Thermodynamic and Electrochemical Investigation of 2-Mercaptobenzimidazole as Corrosion Inhibitors for Mild Steel C35E in Hydrochloric Acid Solutions

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Abstract-2-Benzimidazolethiol (BIZT) was tested as a corrosion inhibitor for mild steel in 1 M HCl solution using different techniques: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The corrosion processes were inhibited by adsorption of BIZT on to the mild steel surface, manner increasing in inhibitor concentration accompanies with corrosion rate decreases, inhibition efficiencies increase and surface coverage degree increases. The rate of corrosion of mild steel rapidly increases with temperature over the temperature range of 298K to 328K both in absence and presence of inhibitor. Quantum chemical parameters are calculated using the Density Functional Theory method (DFT). Correlation between theoretical and experimental results is discussed. Langmuir adsorption isotherm fits well with the experimental data. The protection efficiency increases with increasing inhibitor concentration (in the range $2,5 \cdot 10^{-4}$ - $30,0 \cdot 10^{-4}$ M) and temperature too. the thermodynamic parameters, such as adsorption equilibrium constant (K_{ads}), free energy of adsorption (ΔG_{ads}), adsorption heat (ΔH_{ads}) and adsorption entropy (ΔS_{ads}) values were calculated and discussed.

Keywords- Corrosion; Inhibition; Mild steel. Protection efficiency; Adsorption, Thermodynamic properties

I. INTRODUCTION

Corrosion is an electrochemical process by which metallic structures are destroyed gradually through anodic dissolution. Iron and its alloys are used in countless applications as construction materials, aerospace, medical devices, and tools. They have remarkable economic and industrial importance, because of its low cost maintenance, good structural properties, and excellent mechanical properties. Mild steel is an alloy form of iron, which undergoes corrosion easily in acidic medium [1-6]. Acidic corrosion protection of steel in acidic media great important both for industrial facilities and theoretical aspects. Inhibitors are generally used to protect materials against deterioration from corrosion. Evaluation of corrosion inhibitors for steel in acidic and basic media is important because of the widespread use of steel in contact with the number of corrosive environments [7-8]. A variety of organic compounds containing heteroatoms (N, O, S) that can donate electron pairs have been used to inhibit corrosion mild steel in various aggressive electrolytes [9-16]. The relationship between the adsorption of organic substances and their molecular structure has attracted the attention of many investigators [17–22]. the inhibition efficiency always depends upon the number of active adsorption centers an inhibitor molecule may have, and the charge density, molecular size, mode of adsorption, and its capability to form metallic complexes [23-28]. The process of adsorption of inhibitors diminishes the overall corrosion rate, thus the film resulting, acts as a barrier blocking of the active sites of metal dissolution and/or hydrogen evolution. the adsorption controls corrosion, acting over the anodic or the cathodic surface or both [29-33]. The protective action of an inhibitor in metal corrosion is often associated with chemical or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other [34-37]. Recent studies have been concerned with the effects of Sulphur containing compounds such as thiourea and its derivatives on the inhibition of aluminium corrosion. 2-Benzimidazlethiol (BIZT) has been shown to be an effective inhibitor of carbon-steel corrosion in aqueous solutions of both nitric and sulphuric acid [38-39]. Here, we extend such studies to examine its corrosion inhibition in a system comprising samples of the mild steel C35E exposed to HCl 1 M. by different electrochemical techniques. The inhibition performance was theoretically evaluated using quantum chemistry calculations and molecular dynamics simulations, and the corrosion inhibition mechanism was analyzed.

II. EXPERIMENTAL

A. Weight loss measurements

Carbon steel specimens of the following chemical composition (wt%) were used in the experiment: 0.18 per cent

(C), 0.02 per cent (Si), 0.47 per cent (Mn), 0.01 per cent (P), 0.02 per cent (S) and the remainder iron, were used in the studies. The samples were polished with emery papers from grade 120 to 1200, washed with distilled water, cleaned with acetone, and dried. After being weighed accurately by a balance with high sensitivity the specimens were immersed in 30 mL 1 M HCl with and without various concentrations of the studied inhibitor at different temperatures. After 6 h of immersion, the specimens were taken out, rinsed thoroughly with distilled water, dried and weighed accurately again. Then the tests were repeated at different temperature immersion time. In order to get good reproducibility, experiments were carried out in duplicate. The corrosion rate (W_L) in (g. $cm^{-2}.h^{-1}$) was calculated using (1):

$$W_L = (W_0 - W_f) / (S.t) \quad (1)$$

Where W_0 is the initial weight before immersion, W_f the final weight after the corrosion test, respectively, S is the total surface area of specimens, t is exposure time. The percentage protection efficiency (P) of BIZT was calculated by applying the following relationship [40]:

$$P = (W_L^0 - W_L^I) / (W_L^0) \; x \; 100 \quad (2)$$

Where W_L^0 and W_L^I are the values of corrosion rate without and with inhibitor, respectively.

B. Electrochemical measurements

A three-electrode cell consisting of carbon steel working electrode (WE), a platinum counter electrode (CE) and saturated calomel electrode (SCE) as a reference electrode, was used for electrochemical measurements. The working electrode (WE) which was in the form of a square embedded in PVC holder using epoxy resin so that the flat surface was the only surface in the electrode. The working surface area was 1.0 x 1.0 cm² and prepared as described above (Section Weight loss determination). Used materiel is EC-Lab SP 200 Research Grad model potentiostat/galvanostat/FRA. Data were analyzed using EC-Lab software. The polarization curves were recorded by using three-electrode system. The working electrode was first immersed into the test solution for 30 minutes to establish a steady state open circuit potential (E_{ocp}). After measuring the open circuit potential, potentiodynamic polarization curves were obtained with a scan rate of 1 mV/s in the potential range between ±10 V relative to the E_{ocp}. Corrosion current densities values were obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. Inhibition efficiency P is defined as:

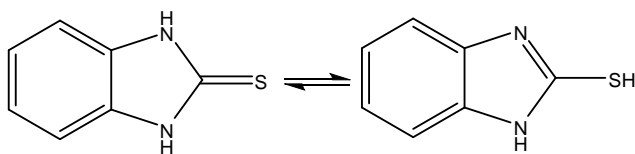$$P = (1 - (i_{corr}^0 / i_{corr}^{inh})) \; x \; 100 \quad (3)$$

Where i_{corr}^0 and i_{corr}^{inh} represent corrosion current density values without and with inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) experiments were performed at potential open circuit in the frequency range from 100 kHz to a 10 MHz, with a signal amplitude perturbation of 10 mV. Inhibition efficiency P is estimated using the following relation:

$$P = ((R_{ct}^{inh} - R_{ct}^0) / (R_{ct}^{inh})) \; x \; 100 \quad (4)$$

Where R_{ct}^0 and R_{ct}^{inh} are charge transfer resistance in the absence and presence of the inhibitor, respectively.

III.   RESULTS AND DISCUSSION

A. Potentiodynamic Polarization Data

Fig. 2 shows typical anodic and cathodic potentiodynamic polarization curves for mild steel in 1 M HCl in the absence and presence of various concentrations ($2,5 .10^{-4}$ - $30,0 .10^{-4}$ M) of BIZT at room temperature. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel line. It could be observed that both the cathodic and anodic reactions were affected with the addition of BIZT, which suggested that the BIZT reduced anodic dissolution and also retarded the cathodic hydrogen evolution reaction. This indicates that BIZT functioned as a mixed-type inhibitor in the acid solutions [41-43].
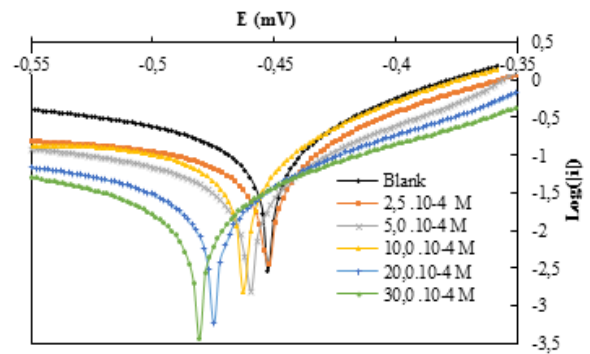

Figure 2. Cathodic and anodic potentiodynamic polarization curves of mild steel C35E in 1 M HCl solution in the absence and presence of various concentrations of BIZT

TABLE I. ELECTROCHEMICAL DATA FROM TAFEL CURVES CARRIED OUT IN 1 M HCL IN ABSENCE AND PRESENCE OF BIZT

C (M)	β_a (mV)	β_c (mV)	E_{corr} (mV/ESC)	I_{corr} (µA/cm²)	P
Blank	58,9	101,1	-451,611	82,073	-
$2,5 .10^{-4}$	58,7	137,7	-461,831	52,500	36,03
$5,0 .10^{-4}$	50,6	107,0	-452,209	42,766	47,89
$10,0 .10^{-4}$	68,3	135,7	-459,155	33,735	58,90
$20,0 .10^{-4}$	94,6	211,6	-472,121	30,059	63,38
$30,0 .10^{-4}$	93,2	153,5	-480,206	17,969	78,11

Figure 1. Molecule of BIZT

The values of associated electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel coefficients for identification of cathodic and anodic polarization (β_c and β_a) and inhibition efficiency P were calculated from these curves and given in Table I. The electrochemical parameter obtained from the Tafel polarization studies observed that the i_{corr} values decreased from 82,073 µA/cm^2 to 17,969 µA/cm^2 with increased concentration of BIZT.

The inhibition value is also found to increase from 36,03 % to 78,11 %. The anodic and cathodic Tafel slopes (β_c and β_a) are approximately constant, these results indicate that this inhibitor acts by simply blocking the available surface area. In other words, the inhibitor decreases the surface area for dissolution without affecting the mechanism of the dissolution of steel. It is also seen that E_{corr} does not shift significantly in the presence of the inhibitor, indicating that the compound is mixed type inhibitor, i.e. it inhibits both anodic and cathodic reactions.

The values of corrosion current densities in the absence (i_{corr}^{0}) and presence of inhibitor (i_{corr}^{inh}) were used to estimate the inhibition efficiency from polarization data P as (3).

Inhibition efficiency increased in the inhibitor concentration in 1 M HCl solution. Decrease in the corrosion current, it reaches a maximum efficiency of 78,11% at a concentration of 30,0.10^{-4} M.

B. Electrochemical impedance spectroscopy (EIS)

Fig. 3 shows the complex-plane impedance plots of mild steel in 1 M HCl without and with various concentrations (2,5 .10^{-4} - 30,0 .10^{-4} M) of BIZT. It is clear that Nyquist plots are imperfect semi-circle in shape corresponding to a charge transfer controlled process. This behavior can be attributed to frequency dispersion. For analysis of the impedance spectra containing one capacitive loop, a simple equivalent circuit consisting of a parallel combination of a capacitor, C_{dl}, and a resistor, R_{ct}, in series with a resistor, R_s, representing the solution resistance as previously reported [44]. The corrosion behavior of mild steel in 1 M HCl solution in the presence of BIZT was investigated by electrochemical impedance spectroscopy at room temperature. Various impedance parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), and inhibition efficiency P are given in Table II. The impedance diagrams were not perfect semicircles. This feature had been attributed to frequency dispersion [45-47]. The charge transfer values (R_{ct}) were calculated from the difference in impedance at the lower and higher frequencies.
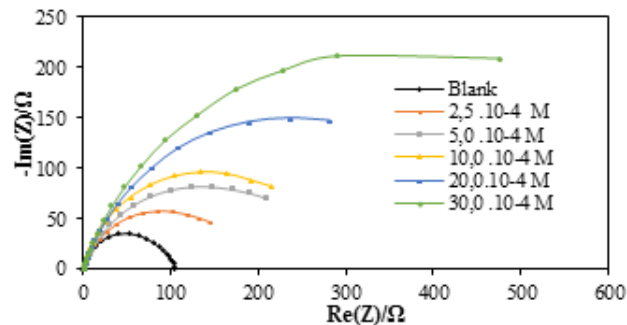

Figure 3.   EIS diagrams of mild steel C35E in 1 M HCl with different concentrations of BIZT at 298K.

To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum ($-Z_{im}^{max}$) was found and C_{dl} values were obtained from (5):

$$C_{dl} = 1/ (2.\pi.f.(-Z_{im}^{max}).R_{ct}) \qquad (5)$$

The values of percentage inhibition efficiency P were calculated from the values of R_{ct} according to (4) [48].

Inhibition efficiency increased in the inhibitor concentration in 1 M HCl solution. The impedance data listed in Table II indicate that the values of both R_{ct} and P are found to increase by increasing the inhibitor concentration, while the values of C_{dl} are found to decrease. The inhibition efficiency values determined using the polarisation curves were lower than those determined by EIS experiments, this difference is probably due the shorter immersion time in the case of the polarisation measurements.

$$C_{dl} = 1/ (2\pi. f_{max}. R_{ct}) \qquad (6)$$

Where f_{max} represents the frequency at which imaginary value reaches a maximum on the Nyquist plot. The electrochemical parameters of Rct, Cdl and Rs are calculated by EC-Lab software and listed in Table II.

This decrease in Cdl may be explained on the basis that the double- layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of the inhibitor on the electrode surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with increase in inhibitor concentration may be attributed to the formation of a protective layer on the electrode surface.

TABLE II.   ELECTROCHEMICAL PARAMETERS DEDUCED BY EIS METHOD FOR MILD STEEL C35E IN 1 M HCL IN THE ABSENCE AND PRESENCE OF VARIOUS CONCENTRATIONS OF BIZT.

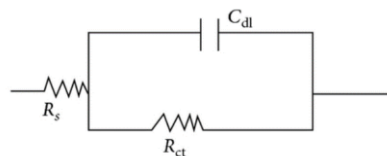| C (M)	R_S (Ω.cm^{-2})	C_{dl} (µF.cm^{-2})	R_{ct} (Ω.cm^{-2})	P
Blank	0,897	1190	95,25	-
2,5 .10^{-4}	1,279	72,69	168,6	43,51
5,0 .10^{-4}	0,861	34,65	250,3	61,95
10,0 .10^{-4}	0,995	73,63	280,3	66,02
20,0 .10^{-4}	1,419	79,18	415,5	77,08
30,0 .10^{-4}	1,135	72,56	609	84,36

Figure 4.   Equivalent circuit used to fit the experimental results.

The thickness of this protective layer increases with increase in inhibitor concentration, since more inhibitor molecules tend to adsorb on the electrode surface, resulting in a noticeable decrease in Cdl. This trend is in accordance with Helmholtz model, given by following (7) [49-50].

$$C_{dl} = (\varepsilon . \varepsilon_0 . A) / d \qquad (7)$$

Where d is the thickness of the protective layer, ε the dielectric constant of the medium, ε_0 the vacuum permittivity and A is the effective surface area of the electrode. Table II also shows an increase in charge transfer resistance R_{ct}, the optimum of R_{ct}, is reached at a concentration of 30,0 .10^{-4} M which is 609 Ω. it is shown that a large charge transfer resistance is synonymous with a slow corrosion, against an effectiveness of an inhibitor is often associated with a capacitance decreasing [51].

The P of impedance results, are in good agreement with the polarisation and electrochemical impedance spectroscopy studies that shows maximum of 78.11 and 84.36% for BIZT, respectively for the maximum concentration of 30. 10^{-4} (M).

C. Weight loss studies

The values of P, corrosion rate W_L (g.m^{-2}.s^{-1}), and the surface coverage (θ) obtained from weight loss measurements of mild steel after 6 h immersion at different temperatures are shown in Table III. The values of θ were calculated using the following equations [52]:

$$\theta = P/100 \qquad (8)$$

It is observed that this compound inhibits the corrosion of mild steel. The inhibition efficiencies increased with inhibitor concentration in the temperature range of 298–318 K. By increasing the inhibitor concentration, the part of metal surface covered by inhibitor molecules increases and that leads to an increase in the inhibition efficiencies. Thus, these results reveal the capability of BIZT coating to act as a corrosion protective layer on mild steel and its thickness significantly affects the corrosion protection properties. The corrosion protection efficiency may be attributed to the presence of π electrons in the aromatic ring and the pairs of electrons on the nitrogen and Sulphur leads to the effective surface modification of mild steel, and electrostatic attraction between the protonated inhibiting organic ions formed in acidic solutions and the electrically charged surface of metal. It has been observed that in the presence of a concentration of 30.10^{-4} M of BIZT, the efficiency is approximately 98,53 % at 318 K, which proves a very good adsorbability on the carbon-steel's surface.

D. Adsorption isotherm

The adsorption mechanism for a given inhibitor depends on such factors, as the chemical structure the electrochemical potential at the metal/solution interface, the pH and the concentration of the inhibitor as well as the functional groups present in its molecule [53]. Adsorption isotherms provide information about the interaction among the adsorbed molecules themselves and also their interaction with the electrode surface. It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface. The high electron density on the S and N atoms in these organic molecules help to get chemisorbed on the metal surface. It is necessary to determine empirically which adsorption isotherm fits best to the surface coverage data in order to use the corrosion rate measurements to evaluate the thermodynamic parameters pertaining to inhibitor adsorption. The Langmuir adsorption isotherm model has been used extensively in the literature for various metal, inhibitor and acid solution systems [54-57]. We supposed that the adsorption of this inhibitor followed the Langmuir adsorption [58-60]:

$$C/\theta = (1/K_{ads}) + C \qquad (9)$$

Where C is the inhibitor concentration, and K_{ads} is the equilibrium constant for the adsorption/desorption process. From the intercepts of the straight lines on the C/θ-axis, where R is the gas constant.

We can calculate K_{ads}, which is related to the standard free energy of adsorption, ΔG_{ads}, as given by (10) [61-64].

$$\Delta G_{ads} = - R. T. \ln(55{,}5 . K_{ads}) \qquad (10)$$

T is the absolute temperature (K). The value of 55,5 is the concentration of water in solution (M). The negative value of ΔG_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. It is generally accepted that, for values of ΔG_{ads} up to -20 kJ.mol^{-1}, the type of adsorption can be regarded as physisorption, in which case inhibition results from the electrostatic interactions between the charged molecules of the inhibitors and the charged metallic surface. In contrast, for values above -40 kJ.mol^{-1}, the adsorption is regarded as chemisorption, which is due to charge sharing or transfer from the inhibitor molecules to the metal surface to form a covalent bond. The results presented in Table IV indicate that the values of free energy of adsorption (ΔG_{ads}) for all the studied systems lie between -34.038 and -45.315 kJ.mol^{-1}, signifying spontaneous adsorption and confirming the chemisorption mechanism [65-67]. The ΔH_{ads} value is positive, suggests that the adsorption of inhibitor's molecules onto metal surface is an endothermic process, meaning that the inhibition efficiency will increase with increasing temperature. This behavior can be interpreted on the basis that increasing the temperature will lead to strong adsorption of the inhibitor molecules from on the steel surface.

TABLE III. CORROSION PARAMETERS OBTAINED OF MILD STEEL C35E IN 1 M HCL SOLUTIONS WITH AND WITHOUT ADDITION OF VARIOUS CONCENTRATIONS OF BIZT AT DIFFERENT TEMPERATURES

| C (M)	W_L (mg .cm^{-2}.h^{-1})			P			θ		
	298K	*308K*	*318K*	*298K*	*308K*	*318K*	*298K*	*308K*	*318K*
Blank	0,1755	0,3052	12,1075	-	-	-	-	-	-
2,5 .10^{-4}	0,1063	0,0614	0,2758	39,43	79,89	97,72	0,3942	0,7989	0,9772
5,0 .10^{-4}	0,0862	0,0734	0,1866	50,87	75,93	98,46	0,5087	0,7593	0,9846
10,0 .10^{-4}	0,0534	0,0715	0,2164	69,58	75,53	98,21	0,6958	0,7553	0,9821
20,0.10^{-4}	0,0689	0,0365	0,1855	60,22	88,02	98,47	0,6022	0,8802	0,9847
30,0 .10^{-4}	0,0742	0,0518	0,1775	57,72	83,03	98,53	0,5772	0,8303	0,9853
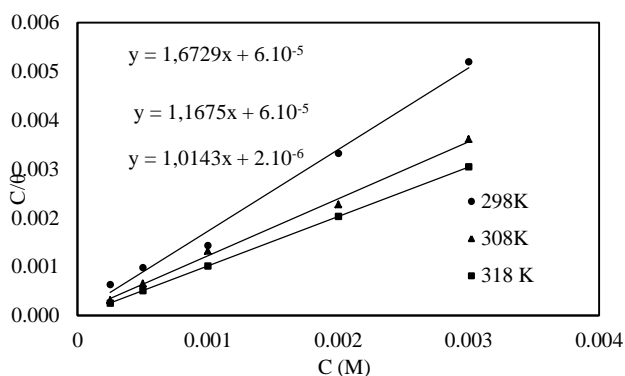
Figure 5. Langmuir adsorption isotherm of BIZT on carbon steel surface in 1 M HC in different temperatures

TABLE IV. ADSORPTION THERMODYNAMICS CONSTANT AND ENTROPY ENERGY OF ADSORPTION OF THE INVESTIGATED INHIBITOR FOR CARBON MILD STEEL IN 1 M HCL IN DIFFERENT TEMPERATURE.

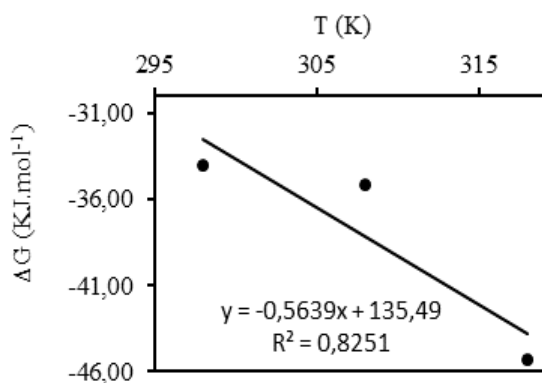| T (K)	Slope	Intercept	R²	K_{ads}	ΔG_{ads} (KJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_{ads} (KJ/mol.K^{-1})
298	1.6729	6 .10^{-5}	0.9904	1,667.10^4	-34,038		
308	1.1604	6.10^{-5}	0,996	1,667.10^4	-34,180	135,49	0,564
318	1.0143	2.10^{-6}	1	5 .10^5	-45,315		

Figure 6. Thermodynamic parameters for the adsorption of BIZT onto the mild steel surface in 1 M HCl.

IV. QUANTUM CHEMICAL STUDIES

DFT is considered as a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. Fig. 7 (a) show the optimized geometry, the HOMO density distribution, the LUMO density distribution and the Mulliken charge population analysis plots for BIMT molecule obtained with DFT at B3LYP/6-31&G (d) level of theory.

From Fig. 7 (b), it could be seen that BIZT might have can have different HOMO and LUMO distributions. The HOMO and LUMO are located on the all molecule structure with preference on the S atom and N atoms, this shows the important role of the S and N atoms in adsorption in metal surface. It is important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some center and is going to back donate a certain amount of charge through the same center or another one [68]. Moreover, unoccupied d orbitals of Fe atom can accept electrons from the inhibitor molecule to form the thiol moiety while the inhibitor molecule can accept electrons from Fe atom with its anti-bonding orbitals to form back-donating bond.

The Mulliken charge of BIZT is shown in Fig. 7 (c), It is clear that the nitrogen atom as well as sulfur atom and some carbons atoms carries negative charge centers which could offer electrons to the mild steel surface to form a coordinate bond. There is a general consensus by several authors that the more negatively charged a heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [69]. Among them, the highest negative charge is domiciled in nitrogen and Sulphur atom. This suggests that this active center with excess charges could act as a nucleophilic reagent. So, the adsorption of the BIZT at the metal surface should also be considered due to the interaction between the unshared electron pairs in the molecule and the metal.

All other important quantum chemical parameters necessary for a meaningful discussion on the reactivity of BIZT are reported in Table V namely the energy of the HOMO (E_{HOMO}), the energy of the LUMO (E_{LUMO}), the E_{HOMO}-E_{LUMO} energy difference (ΔE) and dipole moment (μ).

It is well established in the literature that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the

LUMO energy, as the E_{HOMO}-E_{LUMO} energy gap decreased and the efficiency of inhibitor improved. Quantum chemical parameters listed in Table V reveal that BIZT has high HOMO and low LUMO with high energy gap making it to exhibit a higher inhibitive effect obtained experimentally. It has also been reported that increasing values of μ may facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [70]. The dipole moment of BIZT is 4,761 Debye, which is higher than that of H_2O 1,52 Debye. Thus, the adsorption of the neutral BIMT molecules could occur due to the formation of links between the d orbital of iron atoms, involving the displacement of water molecules from the metal surface [71].

TABLE V.   SOME MOLECULAR PROPERTIES OF BIZT CALCULATED USING DFT AT THE B3LYP/6-311G (D) BASIS SET IN AQUEOUS PHASE.

Parameter	Value
Ionization potential (I)	5,708 eV
Electron affinity (A)	1,128 eV
Absolute hardness (η)	5,144 eV
Absolute electronegativity (χ)	6,272 eV
Softness (σ)	0,194

TABLE VI.   SOME MOLECULAR PROPERTIES OF BIZT CALCULATED USING DFT AT THE B3LYP/6-311G (D) BASIS SET IN AQUEOUS PHASE.

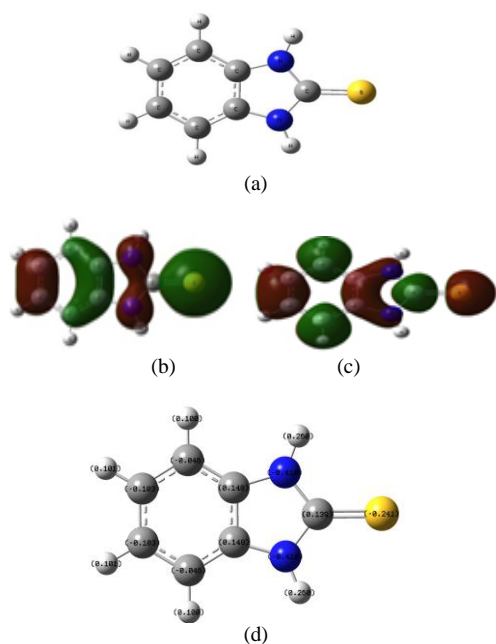| Molecular parameters	Total Energy (a. u.)	Dipole moment (D)	E_{HOMO} (eV)	E_{LUMO} (eV)	Energy gap (ΔE) (eV)
Calculated values	-778.199	4.761	-5,708	-1,128	4,580

Figure 7.   (a) Optimized geometry of BIZT, (b) The highest occupied molecular orbital (HOMO) density and (c) The lowest unoccupied molecular orbital (LUMO) density of BIZT (d) basis set level. (d) The Mulliken charge of BIZT. Using DFT at the B3LYP/6-311G (d) basis set level.

V.   CONCLUSION

- The 2-Benzimidazolethiol inhibitor studied in this work shows excellent inhibition properties for the corrosion of carbon steel in 1M HCl at 318 K, and the inhibition efficiency decreases with the decreasing of the 2-Benzimidazolethiol concentration.

- The inhibition efficiency dependence of the concentration as calculated from electrochemical studies and weight loss measurements were in good agreement. Based on the polarization results, the investigated 2-Benzimidazolethiol acts predominantly as a mixed-type inhibitor.

- The value of ΔG_{ads} and ΔH_{ads} in our measurement suggest that the adsorption of 2-Benzimidazolethiol involves chemisorption.

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