

Synthesis and Identification of 2-Pentadecyl-Quinazolinylthiourea (PQT) As Corrosion Inhibitor for Carbon Steel in Acidic Solution

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Abstract: A new fatty chain derivative of quinazolinone has been synthesized from the two simple precursors of 2-amino benzoic acid and palmitoyl chloride. The novel quinazolinone derivative is obtained via the nucleophilic interaction of 2-palmitoyl-4H-1, 3-benzoxazine -4-one with thiosemicarbazide that yield 2-pentadecyl-quinazolinylthiourea (PQT). Newly synthesized compound was identified via spectral methods; their [FTIR, ¹H-NMR and ¹³C-NMR] and measurement of some of its physical properties. Furthermore the inhibition effect of synthesized compound on the corrosion of carbon steel in 2N HCl was studied by potentiodynamic polarization. Morphology of the carbon steel was examined using scanning electron microscopy (SEM) in presence and absence of inhibitor.

Keywords: Quinazolinone derivatives, Acid corrosion, Carbon steel, Corrosion inhibitor.

I. Introduction

Corrosion is a fundamental process playing an important role in economics and safety, especially for metals. The use of inhibitors is one of the most practical methods for protection against corrosion, particularly in acidic media [1]. Most well-known acid inhibitors are organic compounds which have π bonds and contains hetero atoms such as nitrogen, sulphur, oxygen and phosphorous which allows the adsorption of compounds on the metal surface [2], thus resulting adsorption film acts as a barrier separating the metal from the corrosive medium and blocks the active sites [3].

Carbon steel is the most important metal used in industry as construction metal for metallurgical industries and is used as construction material for pipes in oil and gas industry and transmission pipelines [4, 5].

Acid solutions are widely used in industry. Some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. In acidic media, the use of hydrochloric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble-free compared to other mineral acids [6].

Quinazolinone derivatives represent one of the most classes of heterocyclic compounds possessing a wide spectrum of biological activity [7]. These derivatives are the subject of many research studies due to their widespread potential biological activities such as antimicrobial [8], anti-inflammatory [9], antitumor [10] and anticancer [11].

The main objective of this investigation is to synthesis and study the inhibitive effect of 2-pentadecyl-quinazolinylthiourea (PQT) for the carbon steel surface in hydrochloric acid solution using potentiostatic polarization method.

II. Experimental

2.1 Synthesis of 1, 3-benzoxazin-4-one derivative:

To a stirred solution of anthranilic acid (1.37gm, 0.01mole) in dry acetone, palmitoyl chloride (3ml, 0.01mole) was added in presence of pyridine as solvent. The mixture was refluxed for 3hrs then concentrated under vacuum. The solid product that separated on cold was filtered off, dried and crystallized from petroleum-ether. The product was heated for 4 hrs under reflux in acetic anhydride then concentrated under vacuum. The pale yellow solid which separated was filtered, washed with water and recrystallized to give yield 70 %. M.P 48-50°C. [12]

2.1.1 Synthesis of 2-pentadecyl-quinazolinyl-3-thiourea (PQT) as corrosion inhibitor:

To a solution of compound (1) (3.57gm, 0.01mole) in 30ml pyridine, thiosemicarbazide (0.908gm, 0.01mole) was added and the reaction mixture was heated under reflux for 8hrs, and poured into cold diluted HCl. the crud solid product that separated was filtered off, washed with water, dried and recrystallized from ethanol to give compound (2) yield 80% M.P 98-100°C. [13]

The compounds (1 and 2) were synthesized as shown in scheme (1).

2.2 preparation of Specimen:

A carbon steel sheet was used as working electrode for polarization method with Area (1 cm²) its composition is:(0.086% C, 0.252% Mn, 0.003% P, 0.016% S and the remainder being Fe was used.). 2N Hydrochloric acid solutions were prepared using distilled water.

2.3Polarization Technique:

By using a Wenking M Lab potentiostat and a three electrode cell, electrochemical studies were performed. Platinum over Titanium (Pt/Ti) electrode was used as the auxiliary electrode and a saturated silver electrode Ag/AgCl as the reference electrode. The corrosion rates are determined by Tafel extrapolation technique. The experiments were conducted at 298k, 308k, 318k and 328k.

III. Results And Discussion

3.1 Synthesis of 2-pentadecyl-quinazolinythiourea (PQT):

The new 2-pentadecyl-quinazolinythiourea (PQT) was synthesized following the reaction sequences depicted in scheme (1). Anthranilic acid reacted with Palmitoyl chloride in dry acetone to produce anthranilamide derivative which was cyclized with acetic anhydride to give 4H,1,3-benzoxazinone (1). Quiazolinythiourea (2) was obtained when compound (1) was reacted with thiosemicarbazide. The structure of compound(1) was confirmed by FT-IR spectrum which showed $\nu(\text{C-H})$ aromatic at 3030 CM^{-1} , $\nu(\text{C-H})$ aliphatic (2923 , 2854) CM^{-1} , $\nu(\text{C=O})$ of benzoxazinone(lacton) 1761 CM^{-1} , $\nu(\text{C=N})$ 1637 CM^{-1} [14] and by ¹H-NMR (DMSO-d⁶) which showed δ 0.8 (t, 3H, terminal CH₃), δ 1.1 – 1.3 (m, 30H, 15CH₂ of alkyl chain), δ 7.0 -7.9(m, 4H, ArH)[15] fig (1). Compound (2) FT-IR spectral data showed absorption $\nu(\text{C-H})$ aromatic at 3062 CM^{-1} , $\nu(\text{C-H})$ aliphatic at (2918,2850) CM^{-1} , $\nu(\text{C=O})$ amide at 1690 CM^{-1} , νNH_2 at (3358 CM^{-1} asym, 3260 CM^{-1} sym) νNH at 3155 CM^{-1} . ¹H-NMR spectrum showed δ 0.9 (t, 3H, terminal CH₃), δ 1.2 – 1.5 (m, 30H, 15CH₂ of alkyl chain), δ 6.8 -7.5(m, 4H, ArH), δ 8.0, 8.5 and 11.1 (s, 3H, NH exchangeable) fig (2). ¹³C-NMR spectrum of compound (1) showed signals at δ = (134) ppm, δ = (127) ppm, δ = (147.00) ppm, δ = (122) ppm, δ = (160.53) ppm, δ = (148) ppm, and at δ = (22-27) ppm belong to (-CH-CH) of C1, (-CH-CH) of C2, (-C-N) of C3, (-C-C=O) of C3, (C=O) ester of C5, (C=N) imine of C6 and long chain C₁₅H₃₁) fig(3). ¹³C-NMR of compound (2) showed absorption at δ = (174.5) ppm belong to (C=S) and another absorption fig (4). Spectral data of compound (1 and 2) were showed in Table (1).

Scheme (1): Synthetic route of inhibitor (PQT)

Table (1) physical properties and Spectral data of compound (1 and 2)

Com. No.	Structures	M.P (C)	Yield %	color	Major FT-IR absorption (CM ⁻¹)	¹ H-NMR (□ ppm)	¹³ C-NMR (□ ppm)
1		48-50	70	Pale yellow	3030 v(C-H) arom, 2923 – 2854 v(C-H) aliph, 1761 v(C=O), 1637 v(C=N)	δ 0.8 (t,3H, CH ₃), δ 1.1 – 1.3 (m, 30H, 15CH ₂), δ 7.0 -7.9(m, 4H,ArH)	134(C1), 127(C2), 147(C3), 122(C4), 160.5(C5), 148(C6), 22-27 (Long chain C7)
2		98-100	80	Off white	(3358, 3260) vNH ₂ , 3155 vNH 3062 v(C-H) arom, 2918-2850 v(C-H) aliph, 1690 v(C=O) amide 1608 v(C=N),	δ 0.9 (t, 3H, terminal CH ₃), δ 1.2 – 1.5 (m, 30H, 15CH ₂), δ 6.8 -7.5(m, 4H,ArH) δ 8.0, 8.5 and 11.1 (s,3H, NH exchangeable)	134(C1), 127(C2), 147(C3), 122(C4), 160.5(C5), 148(C6), 22-27 (Long chain C7) 174.5(C8)

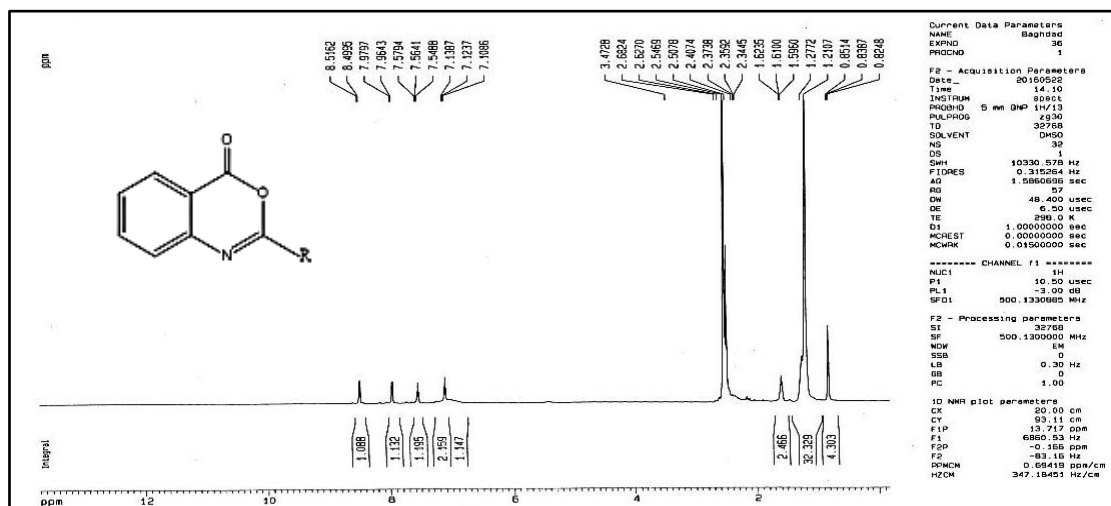


Fig (1) ¹H-NMR spectrum of compound (1)

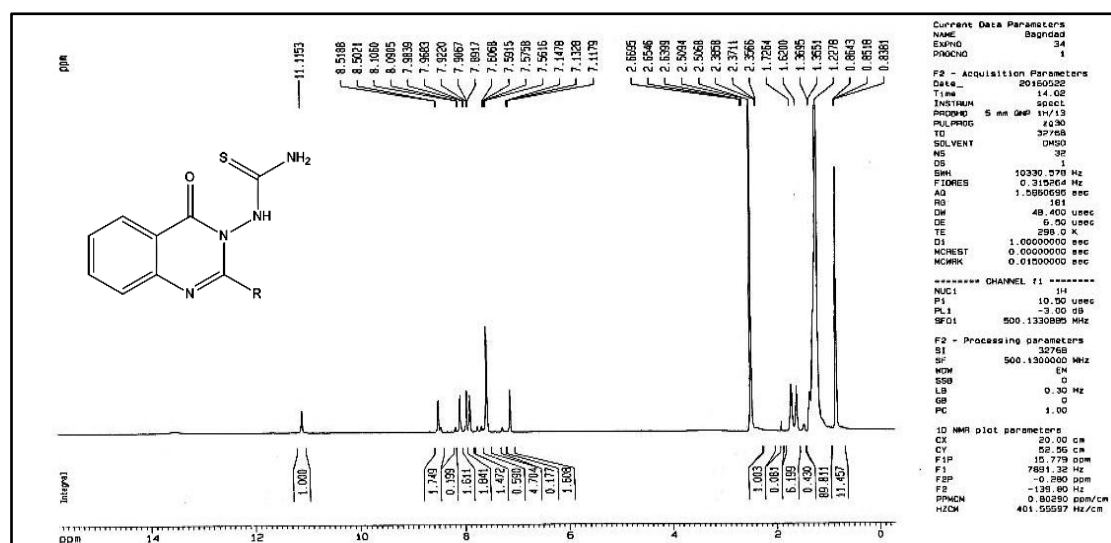


Fig (2) ¹H-NMR spectrum of compound (2)

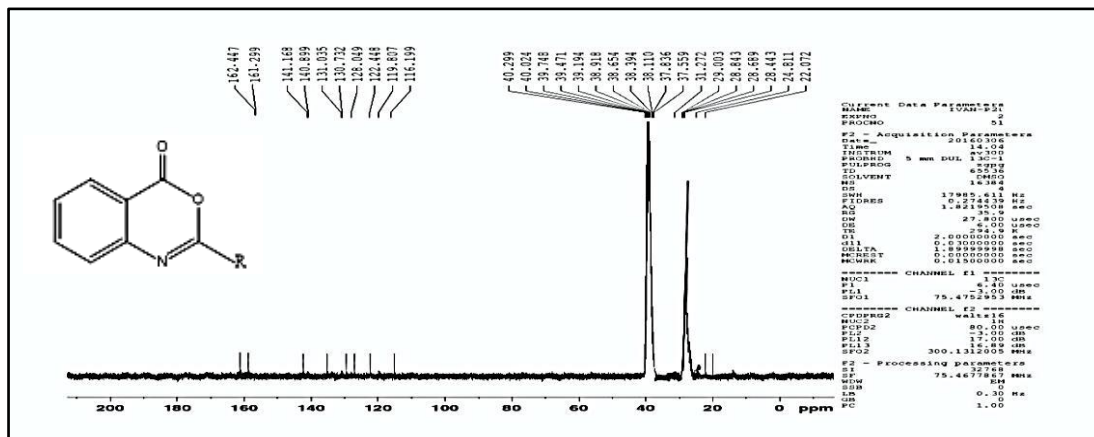


Fig (3) ¹³C-NMR spectrum of compound (1)

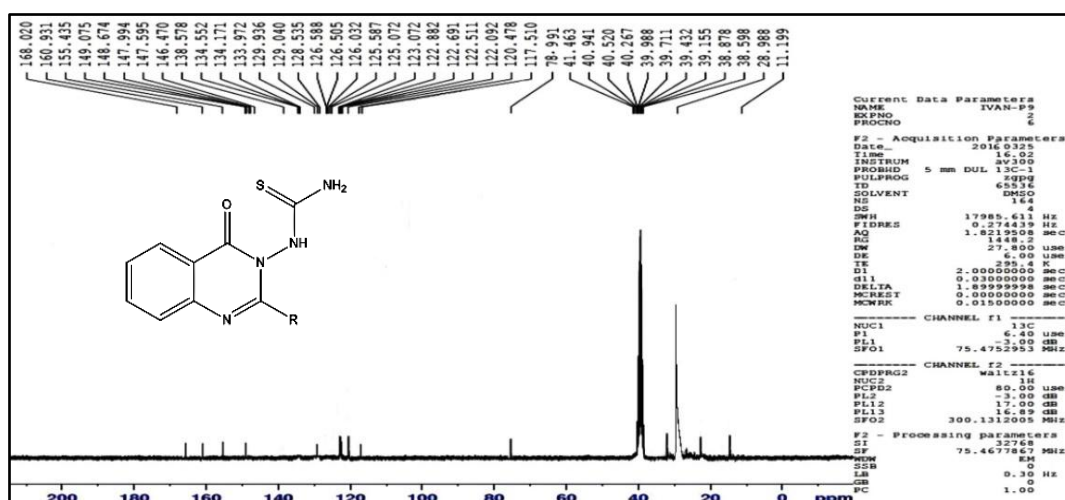


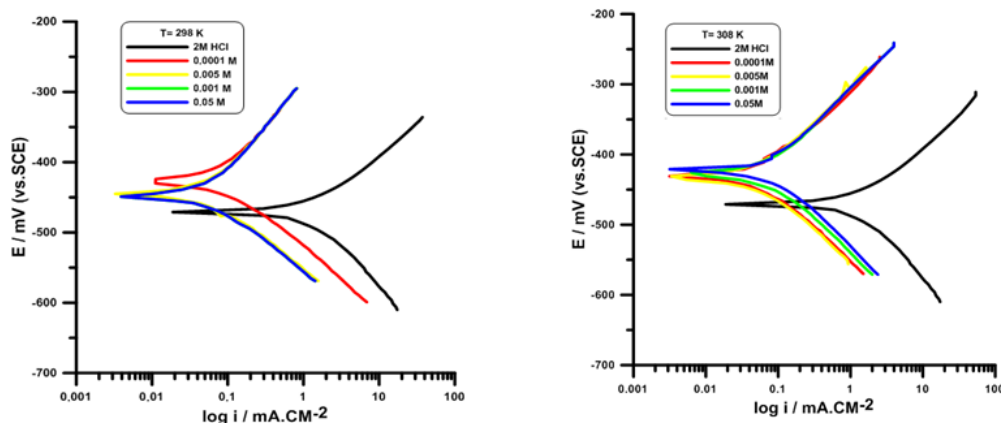
Fig (4) ¹³C-NMR spectrum of compound (2)

3.2 Potentiodynamic polarization:

The Tafel polarization behaviors of carbon steel in 2NHCl with the addition of various concentration of PQT at different temperature are shown in Fig (5). The corrosion kinetic parameters derived from these curves are presented in Table (2). From Table (2) it's clear that the corrosion current (*I*_{corr}), values of carbon steel decreases with the addition of PQT in 2NHCl. The inhibition efficiency %IE was calculated from the measured *I*_{corr} values using the equation (1):

$$\%IE = \frac{I_{corr}(un) - I_{corr}(i)}{I_{corr}(un)} * 100 \quad (1)$$

Where *i*_{corr} (un) and *i*_{corr} (i) are the uninhibited and inhibited corrosion current densities, respectively, which evaluated by extrapolated cathodic and anodic Tafel lines to corrosion potential.



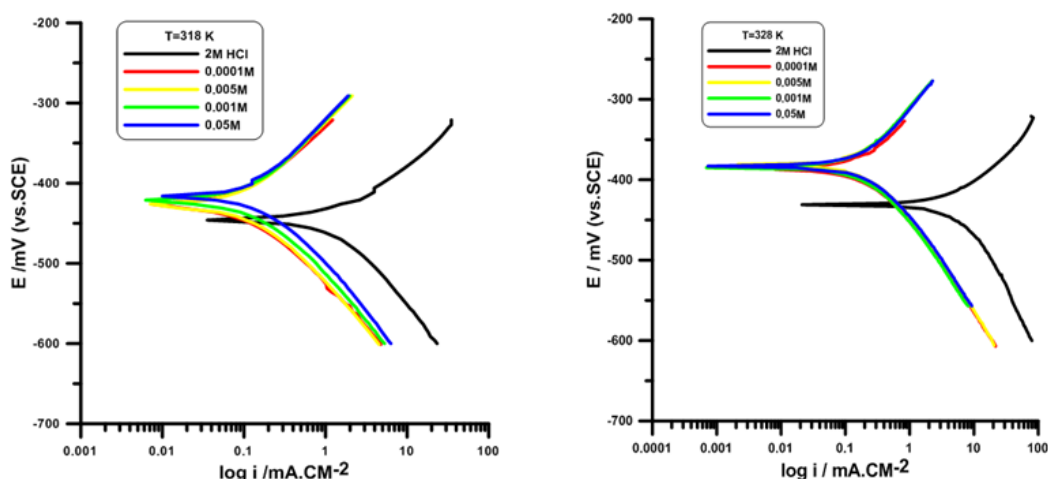


Fig (5) Typical Tafel plots of CS in 2NHCl in presence and absence of different concentration of (PQT) at 298, 308, 318 and 328K.

Table (2) Corrosion parameters obtained for carbon steel in 2N HCl at different temperatures and concentrations of (PQT)

Concentration(N)	T/K	E _{corr} (mV)	I _{corr} (□A.cm ⁻²)	B _c (mV.dec ⁻¹)	B _a (mV.dec ⁻¹)	PE%	□
2NHCl	298	-458.6	959.34	-84.6	69.7	—	—
	308	-472.2	803.55	-78.5	68.5	—	—
	318	-447.7	853.12	-81.8	62.9	—	—
	328	-430.2	3240	-79.2	58.7	—	—
0.0001	298	-472.6	51.54	-62.8	94.3	94.63	0.946
	308	-429	30.34	-67.6	65.9	96.22	0.962
	318	-425.9	65.92	-74.5	75.2	92.27	0.923
	328	-385.8	122.13	-65.3	96.2	96.23	0.962
0.005	298	-445	39.68	-68.8	59.8	95.87	0.959
	308	-426.7	35.57	85.6	72.3	95.57	0.956
	318	-426.7	71.64	-73.9	80.9	91.60	0.916
	328	-379.7	127.81	-69.1	68.9	96.06	0.961
0.001	298	-450.8	37.79	-62.2	100	96.06	0.961
	308	-427	44.84	-71.4	75.5	94.42	0.944
	318	-420.3	83.05	-78.8	81.4	90.27	0.903
	328	-377.2	107.28	-72.5	55.8	96.69	0.967
0.05	298	-449.2	39.02	-65.5	101.7	95.93	0.959
	308	-421.5	53.48	-74.2	80.2	93.34	0.933
	318	-414.6	94.29	-74.1	84	88.95	0.889
	328	-379.6	135.3	72.4	69.7	95.82	0.958

3.3 Adsorption Isotherm Studies:

The adsorption of isotherm study describes the adsorptive behavior of inhibitor in order to know the adsorption mechanism of inhibitor to the metal surface. The most frequently used adsorption isotherms are Langmuir, Frumkin, Temkin and Freundlich isotherms. The Langmuir adsorption isotherm was found to provide the best description of the adsorptive behavior Fig (6). The Langmuir adsorption isotherm is given by the following equation: [16]

$$C/\theta = 1/K_{ads} + C \tag{2}$$

Where C is concentration of inhibitor and K_{ads} is adsorptive equilibrium constant representing the degree of adsorption (i.e., the higher value of K_{ads} indicates that the inhibitor is strongly adsorbed on the metal surface); The Plot of C/θ Vs. C well yields a straight line, Fig(6) with regression coefficient, R², almost equal to 1. This suggests that PQT in the present study obeyed the Langmuir isotherm, and there is a negligible interaction between the adsorbed molecules. The values of equilibrium constant K_{ads} decreased with increasing temperature, which indicated that PQT is easily and forcefully adsorbed onto the C.S. surface at a lower temperature, weak and challenging at higher temperature

Free energy of adsorption was calculated using the following relations[17].

$$K_{ads} = 1/55.5 \text{ Exp}(-\Delta G_{ads}/ RT) \tag{3}$$

$$\Delta G_{ads} = -2.303RT \log (55.55 K_{ads}) \tag{4}$$

$$\text{Log}k_{ads} = -\Delta H_{ads}/2.303RT + \Delta S_{ads} / 2.303R + \text{Log} 1/55.55 \tag{5}$$

The value 55.55 in the equation above is the concentration of water in solution in mol.L⁻¹. The slope of variation of log (K_{ads}) vs. 1/T = (-ΔH_{ads} / 2.303R), so ΔH_{ads} = -2.59808 kJ mol⁻¹ (Fig. 7). A negative value of the ΔH_{ads} indicated that the adsorption process of inhibitor is an exothermic process; in an exothermic process physisorption is distinguished from chemisorption by considering that an exothermic value of a physisorption process is lower than -40 kJ.mol⁻¹ while the adsorption heat of chemisorption process approaches -100 kJ mol⁻¹ [18]. In this study the standard adsorption heat is ΔH_{ads} = -2.59808 kJ.mol⁻¹ postulates that physical adsorption is more favored. The negative value of standard adsorption entropy suggested that the adsorption was coupled with an increase of system order due to the adsorption of PQT on the C.S. surface. The data obtained from Langmuir adsorption isotherm reported in Table (3). The negative values of ΔG_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface.

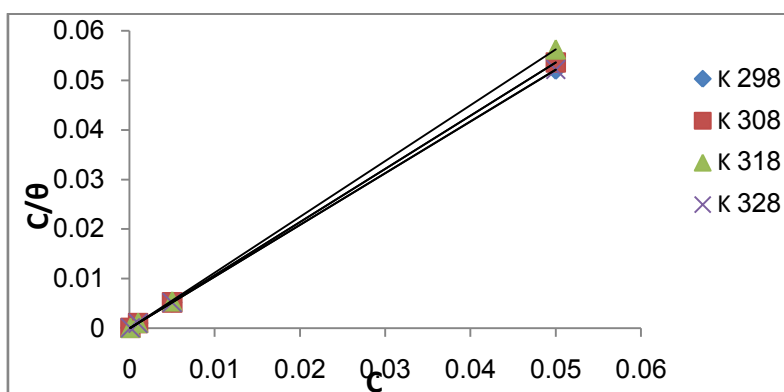


Fig (6) Langmuir adsorption isotherm of (PQT) on carbon steel in 2N HCl at different temperatures

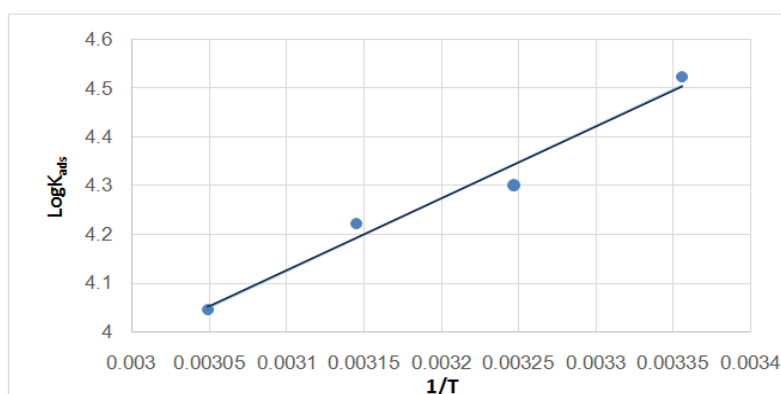


Fig (7) Plot of log Kads versus 1/T

Table (3) Thermodynamic parameters for adsorption of (PQT) on carbon steel surface in 2N HCl at different temperatures

T/K	K _{ads}	ΔG/kJ.mol ⁻¹	R ²	ΔH/kJ.mol ⁻¹	ΔS/J. mol ⁻¹ .K
298	33333.33	-35.7618	0.9999	-2.59808	-0.02269
308	20000.0	-34.4959	1		
318	16666.67	-34.0441	1		
328	11111.11	-33.0394	0.9998		

3.4 Corrosion Kinetic and Thermodynamic Study:

To study the effect of temperature on the inhibition efficiencies of PQT, potentiostat polarization measurements were carried out in the temperature range 298–328K in absence and presence of different PQT concentration.

The equation used to calculate the activation parameters of the corrosion process is Arrhenius Eq. (6). Moreover, transition state Eq. (7) was used. [19]

$$\text{Log (Icorr)} = \text{Log A} - \text{Ea}/2.303\text{RT} \quad (6)$$

$$\text{Log (Icorr/T)} = \text{Log (K/h)} + \Delta\text{S}^*/2.303\text{R} - \Delta\text{H}^*/2.303\text{RT} \quad (7)$$

Where I_{corr} is corrosion current density, Ea is the apparent activation energy, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is temperature in K, A is the Arrhenius pre-exponential factor, h is the Planck's constant (6.626 x 10⁻³⁴ J.s), N is the Avogadro's number (6.022 x 10²³ mol⁻¹), K is the Boltzmann constant,

ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation. The plot of $\log I_{corr}$ against $1/T$ presented a linear relation with a slope $(-E_a / 2.303 R)$ and the intercept of the extrapolated line $\log A$.

The result is listed in table (4) and Straight lines were obtained from the plots of $\log I_{corr}/T$ vs. $1/T$, which are shown in Fig. (8). with the slope of $(-\Delta H^*/2.303 R)$ and an intercept of $[(\log (R/Nh) + (\Delta S^*/2.303 R))]$ from which the values of ΔH^* and ΔS^* , respectively were calculated. From the corrosion current densities obtained from polarization curves at different temperatures in the absence and the presence of PQT as corrosion inhibitor, Arrhenius plots are shown in Figure (9) for a temperature range of (298-328 K) in 2N acid concentration.[20]

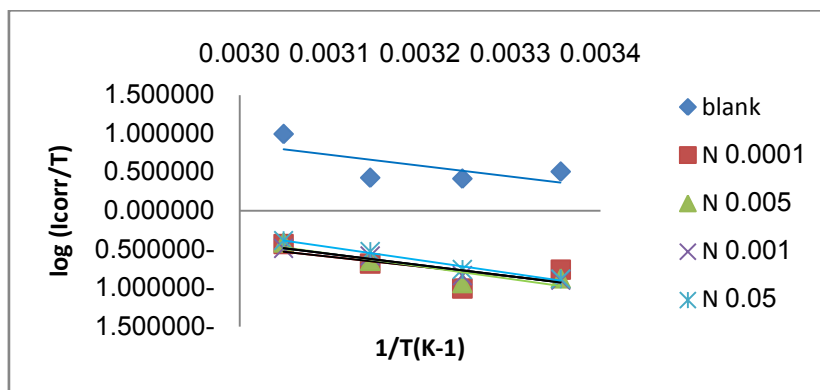


Fig (8) Transition state plot of carbon steel in 2N HCl contains different concentrations of (PQT) at different temperatures

ΔH^* value for the corrosion of C.S in 2N HCl solution was $26.768 \text{ kJ.mol}^{-1}$ in absence of PQT, while in the presence of PQT inhibitor ΔH^* values range are $(+24.125 \text{ to } +32.286) \text{ kJ.mol}^{-1}$, the highest ΔH^* value occurred with 0.05N of PQT. However, the negative values of ΔS_{act} pointed to a greater order produced during the process of activation[21]. This can be achieved by the formation of activated complex and represents association or fixation with consequent loss in the degrees of freedom of the system during the process. The highest value of activation energy is $(58.7567) \text{ kJ.mol}^{-1}$ was obtained with 0.005N.

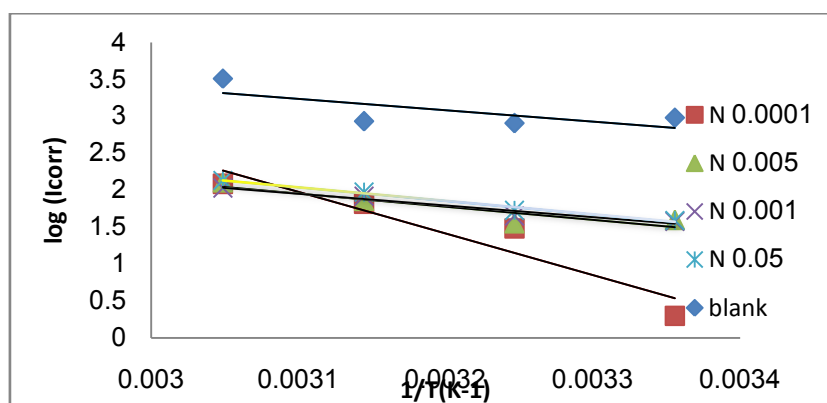


Fig (9) Arrhenius plot of carbon steel in 2N HCl contains different concentrations of (PQT) at different temperatures

Table (4) Corrosion kinetic parameters for carbon steel in 2NHCl in the absence and presence different concentration of (PQT)

$C_{PQT/N}$	$\square G/\text{kJ.mol}^{-1}$				$\square H^*/\text{kJ.mol}^{-1}$	$-\square S^*/\text{kJ.mol}^{-1} \cdot \text{K}^{-1}$	$E_a/\text{kJ.mol}^{-1}$	$A \text{ Molecules.cm}^{-2} \cdot \text{S}^{-1}$
	298	308	318	328				
2NHCl	56.775	57.782	58.789	59.796	26.768	0.1007	29.3660	$5.86 \cdot 10^{32}$
0.0001	64.109	65.450	66.792	68.134	24.125	0.1342	53.9944	$1.55 \cdot 10^{31}$
0.005	64.425	65.539	66.652	67.766	31.231	0.1114	58.7567	$1.62 \cdot 10^{30}$
0.001	64.167	65.388	66.609	67.830	27.786	0.1221	52.7739	$4.48 \cdot 10^{29}$
0.05	85.586	87.375	89.163	90.952	32.286	0.1789	34.8803	$2.91 \cdot 10^{29}$

3.5 Scanning Electron Microscopy (SEM):

The SEM micrograph of the corroded carbon steel in 2NHCl in the prescienceand absence of PQT are shown in Fig (10 A–B). In figure A (absence of inhibitor) of bare carbon steel surface, notches and defects were observed, while a layer of closely packed film was obtained in figure b, and the surface was free from pits and it was smooth. It was concluded from figure a-b that corrosion does not occur in prescience of PQT and hence corrosion was inhibited strongly when the inhibitor was present in the solution, then scanning electron microscopy observation, confirmed the existence of adsorbed protective film on the carbon steel surface.

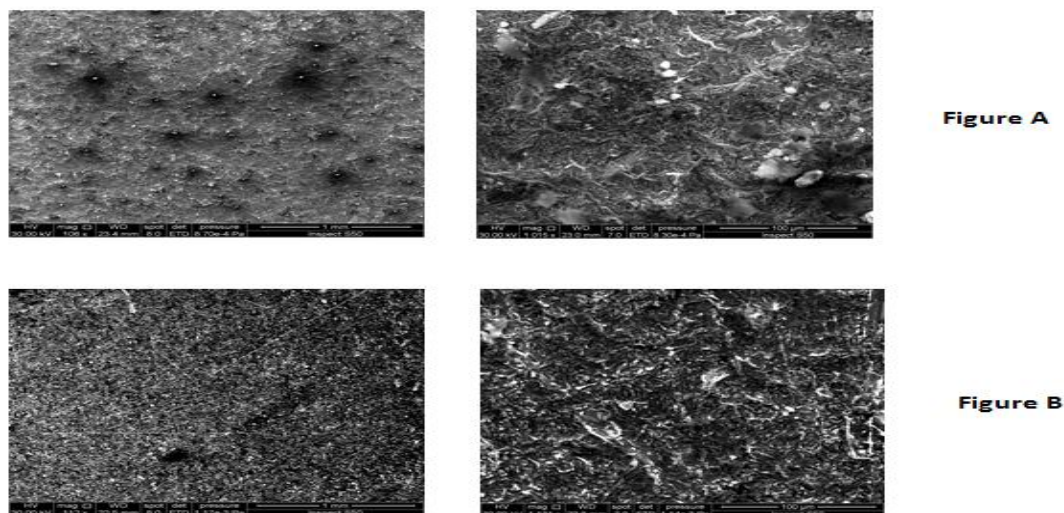


Fig (10) surface characterization by SEM for carbon steel in 2NHCl
(A) in the absence of inhibitor PQT
(B) in the presence of inhibitor PQT

IV. Conclusion

From the overall experimental results the following conclusions can be deduced:

- 1- The result obtained from all electrochemical measurement showed that the inhibition efficiency is good at all the concentrations of inhibitor.
- 2- The inhibition efficiency obtained by the PQT is very good at all the temperature but it decreased at 328k.
- 3- The adsorption of PQT on C-steel surface in 2NHCl solution follows Langmiur isotherm.
- 4- The Maximum inhibition efficiency is about 96.69 at 328k and 0.01N concentration of PQT.
- 5- The inhibitive mechanism was proposed when PQT introduced into 2NHCl solution a thin film formed on the C-steel surface which cause decrease of the C-steel roughness and effectively protect C-steel from corrosion.

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