



## Corrosion inhibition of mild steel by hexyltriphenylphosphoniumbromide in acid medium. Part-III

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The efficiency of hexyltriphenylphosphoniumbromide (HTPPB) as corrosion inhibitor for mild steel in  $H_2SO_4$  ( $10^{-3} M$ ,  $10^{-5} M$ ,  $10^{-7} M$ ) was investigated by electrochemical methods like steady state galvanostatic and potentiostatic polarization measurements. The dissolution parameters such as corrosion current, passive current, flade potential, cathodic and anodic Tafel slopes and efficiencies were determined and studied at four different temperatures (298 K, 308 K, 318 K, 328 K). The optimum concentration of this compound for maximum inhibition efficiency was determined by galvanostatic method. HTPPB gave more than 92% inhibition in presence of  $10^{-3} M H_2SO_4$  at 298 K. Potentio dynamic polarization studies revealed that HTPPB is mixed inhibitor and good passivator in  $1 M H_2SO_4$ . According to temperature kinetics HTPPB obeyed Temkin's and Freundlich adsorption isotherm.

Keywords: Corrosion, inhibition efficiency, mild steel, hexyltriphenylphosphonium bromide.

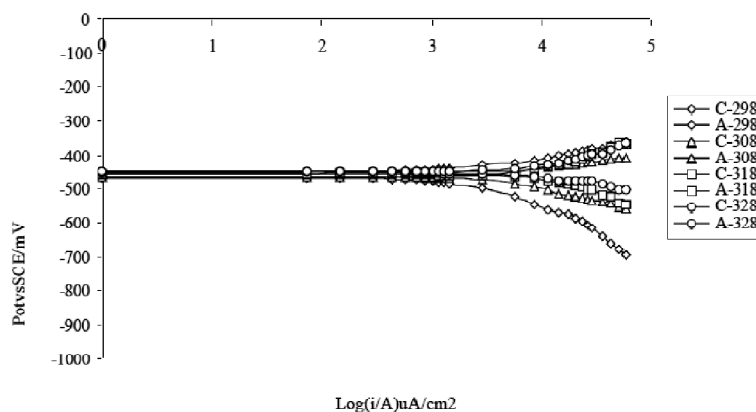
### Introduction

In the contemporary world metal has become integral part of life of human beings and therefore there is an urgent need for it to be prevented to the maximum extent possible from getting corroded, if it is not possible to stop corrosion completely. For that the urgent need is to investigate and detect inhibitor to determine the effect of inhibition and investigate the mode of inhibition. The mechanism of adsorption of hexyltriphenylphosphoniumbromide (HTPPB) which acts as corrosion inhibitor in acidic solution<sup>1-7</sup>. This present study describes the role of HTPPB<sup>8,9</sup> as an inhibitor at the time of cathodic reduction of oxygen and anodic dissolution of mild steel. The primary data indicates that corrosion of mild steel using HTPPB as an inhibitor in acid medium. The result is supplemented with temperature kinetics<sup>10,11</sup>, infrared studies<sup>12</sup>, scanning electron microscopy<sup>13</sup> and quantum chemical studies<sup>14-22</sup>.

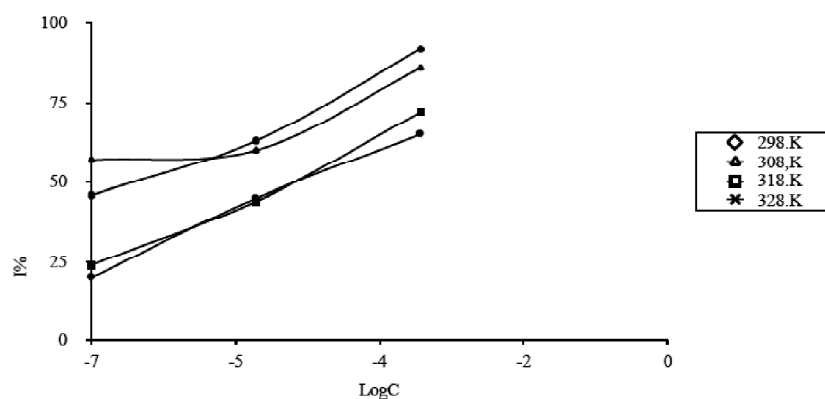
### Results and discussion

*Galvanostatic polarization studies:* Study of galvanostatic polarization of mild steel carried out at four different temperatures (298 K, 308 K, 318 K and 328 K) and  $1 M H_2SO_4$  gave the 'cathodic and anodic polarization' curves (Fig. 1).

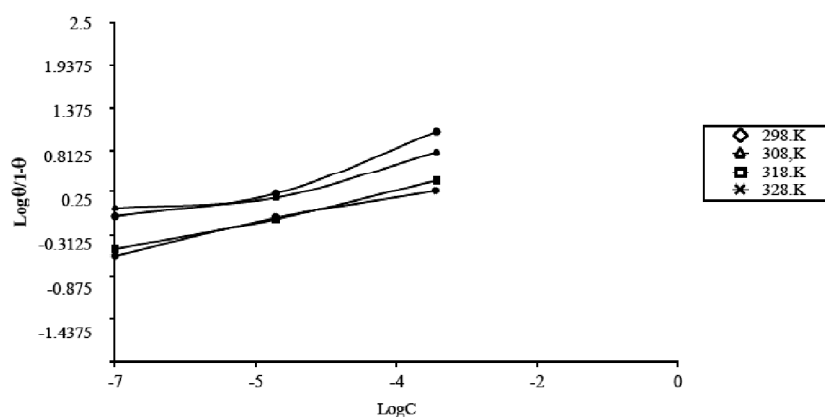
Log of current density vs the corresponding electrode potential (Fig. 3). The mechanism of hydrogen evolution and anodic metal dissolution reaction can be calculated by Tafel slopes of cathodic and anodic process. Corrosion parameters for mild steel in  $1 M H_2SO_4$  are given in Table 1. As the temperature increases the corrosion current value also increases i.e. temperature and corrosion current are directly proportional. Galvanostatic studies in presence of hexyltriphenylphosphoniumbromide (HTPPB)  $1 M H_2SO_4$  containing various concentration of HTPPB was used for polarization studies at 298 K, 308 K, 318 K and 328 K. According to graph plotted between the polarizing potential and logarithm of current densities, give the following results which are mentioned in Table 1. The following information regarding inhibitor can be received by Tafel slopes. HTPPB has shown no appreciable shift in open circuit potential (OCP) towards any direction at the same time (Table 1). It can be clearly seen that there is no appreciable change in  $E_{corr}$  value which makes this compound a mixed type of inhibitor. There is decrease in corrosion current  $I_{corr}$  value at lower temperature (298 K) as compared to the change in corrosion current value at higher temperature (328 K) as the concentration changed from  $10^{-7} M$  to  $10^{-3} M$ . The more is the corrosion current



**Fig. 1.** Tafel polarization curves by galvanostatic polarisation studies of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> at four different temperatures 298 K, 308 K, 318 K and 328 K.



Inhibition efficiency vs concentration of HTPPB at different temperature



Variation of surface coverage vs concentration of HTPPB at four temperature

**Fig. 2**

value, the more will be the corrosion. That is why HTPPB belongs to Putilova's first class of inhibitor. The variations in

Tafel slopes in irregular manner, shows that the reduction in  $i_{corr}$  value by increasing temperature and decreasing inhibi-

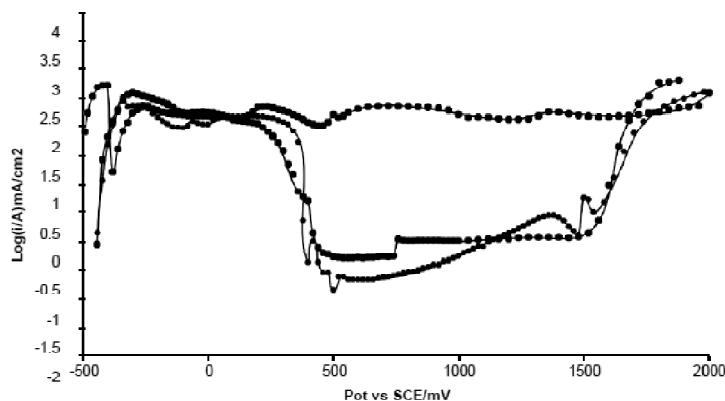


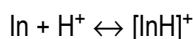
Fig. 3. Logarithm of current density against the corresponding electrode potential.

Table 1. Galvanostatic studies of mild steel in H<sub>2</sub>SO<sub>4</sub> in the presence of HTPPB

Temp. (K)	Conc. (mol dm <sup>-3</sup> )	-E <sub>corr</sub> (mv)	b <sub>c</sub> (mv/decade)	I <sub>corr</sub> (mA/cm <sup>2</sup> )	I (%)
298	10 <sup>-3</sup>	454	175	0.32	92
	10 <sup>-5</sup>	478	125	1.7	63
	10 <sup>-7</sup>	476	110	2.5	46
308	H <sub>2</sub> SO <sub>4</sub>	470	140	4.6	-
	10 <sup>-3</sup>	487	195	0.71	86
	10 <sup>-5</sup>	523	100	2.0	60
	10 <sup>-7</sup>	518	80	2.7	57
318	H <sub>2</sub> SO <sub>4</sub>	465	55	5.1	-
	10 <sup>-3</sup>	507	240	2.5	72
	10 <sup>-5</sup>	519	60	5.4	4.4
	10 <sup>-7</sup>	489	50	6.8	24
328	H <sub>2</sub> SO <sub>4</sub>	455	45	9.0	-
	10 <sup>-3</sup>	510	280	4.2	65
	10 <sup>-5</sup>	520	50	6.5	45
	10 <sup>-7</sup>	510	40	9.6	20
	H <sub>2</sub> SO <sub>4</sub>	450	35	12.0	-

tor concentration is governed by some other mechanism including the adsorption of the inhibitor on the surface. According to polarization data it is clear that inhibitor can work by two ways i.e.

(i) By blocking the active site of cathodic polarization reaction. The active site of Br<sup>-</sup> providing synergistic effect to inhibition process. HTPPB (In) therefore, in acidic media undergoes small protonation reaction and form protonated species. As given below



(ii) During anodic polarization the adsorption takes places between the positive metal ion and the delocalized additive system, because of which the metal dissolution retards. The structure shows that the *p*-electron of inhibitor molecule overlap with the vacant *d*-orbital of Fe<sup>2+</sup>, Fe<sup>3+</sup>. As the anodic current value increases the surface metal atom attached with the ions of Br<sup>-</sup>, OH<sup>-</sup> and ions which is present in the solution and formed metal hydroxide (M-OH)<sub>ads</sub> which is present in the form of adduct of the type (M-In)<sub>ads</sub> or type (M-OH-In)<sub>ads</sub> / (M-In-Br)<sub>ads</sub> / (M-In-OH-Br)<sub>ads</sub> / (M-In-Br-OH)<sub>ads</sub> / (M-Br-OH-In)<sub>ads</sub>.

*Thermodynamic and adsorption studies of mild steel in the presence of HTPPB in acid medium:*

Since corrosion rates directly related with corrosion current, inhibitor efficiencies I% of HTPPB at (298 K, 308 K, 318 K, and 328 K) and different concentration are given in Table 3. At 298 K (in graph) the inhibition efficiency increases with increase in concentration, but decrease with concentration is very less, whereas at higher temperature this decreases occurs sharply. The plot of I% vs log C (Fig. 2) shows that HTPPB at higher temperature follows Langmuir's adsorption isotherm because adsorption and desorption time lag becomes shorter and therefore, it becomes monomolecular at any point of time. This is primarily due to nonlinearity of the molecule, irregular protonation and intermolecular repulsion. But a general trend, that surface coverage decreases with increase in temperature, is very much obvious. The data for HTPPB fits better in Temkin's and Freundlich's adsorption isotherm where surface coverage (θ) shows (linear relationship with concentration). For calculating an approximate

heat of adsorption ( $Q$ ) of HTPPB over metal surface in 1 M  $H_2SO_4$ , with the help of graph drawn between  $\log \theta/1-\theta$  vs  $1/T$ , the value of  $Q$  are calculated from the straight line portion of the curve for  $10^{-3}$  M,  $10^{-7}$  M inhibitor reported in Table 2. The value of  $Q$  obtained, support the chemisorption and that is the reason that the corrosion inhibition efficiency is more than 92%. In case of HTPPB donation of electron from species with the loosely bounded electron such as  $p$ -electron in aromatic ring, or multiple bonds, or unpaired electrons in functional group that contain atom such as  $p$  and

**Table 2.**  $Q$  and  $E_{eff}$  calculated values for the corrosion of mild steel in 1 M  $H_2SO_4$  in the presence of HTPPB

HTPPB concentration (mol/L)	$-Q$ (kcal/mol)	$E_{eff}$ (kcal/mol)
$10^{-3}$	15.18	29.90
$10^{-5}$	17.08	20.70
$10^{-7}$	28.52	18.4
$H_2SO_4$	–	13.80

vacant ( $d$ -orbital) of the transition element ( $Fe^{2+}$ ,  $Fe^{3+}$ ). Energy of activation can be calculated by various concentration through the plot of  $\log I_{corr}$  vs  $1/T$  as shown in Table 3. The effective activation energies in the case of HTPPB are

**Table 3.** Thermodynamic studies data of corrosion of mild steel in 1 M  $H_2SO_4$  in the presence of HTPPB

Temp. (K)	Conc. (mol L <sup>-1</sup> )	$I_{corr}$ (mA/cm <sup>2</sup> )	$\log I_{corr}$	$I$ (%)	$\theta$	$\theta/1-\theta$
298	$10^{-3}$	0.32	-0.4948	92	0.92	11.5
	$10^{-5}$	1.7	0.2304	63	0.63	1.7
	$10^{-7}$	2.5	0.3979	46	0.46	0.85
	$H_2SO_4$	4.6	0.6627	–	–	–
308	$10^{-3}$	0.71	-0.1487	86	0.86	6.14
	$10^{-5}$	2.0	0.3010	60	0.60	1.5
	$10^{-7}$	2.7	0.4313	57	0.57	1.09
	$H_2SO_4$	5.1	0.7075	–	–	–
318	$10^{-3}$	2.5	0.3979	72	0.72	2.55
	$10^{-5}$	5.4	0.7323	44	0.44	0.78
	$10^{-7}$	6.8	0.8325	24	0.24	0.31
	$H_2SO_4$	9.0	0.9542	–	–	–
328	$10^{-3}$	4.2	0.6232	65	0.65	1.85
	$10^{-5}$	6.5	0.8129	45	0.45	0.81
	$10^{-7}$	9.6	0.9822	20	0.20	0.25
	$H_2SO_4$	12.0	1.0791	–	–	–

found to be higher than the  $E_{eff}$  of the corrosion process in 1 M  $H_2SO_4$ . This conclusion shows that the HTPPB additive is very well adsorbed over the metal surface at lower temperatures and due to shortness of time lag between adsorption and desorption at 318 K to 328 K, the relationship becomes linear. This is also an indication that HTPPB belongs to first category of inhibitor as classified by Putilova. The two processes that mainly govern through adsorption behaviour of HTPPB at certain temperature:

(i) Because of high charge density of the phosphorous atom adsorption increases.

(ii) Interaction of HTPPB film (delocalized  $p$ -electron) interacted with the metal surface vacant  $d$ -orbital.

**Potentiostatic polarization:** The effects of HTPPB from the graph (Fig. 3), parameters of anodic dissolution ( $i_c$ ,  $I_p$ ,  $E_{pp}$ ) of mild steel in 1 M  $H_2SO_4$  solution of different concentration of the HTPPB can be calculated in Table 4. The value of  $I_c$  is comparatively higher than the average passive current  $I_p$ . The  $I_c$  increase when concentration decreases. At higher concentration of inhibitors show low value of  $I_c$ , that is why HTPPB shows passivating behaviour at all the concentrations. The synergistic effect is very much effective in the presence of Br.

**Table 4.** Anodic dissolution parameters of mild steel in 1 M  $H_2SO_4$  in the presence of HTPPB, electrochemical data

Inhibitor	Strength of solution	$I_c \times 10^2$ (mA/cm <sup>2</sup> )	$I_p$ (mA cm <sup>-2</sup> )	$E_{pp}$ (mV) (Range)
HTPPB	$10^{-3}$	–	–	–
	$10^{-5}$	3.54	0.15	520–1520
	$10^{-7}$	3.98	0.63	485–1515

The overall electron density on the molecules increases because of delocalised electrons of inhibitor and it has been equally adsorbed. The HTPPB is able to form passive layer for all concentrations due to their better adsorption and less steric hindrance at higher concentration of  $10^{-3}$  M. Because of the reduction  $I_c$  and  $I_p$  considerably it adsorb on the metal surface and form complex different type i.e.  $(M-In-A)_{ads}$ ,  $(M-In)_{ads}$  or  $(M-A-In)_{ads}$  it influences the parameters of anodic dissolution at the passive range. Mild steel has a passive film which is a combination of above complex.

*Studies of infrared spectra:*

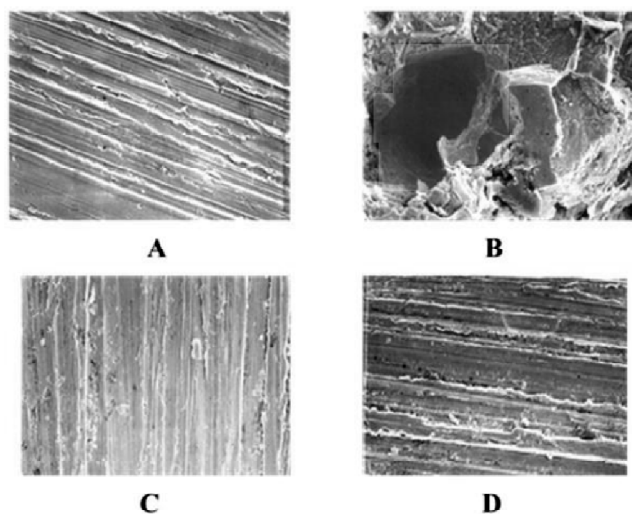
Comparative IR spectra of pure additive and that adsorbed are in Table 5. From IR got the result that many predominant peaks moved towards higher frequencies or disappeared and it may appear with reduced intensities. Now it has been confirmed that, these additive adsorption happens on silica gel. The purpose of IR adsorption studies is about these additive are adsorbed to a certain extent on silica gel. This adsorption shall also occur on mild steel surface. Because it has iron as a major constituent. The vacant *d*-orbital of Fe will be expected to have some interaction with the delocalized electrons associated with this additive.

**Table 5.** HTPPB infrared bands for pure and adsorbed (on silica gel)

Inhibitor	(C-H) bend. Ar. sub. (cm <sup>-1</sup> )	(P-Ar) str. (cm <sup>-1</sup> )	(P-CH <sub>2</sub> ) str. (cm <sup>-1</sup> )	(C-C) Ar str. (cm <sup>-1</sup> )
HTPPB	690.57, 791.24	1482, 1156.40, 996	1433	1585
(HTPPB) <sub>ads</sub>	691.82, 796.28	–	1442	–

*Scanning electron microscopy:*

SEM (scanning electron microscopy) of mild steel surface in presence of 1 M H<sub>2</sub>SO<sub>4</sub> in 10<sup>-3</sup> M and 10<sup>-7</sup> M HTPPB concentrations respectively at magnification, from Fig. 4(c) and (d) shows almost 92% metal surface is being covered by inhibitor molecule. The overall result gives an idea that

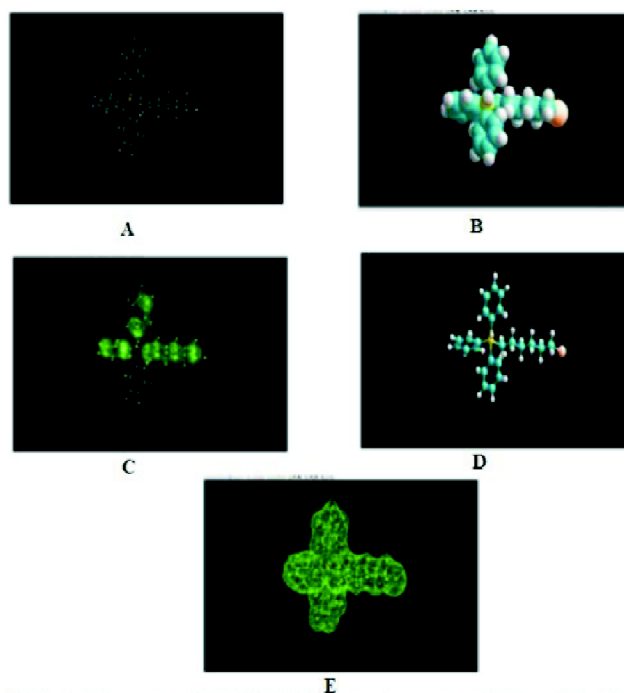


**Fig. 4.** SEM images of (A) mild steel, (B) mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> and (C) 10<sup>-3</sup> M HTPPB and (D) 10<sup>-7</sup> M HTPPB.

the HTPPB is a very effective inhibitor at 298 K and supplement the earlier results obtained from galvanostatic and potentiostatic techniques.

*Quantum chemical analysis:*

The relation between inhibition characteristics and quantum chemical data shows that log *I*<sub>corr</sub> mostly depends upon the energy of the HOMO and LUMO. In addition to the data, it can also be related to dipole moment charge on phosphorous and the shapes of the additive. The energy of HOMO is the theoretical analogue of the ionization potential of the additive whereas, the energy of LUMO represent electron affinity of the substance, that is why good donor and bad acceptor will be indicator of good inhibitor. Dipole charge value indicate that there is a possibility of donation of electron in the metal surface. In case of HTPPB, as shown in Fig. 5(a) and (b), do not make them a perfect donor of electron as is expected from quantum calculation and the cause of the cracks in protective layer, that's why it is a good passivator at low concentration and not at high concentration. But the high value of synergistic effect, Br<sup>-</sup> and less steric hindrance



**Fig. 5.** Optimized geometry of HTPPB: (A) optimized geometry, (B) space filled model, (C) isosurface of total charge density, (D) ball and stick model and (E) electrostatic potential mapped onto 3-D isosurface of total charge density.

makes HTPPB a better inhibitor. From the HOMO and LUMO value it can be seen that additive could be an effective inhibitor because of synergetic effect of  $\text{Br}^-$ , with the help of Table 6.

**Table 6.** Optimized AM1 parameters for HTPPB using Hyperchem

Sl. No.	Inhibitors	HTPPB
1.	No. of electrons	136
2.	Total energy (kcal/mol)	-86427.450
3.	HOMO (eV) energy	-8.732602
4.	LUMO (eV) energy	-0.1540903
5.	Binding energy (kcal/mol)	-5574.190893
6.	Energy (kcal/mol) of isolated atom	-80853.3188
7.	Electronic energy ((kcal/mol)	-733047.9526
8.	Core-core interaction (kcal/mol)	646620.5023
9.	Enthalpy of formation (kcal/mol)	88.3951071

## Experimental

*Preparation of HTPPB:* All the chemicals used were of A.R. grade. 1.0 ml of triphenylphosphine was dissolved in minimum quantity of toluene and 1.2 mol of hexylbromide was added to it. The mixture was refluxed for 4–6 h. The solid was filtered and washed with excess toluene. The white crystals of HTPPB were obtained. The solid was crystallized from  $\text{CHCl}_3$ /petroleum ether, characterized by standard techniques and melting point was recorded 442 K. Mild steel grade IS: 226 sample used for corrosion studies.

The dimensions of specimen were 0.8 cm×0.8 cm×0.2 cm. Each mild steel specimen were made by covering with epoxy resin (araldite) and grinded so well to make it flat and shinning for corrosion studies. The electrochemical cell (assembly of three electrode) system has been used for Tafel polarization and potentiodynamic polarization studies. Corrosion studies has occurred in 1 M  $\text{H}_2\text{SO}_4$  at different concentration  $10^{-3}$  M,  $10^{-5}$  M,  $10^{-7}$  M of HTPPB. A saturated calomel electrode was used as reference electrode (platinum) as counter electrode and working electrode (mild steel). JULABO-40 thermostat was used for controlling the temperature of the cell. Perkin-Elmer Infrared Spectroscope IR-37 was used for recording the IR spectra in KBr medium. In dry chloroform, a saturated solution of the inhibitor was prepared. A small quantity of silica gel was added in solution and stirred vigorously. The solvent get evaporated and the sample was dried. Small quantity of dry sample used for FTIR analysis.

Surface analytical technique was performed on JEOL-840 (SEM). Specimen were washed thoroughly in double distilled water and dried in a desicator before SEM investigation.

## Conclusion

According to data of adsorption of HTPPB on mild steel surface in acid solution draw the conclusion with the help of galvanostatic, temperature kinetics, potentiostatic polarisation studies, surface characterization, SEM, IR and quantum chemical calculation. It has been found that:

(i) HTPPB retard corrosion at ordinary temperature but enhance it at higher temperature. This shows that they belong to Putilovas 1st category of inhibitor.

(ii) HTPPB are mixed inhibitor shows neither appreciable shift of  $E_{\text{corr}}$  towards any direction nor insignificant shift of OCP value (Open Current corrosion Potential).

(iii) Tafel slope shows irregular trend indicates that adsorption of the inhibiting species is governed by other ions present in the solution.

(iv) Temkin's and Freundlich's theory is adequate for explaining adsorption isotherm at all temperatures because it is multilayer adsorption.

(v) Value of  $Q$  and  $E_{\text{eff}}$  indicate HTPPB is chemisorbed on the mild steel.

(vi) Inhibition efficiency decrease with increase in temperature but it shows better inhibiting properties over wider range of temperature.

(vii) According to potentiodynamic studies concluded that this inhibitor strongly adsorbed above metal surface and is very good passivators in 1 M  $\text{H}_2\text{SO}_4$ . This passivation depends of already adsorbed anions which is present in the medium.

(viii) Quantum chemical calculation shows that HTPPB is a better inhibitor because of synergistic effect of  $\text{Br}^-$ .

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