Int. J. Electrochem. Sci., 7 **(2012)** 11718 - 11733

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Inhibitive Action of Benzaldehyde Thiosemicarbazones on the Corrosion of Mild Steel in 3 M H_3PO_4

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Received: 15 September 2012 / *Accepted:* 22 October 2012 / *Published:* 1 December 2012

The inhibition efficiency of some Benzaldehyde thiosemicarbazone derivatives_for mild steel corrosion in 3.0 mol/L H_3PO_4 at 30.0 ±0.1 ^{0}C were investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). These compounds inhibit the corrosion rate even at very low concentrations and the order of increasing inhibition efficiency was correlated with the modification of the molecular structure of the inhibitors. Polarization curves indicated that these compounds acted primarily as mixed-type inhibitors. Electrochemical impedance spectroscopy results indicated that dissolution process of steel in phosphoric acid occurs under activation control. The effect of temperature on the inhibitive action of these compounds was evaluated for the corrosion of mild steel in 3.0 mol/L H_3PO4 acid. Theoretical fitting of the kinetic–thermodynamic model of the adsorption of inhibitors at the metal surface are tested to clarify the nature of adsorption.

Keywords: Potentiodynamic; EIS; molecular structure; mild steel; Phosphoric acid.

1. INTRODUCTION

Steel corrosion in phosphoric acid solution is attracting the attention of researchers [1, 2]. Using inhibitors is an effective method to reduce corrosion rate [3].The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [4]. Mild steel is widely applied as constructional material in many chemical and petrochemical industries due to its excellent mechanical properties and low cost [5].Phosphoric acid (H_3PO_4) is widely used in the surface treatment of steel such as chemical and electrolytic polishing, chemical coloring, chemical and electrolytic etching, removal of oxide film, phosphating, passivating, and surface cleaning [6, 7]. There is a great need to protect steel in the phosphoric acid medium. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms which can donate lone pair of electrons [8-11]. Added improvements in inhibitor performance can also be achieved by substitution and addition of appropriate electron donating groups. Thiosemicarbazones and their derivatives has been reported to be a potential inhibitors for steel [12-14]. Previous studies in our laboratory on the inhibition of the acidic corrosion of steel by thiosemicarbazones have shown their value as corrosion inhibitors [15-17]. Little work [18-20] appears to have been done on the inhibition of steel in H_3PO_4 solution. The purpose of this paper is to evaluate the corrosion of mild steel in the absence and the presence of three thiosemicarbazone derivatives in 3 M H_3PO_4, to establish a correlation between the inhibition efficiency of these organic compounds, molecular structure and the presence of substitutions on the benzene ring.

2. EXPERIMENTAL

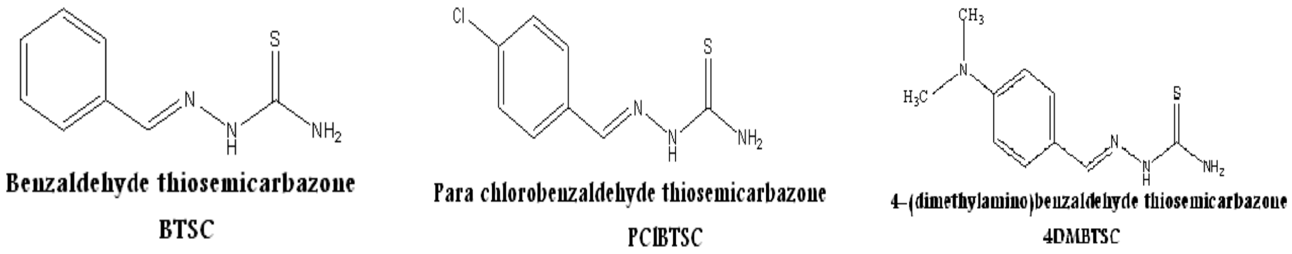
2.1. Electrochemical tests

Electrochemical impedance spectroscopy and polarization curves measurements were achieved using frequency response analyzer (FRA) / potentiostat (Gill AC) supplied from ACM instruments (UK). The frequency range for EIS measurements was 0.1 - $3x10^3$ Hz with applied potential signal peak to peak amplitude of 10 mV around the rest potential. The data were obtained in a three-electrode mode; platinum sheet and saturated calomel electrodes were used as counter and reference electrodes respectively. The material used for constructing the working electrode was mild steel (UNS G10100) that had the following chemical composition (wt. %): 0.1C, 0.1 Cr, 0.1Sb, 0.3Mn and balance Fe. The mild steel was encapsulated in 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 Analytical grade reagent (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 10 min to attains the open circuit potential (ocp) at which the change of ocp with time is 2 mV/min, i.e., the system had been stabilized. Polarization curve measurements were obtained at a scan rate of 30 mV/min starting from cathodic potential (E_{corr} – 300 mV) going to anodic direction. This wide range of potential allows the Tafel slopes (β_a and β_c) to be determined and the corrosion current estimated, by extrapolating the linear Tafel regions to the corrosion potential. All the measurements were done at 30.0 ±0.1 ^oC in solutions open to the atmosphere under unstirred conditions. Initially, the procedures of both Polarization curves and impedance measurements were repeated two times for calibration and to assure the reproducibility of the data.

2.2. Solutions preparation

Solutions of 3 M H_3PO_4/l0% EtOH at a temperature of 30 ^0C ± 0.1 ^oC were used as the corrosive medium. The compounds examined in this study are indicated in Figure 1.

Thiosemicarbazones were prepared by condensation of the suitable carbonyl compound with thiosemicarbazide in the presence of an acid catalyst. As follows: solution of either benzaldehyde, Para Chloro Benzaldehyde, or 4-dimethyl amino benzaldehyde in ethanol in presence of an acetic acid catalyst was added to a solution of Thiosemicarbazide(TSC) soluble in ethanol. The reaction mixture was refluxed with stirring for 2 hours. Upon cooling, the precipitated products were filtered off, washed with ethanol, ether and dried in vacuum, recrystallized twice from ethanol [21, 22]. The reaction products obtained were purified and characterized by NMR and IR spectroscopy.All test solutions contained 10% vol of ethanol to maintain the solubility of the inhibitors.



Benzaldehyde thiosemicarbazone
BTSC

Para chlorobenzaldehyde thiosemicarbazone
PClBTSC

4-(dimethylamino)benzaldehyde thiosemicarbazone
4DMBTSC

Figure 1. Molecular structure of thiosemicarbazone derivatives.

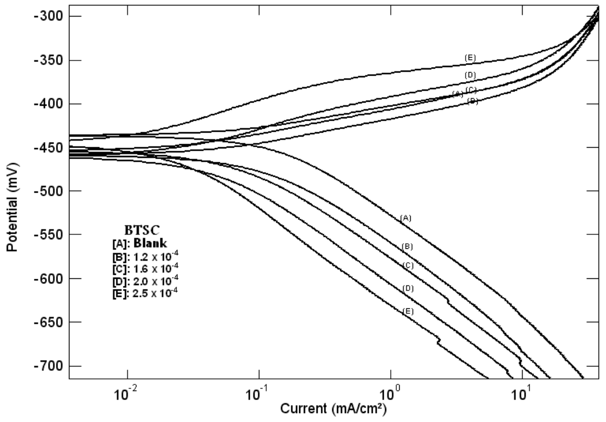
3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization results

Figure 2 shows the effect of the concentration of thiosemicarbazone derivatives on the potentiodynamic polarization curves for steel in 3 M phosphoric acid. The measured parameters such as corrosion potential, E_{corr}; anodic and cathodic Tafel slopes, β_a, β_c; corrosion current density (i_{corr}) and protection efficiency (*P %)* are listed in Table1. the inhibition efficiency is given by:

$$\%P= [(I_{Corr}– I_{Corr(inh)}) / I_{Corr})]x100 \tag{1}$$

Where I_{corr} and I_{corr}(inh) are corrosion current densities without and with inhibitors respectively, as determined by extrapolation of Tafel lines.



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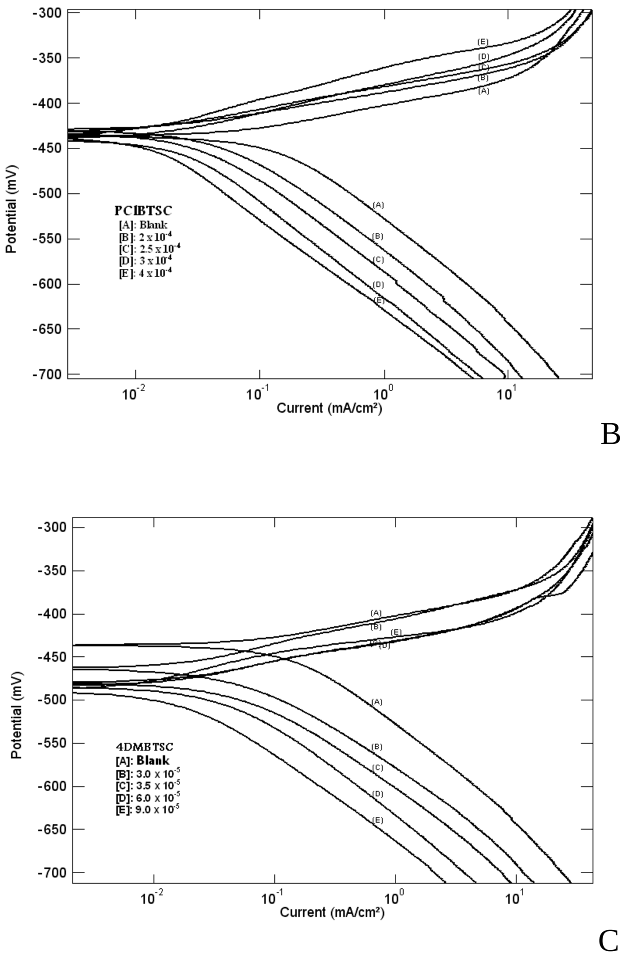


Figure 2. Potentiodynamic polarization curves for mild steel in 3.0 M H_3PO_4 in absence and presence of different concentrations of BTSC (a), PClBTSC (b) and 4DMBTSC (c) at 30 ^{o}C.

The results showed that the three compounds affect both the cathodic and anodic polarization curves indicating that these compounds act as mixed-type inhibitors. The obtained data illustrate that addition of the thiosemicarbazones to the acid solution has a slight effect on the corrosion potential (E_{corr}). However, increasing concentrations of these compounds, the corrosion current densities (i_{corr}) decrease. The obtained data illustrate that addition of the thiosemicarbazones to the acid solution decreases the corrosion current and slightly affects the corrosion potential (E_{corr}). It was reported that [23, 24] pickling inhibitors, in spite of leaving the corrosion potential (E_{corr}) virtually unchanged, cause a significant decrease in the corrosion rate. Therefore, it could be predicted that thiosemicarbazones could be used as pickling inhibitors. The numerical values of anodic and cathodic Tafel slopes, β_a and β_c show a slight variation suggesting that increasing concentrations of these compounds do not change the mechanism of the corrosion reaction [25]. Moreover, it suggests that they don't impact the kinetics of either the anodic or the cathodic reactions taking place at the surface as a function of applied potential. This implies that both these compounds act by adsorption at either and both the local anodic as well as cathodic sites thereby decreasing the rate of the anodic dissolution and hydrogen evolution reactions [26, 27].

Table 1. Electrochemical polarization parameters of mild steel in 3.0 M H_3PO_4 at various concentrations of BTSC, PClBTSC and 4DMBTSC at 30 ^oC.

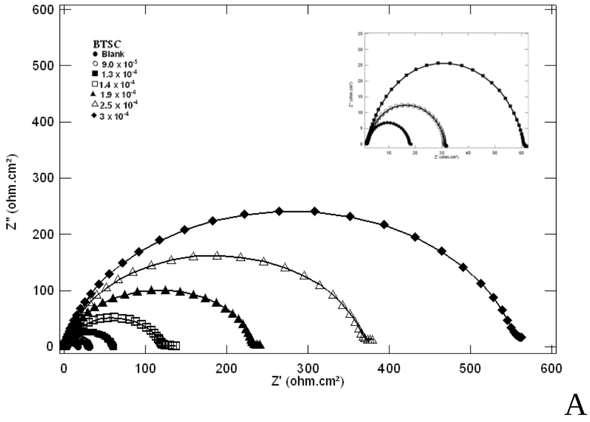
Compound	Conc, mol. L^{-1}	Electrochemical parameters					
		- E_{corr} mV	β_a mV/decade	-β_c mV/decade	i_{corr} mA/cm^2	Rate mm/y	% inh
BTSC	0.0	443	38	104	0.151	1.75	---
	1.2 x 10^{-4}	461	40	106	0.120	1.39	20
	1.3 x 10^{-4}	456	36	105	0.091	1.05	39
	1.6 x 10^{-4}	450	34	102	0.058	0.67	61
	1.7 x 10^{-4}	448	29	104	0.042	0.48	71
	1.8 x 10^{-4}	438	28	108	0.031	0.35	79
	2.0 x 10^{-4}	440	31	105	0.027	0.31	81
	2.2 x 10^{-4}	421	25	113	0.017	0.19	88
	2.5 x 10^{-4}	406	19	111	0.009	0.10	93
	3.0 x 10^{-4}	402	15	112	0.005	0.05	96
PClBTSC	1.5 x 10^{-4}	461	39	93	0.061	0.70	59
	1.8 x 10^{-4}	488	45	105	0.054	0.62	63
	2.0 x 10^{-4}	428	28	100	0.046	0.53	69
	2.2 x 10^{-4}	448	36	113	0.030	0.34	79
	2.5 x 10^{-4}	421	24	100	0.023	0.26	84
	2.7 x 10^{-4}	439	29	97	0.021	0.24	86
	3.0 x 10^{-4}	431	29	106	0.019	0.22	87
	4.0 x 10^{-4}	432	36	101	0.011	0.12	92
4DMBTSC	3.0 x 10^{-5}	473	49	101	0.092	1.06	38
	3.5 x 10^{-5}	500	51	94	0.088	1.02	41
	4.0 x 10^{-5}	518	54	95	0.073	0.84	51
	6.0 x 10^{-5}	508	52	109	0.069	0.80	54
	7.0 x 10^{-5}	520	53	109	0.049	0.56	67
	7.5 x 10^{-5}	520	44	104	0.026	0.30	82
	8.0 x 10^{-5}	464	22	94	0.011	0.12	92
	9.0 x 10^{-5}	464	18	97	0.009	0.10	93

Their effect on the anodic partial reaction could be attributed to their chemisorption on the metal surface that might take place through coordination bond formation between the metal and the electron pair on S-atom [28]. Furthermore, this adsorption may cause steric hindrance to the escape of Fe^{2+} ions [29]. On the other hand, the inhibitive effect of these compounds molecules might result from the electrostatic attraction of the protonated species and their physical adsorption on the cathodic regions of the metal surface at which the hydrogen evolution reaction occrs [30, 31]. Also, these protonated forms obstruct the passage of ions to the cathodic surface. Moreover, the steric hindrance of the adsorbed molecules would affect the combination of the adsorbed hydrogen atoms to form hydrogen molecules and inhibit the cathodic reaction. Moreover, upon increasing the inhibitor concentration, more and more molecules would be adsorbed due to Van der Waals forces of interaction between the inhibitor molecules. Thus increasingly, close-packed film will be building up and segregated the metal surface from the solution. A similar mechanism was suggested for the inhibition of steel in acidic medium by 4-amino, 3-substituted, 5-mercapto 1,2,4-triazoline and some related compound [32]; n-alkylquaternary ammonium compounds.[33,34], and also with some S-alkylisothiouronium iodides [35].

3.2. Electrochemical Impedance Spectroscopy results

The corrosion behavior of mild steel in 3 M H_3PO_4, in the both absence and presence of thiosemicarbazone derivatives was investigated by EIS to gain further mechanistic information's. Nyquist plots of mild steel at different concentrations of BTSC, PClBTSC and 4DMBTSC are shown in Figure 3. Nyquist plots show depressed semicircles indicating that the dissolution mechanism of mild steel is being controlled by the rate of the charge transfer process across the phase boundary in the uninhibited and inhibited acid solutions. Therefore, it could be concluded that addition of these compounds to the acid solution does not alter the mechanism of steel dissolution [36]. Moreover, it is clear that the size of semicircle increases with increasing concentrations. Lorenze and Mansfeld [37] classify the modes of inhibition effect of interface inhibitors into three categories: that caused by (i) the geometric blocking effect of adsorbed inhibitive species on the metal surface (ii) the effect of the blocking of the active sites on the metal surface by adsorbed inhibitive species (iii) the electro-catalytic effect of the inhibitor or its reaction products. Therefore, the increase in the values of R_{ct} might be related to the extent and the mode of adsorption of the three thiosemicarbazone derivatives on the steel/solution interface.

This adsorption (geometric blocking effect) of molecules reduces the reaction area on the steel surface; by which the corrosion inhibition takes place. The equivalent circuit model of the mild steel-phosphoric acid interface is shown in Figure 4, included the solution resistance, R_s and the charge transfer resistance, R_{ct} and the double layer capacitance, C_{dl} [38, 39].



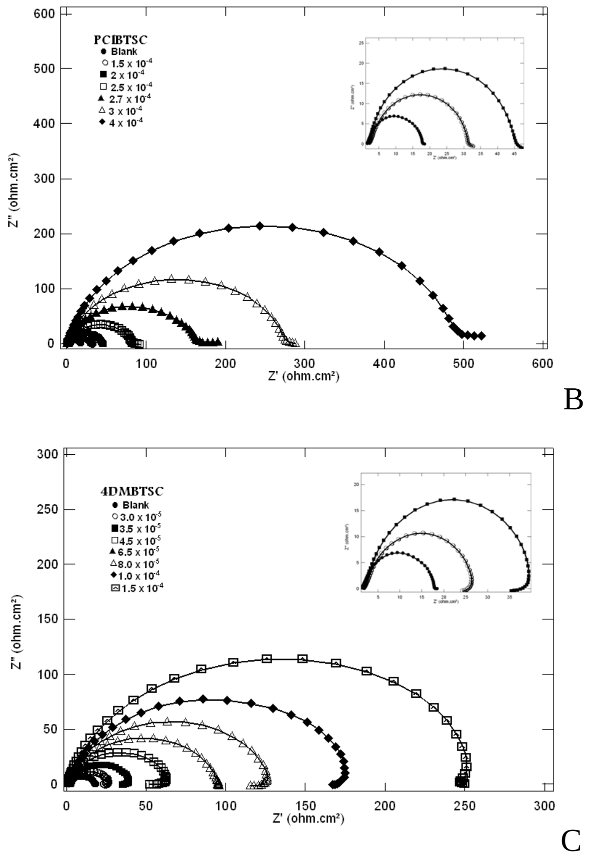


Figure 3. Nyquist plots for mild steel in 3.0 M H_3PO_4 in absence and presence of different concentrations of BTSC (a) ,PClBTSC (b) and 4DMBTSC (c) at 30 ^oC.

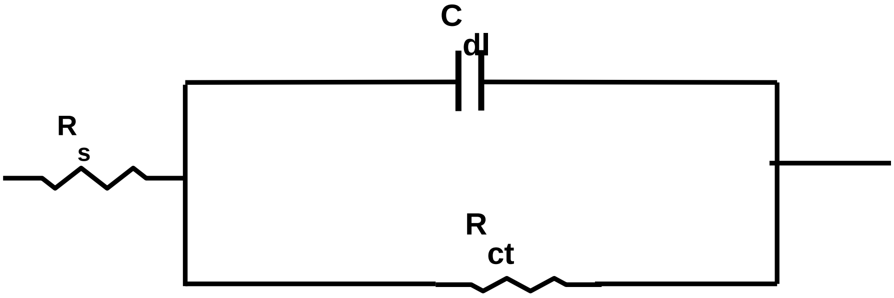


Figure 4. Equivalent circuit model to fit the EIS data of mild steel in 3.0 M H_3PO_4 in absence and presence of the inhibitors.

Electrochemical parameters derived from this electrical model, calculated using ACM analysis v4 software, are given in Table 2. Inhibition efficiency (% inh) was calculated according to following equation:

$$\% \text{ inh} = [(R_{ct} - R_{cto}) / R_{ct}] \text{ x100} \qquad (2)$$

Where R_{ct} and $R_{ct\mathbf{o}}$ are charge transfer resistances with and without inhibitors, respectively. The values of C_{dl} for steel in 3 M phosphoric acid containing different concentrations of thiosemicarbazone derivatives concentrations are shown in Table 2. The data point to decrease in C_{dl} values with increasing inhibitors concentration that might be attributed to the substitutional adsorption of these molecules to the acid anion and the adsorbed water molecules at the metal surface decreasing the extent of the dissolution reaction [40-42].

It is observed that the numerical values of the percentage of corrosion inhibition determined from the polarization curves and EIS measurements Tables (1, 2) are different. This was discussed by Abdel-Gaber et al [43] as: in air saturated media, dissolved oxygen could react with hydrogen atoms adsorbed at random on the iron surface resulting in acceleration of the cathodic reaction. In polarisation curve measurements, the Tafel plots can be difficult to use when there is more than one reduction reaction or where concentration polarization is strong. These limitations make the Tafel region less distinct, and it becomes difficult to make extrapolation to obtain corrosion rates. In impedance measurements, the rate of corrosion is taken as the reciprocal of the charge transfer resistance. This approximation is based on the assumption that the cathodic and anodic Tafel slopes are constant within the concentration under study.

Table 2. Electrochemical impedance parameters of mild steel in 3.0 M H_3PO_4 at various concentrations of BTSC, PClBTSC and 4DMBTSC at 30 ^oC.

Compound	Conc, mol. L^{-1}	Impedance parameters			
		R_s Ohm.cm^2	R_{ct} Ohm.cm^2	C_{dl} $\mu F/cm^2$	% inh
BTSC	0.0	1.5	16	454	----
	8.0 x10^{-5}	1.5	18	382	9
	9.0 x10^{-5}	1.5	29	259	43
	1.2 x10^{-4}	1.5	49	154	66
	1.3 x10^{-4}	1.5	59	133	72
	1.4 x10^{-4}	1.4	119	87	86
	1.5 x10^{-4}	1.7	121	76	86
	1.7 x10^{-4}	1.5	159	68	89
	1.8 x10^{-4}	1.5	179	72	90
	1.9 x10^{-4}	2.1	231	50	92
	2.0 x10^{-4}	1.4	248	56	93
	2.2 x10^{-4}	1.5	324	52	94
	2.5 x10^{-4}	1.2	368	48	95
	3.0 x10^{-4}	1.1	557	31	97
PClBTSC	1.2 x10^{-4}	2.0	21	416	23
	1.5 x10^{-4}	2.1	29	326	43
	1.7 x10^{-4}	1.9	36	320	54
	2.0 x10^{-4}	1.6	43	252	62
	2.2 x10^{-4}	2.2	54	201	69
	2.5 x10^{-4}	1.5	80	140	79
	2.7 x10^{-4}	1.6	162	94	89
	3.0 x10^{-4}	1.4	274	66	93
	4.0 x10^{-4}	1.5	488	49	96
4DMBTSC	3.0 x10^{-5}	1.7	25	344	34
	3.5 x10^{-5}	1.4	38	154	56
	4.0 x10^{-5}	1.4	45	170	63
	4.5 x10^{-5}	1.4	62	105	73
	6.5 x10^{-5}	1.5	93	116	82
	8.0 x10^{-5}	1.3	126	82	86
	1.0 x10^{-4}	1.7	174	80	90
	1.5 x10^{-4}	1.3	252	61	93

Correlation between the chemical structure of the studied compounds and their inhibition efficiency
(a) Protection efficiency

Figure 5 shows the variation in the percentage inhibition efficiency, obtained from impedance measurements (EIS), for different inhibitor concentrations in 3.0 M H_3PO_4. This is because electrochemical impedance spectroscopy (EIS) is a powerful nondestructive technique that has been used extensively to investigate electrochemical systems. In addition, large numbers of data points were obtained using EIS technique.

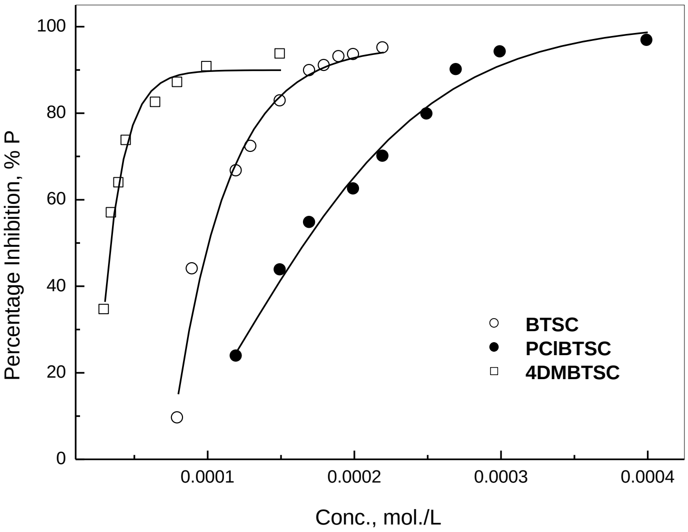


Figure 5. Variations of protection efficiency with the concentration of BTSC, PClBTSC and 4DMBTSC for mild steel in 3.0 M H_3PO_4 solutions at 30 ^{o}C.

As seen, the curves show the order of the increase in the protection efficiency respect to the change in the molecular structure of these compounds are given as PClBTSC < BTSC < 4DMBTSC. It is clearly observed that a low concentration of 4DMBTSC can gives the same percentage of inhibition (e.g. 80%) of high PClBTSC concentration. This behavior can be discussed on the basis that; the lower value of the efficiency for Para chloro benzaldehyde thiosemicarbazone may be attributed to the electron withdrawing inductive effect of the chlorine atom which decreases the electron availability on the adsorpation center reaction site and causes less adsorption. On the other hand the superior performance for 4-(Dimethylamino) benzaldehyde thiosemicarbazone can be attributed to the presence of the effective electron releasing group ($N(CH_3)_2$) on the benzene ring leading to increase in the electron density on the adsorption center which is mainly (>C=S) [44-46].

b) Double layer Capacitance

Figure 6 illustrates the dependence of the double layer capacitance of mild steel on the concentration of the inhibitors BTSC, PClBTSC and 4DMBTSC. In general, the presence of the inhibitors in the solution caused a lowering of the capacitance of the steel interface, and the magnitude of the effect of the inhibitor depends on its molecular structure. The order of the decrease in the capacitance is PClBTSC< BTSC < 4DMBTSC. This behavior can be discussed on the same bases discussed above for the inhibition efficiency changes the effect of the substituent (− Cl or −N $(CH_3)_2$) on the electron density on the adsorption center. In the case of the chloro substitution the decrease of the electron density on the adsorption center leads to the weak adsorption of the compound. However in case of 4-dimethyl derivative the increase of electron density on the adsorption center leads to a strong adsorption of the compound.

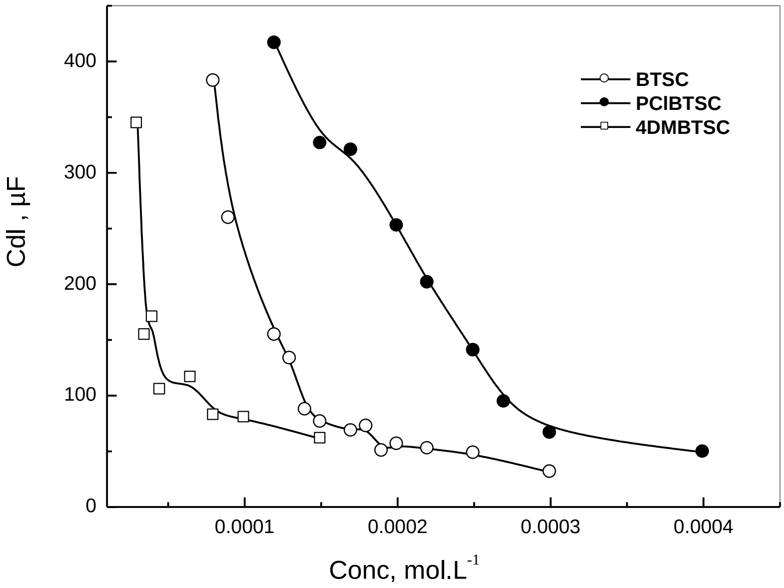


Figure 6. Variation of the double layer capacity the concentration of BTSC, PClBTSC and 4DMBTSC for mild steel in 3.0 M H_3PO_4 at 30 °C.

3.3. Application of the Kinetic-Thermodynamic model

To clarify the nature of adsorption, theoretical fitting of different isotherms, Langmuir and the kinetic–thermodynamic model are tested.

The degree of surface coverage (θ) of the metal surface by inhibitor molecules is calculated from impedance measurements using the equation:

$$\theta = (R_{ct} – R_{cto})/R_{ct} \qquad (3)$$

where R_{cto} and R_{ct} are the charge-transfer resistance for steel in 3.0 M H_3PO_4 in the absence and presence of inhibitor.

The Langmuir isotherm is given by [47]

$$[\theta / (1- \theta)]=K [C] \qquad (4)$$

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

It is found that the Langmuir isotherm is unsuitable to fit the data of the used inhibitors indicating that there might be non-ideal behaviour in the adsorption processes [48] of the inhibitors on the steel surface.The kinetic - thermodynamic model is given by [49, 50]

$$\text{Log}\,[\theta/(1-\theta)] = \text{Log}K' + y\,\text{Log}\,C \qquad (5)$$

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

$$K = K'^{(1/y)} \qquad (6)$$

Figure (7) shows the application of the kinetic - thermodynamic model to the data of the three compounds for steel surface in 3.0 M H_3PO_4.The adsorption parameters obtained from Figure 7 were listed in Table 3.The values of y greater than one imply the formation of multilayers of the inhibitor on the surface of the metal, however, values of y less than one mean that a given inhibitor molecule will occupy more than one active site. Since the efficiency of a given inhibitor was essentially a function of the magnitude of its binding constant K, large values of K indicate better and stronger interaction, whereas small values of K mean that the interaction between the inhibitor molecules and the metal is weaker [51].The values of the binding constant K of these inhibitors have the following order: 4DMBTSC > BTSC > PClBTSC.

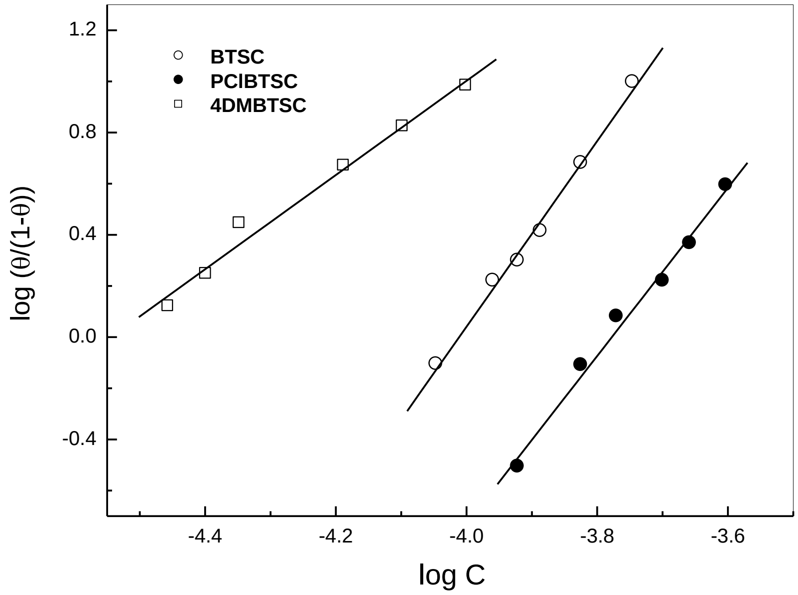


Figure 7. Linear fitting of the data of the three compounds to Kinetic-Thermodynamic model.

As it can be seen the increase of the efficiency of these inhibitors leads to an increase of the value of the binding constant,K. Values of y is greater than one indicate the formation of multilayers of the inhibitor on the surface of the metal. The higher inhibition efficiency of these inhibitors for steel could be explained on the basis of the mechanism that suggests strong adsorption of these inhibitors on the surface of metal acting as a film forming species decreasing the active area available for acid attack**.**

Table 3. Kinetic-thermodynamic parameters for BTSC, PClBTSC and 4DMBTSC on mild Steel surface in 3.0 M H_3PO_4 solution at 30 ^oC.

Compound	kinetic-thermodynamic parameter	
	1/y	K
BTSC	0.27	10,261
PClBTSC	0.3	5.992
4DMBTSC	0.54	34,991

3.4. Effect of Temperature on the dissolution reaction of steel in absence and presence of benzaldehyde thiosemicarbazones

The Nyquist plots for mild steel in 3 M phosphoric acid (3.0 M H_3PO_4) solution in the absence and presence of $1.7x10^{-4}$ M BTSC, $2.7x10^{-4}$ M PClBTSC and $1.0x10^{-4}$ M 4DMBTSC at 30, 40, 50, 60 and 70 ^oC where recorded. The data showed that the size of the capacitive semicircle in absence or presence of these compounds decreases with increasing temperature. This indicates that the corrosion rate in both cases increases with raising temperature. It has been pointed out by number of authors [52, 53] that the logarithm of the corrosion rate (k) is a linear function with the reciprocal of the absolute temperature1/T (Arrhenius equation):

$$\ln k = - E_a / RT + A \qquad (7)$$

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:

$$k = (RT/Nh) \exp (\Delta S^* /R) \exp (-\Delta H^*/RT) \qquad (8)$$

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 mild steel dissolution in 3 M phosphoric acid in the absence and presence of inhibitors are obtained from linear square fit of ln (k) and ln (k/T) data *vs.* (1/T) as shown in figures (8, 9).

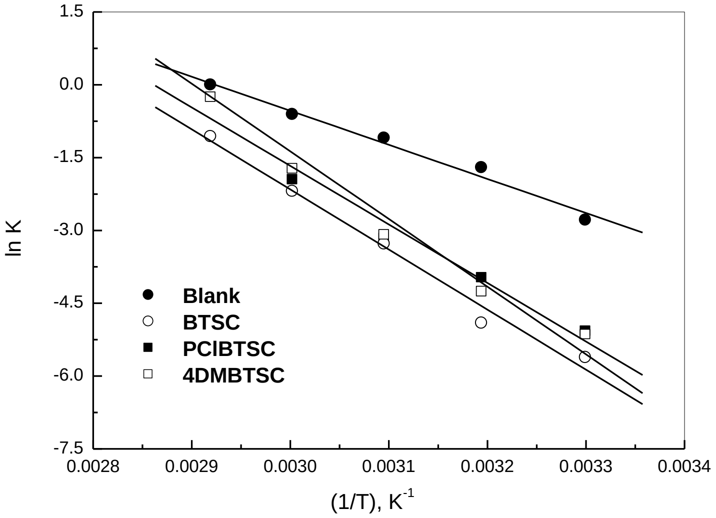


Figure 8. Linear Square fit of ln (k) vs. (1/T) for mild steel in 3.0 M H_3PO_4 in absence and presence of $2.7x10^{-4}$ M PClBTSC, $1.7x10^{-4}$ M BTSC and $1.0x10^{-4}$ M 4DMBTSC.

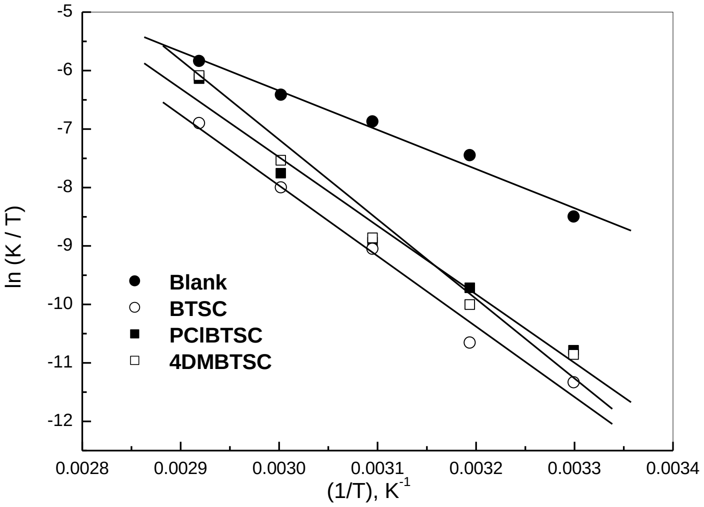


Figure 9. Linear Square fit of ln (k/T) vs. (1/T) for mild steel in 3.0 M H_3PO_4 in absence and presence of $2.7x10^{-4}$ M PClBTSC, $1.7x10^{-4}$ M BTSC and $1.0x10^{-4}$ M 4DMBTSC.

The resulting values for the activation parameters are given in Table 4.As observed, E_a and ΔH^* for the inhibited solutions were higher than that for the uninhibited solutions indicate that when the temperature is raised a decrease in protection efficiency is obtained [52]. Which suggested a physical type of adsorption of the benzaldehyde thiosemicarazones molecules at the steel surface [54]. The values of the activation energy, E_a in the inhibited gave an indication of the dependence of E_a and ΔH^* values on the molecular structure of the inhibitor [55].

Table 4. The activation parameters E_a, ΔH^* and ΔS^* for mild steel in 3.0 M H_3PO_4 in the presence and absence of inhibitors.

Solution	Activation parameters		
	E_a J / mol.	ΔH^* J / mol.	ΔS^* J / mol. K
3.0 M H_3PO_4	58300	55637	-83.36
2.7×10^{-4} M PClBTSC	100190	96750	32.73
1.7×10^{-4} M BTSC	101940	99360	36.99
1.0×10^{-4} M 4DMBTSC	106790	103250	53.19

The table illustrates that ΔS^* has negative values for the test solution implies that the activated complex represents an association rather than a dissociation step, meaning that a decrease in disordering takes place going from reactants to the activated complex [56] . In the presence of the three Thiosemicarbazone derivatives ΔS^* values turned positive and increased in the following order: PClBTSC < BTSC < 4DMBTSC. This result indicates that the corrosion system passes from a more orderly to a random arrangement with increasing the inhibitory character of the studied compounds. Similar results was recorded for some cyclic amines [49] and thiol [57] compounds when they were studied as effective corrosion inhibitors for mild steel in HCl and H_2SO_4 solutions, respectively. However, mild steel corrosion in the free acid was characterized by the more negative ΔS^* value which implies that the activation complex in the rate determining step required association rather than dissociation [59].This can be explained on the basis that, in acid-free solutions, the rate-determining step for the hydrogen evolution reaction on steel is the recombination of the adsorbed hydrogen atom to form H_2 molecules [60-61]. Therefore, the transition state of the rate-determining recombination step represents a more orderly arrangement relative to the initial state, and, hence, a negative value of the entropy of activation is obtained. On the other hand, in the presence of the studied compounds, the inhibition of steel dissolution by a simple blocking of the steel surface leads to the decrease in the surface area required for the recombination of adsorbed hydrogen atom and decreases the magnitude of the entropy of activation [62].

4. CONCLUSIONS

(1) BTSC, PClBTSC and 4DMBTSC were found to act as corrosion inhibitors for mild steel corrosion in 3.0 mol/L H_3PO_4 .Potentiodynamic polarization studies have shown that these compounds act as mixed-type inhibitors.

(2) The results of the investigation show that the inhibition efficiency increases in the sequence of PClBTSC<BTSC<4DMBTSC.

(3) The three Thiosemicarbazone derivatives were found to follows the kinetic-thermodynamic model.

ACKNOWLEDGEMENTS

The author wishes to express his great thanks to Prof. Dr. Elewady, Y.A., Pickering, distinguished professor of Physical Chemistry, Chemistry Dept. Fac. of Science, Mansoura Univ., Egypt, for his keen interest in the study.

References

1. X. Li, Sh. Deng, H. Fu, *Corr. Sci.*, 55(2012)280.
2. X. Li, Sh. Deng, H. Fu, G. Mu, *Corros Sci* ; 52(2010)1167.
3. A. Ghanbari, M.M. Attar, M. Mahdavian. *Mater. Chem. & Phys;* 124 (2010) 1205.
4. Lin Wang, Jian-Xin Pu, Hui-Chun Luo. *Corros. Sci*; 45 (2003) 677.
5. I.B. Obot, N.O. Obi-Egbedi. *Curr. Appl. Phys*; 11 (2011) 382.
6. M. Donovan, J. W. Scott, L. L. Shreir, *Journal of Applied Chemistry*, 8(1958)87.
7. J.C. Galván Jr, J. Simancas, M. Morcillo, J.M. Bastidas, E. Almeida, S. Feliu, *Electrochimica Acta*, 37(1992)1983.
8. L. Wang, *Corros Sci ; Volume* 43(2001)2281.
9. L. Tang, X. Li, G. Mu, L. Li, G. Liu, *Applied Surface Science*, 253 (2006) 2367.
10. X. Li, Sh. Deng, H. Fu, *Corros Sci* ; 53(2011)664.
11. T. Poornima, J. Nayak, A. N. Shetty , *Corros Sci* ; 53(2011) 3688.
12. E.E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, U.J. Ibok, *Materials Chemistry and Physics*, 60(1999)79.
13. U.J. Ekpe, U.J. Ibok, B.I. Ita, O.E. Offiong, E.E. Ebenso,*Materials Chemistry and Physics*, 40(1995)87.
14. G.E. Badr, *Corros Sci* ; 51(2009)2529.
15. B.A.Abd El-Nabey,E.Khamis , M.A.E.Shaban,G.E. Thompson and J.L.Dawson. *Surf. and Coat. Tech*; 28 (1986)67.
16. B.A.Abd El-Nabey,E.Khamis , G.EThompson and J.L.Dawson. *Surf. Tech*; 28 (1986)83.
17. B.A.Abd El-Nabey,E.Khamis ,G.EThompson and J.L.Dawson. *Surf. Tech*; 30 (1987)199.
18. Xianghong Li, Shuduan Deng, Hui Fu. *Progress in Organic Coatings*; 67 (2010) 420.
19. N.J. Walton, M.J. Mayer, A. Narbad. *Phytochemistry;* 63 (2003) 505.
20. K.C. Emregül, M. Hayval. *Mater. Chem. Phys*; 83 (2004) 209.
21. A.E. El Sayed, Fouda, H. Abu El-Nadar and M. N.Moussa. *Acta Chim. Hung*., 124, (1987) 581.
22. A.A. El-Shafei, M.N.H.Moussa and A.A. El-Far. *Mater. Chem. & Phys*., 70, (2001) 175.
23. K. Aramaki, M. Hagiwara and H. Nishihara. *Corro. Sci*., 5 (1987) 487.
24. G. Lyberatos, L. Kobotiatis. *Corrosion*; 47 (1991) 820.
25. B.G. Ateya, B.E. El-Anadouli, and F. F.M.A. El-Nizamy, *Bull. Chem. Soc.Jpn*; 54 (1981) 3157.
26. T. P. Hoar and R. D. Holliday. *J. Appl. Chem*., 3 (1953) 502.
27. N. Hackerman and J. D. Sudbury. *J.Electrochem. Soc.*, 97 (1950) 109.
28. N. Hackerman and A.C. Makrides, *J. Phys. Chem*., 59 (1955) 707.
29. M. A. Abdel Rahim, H. B. Hassan, M. W. Khalil, 28 (1997)198.
30. N. Hackerman and E.L. Cook. *J. Electrochem. Soc*., 1 (1950) 97.
31. A.C. Makrides and N.Hackerman. *Ind. Eng. Chem*., 14 (1955)1773.
32. B. Abd-El Nabey, A. El-Toukhy, M. El-Gamal, F. Mahgoop, *Surf. Technol*. 27(1986) 325.
33. R. Meakins, *J. Appl. Chem*. 13(1963)339.
34. R. Driver, R. Meakins, *Br. Corrosion. J*. 9(1974) 233.
35. S.T. Arab and E.A. Noor, *Corrosion* 49(1993)122.

36. Z. Szklaraska, Smialowska. "Electrochemical and Optical Techniques for Studying of Metallic Corrosion" (1991).
37. W.J. Lorenz, F. Mansfeld, in : Proceedings of the 6th symposium on European Inhibition of Corrosion , University of Ferrara, Ferrara , 1985, p. 23.
38. A.M. Abdel-Gaber, B.A. Abd-El Nabey, I.M. Sidahmed, A.M. El-Zayady,* and M. Saadawy, CORROSION 62 (2006) 293
39. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady, M. Saadawy, *Corros Sci* ; 48 (2006) 2765.
40. F. Bentiss, M. Lagrenee, M. Traisnel and J. C. Hornez. *Corros. Sci.*, 41 (1999) 789.
41. L. Larabi, O. Benali and Y. Harek *Mater.Letters*; In Press (2006).
42. N.S. Rawat and G. Vdaybanu, Proc. of the 10th International Conference on Metallic.Corrosion, III, India (1987).
43. A.M. Abdel-Gaber, N. Khalil and A. Abou El-Fetouh; *Anti-Corrosion Methods and Materials*; 50(2003)442.
44. A. Subramania, N.T. Kalyana Sundaram, R. Sathiya Priya, K. Saminathan, V.S. Muralidharan and T. Vasudevan, *Journal of Applied Electrochemistry* 34 (2004) 693.
45. A.A. Al-Sarawy, A.S. Fouda, W.A. Shehab El-Dein, *Desalination* 229 (2008) 279
46. I.B. Obot, N.O. Obi-Egbedi, *Corros Sci* ; 52 (2010) 657.
47. I. Langmuir, *J. Am. Chem. Soc.* 38(1916) 2,221.
48. G. Lyberatos, L. Kobotiatis, *Corrosion* 47 (1991) 820.
49. A. A. El-Awady, B. A. Abd-El-Nabey and S.G. Aziz; *J.Electrochem. Soc*., 139 (1992)2149.
50. A.A.El- Awady, B.A.Abd-El-Nabey, S.G.Aziz, M.Khalifa and R.A.Al Ghamdey, Internt. J. Chem., 1(1990)169.
51. A.A.El- Awady, B.A.Abd-El-Nabey and S.G.Aziz. *Chem. Soc. Faraday Trans*; 89(1993)795.
52. G .Lyberatos and L Kobotiatis; *Corrosion* 47 (1991) 820.
53. S.S.Abd El-Rehim, M.A.M. Ibrahim, and K.F. Khaled. *J; Appl.Electrochem*; 29(1999) 593.
54. A.M. Abdel-Gaber, B.A. Abd-El Nabey, I.M. Sidahmed, A.M. El-Zayady, and M. Saadawy. *Corrosion;* 62(2006)293.
55. B.Ateya,B.El-Anadouli, and F.El-Nizamy *Corros.Sci*.,24(1984)509.
56. H. Ashassi-Sorkhabi and N. Ghalebsaz-Jeddi. *Mater. Chem. Phys.*, 92 (2005) 480.
57. M.Th. Makhlouf, M.H. Wahdan. *Pol. J. Chem*; 69 (1995) 1072.
58. S.S. Abd-El-Rehim, S.A.M. Refaey, F. Taha, M.B. Saleh, R.A. Ahmed. *Appl. Electrochem*; 31(2001) 429.
59. V.P. Grigoryev, V.U. Eklik. *Prot. Met.* ; 4(1968) 517.
60. V.P. Grigoryev, O.A. Osipov. 3rd Europ. Symp. Corrosion Inhibitors (Ferrara, Italy:University of Ferrara; 1970) 473.
61. L. I. Antropov, Y.A. Suvgira. *Prot. Met.* ;3 (1967) 597.
62. B.A. Abd-El-Nabey, E. Kamis, M.Sh. Ramadan, A. El-Gindy. *Corrosion;* 52 (1996) 671.