Corrosion Inhibition characteristics of Reinforced Steel in H₂SO₄ by benzoyl Thiourea

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Keywords:	A B S T R A C T
Each keyword to start on a new Corrosion Reinforced steel Acidic medium Weight loss Adsorption isotherm Inhibition efficiency Benzoylthiourea inhibitor DFT calculation	In The adsorption and corrosion inhibition performance of 3,3-diethyl(4-Chloro)benzoylthiourea, ClDEBT, at reinforced steel in H₂SO₄ interface was examined using gravimetric method at 303.15 K. The inhibition effectiveness of ClDEBT was improved by increasing the concentration. The adsorption data of ClDEBT on the reinforced steel surface were fitted to Langmuir, Temkin and thermodynamic–kinetic adsorption isotherms, and some thermo-dynamics functions as α, y, f, ΔG_{ads} and K_{ads} were obtained. Activation energies of 35.69 and 55.99 kJ mol⁻¹ for the corrosion processes of reinforced steel were observed in presence and absence of benzoylthiourea inhibitor, respectively. The adsorption of thiourea inhibitor on the surface of reinforced steel was found to be spontaneous and exothermic. Quantum parameters as the highest & lowest occupied molecular orbital energy (E_{HOMO}) & (E_{LUMO}), energy gap (ΔE), were determined and correlated to the experimental data.

دراسة خصائص الامتزاز وتثبيط التأكل للحديد الصلب في H₂SO₄ بواسطة مثبط البنزويل ثيوريا

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طريقة الفقد في الوزن

كفاءة تثبيط

منحنيات الإدمصاص

نظرية الكثافة الالكترونية

الملخص

تم التحقق من سلوك الامتزاز وتثبيط تأكل الحديد الصلب في وسط H₂SO₄ بواسطة مركب 3،3-ثنائي إيثيل (4-كلورو بنزويل ثايويوريا، ClDEBT ، وذلك باستخدام طريقة الفقد الوزني عند 303.15 K . لوحظ زيادة كفاءة تثبيط بزيادة تركيز ClDEBT. تم تطبيق منحنيات الإدمصاص مثل منحنيات لانجمير وتيمكين والنموذج الثرموديناميكي الحركي عند درجة حرارة ثابتة ، وتم الحصول على بعض الدوال مثل ΔG_{ads}.أشارت النتائج إن معدل التأكل يزداد بزيادة درجة الحرارة وان طاقة التنشيط لعملية التثبيط كانت 35.69 و 55.99 (kJ mol⁻1) في غياب ووجود مركب البنزويل ثايويوريا على التوالي. وإن عملية الإدمصاص على سطح الحديد الصلب هي عملية تلقائية وطاردة للحرارة. تم حساب المعاملات الكيميائية الكمومية مثل (E_{HOMO}) و(E_{LUMO}) وفجوة الطاقة (ΔE) ، وتم ربط نتائج الحسابات النظرية ومقارنتها وربطها بالبيانات التجريبية.

Introduction

Corrosion is the deterioration of metal by chemical attack or electrochemical reaction with its environment[1]. The corrosion is one of the main problems by the industrial system[2], the acid are used in the daily processes as the acid cleaning, acid descaling [3, 4]. The inhibitors adding to the acid media has been considered to be cost-effective way of reducing the metallic corrosion that accoutring under conditions of moderate acid concentration and temperature [5]. The most industrial efficient inhibitors are organic molecules [6]. The use of organic compounds is the most practical AQ to protect metals against corrosion. The organic molecules having nitrogen (N), sulphur (S) and oxygen (O) atoms are capable of retarding metallic

corrosion [4]. Thiourea compounds have been investigated as effective reinforced steel corrosion inhibitors [7, 8].

The inhibition characteristic of Benzoyl thiourea compounds on reinforced steel and the other alloys have received more attention of researchers [9]. On the of the previous observation and related to our previous work [10-13], we aimed to investigate the corrosion inhibition properties of inhibitor(Scheme. 1) namely 3,3-diethyl,4-chlorobenzoylthiourea (ClDEBT) on reinforced steel in 1N H₂SO₄ solution, as part of undertaken investigation in our laboratory on the corrosion inhibiting behaviour of reinforced steel. *Benzoylthiourea,* the inhibitor used here was selected as a corrosion inhibitor based on its molecular structure that has O, N & S active centre atoms.
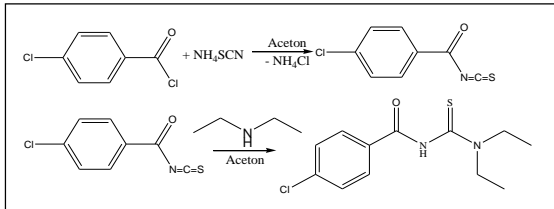
Scheme 1: Synthesis of the of ClEBT molecule

2. Experimental method
2.1. Material
Tests were accomplished on a freshly cleaned cylinder of reinforced steel (specimens were collected from Musrata steel plant) of the chemical composition (wt. %): 0.57% Mn, 0.30% C, 0.0004% S, 0.011% P, 0.23% Si, and the balance iron. Specimens used in the mass loss experiment were mechanically cut into 4.0 cm length and 1cm diameter, then abraded with SiC abrasive papers 400-1200 grit, respectively, washed in absolute ethanol, chloroform and acetone, dried in room temperature and stored in a moisture free desiccators before their use in corrosion studies.

2.2. Solutions
The aggressive solutions of 0.5 M H₂SO₄ were prepared by dilution of analytical grade 98 % of H₂SO₄, with second water. The concentration range of *benzoylthiourea* inhibitor prepared and used in this investigation were 0.0001M - 0.01 M. The benzoylthiourea solution was prepared by dissolving the appropriate amount in ethanol.

2.4. Gravimetric measurements
In this research, weight loss technique was used to examine the inhibition characteristic of ClDEBT inhibitor. Typically, the reinforced steel bars was weighed and entirely immersed in the test solution. The beaker was place into a thermostatic water bath maintained at 313 K. The bars were retrieved after 90 min interval, rinsed and cleaned and dried, then weighed. The mass loss was taken as the difference in the weight of the reinforced steel bars before and after immersion in tested solutions. In addition, the experiments were done at different temperatures from 293 to 323 K. All experiments were carried out in triplicate to get good reproducibility. The corrosion rate (R_{corr}) was calculated in mg cm⁻² min⁻¹ unite from equation (1):

$$R \ (mg \ cm^{-2} min^{-1}) = \left(W \ / At \right) \qquad (1)$$

where W, is the mass loss of reinforced steel cylinder; t, is the involvement time (90 min), and A, is the entire surface area of the reinforced steel bar. The efficiency (%I) of the inhibitor and degree of surface coverage (Θ) were calculated using equations 2 & 3, respectively.

$$I\% = \left(1 - \frac{R_{inh}}{R_0}\right) \times 100 \qquad (2)$$

$$\theta = \left(1 - \frac{R_{inh}}{R_0}\right) \qquad (3)$$

where R_0 and R_{inh} are the corrosion rate for reinforced steel in the absence and presence of the benzoylthiourea solutions in the acidic media,

2.5. Computational study
The HOMO & LUMO orbitals and the overall electronic composition of inhibitor was computed at the density function theory with Materials Studio suite (version 5.5) using DMol³. A generalized gradient approximation (GGA) function [14, 15] and BLYP function, (Becke-Lee-Yang-Parr) [16, 17], were used to perform the optimization process. To map the orbital structure of the compound, the polarization with a double numeric plus (DNP) basis set was used.

3. Results and discussion
The loss in mass method is undoubtedly one of the most commonly used technique of inhibition inspection based on the sincerity and reliability of the measurement.

3.1. The inhibitor concentration Effect
The corrosion rate of reinforced steel in the presence and absence of ClDEBT molecules were investigated at 303.15 K using the mass loss system. The calculated corrosion rates values in mg cm⁻²min⁻¹, are presented in Table 1 & Figure 1. The inhibition efficiency (I%) results are ploted in Figure 2. From the achieved values, it is observable that there is a decrease in the rate of corrosion in the presence of ClDEBT inhibitor when compared to the blank one (free H₂SO₄).
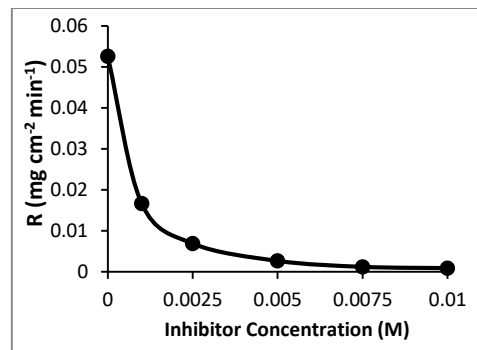

Fig.1: ClDEBT concentration Effect on the corrosion rate of reinforced steel in 0.5M H₂SO₄ at 303.15K.
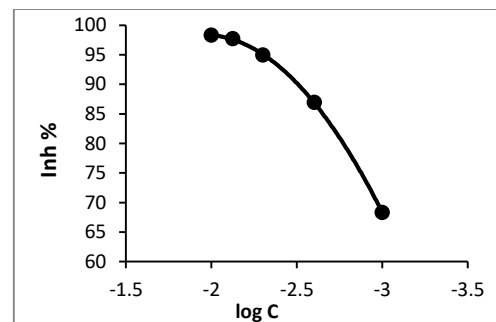

**Fig. 2:** The ClDEBT inhibition efficiency at 303.15K

The values obtained show a decrease in the corrosion rate of reinforced steel in the presence of (ClDEBT).

Table 1: Corrosion rate and inhibition efficiency in the absence and presence of ClDEBT

ClDEBT Conc. (M)	R (mg cm⁻² min⁻¹)	I%
0	0.052579	-
0.001	0.016655	68.324
0.0025	0.006876	86.923
0.005	0.002651	94.954
0.0075	0.0012	97.718
0.01	0.0009	98.288

3.2. Adsorption process and isotherms

The isotherm of adsorption process can afford a elementary knowledge on the inhibitor interaction with the surface of the reinforced steel. The dissolution of metal occur at steel sites; when an insufficient Fe-(Inh)$_{ads}$ species to cover the metal surface. As concentration of inhibitor increased; the dense inhibitor layer is formed on the surface of steel. This layer was able to reduce the chemical attack on the metal surface. The adsorption of an organic molecules on the metal surface is considered as a replacement process between the organic molecules in aqueous phase Org$_{(aq)}$ and the adsorbed water molecules H$_2$O$_{(s)}$ on the surface of steel as in chemical equation 1.

$$org_{(aq)}xH_2O_{(ads)} \rightarrow org_{(ads)}xH_2O_{(aq)} \qquad (1)$$
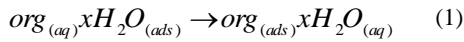
Where x is the number of water molecules substituted by one organic molecule. The surface coverage degree (Θ) has been calculated using the equation 3. Efforts were made to fitting the Θ values to Langmuir, El-Awady and Temkin adsorption isotherm.

Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{asd}} + C_{inh} \qquad (4)$$

where K$_{ads}$ represents the adsorption process equilibrium constant. The C/Θ against C plot is shown in figure 3. Linear plots with very good correlation coefficient were obtained, which indicates the physisorption adsorption mode.
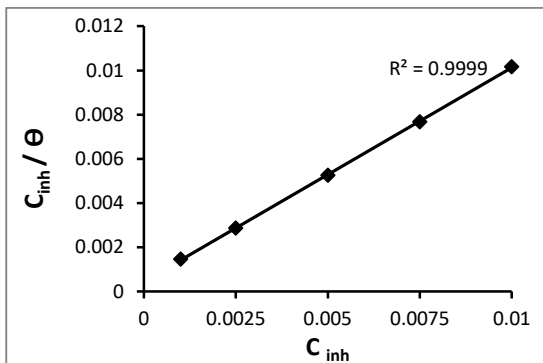

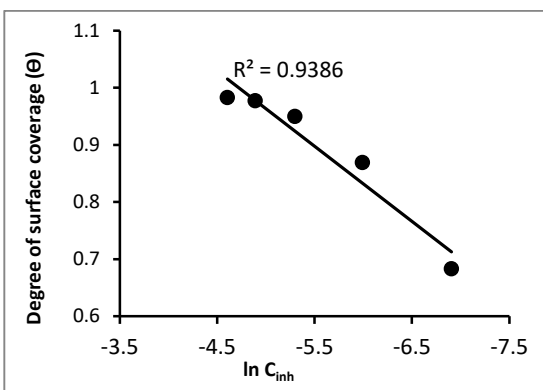**Fig. 3:** Langmuir adsorption isotherm at 303.15K

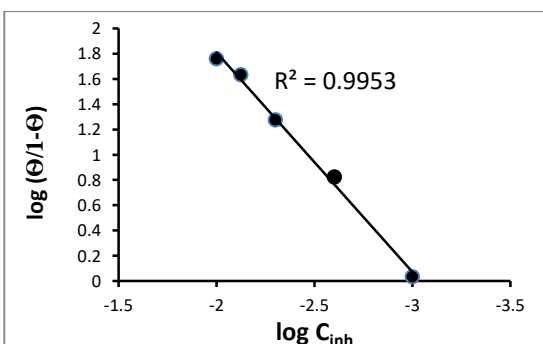**Fig. 4:** Temkin adsorption isotherm plot at 303.15K

Fig. 5: Kinetic-thermodynamic model of El-Awady adsorption isotherm at 303.15K

Furthermore, Temkin isotherm of adsorption (equation 5) was established for the experimental data.

$$\theta = \frac{1}{-2\alpha}\ln C + \frac{1}{-2\alpha}\ln K \qquad (5)$$

α is the factor of the interaction. The ө versus inhibitor concentration (lnC) plot gives a straight line with a slope is equal to α and the intercept is equal to lnK (see Figure 4).

El-Awady, et.al [18, 19] developed a kinetic model for the typical corrosion experiment of the type studied in this work. This corrosion experiment carries all the features of kinetic investigation. Kinetically speaking, the inhibition process take place through the inhibitor molecule adsorption as in chemical balnced eq. 2.

$$S_M + y\,I \rightarrow S\,I_y \qquad (2)$$
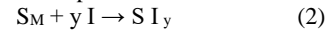
Then, the Kinetic-thermodynamic isotherm equation is set byeq. 6.

$$\log\left(\frac{\theta}{1-\theta}\right) = \log k^{\square} + y\log C_{inh} \qquad (6)$$

Where surface of reinforced steel is donated by S$_M$, the number of inhibitor molecules occupying one active site is expressed by y, and $k^\sim$ is a constant related to the adsorption binding constant. It is significant to recognize that, when the y values are greater than one is suggesting the a multilayers formation of inhibitor molecules on the surface of metal. However, when the y values are less than one is suggesting that, a inhibitor molecules occupies more than one active site. The plot of log(C$_{inh}$) versus $log\left(\frac{\theta}{1-\theta}\right)$ gives a straight line having a slope is equal to y and intercept is equal to log $k^\sim$ as estimated in Figure 5. This straight lines indicates that, the ClDEBT molecules adsorbed on the steel surface is fitted to the Kinetic-thermodynamic model of isotherm (Eq. 6).

The adsorption constant at equilibrium K$_{ads}$ is used to calculate the free energy of adsorption process, $\square G^o_{ads}$, by applying a eq. 7.

$$\square G^o_{ads} = -RT\ln(55.5 K_{ads}) \qquad (7)$$

Where the adsorption free energy is expressed by $\square G^o_{ads}$, R is the gas constant and T is a system temperature. In general, when $\square G^o_{ads}$ values is -20 kJ mol^{-1} or less; the electrostatic interaction are compatible between the charged metal and the charged inhibitor molecules (physical adsorption). However, when the $\square G^o_{ads}$ values is greater than -40 kJ mol^{-1} ; chemical adsorption take place by involving a chemichal reaction at the metal surface as to form a type of coordinated bond [20, 21]. obtained values of the free energies are furthermore interdused in Table 2.

Table 2: parameters from Langmuir, Temken and thermodynamic–kinetic models at 303.15K

Parameter	Value
α	-3.81
y	1.738
f	7.62
K$_{ads}$	2x10^3
$\square G^o_{ads}$	-29.28 KJ/mol

The calculated $\square G^o_{ads}$ value (Table 2) was −29.28 kJ mol^{-1}, which indicates that, the mechanism of ClDEBT adsorption on the surface of reinforced steel in H$_2$SO$_4$ media at 303.15K is a mixture of chemisorption and physisorption [22]. The great value of K$_{ads}$ indicates a stronger adsorption on the surface of reinforced steel. It has been stated that the greater the K$_{ads}$ value (>100), the more stable and stronger the adsorbed layer on metal surface of the inhibitor and consequently; the greater the efficiency [23, 24]. The value of α 'the molecular interaction' which obtained by Temkin isotherm of adsorption was negative, indicating a repulsive forces between the molecules of ClDEBT inhibitor. Moreover, y values (table 2) displayed that, every active site occupy by two of inhibitor molecules.

3.3. The Effect of Temperature

The thermodynamic functions (activation energy, entropy and enthalpy) of inhibition process are calculated by using Arrhenius equation (8) and Transition–State equation (9).

$$\ln R = \left(-\frac{\Box E_a^*}{RT} \right) + \ln A \qquad (8)$$

$$\ln \left(R / T \right) = \left[\ln \frac{R}{N^o h} + \frac{\Box s_a^*}{R} \right] - \frac{\Box H_a^*}{RT} \qquad (9)$$

Where R is the rate of corrosion, $\Box E_a^*$ is a activation energy, A is pre-exponential frequency factor, T is the Kelvin temperature, R is the a gas constant and both $\Box H_a^*$ and $\Box S_a^*$ are the entropy and enthalpy of activation for the corrosion process, respectively, and h is Plank constant, N° is Avogadro's number, [11]. Arrhenius straight line gives slope of $-\Box E_a^*/R$ which used for $\Box E_a^*$ calculation. Whereas, the activation entropy and enthalpy are deduced by the intercept and slope of the straight line of eq. 9. The temperature impact on inhibition properties of reinforced steel in H₂SO₄ were presented in Figures of 6, 7 and Table 3. The recorded data indicateS that, the corrosion rate increased as the T increases from 293K to 323K.

Table 3: Computed values of the thermodynamic functions in the presence and the absence of ClDEBT

Tested solution	$\Box E_a^*$ KJmol⁻¹	$\Box H_a^*$ KJmol⁻¹	$\Box S_a^*$ Jmol⁻¹
Free acid	+35.69	+33.147	-159.66
PBT	+55.99	+53.410	-106.09

The activation energy($\Box E_a^*$)increases in the presence of inhibitor molecules suggests that the adsorbtion of this molecules on the surface of reinforced steel is a physical adsorption mechanism [20].
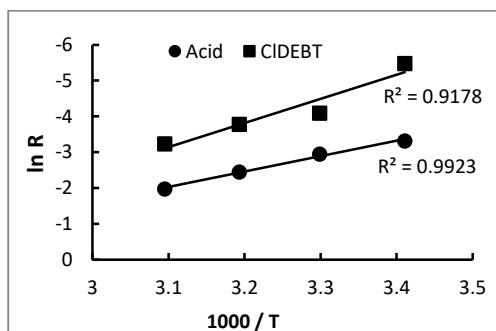

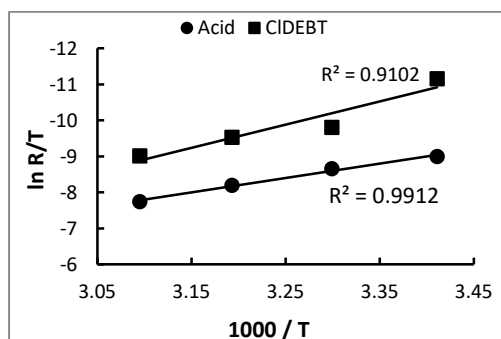**Fig. 6:** Arrhenius plot for the corrosion rate of reinforced steel versus the temperature

Fig. 7: Transition–State plot for the corrosion rate of reinforced steel versus the temperature

3.3. Theoretical calculation
A chemical quantum calculations were accomplished to explore the structural parameters that influence the inhibition efficiency of tested inhibitor. the electronic structures were computed by the energy optimization of bonds angles & lengths. The optimized structures

with their minimum energies acquired from the DFT calculations are presented in Figure 8.
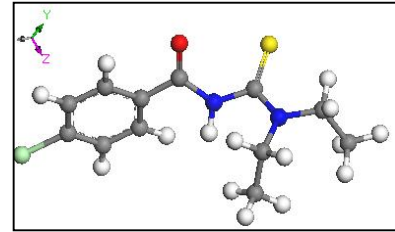

Fig. 8: Optimized inhibitor molecule by DFT, (b)planarity of inhibitor molecules

The LUMO & HOMO orbitals (Figure 9) were used to predict the active site of the adsorbed inhibitor molecule. Based on the theory of frontier molecular orbital [25-29], a transition state formation of the inhibitor molecules is based on the interaction between LUMO and HOMO. The electron donating ability of a molecule describes by HOMO energy which indicates the tendency of electrophiles to attack the inhibitor molecule. A value of E_{HOMO} (-5.226 eV) designates a tendency of inhibitor molecules to provide electrons to acceptor molecules with an empty electron orbital or low energy of molecular orbital [25, 28].

The value of E_{LUMO} (-2.763) specifies an electron accepting ability of an inhibitor molecules (the lowest E_{LUMO} energy; the higher accepting tendency of electrons) [25].
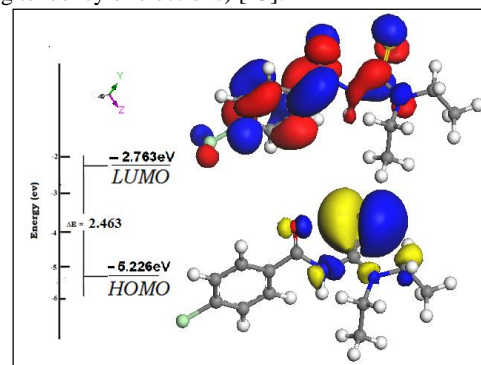

Fig. 9: HOMO and LUMO of the neutral inhibitor molecule by DFT

Table 4: Chemical reactivity parameters with

Parameters	quantities
E_{HOMO}	-5.226
E_{LUMO}	-2.763
Energy band gap (ΔE)	2.463

The molecules of ClDEBT inhibitor adsorbed on the reinforced iron surface through the chemisorption mechanism concerning the movement of water molecules from the iron surface and the electrons sharing between iron and oxygen & nitrogen atoms [30]. The molecules of ClDEBT can be adsorbed similarly on the metal surface based on the interactions between vacant d-orbitals of iron and the π-electrons of the phenyl ring on ClDEBT molecules. The inhibitor molecules of ClDEBT are present as protonated in the form of NH₃⁺ in the acid medium; indicating the electrostatic interaction with the negatively charged surface of steel (FeCl$_{ads}^-$) [31, 32]. Furthermore, the protonated ClDEBT molecules could be adsorb via electrostatic interactions between the negatively charged metal surface and the positively charged molecules.

4. Conclusion

Tested Benzoylthiourea molecules of ClDEBT was establish to be an good inhibitor for the corrosion of the reinforced steel in H₂SO₄ medium. The inhibition efficiency was increased as a concentration of ClDEBT increased. The adsorption of the ClDEBT molecules were successfully fitted to the Langmuir, Temkin and kinetic–

thermodynamic adsorption isotherms. The adsorption mechanism of ClDEBT on reinforced steel in H_2SO_4 media at the examined temperatures is a mixture of both chemisorption and physisorption mechanism. Figures obtained from quantum DFT calculations displays LUMO, HOMO spread along the molecules of ClDEBT inhibitor. In contrast, the oxygen (O) atom in the inhibitor molecules is only homo contributed.

Acknowledgment

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