_3PO_4. The diameter of the capacitor loop increases tremendously in the presence of BTPPC as compared to that of the acid which indicates high inhibition of corrosion. The value of R_{ct} (charge transfer resistance) increases in the presence of inhibitor which in turn leads to a decrease in the corrosion current for mild steel in 0.3 M H_3PO_4. The C_{dl} double layer capacitance value shows a decrease on the addition of inhibitor as compared to that of the acid, indicating a complete film formation on the metal surface in the presence of the inhibitor. Surface morphology study (SEM) reveals that the extent of corrosion inhibition is more at higher concentrations as compared to lower concentrations.

ACKNOWLEDGEMENTS
The authors acknowledge University of Delhi for providing financial assistance and University of KwaZulu-Natal for a postdoctoral scholarship for Dr I. Bahadur.

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