THEORETICAL AND WEIGHT LOSS STUDIES OF POLYETHYLENE GLYCOL TRIPHENYL PHOSPHINE AS CORROSION INHIBITOR FOR CARBON STEEL IN SULPHURIC ACID

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ABSTRACT
The Polyethyleneglycol Triphenyl phosphine (PEGTPP) was observed to be an efficient inhibitor for carbon steel corrosion in acidic sulphuric acid medium with the help of quantum chemical calculations and weight loss methods. High surface coverage on metal surface was revealed by the inhibition efficiencies at different concentrations of inhibitor. Corrosion rates are controlled to an apparent level in the presence of inhibitor into the corrosive medium. With increase in the concentration, the degree of adsorption of inhibitor molecules increases on carbon steel increases. The inhibition efficiency decreases with temperature. The negative values of binding energies and the heat of formation suggest that PEGTPP molecules are very stable and less prone to decompose. This paper presents a general review of the inhibitive action of Polyethyleneglycol triphenyl phosphine against corrosion of carbon steel in acidic media.

KEYWORDS*: Carbon steel; Weight loss method; Acidic medium; Quantum chemical calculations; Corrosion inhibition

INTRODUCTION
Corrosion is the deterioration of a material when exposed to its environment [i]. It is a challenge for human architect since ancient times but with modernization the issue become vast as it grubs a big share of world's economy [ii-v]. On average in every country, 3-5% of its GDP is lost due to corrosion problems. This is direct loss but indirectly it costs much more than our estimate. . In India, corrosion costs Rs. 2 lakh crores loss a year [vi]. There are many sectors like transportation, aircraft, automobiles, oil refineries where losses due to corrosion is very high. Corrosion is a continuous process, often difficult to eliminate completely. Metal are highly prone to corrosion in almost every environment and loss of strength, aesthetic and structural

property are the major aftermaths. Carbon steel is largely used for structural materials due to extra strength. Acidic environments damage the metal to large extent as comparison to other medium. Various strategies are taken into consideration to deal with the corrosion loss in acidic medium but use of corrosion inhibitor is among the most widely used techniques. One major advantage to use inhibitor for metal corrosion in acidic medium is that in this environment dissolution of corrosion products (e.g. metal oxides) take place so the direct interaction of inhibitor molecules with metal substrate occur which is not possible into aqueous or alkaline medium.

Most of the well-known inhibitors in acidic environments are organic compound with aromatic character with hetero atoms and π bonds. They generally exhibit good inhibitor properties due to interaction of electron rich centres of inhibitor molecules with vacant d orbitals of metal. It is well established fact that electron rich groups containing N, S, O and P attached to organic compounds show extra corrosion mitigation [vii-xxvii]. Corrosion protection mechanism is broadly by adsorption of inhibitor molecules at the metal-solution interface.

Polymers are used as corrosion inhibitors because, of the extra adsorbing power due to repetition of similar units thereby blanketing the surface to a large extent. Mostly amine containing or conjugated polymers have been reported in the literature [xxviii-xxxi] but, so far, no attention has been paid on phosphorous based polymer. Uses of Phosphorous or phosphonium moieties generally provide biocidal properties and thermal stability [xxxii-xxxiii]. So in addition to adsorption mechanism, the used corrosion inhibitor, Poly ethylene glycol triphenyl phosphine is expected to provide biocidal effects as well as it can be used at high temperature due to extra thermal stability.

In this work, the behaviour of triphenyl phosphine was first theoretically evaluated as an corrosion inhibitor using quantum chemical calculations and further theoretical results are verified for carbon steel corrosion in 0.5 M H2SO4 at 298K, 308K, 318 K and 328K by weight loss methods. The adsorption mechanism of PEGTPP was evaluated and the various corrosion parameters were calculated and discussed.

EXPERIMENTAL:
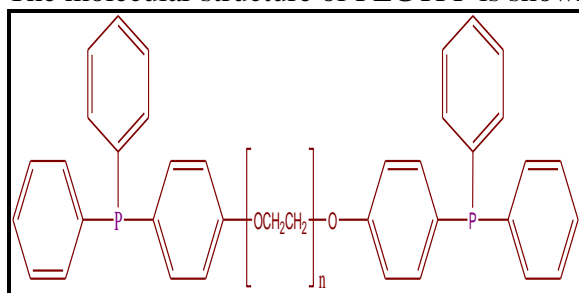The molecular structure of PEGTPP is shown in Fig 1:

Fig 1: Molecular structure of the studied inhibitor PEGTPP

Carbon steel studied is the one which usually used for structural applications. The experiments were performed with carbon steel specimen with the chemical composition (in wt% of carbon steel) as given below:

C	Si	S	P	Mn	Fe
0.15	0.31	0.025	0.025	1.02	Balance

The measurements were carried out in the aggressive solution. The aggressive solutions (test solutions) were made from AR grade H_2SO_4. 0.5 molar concentration of acid was prepared by diluting AR acids with double distilled water. The polymer based phosphonium compound

PEGTPP (Aldrich, >98 %) was used as inhibitor as received. Various concentrations of PEGTPP (150 ppm, 100 ppm, and 50 ppm) were prepared by dissolving the calculated weights in 0.5 M H_2SO_4 solution.

Weight Loss Technique
The gravimetric study was assessed at 298, 308,318 and 328 ± 2 K for all three studied concentrations of polymer with plunging time of 6 hours. For each set of observation, a freshly grinded steel coupon with surface area 1cm^2 was immersed into 50 mL of test solution; reproducible results were obtained by repeating the set twice under same conditions The rate of corrosion process C_R is calculated by dividing the actual weight loss, W (mg) of coupons by the product of Area, A (cm^2) of coupon and exposure time, t (hours) i.e C_R=W/At [xxxiv]. The corrosion inhibition efficiency IE_{WL} (%) was calculated by using the formula:

$$IE_{WL}(\%) = \frac{C_R - C_R(i)}{C_R} x100 \qquad (1)$$

Where C_R is the corrosion rate in the presence of 0.5 M H_2SO_4 solution only and and C_R (i) is the corrosion rate in with the addition of the inhibitor in 0.5 M H_2SO_4 solution. The degree of surface coverage (θ) of polymer molecules on the substrate was calculated by using the following equation:
$$\theta = IE_{WL}(\%)/100 \qquad (2)$$
Where IE is the inhibition efficiency of a PEGTPP.

The theoretical Quantum chemical analysis was completed using the PM3 mode of the quantum chemical package MOPAC 6.0 of Hyperchem 7.5. The geometries of the Inhibitor molecules were fully optimized by using the MM$^+$ (Molecular Mechanics) and then re-optimized by AM1 with Polak Ribiere gradient method. The calculations for the various molecular parameters were performed through UHF (single state calculation) method. For accuracy, the convergence limit was fixed at 0.1 kcal and the criterion of RMS gradient is at 0.1 kcal/mol.

RESULTS AND DISCUSSION
Effect of Concentration on Inhibition Efficiency:
The inhibition efficiencies for carbon steel corrosion in 0.5 M H_2SO_4 for all studied concentrations of PEGTPP at all considered temperatures (298 K, 308 K, 318 K and 328 K) are tabulated in Table 1 and variation of percentage inhibition efficiencies (IE %) against concentration of inhibitor are given in Fig.2. It is clearly seen from the Table 1 that IE % increases with increase in the concentration of additives. Maximum IE% i.e.~ 90% was shown by inhibitor at highest concentration (150 ppm) at 298 K and minimum IE% i.e.~ 49% was shown by inhibitor at lowest concentration (50 ppm) 328 K. The high value of surface coverage (θ) leads to the fact that adsorption of polymer molecules on the active site of carbon steel surface is one of the possible mechanisms of inhibition.
Further close analysis of Table 1 shows that the corrosion rate is found to decrease with increase in concentration of PEGTPP as compare to acid at all four temperatures. The inhibition efficiencies decrease with decrease in concentration of the inhibitor and it was seen that at 298 K, the inhibition efficiency for 150 ppm is found to be 90.04% and it is reduced to 76.01 % when the concentration is reduced to 50 ppm. With the decrease in the concentration of this inhibitor surface coverage decreases and a large area of unprotected specimen gets corroded resulting in lesser inhibition efficiency. The lower surface coverage at high temperature specifies that elevated temperature fast ionic mobility, leads to dissolution of the film on the

metal surface. The decrease in inhibition efficiency with increasing temperature may be due to decreasing the tendency of inhibitor to be adsorbed on the carbon steel surface [xxxv].

Table 1: Corrosion parameters of carbon steel in 0.5 M H$_2$SO$_4$ in the presence Polyethyleneglycol triphenylphosphine (PEGTPP)

| Temp. (K)	Conc. of PEGTPP (ppm)	Initial Weight I$_w$ (g)	Final Weight F$_w$ (g)	Weight Loss (g)	C$_R$ (mgcm^{-2}h^{-1})	IE (%)
H$_2$SO$_4$						
298	0.5 M	11.6248	11.6381	0.0133	2.21	
308	0.5 M	10.2346	10.2513	0.0167	2.78	
318	0.5 M	12.3426	12.3615	0.0189	3.15	
328	0.5 M	10.4689	10.4901	0.0212	3.53	
PEGTPP						
298	150	10.4545	10.4558	0.0013	0.22	90.04
	100	10.7836	10.7860	0.0024	0.40	81.90
	50	11.3946	11.3978	0.0032	0.53	76.01
308	150	11.5648	11.5667	0.0019	0.32	88.48
	100	12.3216	12.3243	0.0027	0.45	83.81
	50	11.9637	11.9673	0.0036	0.6	78.01
318	150	10.7741	10.779	0.0049	0.82	73.96
	100	10.6794	10.6863	0.0069	1.15	63.49
	50	11.4527	11.4608	0.0081	1.35	57.14
328	150	10.8466	10.8533	0.0067	1.12	68.27
	100	10.9532	10.9618	0.0086	1.43	59.49
	50	10.3427	10.3535	0.0108	1.8	49.00
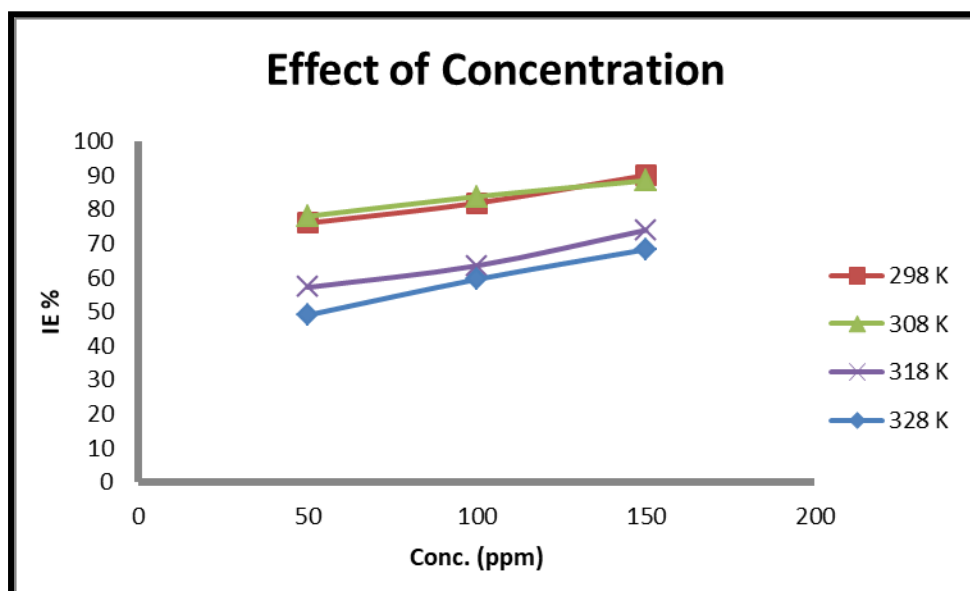
Fig 2. Effect of inhibitor concentration on corrosion inhibition efficiency for PEGTPP at 298 K, 308 K, 318 K and 328 K

Quantum Chemical Analysis:

Quantum chemical analysis explains the theoretical concepts of quantum chemical calculations. Various optimized AM1 parameters for the inhibitor using Hyperchem 7.5 are tabulated in Table 2. In the Figs. 3 (a)-(e), cyan colour represents hydrogen atom, brown colour represents the carbon atoms and red colour represents phosphorous atom. The green colour represents the oxygen atoms and the yellow colour represents bromine. In all these diagrams, green colour represents positive electron density and pink colour indicates negative electron density. From these figs., electron density contours of the inhibitor molecules can be clearly seen. It is seen that the inhibitor chosen have an electron cloud to some extent which is available for donation to the metal surface for adsorption. The negative values of binding energies and heat of formation of this inhibitor are found to be negative which suggest that these inhibitor molecules are very stable and less prone to decompose. There is no correlation between dipole moment and observed inhibition efficiencies. This may be due to some other factors like behaviour of molecules in the solvent and mechanism of adsorption, which play important role in the corrosion inhibition. The difference in the order of inhibition may be due to the extent of delocalization of the electrons available and non-linearity leading to the stearic hindrance of this phosphonium compound which obstructs the adsorption process thereby leading to the decrease in extent of inhibition.

Table 2: Optimized AM1 parameters for the inhibitor using Hyperchem 7.5

Inhibitor	Binding Energy (kcal/mol)	Heat of Formation (kcal/mol)	E_{HOMO} (eV)	E_{LUMO} (eV)	Dipole Moment (Debye)	E_{LUMO}-E_{HOMO}
PEGTPP	-8542.81	-96.94	-9.28	0.002	2.00	9.28
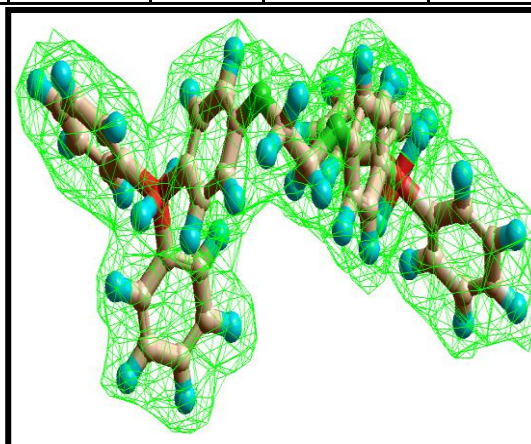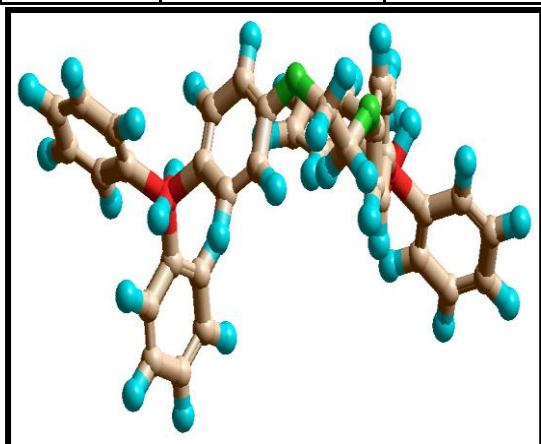
Fig.3 (a): Ball and Stick Model of Optimized Geometry of PEGTPP

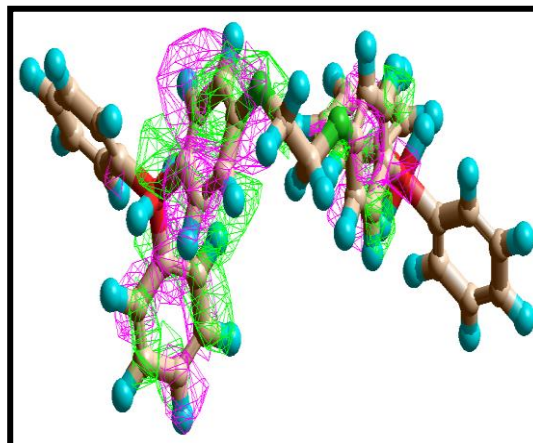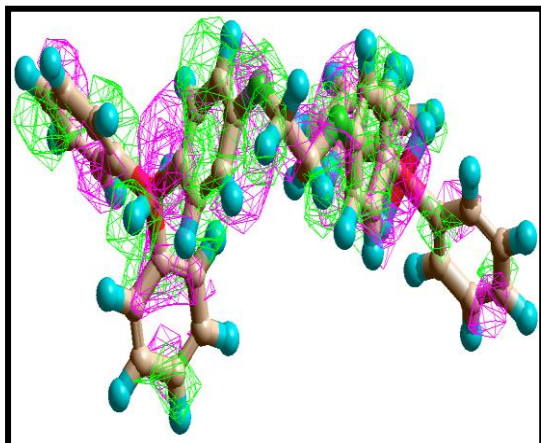***Fig.3 (b): 3-D Isosurface of Total Charge Density on PEGTPP***

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Fig.3 (c): 3-D Isosurface of Total Charge Density on PEGTPP (HOMO) ***Fig.3 (d): 3-D Isosurface of Total Charge Density on PEGTPP (LUMO)***
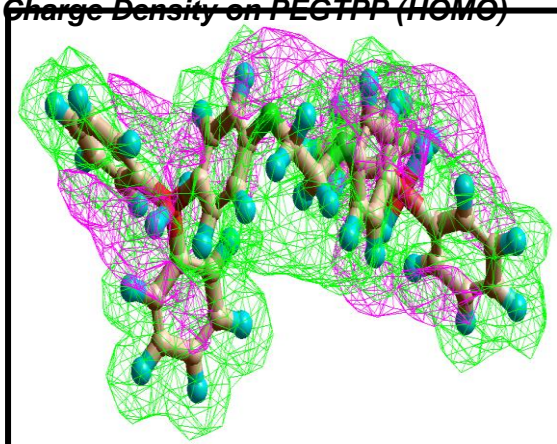

Fig.3 (e): Electrostatic Potential Mapped on to 3-D Charge Density of PEGTPP

CONCLUSION

PEGTPP showed excellent inhibition performance to carbon steel corrosion in 0.5 M H_2SO_4 at 298 K, 308 K, 318K and 328K. The inhibition efficiency increased with inhibitor concentration but was decreased in irregularly with temperature. The negative values of binding energies and heat of formation of this inhibitor are found to be negative which suggest that these inhibitor molecules are very stable and less prone to decompose.

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