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Adsorption and corrosion inhibition of mild steel in 0.5 M H_2SO_4 by a new thiazine derivative 2H-benzo[b][1,4]thiazin-3(4H)-one using experimental and theoretical approaches

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ABSTRACT

The inhibition effect of 2H-benzo[b][1,4]thiazin-3(4H)-one (T1) on the corrosion of mild steel in 0.5 M H2SO4 was studied by weight loss, electrochemical impedance spectroscopy (EIS) techniques and potentiodynamic polarization methods. The results showed that (T1) was a good inhibitor in 0.5 M H2SO4 and inhibition efficiency increases with (T1) concentration to attain 91% at 10-3M at 308 K. E(%) values obtained from various methods used are reasonably good agreement. The adsorption of (T1)obeyed the Langmuir adsorption isotherm. Polarization curves showed that (T1) acted as a mixed-type inhibitor in sulfuric acid. 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, benzothiazine, EIS, Corrosion, Weight loss, Electrochemical, DFT.

INTRODUCTION

Acid solutions are commonly used for removal of undesirable scale and rust in metal working,cleaning of boilers and heat exchangers, oil-well acidizing in oil recovery[1–4].Corrosion of metals/alloys is a natural phenomenon that can be controlled upon introducing small quantities of inhibitors into the corrosion environment. Several organic substances were studied for corrosioninhibition of metals/alloys at different corrosive environments [5-8].Inhibitors are used in these processes to control metal dissolution as well as acid consumption. The uses of inhibitors are one of the most practical methods to inhibit corrosion of metals in many environments, especially in acidic media [9].The inhibition efficiency should increase in the order O<N<S<P [10]. In our laboratory, many studies have been published on the use of natural products as corrosion inhibitors in acidic media [11], but little work appears to have been done on the corrosion inhibition of steel alloys in sulphuric acid using pyridazinium derivatives.One technique that has been used to evaluate organic corrosion inhibitors is molecular modeling. Through quantum chemical calculations, it is possible to obtain structural parameters, such as the energies of the frontier molecular orbitals, the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), and the dipole moment. These parameters influence the potential inhibition and are generally strongly correlated with the experimentally obtained inhibition efficiency [12–13].The aim of this paper is to study the inhibiting action of a new organic compound containing nitrogen, sulfur and aromatic ring. The electrochemical behaviour of steel in acidic media in the absence and presence of inhibitor has been studied by electrochemical impedance spectroscopy and gravimetric methods as well as quantumchemical calculations were studied.

MATERIALS AND METHODS

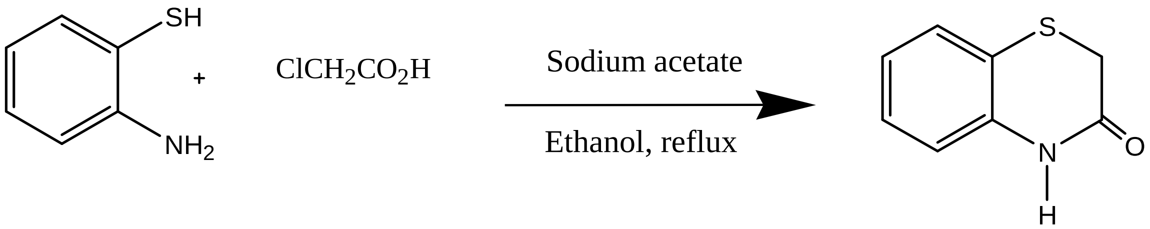
2.1. Materials and solutions

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.

The aggressive solutions of 0.5 M H_2SO_4 was prepared by dilution of analytical grade 98% H_2SO_4 with distilled water. The concentration range of (T1) employed was 10^{-6}–10^{-3} M.

2.2. Synthesis of inhibitors

Sodium acetate (0.24 mol) was added to a stirred solution of 2- aminothiophenol (0.16 mol) and chloroacetic acid (0.16 mol) in ethanol (200 mL). The resulting reaction mixture was heated under reflux for 6 h and the completion of reaction was checked by TLC (Pet ether:Ethyl acetate, 5:5). The reaction mixture was concentrated by evaporation and then poured into ice-cold water to get 2H-benzo[b][1,4]thiazin-3(4H)-one (T1) as a white solid. It was then filtered, dried and recrystallized from ethyl acetate. Yield 83%; (m.p. 176-178 °C). The molecular structure of T1 is shown in scheme 1.



Scheme 1: Synthesis and characterization of2H-benzo[b][1,4]thiazin-3(4H)-one (T1)

The analytical and spectroscopic data are conforming to the structure of compound formed.(P1):Yield = 85%; M.p.176-178K; RMN1H (DMSO-d6) δ ppm:3.43(s, 2H, SCH_2); 6.92-7.30 (m, 4H, Har); 10.51(s, 1H; NH).; RMN13C (DMSO-d6) δ ppm : 30.2(SCH_2); 117.7, 123.3, 127.5, 127.8 (CH_{ar}); 119.5, 137.8 (Cq); 165,7(C=O).
1,4-benzothiazine and its derivatives constitute an important class of heterocyclic compounds which possess a wide range of therapeutic and pharmacological properties[14-17].So as to synthesis of the new derivatives we prepared 2H-benzo[b][1,4]thiazin-3(4H)-one (T1), by the condensation of 2 -aminothiophenol with chloroacetic acid in the presence of sodium acetate in ethanol to reflux (general scheme1).

RESULTS AND DISCUSSION

3.1 Weight Loss Measurements

The weight loss data made primarily at 6 hours of immersion at room temperature (308 K) were given in Table 1, where the inhibition efficiency was calculated using the following equation (1):

$$\text{Ew}\ \% = \frac{V0-V}{V0}\ \text{X}\ 10 \qquad \textbf{(1)}$$

where V_0 and V are the values of corrosion rate without and with inhibitor, respectively.

The fractional surface coverage θ can be easily determined from the weight loss measurements by the ratio Ew (%)/100, where Ew (%) is inhibition efficiency and calculated using Relation (1). The data obtained suggest that the T1 get adsorbed on the mild steel surface at studied temperature and corrosion rates increased in presence of inhibitor in 0.5 M H_2SO_4 solutions.

Table 1.*Corrosion rate and inhibition efficiency in the absence and presence of T1 in 0.5 M H_2SO_4solution at 308K.*

Inhibitor	**Concentration** (M)	***v*** (mg.cm^{-2} h^{-1})	**Ew (%)**
0.5 H_2SO_4	**0.5**	1.450	--
2H-benzo[b][1,4]thiazin-3(4H)-one**T1**	**10^{-3}**	0.091	**91**
	10^{-4}	0.154	85
	10^{-5}	0.201	79
	10^{-6}	0.301	70

Table 1 indicates that the corrosion rate of mild steel decreased on increasing concentration. This behavior could be attributed to the increase in adsorption of T1 at the metal/ solution interface on increasing its concentration. Indeed, the adsorption of the T1 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, and the lone sp2 electron pairs present on the S and/or N atoms [18, 19].

3.2. Adsorption isotherm

The mechanism of the interaction between inhibitor and the electrode surface can be explained using adsorption isotherms. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to provide best description of the adsorption behavior of the investigated inhibitor. The Langmuir isotherm is given by the equation [20]:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad \textbf{(2)}$$

$$\text{With } \Delta G°_{ads} = -RT.\ln(55{,}5.K) \quad \textbf{(3)}$$

Where C_{inh} is the concentration of inhibitor, K the adsorptive equilibrium constant, ΔG_{ads} is the standard free energy of adsorption reaction, R is the universal gas constant, T is the absolute temperature in Kelvin, θ is the fraction of the surface covered calculated as follows θ = Ew(%)/100 and the value of 55.5 is the concentration of water in the solution in mol/L. Figure. 2 shows the dependence of the ratio C_{inh}/θ as function of C_{inh}. Linear plot is obtained with slope and correlation coefficient close to 1.

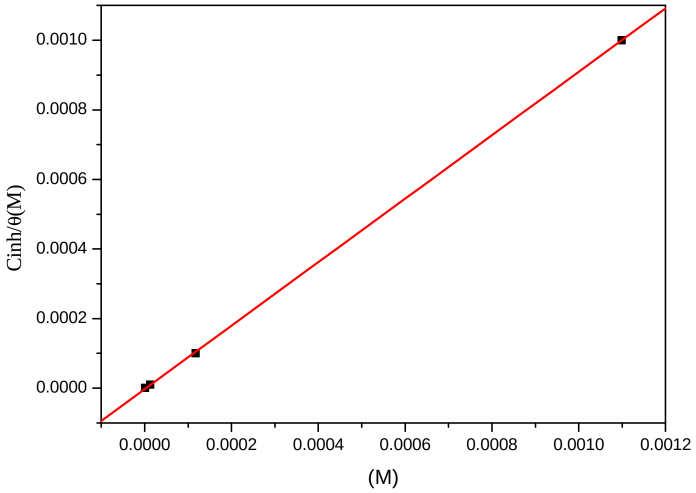


Figure 2:Langmuir adsorption plot of mild steel in 0.5 M H2SO4 solution containing various concentrations of T1

The equilibrium adsorption constant obtained from this isotherm are about 4×10^5 M^{-1}. This is in good agreement with values of inhibition efficiency obtained from the electrochemical and weight loss measurements. Moreover, the largest negative values of ΔG_{ads}= -43.55kJ/mol indicate that this inhibitor is strongly and spontaneous adsorbed onto the mild steel surface. We can note that a plausible mechanism of corrosion inhibition of carbon steel in 0.5 M H_2SO_4 by the compound under study may be deduced on the basis of adsorption. In acidic solutions, this inhibitor exist as cationic species which may be adsorbed on the cathodic sites of the mild steel and reduce the evolution of hydrogen [21]. The protonated inhibitor can also be adsorbed on the metal surface on specifically adsorbed chloride ions [22-23], which act as a bridge between the metal surface and the electrolyte. Moreover, the adsorption of this compound on anodic sites through lone pairs of electrons of S and N atoms and through π-electrons of C=O and phenyl group will then reduce the anodic dissolution of carbon steel.

Generally, the standard free energy values of −20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of −40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [24]. The calculated standard free energy of adsorption value is closer to −40 kJ mol^{-1}. Therefore, it can be concluded that the adsorption is more chemical than physical adsorption [25].

3.2. Polarisation results

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster 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 (Ep%) is defined as Equation 4, where $i_{corr(0)}$ and $i_{corr(inh)}$ represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{\text{icor}(0)-\text{icor}(\text{inh})}{\text{icor}(0)} \text{x } 100 \qquad \textbf{(4)}$$

Anodic and cathodic polarization curves for mild steel in 0.5 M $H_2SO_4$with and without various concentrations of used inhibitor are shown in figure 3.

The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (Ecorr), corrosion currents densities (Icorr) and cathodic Tafel slope (βc) are listed in Table 2.

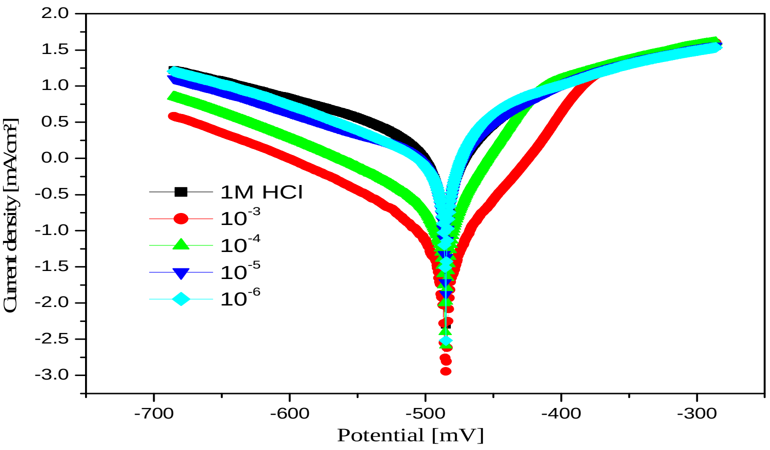


Figure 3. Tafel plot of mild steel with different concentrations of T1 in 0.5 M H_2SO_4solution

It is clear from the Figure 3, that both anodic metal dissolution and cathodic hydrogen reduction reactions were inhibited when the T1 inhibitor was added to 0.5 M H_2SO_4. The corrosion potential is almost unchanged. The corrosion current density as well as corrosion rate of mild steel considerably reduced in the presence of the inhibitor.

Table 2.Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 0.5 M H_2SO_4without and with addition of various concentrations of (T1) at 308k

Inhibitor	**Concentration** (M)	**E**$_{corr}$ (mV/ECS)	**I**$_{corr}$ (µA/cm^2)	**-β**$_c$ (mV/dec)	**Ep** (%)
H_2SO_4	**0.5**	-485	1975	190	
2H-benzo[b][1,4]thiazin-3(4H)-one**T1**	**10^{-3}**	-492	170	146	**91**
	10^{-4}	-492	238	126	88
	10^{-5}	-492	675	163	66
	10^{-6}	-496	992	205	50

The results are indicative of the adsorption of inhibitor molecules on the mild steel surface. The inhibition of both anodic and cathodic reactions is more marked with the increasing inhibitor concentration while the corrosion potential nearly remained the same in comparison with corrosion potential observed in blank solution. These results indicate that the T1 is a mixed-type inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4[26]. The inspection of results in Table 2 indicate that T1inhibits the corrosion process in the studied range of concentrations and Ep (%) increases with these later, reaching its maximum value, 91%, at 10^{-3}M.

3.3. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr 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 30 min of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (E_R%) is estimated using the equation 4, where $R_t(0)$ and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$ER\% = \frac{\mathrm{Rt(inh)} - \mathrm{Rt(0)}}{\mathrm{Rt(inh)}} \times 100 \qquad \mathbf{(4)}$$

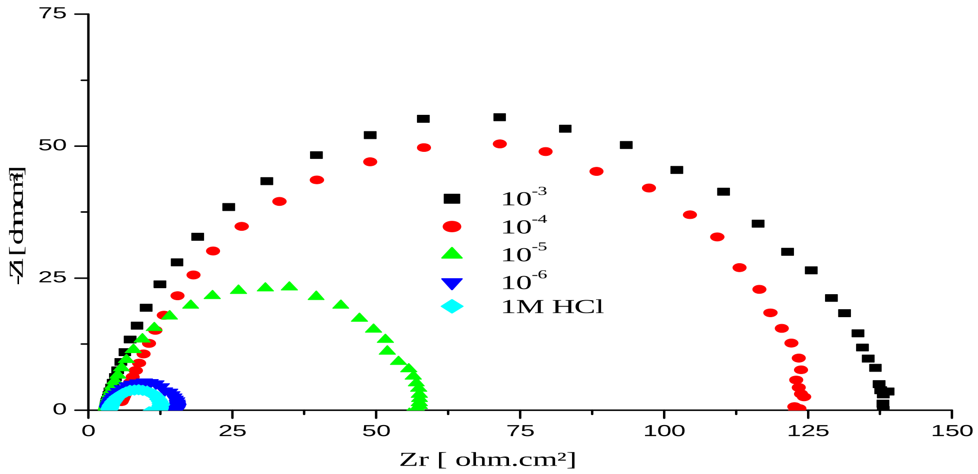


Figure 4:Nyquist plots of the corrosion of mild steel in 0.5 M H_2SO_4 without and with different concentrations of T1 at 308K

Figure4show the Nyquist plot for mild steel in 0.5 M H2SO4 solution in the absence and presence of different concentrations of investigated inhibitor. The impedance diagrams have an approximately semi-circular appearance shows that the corrosion of mild steel in 0.5 M H_2SO_4 is controlled by a charge transfer resistance process. The capacitive loop at high frequene indicates that the corrosion of carbon steel is mainly controlled by a charge transfer process, as is usual in EIS studies, the high frequencies capacitive loop is related to the charge-transfer process occurring during metal corrosion and the double-layer behaviour [27]. The diameters of capacitive loops increase with the increase in T1 concentration, which indicates the increase of charge transfer resistance and improvement in inhibiting effect on carbon steel corrosion (Figure4). It is also observed that the shapes of the impedance plots for the inhibited electrodes are not essentially different from those of the uninhibited electrodes.

Table 3.Impedance parameters of mild steel in 0.5M H_2SO_4 containing different concentrations of T1

Inhibitor	**Concentration (M)**	**R_t** (Ω cm^2)	**C (µf/cm^2)**	**E (%)**
H_2SO_4	**0.5**	12	134	--
2H-benzo[b][1,4]thiazin-3(4H)-one**T1**	**10^{-3}**	135	12	**91**
	10^{-4}	54	26	78
	10^{-5}	46	103	74
	10^{-6}	29	118	59

Table 3 shows the EIS data where the Cdl values decrease and the Rct values increase with the increase of the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, and decreasing the extent of dissolution reaction. The high (Rt) values are generally associated with slower corroding system [28, 29]. The decrease in the Cdl can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [30] suggested that the inhibitor molecules function by adsorption at the metal/solution interface[31,32]. These results again confirm that T1 exhibit good inhibitive performance for mild steel in H_2SO_4 solution.

The order of the inhibition efficiency from the weight loss measurements are in good agreement with those obtained from the EIS and potentio- dynamic polarization methods.

3.5. Theoretical calculations

All quantum chemical study was carried out using the Density Functional Theory (DFT) with hybrid functional B3LYP, based on Becke's three-parameter functional including Hartree–Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke [33,34] together with the nonlocal correction for the correlation energy provided by Lee and al.[35].

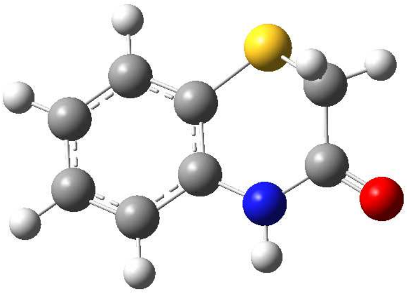


Figure 5: Optimized structures of compound(T1)

Parameters obtained from the quantum chemical calculations including the energy of highest occupied molecular orbital (EHOMO), the energy of lowest unoccupied molecular orbital (ELUMO), the separation energy (ΔE = ELUMO - EHOMO) and the dipole moment (μ) are shown in Table4.

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 [36, 37]. The other important parameter is dipole moment, which can lead to increase of inhibition and can be related to the dipole–dipole interaction of molecules and metal surface [38, 39].

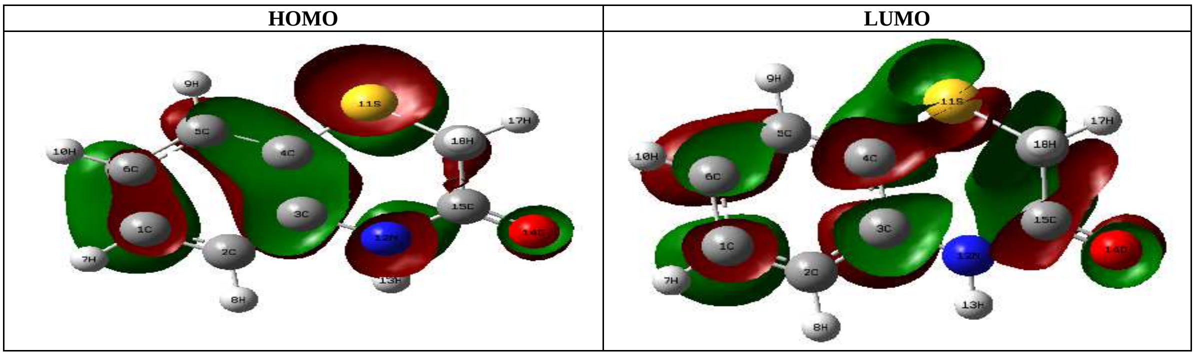


Figure6.The frontier molecular orbital density distribution of benzothiazine compound

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 6, 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, O atoms and N-atom. This means that these are active sites of the molecules responsible for interaction with metal surface.

Table 4.Calculated quantum chemical parameters of the studied compound (T1)

Quantum parameters	**T1**
E_{HOMO}(u.a.)	-0.30774
E_{LUMO}(u.a.)	-0.00947
ΔEgap (u.a.)	0.29827
μ (debye)	**2.6718**

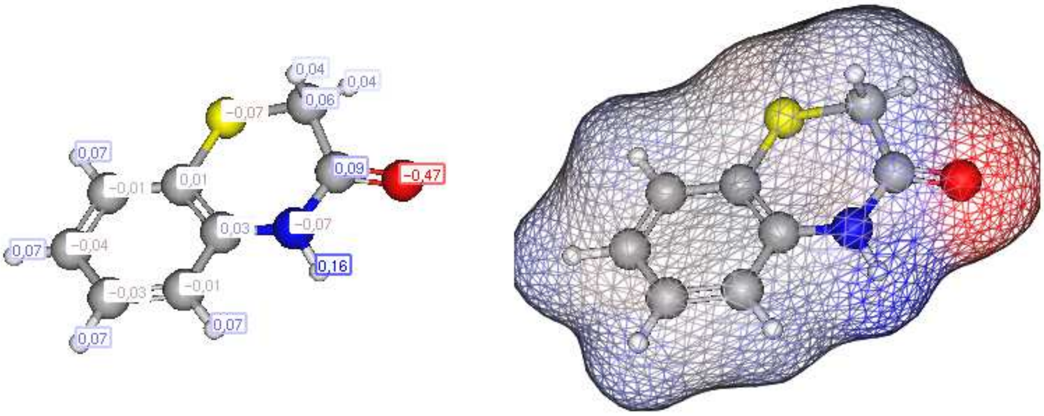


Figure7: Charge repartition of compound (T1).

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 [40, 41].Figure7 shows the Mulliken charges of the atoms in T1 molecule. By careful inspection of the values of Mulliken charges, the largest negative atom is found on the N and S(-0.07) of the benzothiazine one ring. This is further supported by Figure7, where the total electron density is located around these atoms.

CONCLUSION

From the principal result of the present work we can conclude that:
- 2H-benzo[b][1,4]thiazin-3(4H)-onewas found to perform in 0.5 M H2SO4.
- Polarization study showed that the compound under investigation was mixed type inhibitor.
- The inhibition efficiency of the **T1**increased with the concentration and reached 91% at 10^{-3}M.
- The weight loss, polarization curves and electrochemical impedance spectroscopy were in good agreement.
- Adsorption of the inhibitor on the carbon steel surface from 0.5 M H2SO4 followed the Langmuir isotherm.

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