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A New Organotellurium Compound Based on N-Substituted Tetrazole as anti-corrosion for C-Steel in 1 M HCl Solution

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Abstract:

The present study includes a study and evaluation of the effect of a new organotellurium compound derived from N-butyl substituted tetrazole compensated namely: di (1-butyl tetrazole-5-yl) tellurium dibromide (Tz) which was prepared in a previous study as a anti-corrosion for the carbon steel alloys in the acid medium 1 M of hydrochloric acid. The work involved evaluating the inhibitor at various temperatures 303, 313 and 323 K for specific concentrations of inhibitor at 5, 10 and 30 ppm. This study was used the supplementary method of polarization curves or the so-called Supplementary Method of Polarization Curves / Tafel plots, to calculate the corrosion variables (corrosion voltage and corrosion current density) . It was observed that as anti-corrosion concentrations were increased as the efficiency of anti-corrosion will be increased. The prepared compound Tz gave a good inhibition efficiency 87% with 30 ppm at 303 K. It was also found that the activation energies are higher with the presence of inhibitor than their absence, especially with the presence of inhibitor Tz in the acid medium (1 M), due to decrease of the corrosion current, so the corrosion rate of the carbon steel alloy will decrease while the charge resistance of the charge will increase.

Keywords: N- substituted tetrazole, organotellurium compound, carbon steel, corrosion inhibitor, Supplementary Method of Polarization Curves / Tafel plots.

1. Introduction:

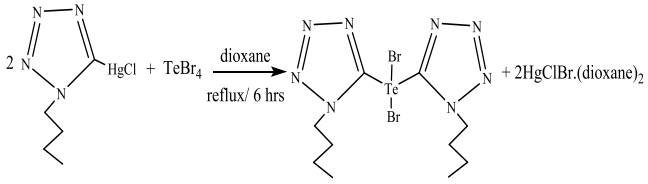
Corrosion is one of the most common problems which faced the industrial field especially those it used acidic media in the daily processes. The destructive attack on a metal or metal alloy by acidic solutions has several dangers and effects for example: decreased strength, downtime about equipment, get away from for liquids, also lost surface properties. [1] . To Protect the metallic surfaces from the general aggression of acid solutions, addition of some organic compounds containing atoms such otherness nitrogen, oxygen, phosphorus or sulfur atoms as well as hetero cyclic containing conjugated double bonds, known as corrosion inhibitors. The heteroatoms in organic inhibitors facilitates act by cover and protect the metal surface. [2] In general, adsorption between inhibitors and metal surface occurs because the p orbitals- electron pair of heteroatom coordinate with the d orbits of the metal surface atoms, [3]. The organic inhibitors are influenced by type of corrosive electrolyte, the nature of surface charge of metal and the chemical structure of inhibitors. In recent years, A great deal of effort has been devoted to developing organic inhibitors to find a new class of corrosion inhibitor with low cost and toxicity and high efficiency. One of the important class of organic inhibitors in acidic media is the N-heterocyclic compounds such as the tetrazole derivatives due to the adsorption of these particles on the surface of the alloys. Accordingly, the purpose of this paper is to think about the restraining activity of a unused organotellurium compounds containing N-substituted tetrazole namely **: di (1-butyl tetrazole-5-yl) tellurium dibromide (Tz)** which was prepared in our a previous study as a anti-corrosion for the carbon steel alloys in the corrosive medium 1 M of hydrochloric acid at different temperatures 303- 323 K in different concentrations of inhibitor at 5, 10 and 30 ppm using the supplementary method of polarization curves or / Tafel plots, to calculate the corrosion variables (corrosion voltage and corrosion current density) . Many researchers have studied how to protect mineral surfaces and by using tetrazoles substituted in different groups in different media that may be base or other acidic and have proven good efficiency because they contain a number of nitrogen atoms.[4] It was not touched on organic tellurium compounds containing tetrazole compensated with butyl and found that the prepared compound gave good efficiency in comparison with it. We did not find any other study included on the organic compounds of tellurium as anti-corrosion and this is a new study of its kind in this field.

2. Experimental Methods:

2.1. Synthesis of di (1-butyl tetrazole-5-yl) tellurium dibromide (Tz)

This compound was prepared according to literature method.

The reaction was subsequently escalated to mix (1-butyl tetrazole-5-yl) mercury (II) chloride (0.72 g, 2.00 mmol) with tellurium tetrabromide (0.446g, 1.00mmol) in 30 mL of dry dioxane solvent for 6 hours under an inert atmosphere of the argon. Then the mixture is filtered hot and allowed to cool to room temperature, then a white precipitate of the HgBrCl. $(dioxane)_2$ complex was separated by filtration. Evaporation of the solvent with the rotary evaporator and under the evacuated pressure, so it will be a yellow precipitate, which has been recycled with ethanol to give the compound in the form of yellow crystals. The yield of the product (**2**) was 72 %, mp 155-157 °C. IR (KBr) cm^{-1}: 2966w, 2924w, 2330w, 1612sh, 1446w, 1288w, 1111sh, 1080w. UV-Vis (λ_{max}, nm (ε L mol^{-1} cm^{-1})): 295 (14780). Molar conductance ($ohm^{-1}.cm^2.mol^{-1}$): 20.50. Rf: 0.72. ^{1}H-NMR (400 MHz, DMSO-d6, d/ppm): 2.735 (t, 2H, N-***CH₂***); 1.465 (quintet, 2H, ***CH₂***-CH_2-CH_3); 1.275 (sextet, 2H, ***CH₂***-CH_3); 0.826 (t, 3H, **CH_3**). ^{13}C NMR (DMSO-d6): 62.656 (**C-Te)**; 38.939 (N-***CH₂***); 28.940 (***CH₂***-CH_2-CH_3); 18.960 (***CH₂***-CH_3); 13.472 (**CH_3**). MS Calculated for $C_{10}H_{18}Br_2N_8Te$ (537.72) Found: M^+ (538); MS/MS (m/z): 523, 509, 495, 481, 468 , 439, 422, 362, ,81 ,69, 57 , 43; Elemental Analysis Calculated: C, 22.34; H, 3.37; N, 20.84. Found: 22.38; H, 3.43; N, 90.91.



(Tz)

2.2. Composition of material

In this study, the alloy used contains the components shown in Table 1:

Table 1: chemical composition the alloy used

Material	Ni	C	Si	Mn	P	S	Cr	Cu	AS
%	0.3	0.13	0.37	0.3	0.04	0.05	0.1	0.3	0.08

And the remainder is HCl was gotten from Aldrich Chemical Co.

2.3. Electro chemical Estimations

Electrochemical estimations have been made the use of potentiostat/galvanostat (ACM) linked to a laptop. Three-pole machine, composed of the carbon alloy fixed as a working pole (WE), an auxiliary pole (CE) platinum plate, and a saturation pole such as a standard electrode (RE). applied electrochemical measurements. The solution temperature was maintained at the specified temperature the usage of a water bathtub. Before indulging in check answers, (We) used sanding paper between 600 and 1200 ranges and gave a reverse image using a sharpening tool. The (WE) is then washed with pure water and soaked in acetone inside the ultrasonic cleaner for about a minute. The WE electrode switched to the immediate setting up of electrical and chemical calculations, after which it was immersed in an open circuit voltage in the test solution for one hour until a strong potential of the nation was achieved before impedance and polarization formation. All trials were conducted in aerobic responses. We were identified by polarization records because diploma of surface coverage (available), percentage inhibition performance (IE percent), and freight transfer resistance.

2.3. Solutions

We prepared 3 different concentrations of the inhibitor used Tz in 1 M HCl. In the above solution the various concentrations of this study were prepared by soluble to obtain concentrations (5, 10, 30 ppm) that were calculated at different temperatures.

3. Results and Discussion

3.1. Polarization Measurements

Typical potentiodynamic polarization curves for C-metallic in 1 M HCl are illustrated in (Fig. 1-9) in the presence and absence of specific concentrations of (Tz). Table 2 shows the respective Tafel parameters, inhibition efficiency (percent IE), floor coverage (almost), corrosion value and charge transfer resistance. It is clear that the shapes of the Tafel plots for inhibited electrodes are similar to those of uninhibited electrodes. The presence of the receptor reduces the conventional density but no longer trades different behavioral influences. The inhibition efficiency of the inhibitory molecules was evaluated according to equation (1).[5]

$$\text{Inhibitor efficiency (E\%)} = \frac{CR^{o} - CR}{CR^{o}} \times 100\% \quad .....(1)$$

Where CR° and CR are the corrosion rates of the C-Steel in presence and absence of inhibitor, respectively. The values presented in the table (2) show that the inhibition efficiency increased with increasing the amount of added additives and decreased with increasing temperature, and this is expected and is consistent with previous studies [6].

Table 2: Electrochemical variables, Θ, and % IE for C-steel in (1 M HCl) in the absent and existence of various concentration of (Tz) at various temperatures.

conc. ppm	T K	Ecorr mv	βa A/V	Bc A/V	Icorr mA/cm2	Rct Ω	CR mpy	%IE	Θ
Blank	303	-684	0.2171	-6.737	2.694	9.537	156.16	-	-
5		-605	10.46	-5.302	5.484×10^{-1}	46.86	31.784	79.6	0.796
10		-695	10.66	-4.418	3.861×10^{-1}	55.56	22.376	85.7	0.85.7
30		-761	8.47	-5.736	3.346×10^{-1}	76.78	19.396	87.6	0.876
Blank	313	-735	1.65E-15	-0.1093	4.101	6.265	237.72	-	-
5		-671	8.394	-7.95	1.149×10^{-1}	22.36	66.6	71.9	0.719
10		-657	9.797	-8.234	1.133×10^{-1}	22.68	65.68	72.4	0.724
30		-663	10.59	-9.045	8.64×10^{-1}	30.036	49.04	79.4	0.794
Blank	323	-699	1.65E-15	-1.647E-15	8.335	3.083	483.2	-	-
5		-690	2.734	-5.728	2.607	9.854	151.12	68.7	0.687
10		-687	3.702	-7.411	2.436	10.55	141.2	70.8	0.708
30		-691	5.001	-7.018	1.987×10^{-1}	12.93	115.2	76.2	0.762

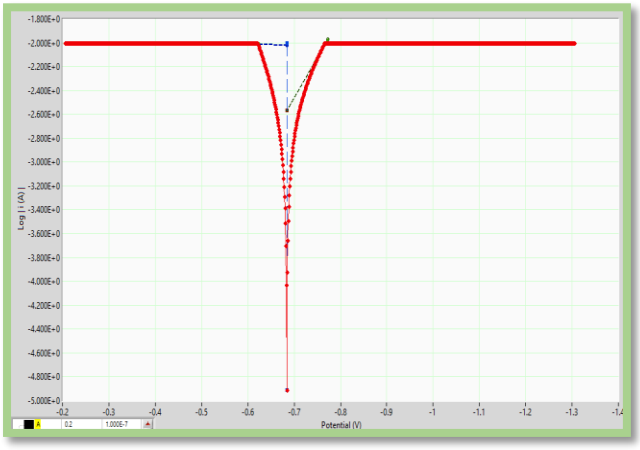


Fig. 1. Tafel curve for C-steel at 303 K in 1 M HCl (blan

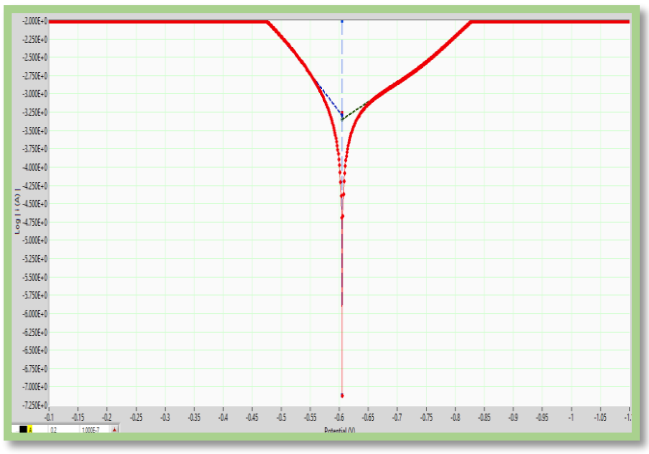


Fig. 2. Tafel curve for C-steel at 303 K in HCl with 5 ppm (Tz).

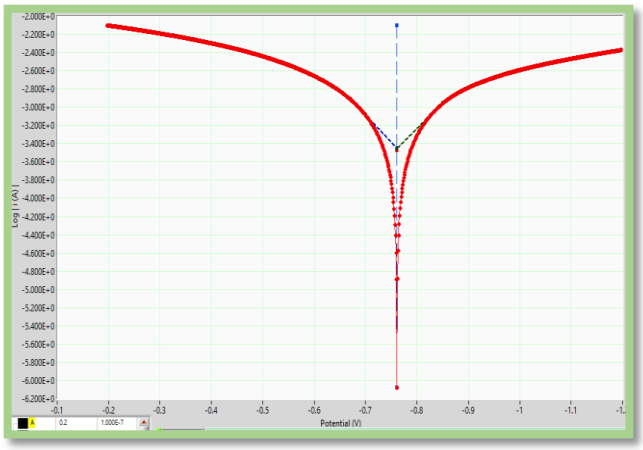


Fig. 3. Tafel curve for C-steel at 303 K in HCl with 30 ppm (Tz).

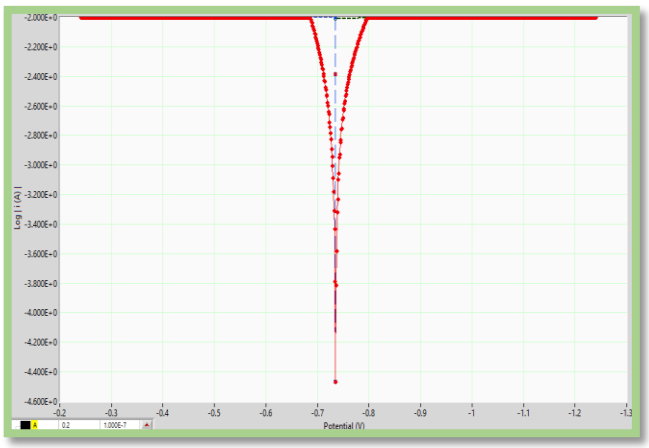


Fig. 4. Tafel curve for C-steel at 313 K in 1 M HCl (blank).

Fig. 5. Tafel curve for C-steel at 313 K in HCl with 5 ppm (Tz).

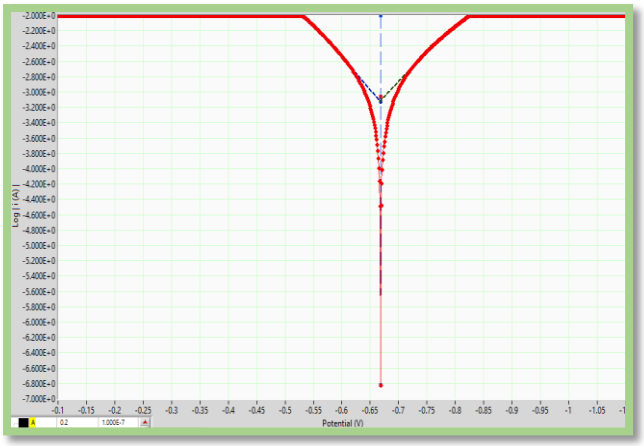


Fig. 6. Tafel curve for C-steel at 313 K in HCl with 30 ppm (Tz).

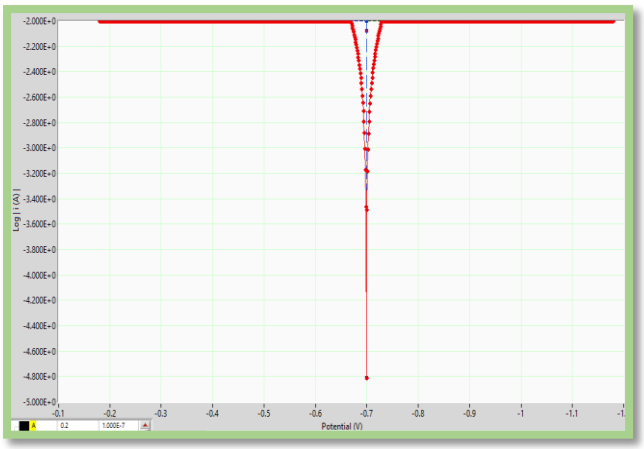


Fig. 7. Tafel curve for C-steel at 323 K in 1 M HCl (blank).

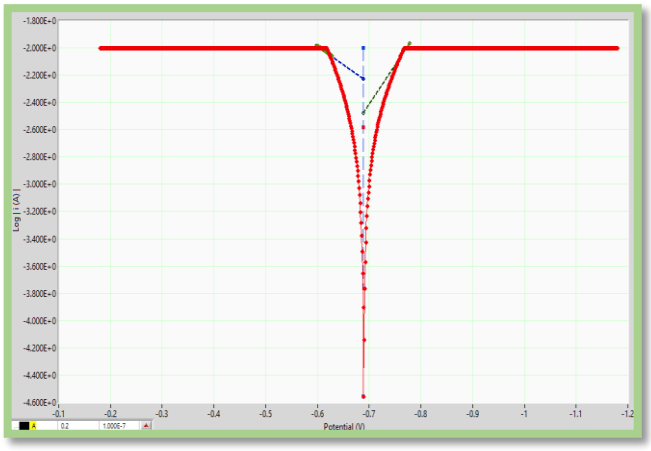


Fig. 8. Tafel curve for C-steel at 323 K in HCl with 5 ppm (Tz).

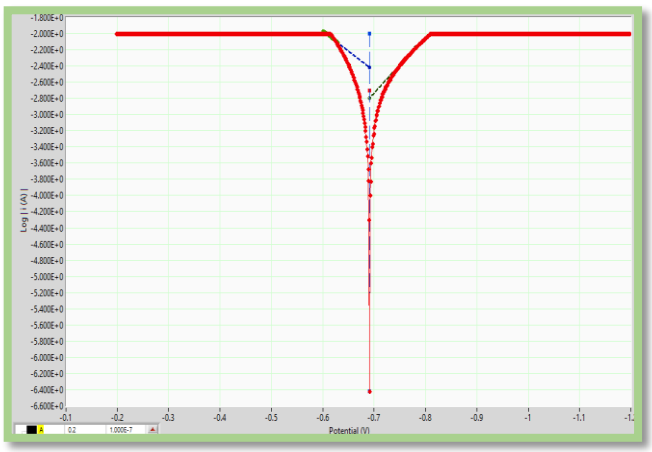


Fig. 9. Tafel curve for C-steel at 323 K in 30 ppm (Tz).

From Table 1 it is clear that the inhibitor's adsorption moved the corrosion potential (Ecorr) in the negative direction. Both the Tafel slopes (ßa and ßc), the anodic and cathodic Tafel slopes are decreased by the introduction of (Tz). This means that (Tz) is a mixed barrier influencing the iron dissolution and the evolution of hydrogen [7] . Reducing the positive and negative currents in the presence of (Tz) can be explained by blocking the active sites by creating a protective film on the electrode surface [8]. At (Tz) concentration of 30 ppm at 303 k the surface coverage and inhibition efficiency values achieved are optimum. As can be seen from Table 1, inhibitor (Tz) greatly decreases corrosion current with a small change in the

potential for corrosion. If the displacement in the corrosion potential is greater than 85 mV, the inhibitor may be classified as a cathodic or anodic form in respect of the corrosion potential of the blank solution [8a]. In the present research, and through the difference of possible corrosion values of the corrosion inhibitor in the presence or absence of the inhibitor, which suggested that the inhibitor studied is a mixed-type inhibitor that is in agreement with some other studies [7b]. The values of (Rct) increases with inhibitor are shown in Table 1 and the value of Rct indicates that of the efficiency inhibitor to prevent carbon-steel erosion in acidic media. The maximum transfer resistance (Rct(inh)) value at (303 K) and a concentration (76.78 ppm) of the inhibitor was (30 ppm). Using (Tz) inhibitor at (323 K) the average value of (Rct) was 12.93 at a concentration (30 ppm), while the value reached 3.083 at the same conditions when there was no inhibitor [9].

3.2. The Temperature Effect:

Temperature is critical facts Whilst studying pyrolysis. At temperature, its impact at the response of acidic minerals is extremely complex. The price of corrosion in acidic solutions, for example, will increase regularly with increasing temperature due to Hydrogen launch reduces. Many adjustments may occur to the floor of the steel, which includes adsorption, absorption, rearrangement, or inhibitor degradation [10] . Very few inhibitors are powerful at high temperatures [11].

It changed into also found that increasing the temperature became laid low with Carbon steel corrosion rate 1 M HCl, and its results are obvious inside the inhibition motion about 30 ppm as shown in Table 3. The inhibitory effect (% IE) dropped from 87.6% from 303 K to 76.2% at 323 K.

Table 3. The effect of temperature on C-Steel's corrosion levels when 30 ppm (Tz) is absent and present.

T(K)	1 M HCl CR (mpy)	Tz CR (mpy)	%IE	Θ
303	156.16	19.396	87.6	0.876
313	237.72	49.04	79.4	0.794
323	483.2	115.2	76.2	0.762

The effective activation energies (Ea) for the corrosion process of C-steel in 1 M HCl were calculated from the Arrhenius equation (2) in the absent and presence of different concentrations of investigated compounds [12].

$$\ln CR = \ln A - \frac{Ea}{RT} \qquad .....(2)$$

Where Ea is the obvious activation corrosion energy, R is the commonplace gas's regular, A is the Arrhenius pre-exponential steady, and T is absolutely the temperature. As shown in (Fig. 10), a plot of ln CR (corrosion rate) versus 1/T gave straight lines.

The entropy of activation (ΔS) and the enthalpy of activation (ΔH) for the intermediate complicated in the transition for the corrosion of ingot in HCl inside the absence and presence of different concentrations of investigated compounds have been obtained through applying the transition-nation equation (3) [13]:

$$\ln \frac{CR}{T} = \ln \frac{R}{Nh} + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad ...(3)$$

where h is Plank's constant, N is Avogadro's number.

When drawing the relationship between ln CR / T vs. 1 / T output a straight line (Fig. 11), its slope is (ΔH / R), and the cutoff is [ln (R / Nh) + ΔS / R] [5, 13], The presence of Tz increased C-metallic activation energies suggesting heavy adsorption of the Tz molecules on the steel ground and the presence of those components induces the adsorption of these additives on the C-steel ground. Values of the activation entropy are negative in the absence and in the presence of the compounds tested. This means that the activated complicated within the rate-figuring

out step represents an affiliation in place of a dissociation step [14]. In this way the activated molecules were better than the ones present at the initial level.

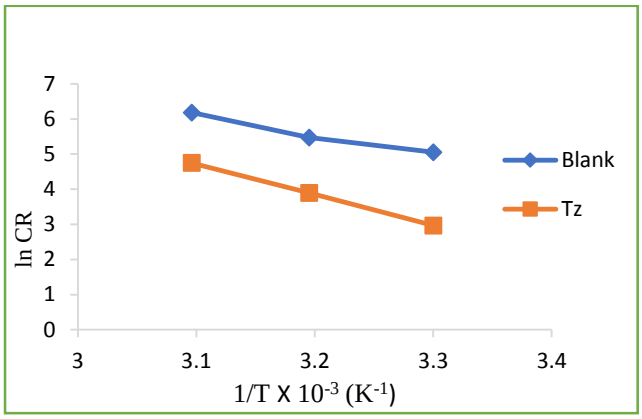


Fig. 10. Arrhenius plots for C-steel in 1 M HCl within the presence and nonattendance of Tz (30 ppm).

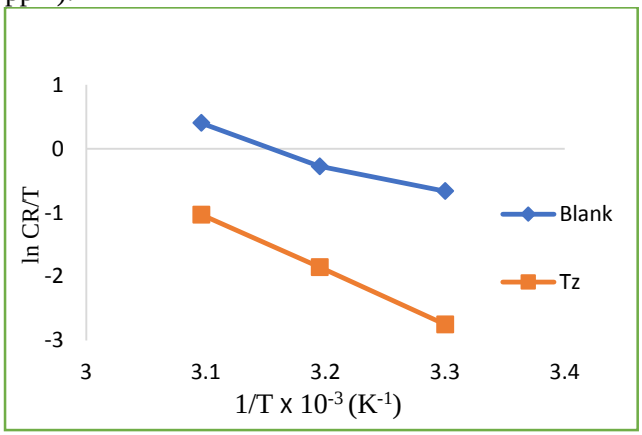


Fig. 11. Transition-state ln (W / T) plots versus 1/T in 1 M HCl in the absence and presence of specific concentrations of Tz

Table 4. In the absence and presence of Tz, thermodynamic conditions for mild steel in 1 M HCl

conc.ppm	Ea (KJ/mol)	ΔH (KJ/mol)	ΔS(KJ/mol.K)
Blank	45.828	43.228	-0.0605
30	72.496	69.895	0.0107

3.3. Adsorption isotherm:

In addition to their interaction with the electrode surface, the Tz adsorption provides details about the interaction between the absorbed molecules themselves. The degree of surface coverage of the various inhibitor molecules concentrations in 1 M HCl was determined using the following equation (4-6) [15].

$$\theta = \frac{CR_{uninh} - CR_{inh}}{CR_{uninh}} \quad .....(4)$$

Are the corrosion rate uninhibited and inhibited respectively.

The interaction of Tz with the carbon metal floor turned into exceptional described using the Langmuir isotherm. This isotherm is: [16].

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

where Kads the constant of the adsorptive balance, θ is the surface covered, and C is the conc. in mol L^{-1} calculated as follows [17]:

$$\Delta G^{\circ}_{ads} = -RT\ln 55.5\, K_{ads} \quad .....(6)$$

In which R is the widespread gasoline steady and T is absolutely the temperature. Standard free energitic for adsorption (ΔG^{o}) of -42.661 kJ mol^{-1} turned into obtained at 30oC. The cost of ΔG^{o} suggests the adsorption spontaneity response of Tz at the carbon metallic surface. It moreover focuses to chemisorption happening within the interaction of Tz and the surface of C-steel where charge sharing or exchange from the inhibitor atoms to the carbon steel surface shapes a arrange sort of bond.

Table 5. Equilibrium constant (K_{ads}), free energy adsorption (ΔG°_{ads}) for adsorption of C-steel inhibitors in 1 M HCl at (303 k).

Tz conc. ppm	**T K**	θ	**ΔG^{0}_{ads} (KJ/mol)**	**K_{ads} L/mol**
5	303	0.796	-42.661	419624.582
10		0.857	-41.997	322250.140
30		0.876	-39.648	126622.101

The negative adsorption free energy values Suggest that the absorption of the inhibitor Tz on the carbon-Steel surfice is automatic And

additionally the strong interplay between the Tz particles and the surface of the metal [18]. However, the adsorption process indicates either chemical or chemical degradation. The value of devices less than (greater than -40 kJ / mol) is associated with chemical degradation between the charged molecule and the charged minerals [19].

On this work it is located the value of ΔG°ads has been determined to be greater than (−40 kJ / mol); meaning: the Tz adsorption function on the superficies of C-metal is especially chemisorption.

Conclusion:

The possibility of preparing a new di-organyltellurium di halide compound containing tetrazole (**Tz**) by reacting the organic mercury derivative with tellurium tetra bromide with DMSO solvent and inert atmosphere of argon gas at a molar ratio of 2: 1.

Electrochemical Display: Tz acts as a C-Steel inhibitor at 1M HCl. Inhibition performance will increase with the amount of inhibitor and decrease with temperature. Kinetic and thermodynamic parameters indicate a strong adsorption of the Tz inhibitor onto the C-Steel surface. The presence of the high number of nitrogen atoms in the tz works to prefer its use as an inhibitor due to the presence of electronic double-edits that help to increase its adsorption on the alloy surface used in this research. The inhibition mechanism is by using a fully automatic adsorption (chemical adsorption) of the inhibitor on the surface of C-steel Electrochemical measurements confirm the mixed inhibition method. As a result, the Tz is considered a good anti-corrosion and can be used to protect metal surfaces from dissolution in acidic media.

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دراسة تثبيط التآكل لمركب عضوي التلوريوم لمشتق التترازول المعوض على ذرة النتروجين لسبيكة الفولاذ الكاربوني في محلول 1 مولاري لحامض الهيدروكلوريك

الاء اياد الياسين، صالح حمزة عباس، عادل علي الفريجي

قسم الكيمياء، كلية العلوم / جامعة البصرة، البصرة / العراق

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الخلاصة

يتضمن البحث الحالي دراسة و تقييم لمركب التلوريوم العضوي المتضمن على التترازول المعوض على ذرة النتروجين المسمى di (1–butyl tetrazole–5–yl) tellurium dibromide (Tz) الذي حضر في دراسة سابقة كمثبط لتآكل سبيكة الصلب الكاربوني في الوسط الحامضي لحامض الهيدروكلوريك بتركيز 1 مولاري عند درجات حرارية مختلفة (303 K و313 و323) وبتراكيز مختلفة منه 5 ppm و10 و30 بأستخدام الطريقة الاستكمالية لمنحنيات الاستقطاب أو ما يسمى بمنحنيات تافل (Supplementary Method of Polarization Curves / Tafel plots). تم حساب جميع متغيرات التآكل مثل جهد التآكل و كثافة تيار التآكل وغيرها ولوحظ ان كلما ازداد تركيز المركب العضوي للترازول المعوض على ذرة النتروجين كلما أزدادت كفاءة التثبيط و قل التآكل في السبيكة. أعطى المركب المحضر Tz كفاءة تثبيط جيدة 87 ٪ بتركيز 30 ppm وعند303 K. كما وجد أن طاقات التنشيط أعلى مع وجود مثبط من غيابه، خاصة مع وجود المانع Tz في الوسط الحمضي(1 M) ، بسبب انخفاض تيار التآكل ، لذلك سينخفض معدل التآكل لسبائك الكربون الصلب بينما ستزداد مقاومة الشحنة.

الكلمات المفتاحية: مركبات التترازول المعوضة على ذرة النتروجين، مركب التلوريوم العضوي، الصلب الكاربوني، مثبطات التآكل، الطريقة الاستكمالية لمنحنيات الاستقطاب أو ما يسمى بمنحنيات تافل.