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The Inhibitive Effect of a (1,3-Dioxolan-2-ylmethyl) –triphenyl phosphonium bromide on the Corrosion of Steel in 0.5 M Phosphoric Acid Solution

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The effect of (1,3-Dioxolan-2-ylmethyl)–triphenylphosphonium bromide (DTPB) on the corrosion of steel in aqueous solution of 0.5 M phosphoric acid was investigated at different temperatures by chemical and electrochemical techniques. The results obtained showed that DTPB could serve as an effective inhibitor for the corrosion of steel in phosphoric acid media. The inhibitive mechanism was discussed assuming the adsorption of DTPB on the electrode surface. Theoretical fitting of different isotherms, Langmuir, Flory-Huggins, and the kinetic-thermodynamic models, were tested to clarify the nature of adsorption. The associated activation parameters were determined and discussed.

Keywords: Phosphoric; Steel; EIS; Polarization; inhibition.

1. INTRODUCTION

Acid solutions are frequently used in removing undesirable scale and rust in metal workings. The main problem is the consumption of working metal due to dissolution in the used pickling or descaling solution. Phosphoric acid (H_3PO_4) is widely used in the production of fertilizers and surface treatment of steel such as chemical and electrolytic polishing or etching, chemical coloring, removal of oxide film, phosphating, passivating, and surface cleaning [1,3]. Phosphoric acid shows strong corrosiveness on ferrous and ferrous alloys. There is a great need to protect steel materials used in the phosphoric acid industry. However, several works [1-7] appears to have been done on the corrosion inhibition of steel in phosphoric acid solutions. Khamis et al. [6] investigated the corrosion inhibition of steel in 35% H_3PO_4 by some thiosemicarbazide derivatives. Their results showed that the protection efficiency of all the compounds reached up to 99%. However, it has been reported [8] that the inhibitors which are useful in hydrochloric acid solutions are generally also effective in H_3PO_4

solutions. Most effective inhibitors are organic compounds which are rich in hetero atoms such as phosphorous, nitrogen, sulphur and oxygen. Phosphorous as heteroatom in homologous series of organic compound is easily polarizable and has lower electronegativity compared to other heteroatoms. Therefore, it is expected that phosphorous based compounds should be most effective in retarding the dissolution of steel in acidic media. Phosphonium compounds are known to act as corrosion inhibitors of steel in acidic solutions [9–12].

The aim of the present work is to test the inhibitive action of (1,3-Dioxolan-2-ylmethyl)–triphenylphosphonium bromide (DTPB) on the acidic corrosion of steel and effect of temperature on its inhibitory effect.

2. EXPERIMENTAL

2.1. Electrochemical tests

Electrochemical impedance and polarization curves measurements were achieved using frequency response analyzer Gill AC instrument (UK). The frequency range for EIS measurements was $0.1 \leq f \leq 1x10^4$ Hz with applied potential signal amplitude of 10 mV around the rest potential. Polarization curves measurements were carried out at a scan rate of 30mV/min starting from cathodic potential (E_{corr}-250 mV) going to the anodic direction. The EIS and polarization measurements were done in an electrochemical cell with three-electrode mode; platinum sheet and saturated calomel electrodes were used as counter and reference electrodes. The specimens used for constructing the working electrode were steel that had the following chemical composition (wt%): C, 0.21; S, 0.04; Mn, 2.5; P, 0.04; Si, 0.35; balance Fe. The steel samples were fixed in poly tetrafluoro ethylene (PTFE) rods by an epoxy resin in such a way that only one surface was left uncovered. The exposed area (1 cm^2) was mechanically abraded with a series of emery papers of variable grades, starting with a coarse one and proceeding in steps to the finest (800) grade. The samples were then washed thoroughly with double distilled water followed with A.R. ethanol and finally with distilled water, just before insertion in the cell. Before polarization and EIS measurements, the working electrode was introduced into the test solution and left for 15 minutes at the open circuit potential. Measurements were done at 30, 40, 50, and $60.0 \pm 0.1^{O}C$ in solutions open to the atmosphere under unstirred conditions.

2.2. Weight loss measurements

The experiments were carried out using rectangular steel coupons, each with an area of 6 cm^2, with the same chemical composition of the steel samples used in the electrochemical measurements. The weighed coupons, after polishing and cleaning, were suspended in beakers containing the test solution. After 24 hours, the coupons were removed from the solution, washed with distilled water, dried with ethanol followed by acetone (CH_3COCH_3), and then reweighed. The weight loss was then determined and the rate of corrosion was expressed in g cm^{-2} h^{-1}.

2.3. Solution Preparation

(1, 3-Dioxolan-2-ylmethyl)–triphenylphosphonium bromide (DTPB), Fig. 1, is purchased from Aldrich Chemicals Company. The solutions were prepared using double distilled water. Stock solutions of 2 M H_3PO_4 and 0.01 M DTPB solutions were used to prepare solutions containing 0.5 M H_3PO_4 and the desired DTPB concentration using appropriate dilutions. The concentration of the stock solution was expressed in terms of moles per litre.

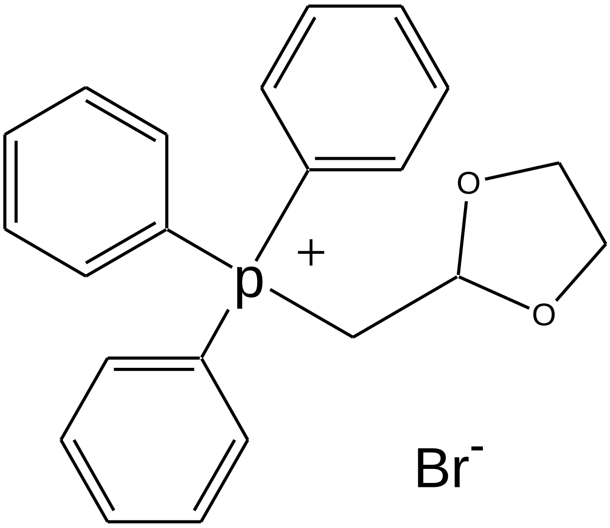

Figure 1. 1, 3-Dioxolan-2-ylmethyl)-triphenylphosphonium bromide (DTPB).

3. RESULTS AND DISCUSSION

3.1. Weight loss measurement results

The variation of the percentage inhibition efficiency (%P) obtained from weight loss measurements of steel coupons in 0.5 M H_3PO_4 in presence and absence of different concentration of DTPB is shown in Fig. 2. The %P values were calculated using the relation:

$$\%P= [(w_o - w)/ w_o] \times 100$$

where w_o and w are the rates of corrosion (g cm^{-2} hr^{-1}) in the absence and presence of DTPB.

The figure indicates that the inhibition efficiency increases exponentially with increasing the DTPB concentration. A considerable value of 96% of inhibition was obtained at $7.5x10^{-4}$ M of DTPB concentration indicating that the DTPB could serve as an efficient corrosion inhibitor for steel in phosphoric acid solution.

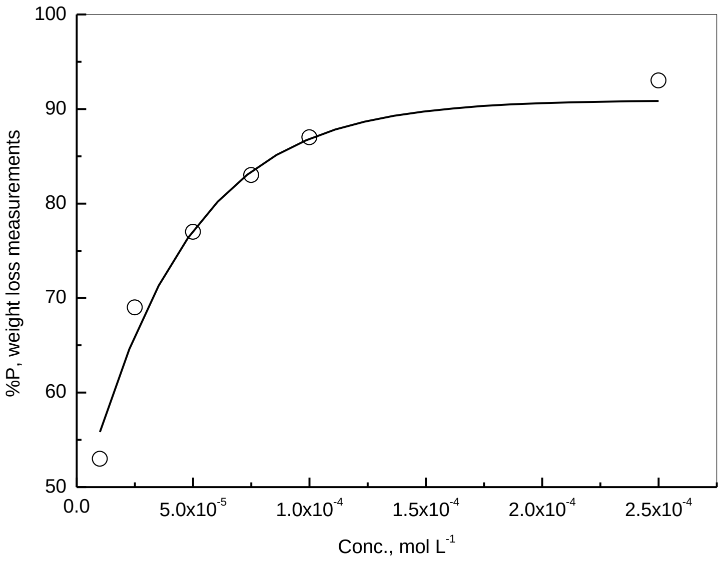

Figure 2. Variation of the percentage inhibition efficiency (%P) obtained from weight loss measurements for steel in 0.5 M phosphoric acid solution with the concentration of DTPB at 30 ^{O}C.

3.2. Potentiodynamic polarization results

Typical potentiodynamic polarization curves for steel in 0.5 M phosphoric acid in the absence and presence of different DTPB concentrations are shown in Fig. 3.

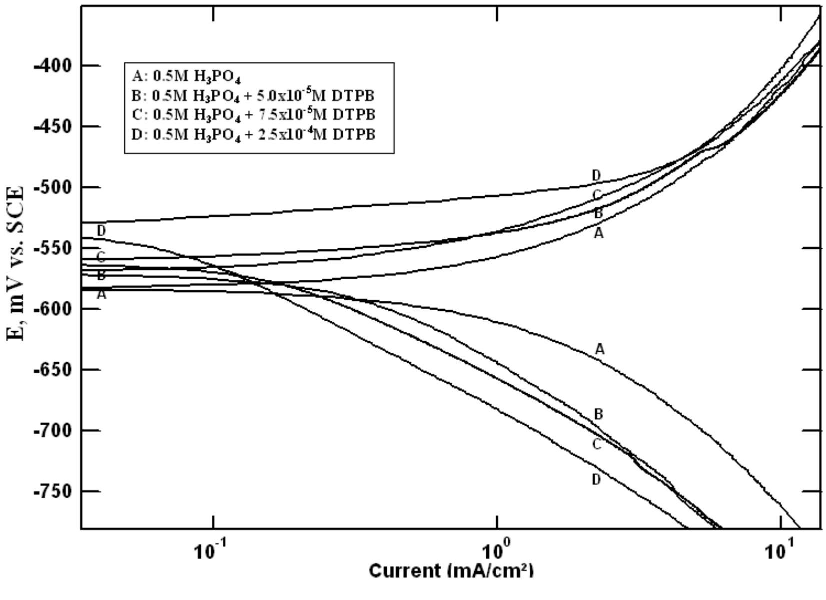

Figure 3. Potentiodynamic polarization curves for steel in 0.5M phosphoric acid in the absence and presence of different DTPB concentrations.

As seen, addition of DTPB affects both anodic and cathodic parts of the polarization curve and slightly shifts the values of the corrosion potential, E_{corr}, to the noble (anodic) direction indicating that DTPB could be classified as a mixed-type inhibitor with predominant anodic character. The corrosion current densities and beta slopes were extracted from the linear portions of anodic and cathodic branches beyond ±50 mV from E_{corr} as defined by Tafel extrapolation method. The values of the electrochemical parameters: corrosion current density, i_{corr}, anodic and cathodic Tafel slopes, β_a, β_c for different concentrations of DTPB are given in Table 1.

Table 1. Electrochemical polarization parameters of steel in 0.5M H_3PO_4 in the absence and presence of different DTPB concentrations.

Conc. (mol L^{-1})	$-E_{corr}$ (V vs. SCE)	β_a (V $decade^{-1}$)	$-\beta_c$ (V $decade^{-1}$)	i_{corr} (A m^{-2})
0.0	0.585	0.109	0.122	7.503
$1.0x10^{-5}$	0.584	0.095	0.123	3.810
$2.5x10^{-5}$	0.583	0.093	0.131	2.502
$5.0x10^{-5}$	0.581	0.091	0.129	2.020
$7.5x10^{-5}$	0.589	0.107	0.111	1.630
$1.0x10^{-4}$	0.577	0.089	0.134	1.131
$2.5x10^{-4}$	0.572	0.104	0.119	0.942
$5.0x10^{-4}$	0.586	0.088	0.139	0.890
$7.5x10^{-4}$	0.555	0.088	0.137	0.790
$1.0x10^{-3}$	0.550	0.102	0.147	0.650

The displayed data show that increasing DTPB concentration decreases the values of i_{corr}. The slight variations in values of β_a and β_c indicate that the inhibiting action takes place by simple blocking of the available cathodic and anodic sites of the metal surface [13].

3.3. Electrochemical impedance spectroscopy results

Figure 4 shows the Nyquist impedance plots of steel in 0.5M phosphoric acid in the absence and presence of different DTPB concentrations. Depressed semicircles of capacitive type were observed indicating that the dissolution process occurs under activation control. The size of the semicircles increases with increasing concentration of the inhibitor. The impedance response is also characterized by inductive loop at the low frequency region. The inductive behaviour has been related with the relaxation of adsorbed species [14,15] or to a surface area modulation or to salt film property modulations (density, ionic conductivity, or thickness) [16].

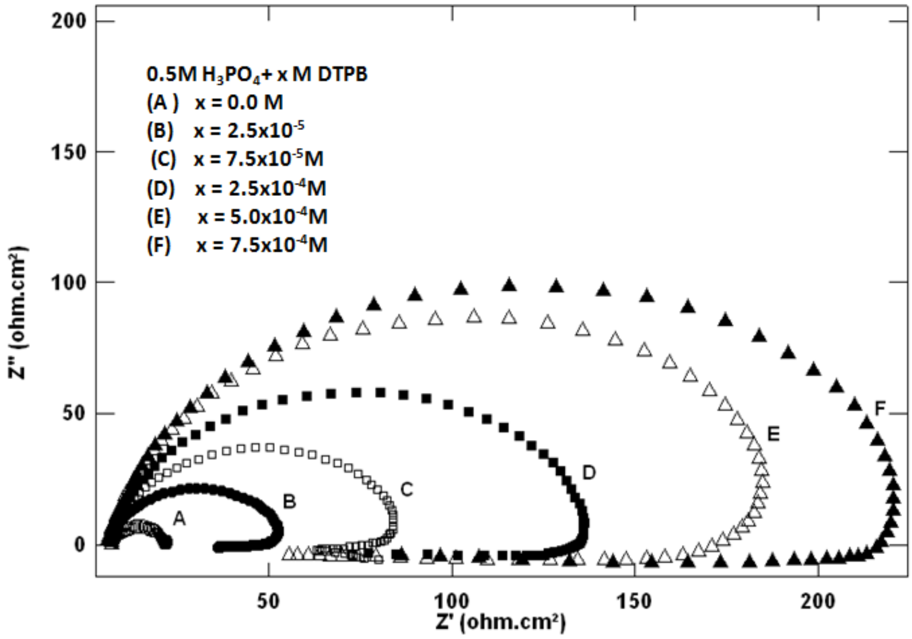

Figure 4. Nyquist Impedance plots of steel in 0.5M phosphoric acid in the absence and presence of different DTPB concentrations.

The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data to an equivalent circuit model, Fig. 5, that includes the solution resistance R_s and constant phase element of the double layer (CPE_{dl}) which is placed in parallel to charge transfer resistance element, R_{ct}.

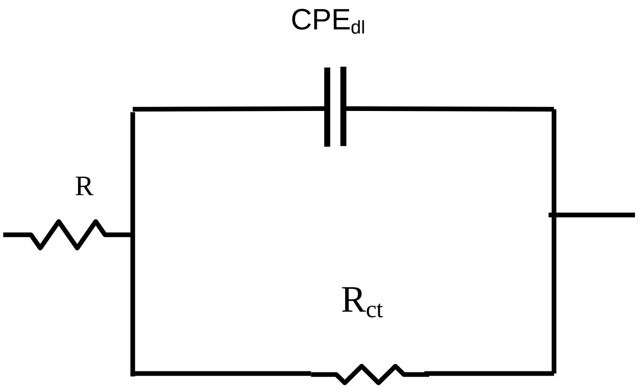

Figure 5. The equivalent circuit model

The R_{ct} value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate. The capacitances were implemented as a constant phase element (CPE) during analysis of the impedance plots. The CPE is defined by two values, Q and n. The impedance, Z, of CPE is presented by

$$Z_{\mathrm{CPE}} = Q^{-1} (i\omega)^{-n}$$

where $i = (-1)^{1/2}$, ω is frequency in rad s^{-1}, $\omega = 2f\pi$ and f is the frequency in Hz.

If n equals one, then Eq. (1) is identical to that of a capacitor, $Z_{\mathrm{CPE}} = (i\omega C)^{-1}$ where C is the ideal capacitance. For a non-homogeneous system, n values range from 0.9 to 1.

The values of R_{ct} and Q_{dl} for steel in 0.5 M phosphoric acid containing different DTPB concentrations are shown in Fig. 6.

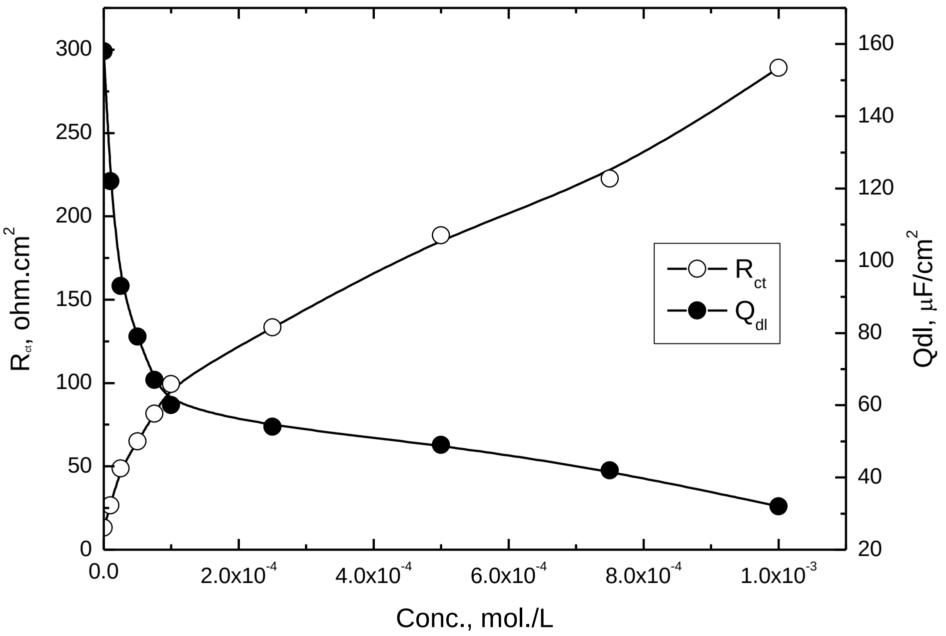

Figure 6. Variation of R_{ct} and Q_{dl} values for steel in 0.5M phosphoric acid containing different DTPB concentrations

The data indicate that the increase of concentration of DTPB leads to increasing charge transfer resistance that is associated with a decrease in Q_{dl}. Since, the double layer capacitance can be expressed in the Helmholtz model by:

$$C_{dl} = (\varepsilon\, \varepsilon_0\, A/d)$$

where “d” is the thickness of electrical double layer, A is the surface of the electrode, ε_0 is the permittivity of vacuum and ε is the medium dielectric constant [17]. Therefore, the decrease in C_{dl} or Q_{dl} values could be related to the decrease of local dielectric constant (ε) or increase of thickness of electrical double layer due to the formation of a protective layer by the adsorption of inhibitor molecules on the mild steel surface [18, 19].

The percentage inhibition efficiency, % P was calculated from impedance measurements using the relation:

$$\% P = [(R_{ct} - R_{ct_o}) / R_{ct}] \times 100$$

where $\mathbf{R_{cto}}$ and $\mathbf{R_{ct}}$ are the charge transfer resistance of steel in 0.5 M phosphoric in the absence and presence of DTPB, respectively. The variation of %P obtained from electrochemical impedance measurements with the concentration of DTPB are shown in Fig. 7. The curve is characterized by an initial rapid increase of the % P followed by steadily rising part indicating a formation of a mono-layer adsorbate film on the steel surface. The % P values are in good agreement with the results obtained previously from weight loss measurement (Figure 2)

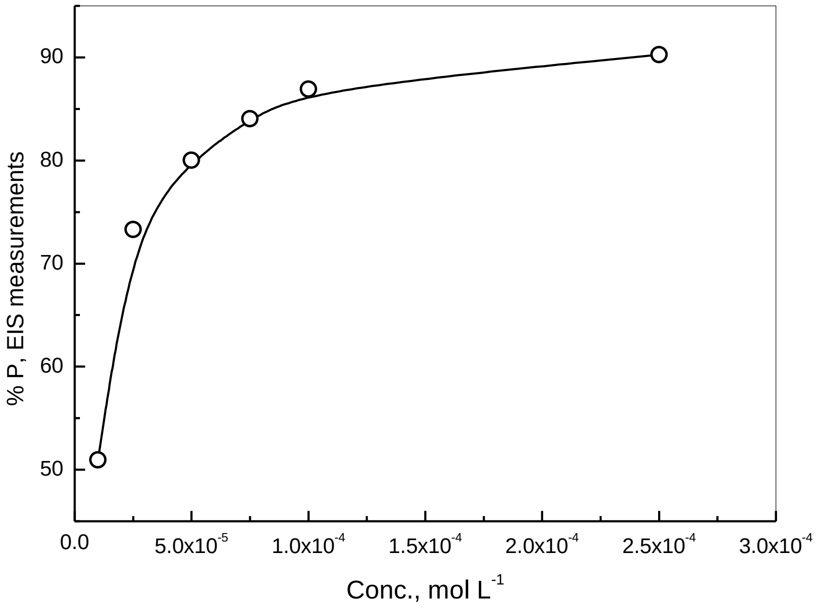

Figure 7. Variation of the percentage inhibition efficiency (%P) obtained from EIS measurements for steel in 0.5 M phosphoric acid solution with the concentration of DTPB 30 ^{O}C.

3.4. Application of adsorption isotherms

Basic information on the interaction between inhibitor and steel surface can be provided by adsorption isotherm. The degree of surface coverage (θ) of the metal surface by an adsorbed inhibitor molecule is calculated from impedance measurements using the equation:

$$\theta = (R_{ct} - R_{cto}) / R_{ct}$$

The Langmuir isotherm is given by [20]:

$$[\theta / (1-\theta)] = K [C]$$

where *K* is the binding constant representing the interaction of the additives with metal surface and *C* is the concentration of the additives.

Flory-Huggins isotherm is given by [21, 22]:

$$\theta / [x (1-\theta)^{x}] = K [C]$$

where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

and the kinetic – thermodynamic model is given by [23]:

$$\log [\theta / (1-\theta)] = \log K' + y \log C$$

where *y* is the number of inhibitor molecules occupying one active site. The binding constant K is given by

$$K = K'^{(1/y)}$$

Figures (8-10) show the application of the above mentioned models to fit the corrosion data of the inhibitor.

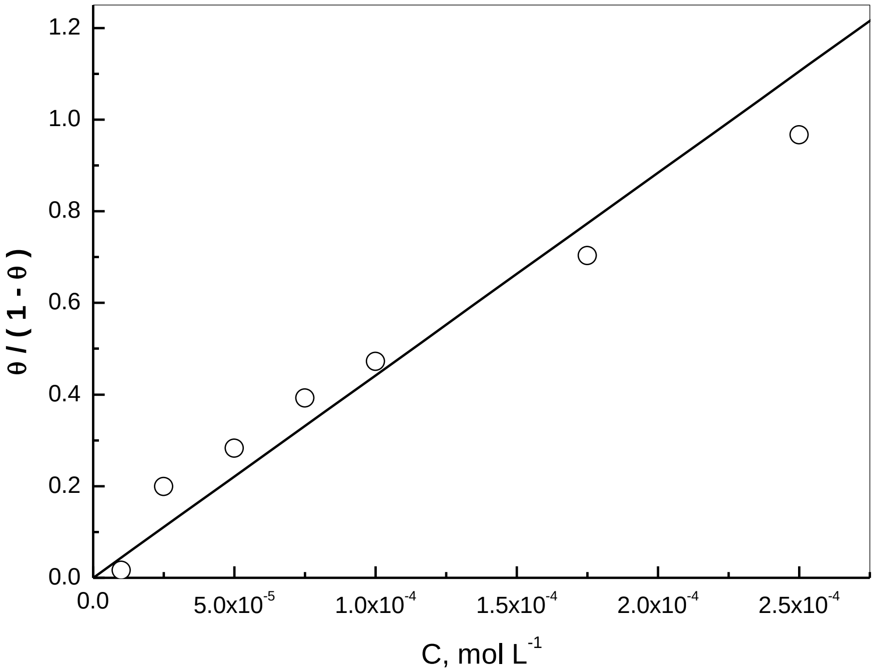

Figure 8. Linear square fit of impedance data to Langmuir isotherm.

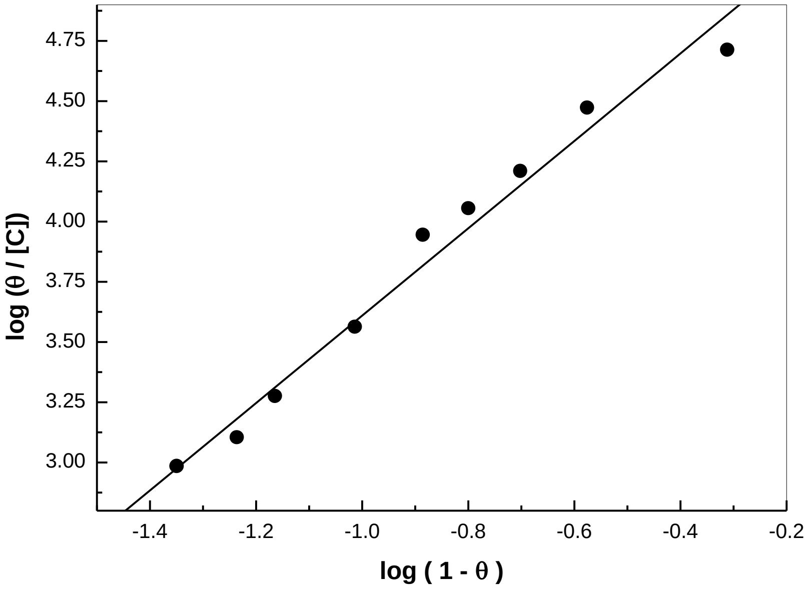

Figure 9. Linear square fit of impedance data to Flory Huggins isotherm.

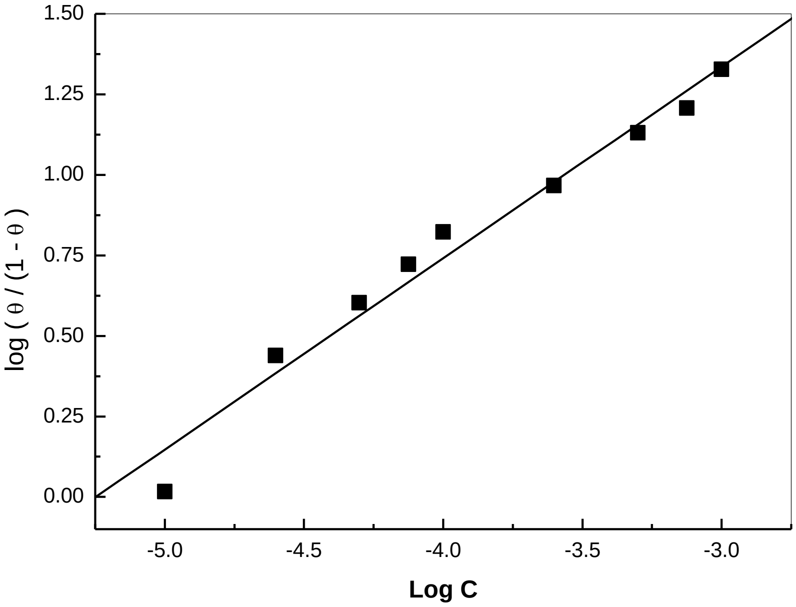

Figure 10. Linear square fit of impedance data to Kinetic-Thermodynamic model.

The parameters obtained from these Figures are given in Table 2. The parameters reveal that Langmuir isotherm is applicable to fit the corrosion data of DTPB indicating an ideal behavior in the adsorption processes on the steel surface [24]. The value of the size parameter *x* indicates that the adsorbed species of DTPB could displace one water molecule from the steel surface. The number of active sites occupied by a single inhibitor molecule, 1/y, are nearly equal to the size parameter x. The 1/y value indicates that the adsorbed molecules cover one active center. The binding constant values

(K) show a fairly good agreement between Langmuir, Flory-Huggins isotherm and Kinetic thermodynamic model.

Table 2. Linear fitting parameters of Langmuir, Flory-Huggins and Kinetic- thermodynamic model for DTPB.

Langmuir	Flory- Huggins		Kinetic-Thermodynamic	
K	X	K	1/y	K
$1.10x10^4$	1.07	$1.16\ x10^4$	1.11	$3\ .00x10^4$

3.5. Activation parameters

Figure 11 shows Nyquist impedance plots for steel in 0.5 M phosphoric acid solution containing $7.5x10^{-5}$ mol/L DTPB at 30, 40, 50 and 60^OC. As seen, the size of the capacitive semicircle decreases and hence the steel corrosion rate in the inhibited solution increases by increasing the temperature.

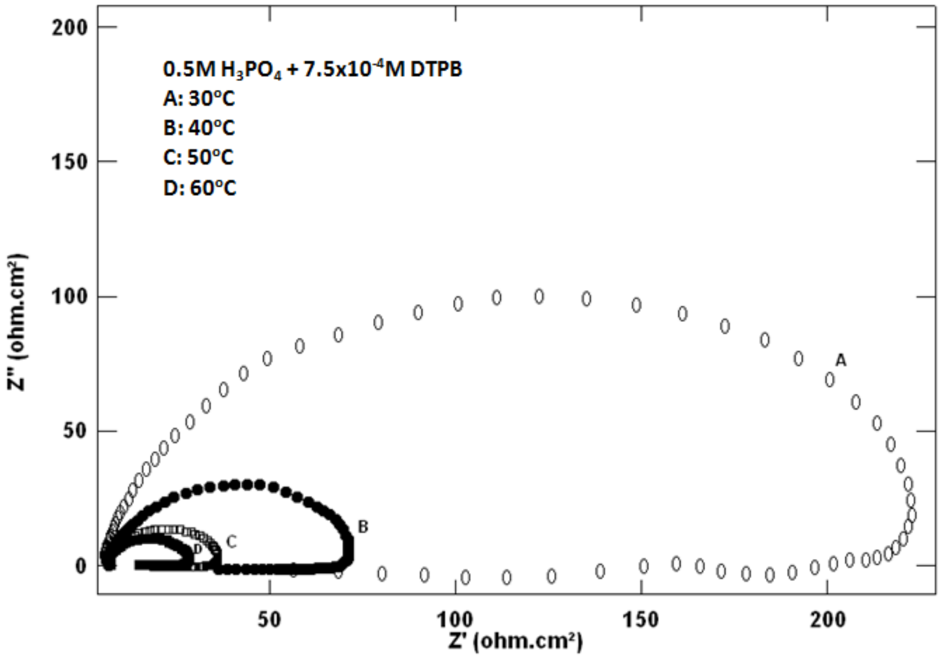

Figure 11. Nyquist impedance plots of steel in 0.5M phosphoric acid solution containing $7.5x10^{-4}$ M DTPB at different temperatures.

It has been pointed out by a number of authors [25, 26] that the logarithm of the corrosion rate (ν) is a linear function with the reciprocal of the absolute temperature 1/T (Arrhenius equation):

$$\ln \nu = - E_a / RT + A$$

where E_a is the apparent effective activation energy, T is the absolute temperature, R is the universal gas constant, and *A* is Arrhenius pre-exponential factor.

An alternative formulation of the Arrhenius equation is the transition state equation:

$$\nu = (RT/Nh) \exp (\Delta S^*/R) \exp (- \Delta H^*/RT)$$

where, N is the Avogadro's number, h is the Plank's constant, ΔH^* is the enthalpy of activation, and ΔS^* is the entropy of activation. The corrosion rates were taken as the reciprocal of the charge transfer resistance.

The activation parameters for steel in 0.5 M phosphoric acid in the absence and presence of 7.5×10^{-5} mol/L DTPB are obtained from linear square fit of ln (ν) and ln (ν/T) data *vs.* (1/T) as shown in Figures (12 and 13).

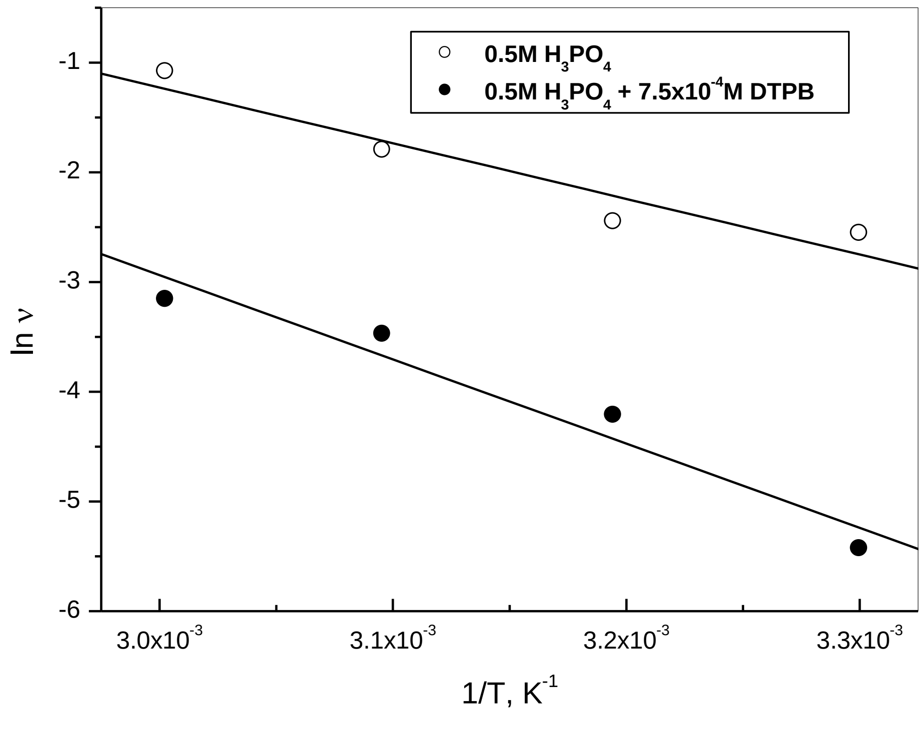

Figure 12. Linear square fit of ln (ν) vs. (1/T).

The resulting values for the activation parameters are given in Table (3). The values of E_a and ΔH^* in the presence of the inhibitor are higher than those of pure acid. This could be attributed to the presence of an energy barrier for the corrosion reaction due to the existence of inhibitor cations at the metal/electrolyte interface. The negative value of ΔS^* implies that the activated complex represents an association rather than a dissociation step meaning that a decrease in disordering takes place on going from reactants to the activated complex [27]. Similar results were recorded for the inhibition of mild steel corrosion in phosphoric acid solutions by some N-heterocyclic compounds in the salt form [5].

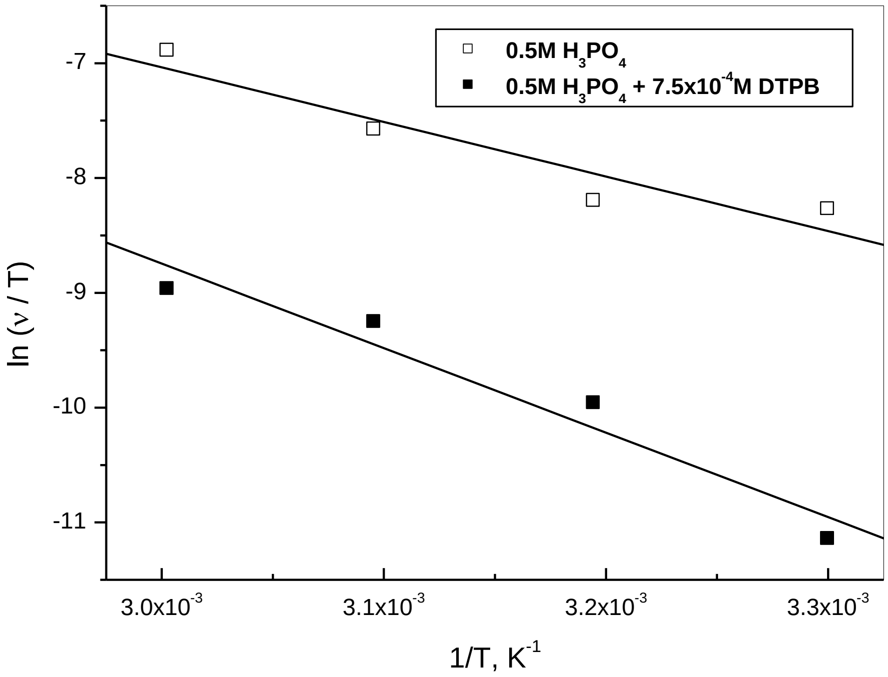

Figure 13. Linear square fit of ln (ν/T) vs. (1/T).

Table 3. Thermodynamic parameters of steel corrosion in 0.5M H_3PO_4, in the absence and presence of 7.5×10^{-4}M DTPB.

Solution	Activation parameters		
	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	ΔS* J mol^{-1} K^{-1}
0.5M H_3PO_4	42.18	39.54	-137.4
0.5M H_3PO_4 + 7.5x10^{-4}M DTPB	63.84	61.20	-86.6

4. MECHANISM OF THE CORROSION INHIBITION

The inhibitive effect of DTPB in H_3PO_4 solution can be explained as follows: in aqueous acidic solutions, the DTPB ionizes to the cation organic part (DTP^+) and the anion inorganic part (Br^-). It is well known that the steel surface charges a positive charge in acid solution [28]. So, it is difficult for DTP^+ to approach the positively charged steel surface due to the electrostatic repulsion. The Br^- ions specifically adsorbed at the steel/solution interface creating an excess negative charge toward the solution [29].

$$Fe + Br^- = (FeBr^-)_s$$

The phosphonium cation adsorbed on the sites of the surface where the anion is chemisorbed [12]. So, Br^- ion acts as an adsorption mediator for bonding metal surface and DTP^+ [30]. This gives rise to the formation of an adsorption composite film in which bromide ions are sandwiched between metal and positively charged part of the inhibitor. This film acts as a barrier facing corrosion process.

$$(FeBr^-)_s + DTP^+ = (FeBr^- \ldots\ldots DTP^+)_s$$

Moreover, it could be suggested that the π-electron system of the benzene rings and unshared lone pair of electron of the oxygen atom in DTP cation possibly overlaps with the vacant d-orbitals of the surface of iron resulting in a strong dπ–pπ interaction. Therefore, the adsorption of DTP cation on mild steel may primarily be through dπ–pπ interaction which is further assisted by synergism provided by Br^- [9, 10]. Therefore, in the process of adsorption, both physical and chemical adsorption would take place.

5. CONCLUSIONS

- DTPB could acts as an effective corrosion inhibitor for the phosphoric acid corrosion of steel.
- DTPB is classified as a mixed-type inhibitor with predominant anodic character.
- the decrease in C_{dl} or Q_{dl} values, obtained from impedance measurements, was related to the decrease of local dielectric constant (ε) or increase of thickness of electrical double layer due to the formation of a protective layer by the adsorption of inhibitor molecules on the mild steel surface
- Application of different isotherms indicated an ideal behavior in the adsorption processes of DTPB on the steel surface.
- The number of active sites occupied by a single inhibitor molecule value indicated that the adsorbed molecules cover one active center.
- The mechanism of inhibition was suggested to be through (i) a cooperative mode of adsorption where Br^- ion acts as an adsorption mediator for bonding metal surface and phosphonium cation and/or (ii) overlaps of the π-electron system of the benzene rings and unshared lone pair of electron of the oxygen atom in DTP cation with the vacant d-orbitals of the surface of iron resulting in a strong dπ–pπ interaction.

References

1. X. Li, Sh. Deng, H. Fu, *Corros. Sci.* 53 (2011) 664–670
2. X. Li, Sh. Deng, H. Fu, Guannan Mu, *Corros. Sci.* 52 (2010) 1167–1178.

3. X. Li, Sh. Deng, H. Fu, *Prog. Org. Coat*. 67 (2010) 420–426.
4. A.Ghanbari, M.M. Attar, M. Mahdavian, *Mater. Chem. Phys*. 124 (2010) 1205–1209
5. E.A. Noor., *Corros. Sci*. 47 (2005) 33–55.
6. E. Khamis, M.A. Ameer, N.M. AlAndis, G. Al-Senani, *Corrosion* 56 (2000) 127–138.
7. M.S. Morad, *Mater. Chem. Phys*. 60 (1999) 188-195
8. G. Schmitt, *Br. Corros. J.* 19 (4) (1984) 165.
9. K. Bhrara, H. Kim, G. Singh, *Corros. Sci*. 50 (2008) 2747–2754.
10. K. Bhrara, G. Singh, *Appl. Surf. Sci*. 253 (2006) 846–853.
11. M.H. Wahdan, A.A. Hermas, M.S. Morad, *Mater. Chem. Phys*. 76 (2002) 111–118.
12. M.S. Morad, *Corros. Sci*. 42 (8) (2000) 1307–1326.
13. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, M. Saadawy, *Corros. Sci.* 51(2009)1038-1042.
14. J. Bessone, C. Mayer, K. Juttner and W.J. Lorenz, *Electrochim. Acta*, 28 (1983) 171.
15. J. Hitizig, K. Juttner, W.J. Lorenz and W. Paatsch, *J. Electrochem. Soc*., 133 (1986) 887.
16. J.B. Bessone, D.R. Salinas, C.E. Mayer, M. Ebert and W.J. Lorenz, *Electrochimica Acta*, 37 (1992)2283.
17. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady, M. Saadawy, *Mater. Chem. Phys*. 98 (2006) 291–297
18. M. Benabdellah, R. Touzani, A. Dafali, B. Hammouti, S. El Kadiri, *Mater. Lett.* 61(2007) 1197–1204.
19. A.Ghanbari, M.M. Attar, M. Mahdavian, *Chem. Phys.* 124 (2010) 1205–1209.
20. I. Langmuir, *J. Am. Chem. Soc*., 38 (1916) 2221.
21. P. J. Florry, *J. Chem. Phys*. 10 (1942) 51.
22. M. L. Huggins, *J. Phys. Chem*. 46 (1942) 151
23. A.A. El-Awady; B.A. Abd-El-Nabey, S.G. Aziz, *J. Electrochem. Soc*., 19 (1992) 2149.
24. G. Lyberatos and L. Kobotiatis, *Corrosion*, 47 (1991) 820.
25. S.S. Abd El-Rehim, Magdy A.M. Ibrahim, and K.F. Khaled, *J. Appl. Electrochem*., 29 (1999) 593
26. I.N. Putilova, S.A.Balezin, V.P. Barannik, Metallic Corrosion Inhibitors (Oxford, U.K. :Pergamon Press, 1960)
27. B.A. Abd-El-Nabey, E. Khamis, M.Sh. Ramadan, and A. El-Gindy, *Corrosion*, 52 (1996) 671.
28. H. Luo, Y.C. Guan, K.N. Han, *Corrosion* 54 (1998) 721.
29. X.H. Li, S.D. Deng, H. Fu, T.H. Li, *Electrochim. Acta* 54 (2009) 4089–4098.
30. X. Li, L. Tang, H. Liu, G. Mu, G. Liu, *Mater. Lett.* 62 (2008) 2321–2324.