Synthesis, Characterization and Study of Some Tetrazole Compounds as New Corrosion Inhibitors for C-steel in 0.5 M HCl Solution

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Abstract : *Two tetrazole compounds were synthesized. The prepared compounds were identified by CHNS analysis FT-IR and ^{1}H-NMR spectroscopy. The inhibition efficiency in the presence of tetrazoles as a steel corrosion inhibitor in 0.5M HCl calculated using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. Results obtained revealed that tetrazole compounds performed excellently as a corrosion inhibitor for C-steel in this medium and its efficiency attains to 91.34% at 5×10^{-3}M at 303 K by potentiodynamic polarization measurements and 91.66% by EIS in the same conditions. The surface morphology studies (SEM and AFM) showed that these types of inhibitors had a smooth surface with deposited compounds on it for the specimen that treated with acidic inhibited solutions as compared with the surface of those specimens which treated with uninhibited acidic solution.*

Keyword: C-steel corrosion, tetrazole, EIS, surface morphology

1. Introduction

Carbon steel is an alloy of iron it is widely used in petrochemical, chemical and metallurgical industries. It is also used as a construction material owing to its excellent mechanical properties and cost effectiveness. However, it is easily undergoes corrosion in various environmental conditions. Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning and oil well acidizing, because of the general aggressiveness of acid solutions, the well-known inhibitors are organic compounds containing heteroatoms such as oxygen, nitrogen or sulphur, and multiple bonds, which allow an adsorption on the metal surface [1–3]. It has been observed that the adsorption of these inhibitors depends on the physico-chemical properties of the functional groups and the electron density at the donor atom. The adsorption occurs due to the interaction of the lone pair and/ or p-orbitals of inhibitor with d-orbitals of the metal surface atoms, which evokes a greater adsorption of the inhibitor molecules onto the surface, leading to the formation of a corrosion protection film [4–6]. Furthermore, adsorption is also influenced by the structure and the charge of metal surface, and the type of testing electrolyte [7]. The choice of effective inhibitors is based on their mechanism of action and electron-donating ability. The significant criteria involved in this selection are molecular structure, electron density on the donor atoms, solubility and dispersibility[8–10]. The extensive studies have been performed to look for new environment-friendly organic inhibitors in recent decades, including triazole derivatives[11], thiazolidin[12], thiadiazole derivatives [13], isoxazolidines[14,15], imidazole derivatives [16] and so on.

For this importance of heterocyclic compounds, the recent work includes synthesis of some tetrazole thiol derivatives, characterization and used them as corrosion inhibitors in acidic medium 0.5 M HCl, using Tafel extrapolation technique and electrochemical impedance spectroscopy. The morphology of the surface of carbon steel is studied by energy X-ray dispersive, scanning electron microscopy and atomic force microscopy.

2. Experimental Methods

Melting points were determined by open capillary and are uncorrected. The CHNS analysis measurements for the synthesized compounds were performed using EuroVector model EA3000A (Italy) and ^{1}H-NMR spectra performed using Bruker model ultra shield 300MHz (Switzerland), at the analytical Laboratory of AL-ALBAYET University, Jordan. DMSO-d6 was used as a solvent and TMS as an internal standard. IR spectra were recorded using KBr disc on Shimadzu FT-IR model 8400 Spectrophotometer at Chemistry Department, College of Education of Pure Sciences, Basrah University, Iraq.

2.1. Synthesis of compounds
2.1.1. Synthesis of tetrazole T1 (1-Phenyl-1,2,3,4-tetrazole-5-thiol)[17]

A mixture of 150ml of water, 0.05 mole (5.98ml) Phenyl *iso*-thiocyanate and 0.075 mole (4.87g) sodium azide was refluxed for 4h. After cooling, the mixture was filtered off, the filtrate was extracted with ether to remove the non reacted of Phenyl *iso*-thiocyanate. The aqueous layer was treated with hydrochloric acid to pH 3, precipitated white solid formed. The Filtered crystals were water washed, dried, and recrystallized from ethanol. The characterizations of the products are listed in Tables 1 & 2.
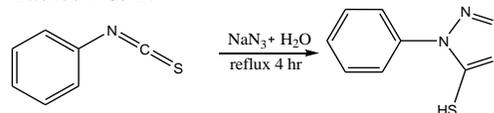
Scheme 1: synthesis of tetrazole T1

2.1.2. Preparation of 5-Benzylthio-1-phenyl-1,2,3,4-tetrazole (T2)

A mixture of 0.015 mole (2.67g) of T1, 0.018 mole of or benzyl chloride and 0.02 mole (1.64g) of sodium acetate in 50 ml of ethanol was heated under reflux for 3 hrs, then allowed to cool, and poured into 100 ml of cold water containing ice. The solid product was collected and recrystallized from ethanol.[17] The characterizations of the products are listed in Tables 1 & 2.
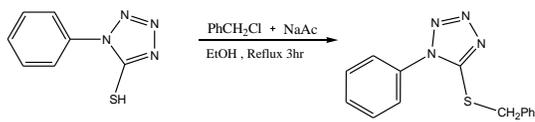
Scheme 2: synthesis of tetrazole derivative T2

Table 1: The characterization of the prepared tetrazole compounds

Compd.	Molecular formula	Molecular weight (g/mole)	Crystal color and shape	m.p. (ºC)	Yield (%)
T1	$C_7H_6N_4S$	178.21	White needle crystal	138-140	90
T2	$C_{14}H_{12}N_4S$	268.34	Yellowish white crystal	114-116	83

Table 2: The CHNS of the prepared tetrazole compounds

Compd.	Elemental analysis Found (Calcd.)			
	C%	H%	N%	S%
T1	47.87 (47.18)	3.26 (3.39)	30.86 (31.44)	17.71 (17.99)
T2	63.00 (62.66)	4.17 (4.5)	20.74 (20.88)	11.64 (11.95)

2.2. Solution preparation

The aggressive solutions, 0.5M HCl, were prepared the by the dilution of AR grade 37% HCl in distilled water. The different concentrations of tetrazole compounds were prepared by dissolving a certain amount of each compound in 0.5M HCl to obtain the following concentration (1×10^{-4}, 5×10^{-4}, 1×10^{-3} and 5×10^{-3}M).

2.3. Tafel extrapolation method[18]

Polarization studies were carried out using Bank EIEIKTRONIK INTELLGENT CONTROLS Model MLab 200-Chemistry Department- Education College of pure science – Basrah University, Iraq. Tafel polarization obtained by changing the electrode potential automatically from (+250 mV to -250 mV) at open circuit potential with a scan rate 0.5 mV S^{-1} to study the effect of inhibitor on mild steel corrosion. The linear Tafel segment of cathodic and anodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}). The inhibition efficiency was evaluated from the calculated I_{corr} values using the relationship:

$$E\% = \left[\frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \right] \times 100 \qquad (1)$$

where I_{corr} and $I_{corr(inh)}$ are the corrosion current in the absence and in the presence of inhibitor, respectively.

2.4. Electrochemical impedance spectroscopy (EIS)

EIS measurements were carried out in a frequency range of 10 KHz to 100 Hz using amplitude of 5 mV peak to peak using a.c. signal at open circuit potential. The software used in

this study are electrochemical impedance software model 6310 (Germany), in Institute of Modern Technologies, Kalashnikov University, Izhevsk, Russia., corrosion software (Model 352–252, version 2.23) and Equivalent circuit software (EQUIVCRT.PAS).

The inhibition efficiency E%EIS can be calculated using the following equation:[19]

$$E_{EIS}\% = \frac{R_{t,i} - R_{t,0}}{R_{t,i}} \times 100 \qquad (2)$$

Where $R_{t,0}$ and $R_{t,i}$ are charge transfer resistances in the absence and presence of inhibitors, respectively

2.5. Surface analysis
2.5.1. Energy dispersive X-ray EDX/SEM analysis

The surface film formed on the metal specimen was examined by energy dispersive X-ray analysis (EDX). This was carried out by Energy Dispersive X-ray (SEM/EDX) Spectroscopy model Geneziz 2000XMS (Germany), in Department of Surface Physics, Faculty of Physics and Energetic, Udmurt State University, Izhevsk, Russia. The spectra were recorded on samples immersed for a period of 24 hrs in 0.5 M HCl in the absence and presence of optimum concentration of the inhibitor. The energy of the acceleration beam employed was 30 kV.

2.5.2. Atomic force Microscopy (AFM)

The carbon steel strips of 2 .5 cm 2.5 cm and 0.4cm cm sizes were prepared as described in section 2.4. After immersion in 0.5 M HCl without and with addition of 1×10^{-4} -5×10^{-3} M of tetrazole inhibitors at 303 K for 24 hrs, the specimen was cleaned with distilled water, dried and then used for AFM.

3. Results and discussion
3.1. FT-IR Spectra

FT-IR Spectra of the synthesized compounds were carried out using KBr disc method. The characterized bands were given in Table 3.

The IR data of the parent tetrazole compound showed a band at 2758 cm^{-1} which is characteristic of the S-H stretching[20]. This band was lacked in the S-substituted derivatives S-R, as shown in Table 3.

Table 3: Characterized bands in FT-IR spectra for prepared tetrazole compounds

T1	T2	Assignment
3043 m	3062 m 3031 m	C-H stretching aromatic
	2943 m	C-H stretching aliphatic
2758 m		S-H stretching
1589 m	1593 s	C=N stretching of tetrazole ring
1564 w 1498 s	1497 s	C=C stretching of aromatic rings
1456 w	1458 m	N=N stretching of tetrazole

		ring
	1384 s	C-H bending aliphatic
1280 m 1049 s	1258 s 1087 s	C-N stretching of tetrazole ring
756 m	765 s	C-H bending aromatic
682 m	692 s	C-S stretching

br = broad, s = strong, m = medium, w = weak

IR spectra of tetrazole compounds showed strong-weak bands at 1589-1593 cm^{-1} and 1497-1564 cm^{-1} which are characteristic of the C=N and C=C ring stretching, respectively. Strong-medium bands at 1258-1280 cm^{-1} and 1049-1087 cm^{-1} which are characteristic for C-N stretching of tetrazole ring[21]. Medium-weak absorption band at 1456 cm^{-1} and 1458 cm^{-1} which are characteristic of N=N stretching of tetrazole ring.

3.2. ^{1}H-NMR

^{1}H-NMR spectra of the prepared tetrazole compounds were performed in deuterated dimethyl sulfoxide solutions with tetramethylsaline as an internal standard. These spectra showed signals at 2.5 ppm which was due to DMSO solvent..

The parent tetrazole T1 has a characteristic singlet signal at 2.768 ppm due to proton of thiol group[20], and this signal is not appeared in the tetrazole derivative compound T2. The compound T2 exhibited a characteristic aliphatic system which gave signals in the highfield range between 4.608 ppm. The two tetrazole compounds exhibited multiplet signals in the downfield range between 7.272-8.168ppm due to the protons of the aromatic systems as shown in Table 4.

Table 4: ^{1}H-NMR data of the tetrazole compounds

Compd.	δ ppm		
	-SH	-CH$_2$-S-	Aromatic
T1	2.768(s)		7.557-8.165(m, 5H)
T5		4.608(s)	7.272-7.636(m, 10H)

s =singlet and m=multiplet

3.3. Potentiodynamic polarization measurements

The electrochemical kinetics of metallic corrosion process can be characterized by determining at least three polarization parameters, such as corrosion current density (I_{corr}), corrosion potential(E_{corr}) and Tafel slopes(βaand/or βc). The corrosion behavior can be determined by a polarization curve (E versus log i). The evaluation of the polarization parameters leads to the determination of the corrosion rate (C_R).

Thus, it was possible to determine I_{corr} for all concentrations of all tested inhibitors, as well as for the blank (solution without inhibitor).The polarization curves for the carbon steel (C-steel) electrode in 0.5 M HCl with different inhibitors at 5x10^{-3}M and at 303 K are shown in Figure 1a&b. The electrochemical parameters, namely, the corrosion potential(E_{corr}), corrosion current density (I_{corr}), anodic (βa) and cathodic (βc) Tafel slopes and inhibition efficiency(E), are listed in Table 5.
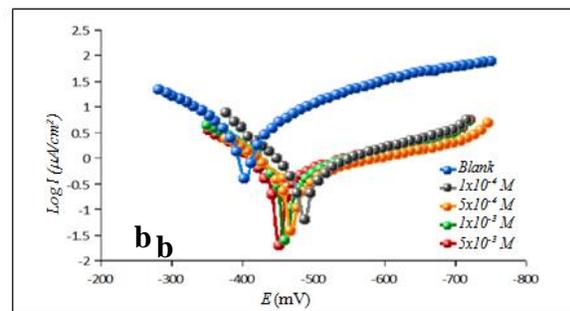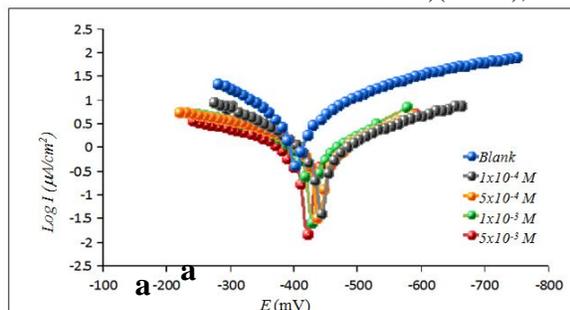
Figure 1: Tafel curves of carbon steel in 0.5M HCl in the absence and presence of 5x10^{-3}M of tetrazole inhibitors at different temperatures a=T1 and b=T5

Table 5: Electrochemical parameters and %IE for corrosion of carbon steel in 0.5M HCl in the presence of different tetrazole inhibitors at various concentrations

Inhib.	Conc. of inhib. (M)	i_{corr} μA/cm^2	E_{corr} mVolt	β c mV/dm	β a mV/dm	%IE
Blank	0	504.77	-402.12	-113.1	95.2	
T1	1x10^{-4}	192.3	-444.65	-117.8	90.8	61.90
	5x10^{-4}	155.3	-438.29	-130.2	83.9	69.23
	1x10^{-3}	108.8	-429.37	-138.4	86.7	78.44
	5x10^{-3}	97.4	-421.21	-133.3	50.6	80.70
T2	1x10^{-4}	156.7	-487.49	-81.4	122.3	68.95
	5x10^{-4}	128.4	-467.62	-87.9	117.2	74.56
	1x10^{-3}	110.2	-459.68	-80.6	116.6	78.16
	5x10^{-3}	43.7	-451.23	-115.9	123.1	91.34

3.4. Electrochemical impedance spectroscopy (EIS) measurements

Figures 2a&b show Nyquist plots for the carbon steel in 0.5 M HCl in the absence and in presence of different concentrations of tetrazoles. It can be seen that Nyquist plots

contain depressed semicircles. Such behavior is the characteristic of solid electrodes and often referred to as frequency dispersion. This frequency dispersion can be attributed to roughness and heterogeneities of the solid surfaces [22].

Figure 2: Nyquist plots of C-steel in 0.5M HCl with various concentration of a=T1 and b=T2 at 303K

Table 6: Electrochemical impedance parameters for C-steel in 0.5M HCl in the various concentration of tetrazole compounds at 303K

Inhib.	Conc. of inhib. (M)	R_t (Ω cm^2)	C_{dl} (mF cm^{-2})	%IE
Blank	0	250.29	636.94	
T1	1×10^{-4}	602	264.51	58.47
	5×10^{-4}	800	199.04	68.75
	1×10^{-3}	1200	110.17	79.17
	5×10^{-3}	1350	117.95	81.48
T2	1×10^{-4}	778	204.67	67.87
	5×10^{-4}	1100	144.76	77.27
	1×10^{-3}	2000	66.10	87.50
	5×10^{-3}	2999	53.10	91.66

3.5. Surface Morphological Studies
3.5.1. Scanning Electron Microscopy studies (SEM)

Scanning electron microscope (SEM) images were taken in order to study the surface morphology of C-steel in the absence and presence of tetrazole inhibitors. SEM image Figure 3a reveals the polished C-steel, while Figure 3b reveals that in the absence of tetrazole inhibitors, the C-steel surface is highly damaged with pitted areas. This shape is typical to pitting corrosion [24]. Figure 3c&d shows a smooth surface with deposited compounds on it for the specimen after immersion in 0.5 M HCl solution containing 5x10-3 M tetrazoles; the best concentration of corrosion inhibitor. By comparison of SEM images at the same magnifications, it is indicated that the pits disappear and C-steel is almost free from corrosion in HCl with tetrazoles solutions. This is because of the formation of an adsorbed film of tetrazoles inhibit pitting corrosion of C-steel in 0.5 M HCl solution.
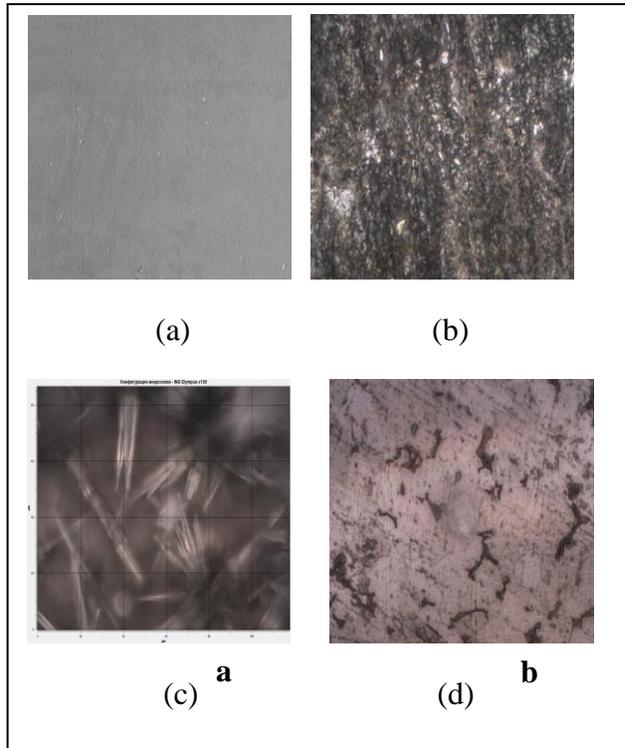
Figure 3: SEM images of the C-steel surface of (a) Polished carbon steel (control), (b) C-steel immersed in 0.5M HCl (blank), (c) C-steel surface after immersion for a period of 24 hrs in 0.5M HCl in presence of T1 and (d) C-steel surface after immersion for a period of 24 hrs in 0.5M HCl in presence of T2

3.5.3. Atomic force microscopy AFM

The atomic force microscope provides a powerful means of characterizing the microstructure. The three-dimensional AFM images are shown in Figure 4a-d. As it can be seen from Figure 4a the C-steel surface before immersion seems smooth compared to the C-steel surface after immersion in uninhibited 0.5 M HCl for 24 hrs. The average roughness of polished C-steel (Figure 4a) and C-steel in 0.5 M HCl without inhibitor (Figure 4b) was calculated to be 24 and 388 nm, respectively. It is clearly shown in Figure 26b that C-steel sample is getting cracked due to the acid attack on C-steel surface. However in the presence of optimum concentration of inhibitors, the average roughness were reduced to 52 and 38 nm for T1 and T2, respectively (Figure 4c&d).

Figure 4: Three dimensional AFM image of C-steel surface, a=fresh, b= immersed in 0.5 M HCl solution, c= immersed in 0.5 M HCl solution + T1 and d= immersed in 0.5 M HCl solution + T2
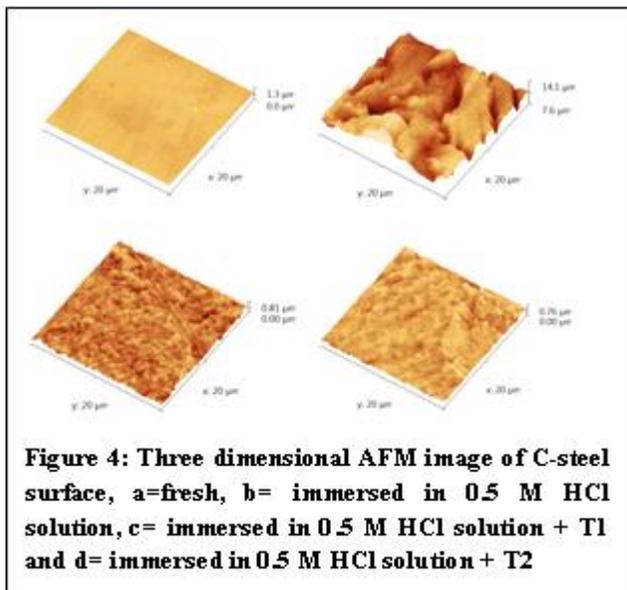
4. Conclusion

The corrosion behavior of C-steel in 0.5M HCl in the absence and presence of tetrazole compounds was investigated using the weight loss method, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. From the results obtained the following conclusions could be drawn:

1- The tetrazoles exhibited very good inhibition efficiency reaches to 91.66%. The results show that its inhibition efficiencies increased with increases the concentration of inhibitors.
2- By increasing the side chain length of alkyl group, the inhibition efficiency was found to be increases.
3- There are good agreements between weight loss and electrochemical techniques to determine the efficiency of corrosion inhibitor.
4- The surface morphology techniques showed that the carbon steel specimens had smoother surface due to formation of protected film of adsorbed inhibitor on the metal surface which prevented it from the corrosion process.

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