

Synthesis, Characterization and Evaluation the Corrosion Inhibition for Carbon Steel in H₂SO₄ Solution of Several New Thiourea Derivatives

Uday H. Al-Jeilawi, Suaad M. Al-Majidi, Khulood A. Al-Saadie

Department of Chemistry, College of Science, University of Baghdad

E-mail: dr.oday2009@gmail.com

Abstract

This research includes synthesis of some new thiourea derivatives by two route, the first route include synthesis of 1-aroyl-3-aryl thiourea derivatives (1-17) by a reaction of substituted carboxylic acids with thionyl chloride then the resultant compounds treated the result with potassium thiocyanate to afford the corresponding 1-aroyl isothiocyanate which react directly with primary and secondary aryl amines. The second route, bromo benzene was allowed to react with potassium thiocyanate to afford the corresponding phenylisothiocyanate which was directly reacted with primary and secondary aryl amines to yield 1-phenyl-3-aryl thiourea derivatives (18-28). The purity of the synthesized compounds were checked by measuring the melting point, Thin Layer Chromatography (TLC) and their structure, were identified by spectral methods [FTIR, ¹H-NMR and ¹³C-NMR]. furthermore, these compounds were investigated as corrosion inhibitors for carbon steel at 303 K in 1M H₂SO₄ solution by using weight loss method, the results showed that maximum inhibition efficiency of some 1-aroyl-3-aryl thiourea derivatives and 1-phenyl-3-aryl thiourea derivatives are ranging between (83-94) %.

Keywords: carbon steel, corrosion inhibition, thiourea derivatives, weight loss

Introduction

Carbon steel has been extensively used under different conditions in petroleum industries [1]. An acid wash process is widely used in many industries and in petrochemical processes [2, 3] in order to cleaning and descaling of steel substrates. Acids are generally used in the pickling processes of metals and alloys [4]. Mostly, sulfuric and hydrochloric acids are employed for such purposes [5]. Metallic corrosion is attracting the attention of researchers. Researchers all over the world are searching for some methods to avoid corrosion damage. Using corrosion inhibitors is an effective method to reduce corrosion rate [6]. Because of aggressive nature of acid

solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials as well as acid pickling. Organic compounds are effective inhibitors of aqueous corrosion of many metals and alloys [7, 8]. The influence of organic compounds containing nitrogen, oxygen and sulphur atoms on the corrosion of the steel in acidic solutions has been investigated by several authors [9-14]. The inhibition efficiency may follow the sequence $O < N < S < P$ [15]. Generally, N-containing inhibitor functions more efficiently in HCl, while S-containing inhibitor in H_2SO_4 [16]. Furthermore, the inhibitor which possesses both N and S atoms simultaneously always exhibits higher inhibition performance than that possesses alone N or S atom [17]. Among various N and S containing compounds, thiourea and thiourea derivatives are known to be an effective corrosion inhibitors for a long time. There are many investigations about thiourea and various thiourea derivatives as good inhibitors of the corrosion of iron or steel in HCl [18–21], H_2SO_4 [22–27], HNO_3 [28], $HClO_4$ [29] and H_3PO_4 [30]. The organic inhibitors function through adsorption on metal surface, blocking the active sites of the metal surface by displacing water molecules and forming a compact barrier film which decrease the corrosion rate [31]. The adsorption of corrosion inhibitors molecules depends mainly on certain physicochemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons and the electronic structure of the molecules [32-34]. The inhibition performance of organic inhibitors is due to physisorption and/or chemisorption on the surface of the metals [35, 36].

In this paper the synthesis of some new thiourea derivatives were synthesized and characterized using [FTIR, 1H -NMR and ^{13}C -NMR].; then evaluation as corrosion inhibitors for carbon steel in 1M H_2SO_4 solution. The surface coverage (θ), inhibition efficiency (% IE) and corrosion rate ($mg/cm^2.h$) of these inhibitors were investigated by weight loss method.

Experimental

Instruments

Melting points were measured with a Gallen Kamp melting point apparatus. The FTIR-spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer using KBr disc. 1H NMR and ^{13}C NMR spectra were recorded on Bruker spectrosin ultra-shield magnets 300 MHz instrument, using $DMSO-d_6$ as solvent and TMS as internal

reference [Al al-Bayt University, Jordan]. The carbon steel was analyzed by using SPECTRO MAX_X device (Germany). 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.

Synthesis of 1-aroyl-3-aryl thiourea derivatives (1-17)[37]

A solution of acid chlorides was synthesized according to literature procedure with modefication (0.01 mole) dissolved in dry acetone (30 ml) was added dropwise to a suspension of potassium thiocyanate (0.9710gm ,0.01 mol.) 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 thiourea derivatives were recrystallized from aqueous ethanol or ethanol, to afford the pure compounds (1-17). Melting points and colors as well as vibrational bands of the dried products were listed in Table (1).

Synthesis of 1-phenyl-3-aryl thiourea derivatives (18-28)

A solution of bromo benzene (0.01 mol.) in dry acetone (20 ml.) was added drop wise to a suspension of potassium thiocyanate (0.9710gm ,0.01 mol.) 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 thiourea derivatives were recrystallized from aqueous ethanol or ethanol, to afford the pure compounds (18-28).Some of the physical properties of the dry products are listed in Table (2).

Specimen

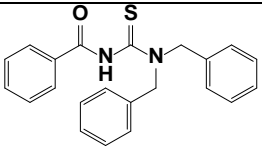
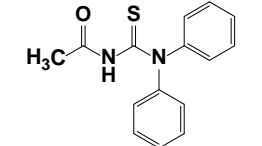
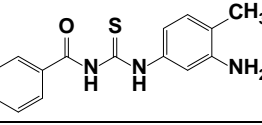
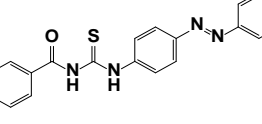
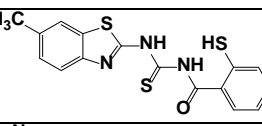
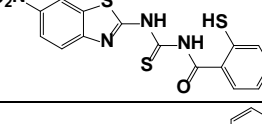
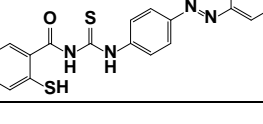
Carbon steel specimens with composition 0.086% C, 0.252%Mn, 0.003%P, 0.016% S and the remainder being Fe were used. Specimens of size 2cm x 1cm x 0.2cm were used for the weight loss. These samples were polished successively with belt grinding polishing machine and polished with emery papers of different grit (80, 150, 220, 240, 320, 400, 1000, 1200 and 2000) in sequence. After polishing the

specimens were washed with distilled water then acetone finally dried and kept in desiccator.

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 was determined within definite time interval,(1-5hrs.,short time term) at 303 ± 1 K of immersion in 1M H_2SO_4 with and without addition of different inhibitors the same concentration 3.5×10^{-4} M ,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 $(mg/cm^2.h)$.

Table (1): Physical properties and FTIR adsorption bands of compounds (1-17)

Comp . No.	Comp. structure	Meltin g point C	Yield %	color	Major FTIR Absorptions cm^{-1}				
					vN-H	vC-H Arom.	vC=O	vC=S	Other bands
1		144-146	90	Light pink	3327	3028	1687	1240	vC-H aliph. 2922,2852 δ N-H 1591
2		132-134	77	Light yellow	3244 3209	3055	1728	1224	v C-H aliph. 2991 δ N-H 1591
3		>300	35	off-white	3151	3029	1679	1257	vNH ₂ 3438,3371 vC-H aliph. 2922, 2852
4		196-198	83	Pale orang	3311 3265	3037 3001	1670	1263	vN=N 1448
5		162-164	55	Light green	3201 3197	3062	1662	1272	vC-H aliph. 2893,2852 v C=N 1606
6		206-208	70	Yellow-green	3361 3292	3095	1654	1299	--
7		132-134	70	Brown	3298 3205	3031	1664	1294	vN=N 1434 δ N-H 1593

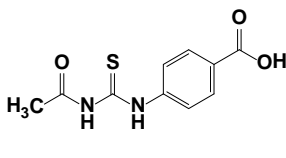
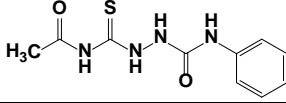
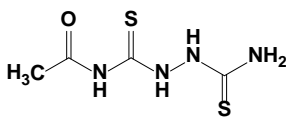
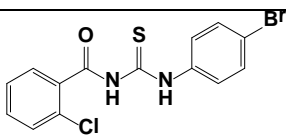
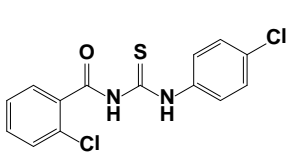
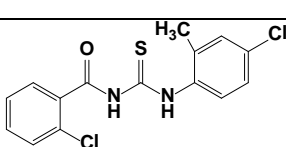
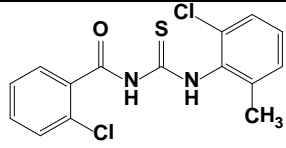
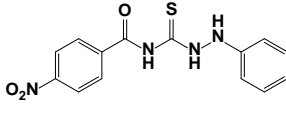
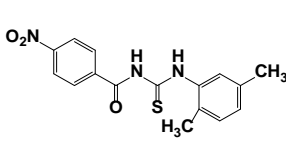
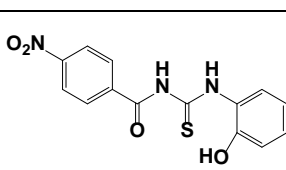
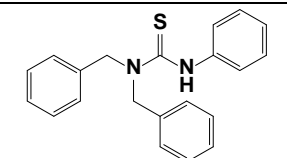
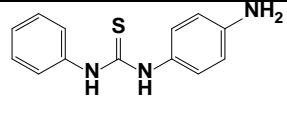
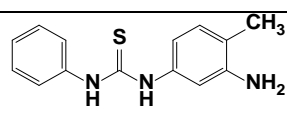
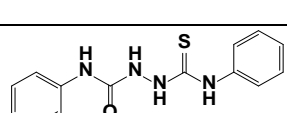
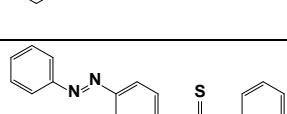
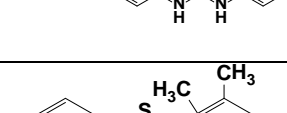
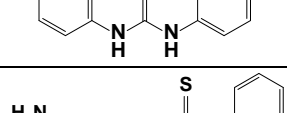
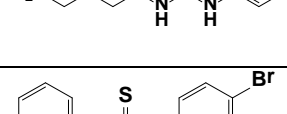
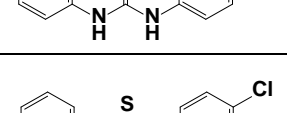
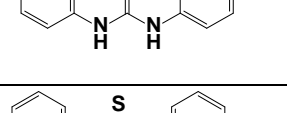
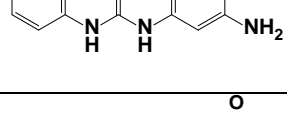
8		236 dec.	56	Off- white	3190	3031	1691	1259	vO-H acid 3300-2775 broad v C-H aliph 2846 δ N-H 1595
9		216- 218	60	Brown	3300 3224	3090	1674	1240	v CH aliph 2927 δ N-H 1600
10		166- 168	45	Pale yellow	3153	-	1693	1236	vNH ₂ 3377,3230 vC-H Aliph 2929,2862 δ N-H 1595
11		176- 178	89	Gray	3199	3058	1693	1251	vC-Cl 862 vC-Br 640 δ N-H 1600
12		180- 182	83	off- white	3195	3020	1679	1249	vC-Cl overlap with para position 831 δ N-H 1622
13		160- 162	87	Light violet	3228 3139	3012	1679	1255	vC-H Aliph 2910,2860 δ N-H 1606
14		206- 208	86	Light violet	3153	3018	1685	1247	v C-H aliph 2927 δ N-H 1595
15		162- 164	50	Pale yellow	3411 3130	3074	1693	1284	δ N-H 1625 v NO ₂ . Asym 1527 Sym 1348
16		185- 187	55	off- white	3236 3149	3078	1728	1267	vC-H Aliph 2916,2862 δ N-H 1600 v NO ₂ . Asym 1521 Sym 1348
17		192- 194	60	yellow	3244 3172	3057	1677	1270	v O-H overlap with v NH ₂ v NO ₂ . Asym 1548 Sym 1330

Table (2): Physical properties and FTIR spectral of compounds (18-28)

Comp . No.	Comp. structure	Meltin g point C	Yield %	color	Major FTIR Absorptions cm ⁻¹				
					vN-H	vC-H Arom	vC-H Aliph.	vC=S	Other bands

18		148-150	98	Pale yellow	3375 3305	3028	2920 2848	1211	--
19		276 dec.	89	Gray	3205 3164	3010	--	1274	ν NH ₂ 3400,3326 δ N-H 1600
20		132-134	68	off-white	3203 3176	3056 3016	2927 2854	1261	ν NH ₂ 3328,3203 δ N-H 1596
21		200-202	50	Brown	3209	3060	--	1242	ν C=O 1672
22		170-172	91	Orang	3210	3037	--	1236	δ N-H 1593
23		152-154	90	White	3260 3163	3099 3008	2935 2858	1249	δ N-H 1593
24		170-172	50	White	3165	3010	2931 2854	1251	ν NH ₂ 3390,3280 δ N-H 1593
25		154-156	85	Violet	3201 3193	3028 3004	--	1242	
26		154-156	97	White	3205 3176	3031 3004	--	1242	ν C-Cl 769 para position 811
27		90-92	75	Black	3199	3043	--	1253	ν NH ₂ 3353,3336 δ N-H 1595
28		>300	55	off-white	3203	3016	--	1286	ν O-H acid 3400-2700 broad ν C=O 1691

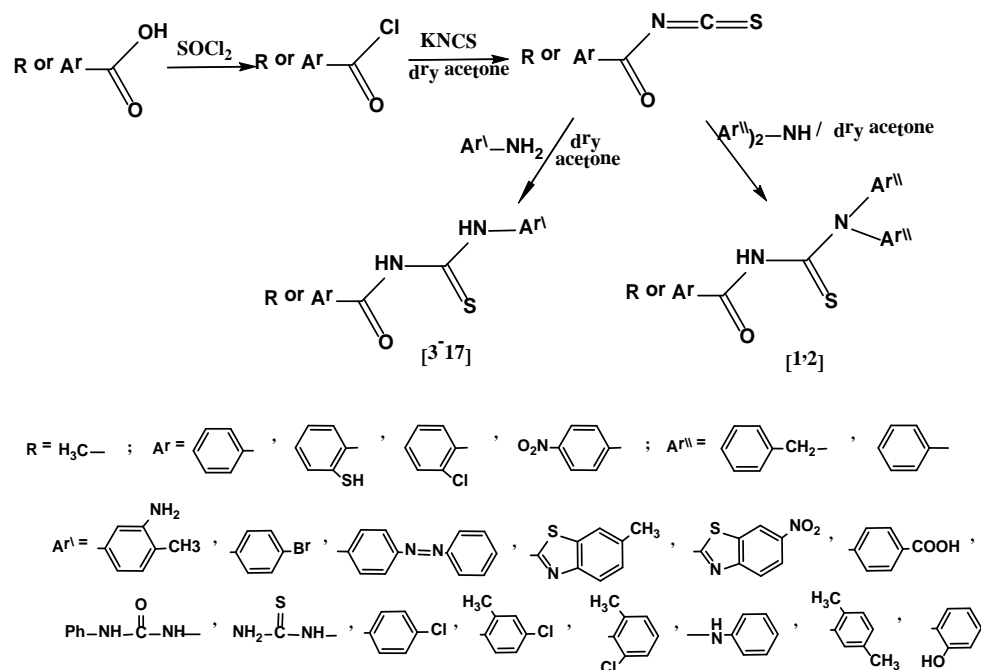
Results and Discussion

Some of new organic compounds containing (N and S) atoms were prepared for using as corrosion inhibitors. Through two routes, the first route include synthesis some of new 1-aryl-3-aryl thiourea derivatives (1-17) show in scheme (1), thiourea derivatives were synthesized according to the method in previous paper [37] with

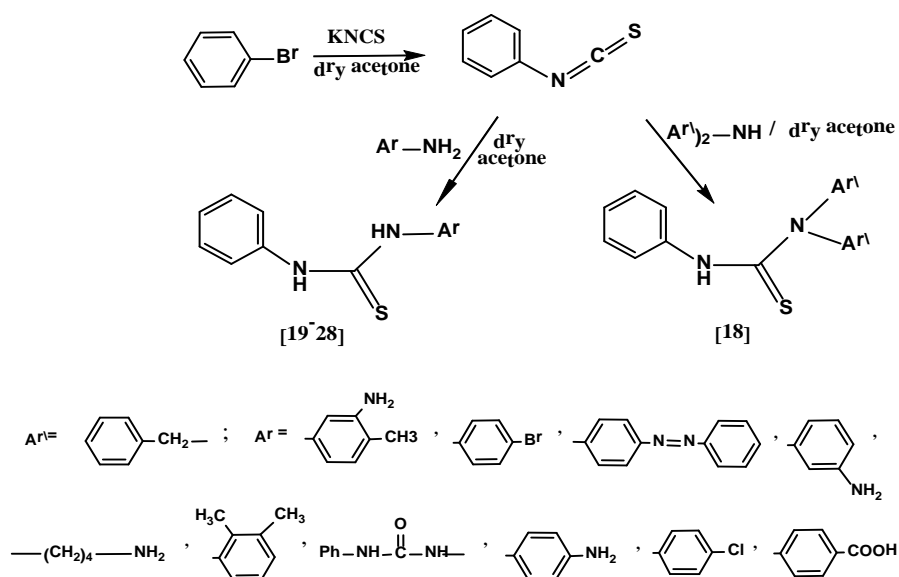
minor modifications. The synthesis involves carboxylic acids converted into corresponding acid chlorides by treatment with thionyl chloride according to standard procedure. The acid chlorides were treated with an equimolar quantity of potassium thiocyanate in dry acetone to afford the corresponding isothiocyanate intermediates which were direct addition to an equimolar of primary or secondary aryl amines in dry acetone to isothiocyanates furnished the 1-aryl-3-aryl thiourea derivatives (1-17). The reaction proceeds via a nucleophilic addition of the amine to the isothiocyanate, and the completion of the reaction was examined by TLC. The structure of these compounds were confirmed by physical properties which were listed in Table (1), and characterized by FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. FT-IR (KBr) spectra showing strong $\nu\text{N-H}$ absorptions at about $3361\text{-}3130\text{ cm}^{-1}$, and displayed absorptions at about $1728\text{-}1654\text{ cm}^{-1}$ and $1299\text{-}1236\text{ cm}^{-1}$ that were assigned to $\nu\text{C=O}$ and $\nu\text{C=S}$ functions respectively. While the $^1\text{H-NMR}$ spectral data for some compounds δ ppm in DMSO-d^6 solvent are listed in Table (3). The signals at 10.78-11.34 are of $[\text{S}, 1\text{H}, -\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-]$; 10.45-10.78 $[\text{S}, 1\text{H}, -\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}-]$ [38]. Generally the $^1\text{H-NMR}$ signals of NH protons for amides are observed in the range of [9-10] δ ppm. 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. $^{13}\text{C-NMR}$ spectral data were listed in Table (4), the spectrum showed the peaks at about δ 183.49-179.81 and 171.77-165.75 for C=S (thioamide) and C=O (amide), respectively [38].

The second route include synthesis of 1-phenyl-3-aryl thiourea derivatives (18-28) show in scheme (2), the synthetic route involves that the bromo benzene treated with an equimolar quantity of potassium thiocyanate in dry acetone to afford the corresponding phenylisothiocyanate intermediate which were direct addition to an equimolar of primary or secondary aryl amines in dry acetone to furnished the 1-phenyl-3-aryl thiourea derivatives (18-28). The structure of these compounds were confirmed by physical properties which were listed in Table (2), and characterized by FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. FT-IR (KBr) spectra showing strong $\nu\text{N-H}$ absorptions band at about $3375\text{-}3163\text{ cm}^{-1}$, and displayed absorptions band at about $1286\text{-}1211\text{ cm}^{-1}$ that assigned to $\nu\text{C=S}$. While the $^1\text{H-NMR}$ spectral data for some compounds δ in ppm in DMSO-d^6 solvent were listed in Table (3). The signals

at 9.33-10.27 assigned to $[S,1H, -\overset{S}{\parallel}C-NH-]$ [38]. ^{13}C -NMR spectral data were listed in Table (4), the spectrum showed that the peaks at δ 180.7-179.83 for C=S (thioamide).



Scheme (1): synthesis of some new 1-Aroyl-3-Aryl thioureas



Scheme (2): synthesis of some new 1-phenyl-3-Aryl thioureas

Table (3): 1H -NMR spectral data (ppm) for some of the prepared compounds

Comp. No.	Compound structure	1H -NMR parameters (ppm) δ -H
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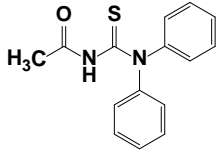
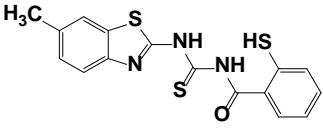
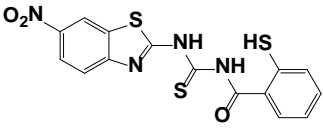
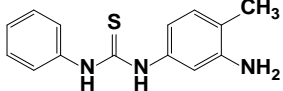
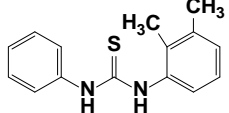
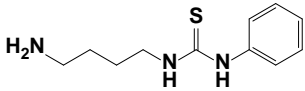
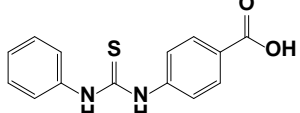
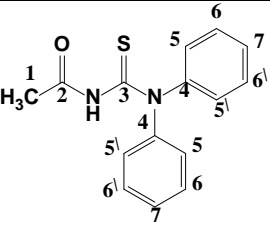
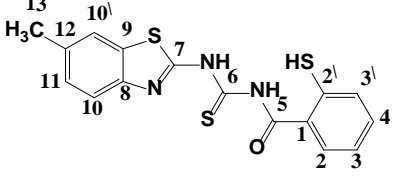
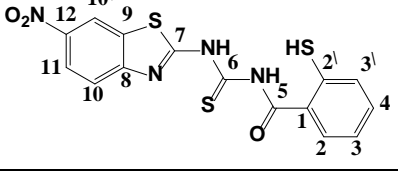
2		1.70(s,3H,-CH ₃);7.79-8.09(m,10H,Ar-H);10.78(s,1H,-NH-).
5		2.28 (s,3H,-CH ₃) ; 3.36(s,1H,S-H) ;7.02-8.47 (m,7H,Ar-H) ; 10.45(s,1H, -C(=S)-NH-);11.34(S,1H, -C(=O)-NH-).
6		3.30(s,1H,S-H);6.58-7.43(m,4H,Ar-H(thioacid));7.92-8.68 (m,3H, Ar- thiazole); 10.50(s,1H, -C(=S)-NH-); 11.33(S,1H, -C(=O)-NH-).
20		2.02(s, 3H,-CH ₃); 4.87(s, 2H,-NH ₂); 6.52-7.50(m, 8H, Ar- H); 9.42-9.52(s, 2H,-NH-).
23		2.12(s, 3H,o-CH ₃); 2.26(s, 3H,m- CH ₃); 7.07-7.50(m, 8H, Ar-H); 9.33-9.48(s, 2H,-NH-).
24		1.5(m, 4H,-(CH ₂) ₂); 3.31(t, 2H,CH ₂ -NH ₂); 3.49(m, 2H,-NH- CH ₂ -);4.45(s, 2H,-NH ₂); 7.07-7.75(m, 5H, Ar-H); 9.44(b, 2H,-NH-).
28		7.14-7.90(m, 10H, Ar-H); 9.75-10.27(s, 2H,-NH-); 9.44(b, 1H,-CO-OH).

Table (4): ¹³C-NMR spectral data for some of the prepared compounds

Comp. No.	Compound structure	¹³ C-NMR data (ppm)
2		22.88(C ₁);116.72-129.08(C _{5,5',6,6',7});143.42(C ₄);165.75(C ₂); 183.49(C ₃).
5		42.16(C ₁₃);114.52-126.31(C _{2,2',3,3',4,10,10',11}) ;131.56(C _{1,9});140.66 (C ₁₂);143.31(C ₈);155.66(C ₈);158.66(C ₇);171.77(C ₅);180.20 (C ₆).
6		112.35-126.31(C _{2,2',3,3',4,10,10',11});131.56(C ₁);140.66 (C ₁₂);140.69 (C ₁₂); 143.21(C ₈); 155.64(C ₉); 158.56(C ₇); 171.73(C ₅); 179.81 (C ₆).

20		16.92(C ₁₀);109-128(C _{3,3} , _{4,7,7} , ₈);129.80(C _{2,2});137.38(C ₉);139.71(C _{1,6});146.68(C ₈);179.64(C ₅).
23		14.15(C ₁₀);20.0(C ₁₁);123-128(C _{3,3} , _{4,7,8,9});133.67(C _{7,8});137.07(C _{2,2});137.47(C ₁);139.59(C ₆);180.56(C ₅).
24		25.91(C ₇);26.10(C ₇);43.57(C _{6,8});123-126(C _{3,3,4});128.53(C _{2,2});139.27(C ₁);180.33(C ₅).
28		121-128(C _{3,3,4});129.19(C _{2,2} , _{7,7} , ₉);139.19(C _{1,8,8});143.48(C ₆);166.89(C ₁₀);179.38(C ₅).

Weight loss measurements

The gravimetric measurements of carbon steel immersed in 1M H₂SO₄ in the absence and presence of 3.5×10^{-4} M different inhibitors of thiourea compound were investigated and determined within definite time interval, (1-5hrs.) of immersion at 303 ± 1 K, Figures (1,2) show the weight loss-time curves for carbon steel in 1M H₂SO₄ solution in the absence and presence of different inhibitors of thiourea derivatives, Table (5,6) reveal that, the curves are characterized by gradual rise in weight loss with time. The curves indicate that, the weight loss of carbon steel depended on type of additive inhibitors and the nature of substituted groups.

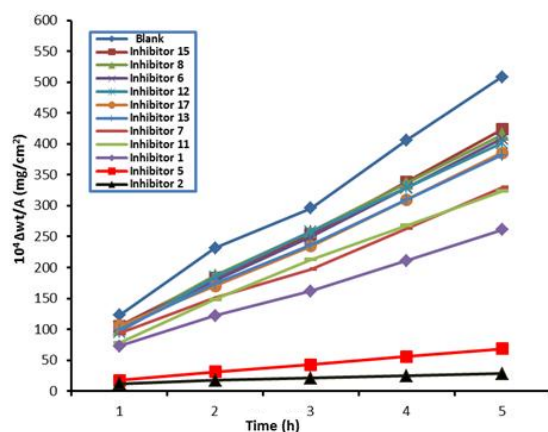


Figure (1): variation of weight loss versus time (h) for carbon steel corrosion in 1M H₂SO₄ in the absence and presence of 3.5×10^{-4} M inhibitors 1-aryl-3-aryl thiourea derivatives at 308 K

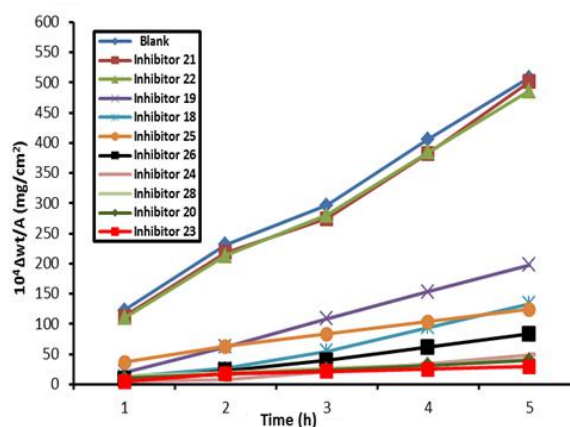


Figure (2): variation of weight loss versus time (h) for carbon steel corrosion in 1M H₂SO₄ in the absence and presence of 3.5×10^{-4} M inhibitors 1-phenyl-3-aryl thiourea derivatives at 308 K

Table (5): weight loss of carbon steel with time (h) in 1M H₂SO₄ solution in the absence and presence of 3.5×10⁻⁴ M inhibitors 1-aryl-3-aryl thiourea derivatives at 303 K

Time(h)	10 ⁴ ΔWt/A (mg/cm ²) by some inhibitors 1-aryl-3-aryl thiourea derivatives											
	Blank	15	8	6	12	17	13	7	11	1	5	2
1	122.5	105.25	100.5	103.75	95.25	105.75	99.25	93	78.25	72.75	17.25	12
2	231.75	183.5	187.25	178.5	184.5	170.25	174	151	148.25	122	31	17.25
3	296.25	253.75	257.75	249.75	258	234.5	237.25	197	213	161.5	42.75	21
4	406	338.75	336.5	329	329.5	310	309.5	263.25	268.25	211.25	55.75	24.5
5	508.25	423.75	415.25	408.25	401	385.5	381.75	329.5	323.5	261	68.75	28

Table (6): weight loss of carbon steel with time (h) in 1M H₂SO₄ solution in the absence and presence of 3.5×10⁻⁴ M inhibitors 1-phenyl-3-aryl thiourea derivatives at 303 K

Time (h)	10 ⁴ ΔWt/A (mg/cm ²) by some inhibitors 1-phenyl-3-aryl thiourea derivatives										
	Blank	21	22	19	18	25	26	24	28	20	23
1	122.5	112.25	110	19.5	12.25	36.25	8.25	4.5	13.25	10.5	4.75
2	231.75	218.25	213.25	62	26.25	62.75	23	7.5	20	17	17.25
3	296.25	274.5	280.5	109	54.5	83	39.75	20.25	26.5	24.5	21
4	406	382.5	384.5	153.5	94.25	103.75	61.5	34	32.5	31.75	25.25
5	508.25	501.25	486.25	198	134	124.5	83.25	48.75	41	39.5	29.5

The corrosion rate R_{corr} of carbon steel was determined using the relation:

$$R_{\text{corr}} = \frac{\Delta Wt}{A * t} \quad (1)$$

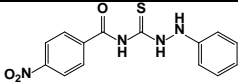
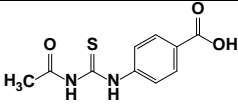
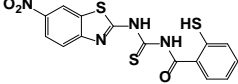
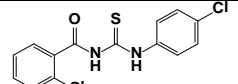
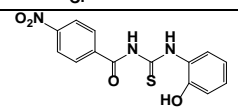
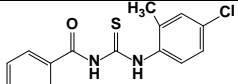
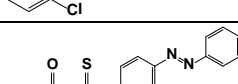
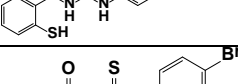
Where ΔWt is the mass loss (mg), A the area (cm²) and t time of immersion period (5 hours). The value of the percentage inhibition efficiency (% IE), and a parameter surface coverage (θ) which represents the part of the surface covered by the inhibitors molecules, for the corrosion of carbon steel were calculated as follows [39]:

$$\% \text{IE} = \frac{(\mathbf{R} - \mathbf{R}_{\text{inh}})}{\mathbf{R}} \times 100 \quad (2)$$

$$\theta = \frac{(\mathbf{R} - \mathbf{R}_{\text{inh}})}{\mathbf{R}} \quad (2)$$

where \mathbf{R} and \mathbf{R}_{inh} are the uninhibited and the inhibited corrosion rate, respectively. The calculated values of corrosion rate R_{corr} ($\text{mg}/\text{cm}^2\cdot\text{h}$), surface coverage (θ) and inhibition efficiency ($\% \text{IE}$) at 303 K are given in Table (7, 8). According to the observed, 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.

Table (7): 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 inhibitors 1-aryl-3-aryl thiourea derivatives at 303 K

Inhibitor structure	Inhibitor No.	$10^4 R_{\text{corr}}$ ($\text{mg}/\text{cm}^2\cdot\text{h}$) (5h)	θ	$\% \text{IE}$
	blank	101.65	--	--
	15	84.75	0.1663	16.63
	8	83.05	0.1830	18.30
	6	81.65	0.1968	19.68
	12	80.2	0.2010	20.10
	17	77.1	0.2415	24.15
	13	76.35	0.2489	24.89
	7	65.9	0.3517	35.17
	11	64.7	0.3635	36.35

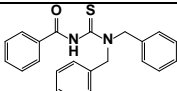
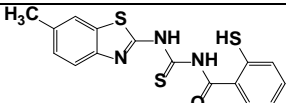
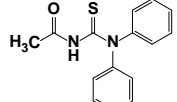
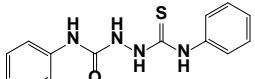
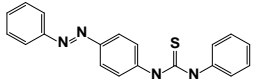
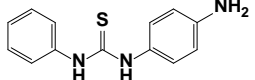
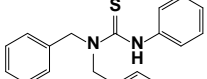
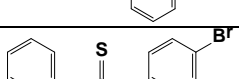
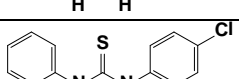
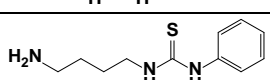
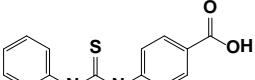
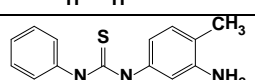
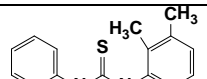
	1	52.2	0.4865	48.65
	5	13.75	0.8647	86.47
	2	5.9	0.9420	94.20

Table (8): corrosion rate, degree of surface coverage and inhibition efficiency for carbon steel in 1M H₂SO₄ solution in the absence and presence of 3.5×10⁻⁴ M of inhibitors

Inhibitor structure	Inhibitor No.	10 ⁴ R _{corr} (mg/cm ² .h) (5h)	θ	% IE
	blank	101.65	--	--
	21	100.25	0.0138	1.38
	22	97.25	0.0433	4.33
	19	39.6	0.6104	61.04
	18	26.8	0.7364	73.64
	25	24.9	0.7550	75.50
	26	16.65	0.8362	83.62
	24	9.75	0.9041	90.41
	28	8.2	0.9193	91.93
	20	7.9	0.9223	92.23
	23	5.9	0.9420	94.20

1-phenyl-3-aryl thiourea derivatives at 303 K

The inhibition action of thiourea compounds toward the corrosion of carbon steel in 1M H₂SO₄, could be attributed to several factors including the structure, the number and types of adsorption sites, the nature of molecule, the metal surface, and the ability to form complexes [40-42]. The inhibition mechanism of thiourea derivatives under investigation is believed to be as a result of complex formation between Fe²⁺ ion, and thiourea derivatives. The complex formed was adsorbed on the metal surface and there by isolating the metal from further corroding attack. To provide an evidence for formation of complex. Also The adsorption of thiourea derivatives can be attributed to the presence of polar unit having atoms of nitrogen, sulphur and oxygen and aromatic/heterocyclic rings. Therefore, the possible reaction centers are unshared electron pair of hetero-atoms and π -electrons of aromatic ring [43]. The adsorption and inhibition effect of thiourea derivatives in 1M H₂SO₄ solution can be explained as follows: In aqueous acidic solutions, thiourea derivatives exist either as neutral molecules or as protonated molecules and may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed SO₄²⁻ ions, (ii) donor–acceptor interactions between the π -electrons of aromatic ring and vacant d orbital of surface iron atoms, (iii) interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms. In general, two modes of adsorption are considered on the metal surface in acid media. In the first mode, the neutral molecules may be adsorbed on the surface of carbon steel through the chemisorption mechanism, involving the displacement of water molecules from the carbon steel surface and the sharing electrons between the hetero- atoms and iron. The inhibitor molecules can also adsorb on the carbon steel surface on the basis of donor–acceptor interactions between π -electrons of the aromatic ring and vacant d-orbitals of surface iron atoms. In the second mode, since it is well known that the steel surface bears positive charge in acid solution [44, 45], so it is difficult for the protonated molecules to approach the positively charged carbon steel surface due to the electrostatic repulsion. Since SO₄²⁻ ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated thiourea derivatives adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus there is a synergism between adsorbed SO₄²⁻ ions and protonated thiourea derivatives.

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تحضير، تشخيص وتقدير تثبيط التآكل على الفولاذ في محلول حامض الكبريتيك لعدد من مشتقات الثايويوريا الجديدة

عدي هادي رؤوف، سعاد محمد حسين، خلود عبد صالح
قسم الكيمياء، كلية العلوم، جامعة بغداد

الخلاصة

تضمن هذا البحث تحضير بعض مشتقات الثايويوريا الجديدة من خلال مسارين، تضمن المسار الأول تحضير عدة مشتقات من 1-أرويل-3-أريل ثايويوريا (1-17) عن طريق تفاعل معوضات حوامض كاربوكسيلية مع الثايونيل كلورايد ثم معاملة الناتج مع ثايوسيانات البوتاسيوم لتعطي مشتقات الثايوسيانات التي تم مفاعلتها بصورة مباشرة مع أمينات اولية وثانوية اروماتية. المسار الثاني، تضمن مفاعلة برومو بنزين مع ثايوسيانات البوتاسيوم لتعطي فنيل ايزوثايوسيانات التي تم تفاعلها مباشرة مع أمينات اولية وثانوية اروماتية لتعطي 1-

فنيـل-3-أريـل ثايويوريـا(18-28). تم تنقية المركبات المحضرة وأثبتتها عن طريق قياس درجة الانصهار، TLC كما تم تشخيص التراكيـب بواسطـة الطرائق الطيفية [FTIR, ¹H-NMR and ¹³C-NMR] وقياس بعض الثوابت الفيزيائية. إضافة الى ذلك، قيمت المركبات المحضرة كمثبطات لتآكل الفولاذ بدرجة 303 كلفن في محيط 1 مولاري حامض الكبريتيك باستخدام طريقة فرق الوزن، وصلت اعلى نسبة كفاءة تثبيط للسطح باستخدام بعض مشتقات 1- أرويل-3-أريل ثايويوريا ومشتقات 1- فنيـل-3-أريـل ثايويوريا بين (83-94)%.