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## Corrosion Inhibition characteristics of Reinforced Steel in $H_2SO_4$ by benzoyl Thiourea

Zianab Abu alqassim<sup>a</sup>, Omhani Almahdi<sup>a</sup>, Omkalthoom Almassri<sup>a</sup> and Aisha AL-abbassi<sup>b\*</sup>

<sup>a</sup>Chemistry Department, Faculty of Education, Sebha University, Ghat, Libya.

<sup>b</sup>Chemistry Department, Faculty of Science, Sebha University, Sebha, Libya.

### Keywords:

Corrosion.  
Reinforced Steel.  
Acidic Medium.  
Weight Loss.  
Adsorption Isotherm.  
Inhibition Efficiency.  
Benzoyl Thiourea Inhibitor.  
DFT Calculation.

### ABSTRACT

In The adsorption and corrosion inhibition performance of 3,3-diethyl(4-Chloro)benzoylthiourea, CIDEBT, at reinforced steel in  $H_2SO_4$  interface was examined using gravimetric method at 303.15 K. The inhibition effectiveness of CIDEBT was improved by increasing the concentration. The adsorption data of CIDEBT on the reinforced steel surface were fitted to Langmuir, Temkin and thermodynamic-kinetic adsorption isotherms, and some thermo-dynamics functions as  $\alpha$ ,  $y$ ,  $f$ ,  $\Delta G_{ads}$  and  $K_{ads}$  were obtained. Activation energies of 35.69 and 55.99  $\text{kJ mol}^{-1}$  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 ( $\Delta E$ ), were determined and correlated to the experimental data.

## دراسة خصائص الامتزاز وتثبيط التآكل للحديد الصلب في $H_2SO_4$ بواسطة مثبط البنزويل ثيوريا

زينب ابوالقاسم<sup>1</sup>، ام هاني المهدي<sup>1</sup>، ام كلثوم المصري<sup>1</sup>، عائشة العباسي<sup>2\*</sup>

<sup>a</sup>قسم الكيمياء، كلية التربية، جامعة سبها، غات، ليبيا.

<sup>b</sup>قسم الكيمياء، كلية العلوم، جامعة سبها، سبها، ليبيا.

### الكلمات المفتاحية:

التآكل.  
الحديد الصلب.  
الاسواط الحمضية.  
طريقة الفقد في الوزن.  
كفاءة تثبيط.  
منحنيات الإدمصاص.  
نظرية الكثافة الالكترونية.

### الملخص

تم التحقق من سلوك الامتزاز وتثبيط تآكل الحديد الصلب في وسط  $H_2SO_4$  بواسطة مركب 3,3-ثنائي إيثيل (4-كلورو بنزويل ثايوريا، CIDEBT)، وذلك باستخدام طريقة الفقد الوزني عند 303.15 K. لوحظ زيادة كفاءة تثبيط بزيادة تركيز CIDEBT. تم تطبيق منحنيات الإدمصاص مثل منحنيات لانجمير وتيمكين والنموذج الثرموديناميكي الحراري عند درجة حرارة ثابتة، وتم الحصول على بعض الدوال مثل  $\Delta G_{ads}$ . أشارت النتائج إن معدل التآكل يزداد بزيادة درجة الحرارة وأن طاقة التنشيط لعملية التثبيط كانت 35.69 و 55.99 ( $\text{kJ mol}^{-1}$ ) في غياب ووجود مركب البنزويل ثايوريا 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 ( $\Delta E$ )، 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 accourting

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

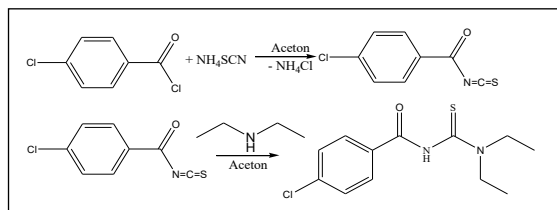
\*Corresponding author:

E-mail addresses: [ais.alabbasi@sebhau.edu.ly](mailto:ais.alabbasi@sebhau.edu.ly), (O. Almahdia) [zawytzawyt06@gmail.com](mailto:zawytzawyt06@gmail.com), (O. Almassria) [thooma1997@gmail.com](mailto:thooma1997@gmail.com), (Z. Abu alqassima) [zin.abuakassm@sebhau.edu.ly](mailto:zin.abuakassm@sebhau.edu.ly)

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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 (CIDEBT) on reinforced steel in 1N H<sub>2</sub>SO<sub>4</sub> 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 CIDEBT 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 H<sub>2</sub>SO<sub>4</sub> were prepared by dilution of analytical grade 98 % of H<sub>2</sub>SO<sub>4</sub>, 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 CIDEBT 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<sup>-2</sup> min<sup>-1</sup> unite from equation (1):

$$R \text{ (mg cm}^{-2}\text{min}^{-1}\text{)} = (W / At) \quad (1)$$

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 ( $\theta$ ) were calculated using equations 2 & 3, respectively.

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

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

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 DMol<sup>3</sup>. 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 CIDEBT molecules were investigated at 303.15 K using the mass loss system. The calculated corrosion rates values in mg cm<sup>-2</sup>min<sup>-1</sup>, are presented in Table 1 & Figure 1. The inhibition efficiency (I%) results are plotted in Figure 2. From the achieved values, it is observable that there is a decrease in the rate of corrosion in the presence of CIDEBT inhibitor when compared to the blank one (free H<sub>2</sub>SO<sub>4</sub>).

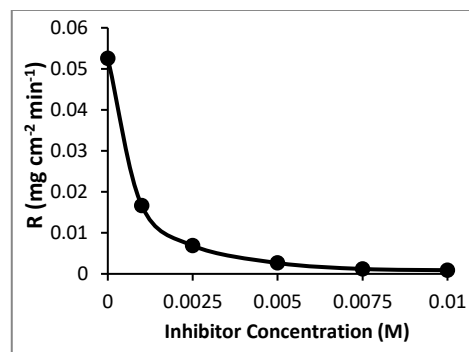


Fig.1: CIDEBT concentration Effect on the corrosion rate of reinforced steel in 0.5M H<sub>2</sub>SO<sub>4</sub> at 303.15K.

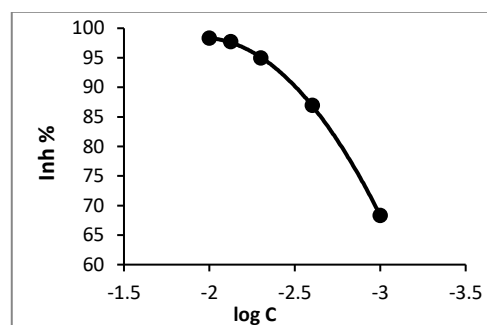


Fig. 2: The CIDEBT inhibition efficiency at 303.15K

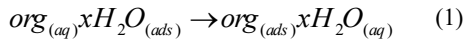
The values obtained show a decrease in the corrosion rate of reinforced steel in the presence of (CIDEBT).

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

| CIDEBT | Conc. ( M) | R<br>(mg cm <sup>-2</sup> min <sup>-1</sup> ) | 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)<sub>ads</sub> 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<sub>(aq)</sub> and the adsorbed water molecules H<sub>2</sub>O<sub>(s)</sub> on the surface of steel as in chemical equation 1.



Where  $x$  is the number of water molecules substituted by one organic molecule. The surface coverage degree ( $\Theta$ ) has been calculated using the equation 3. Efforts were made to fitting the  $\Theta$  values to Langmuir, El-Awady and Temkin adsorption isotherm.

Langmuir isotherm is given by the expression:

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

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

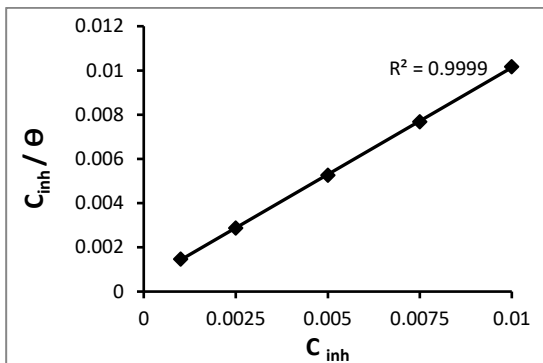


Fig. 3: Langmuir adsorption isotherm at 303.15K

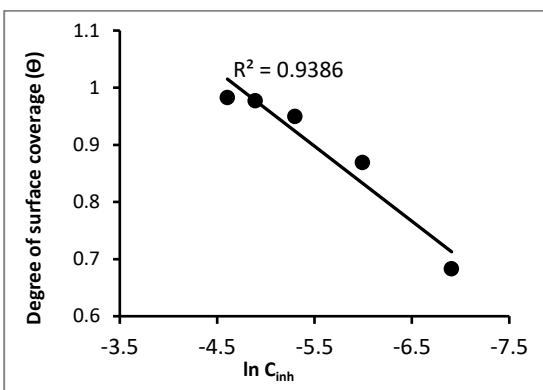


Fig. 4: Temkin adsorption isotherm plot at 303.15K

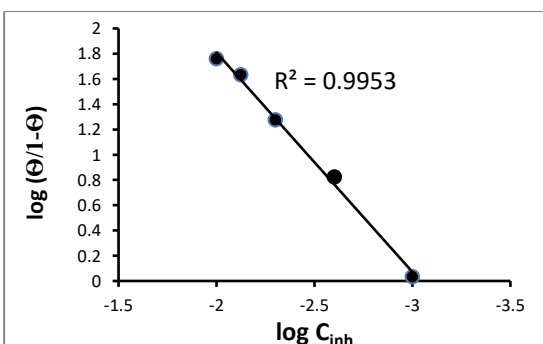


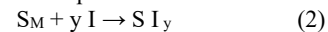
Fig. 5: Kinetic-thermodynamic model of El-Awady adsorption isotherm at 303.15K

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

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

$\alpha$  is the factor of the interaction. The  $\theta$  versus inhibitor concentration ( $\ln C$ ) plot gives a straight line with a slope is equal to  $\alpha$  and the intercept is equal to  $\ln K$  (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 balanced eq. 2.



Then, the Kinetic-thermodynamic isotherm equation is set byeq. 6.

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

Where surface of reinforced steel is donated by  $S_M$ , the number of inhibitor molecules occupying one active site is expressed by  $y$ , and  $k^{\square}$  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  $\log k^{\square}$  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,  $\square G_{ads}^o$ , by applying a eq. 7.

$$\square G_{ads}^o = -RT \ln(55.5 K_{ads}) \quad (7)$$

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

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

| Parameter           | Value           |
|---------------------|-----------------|
| $\alpha$            | -3.81           |
| $y$                 | 1.738           |
| $f$                 | 7.62            |
| $K_{ads}$           | $2 \times 10^3$ |
| $\square G_{ads}^o$ | -29.28 KJ/mol   |

The calculated  $\square G_{ads}^o$  value (Table 2) was  $-29.28 \text{ kJ mol}^{-1}$ , which indicates that, the mechanism of ClDEBT adsorption on the surface of reinforced steel in H<sub>2</sub>SO<sub>4</sub> 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  $\alpha$  '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).

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

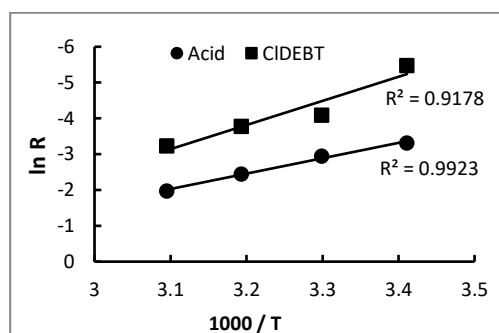
$$\ln \left( \frac{R}{T} \right) = \left[ \ln \frac{R}{N^o h} + \frac{S_a^*}{R} \right] - \frac{H_a^*}{RT} \quad (9)$$

Where  $R$  is the rate of corrosion,  $E_a^*$  is a activation energy,  $A$  is pre-exponential frequency factor,  $T$  is the Kelvin temperature,  $R$  is the a gas constant and both  $H_a^*$  and  $S_a^*$  are the entropy and enthalpy of activation for the corrosion process, respectively, and  $h$  is Plank constant,  $N^o$  is Avogadro's number, [11]. Arrhenius straight line gives slope of  $-E_a^*/R$  which used for  $E_a^*$  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 H<sub>2</sub>SO<sub>4</sub> 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.

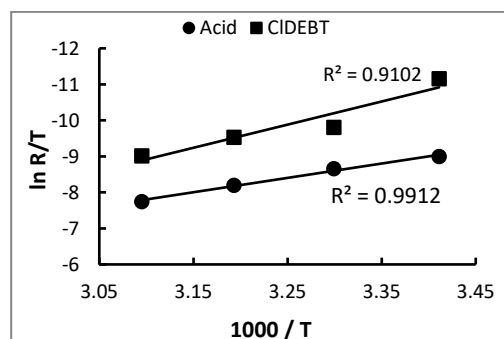
**Table 3:** Computed values of the thermodynamic functions in the presence and the absence of CIDEBT

| Tested solution | $E_a^*$<br>KJmol <sup>-1</sup> | $H_a^*$<br>KJmol <sup>-1</sup> | $S_a^*$<br>Jmol <sup>-1</sup> |
|-----------------|--------------------------------|--------------------------------|-------------------------------|
| Free acid       | +35.69                         | +33.147                        | -159.66                       |
| PBT             | +55.99                         | +53.410                        | -106.09                       |

The activation energy( $E_a^*$ )increases in the presence of inhibitor molecules suggests that the adsorption 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

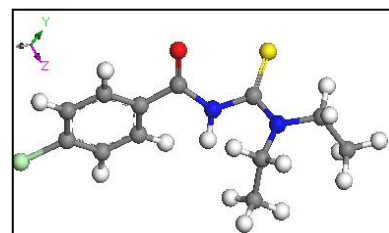


**Fig. 7:** Transition-State plot for the corrosion rate of reinforced steel versus the temperature

### 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

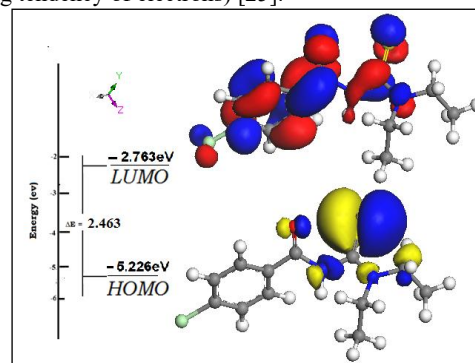
with their minimum energies acquired from the DFT calculations are presented in Figure 8.



**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 ( $\Delta E$ ) | 2.463      |

The molecules of CIDEBT 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 CIDEBT can be adsorbed similarly on the metal surface based on the interactions between vacant  $d$ -orbitals of iron and the  $\pi$ -electrons of the phenyl ring on CIDEBT molecules. The inhibitor molecules of CIDEBT are present as protonated in the form of  $NH_3^+$  in the acid medium; indicating the electrostatic interaction with the negatively charged surface of steel ( $FeCl_{ads}^-$ ) [31, 32]. Furthermore, the protonated CIDEBT molecules could be adsorb via electrostatic interactions between the negatively charged metal surface and the positively charged molecules.

### 4. Conclusion

Tested Benzoylthiourea molecules of CIDEBT was establish to be an good inhibitor for the corrosion of the reinforced steel in H<sub>2</sub>SO<sub>4</sub> medium. The inhibition efficiency was increased as a concentration of CIDEBT increased. The adsorption of the CIDEBT molecules were successfully fitted to the Langmuir, Temkin and kinetic–

thermodynamic adsorption isotherms. The adsorption mechanism of CIDEBT on reinforced steel in H<sub>2</sub>SO<sub>4</sub> 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 CIDEBT inhibitor. In contrast, the oxygen (O) atom in the inhibitor molecules is only homo contributed.

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