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Investigation of corrosion inhibition of mild steel in 1 M HCl by 3-oxo-[1,4]-benzothiazine derivative (T1) using experimental and theoretical approaches

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ABSTRACT

(Z)-2-benzylidene-2H-[1,4]benzothiazin-3-one (T1) has been evaluated as a corrosion inhibitor for mild steel using weight loss and electrochemical polarization (EIS). The study was also complemented by quantum chemical calculations. The inhibition efficiency (E%) increased with increasing (T1) concentration, showing a maximum E% of 95% at 308 K at 10-3M. The electrochemical study reveals that this compound is an cathodic inhibitor and corrosion current density is the order 120 $\mu\text{A}/\text{cm}^2$ of (T1) at the optimum concentration. EIS results show that the change in the impedance parameters (R_{ct} and C_{dl}) with concentration of (T1) is indicative of the adsorption of molecules leading to the formation of a protective layer on the surface of mild steel. A good fit to Langmuir adsorption isotherm was obtained between surface coverage degree and inhibitor concentration. The results obtained by weight loss measurements are consistent with the results of the electrochemical study. Quantum chemical approach used to calculate electronic properties of the molecule to ascertain the relation between inhibitive effect and molecular structure.

Key words: Mild steel, 1,4-benzothiazine, Inhibition, Corrosion, HCl, Quantum chemical.

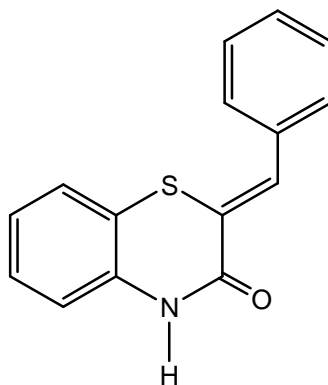
INTRODUCTION

In recent days, studies on steel corrosion phenomena have become an industrial and academic topic, especially in acid media [1,2]. This is because of the increasing industrial applications of acid solutions. The most important fields of applications are acid pickling, industrial cleaning, acid descaling, oil-well acidizing in oil recovery and the petrochemical processes. Aqueous solutions of acids are among the most corrosive media. So, the rate of corrosion at which metals are destroyed in acidic media is very high, especially when soluble corrosion products are formed. Therefore, investigating and exploring corrosion inhibitors for steel corrosion in acid solutions are not only important from an academic point of view but also for its practical applications [3-7].

An inhibitor is a substance that retards the rate of corrosion of metals when added in minute quantity. The chemistry of heterocyclic 1, 4-Benzothiazines possess a wide spectrum of biological and pharmacological activities due to presence of a fold along the nitrogen and sulfur axis, which is considered to be responsible as one of the structural features to impart their activities [8-10]. Different classes of 1,4-Benzothiazines compounds possess an extensive spectrum of pharmacological activities, moiety has been found to have important activities such as analgesic [11,12], antibacterial [13,14], anticancer [15, 16], anticonvulsant [17], antidiabetic [18]. Most inhibitors in use are synthesised from cheap raw materials, some are chosen from compounds having hetero atoms (N, S, O, P) in their aromatic or long carbon chain [19-21]. Several attempts have been made to predict corrosion inhibition efficiency with a number of

individual parameters obtained via various quantum chemical calculation methods as a tool for studying corrosion inhibitors[22-25]. These trials were aimed at finding possible correlations between corrosion inhibition efficiency and a number of quantum chemical properties/descriptors such as dipole moment, highest occupied (EHOMO), lowest unoccupied (ELUMO) molecular orbital, the difference between them (LUMO-HOMO gap) and the dipole moment(μ) as well as some structural parameters.

The present investigation is concerned with the mechanism and efficiency of 3-oxo-[1,4]-benzothiazine derivative (T1) as corrosion inhibitor of mild steel in 1M HCl solution (Scheme 1).

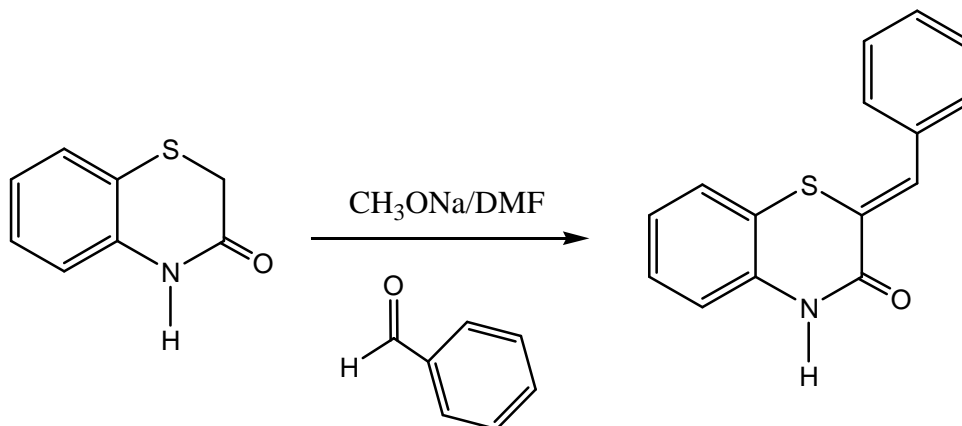


Scheme 1: (Z)-2-benzylidene-2H-[1,4]benzothiazin-3-one:(T1)

MATERIALS AND METHODS

2.1. Synthesis of Inhibitors (T1)

A solution of the 2H-[1,4]-benzothiazin-3-one (2.84mmol) in 10 ml of DMF was added sodium methoxide in excess and benzaldehyde (6.24 mmol). Under stirring, the mixture is led to reflux for 48 h. After filtration of the salts, the filtrate was concentrated under reduced pressure. The residue is purified on silica gel column and recrystallized with hexane.



Scheme 2: Synthesis and characterization of (Z)-2-benzylidene-2H-[1,4]benzothiazin-3-one: (P1)

The analytical and spectroscopic data are conforming to the structure of compound formed.(P1):Yield = 65%; M.p.110-112K; RMN1H (DMSO-d6) δ ppm : 6.99-7.66 (m, 9H, Har); 7.78(s, 1H; =CH-C6H5); 11.02(s, 1H; NH); RMN13C (DMSO-d6) δ ppm : 117.2, 123.7, 125.7, 127.5, 129.2, 129.2, 129.4, 130.3, 130.3, 131.2, (CHar); 115, 4, 120.8, 134.6, 134.7 (Cq), 159.1 (C=O).

2.2. Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of green inhibitor employed was 10⁻³ – 10⁻⁵ (M).

2.3. Weight loss measurements

Coupons were cut into 1.5× 1.5 × 0.05 cm³ dimensions having composition (0.09%P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed

thoroughly with bidistilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm³. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (*v*) is calculated using the following equation:

$$v = \frac{W}{S.t} \quad (1)$$

where *W* is the average weight loss, *S* the total area, and *t* is immersion time. With the corrosion rate calculated, the inhibition efficiency (*E_w*) is determined as follows:

$$E_w \% = \frac{V_0 - V}{V_0} \times 100 \quad (2)$$

where *V₀* and *V* are the values of corrosion rate without and with inhibitor, respectively.

2.4. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from -800 mV to -200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (*E_p*%) is defined as Equation3, where *i_{corr}(0)* and *i_{corr}(inh)* represent corrosion current density values without and with inhibitor, respectively.

$$E_p \% = \frac{i_{corr(0)} - i_{corr(inh)}}{i_{corr(0)}} \times 100 \quad (3)$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at *E_{corr}* after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (*E_R*%) is estimated using the relation 4, where *R_{t(0)}* and *R_{t(inh)}* are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$E_R \% = \frac{R_{t(inh)} - R_{t(0)}}{R_{t(inh)}} \times 100 \quad (4)$$

2.5. Quantum chemical calculations

For the theoretical study, complete geometry optimizations of the molecules were performed using the Density Functional Theory (DFT) with the Beck's three parameter exchange functional and the Lee-Yang-Parr non-local correlation functional (B3LYP) with 6-311G(d,p) basis set of atomic orbitals as implemented in Gaussian 03 program package [26]. Some electronic properties such as energy of the highest occupied molecular orbital (*E_{HOMO}*), energy of the lowest unoccupied molecular orbital (*E_{LUMO}*), energy gap (ΔE) between LUMO – HOMO and dipole moment. The optimized molecular structures and HOMO, LUMO surfaces were visualized using Gauss View [27].

RESULTS AND DISCUSSION

Mild steel corrosion behavior in 1 M HCl was investigated in the absence and presence of 3-oxo-[1,4]-benzothiazine derivative (T1) with the help of weight loss and electrochemical techniques. It was seen that mild steel dissolution rate was very high in 1 M HCl alone but presence of inhibitor significantly decreased the corrosion rate of mild steel.

3.1. Weight loss measurements

The inhibition efficiency (*E_w*) and corrosion rate (*v*) with different concentrations of 3-oxo-[1,4]-benzothiazine derivative (T1) for mild steel in 1.0 M HCl solution at 308k were summarized in Table 1.

Table 1. Corrosion rate and inhibition efficiency in the absence and presence of 3-oxo-[1,4]-benzothiazine derivative (T1) in 1.0M HCl solution

Inhibitor	Concentration (M)	ν (mg.cm ⁻² .h ⁻¹)	Ew (%)
1M HCl	-	0.82	---
3-oxo-[1,4]-benzothiazine (T1)	10 ⁻⁵	0.31	62
	5.10 ⁻⁵	0.19	77
	10 ⁻⁴	0.11	87
	5.10 ⁻⁴	0.07	92
	10 ⁻³	0.04	95

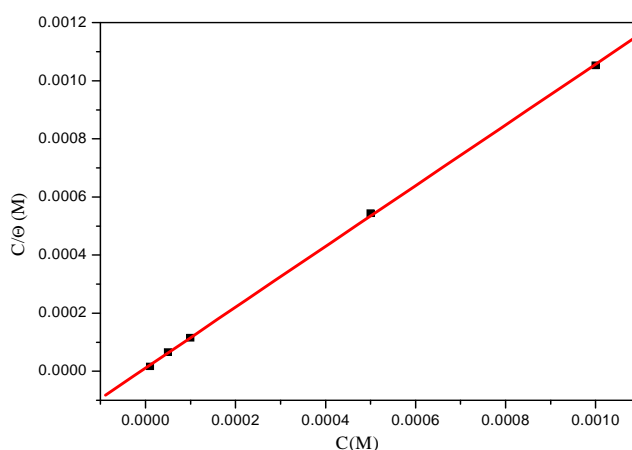
Table 1 shows the results of weight loss of steel in 1 M HCl with and without the addition of various concentrations of T1. It is clear that the corrosion rate decreases with the concentration of the compound tested (T1). The inhibition efficiency, E%, attain 95% at 10⁻³ M.

The protective properties of T1 are probably due to the interaction between τ - electrons of the tow aromatic rings of the 3-oxo-[1,4]-benzothiazine derivative (T1) and the free pairs of electrons of S, N and O atoms with the positively charged steel surface.

3.2. Adsorption isotherm

As known, the adsorption isotherms provide important information on interaction between the inhibitor and the metal surface [28]. In this way, Langmuir adsorption isotherm is generally applied because the inhibitors mostly obey this isotherm [29, 30]. According to Langmuir isotherm, there is a relation between the surface coverage, θ , and inhibitor concentration in mol/L, C, as follows:

$$\frac{C}{\theta} = \frac{1}{k} + c \quad (5)$$

**Figure 1: Langmuir adsorption isotherm of both inhibitor in 1 M HCl at 308K**

Considering Eq. (5), the value of equilibrium constant, K_{ads} , is calculated from the reciprocal of the intercept of C/ θ -axis. R-squared values corresponding to T1 (more than 0.999) show that present inhibitor have a good correlation with Langmuir isotherm (see Figure 1). Afterward, the standard free energy of inhibitor adsorption, ΔG°_{ads} , on metal surface can be calculated using following equation [31]:

$$\Delta G^{\circ}_{ads} = -RT \ln(55.55 K_{ads}) \quad (6)$$

In this expression, R is gas constant, T is absolute temperature and 55.55 is molar concentration of water in one liter solution. It is reported that the high absolute value of ΔG°_{ads} refers to the superior adsorption ability of organic compounds onto the metal surface [32]. The ΔG°_{ads} values calculated for T1 is -39.42 kJ/mol. In general, the values around -40 or more negative are considered as an indication of charge sharing or charge transferring from an organic specie to the metal surface to form a coordinate type of metallic bond (chemisorption) while those values of approximately -20 or less negative are assumed for existing electrostatic interactions between inhibitor and the charged metal surface (physisorption) [33, 34].

3.3. Polarisation results

The potentiodynamic polarization curves for mild steel in 1 M hydrochloric acid solution containing different concentration of thiazin derivative(T1) at 308 K is shown in Figure 2. The intersection of Tafel regions of cathodic and anodic branches gives the corrosion current density (i_{corr}) and the corrosion potential (E_{corr}). Table 2 shows the electrochemical parameters (i_{corr} , E_{corr} , β_c and β_a) obtained from Tafel plots for the steel electrode in 1 M HCl solution without and with different concentrations of 3-oxo-[1,4]-benzothiazine derivative (T1).

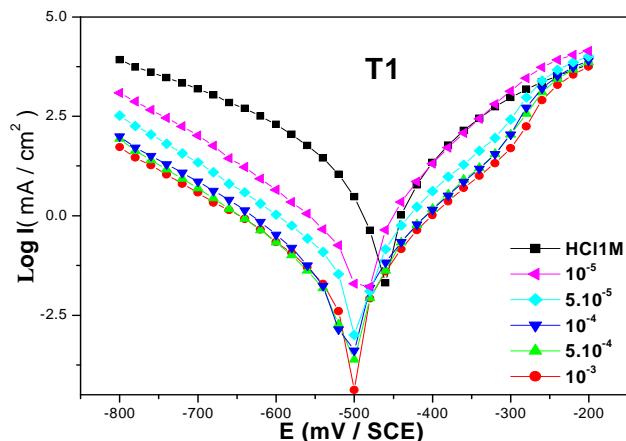


Figure 2: Potentiodynamic polarization curves of mild steel in 1 M HCl at various concentration of T1

Table 2. Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of 3-oxo-[1,4]-benzothiazine derivative (T1) at 308k

Inhibitor	Concentration (M)	$-E_{corr}$ (mV/ECS)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$ (mV/dec)	$-\beta_a$ (mV/dec)	E_p (%)
1M HCl	-	464	1386	184	135	--
3-oxo-[1,4]-benzothiazine (T1)	10^{-5}	488	374	152	109	73
	5.10^{-5}	494	226	162	128	84
	10^{-4}	500	158	163	126	89
	5.10^{-4}	510	144	155	122	90
	10^{-3}	505	120	153	119	92

As it is shown in Figure 2 and Table 2, cathodic polarisation curves rise to parallel Tafel lines, indicating that the hydrogen evolution reaction is activation controlled. Thus, the presence of 3-oxo-[1,4]-benzothiazine derivative (T1) does not affect the mechanism of this process[35]. The addition of molecules tested causes a decrease of the current density. The values of corrosion potential (E_{corr}) and cathodic Tafel slope (β_c) remain almost constant upon the addition of inhibitor concentration. The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration to attain 92 % at 10^{-3} M.

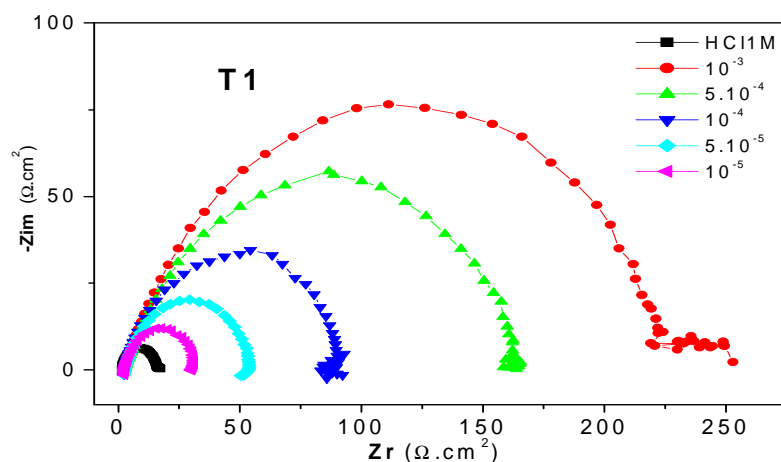


Figure 3. Nyquist plots of mild steel in 1M HCl in presence of different concentrations of inhibitors T1

3.4. Electrochemical impedance spectroscopy

In order to confirm the results extracted from polarization curve and to acquire more information about corrosion mechanisms, EIS measurements were carried out at corrosion potential. The obtained results after immersion in 1 M HCl with and without T1 is presented in Figure.3.

For Nyquist plots (Figure 3) it is clear that the impedance diagrams in most cases does not show perfect semicircle. This behavior can be attributed to the frequency dispersion [36, 37] as a result of roughness and in homogenates of the electrode surface. The impedance response consisted of characteristic semicircles for solutions examined indicating that the dissolutions of mild steel process occurs under charge transfer control in other words under activation control and the presence of the inhibitor does not change the mechanism of the acid dissolution. These semicircles are of a capacitive type whose diameters increase with increasing inhibitor concentration.

Table.3. Impedance parameter values for the corrosion of mild steel in 1M HCl

Inhibitor	Concentration (M)	R _{ct} (Ω cm ²)	C (μf/cm ²)	E _{Rt} (%)
1M HCl	-	14.57	200	--
3-oxo-[1,4]-benzothiazine (T1)	10 ⁻⁵	30	54.29	51.43
	5.10 ⁻⁵	54	48.72	73.02
	10 ⁻⁴	90	28.31	83.81
	5.10 ⁻⁴	162	19.68	91.01
	10 ⁻³	225	17.62	93.52

The values of R_{ct}, C_{dl} and %E for mild steel in 1M hydrochloric acid containing different concentrations for the used inhibitor is shown in Table (3). The data indicate that increasing charge transfer resistance is associated with a decrease in the double layer capacitance and increase in the percentage inhibition efficiency. The decrease in C_{dl} values could be attributed to the adsorption of the inhibitor molecules at the metal surface. It has been reported that the adsorption of organic inhibitor on the metal surface is characterized by a decrease in C_{dl} [38]. Furthermore the decreased values of C_{dl} may be due to the replacement of water molecules at the electrode interface by organic inhibitor of lower dielectric constant through adsorption.

3.5. Quantum chemical studies

The effectiveness of an inhibitor can be related to its spatial molecular structure, as well as with their molecular electronic structure [39, 40]. Inhibitor efficiency depends on the structure and the chemical properties of the inhibitor being adsorbed.

The final geometries and the computational results parameters of T1 are given in Figure. 4 and table 4.

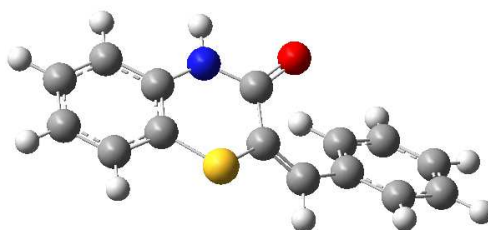


Figure 4. Optimized Structures of T1

The calculated quantum chemical parameters related to the inhibition efficiency of the studied molecule, such as the FMO energies (E_{HOMO}, E_{LUMO}), the gap energy (ΔE) and the dipole moment(μ); are collected in Table 4.

Table 4. Quantum chemical parameters of T1

Quantum parameters	T1
E _{HOMO} (eV)	-0.283
E _{LUMO} (eV)	-0.206
ΔE _{gap} (eV)	0.077
μ (debye)	2.0382

In terms of the frontier molecular orbital theory, HOMO and LUMO energies may be used to predict the adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms. As E_{HOMO} is often associated with the electron donating ability of the molecule, high values of E_{HOMO} mean that the molecule is tended to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Conversely, lower E_{LUMO} values indicate the stronger ability of the molecule to accept electrons. Therefore, the ΔE value

represents an important stability index that helps to predict the inhibitive effect of the calculated molecules [41, 42]. The dipole moment (μ) provides information on the polarity of the whole molecule. High dipole moment values are reported to facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [32]. Several authors have stated that the inhibition efficiency increases with dipole moments values [43, 44]. On the other hand, literature survey reveals that many irregularities appear in the correlation of dipole moments with inhibition efficiency [45, 46]. The dipole moments of T1 is 2.0382D, which is higher than that of H₂O ($\mu = 1.88$ D). The high dipole moment value of this compound probably indicates strong dipole–dipole interactions between them and metallic surface [47]. Accordingly, the 3-oxo-[1,4]-benzothiazine molecule (T1) adsorption in aqueous solution can be regarded as a quasi-substitution process of the water molecules by the inhibitor molecules at metal surface (H₂O_{ads}).

The optimized geometries of the studied compound in the neutral form including their HOMO and LUMO distributions density are shown in Figure. 5.

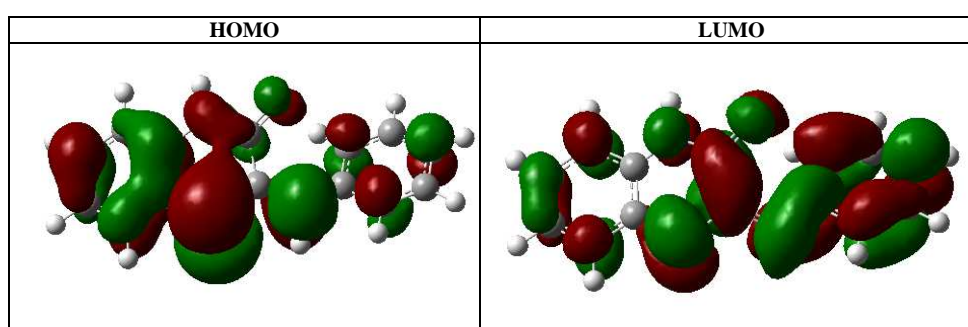


Figure.5. The frontier molecular orbital density distribution of 3-oxo-[1,4]-benzothiazine derivative(T1)

As we know, frontier orbital theory is useful in predicting the adsorption centres of the inhibitors responsible for the interaction with surface metal atoms. Figure.5, show the HOMO and LUMO orbital contributions for the studied inhibitor molecule(T1). For the molecule, the HOMO and LUMO densities were concentrated on rings, S atom and N-atom. This means that these are active sites of the molecules responsible for interaction with metal surface.

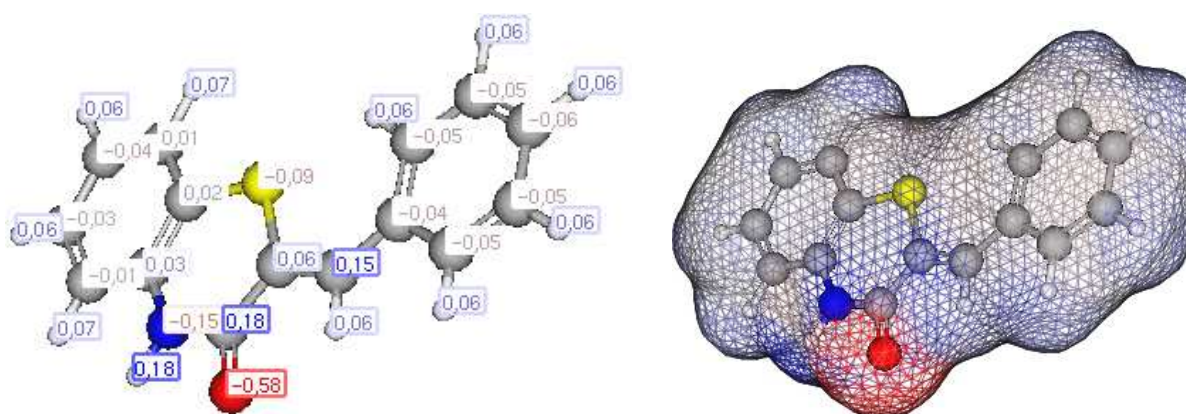


Figure.6. Charge repartition of thiazine derivative(T1)

It has been reported that the more negative the atomic charge of the adsorbed centre, the more easily the atom donates its electrons to the unoccupied orbital of metal [48, 49]. Figure. 6 shows the Mulliken charges of the atoms in thiazine molecule. By careful inspection of the values of Mulliken charges, the largest negative atom is found on the S (-0.09) of the thiazine derivative ring. Other atoms with excess negative charges include N of 3-oxo-[1,4]-benzothiazine group. This is further supported by Figure.6, where the total electron density is located around these atoms.

CONCLUSION

The inhibition efficiency of mild steel corrosion in 1 M HCl by 3-oxo-[1,4]-benzothiazine derivatives has been investigated using electrochemical measurement, weight loss measurements and quantum chemical calculations at (DFT/B3LYP/6-31G (d, p)) level of theory. The following conclusions were drawn from this study:

- Reasonably good agreement was observed between electrochemical measurement and weight loss measurements.
- The examined thiazine derivative (T1) is effective corrosion inhibitor for mild steel in 1M HCl solution.
- The adsorption of (T1) on the mild steel surface was found to obey Langmuir adsorption isotherm.
- The smaller gap between E_{HOMO} and E_{LUMO} favors the adsorption of the synthesized inhibitor on steel surface and enhancement of corrosion inhibition.
- The density distributions of the frontier molecular orbitals (HOMO and LUMO) show that T1 adsorb through the active centers S, N; O and π electrons of the thiazine ring.

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