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Corrosion Inhibition Effects of Some New Synthesized N-Aroyl-N\-Aryl thiourea Derivatives for Carbon Steel in Sulfuric Acid Media

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Abstract

This research includes the synthesis of some new N-Aroyl-N\-Aryl thiourea derivatives namely: N-benzoyl-N\-(p-aminophenyl) thiourea (STU1), N-benzoyl-N\-(thiazole) thiourea (STU2), N-acetyl-N`-(dibenzyl) thiourea (STU3). The series substituted thiourea derivatives were prepared from reaction of acids with thionyl chloride then treating the resulted with potassium thiocyanate to affored the corresponding N-Aroyl isothiocyanates which direct reaction with primary and secondary aryl amines, The purity of the synthesized compounds were checked by measuring the melting point and Thin Layer Chromatography (TLC) and their structure, were identified by spectral methods [FTIR,^{1}H-NMR and ^{13}C-NMR].These compounds were investigated as a corrosion inhibitor for carbon steel in 1M H_2SO_4 solution using weight loss, potentiostatic polarization methods; the obtained results showed that the substituted thioureas retard both cathodic and anodic reactions in acid media, by virtue of adsorption on the carbon steel surface. This adsorption obeyed Langmuir's adsorption isotherm. The inhibition efficiency of (STU1-3) is ranging between (60-95)%. By using different (STU3) derivative concentration and temperature, the carbon steel corrosion rate was decreased with increasing (STU3) concentration and the highest inhibition efficiency reach to 98.5% by using 5×10^{-4} M (STU3) concentration at 338 K, the inhibition efficiency increases with increasing temperature in the range of (308-338)K.

Keywords: thiourea derivatives, carbon steel, polarization, corrosion inhibition.

Introduction

Carbon steel is a very prominent material of construction and frequently comes in contact with aqueous solution, which may be acidic in nature, as a part of industrial process[1]. The study of corrosion of steel in acid media is of both academic and industrial significance that has received considerable attention[2,3]. Acid solution are widly used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling, gas and oil well acidizing[4]. Acids are also used in numerous manufacturing processes in different industries [5]. Most of the efficient inhibitors used in industry are organic compounds [6]. The addition of inhibitors to the acid media has been found to be cost-effective way of mitigating metallic corrosion under conditions of moderate acid concentration and temperature [7]. The effect of temperature on the inhibiting process is of great importance in industry. Most of the well-known acid inhibitors are compound containing heteroatom phosphorus, sulfur, nitrogen and oxygen, which are capable of retarding metallic corrosion [8]. Generally, N-containing inhibitor functions more efficient in HCl, while S-containing inhibitor in H_2SO_4 [9]. Furthermore, the compounds containing both N and S can provide excellent inhibition, compared with compounds containing only N or S [10]. There are many investigations about thiourea and various thiourea derivatives as good inhibitors of the corrosion of iron or steel in HCl [11-13], H_2SO_4 [14-16], HNO3 [17], $HClO_4$ [18], H_3PO_4 [19]. Such compounds can adsorb on the surface of the metal, blocking the active centers on the surface and thus reduces the corrosion rate [20]. The inhibition performance of organic inhibitors is due to physisorption and/or chemisorption on the surface of the metals [21, 22].

In this research some new thiourea derivatives (STU1-3) were synthezied; then evaluated as corrosion inhibitors for carbon steel in 1M H_2SO_4 solution. weight loss and potentiostatic polarization have been used to determine; surface coverage (θ), inhibition efficiency (% IE) and the inhibitor adsorption isotherm on carbon steel in the corrosive media.

Experimental

Instruments

Melting points were measured with a Gallen Kamp melting point apparatus. Model the FTIR-spectra of compounds were recorded on a Shimadzu FTIR-8300 spectrophotometer using KBr disc. ^{1}HNMR and ^{13}CNMR spectra were recorded on Bruker spectro spin ultra-shield magnets 300 MHz instrument, using DMSO-d^{6} as solvent and TMS as internal reference. The Weight loss were measured with Sartorius Ag. Gottigen BL210S (Germany) Electronic precision balance and preions metal scale with capacities ranging 0.1mg to 12kg.

Polarization measurements were conducted using advanced potentiostat winking MLab-200 (2007) [Bank Elektronik-Intelligent controls GmbH] with all accessories, a three electrodes cell were used. The working polished carbon steel electrode with exposed area 1 cm^{2} was dipped in the test solution. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the counter electrodes, respectively. All potentials were measured *vs*. SCE.

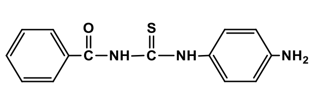
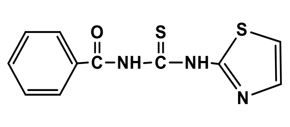
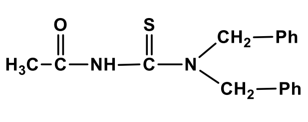
Chemicals

All Starting chemical compounds were obtained from Fluka and Aldrich or BDH.

synthesis of N-Aroyl-N$^{\backslash}$-Aryl thiourea derivatives (STU1-3)[23]

A solution of acid chloride was synthesized according to literature procedure (0.01 mole) dissolved in dry acetone (30 ml) was added dropwise to a suspension of potassium thiocyanate (0.01 mole,0.9710gm) in dry acetone (30 ml), the reaction mixture was refluxed for 1hr. After cooling to room temperature,a solution of primary and secondary aryl amines (0.01 mole) in dry acetone (20 ml) was added and the resulting mixture refluxed for 3-4 hrs., then the reaction mixture was poured into cold water and the precipitated thioureas were recrystallized aqueous ethanol or ethanol, to afford the pure compounds (STU1-3).Some of the measured physical properties of the dry products are listed in Table (1).

Table (1)
Physical properties and FTIR spectral of compounds (STU1-3).

Comp. No.	***Comp. structure***	***Melting point c°***	***Yield %***	***color***	***Major FTIR Absorptions cm^{-1}***				
					νN-H	***νC-H arom.***	***νC=O***	***νC=S***	***Other bands***
STU1		204-205	88	deep yellow	3232	3043	1662	1271	ν NH$_2$ asym. 3410 sym.3320 νp-position 825
STU2		148-150	59	yellow	3305 3120	3050	1676	1298	νC=N 1649
STU3		121-122	80	off white	3250	3031	1685	1238	νC-H aliph. 2939;2862

Specimen

Carbon steel specimens with composition 0.086% C, 0.252%Mn, 0.003%P, 0.016% S and the remainder being Fe were used. Specimens of size 2cm x 1cm x 0.2cm were used for the weight loss and of 1.5cm diameter specimen were used for polarization method**.** These samples were polished successively with belt grinding polishing machine and polished with emery papers of different grit

(80, 150, 220, 240, 320, 400, 1000, 1200 and 2000) in sequence. After polishing the specimens were washed with distilled water and finally dried.

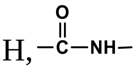
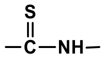
Weight loss method

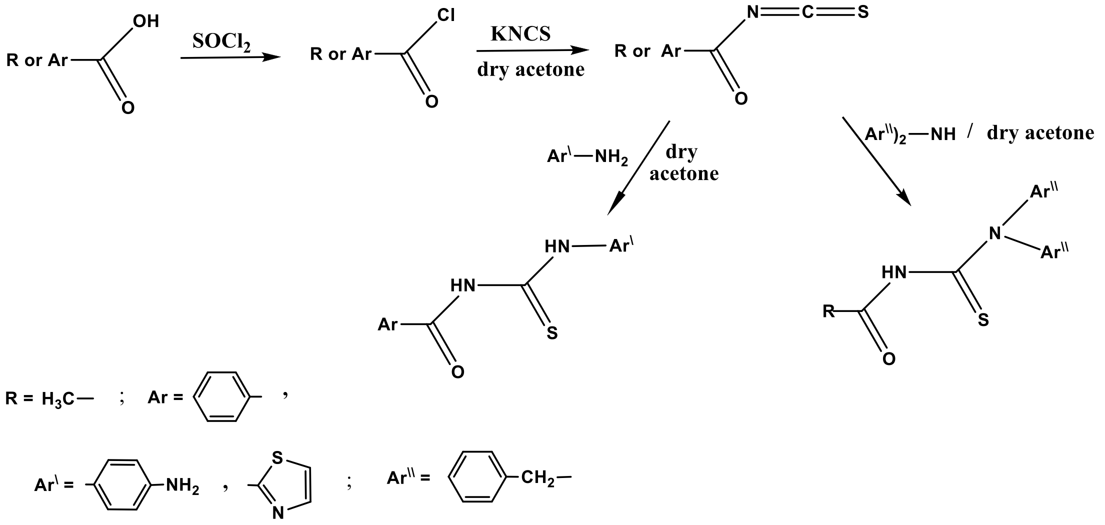
Weight loss was carried out in a glass vessel containing 75 ml test solution. A clean weighed carbon steel specimen was completely immersed at an inclined position in the vessel. After a period of time up to 5 hour at 303±1 k of immersion in 1M H_2SO_4 with and without addition of inhibitor (STU1-3), the specimen was withdrawn, rinsed with distilled water, washed with acetone, dried and weighted using the analytical balance. The average weight loss for each two identical experiments was taken and expressed in (g/m^2.d).

Potentiostatic polarization study

The electrode potential was allowed to stabilize 15 min before starting the measurements. Tafel polarization curves were obtained by changing the electrode potential automatically from -200 mV versus open circuit potential (OCP) to +200mV versus OCP with scan rate of 2.0 mV s^{-1}. All experiments were conducted at 308±1K.Inhibitor concentration of (1.7×10^{-4}, 3.5×10^{-4}, 5×10^{-4})M were examined. Tafel lines of potential versus, I_{corr} in a logarithm scale were plotted and corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined in the absence and presence of inhibitor.

Corrosion inhibitors synthesis

Most of the hetero compounds are very important organic compound having wide spectrum of corrosion inhibitors of carbon steel in acid media. The initial mechanism in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface and can be facilitated by the presence of hetro atoms such as (N,O,P and S) [8]. Therefore, there is need for preparation of new organic compounds containing (N and S) atom for used as a corrosion inhibitors. The synthetic sequence leading to the thioureas(STU1-3) show in Scheme (1). All thioureas (STU1-3) were synthesized according to the method in previous paper [23] with minor modifications. The obtained yields ranging from (59–88)%. The synthesis involves acids converted into corresponding acid chlorides by treatment with thionyl chloride according to standard procedure. The acid chlorides were treated with an equimolar quantity of potassium thiocyanate in dry acetone to afford the corresponding isothiocyanates intermediates which were direct addition of an equimolar of primary and secondary aryl amines in dry acetone to isothiocyantes furnished the N-Aroyl-N$^{\backslash}$-Aryl thiourea derivatives (STU1-3). The reaction proceeds via a nucleophilic addition of the amine to the isothiocyanates, and the end point of the reaction was examined by TLC. The structure of these compounds (STU1-3) were confirmed by physical properties are listed in Table (1), and characterized by FTIR, 1H-NMR and 13C-NMR spectroscopy. FT-IR (KBr) spectra showing strong υN-H absorptions at about 3305-3120 cm-1, and displayed absorptions at about 1685-1662 cm-1 and 1298-1238 cm-1 that were assigned to υC=O and υC=S functions respectively. While the ^{1}H-NMR spectra data of compounds (STU1-3) [24] δ ppm in DMSO-d^6 solvent are listed in Table (2). The signals in the range of 10.7-12.8 [S,1H,  $-\overset{O}{\overset{\|}{C}}-NH-$]; 10.5-12.2 [S,1H,  $-\overset{S}{\overset{\|}{C}}-NH-$]. Generally the1 H-NMR signals of NH protons for amides are observed in the range of [9-10] δppm. The low-field shift of the signal for the imine proton for synthesized compounds can be attributed to the deshielding effect of the electron-withdrawing carbonyl and thiocarbonyl group. 13C-NMR spectra data were listed in Table (3), spectrum showed the peaks at about δ 182.7-178.1 and 168.1-164.3 for C=S (thioamide) and C=O (amide), respectively.



Scheme (1): synthesis of some new N-Aroyl-N\-Aryl thioureas

Table (2)
^{1}H-NMR spectral data(ppm) for some of the prepared compounds (STU1-3).

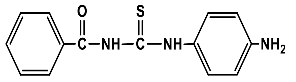
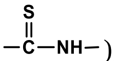
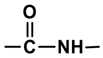
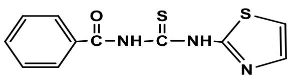
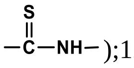
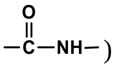
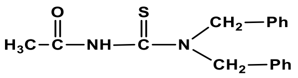
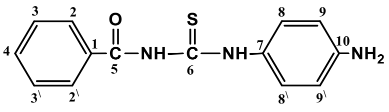
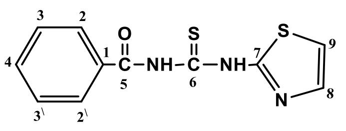
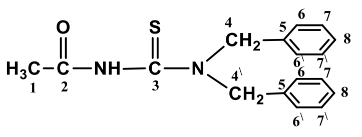
Comp. No.	*Compound structure*	*^{1}H-NMR parameters (ppm) δ-H*
STU1		5.18(s,2H, -NH$_2$);6.5-7.9(m,9H,Ar-H); 10.5(s,1H,  $-\overset{S}{\overset{\|}{C}}-NH-$);11.32(S,1H,  $-\overset{O}{\overset{\|}{C}}-NH-$)
STU2		7.27-7.36(d,2H,H-thiazole);7.5-8.6(m,5H,Ar-H); 12.2(s,1H,  $-\overset{S}{\overset{\|}{C}}-NH-$);12.8(S,1H,  $-\overset{O}{\overset{\|}{C}}-NH-$)
STU3		2.00(s,3H,-CH$_3$);4.63-5.13(s,4H,-CH$_2$-);7.15-7.35(m,10H,Ar-H);10.59(s,1H,-NH-)

Table (3)
^{13}C-*NMR spectral data for some of the prepared compounds(STU1-3).*

Comp. No.	*Compound structure*	*^{13}C-NMR data (ppm)*
STU1		113.4-128.61($C_{2,2^{\backslash},3,3^{\backslash},4,8,8^{\backslash},9,9^{\backslash}}$);132.23($C_7$);132.95($C_1$); 147.29($C_{10}$);168.15($C_5$);178.18($C_6$).
STU2		113.79(C_9);114.53-129.23($C_{2,2^{\backslash},3,3^{\backslash},4}$);132.99($C_8$);133.31 ($C_1$);137.97($C_7$);164.39($C_5$);178.81($C_6$).
STU3		23.14(C_1);55.27($C_{4,4^{\backslash}}$);127.27-128.6($C_{5,6,6^{\backslash},7,7^{\backslash},8}$); 167.50($C_2$);182.72($C_3$).

Weight loss measurements

The gravimetric measurements of carbon steel immersed in 1M H_2SO_4 in the absence and presence of different inhibitors of thiourea derivatives (STU1-3) were investigated and determined after 4 hour of immersion time at 303 K, 3.5×10^{-4} M concentration of these inhibitors was chosen to compare the inhibition efficiency of the three compounds, weight loss of carbon steel samples are decreased in the present of the three compounds. This means that these compounds retards the corrosion of carbon steel in 1 M H_2SO_4 or in other words, these compounds act as inhibitors. The corrosion rate of carbon steel was determined using the relation:

$$R = \frac{\Delta m}{A * t} \quad \text{...(1)}$$

where Δm is the mass loss (mg), A the area (cm^2) and t immersion period (4 hours). The value of the percentage inhibition efficiency (% IE), and a parameter surface coverage (θ) which represents the part of the surface covered by the inhibitors molecules, for the corrosion of carbon steel were calculated as follows [25]:

$$\%\,IE = \frac{(R - R_{inh})}{R} \times 100 \quad \text{........................(2)}$$

$$\theta = \frac{(R - R_{inh})}{R} \quad \text{...................................(3)}$$

where R and R_{inh} are the uninhibited and the inhibited corrosion rate, respectively. The calculated values of corrosion rate ($g/m^2.d$), surface coverage (θ) and inhibition efficiency (% IE) at 303 K are given in Table (4). According to this data, it is clear that using 3.5×10^{-4} M of all thiourea derivatives reduces the corrosion rate of carbon steel in sulfuric acid solution, the order of inhibition efficiency (% IE) of investigated thioureas is as follows: STU3> STU2> STU1.

Table (4)

Data of corrosion rate, degree of surface coverage and inhibition efficiency for carbon steel in 1M H_2SO_4 solution in the absence and presence of 3.5×10^{-4} M of the three inhibitors at 303 K.

inhibitor	*R ($g/m^2.d$)*	*θ*	*% IE*
blank	474.46	--	--
STU1	99	0.79	79.12
STU2	86.22	0.81	81.82
STU3	21.37	0.95	95.49

Polarization measurements

Potentiostatic polarization curves were plotted for the corrosion of carbon steel in 1M H_2SO_4 solution in the absence and presence of 3.5×10^{-4} M thioureas (STU1-3) at 308 K as shown in (Fig. (1)).

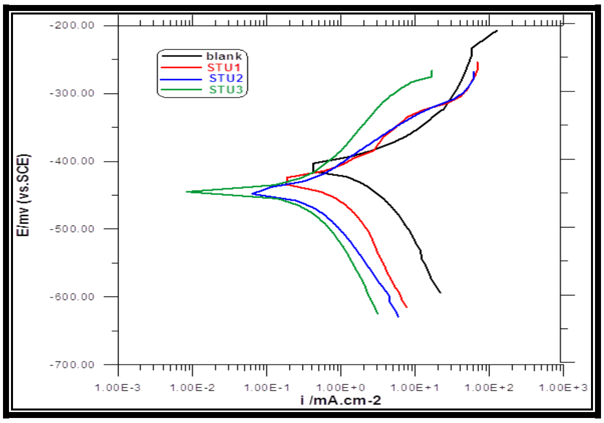


Fig.(1) Polarization curves of carbon steel in 1M H_2SO_4 in the absence and presence of 3.5×10^{-4} M thioureas (STU1-3) at 308 K.

A linear region with apparent Tafel was observed, the cathodic reaction was activation-controlled and the addition of the compounds tested decreased the current densities in large anodic and cathodic domains of potential. This result indicated that the compounds studied acted as mixed-type inhibitors. Generally, the addition of mixed inhibitors in solution does not change corrosion potential significantly because they inhibit both the anodic and cathodic reactions. Small changes in potentials can be a result of the competition of the anodic and the cathodic inhibiting reactions, and of the metal surface condition [26]. The values of various electrochemical parameters are summarized in Table (5), the percentage inhibition efficiency (% IE), and a parameter surface coverage (θ) which represents the part of the surface covered by the inhibitors molecules, for the corrosion of carbon steel were calculated as follows [27]. Where I_{corr} and $I_{corr(inh)}$ are the corrosion currents densities in the absence and in presence of the inhibitor,respectively which determined by extrapolation of the cathodic and anodic Tafel lines to corrosion potential (E_{corr}).From Table (5), it was clearly seen that cathodic slope were found similar indicating that the reduction of hydrogen did not modified in the presence of the inhibitors tested.Thus, the presence 3.5×10^{-4} M of thioureas led to decrease in the values of I_{corr}, which was particularly significant in the case of(STU3).

Table (5)
polarization parameters of carbon steel in 1M H_2SO_4 in the absence and presence of 3.5×10^{-4} M thioureas (STU1-3) at 308 K.

Solution	*E_{corr} mv (SCE)*	*I_{corr} $\mu A/cm^2$*	*βc mV/dec*	*βa mV/dec*	*W.L $g/m^2.d$*	*Penetration loss mm/a*	*θ*	*% IE*
blank	-411.8	1450	-109.2	70.5	363	16.9	--	--
STU1	-429.8	585.93	-123.2	79.6	146	6.80	0.5959	59.59
STU2	-443.4	281.27	-107.5	73.7	703	3.26	0.8060	80.60
STU3	-448.4	236.24	-112.0	105.1	59.1	2.74	0.8370	83.70

Effect of inhibitor (STU3) concentration

Effect N-acetyl-N\-(dibenzyl) thiourea (STU3) was investigated in the concentration range (1.7×10^{-4} - 5×10^{-4})M. (Fig. (2)) shows the Tafel polarization value of carbon steel immersed in 1M H_2SO_4 at 308 K with and without (STU3) inhibitor. polarization parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (βc and βa) and corrosion current density (I_{corr}) were extracted by extrapolating the anodic and cathodic branches of Tafel curves at potentials beyond the region of Ecorr ±200 mV, and are listed in Table (6). From the results collected in Table (6), it can be seen that by increasing the inhibitor concentration, the corrosion rate is decreased in acid media and inhibition efficiency increased as shown in Fig.(3). Therefore, it can be concluded that they impede the corrosion by merely blocking the reaction sites on carbon steel surface without interfering the anodic and cathodic reactions. Moreover, this inhibitor cause no significant changes in the anodic and cathodic Tafel slopes, this suggest that this inhibitor behave as a mixed-type inhibitor. Indicating that the inhibitor can be classified as adsorptive-type [26].

Table (6)
Polarization parameters of carbon steel in 1M H_2SO_4 in the absence and presence of different concentrations of (STU3) at 308 K.

Inhibitor conc. (M)	*E_{corr} mv (SCE)*	*I_{corr} $\mu A/cm^2$*	*βc mV/dec*	*βa mV/dec*	*W.L $g/m^2.d$*	*Penetration loss mm/a*	*θ*	*% IE*
0	-411.8	1450	-109.2	70.5	363	16.9	--	--
1.7×10^{-4}	-454.9	456.44	-151.8	123.5	114	5.30	0.6852	68.52
3.5×10^{-4}	-448.4	236.24	-112.0	105.1	59.1	2.74	0.8370	83.70
5×10^{-4}	-458.8	206.92	-73.6	64.4	51.7	2.40	0.8572	85.72

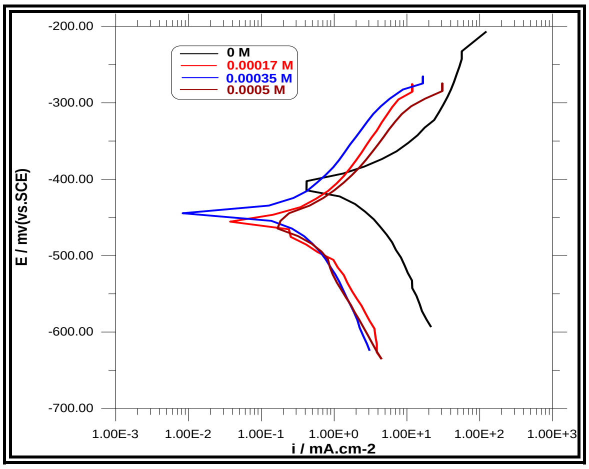


Fig.(2) Polarization curves of carbon steel in 1M H_2SO_4 in the absence and presence of inhibitor (STU3) different concentration at 308 K.

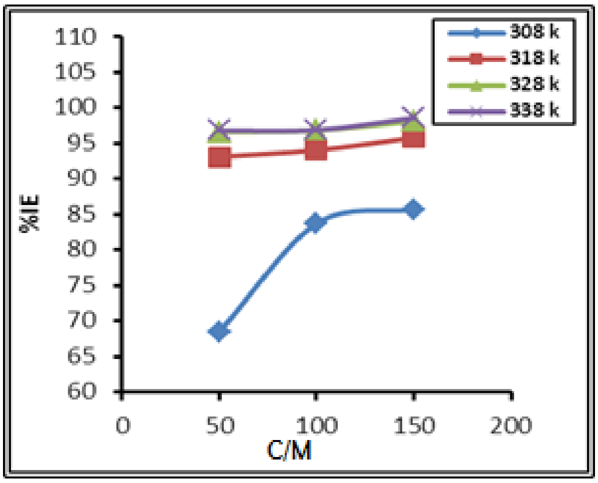


Fig.(3) Relationship between inhibition efficiencies and various concentrations from inhibitor(STU3) for carbon steel in 1M H_2SO_4.

Adsorption isotherms

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms [28]. The adsorption of an organic adsorbate at metal–solution interface can occur as a result of substitutional adsorption process between organic molecules presented in the aqueous solution ($Org_{(sol)}$), and the water molecules previously adsorbed on the metallic surface ($H_2O_{(ads)}$) [29]:

$$Org_{(sol)} + xH_2O_{(ads)} = Org_{(ads)} + xH_2O_{(sol)} \quad \text{..........(4)}$$

where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively,$H_2O_{(ads)}$ is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic adsorbate. In order to obtain the adsorption isotherm, the degree of surface coverage, θ, for different concentrations of inhibitor in 1M H_2SO_4 solution has been evaluated by equation (5). The θ values are presented in Table (7). According to the Langmuir's isotherm, the surface coverage (θ) is related to inhibitor concentration (C) by the following equation [30]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{...(5)}$$

Where K_{ads} is the equilibrium constant of the inhibitor adsorption process. A straight line is obtained on plotting C/θ versus C as shown in Fig. (4). The linear correlation coefficient (r^2) is equal to (r^2 =0.9988-1) and the slope is very close to 1, indicating the adsorption of synthesized inhibitor (STU3) on the carbon steel surface obeys the Langmuir adsorption isotherm. The high correlation facter (r^2) of the Langmuir adsorption isotherm may confirm the validity of this approach. The equilibrium constant (K_{ads}) for the adsorption–desorption process of tested inhibitor can be calculated from reciprocal of the intercept. The adsorptive equilibrium constant (K_{ads}) values are listed in Table (7). The most important thermodynamic adsorption parameters are the free energy of an adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation [31]:

$$\Delta G_{ads} = -2.303RT\log(55.5K_{ads}) \quad \text{................(6)}$$

where R is the gas constant, T is the absolute temperature and the value 55.5 is the concentration of water in solution expressed in M, K_{ads} is the equilibrium constant of the inhibitor adsorption process .Values of ΔG_{ads} are listed in Table (7). The values of ΔG_{ads} negative sign are usually characteristic of a strong interaction and a high efficient adsorption. Generally, values of ΔG_{ads} around -20 kJ mol^{-1} or lower negative are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Whereas, the more negative values than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [32]. Calculated ΔG_{ads} values indicate that the adsorption mechanism of the synthesized inhibitor on carbon steel in 1M H_2SO_4 solution is chemical adsorption.

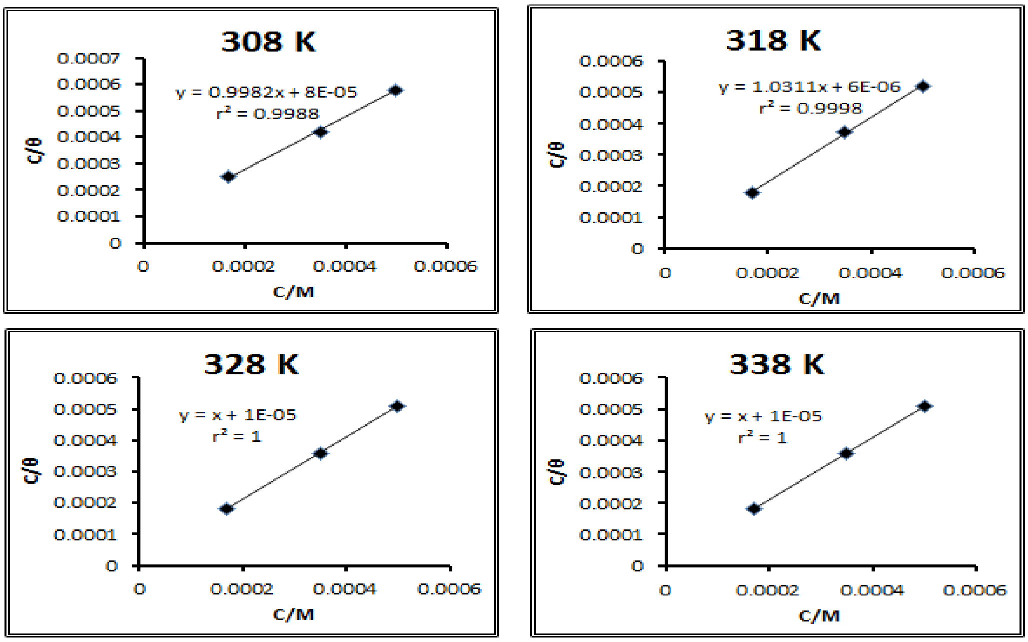


Fig.(4) The Langmuir isotherm adsorption for carbon steel in 1M H_2SO_4 in the different concentrations of inhibitor (STU3) at (308-338) K.

Table (7)

Data of free energy of adsorption and the parameter of adsorption isotherm for carbon steel in 1M H_2SO_4 solution in different concentrations of inhibitor (STU3) at (308-338) K.

T/K	$(1/T)*10^{-3}$ K^{-1}	C/M	θ	C/θ	K_{ads} (M^{-1})	ΔG_{ads} $KJ.mol^{-1}$	r^2
308	3.2	1.7×10^{-4}	0.6852	0.00025	12500	-34.44	0.9988
		3.5×10^{-4}	0.8370	0.00042			
		5×10^{-4}	0.8572	0.00058			
318	3.1	1.7×10^{-4}	0.9310	0.00018	166666	-42.42	0.9998
		3.5×10^{-4}	0.9403	0.00037			
		5×10^{-4}	0.9578	0.00052			
328	3.0	1.7×10^{-4}	0.9657	0.00018	100000	-42.36	1
		3.5×10^{-4}	0.9681	0.00036			
		5×10^{-4}	0.9810	0.00051			
338	2.9	1.7×10^{-4}	0.9679	0.00018	100000	-43.65	1
		3.5×10^{-4}	0.9685	0.00036			
		5×10^{-4}	0.9856	0.00051			

Effect of temperature

The change in the rate of the corrosion process with temperature was studied in 1 M H_2SO_4 with and without (STU3) inhibitor at various concentrations (1.7×10^{-4} - 5×10^{-4})M. The aim was to evaluate the apparent activation energy and the pre-exponential Factor (A) of the corrosion process. This was carried out by studying the temperature dependence of the corrosion current obtained with the potentiostatic polarization method. The polarization exhibits Tafel behaviour. The Polarisation curves which are not presented here show that both the anodic and cathodic polarizations decrease upon heating while I_{corr} increases. Several electrochemical Parameters were calculated from these curves and the results are summarised in Table (8). I_{corr} increases upon heating both in uninhibited and inhibited solutions. The Efficiency of STU3 increases with temperature increase in the studied temperature range. The fact that (%IE) increases with temperature was considered by Ivanov [33] as due to Change in the nature of the adsorption mode. The inhibitor is physically adsorbed at lower temperatures, while Chemisorption is favoured at higher temperatures Fig. (5).

Table (8)

The effect of temperature on the corrosion parameters of carbon steel in 1 M H_2SO_4 containing different concentrations of inhibitor (STU3).

Conc. (M)	***Temp. K***	***E_{corr} Mv (SCE)***	***I_{corr} $\mu A/cm^2$***	***βc mV/dec***	***βa mV/dec***	***W.L $g/m^2.d$***	***Penetration loss mm/a***	***θ***	***% IE***
0	308	-411.8	1450	-109.2	70.5	363	16.9	--	--
	318	-394.7	6150	-134.4	102.6	1540	71.4		
	328	-381.2	13390	-153.6	128.8	3350	155		
	338	-372.3	21510	-243.2	137.4	5380	250		
1.7×10^{-4}	308	-454.9	456.44	-151.8	123.5	114	5.30	0.68	68.52
	318	-438.9	424.14	-147.4	109.1	106	4.92	0.93	93.10
	328	-432.1	458.46	-110.3	104.1	115	5.32	0.96	96.57
	338	-421.7	688.68	-74.6	77.7	172	7.99	0.96	96.79
3.5×10^{-4}	308	-448.4	236.24	-112.0	105.1	59.1	2.74	0.83	83.70
	318	-441.7	366.72	-119.6	104.4	91.7	4.26	0.94	94.03
	328	-440.0	426.46	-88.4	70.5	107	4.95	0.96	96.81
	338	-432.0	675.42	-101.1	83.0	169	7.84	0.96	96.85
5×10^{-4}	308	-458.8	206.92	-73.6	64.4	51.7	2.40	0.85	85.72
	318	-440.5	259.22	-110.2	89.1	64.8	3.01	0.95	95.78
	328	-433.6	253.11	-107.8	93.0	63.3	2.94	0.98	98.10
	338	-423.4	307.77	-123.0	90.6	76.9	3.57	0.98	98.56

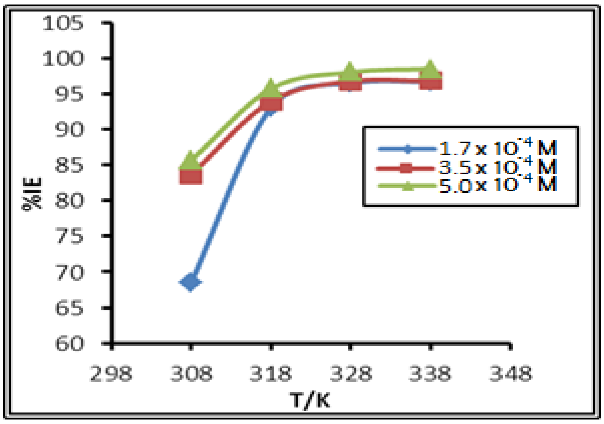


Fig.(5) Relationship between inhibition efficiencies and different temperature(308-338) K for carbon steel in 1M H_2SO_4 for inhibitor(STU3).

Although the adsorption process was sufficiently elucidated by the thermodynamic model, the kinetic model is another way to explain the mechanism of corrosion inhibition. The corrosion reaction can be regarded as an Arrhenius modified Arrhenius equation [28]:

$$\log i_{corr} = \log A - \frac{E_a^*}{2.303RT} \quad \text{.........................(7)}$$

Where i_{corr} is the corrosion current density, E_a^* is the apparent activation energy of the corrosion reaction, R is the gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential factor. Fig.(6) presents the Arrhenius plots of the natural logarithm of the current density *vs* 1/T, for 1M solution of H_2SO_4, in presence and absence of different concentrations of compound (STU3).

Values of E_a^* and A for the corrosion reaction in the absence and presence of different concentrations of the (STU3) inhibitor are calculated by a linear regression method and given in Table (9). It is found that the activation energy is lower in the presence of inhibitor than in its absence.

Enthalpy and entropy of activation ($\Delta H^*$and ΔS^*) are calculated from the transition state equation [34]:

$$\log\left(\frac{i_{corr}}{T}\right) = \left(\log\left(\frac{R}{N_A h}\right) + \left(\frac{\Delta S^*}{2.303R}\right)\right) - \frac{\Delta H^*}{2.303R} \times \frac{1}{T} \quad \text{..........(8)}$$

where h is Planck's constant, N_A is Avogadro's number, R is the universal gas constant, $\Delta H^*$is the enthalpy of the activation and ΔS^* is the entropy of activation. Plotting of log (i_{corr}/T) against 1/T, (Eq. (8)), for carbon steel in 1M H_2SO_4 in the absence and presence of different concentrations from the synthesized inhibitor, gives straight lines as shown in Fig. (7). Data in Table (9) represent the values of $\Delta H^*$and ΔS^* which are calculated from the slope ($-\Delta H^*/2.303R$) and the intercept [log (R/N_Ah) + $\Delta S^*/2.303R$] of the straight lines. Values of ΔH^* and ΔS^* are calculated and listed in Table (9).

E_a^* decreases with increasing the synthesized inhibitor (STU3) concentration. It is obvious that concentration of the synthesized inhibitor is playing a role in decreasing the activation energy value, thereby indicating a more efficient inhibiting effect. The decrease in E_a^* with the synthesized inhibitor concentration is typical of chemisorption process [35]. This was attributed by Hoar and Holliday [36] to a slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at the higher temperature. But, Riggs and Hurd [37] explained that the decrease in activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one. Schmid and Huang [38] found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but that the reaction rate on the covered area is substantially less than on the uncovered area like that in this work Table (9). According to Eq. (7) low values of A and high values of E_a^* lead to lower corrosion rates. For the present study, E_a^* is lower in the presence of (STU3). Therefore, the decrease in the steel corrosion rate is decided by the pre-exponential factor A, which reflects the effect of the variation of entropy ΔS^* during activation. It was found that A and consequently ΔS^* significantly decreased with inhibitor concentration reducing the corrosion rate of the steel. As a result, the corrosion rate of steel decreased with increasing inhibitor concentration. Clearly, the reduction of A is an important factor that determines the corrosion rate of steel in 1M H_2SO_4 in the presence of (STU3). Generally one can say that the nature and the concentration of electrolyte affect greatly the activation energy for the corrosion process.

The positive signs of the enthalpy ΔH^* reflect denoting that transition state (the activated complex) is endothermic process. Negative values of entropies ΔS^* and addition to the value of ΔS^* decreases gradually with increasing the synthesized inhibitor concentrations imply that the activated complex in the rate determining step represents an association rather than a dissociation step. This meaning that a decrease in disordering takes place on going from reactants to the activated complex [39, 40].

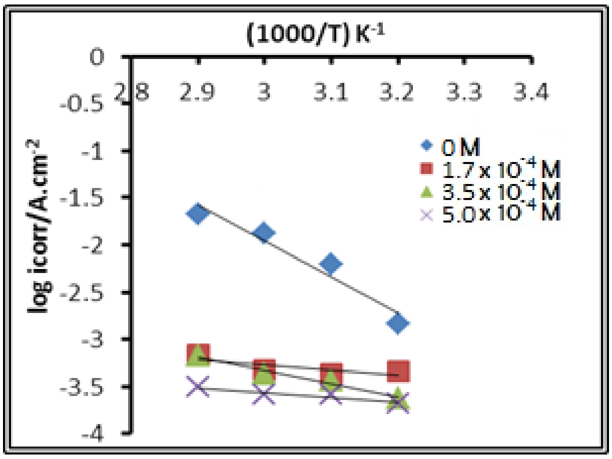


Fig. (6) Arrhenius plots of log i_{corr} versus 1/T in presence and absence of different concentrations of inhibitor (STU3).

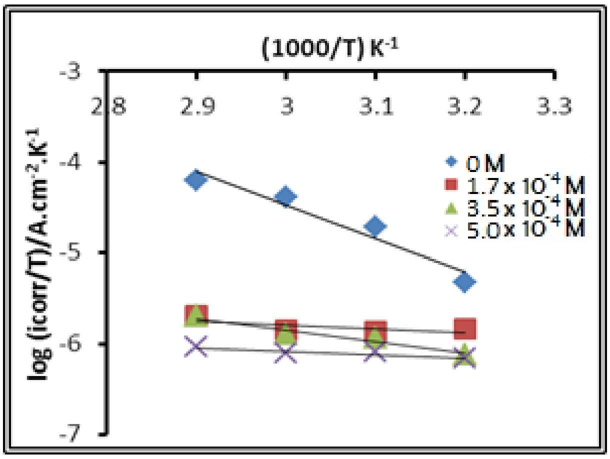


Fig. (7) Arrhenius plots of log (i_{corr}/T) versus 1/T for carbon steel in 1M H_2SO_4 solution without and with different concentrations of the inhibitor (STU3).

Table (9)

The thermodynamic parameters of activation of the synthesized inhibitor (STU3) at different concentrations for carbon steel in 1M H_2SO_4.

C M	A $A.cm^{-2}$	E_a^* $KJ.mol^{-1}$	ΔH^* $KJ.mol^{-1}$	ΔS^* $J.mol^{-1}.K^{-1}$
0	3.9×10^{9}	73.74	71.04	-950.86
1.7×10^{-4}	2.94×10^{-2}	11.1	8.42	-1163.89
3.5×10^{-4}	799×10^{-2}	26.9	25.08	-1115.04
5×10^{-4}	0.860×10^{-2}	9.57	7.08	-1173.58

Conclusion

The inhibiting effect of N-Aroyl-N$^{\backslash}$-Aryl thiourea derivatives (STU1-3) in 1 M H_2SO_4 on carbon steel was studied by various methods. The results are in good agreement and the main conclusions are as follows.

1. The chemical structure of the synthesized inhibitors are confirmed by FTIR,^{1}H- NMR and ^{13}C-NMR.
2. The corrosion inhibition efficiency (**%** IE) of thiourea derivatives follows the sequence: STU3 > STU2 > STU1.
3. STU3 was found to be the best inhibitor for carbon steel in 1M H_2SO_4.
4. The inhibition efficiency of STU3 increases with increase of inhibitor concentration. Its presence in the solution decreases the value of the apparent activation corrosion energy.
5. The adsorption of STU3 on the steel surface in sulphuric acid obeys the Langmuir adsorption isotherm model and leads to the formation of a protective film.
6. The analysis of the experimental data leads to the suggestion of chemisorption of the inhibitor on the metal surface. In fact, the apparent activation energy of the corrosion that is lower in presence of STU3 than in its absence and the higher values of the free energy of adsorption verify the chemisorptive character of the adsorption.
7. The substance is adsorbed with the heteroatoms forming donor–acceptor bonds between unpaired electrons of the heteroatoms and the active centres of the metal surface.

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الخلاصة

يتضمن البحث تحضير بعض مشتقات الثايويوريا الجديدة وهي: N- بنزويل-$N^{\backslash}$- باراأمينوفنيل ثايويوريا (STU1), N- بنزويل- $N^{\backslash}$- ثايوزول ثايويوريا (STU2) , N- اسيتايل- $N^{\backslash}$- داي بنزايل ثايويوريا (STU3). سلسلة معوضات الثايويوريا المعوضة حضرت من تفاعل الحوامض مع الثايونيل كلورايد ثم معاملة الناتج مع ثايوسيانات البوتاسيوم لتعطي مشتقات الثايوسيانات التي تتفاعل مباشرة مع أمينات اروماتية اولية وثانوية. تم تنقية المركبات المحضرة وأثباتها عن طريق قياس درجة الانصهار، TLC كما تم تشخيص التراكيب بواسطة الطرائق الطيفية [FTIR,^{1}H-NMR and ^{13}C-NMR] وقياس بعض الثوابت الفيزياوية. تمت دراسة تأثير المركبات المحضرة كمثبطات لتآكل حديد الصلب الكربوني في محيط 1 مولاري حامض الكبريتيك باستخدام تقنيتي فرق الوزن وطريقة قياس منحني الاستقطاب بالمجهاد الساكن. بينت النتائج ان مشتقات الثايويوريا المحضرة قللت من سرعة التفاعل الانودي والكاثودي على حدّ سواء في المحيط الحامضي وان هذه الاعاقة ناتجة من أمتزازها على سطح الفولاذ. وعملية الأمتزاز كانت تطيع متساويات الحرارة من نوع لانكماير. وصلت نسبة كفاءة التثبيط للسطح باستخدام المشتقات الثلاثة (60-95%). تمت دراسة تأثير تراكيز مختلفة من المشتق STU3 ودرجات حرارة مختلفة وتبين ان زيادة تركيزه تؤدي الى زيادة كفاءة التثبيط ووصلت أعلى نسبة 98.5% عند استخدام 5×10^{-4} M عند درجة 338K وتزداد كفاءة التثبيط بزيادة درجات الحرارة K(308-338).