Corrosion Inhibition of Mild Steel by Ethyltriphenylphosphoniumbromide (ETPPB) in Acid Medium

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Abstract: The efficiency of ethylxyltriphenylphosphoniumbromide (ETPPB) as an inhibitor to investigate corrosion inhibition for mild steel in the presence of phosphoric acid. Electrochemical techniques such as galvanostatic and potentiostatic polarization studies which was used to study the inhibitor behavior. Corrosion parameters was calculated by Tafels slopes at four different temperatures (298 K, 308 K, 318 K, 328 K). It suggests that ETPPB shows inhibition efficiency more than 90%. Inhibitor is well absorbed at the metal surface at higher temp also, due to lag of time between adsorption and desorption make it Putilova's first class of inhibitor. Potentiodynamic polarization studies suggest that ETPPB is mixed type of inhibitor. Themodynamic studies revealed that ETPPB obeyed Temkin's and Freundlich adsorption isotherm

Keywords: Ethyltriphenylphosphonium bromide; Galvanostatic Studies, Potentiostatic Polarization studies, Thermodynamic studies, Infrared spectroscopy, Quantum chemical calculations, Electrochemical impedance spectroscopy, Scanning electron microscopy

1. INTRODUCTION

A thing which comes into existence with human resources is bound to revert back to it's original form unless it is prevented by human being by some scientific method. Metal has become an integral part of human being from middle age to present B-52 Fighter plane. The growing need of metal in every walk of life and loss of it by corrosion has put a big question mark before the mankind regarding how to prevent it from being corroded so that it can be used to its maximum extent. One of the most widely and easy method to protect metal from being corroded is the use of corrosion inhibitor. There are many types of corrosion inhibitors such as cathodic inhibitor, anodic inhibitor, Passivating inhibitor, Organic inhibitor, volatile inhibitor, Neutralizing inhibitor, Precipitators, Absorbents, Inorganic inhibitors. The inhibiting effect of phosphonium based compound occurs because phosphorous act as heteroatom in homologous series of organic compound is easily polarizable because of its large size and lower electronegativity compared to other heteroatom. Mostly, the good inhibitors with an aromatic character having pi bond which inter act with metal surface very easily. Some of the electron donating groups having N (1-11), S(12-18), O(19-21) attached with the organic compounds increases inhibition efficiency. Now a day's series of quaternary phosphonium compounds are using as a biocide against micro and macro organism. Biocidal properties of phosphonium compounds make it environment friendly and synergistic effect shown by bromide boost its biocidal properties. Phosphonium compound also used in ionic liquids, lubricants, and other materials (22-30).

In this investigation H_3PO_4 is used instead of H_2SO_4 and HCI of corrosion inhibitor. The key component of phosphoric acid is phosphorous which is present in body naturally it works with calcium to form strong bones, helps kidney and muscles recovery. Now its environment friendly nature makes it good solvent. It is a good fertilizer for plant. Phosphoric acid is made from the mineral phosphorous. Phosphoric acid is a major chemical product which has many important uses especially in the production of fertilizers. It is also used as dust remover from metal surface and when the ferric phosphate which has been produced by ferric oxide is wiped off, it gives new appearance to the metal surface. Therefore, the inhibition efficiency of ETPPB for mild steel in 0.5 M H_3PO_4 solution have been studied by following characteristics: Galvanostatic studies, Potentiodynamic polarization, thermodynamics study and scanning electron microscopy.

2. EXPERIMENTAL

2.1. Materials

The working electrode were made by a mild steel rod having composition of

(wt %): C (0.15), Si (0.31), S (0.025), Mn (1.02) and Fe.

2.2. Solutions

All solutions were prepared from double distilled water, conductivity is 5.5×10^{-6} S.m^{-1} and AR grade with $\geq 98\%$ purity of H_3PO_4 was used. The inhibitor concentration was $10^{-3}, 10^{-5}, 10^{-7}$ in 0.5 M Phosphoric acid.

2.3. Electrochemical measurements

The working electrode was made by cutting mild steel rod and one end of copper wire was soldered and embedded in epoxy resin (ARALDITE) and left 1 cm^2 exposed surface area for the studies. The platinum electrode act as counter electrode while saturated calomel electrode worked as a reference electrode coupled by a lugging capillary. The potential of the metal electrode versus reference electrode was measured. A detailed study of the steady state Potentiostatic behaviour of the anodic dissolution of mild steel in the presence and absence of various concentration of an inhibitor. Potentiodynamic polarization curve were attained with a scan rate of 0.01 Vs^{-1} the range from -1.2 V to 0.2 V relative to the corrosion potential (E_{corr}). During the course of SEM well grinded and polished samples of mild steel (1cm x 1cm x 1cm) is being required. These sample of MS dipped completely in 0.5 M H_3PO_4, 10^{-3}M ETPPB, 10^{-5} ETPPB, 10^{-7} M ETPPB in inhibitors solution for 24 Hours at room temp. After 24 Hours sample was taken out from the solution and dried inside the desiccator for 24 Hours and sample was ready for SEM. Images of SEM were received by using operative voltage of (15-30) kV with digital imagine and 35 mm photography system.

2.4. The structure of ETPPB

ETPPB, the organic additive $C_2H_5P(C_6H_5)_3Br$ is shown in figure 1.

The Physical properties of ETPPB; M.Wt = 388.88g, Assay 97% and M.P = 325-330 ^{0}C
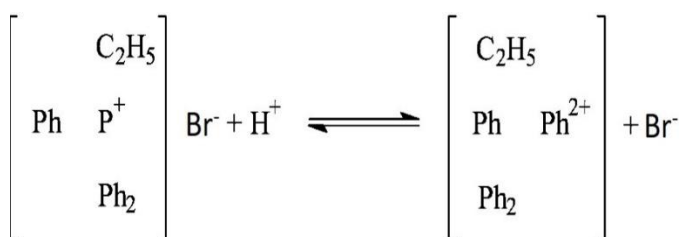

Fig. 1. Molecular structure of ETPPB.

3. RESULTS AND DISCUSSION

Galvanostatic polarization studies

During the course of galvanostatic studies of mild steel at four different temperature i.e. 298 K, 308 K, 318 K and 328 K and 0.5M H_3PO_4 all the parameters have been calculated by cathodic and anodic polarization curves (Fig 1.2-1.4) with the help of Log of current density vs corresponding electrodes. Tafel slopes in graph describes the mechanism of hydrogen evolution and metal dissolution by plotting graph potential versus Logarithm of current density. The open circuit potential against SCE always measured before each cathodic and anodic polarization studies. As graph shows that corrosion current value directly proportional to temperature and the change in Tafel slopes value suggest that the reduction in E_{corr} is being caused by delocalization of three phenyl ring and also assisted by Br- ion which is having synergistic effect.

The decrease in corrosion current density with increase in inhibitor concentration is observed at all four temperatures. During cathodic polarization the adsorption will be because of the overall resultant positive charge on the additive. Therefore, ETPPB in acidic media gets ionized and there is a distinct probability of this getting protonated species as per reaction below:
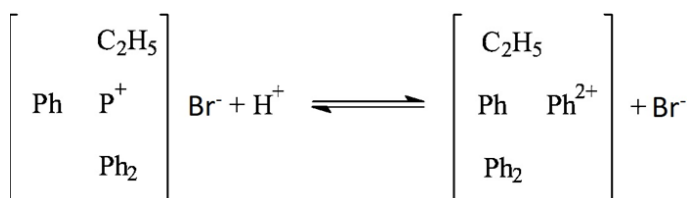

In the process of corrosion inhibition both molecular and protonated species would be absorbed by blocking active sites along with synergistic effect of Br- at the time of cathodic polarization. As the number of different species involved in blocking the active sites, Hence Tafel slopes value shows irregular trends for both the polarization cathodic and anodic when concentration increases both molecular and protonated species increases but the molecular species are always higher therefore extent of inhibition is higher at higher concentration. At lower concentration and higher temperature the adsorption becomes weaker because time gap between adsorption and desorption becomes shorter that will lead to greater exposure of the bare surface that leads to lesser inhibition. At 298K, 308K, 318K and 328K. After plotting the graph between the polarizing potential and logarithm of current densities results

are mentioned in table 1.1 and 1.2. Information is being gathered by Tafel slopes shows that ETPPB do not show any shift in OCP (Open circuit potential) towards any direction. Table 1.2 clearly indicates by showing no appreciable change in Ecorr value which signifies that, It is mixed type of inhibitor There is decrease in corrosion current I_{corr} value at lower temperature (298K) as compared to the change in corrosion current value at higher temperature (328K) as the concentration changed from 10^{-3} and 10^{-7} M. The corrosion current value is inversely proportional to the corrosion. So that ETPPB belongs to Putilova's first class of inhibitor. Irregular trend of Tafel slopes shows that by increasing temperature Icorr value decreases and process of inhibition also decreases. It belongs to Putilova's first class of inhibitor.

Polarization data reveals the functioning of the inhibitor by following ways:

(i) It occurs by blocking cathodic polarization reaction active site and Br- provides synergistic effect to inhibition process. Therefore, ETPPB in acidic medium undergoes protonation and form protonated species given below.

(ii) $In + H^+ \leftrightarrow [In\ H]^+$
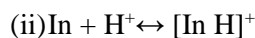
At the time of anodic polarization adsorption occurs between the metal ion and the delocalized additive system .On the basis of structure of inhibitor ,It has been clear that p electron of inhibitor molecule overlap with the vacant d orbital of Fe^{2+}, Fe^{3+} which retards metal dissolution when the anodic current value increases the ions Cl^-, OH^- which has been present in the solution attached with the metal surface formed metal hydroxide $(M-OH)_{ads}$ which is present in the form of adduct of the type $(M-In)_{ads}$ or type $(M-OH-In)_{ads}$ / $(M-In-Br)_{ads}$ / $(M-In-OH-Br)_{ads}$ / $(M-In-Br-OH)_{ads}$ / $(M-Br-OH-In)_{ads}$.

Thermodynamic and adsorption studies of mild steel in the presence of ETPPB in acid medium

The plot of I% vs Log C (Fig 2.1) gives following information related with heat of adsorption and activation energy. It follows Langmuir adsorption isotherm because time lag between absorption and desorption is very short at higher temperature and it becomes monomolecular at any time but the data for ETPPB usually fits in Temkin and Freundlich's adsorption isotherm where heat of adsorption (Q) of ETPPB is being calculated by graph between $log\Theta/1-\Theta$ vs 1/T, (Fig 2.2-2.6) the value of heat of adsorption is calculated by straight line portion of the curve for 10^{-3} to 10^{-7} inhibitor shown in Table 2.1 and table 2.2. The value of Q support the chemisorption that's why the corrosion inhibition efficiency is above 92% Since corrosion rates directly related with corrosion current, inhibitor efficiencies. The plot between log i_{corr} vs 1/T (Fig 2.4) shows energy of activation at various concentration and it has been found that ETPPB has higher E_{eff} than 0.5M H_3PO_4 in the corrosion process. On the basis of above discussion result come out, that the ETPPB inhibitor is well absorbed at the metal surface and at higher temp due to lag of time between adsorption and desorption make it Putilova's first class of inhibitor.

Potentiostatic polarization

The graph Fig describes the effect of ETPPB. All the parameters of the anodic dissolution (i_c, I_p, Epp) of mild steel in the solution of 0.5M H_3PO_4 at different concentration of the ETPPB has given in table 3.1 (Fig 3.1-3.2). The corrosion current(i_c) value is usually higher than the average passive current

(Ip) value. The concentration of inhibitors is inversely proportional to the value of i_c. So that ETPPB shows passivation at all the concentrations and presence of Br- increases synergistic effect and plays crucial role in passivation. Inhibitors are equally absorbed on molecules because electron density increases due to delocalized electrons of inhibitors due to better adsorption and less stearic hinderance ETPPB form passive layer at all concentrations. Mild steel possesses passive film which is a combination of $(M-In-A)_{ads}$, $(M-In)_{ads}$ or $(M-A-In)_{ads}$. These complexes form due to reduction of I_c and I_p.

Studies of Infrared Spectra

By comparing the studies of additive on silica gel and surface of mild steel. The interaction takes place between vacant d-orbital of iron and delocalized electrons of additive. The main objective of IR studies is too familiar with the additive's adsorption on silica gel and mild steel. Conclusion drawn from this study that many predominant peaks moved towards higher frequencies or disappeared, it is also possibility that it may appear with reduced intensities. Now it is very much clear that adsorption which is happened on silica gel and mild steel (iron is major constituent).The vacant d-orbital of Fe shows some interaction with the additive's delocalized electrons.

Scanning electron microscopy (SEM)

The overall result of SEM for ETPPB shows that it is very effective inhibitor at 298K in the presence of 0.5 M H_3PO_4 and 10^{-3}M ETPPB, 10^{-5}M ETPPB, 10^{-7}M ETPPB, concentration respectively at different magnification. It shows almost 92% surface of mild steel covered by inhibitor molecule.

4.   CONCLUSION

On the basis of experimental data of adsorption of ETPPB at the surface of mild steel in acid solution. The result obtained while doing the galvanostatic, Potentiostatic, temperature kinetics, surface characterization, SEM and IR. These conclusions have been drawn.

1)   There is no appreciable shift of Ecorr towards any direction and no insignificant shift of OCP (Open circuit potential) that's why ETPPB is a mixed type of inhibitor.

2)   Irregular trend of Tafel slope shows that the other ions present in the solution is governed by the adsorption behaviour of inhibiting species.

3)   It is multilayer adsorption that's why Temkin's and Freundlich's theory is sufficient to explain adsorption isotherm at all temperature.

4)   ETPPB is chemisorbed on the mild steel explain by the value of Q and E_{eff}.

5)   While increasing temperature inhibition efficiency decreases but it gives better properties under wide range of temperature

6)   Potentiodynamic studies shows that the inhibitors are very good passivator due to strong absorption over metal surface in 0.5M H_3PO_4.

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TABLE 1.1: Corrosion parameter for mild steel in 0.5N H_3PO_4

TEMP	$-E_{CORR}$	B_C	I_{CORR}
(K)	(mv)	(mv/dec)	mA/cm^2
298	470	140	4.6
308	465	55	5.1
318	455	45	9.0
328	450	50	12.0

TABLE 1.2: Galvanostatic data of mild steel in 0.5N H_3PO_4 in presence of ETPPB

Temp	Conc.	$-E_{Corr}$	b_c	I_{Corr}	I
(K)	(mol^{-1})	(mv)	(mv/dec)	mA/cm^2	(%)
298	10^{-3}	493	181	.20	93%
	10^{-5}	497	127	.78	80%
	10^{-7}	470	80	1.1	68%
	H_3PO_4	470	135	4.6	–
308	10^{-3}	494	175	.30	91%
	10^{-5}	497	75	1.1	71%
	10^{-7}	468	94	1.3	68%
	H_3PO_4	465	55	5.1	–
318	10^{-3}	495	240	1.0	80%
	10^{-5}	500	70	3.8	51%
	10^{-7}	440	75	5.5	30%
	H_3PO_4	455	45	8.0	–
328	10^{-3}	500	245	2.5	65%
	10^{-5}	481	55	4.2	50%
	10^{-7}	442	60	6.0	31%
	H_3PO_4	440	245	11.0	–

TABLE 2.1:   Calculated values of Q and E_{eff} for the corrosion of Mild Steel in 0.5 M H_3PO_4 in the presence of ETPPB

Concentration mol l^{-1}	−Q (Kcal mol^{-1})	E_{eff} (Kcal mol^{-1})
10^{-3}	27.65	26.60
10^{-5}	20.10	23.30
10^{-7}	21.20	23.84
H_3PO_4	−	13.80

TABLE 2.2 : Thermodynamic studies of Corrosion of mild steel in 0.5 H_3PO_4 in the presence of ETPPB

Temp (K)	Conc. (mol l^{-1})	i_{corr} (mA/cm^2)	log i_{corr}	I%	Ө	Ө/1-Ө
298	10^{-3}	.20	−0.6989	94	.94	15.0
	10^{-5}	.78	−0.1071	80	.80	5.00
	10^{-7}	1.1	0.0413	70	.70	2.33
	H_3PO_4	4.6	0.6627	−	−	−
308	10^{-3}	.30	−0.5228	92	.92	11.50
	10^{-5}	1.1	0.0413	73	.73	2.70
	10^{-7}	1.3	0.1139	69	.69	2.22
	H_3PO_4	5.1	0.7075	−	−	−
318	10^{-3}	1.0	0.0000	81	.81	4.26
	10^{-5}	3.8	0.5797	52	.52	1.08
	10^{-7}	5.5	0.74036	30	.30	0.42
	H_3PO_4	8.0	0.9542	−	−	−
328	10^{-3}	2.5	0.39794	68	.68	2.12
	10^{-5}	4.2	0.62324	61	.61	1.56
	10^{-7}	6.0	0.77815	40	.40	0.66
	H_3PO_4	11.0	1.04139	−	−	−

TABLE 3.1 Electrochemical parameters for anodic dissolution of mild steel in 0.5M H_3PO_4 in the presence of ETPPB

Solutions	Concentrations	$i_c \times 10^2$ (mA cm^{-2})	i_p (mA cm^{-2})	Epp mV (Range)
H_3PO_4	0.5 M	2.81	1.25	475-1550
HTPBB	10^{-3}	2.18	0.46	495-1395
	10^{-5}	3.10	0.79	500-1450
	10^{-7}	3.68	2.21	480-1490
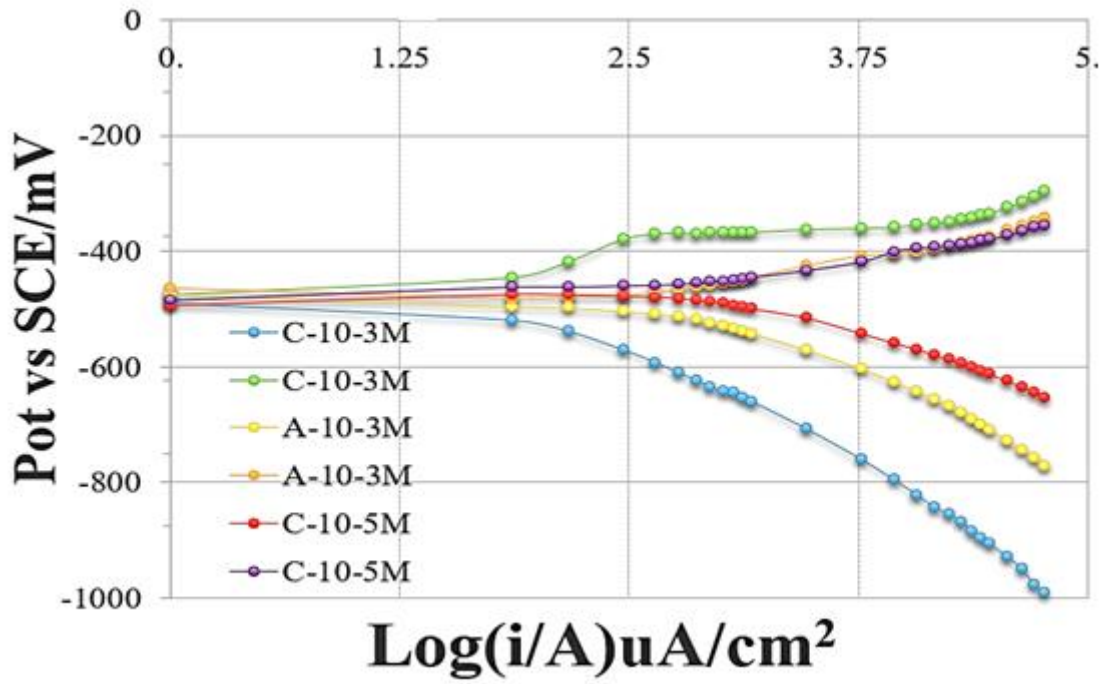
Fig 1.1: Tafel Polarization Curves for mild steel in 0.5N H₃PO₄ solution containing various concentration of ETPPB at 308 K
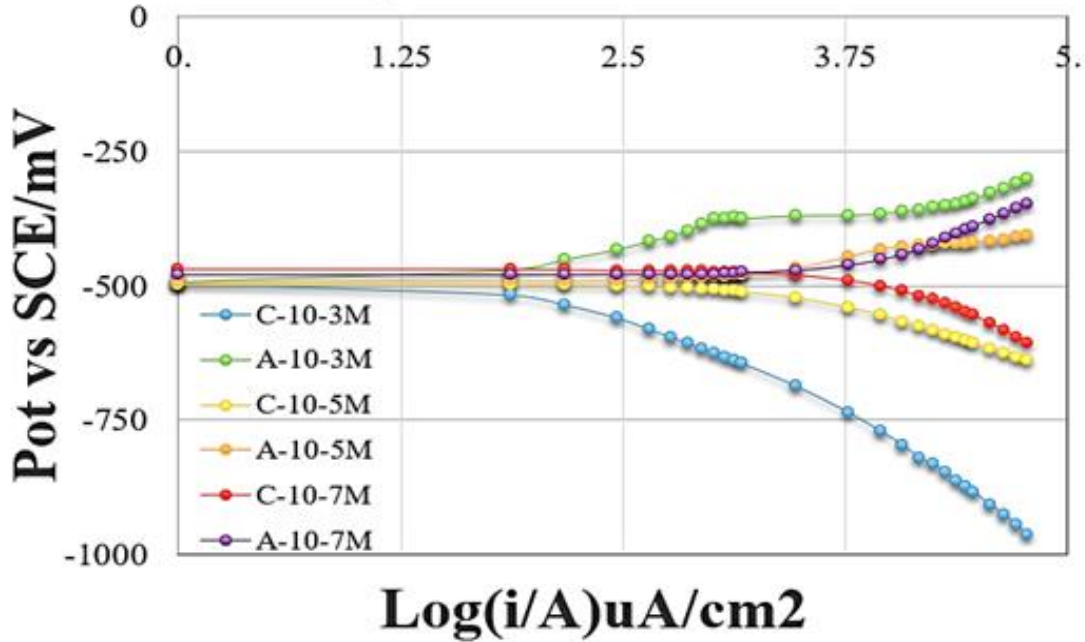

Fig 1.2: Tafel Polarization Curves for mild steel in 0.5N H₃PO₄ solution containing various concentration of ETPPB at 308 K
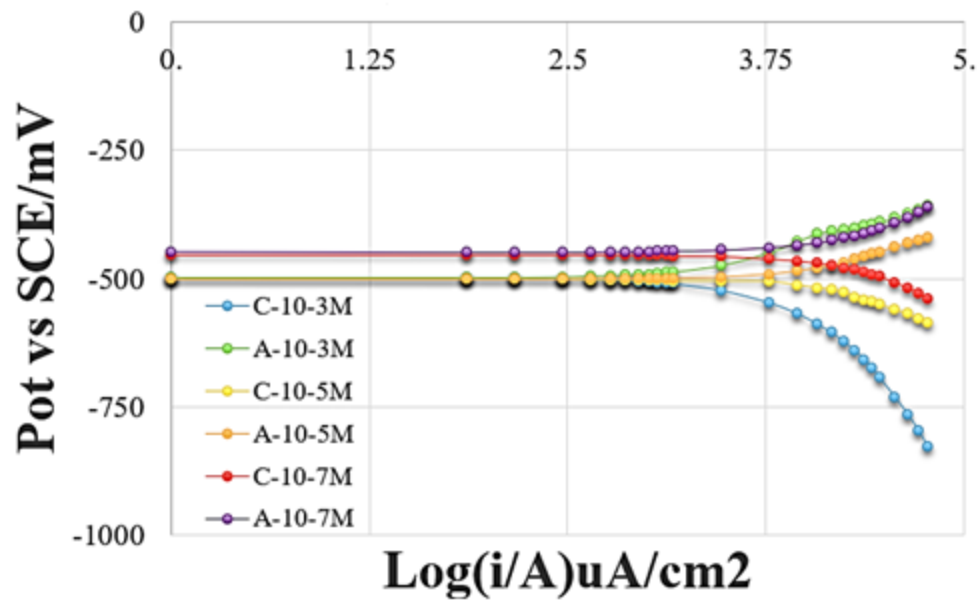
Fig 1.3: Tafel Polarization Curves for mild steel in 0.5N H₃PO₄ solution containing various concentration of ETPPB at 318 K
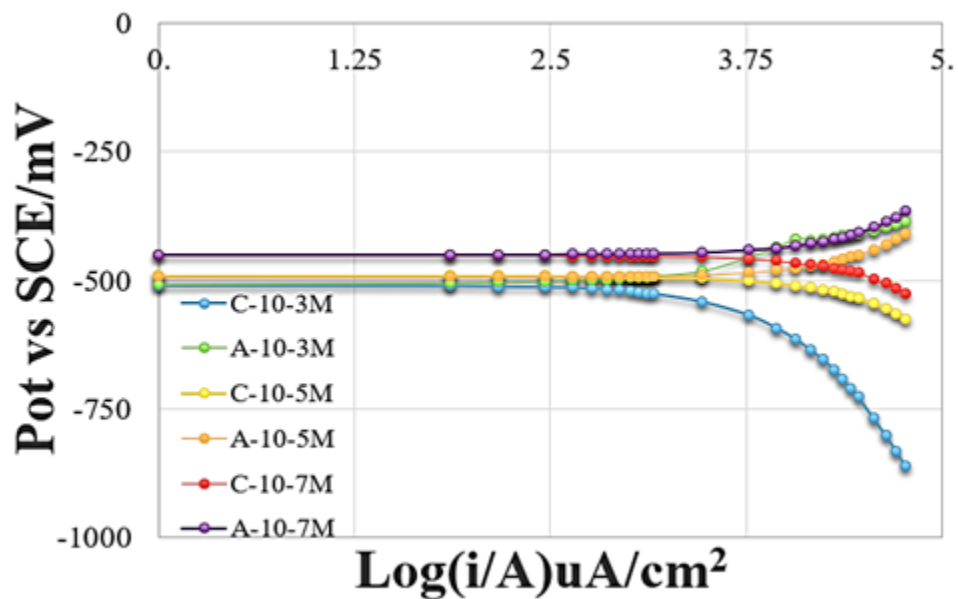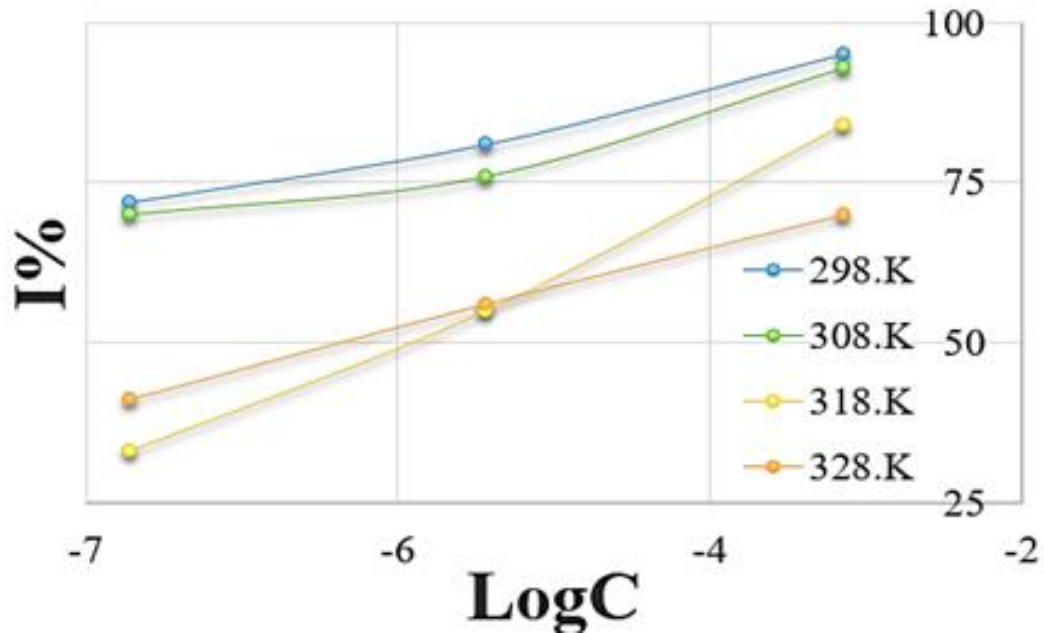

Fig 1.4: Tafel Polarization Curves for mild steel in 0.5N H₃PO₄ solution containing various

concentration of ETPPB at 328 K

Fig 2.1: Inhibition efficiency Vs concentration of ETPPB at different temperature
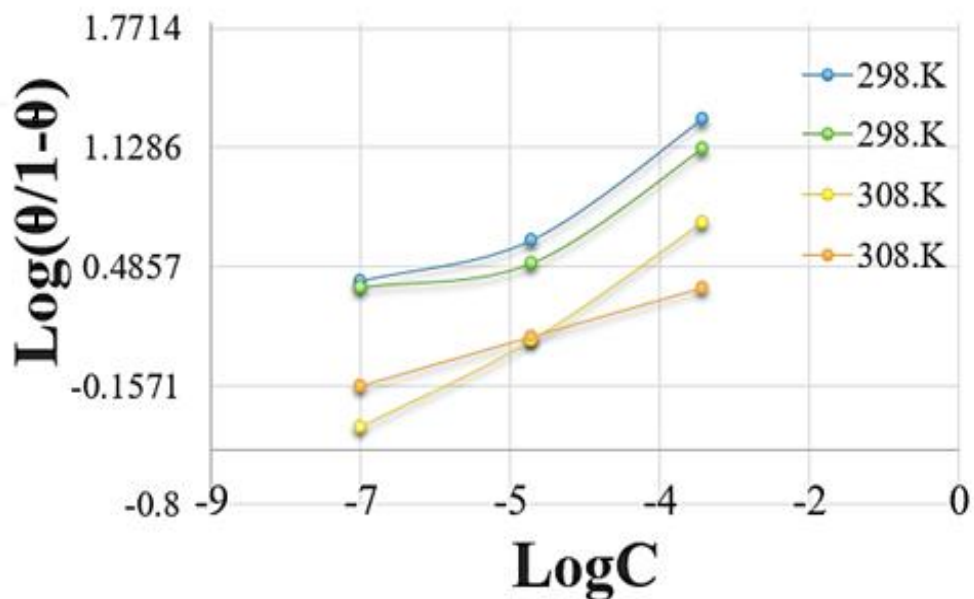
Fig 2.2 Variation of Surface coverage Vs Concentration of ETPPB at different temperature
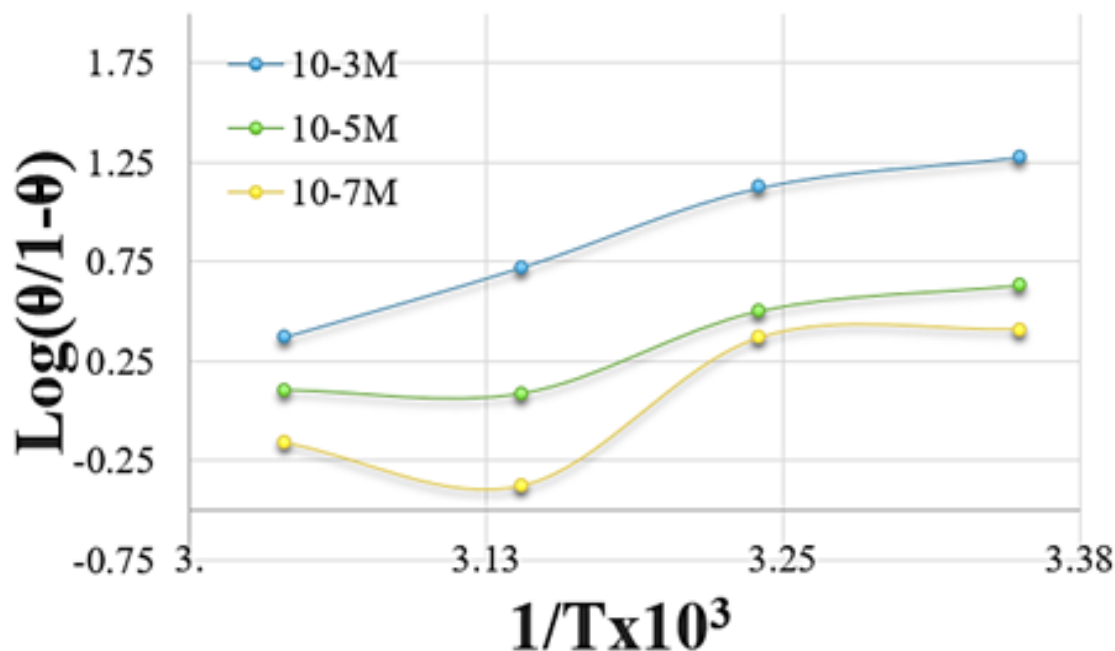
Fig 2.3 Variation of Surface coverage Vs reciprocal of temperature at different concentration of ETPPB
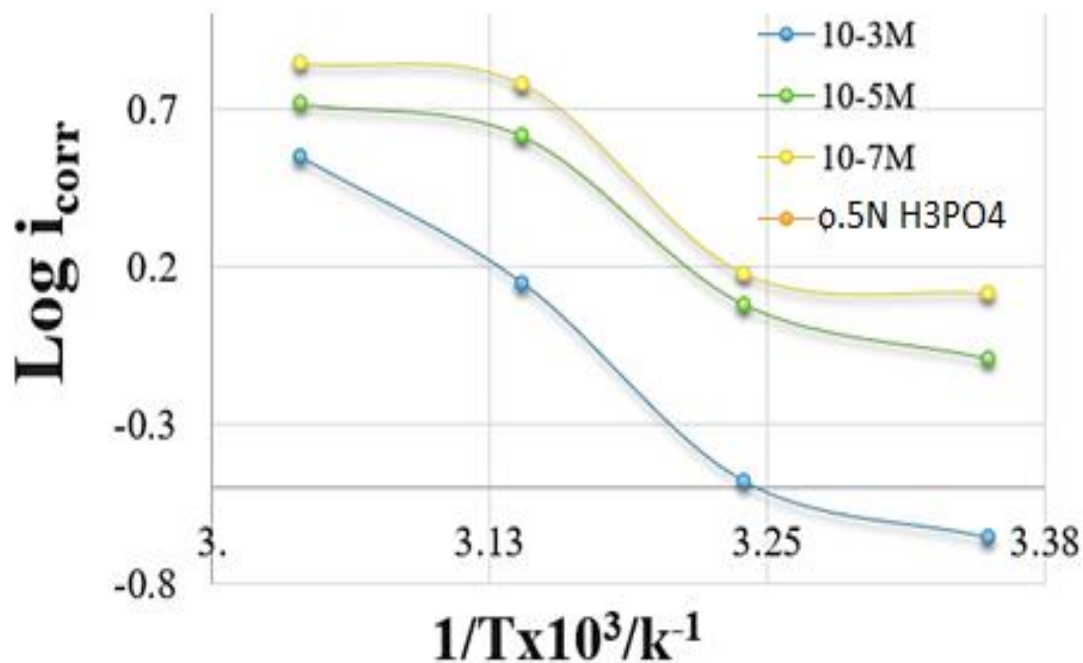
Fig 2.4 Variation of corrosion current Vs reciprocal of temperature at different concentration of ETPPB
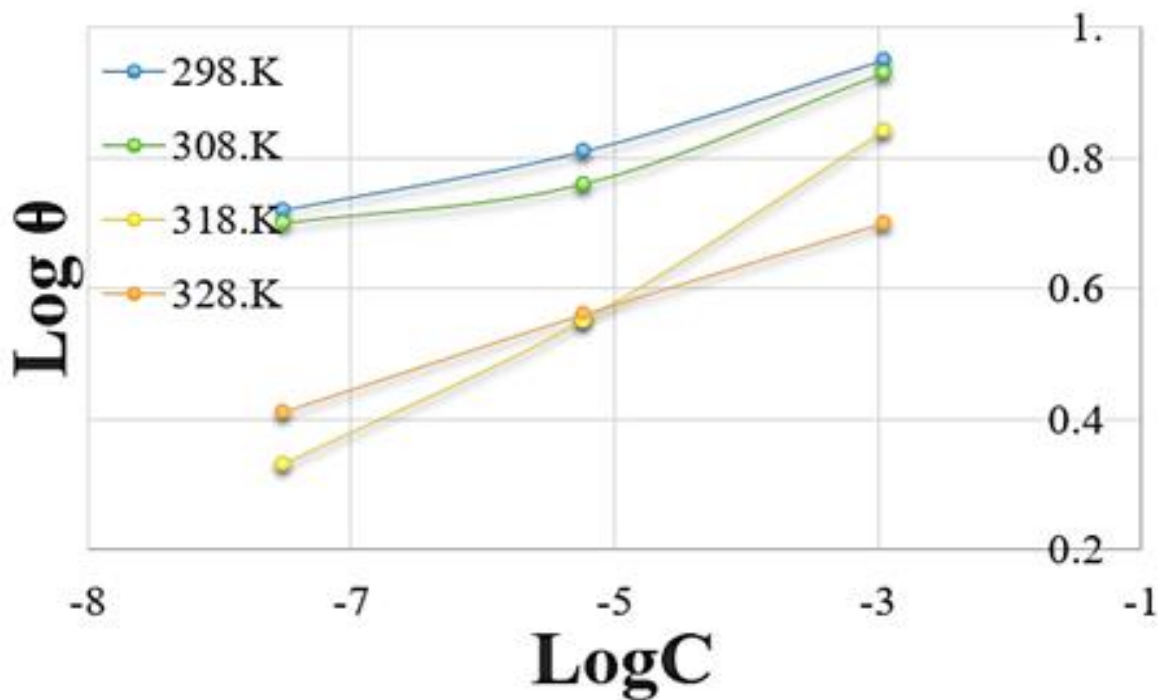
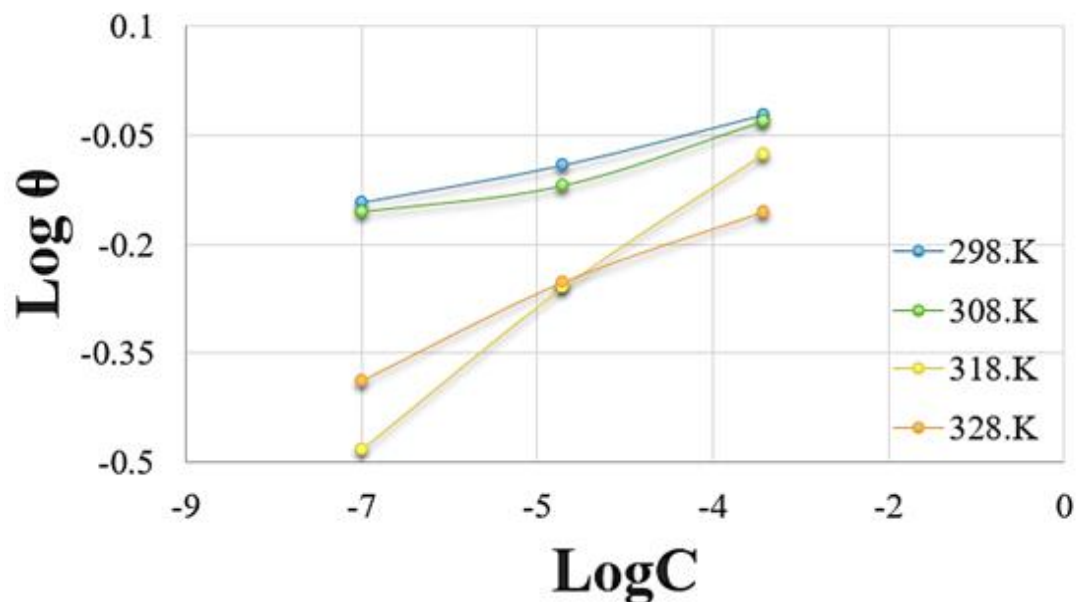**Fig 2.5 Surface coverage Vs Concentration of ETPPB at different temperature (Temkin's isotherm)**

Fig 2.6 Surface coverage Vs Concentration of ETPPB at different temperature (Freundlich isotherm)
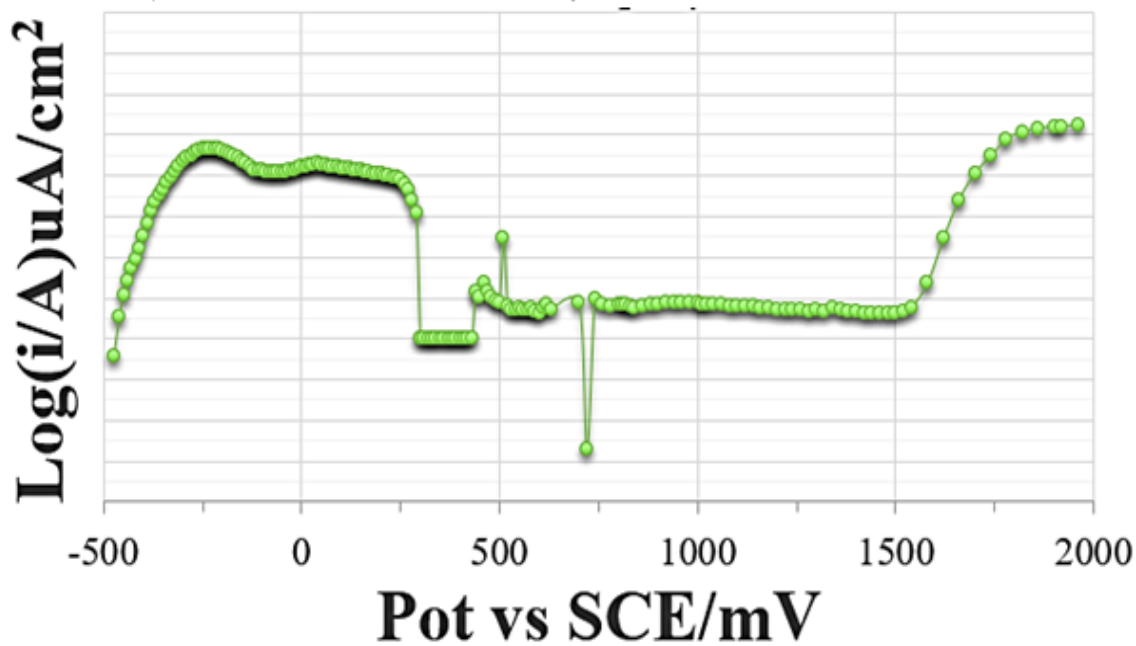
Fig 3.1 Potentiodynamic polarization curves for mild steel dissolution in 0.5N H₃PO₄ at 298 K
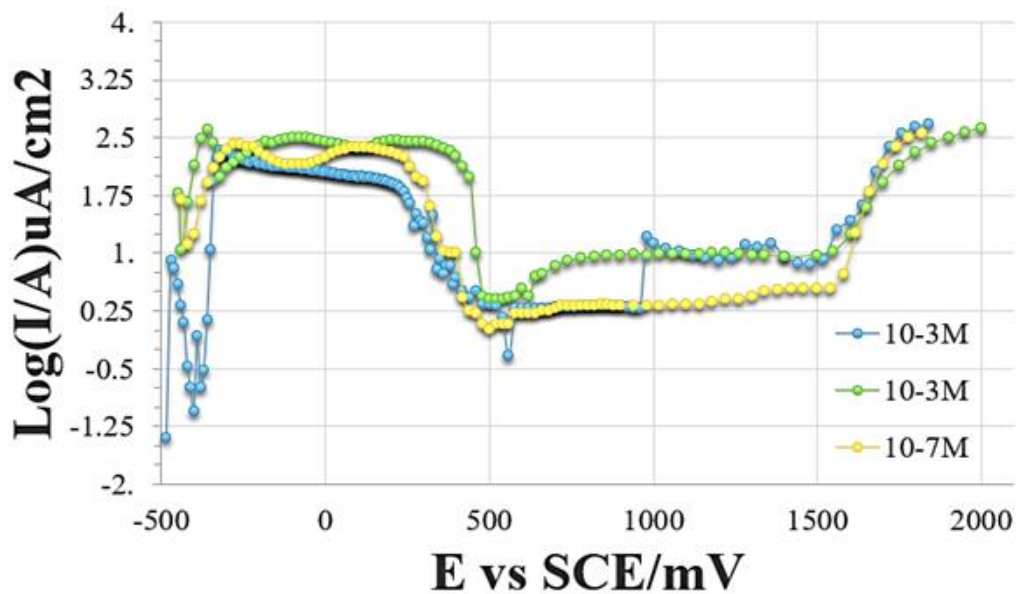

Fig 3.2 Potentiodynamic polarization curves for mild steel in 0.5N H₃PO₄ containing various concentration of ETPPB at 298 K