

Inhibiting Effect of Thiosemicarbazide and 4-Phenyl Thiosemicarbazide Towards the Corrosion of Carbon Steel in H_3PO_4 Solutions

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Corrosion inhibition of C-steel in 2 N H_3PO_4 solution using thiosemicarbazide (TSC) and 4-phenyl thiosemicarbazide (PTSC) at different concentrations was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The presence of these compounds in the solution decreases the double layer capacitance and increases the charge transfer resistance. Potentiodynamic polarization studies were shown that the investigated compounds are mixed type inhibitors. The effect of temperature on corrosion inhibition has been studied and thermodynamic activation parameters were calculated. The inhibition was found to increase with increasing the inhibitor concentration and decreases with rise in temperature. The adsorption of these compounds on C- steel surface has been found to obey Langmuir's adsorption isotherm.

Keywords: Corrosion inhibition, thiosemicarbazide, 4-phenyl thiosemicarbazide, carbon steel, phosphoric acid

1. INTRODUCTION

Inhibition of C-steel corrosion has more interest because it is widely used as constructional material in many industries due to its low cost and excellent mechanical properties. H_3PO_4 is a major chemical product, which has many important uses especially in the production of fertilizers. Recently, number of studies have been appeared [1-5] on the topic of the corrosion inhibition of C-steel in acidic media because acids play a very important part in most processes such as industrial acid cleaning, oil well acidizing, acid pickling, manufacturing process and vapor-liquid system.

Several organic compounds which contain nitrogen are used as corrosion inhibitor for metals in acid environment [6-11]. A number of organic compounds [12-27] are known to be applicable as

corrosion inhibitors for steel in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system, and function via adsorption of the molecules on the metal surface, creating a barrier to corrosive attack. Thiosemicarbazide derivatives have special affinity to inhibit corrosion of metals in acidic solutions [28-30].

This work deals with the study of the corrosion inhibition of C-steel in H_3PO_4 solution by thiosemicarbazide and 4-phenyl thiosemicarbazide using different techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL TECHNIQUES

2.1. Materials

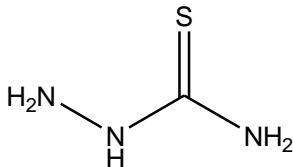
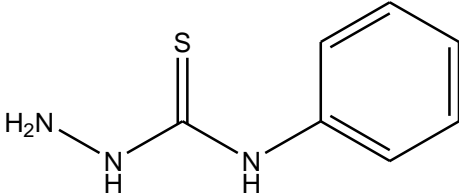
The chemical composition (weight %) of C- steel is: 0.200 C, 0.91 Mn, 0.007 P, 0.002 Si and the remainder iron.

2.2 Solution

Acid solutions which used as corrosive media in this study was made of analytical reagent grade phosphoric acid and distilled water.

2.3. Inhibitors

The inhibitors which used in this investigation are thiosemicarbazide and 4-phenyl thiosemicarbazide and their chemical structures, names and molecular formulas are shown in Table (1):

No.	Names	Chemical structures	Molecular Weights
TSC (A)	thiosemicarbazide		91.15
PTSC (B)	4-phenyl thiosemicarbazide		167.242

2.4. Potentiodynamic polarization measurements

Electrochemical polarization experiments were carried out in a glass cell with three different types of electrodes. a platinum electrode and a saturated calomel electrode (SCE) were used as a counter and a reference electrodes, respectively. The C-steel specimen was embedded in PVC holder using epoxy resin with an exposed area of 1cm^2 and used as working electrode. The working electrode was polarized at -0.8 V to $+0.8\text{V}$ with a scanning rate of 1 mV S^{-1} using Gamry frame work instruments. From this study we obtained, corrosion current density (i_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c) and (β_a), respectively, degree surface coverage (θ). The inhibition efficiency was calculated from corrosion current density using the following formula [31].

$$\%IE = 100 \times (i_{\text{corr}} - i'_{\text{corr}}) / i_{\text{corr}} \quad (1)$$

where i_{corr} and i'_{corr} are the corrosion current densities in the absence and presence of the inhibitors, respectively.

2.5. Electrochemical impedance spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy experiments were conducted at 25°C with respect to corrosion potential, (E_{corr}) over a frequency range of 100 kHz to 0.2 Hz with a signal amplitude perturbation of 5 mV and time interval 20 min. using Potentiostat / Galvanostat (Gamry PCI 300/4) and personal computer with EIS 300 soft ware for calculation. Data were presented as Nyquist and Bode plots. Degree of surface coverage (θ) and $\%IE$ were calculated using the following equations:

$$\%IE = 100 \times \theta = [1 - (R'_{\text{ct}} / R_{\text{ct}})] \quad (2)$$

where R'_{ct} and R_{ct} are the charge transfer resistance values in the absence and presence of the inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic Polarization

Potentiodynamic polarization parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), degree of surface coverage (θ), polarization resistance (R_p) and percentage inhibition efficiency (IE%) are summarized in Table (2) for the corrosion of C-steel in $2\text{ N H}_3\text{PO}_4$ in the absence and presence of different concentrations of inhibitors. The results show that the corrosion current (i_{corr}) decreases with increasing the inhibitor concentration and hence, the inhibition efficiency increases. The order of inhibition efficiency of investigated compounds is as follows: $\text{PTSC} > \text{TSC}$ as shown from Table (3). The potentiodynamic polarization curves in the absence and presence of different concentrations of inhibitor (PTSC) shown in Figure (1). Similar curves were obtained for another inhibitor (not shown). The addition of these compounds: a) does not affect E_{corr} and ii) affect both anodic and cathodic polarization curves, which means that, addition of inhibitors affect both hydrogen evolution and metal dissolution.. These results of (i) and (ii) indicate that PTSC and TSC act as mixed type inhibitors.

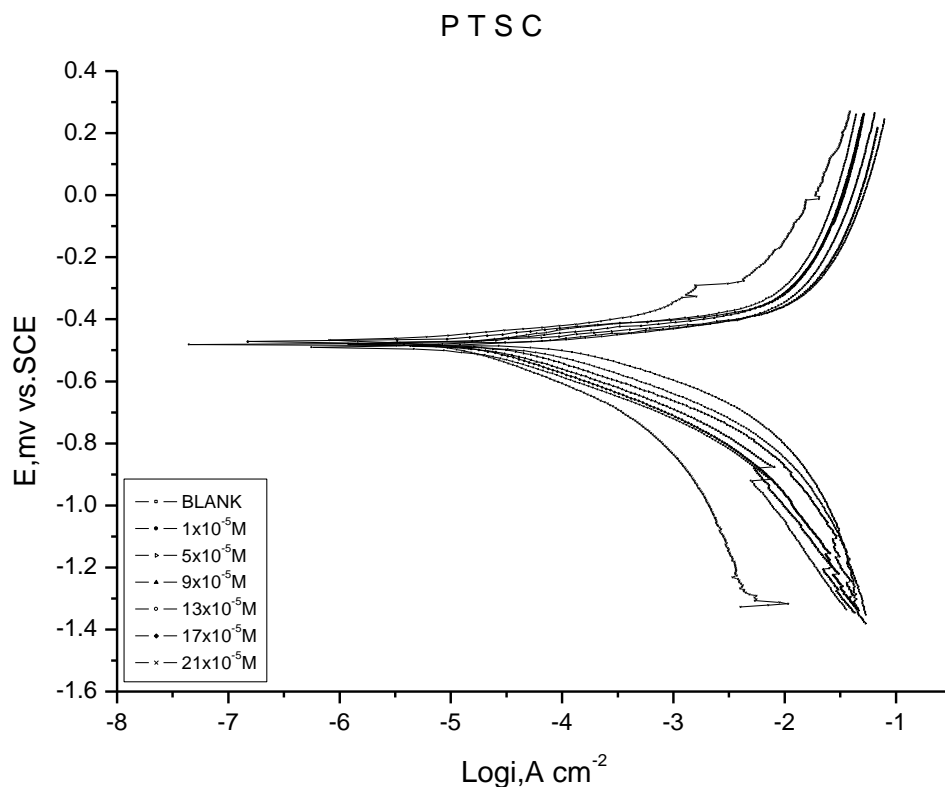


Figure 1. Polarization curves for the dissolution of C-steel in 2 N H₃PO₄ in the absence and presence of different concentrations of compound (PTSC) at 25°C

Table 2. Potentiodynamic polarization parameters for corrosion of C-steel in 2 N H₃PO₄ in the absence and presence of different concentrations of inhibitors (TSC, PTSC) at 25°C

Inh.	Conc. x 10 ⁵ M	-E _{corr} mV	i _{corr} μA cm ⁻²	β _a mV dec ⁻¹	β _c mV dec ⁻¹	R _p x 10 ² Ω cm ²	θ	IE%
Blank	0	481	814.9	351	436	1.035	-----	-----
TSC (A)	1	499	565.7	314	414	1.371	0.306	30.6
	5	484	421.4	291	381	1.701	0.483	48.3
	9	473	295.5	253	351	2.162	0.637	63.7
	13	522	222.7	265	348	2.935	0.727	72.7
	17	521	152.5	260	330	4.141	0.813	81.3
	21	491	47.7	223	273	11.18	0.941	94.1
PTSC (B)	1	487	344.2	279	357	1.977	0.578	57.8
	5	480	172.8	246	334	3.560	0.788	78.8
	9	480	97.60	246	306	6.072	0.880	88.0
	13	490	75.18	248	295	7.779	0.908	90.8
	17	471	62.22	231	281	8.837	0.924	92.4
	21	468	45.46	231	380	13.71	0.944	94.4

Table 3. Inhibition efficiency of C-steel dissolution in 2 N H₃PO₄ in the presence of different concentrations of inhibitors (TSC, PTSC) at 25° C

Conc. x 10 ⁻⁵ M	% IE	
	TSC(A)	PTSC(B)
1	30.6	57.8
5	48.3	78.8
9	63.7	88.0
13	72.7	90.8
17	81.3	92.4
21	94.1	94.4

3.2 Adsorption isotherms

The electrochemical processes on the metal surface which related to the adsorption of the inhibitor [32] and the adsorption depend on the chemical structure of the inhibitor. The adsorption of the inhibitor molecules from aqueous solutions can be regarded as quasi substitution process [33-35] between the organic compound in the aqueous phase and water molecules at the electrode surface. By examining the degree of surface coverage (θ) which determined by potentiodynamic polarization technique to various isotherms .The best isotherm obtained was Langmuir's adsorption isotherm. A plot of (C/ θ) against inhibitor concentrations (C) of compounds (TSC, PTSC) are represented in Figure (2) a straight line relationship was obtained according to the following equation:

$$C/\theta = 1/K_{ads} + C \tag{3}$$

where K is equilibrium constant for the adsorption process , which obtained from the intercept of the straight lines and its value is recorded in Table (4) and it is related to the standard free energy of adsorption (ΔG°_{ads}) by the equation:

$$K_{ads} = 1/55.5 \exp (-\Delta G^{\circ}_{ads} /RT) \tag{4}$$

where 55.5 is the molar concentration of water in the solution in mol L⁻¹, R is the universal gas constant and T is the absolute temperature.

According to the kinetic thermodynamic model of El-Awady et al [36] the adsorption isotherm relationship is represented by the following equation:

$$\log (\theta /1-\theta) = \log K^{\lambda} + y \log C \tag{5}$$

where y is the number of inhibitor molecules occupying one active site of the metal surface and 1/y is the number of the surface active sites occupied by one inhibitor molecule. To plot log ($\theta /1-\theta$) against log C the straight line obtained as shown in Figure (3) with intercept of (log K^{\lambda}), slope of (y) and K_{ads} calculated from $K = K^{\lambda(1/y)}$ as shown in Table (5).

Table 4. Equilibrium constant (K_{ads}), adsorption free energy (ΔG°_{ads}) and number of active sites ($1/y$) for the adsorption of inhibitors on C-steel in 2 N H_3PO_4 at 25°C

Inhibitor	Langmuir isotherm			Kinetic model		
	Intercept $\times 10^5$	$K_{ads} \times 10^{-4}$ M^{-1}	ΔG°_{ads} - $kJ mol^{-1}$	$1/y$	$K_{ads} \times 10^{-4}$ M^{-1}	ΔG°_{ads} - $kJ mol^{-1}$
TSC(A)	4.5	2.2	34.7	1.01	3.0	35.5
PTSC(B)	0.99	10.1	38.5	1.23	13.0	39.1

From previous results, the large values of K_{ads} imply better efficient adsorption and better inhibition efficiency [37]. The negative values of ΔG°_{ads} indicate that the adsorption process is spontaneous. The higher values of ΔG°_{ads} and K_{ads} indicate the strong adsorption of these inhibitors and the stability of the adsorbed layer on the C-steel surface [38]. It is well known that ΔG°_{ads} values up to $-20 kJ mol^{-1}$ are consistent

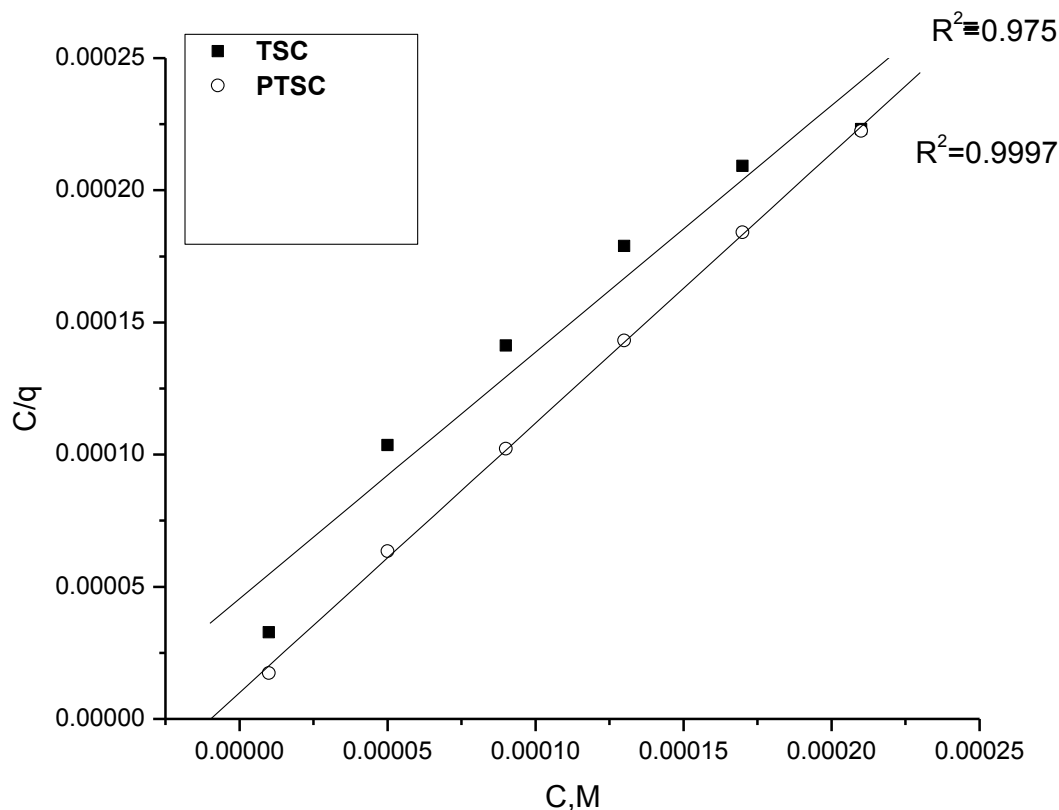


Figure 2. Langmuir adsorption isotherm for carbon steel in 2 N H_3PO_4 in the presence of different concentrations of TSC and PTSC at 25°C

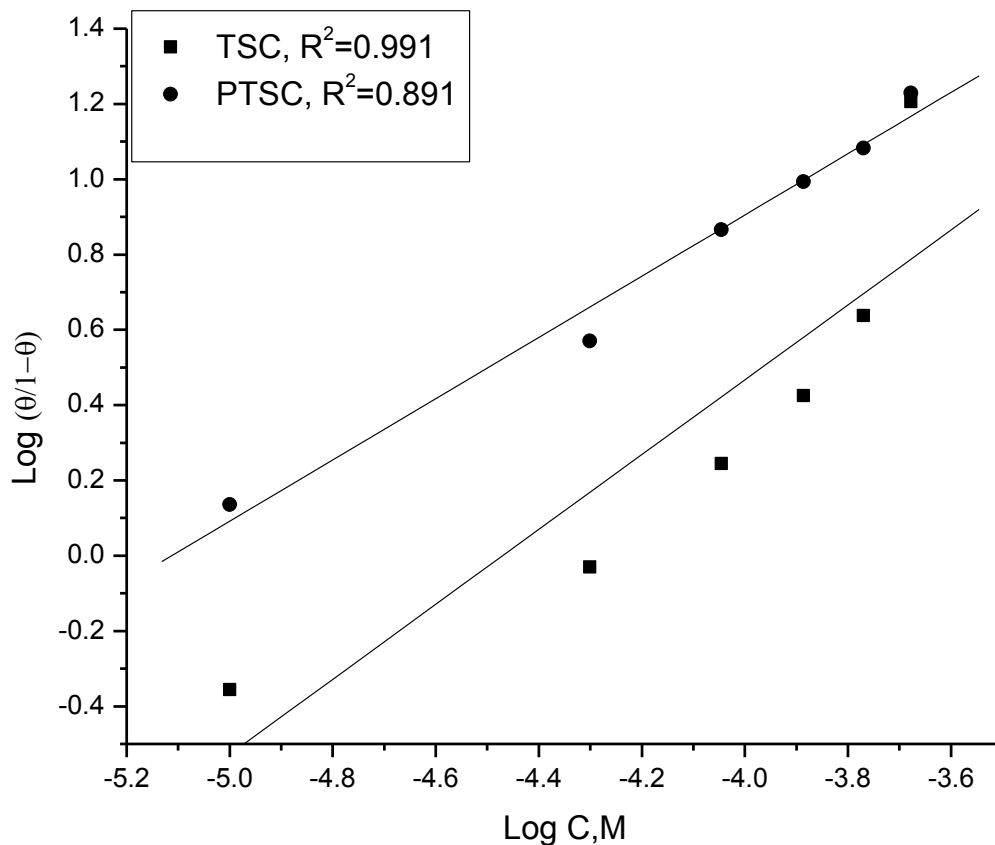


Figure 3. El-Awady model plotted as $\log (\theta/1-\theta)$ vs. $\log C$ of the investigated inhibitors for corrosion of C-steel in 2 N H_3PO_4 solutions at 25°C

with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 kJ mol^{-1} involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate bond (chemisorption) [39]. The values of $\Delta G_{\text{ads}}^{\circ}$ obtained are less negative than -40 kJ mol^{-1} which indicating that the adsorption mechanism of thiosemicarbazide and 4-phenyl thiosemicarbazide on C-steel in 2 N H_3PO_4 solutions was physical adsorption.

3.3 Effect of temperature

The effect of temperature (25 - 55°C) on the corrosion behavior of C-steel in 2 N H_3PO_4 in the absence and presence of $21 \times 10^{-5} \text{ M}$ of inhibitors was studied using potentiodynamic polarization measurements. The activation energy (E_a^*) for the corrosion process can be calculated from Arrhenius equation:

$$i_{\text{corr}} = A \exp (-E_a^* / RT) \tag{6}$$

where A is the Arrhenius pre-exponential constant depends on the metal type and electrolyte. Arrhenius plots of $(\log i_{\text{corr}})$ against $(1/T)$ are shown in Fig. (4), a straight lines obtained and from the slopes of these lines E_a^* can be determined. The values of E_a^* obtained are listed in Table (6). These results show that the E_a^* value of 2 N H_3PO_4 containing inhibitors is higher than that without

inhibitors. The higher values of E_a^* indicated the presence of energy barrier on the C-steel surface. [40]. The activation energy increases with increasing the efficiency of the investigated compound as follows: PTSC > TSC.

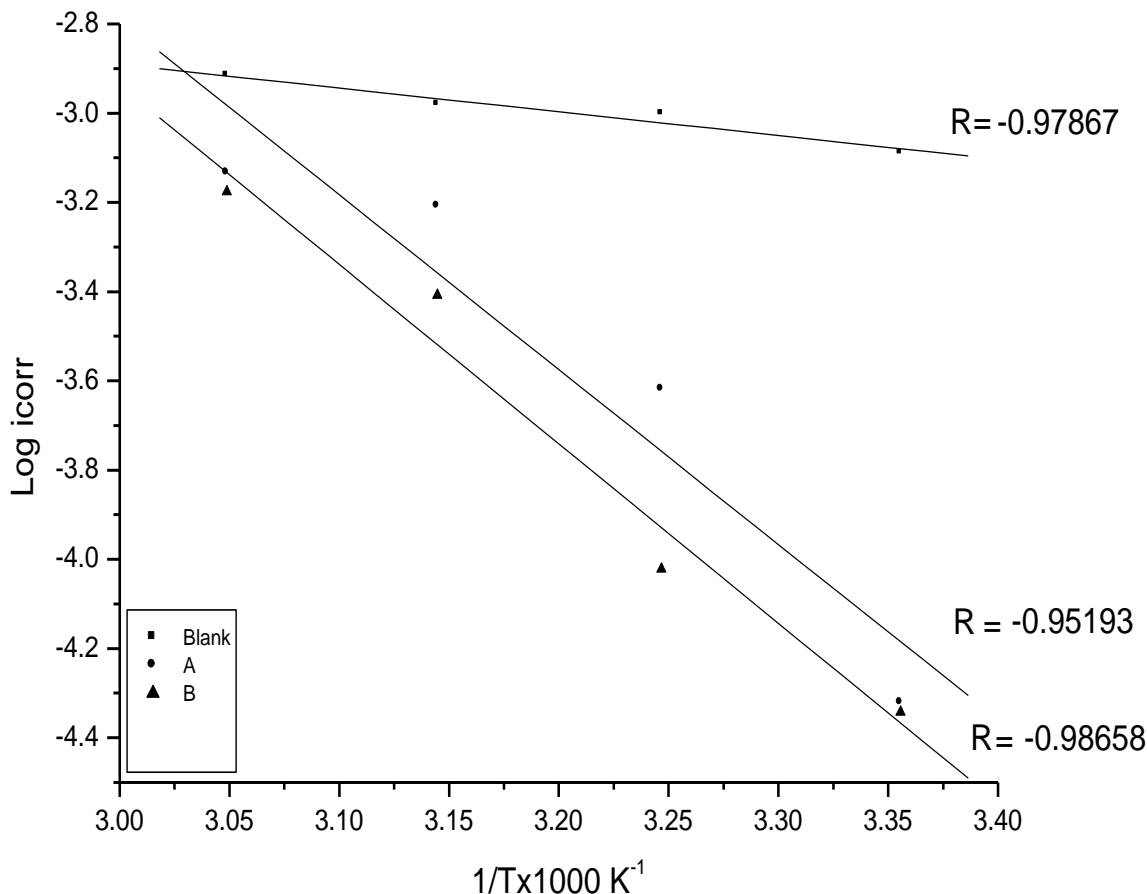


Figure 4. Arrhenius plots ($\log i_{\text{corr}}-1/T$) for C-steel dissolution in 2N H_3PO_4 in the absence and presence of 21×10^{-5} M of TSC, PTSC

Enthalpy and entropy of activation (ΔH^* and ΔS^*) are calculated from transition state theory using the following equation [41]:

$$k = RT/Nh \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \tag{7}$$

where N is Avogadro's number and h is Planck's constant. A plot of $(\log i_{\text{corr}} / T)$ against $1/T$ straight lines obtained as shown in Figure (5). The value of ΔH^* calculated from the slopes of these lines and the value of ΔS^* calculated from the intercepts of these lines are recorded in Table (6). The positive values of ΔH^* reflect the endothermic corrosion process and its higher values reflects strong adsorption of these compounds on C-steel surface. The values of ΔS^* in the absence and presence of inhibitors are large and negative this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step.

Table 6. Activation parameters for dissolution of C-steel in 2 N H₃ PO₄ in the absence and presence of 21x10⁻⁵ M of TSC and PTSC

Inhibitors	E _a [*] kJ mol ⁻¹	H [*] ·Δ kJ mol ⁻¹	S [*] ·-Δ J mol ⁻¹ k ⁻¹
Blank	10.2	7.6	278.5
TSC (A)	75.0	72.4	82.0
PTSC (B)	77.0	74.4	78.9

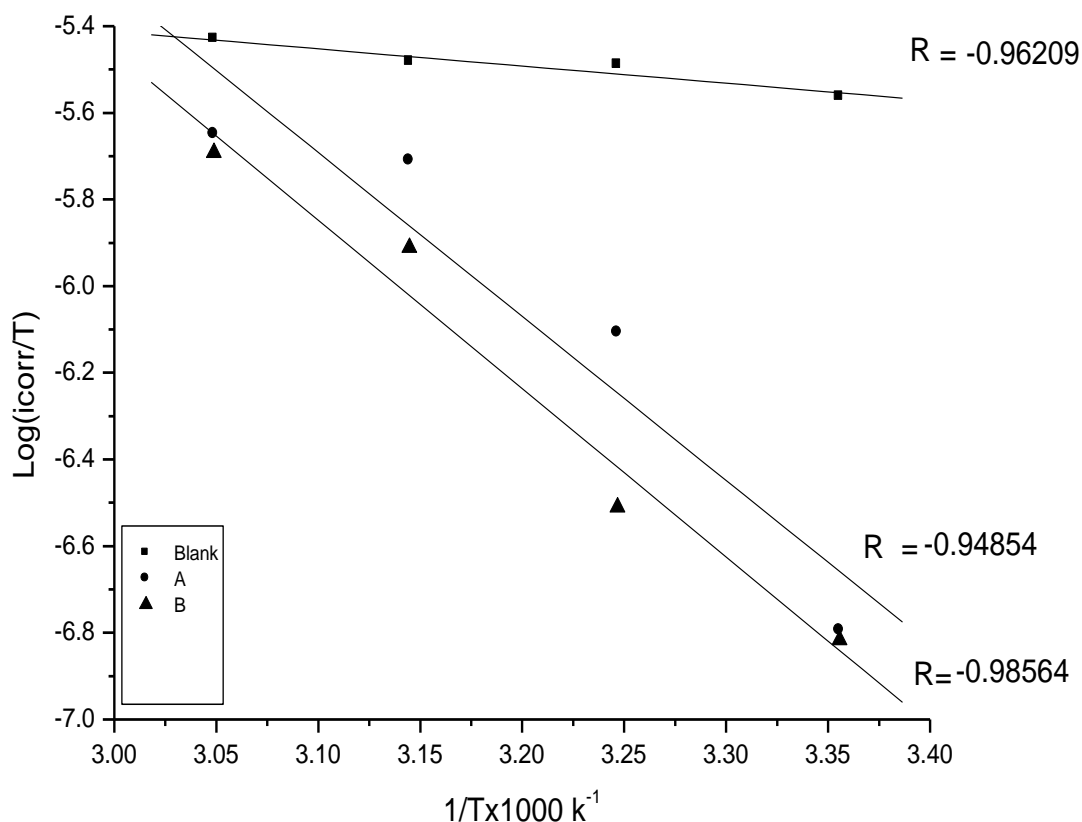


Figure 5. Arrhenius plots (log i_{corr}/T vs. 1/T) for C-steel dissolution in 2 N H₃PO₄ in absence and presence of 21x10⁻⁵ M of TSC, PTSC

3.4 Electrochemical impedance spectroscopy (EIS)

EIS measurements were carried out for corrosion behavior of carbon steel in 2 N

H₃ PO₄ in the absence and presence of various concentrations of inhibitors at 25°C. The obtained Nyquist plot for compound (PTSC) is shown in Figure (6) similar curves were obtained for inhibitor (TSC) (not shown). The impedance diagrams have an approximately semicircular appearance shows that the corrosion of carbon steel is controlled by a charge transfer process. The diameters of the capacitive loop obtained increases in the presence of inhibitors TSC, PTSC and were indicative of the degree of inhibition of the corrosion process. The Bode plot of compound (PTSC) is shown in Figure 7

the high frequency limits corresponds to the solution resistance $R_s(\Omega)$, while the lower frequency limits corresponds to $(R_{ct} + R_s)$. The low frequency contribution shows the kinetic response of the charge transfer reaction [42]. The impedance parameter such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency (% IE) were calculated and are listed in Table (7). The result obtained show that the value of charge transfer resistance (R_{ct}) for carbon steel in phosphoric acid changed after the addition of inhibitors. The R_{ct} values increases and the C_{dl} values decreases with increasing the concentrations of inhibitors. This lead to an increase of percent inhibition (% IE). The high R_{ct} values associated with slower corroding system [43, 44]. The inhibition efficiency obtained from impedance measurements are in good agreement with those obtained from potentiodynamic polarization studies (PTSC > TSC).

Table 7. Electrochemical impedance spectroscopy (EIS) parameters for C-steel in 2 N H_3PO_4 in the absence and presence of different concentrations of inhibitors TSC and PTSC at 25 °C

Compound	Conc. x 10 ⁻⁵ M	C _{dl} , μF cm ⁻²	R _{ct} , Ω cm ²	θ	IE%
	0	81.27	19.91	0	0
TSC(A)	5	82.65	94.87	0.790	79.0
	13	58.16	180.2	0.890	89.0
	17	49.76	204.7	0.903	90.3
	21	33.76	323.4	0.938	93.8
	PTSC(B)	5	67.47	148.5	0.866
	13	35.69	396.0	0.950	95.0
	17	27.76	1210	0.984	98.4
	21	24.61	1868	0.989	98.9

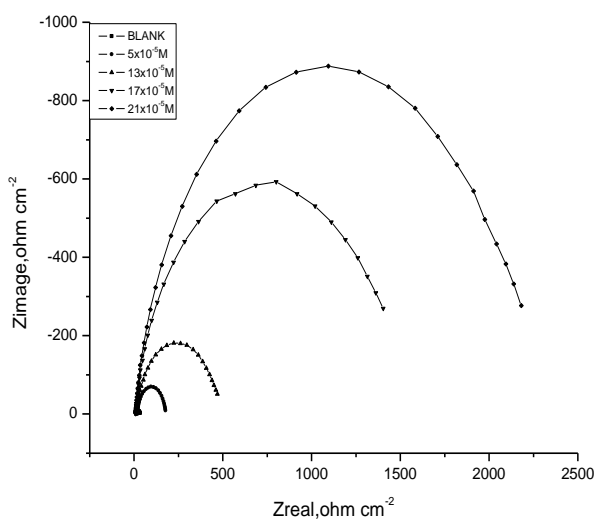


Figure 6. The Nyquist plots for C-steel dissolution in 2 N H_3PO_4 in the absence and presence of different concentrations of PTSC at 25 °C

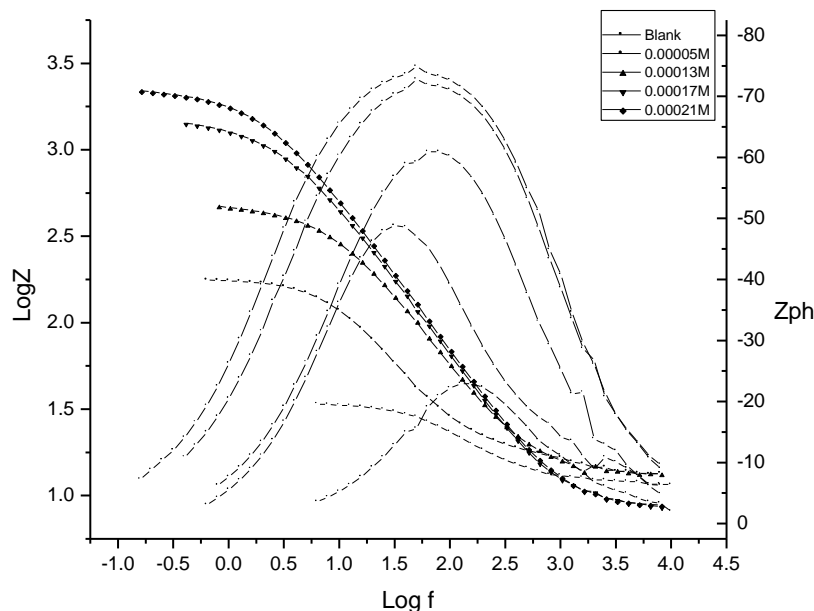


Figure 7. The Bode plots for C-steel dissolution in 2 N H_3PO_4 in the absence and presence of different concentrations of PTSC at 25°C

3.5. Mechanism of inhibition

All previous results support that PTSC and TSC were actually inhibits the corrosion of C-steel in phosphoric acid solutions. The corrosion inhibition is due to their physical adsorption and formation of protective film of the adsorbate on the C-steel surface. The inhibitive effect of PTSC and TSC may be attributed to the accumulation of the inhibitor molecules on to the metal surface, which reduces the direct contact of the metal with the corrosive environment. The order of inhibition efficiency is as follows: PTSC > TSC. Compound PTSC exhibits very good inhibition efficiency, probably because of the presence of three nitrogen atoms and one sulphur atom as well as the presence of one aromatic ring in the molecule and in other hand it has the highest molecular size. This molecule may be adsorbed flat on C-steel surface. But compound TSC comes after compound PTSC in inhibition efficiency due to it contain three nitrogen atoms and one sulphur atom only and it has lesser molecular size.

4. CONCLUSIONS

Thiosemicarbazide and 4-phenyl thiosemicarbazide act as corrosion inhibitors of carbon steel in 2 N H_3PO_4 solutions. The inhibition efficiency increases with increase in inhibitors concentrations and decreases with raising temperature. The adsorption of the investigated compounds follows the Langmuir's adsorption isotherm. The investigated compounds were mixed type inhibitors, but cathode is more polarized than anode. The negative value of $\Delta G_{\text{ads}}^\circ$ obtained indicates that these compounds

are spontaneously adsorbed on carbon steel surface. The percent inhibition obtained from all studied methods have the same order (PTSC > TSC).

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