JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008

Study of corrosion of mild steel in Propyl Triphenyl Phosphonium Bromide/ Sulfuric Acid solution by conventional weight Loss and Electrochemical methods

Kalpana Bhrara[a] and Gurmeet Singh[b]*

[a,b] Department of Chemistry, University of Delhi, Delhi-110007, India.
Email: gurmeet123@yahoo.com, kbhrara@yahoo.com, Tel.:91-011-27667725 Ext.1628

ABSTRACT

Propyl Triphenyl Phosphonium Bromide (PTPPB) has been evaluated as a corrosion inhibitor for mild steel in 0.5M H_2SO_4 solutions using weight loss measurements. The data showed that the presence of PTPPB in aerated 0.5 M H_2SO_4 solutions decreases corrosion rate to a great extent and the corrosion rate decreases with increasing inhibitor concentration at a constant temperature. At 298K, inhibition efficiency was found to be 93.5% for 10^{-7} M PTPPB which increased to about 99% for the PTPPB concentration of 10^{-2} M. The effect of temperature on the corrosion behavior of mild steel was studied at five different temperatures ranging from 298 to 338K. Adsorption on the mild steel surface follows the Langmuir isotherm. The values of free energy of adsorption indicate strong adsorption of PTPPB on mild steel surface.

The weight loss results were found to be in agreement with the electrochemical results. The polarization curves clearly indicate that PTPPB acts as a mixed type inhibitor.

Key Words

Propyl triphenyl phosphonium bromide, weight loss studies, Langmuir's isotherm, potentiodynamic polarization.

---

* Author for Correspondence

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008

Introduction

A considerable amount of interest has been generated in the study of organic compounds as corrosion inhibitors owing to their usefulness in several industries: during the pickling of metals, cleaning of boilers, acidification of oil wells, etc [1]. Most effective inhibitors are organic compounds which are rich in hetero atoms such as phosphorous, nitrogen, sulfur and oxygen. Such compounds and their derivatives are excellent inhibitors for iron and mild steel in sulfuric acid [2-26].

Phosphonium compounds are known to act as corrosion inhibitors of various metals in acidic solutions [27-39]. In the present study, Propyl Triphenyl Phosphonium Bromide (PTPPB) has been evaluated as a corrosion inhibitor for mild steel in 0.5M H_2SO_4 solutions using weight loss studies. The study was also complemented by potentiodynamic polarization studies.

Experimental

Mild Steel (C=0.15%, Si=0.08%, S=0.025%, P=0.025% and Mn=1.02%) specimens of dimensions 2 cm x 0.8 cm x 0.8 cm were abraded successively by emery papers of different grades, i.e. 150, 320, 400 and 600 and finely polished with a 4/0 polishing paper to obtain mirror like finish. The specimens were degreased in an ultrasonic cleaner, dried in dessicator for 24 hours and weighed. They were dipped in 0.5M sulfuric acid solution and in 0.5M sulfuric acid solution containing 10^{-2}M, 10^{-3}M, 10^{-5}M and 10^{-7}M inhibitor. After six hours samples were taken out of the medium, washed with water to remove corrosion products, dried in dessicator for 24 hours and weighed again to calculate weight loss.

The detailed procedure for potentiodynamic polarization studies is described in [36-38]. 0.5M sulfuric acid solution containing 10^{-2}, 10^{-3}, 10^{-5} and 10^{-7}M PTPPB were used for corrosion studies. The cathodic and anodic polarization studies were conducted at 298, 308, 318, 328 and 338K. Typical polarisation curves for the aerated solutions of 0.5M sulfuric acid with various concentrations of PTPPB at different temperatures were plotted. The corrosion current for different sets of solution were found from the extrapolation of the polarization curves back to the OCP.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008

Results

Weight Loss Studies:

Inhibitor efficiency was calculated using mass loss data from the equation:

$$I\% = ((w_0 - w_I) / w_0) \times 100$$

Where w_0 and w_I are weight losses in the absence and presence of inhibitor. The various data, i.e. corrosion rate, I%, surface coverage (θ) etc. are reported in table 1 for the adsorption of PTPPB on mild steel in 0.5M sulfuric acid.

Table 1.
Mass Loss data for corrosion of mild steel in 1N sulfuric acid in the absence and the presence of PTPPB

Concentration mol l^{-1}	Weight Loss g	Corrosion Rate g cm^{-2} day^{-1}	Efficiency %	θ
298K				
10^{-2}	0.00120	0.00062	99.0	0.99
10^{-3}	0.00156	0.00081	98.7	0.99
10^{-5}	0.03113	0.01621	74.0	0.74
10^{-7}	0.00708	0.00369	93.5	0.93
H_2SO_4	0.11975	0.06237	-	-
308K				
10^{-2}	0.00136	0.00071	99.0	0.99
10^{-3}	0.00136	0.00071	99.0	0.99
10^{-5}	0.11896	0.06196	12.3	0.12
10^{-7}	0.09767	0.05087	28.0	0.28
H_2SO_4	0.13565	0.07065	-	
318K				
10^{-2}	0.00157	0.00082	99.0	0.99
10^{-3}	0.00188	0.00098	98.8	0.99
10^{-5}	0.00721	0.00375	95.4	0.95
10^{-7}	0.11158	0.05811	28.8	0.29
H_2SO_4	0.15671	0.08162	-	-
328K				
10^{-2}	0.00180	0.00094	98.9	0.99
10^{-3}	0.00180	0.00094	98.9	0.99
10^{-5}	0.01361	0.00709	91.7	0.92
10^{-7}	0.01755	0.00914	89.3	0.89
H_2SO_4	0.16402	0.08543	-	-
338K				
10^{-2}	0.00188	0.00098	98.9	0.99
10^{-3}	0.00342	0.00178	98.0	0.98
10^{-5}	0.11978	0.06238	30.0	0.30
10^{-7}	0.11123	0.05793	35.0	0.35
H_2SO_4	0.17112	0.08912	-	-

Various adsorption isotherms were studied but Langmuir's isotherm was found to be the best fit for the concentrations and temperatures studied with average $R^2 = 1.0000$ for the adsorption of PTPPB. Langmuir's isotherm is given by

$$C / \theta = 1/ K + C$$

Where C is inhibitor concentration in mol l^{-1} and K is an equilibrium constant of adsorption, K which is related to standard free energy of adsorption G^0_{ads} by the equation

$$K= (1/55.55) \exp (- G^0_{ads} / RT)$$

Fig.1 shows the dependence of C/θ as a function of C. From the intercepts, the values of K and G^0_{ads} are calculated and are given in Table 2.

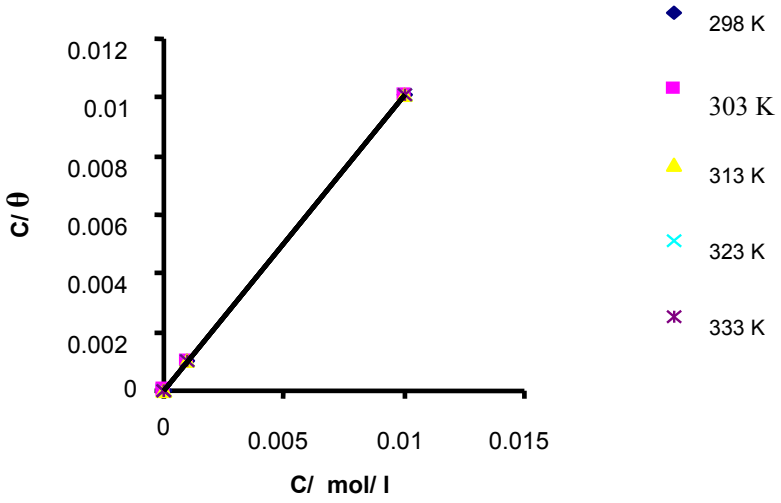

Fig. 1 Langmuir isotherm for the adsorption of PTPPB

Table 2
Various parameters calculated from the Langmuir isotherm for PTPPB

Temperature K	R^2	Slope	K	$-\Delta G_{ads}$ kJ mol^{-1}
298	1.0000	1.010	1.00×10^6	44.19
308	1.0000	1.007	3.33×10^4	36.96
318	1.0000	1.010	5.00×10^6	51.41
328	1.0000	1.010	3.33×10^6	51.92
338	1.0000	1.009	1.00×10^5	43.65

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008

Potentiodynamic Polarization Studies:

Polarization studies on mild steel in 0.5M sulfuric acid solution containing 10^{-2}M, 10^{-3} M, 10^{-5}M and 10^{-7}M PTPPB were performed. Fig. 2 shows the representative cathodic and anodic polarization curves for mild steel in 0.5M sulfuric acid in presence of 10^{-2} M PTPPB at 298K. The corrosion currents for different sets of solution were found from the extrapolation of the polarization curves back to the OCP. The inhibitor efficiency was calculated using:

$$\mathbf{I\% = (i_0 - i_{corr})/i_0 \times 100}$$

in which i_0 and i_{corr} are the corrosion currents (A cm^{-2}) in uninhibited and inhibited solutions respectively . From the polarisation curves at various temperatures, corrosion parameters e.g. OCP, corrosion current and inhibition efficiencies etc. of acid corrosion of mild steel in the presence of PTPPB were calculated and are given in Table3.

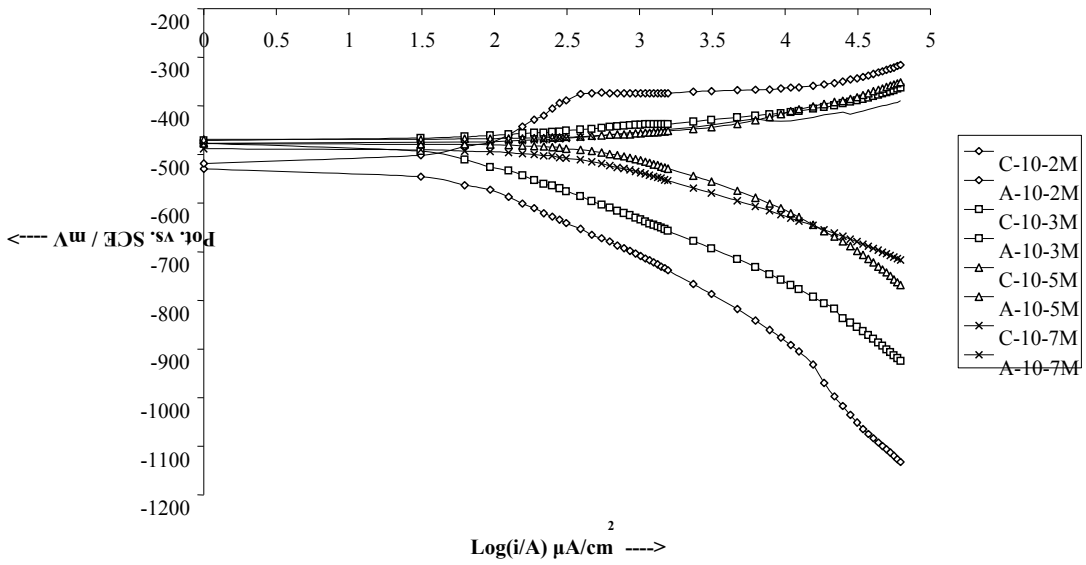

Figure 2 Galvanostatic Polarisation curve of Mild Steel in 0.5M sulfuric acid in presence of PTPPB at 298K

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008

TABLE 3

Corrosion Parameters of Mild Steel 1N H_2SO_4 in the presence of PTPPB

Conc. (mol l^{-1})	-OCP (mV)	i_{corr} (mA/cm^2)	I (%)
298 K			
10^{-2}	530	0.060	99.1
10^{-3}	480	0.072	99.0
10^{-5}	479	1.820	74.3
10^{-7}	487	0.389	94.5
H_2SO_4	481	7.080	-
308K			
10^{-2}	491	0.072	99.0
10^{-3}	474	0.072	99.0
10^{-5}	490	7.080	2.3
10^{-7}	480	6.026	16.8
H_2SO_4	474	7.244	-
318K			
10^{-2}	510	0.145	98.9
10^{-3}	506	0.204	98.4
10^{-5}	473	0.589	95.4
10^{-7}	483	11.749	8.8
H_2SO_4	501	12.883	-
328K			
10^{-2}	507	0.229	98.5
10^{-3}	527	0.263	98.3
10^{-5}	477	1.259	91.7
10^{-7}	478	1.622	89.3
H_2SO_4	483	15.136	-
338K			
10^{-2}	509	0.282	98.4
10^{-3}	498	0.417	97.6
10^{-5}	477	13.183	24.1
10^{-7}	480	13.183	24.1
H_2SO_4	477	17.378	-

Discussion:

The corrosion rate increases and then decreases with the increase in concentration of the inhibitor at lower temperatures. At higher temperatures corrosion rate decreases with the

increase in concentration of the inhibitor. For 10^{-2} and 10^{-3}M PTPPB, corrosion rate almost remains constant with increase in temperature whereas for 10^{-5} and 10^{-7}M PTPPB it increases and then decreases, passes through a minimum and then increases again. For the lower concentrations studied, the minimum in corrosion rate (maximum in I %) is observed at 328K. It can be clearly seen (Table 1) that PTPPB is a very efficient inhibitor at most of the temperatures studied especially at higher concentrations. It performs best at 318 and 328K where inhibitor efficiencies are in the range of 89.3-99.0%. Its performance decreases considerably at 338K at lower concentrations.

The fact that inhibition efficiencies are higher at higher temperatures than those at 298K also indicates that the adsorption of PTPPB is not merely a physical or a chemical adsorption but a comprehensive adsorption [40].

Table 2 shows that all the linear correlation coefficients (R^2) are almost equal to 1 and all the slopes are very close to 1, which indicates the adsorption of inhibitor onto steel surface accords with the Langmuir adsorption isotherm. The result also indicates that there were no interactions among the adsorbed species [41, 42].

The negative values of ΔG^0_{ads} along with high K indicate a spontaneous adsorption process and a good chemical stability of inhibitor, which may be derived from the chemical bond between metal and inhibitor molecules. Magnitudes of K and ΔG^0_{ads} values confirm that PTPPB is adsorbed on the metal surface at all the temperatures but is most efficient at 328K.

The inhibitor efficiencies remain almost constant (98-99%) with temperature at higher concentrations. The π- electron system of this inhibitor molecule possibly overlaps with the vacant d-orbitals of the metal surface resulting in a strong dπ-pπ interaction [27] which is further assisted by the synergistic effect of Br^- ions [29]. This electrostatic interaction probably leads to a stronger adsorption of the inhibitor and formation of a barrier between the metal surface and reactive sites.

At 10^{-5}M PTPPB, efficiency decreases and then increases with temperature and shows maxima at 318K. This is clear indicative of the fact that the PTPPB undergoes change in orientation of phenyl rings as the temperature is increased. At 318K, they may be in the same plane, therefore enhancing the adsorption on the metal surface. These changes in

ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008

orientation of phenyl rings are not possible beyond a certain temperature because of the shorter time lag between adsorption-desorption processes.

At 10^{-7}M PTPPB, efficiency is maximum at 298K, decreases and then shows maxima at 328K. The adsorption of PTPPB is assisted by other anions present in the solution and therefore maximum adsorption at room temperature whereas the maxima at 328K can be explained due to maximum adsorption through π-electron density because of planar orientation of four phenyl rings.

Table 3 shows that the electrochemical results supplement the weight loss results. OCP remains more or less constant with a slight shift towards cathodic direction for all the temperatures. Therefore, PTPPB is a mixed type of inhibitor. It acts in both ways affecting cathodic and anodic partial processes by blocking the active sites of the metal surface.

Conclusions

From the overall data of adsorption of PTPPB on mild steel surface in acid solution studied, it may be concluded that

(i) PTPPB retards corrosion at ordinary temperatures and shows better inhibition efficiency at higher temperatures especially at 318K and 328K.

(ii) The Langmuir adsorption isotherm was found to be closest to the description of the adsorption behavior of the studied inhibitor.

(iii) The negative values of ΔG^0_{ads} along with high K indicate a spontaneous adsorption process at all the temperatures but is most efficient at 318 and 328K.

(iv) The electrochemical results are in good agreement with the weight loss data.

(v) PTPPB is a mixed type of inhibitors. OCP values in the presence of PTPPB shows a slight predominance in cathodic direction.

References

1. B.G. Clubley, 'Chemical inhibitors for corrosion control', 1990, Cambridge, Royal Society of Chemistry.
2. J. Rawat and M. A. Quraishi: *Brit. Corros. J.*, 1999, **34**(3), 220-224.
3. B. Ramesh Babu and R. Holze: *Brit. Corros. J.*, 2000, **35**(3), 204-209
4. M. Özcan, İ. Dehri and M. Erbil: *Appl. Surf. Sci.*, 2004, **236**(1-4), 155-164
5. M. Bouklah, A. Attayibat, S. Kertit, A. Ramdani and B. Hammouti: *Appl. Surf. Sci.*,

ISSN 1466-8858 Volume 11, Preprint 2 submitted 20 May 2008
2005, **242**(3-4), 399-406.
6. C. Jeyaprabha, S. Sathiyanarayanan and G. Venkatachari: *Appl. Surf. Sci.*, 2005, **246**(1-3), 108-116
7. M. Bouklah, A. Ouassini, B. Hammouti and A. El Idrissi: *Appl. Surf. Sci.*, 2005, **250**, 50–56.
8. V.S. Sastri, J.R. Perumareddi and M. Elboujdaini: *Corros. Eng. Sci. Tech.*, 2005, **40**(3), 270-272.
9. A. Ouchrif, M. Zegmout, B. Hammouti, S. El-Kadiri and A. Ramdani: *Appl. Surf. Sci.*, 2005, **252**(2), 339-344.
10. C. Jeyaprabha, S. Sathiyanarayanan, K.L.N. Phani and G. Venkatachari: *Appl. Surf. Sci.*, 2005, **252**(4), 966-975.
11. Xianghong Li and Guannan Mu: *Appl. Surf. Sci.*, 2005, **252**(5)**,** 1254-1265.
12. Lin Niu, Hu Zhang, Fenghua Wei, Suxiang Wu, Xiaoli Cao and Pengpeng Liu: *Appl. Surf. Sci.*, 2005, **252**(5)**,** 1634-1642.
13. S.A. Ali, A.M. El-Shareef, R.F. Al-Ghamdi and M.T. Saeed: *Corros. Sci.*, 2005, **47**(11)**,** 2659-2678.
14. M. Bouklah, B. Hammouti, M. Lagrenée and F. Bentiss: *Corros. Sci.*, 2006, **48**(9), 2831-2842.
15. Libin Tang, Xueming Li, Yunsen Si, Guannan Mu and Guangheng Liu: *Mater. Chem. Phys.*, 2006, **95**(1), 29-38.
16. M. Lebrini, F. Bentiss, H. Vezin and M. Lagrenée: *Corros. Sci.*, 2006, **48**(5), 1279-1291
17. M. Bouklah, B. Hammouti, M. Lagrenée and F. Bentiss: *Corros. Sci.*, 2006, **48**(9), 2831-2842.
18. M.S. Morad and A.M. Kamal El-Dean: *Corros. Sci.*, 2006, **48**(11), 3398-3412.
19. A.B. Silva, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro and E. D'Elia: *Corros. Sci.*, 2006, **48**(11), 3668-3674.
20. Lian Zhong, Shuhu Xiao, Jie Hu, Hua Zhu and Fuxing Gan: *Corros. Sci.*, 2006, **48**(12), 3960-3968.
21. S.A. Hossain and A.I. Almarshad: *Corros. Engg. Sci. and Tech.*, 2006, **41**(1), 77-81.
22. M. Bouklah, A. Ouassini, B. Hammouti and A.El Idrissi: *Appl. Surf. Sci.*, 2006, **252**(6)**,** 2178-2185.
23. M. Kissi, M. Bouklah, B.Hammouti and M. Benkaddour: *Appl. Surf. Sci.*, 2006, **252**(12)**,** 4190-4197.
24. G. Quartarone, L. Bonaldo and C. Tortato: *Appl. Surf. Sci.*, 2006, **252**(23)**,** 8251-8257.
25. C. Jeyaprabha, S. Sathiyanarayanan and G. Venkatachari: *Appl. Surf. Sci.*, 2006, **253** (2), 432-438.
26. Rovshan Hasanov, Murat Sadıkoğlu and Semra Bilgiç: *Appl. Surf. Sci.*, 2007, **253**(8), 3913-3921
27. P. Mutombo, N. Hackerman: *Anti-Corros. Met. Mater.*, 1998, **45**(6), 413.
28. M.S. Morad, *J. Appl. Electrochem.*, 1999, **29**(5), 619-626.
29. E. Khamis, E.S.H.El-Ashry and A.K. Ibrahim: *Brit. Corros. J.*, 2000, **35**(2), 150-154.
30. M.S. Morad: *Corros. Sci.*, 2000, **42**(8), 1307-1326.
31 M.S. Abdel-Aal and M.S. Morad: *Brit. Corros. J.*, 2001, **36**(4), 253-260

32. A.A. Hermas, M.S. Morad and M.H. Wahdan: *J. Appl. Electrochem.*, 2004, **34**(1), 95–102.
33. M. Troquet and J. Pagetti: *Werkst. und Korros.*, 2004, 34(11), 557-562.
34. K.F. Khaled: *Appl. Surf. Sci.*, 2004, **230**(1-4), 307-318.
35. F. Said, N. Souissi, A. Dermaj, N. Hajjaji, E. Triki and A. Srhiri: *Werkst. und Korros.,* 2005, **56**(9), 619-623.
36. M. Walia and Gurmeet Singh: Surf. Engg., 2005, **21**(3), 176-179.
37. K. Bhrara and G. Singh: Surf. Engg., 2005, **21**(3), 165-171.
38. Kalpana Bhrara and Gurmeet Singh: *Appl. Surf. Sci.*, 2006, **253**(2), 846-853.
39. Kalpana Bhrara and Gurmeet Singh: *Corros. Engg. Sci. Tech.*, 2007, **42**(2), 137-144.
40. B.A. Abd-El-Nabey, E. Khamis, M.Sh. Ramadan, A. El-Gindy: *Corrosion*, 1996, **52**(9), 671.
41. A.Y. El-Etre: *Corros. Sci.*, 2001, **43**(6), 1031-1039.
42. F. Bentiss, M. Lagrene´e, M. Traisnel, J.C. Hornez: *Corrosion*, 1999, **55**(10), 968.