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Inhibition study of mild steel corrosion in hydrochloric acid by new class synthesized 1,4-benzothiazine derivative

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ABSTRACT

Inhibition performance of 2-(3-oxo-2,3-dihydro[1,4]benzothiazin-4-yl)acetic acid named (P1), newly synthesized on the electrochemical behavior of mild steel in molar hydrochloric acid was investigated by using the weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. EIS diagrams show that adsorption of (P1) increases the transfer resistance and decrease the capacitance of interface metal/solution. The inhibition efficiency for this compound studied increased with the increase in the inhibitor concentrations to attain 93% at the 10-3M of (P1). Effect of temperature is also studied between 308 and 353 K. Correlation between quantum chemical calculations and inhibition efficiency of the investigated compound is discussed using the Density Functional Theory method (DFT).

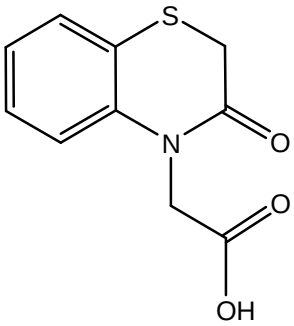
Key words: Mild steel, benzothiazine, EIS, Corrosion, Weight loss, Electrochemical, DFT.

INTRODUCTION

The study of corrosion inhibition is a very active field of research. Several classes of organic compounds are widely used as corrosion inhibitors for metals in acid environments [1–5]. Experimental means are useful to explain the inhibition mechanism but they are often expensive and time-consuming. Ongoing hardware and software advances have opened the door for the powerful use of theoretical chemistry in corrosion inhibition research. Several quantum chemical methods and molecular modeling techniques have been performed to correlate the inhibition efficiency of the inhibitors with their molecular properties [6–10]. Using theoretical parameters helps to characterize the molecular structure of the inhibitors and to propose their interacting mechanism with surfaces [11]. Some studies have shown that the inhibition of the corrosion process is mainly described by the formation of donor–acceptor surface complexes between free or p–electrons of an organic inhibitor, mostly containing nitrogen, sulfur or oxygen atoms, and a vacant d-orbital of a metal [12–18]. Over the years, 1,4-benzothiazines have constituted an important class of heterocyclic which, even when part of a complex molecule [19], possess a wide spectrum of biological activities [20-21], due to the presence of a fold along the nitrogen sulfur axis, the biological activity of some 1,4-benzothiazines is similar to that of phenothiazines, featuring the same structural specificity [22-24]. The role of 1, 4-benzothiazine in medicinal chemistry was reviewed earlier [25]. Generally, benzothiazine and derivatives have

found widespread application as analgesic [26-27], antibacterial [28-29], anticancer [30], anticonvulsant [31], anthelmintic [32].

The present study aimed to test new compounds named [2-(3-oxo-2,3-dihydro[1,4]-benzothiazin-4-yl)acetic acid]:(P1) on the corrosion of mild steel in 1 M hydrochloric acid solution. In this work, we are interested in the synthesis of the title compound for biological activities, by realized the hydrolysis reaction with solution of potassium hydroxide, in water was added to the solution of ethyl 2-(3-oxo-2,3-dihydro[1,4]-benzothiazin-4-yl)acetate in ethanol. The resulting reaction mixture was poured into water and acidified with 4 M HCl to form compound (P1) Scheme 1.



Scheme 1: 2-(3-oxo-2,3-dihydro[1,4]-benzothiazin-4-yl)acetic acid:(P1) [33]

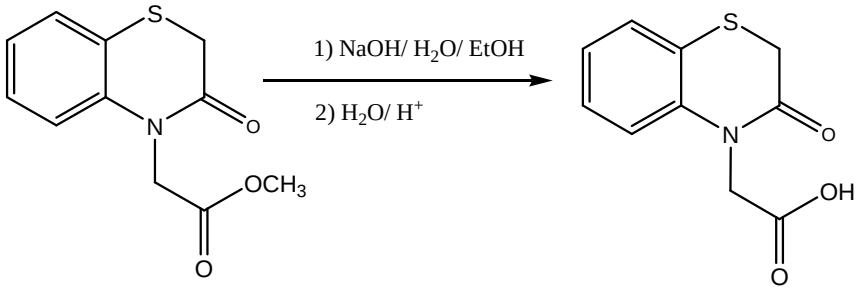
MATERIALS AND METHODS

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 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of inhibitors employed was 10^{-5} - 10^{-3} (mol/l).

2.2. Synthesis of inhibitors

A solution of potassium hydroxide (12.5 mmol) in water (5 ml) was added to the solution of ethyl 2-(3-oxo-2,3-dihydro[1,4]-benzothiazin-4-yl)acetate (3.07 mmol) in ethanol (10 ml). The resulting reaction mixture was stirred at room temperature for 6 h and the reaction completion was checked by TLC. The reaction mixture was poured into water and acidified with 3 M HCl to form 2-(3-oxo-2,3-dihydro[1,4]-benzothiazin-4-yl)acetic acid as colorless solid. Single crystals suitable for X-ray analysis were obtained by crystallization from dichloromethane under slow evaporation (M.p 88-90 K).



Scheme 2: Characterization of 2-(3-oxo-2,3-dihydro[1,4]-benzothiazin-4-yl)acetic acid (P1)

The analytical and spectroscopic data are conforming to the structure of compound formed.

(P1):Yield = 72%; M.p.88-90K; RMN1H (DMSO-d6) δ ppm : 13.32(s, 1H ; OH); 3.66 (s, 2H ; CH2); 4.58 (s, 2H ; NCH2); 7.04-7.41 (m, 4H, Har); RMN13C (DMSO-d6) δ ppm : 30.6(SCH2); 46.8 (NCH2); 118.2, 123.9, 127.8, 128.5 (CHar); 123.1, 139.8(Cq); 165.9, 170,2 (C=O).

RESULTS AND DISCUSSION

Mild steel corrosion behavior in 1 M HCl was investigated in the absence and presence of 1,4-benzothiazine derivative (P1) 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 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):

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

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

It is clear that with the rise in 1,4-benzothiazine derivative (P1) concentration, corrosion rate decreased and then the inhibition efficiency increased. The highest inhibiting efficiency attained 93% at 10-3M. This excellent inhibitory effect merits to be studied at elevated temperatures.

Table 1. Corrosion rate and inhibition efficiency in the absence and presence of 1, 4-benzothiazine derivative (P1) in 1.0 M HCl solution at 35°C

Inhibitor	Concentration (M)	C_R ($mg.cm^{-2} h^{-1}$)	η (%)
1M HCl	**-**	**0.82**	**---**
1, 4-benzothiazine (P1)	**10-6**	**0.21**	**74**
	10-5	**0.17**	**79**
	10-4	**0.11**	**87**
	10-3	**0.06**	**93**

3.2. Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition [34]. The change of the corrosion rate at selected concentrations of the benzothiazine derivative during 1 h of immersion with the temperature was studied in 1 M HCl, both in the absence and presence of benzothiazine derivative . For this purpose, gravimetric experiments were performed at different temperatures (313–353 K).

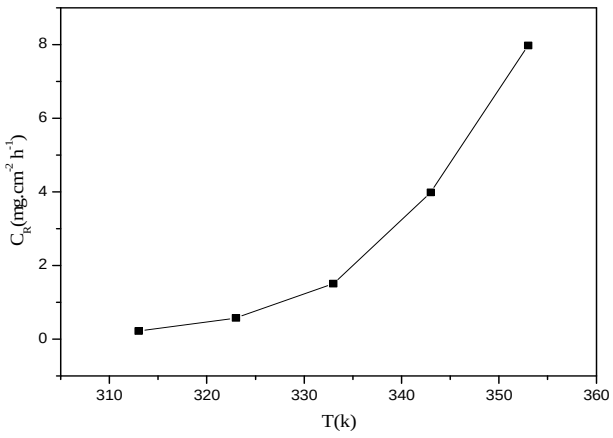


Figure 1: Variations of the corrosion rate (CR) of mild steel in 1 M HCl with 1, 4-benzothiazine derivative (P1) for the temperatures shown in the inset

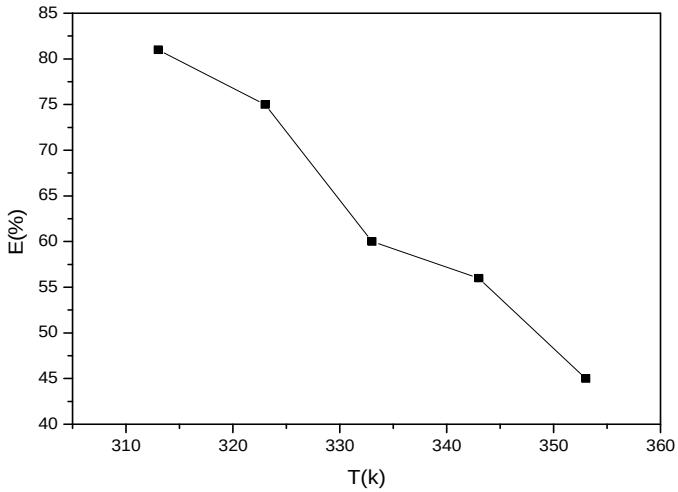


Figure 2: Corrosion inhibition of steel expressed as inhibition efficiency in percentage E(%) as a function of 1,4-benzothiazine derivative (P1) in 1 M HCl solution at different temperatures

It is clear that the corrosion rate increased considerably with the rise of temperature for blank solution. In the presence of the tested molecule, the corrosion rate is highly reduced at moderate temperatures. We observed that the efficiency depends on the temperature and decreases with temperature up to 45% at 353 K. This can be explained by the decrease of the strength of the adsorption processes at elevated temperature, suggesting a physical adsorption mode [35].

The logarithm of the corrosion rate of steel C_R can be represented as a straightline (Fig. 3) function of 1000/T (Arrhenius equation, equation 2), where T is the temperature in Kelvin:

$$Wcorr = K \exp(-Ea/RT) \text{ and } W0corr = K' \exp(-Ea'/RT) \quad (2)$$

Ea'= 94.58 and Ea = 55.24 kJ/mol are the activation energy with and without 1,4-benzothiazine derivative (P1) respectively.

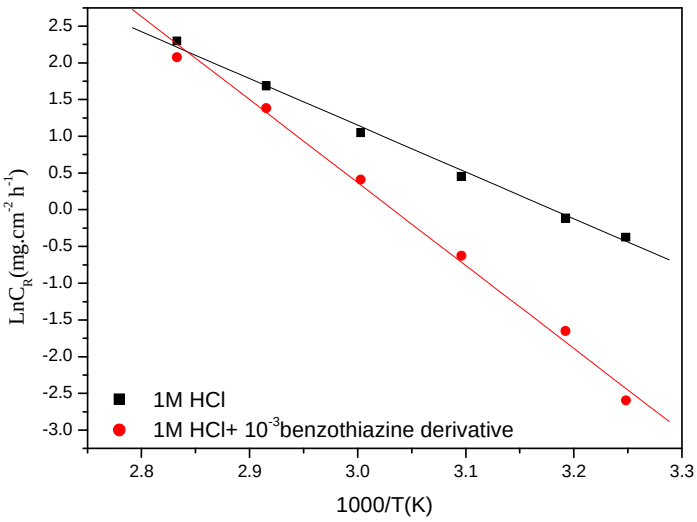


Figure 3: Arrhenius plots of steel in 1 M HCl in the absence and presence of 10-3 M 1,4-benzothiazine derivative (P1)

It is observed that Ea increases in the presence of inhibitor, which indicates poor performance of 1,4-benzothiazine derivative (P1) at higher temperatures. This increase of activation energy is generally interpreted as an electrostatic adsorption process of inhibitor on the steel surface [36].

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 3, where $i_{corr(0)}$ and $i_{corr(inh)}$ represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{icor(0)-icor(inh)}{icor(0)} \text{ x } 100 \quad (3)$$

Anodic and cathodic polarization curves for mild steel in 1.0 M HCl with and without various concentrations of used inhibitor are shown in Figures 4.

Various corrosion parameters such as corrosion potential (Ecorr), corrosion current density (I_{corr}) and the inhibition efficiency (E%) were determined by Tafel extrapolation method [37] and are given in Table 2.

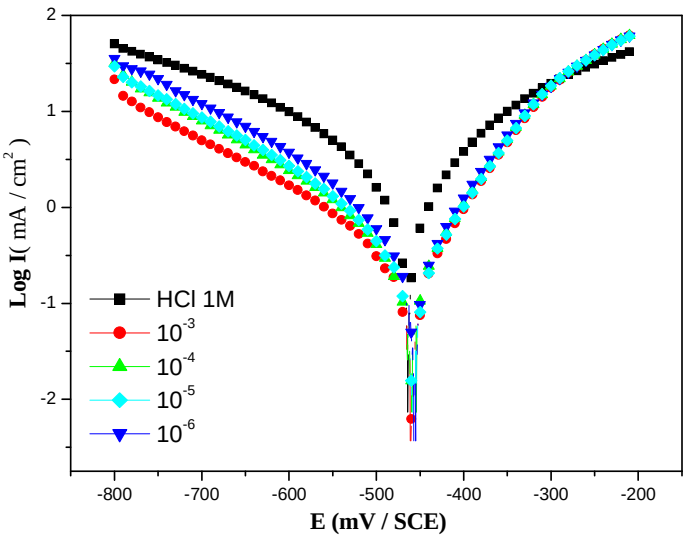


Figure 4. Tafel plot of mild steel with different concentrations of 1,4-benzothiazine derivative (P1) in 1M HCl solution

The analyse of the data in Table 2 revealed that the corrosion current density (i_{corr}) decreases considerably with increasing benzothiazine derivative concentration, while no definite trend was observed in the shift of E_{corr} values. The cathodic Tafel slope (βc) show slight changes with the addition of 1,4-benzothiazine derivative (P1), which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing benzothiazine derivative concentration. The dependence of E(%) versus the inhibitor concentration of benzothiazine derivative is also presented in Table 2. The obtained efficiencies indicate that benzothiazine derivative acts as effective inhibitor. Indeed, the values of E (%) increase with inhibitor concentration, reaching its maximum value, 92%, at 10^{-3} M.

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 1,4-benzothiazine derivative (P1) at 35°C

Inhibitor	Concentration	-E_{corr} (mV/ECS)	I_{corr}	-β_c	η

	(M)		($\mu A/cm^2$)	(mV/dec)	(%)
1M HCl	**-**	**454**	**1205**	**184**	**--**
1, 4-benzothiazine (P1)	**10-6**	**455**	**279**	**128**	**77**
	10-5	**461**	**230**	**128**	**81**
	10-4	**463**	**182**	**135**	**85**
	10-3	**460**	**97**	**152**	**92**

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 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 equation 4, where $R_t(0)$ and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

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

Electrochemical impedance spectroscopy (EIS) is commonly used technique in corrosion researches to explain the mechanisms and adsorption phenomena [38-39]. Especially, in inhibition studies, a single semi-circular shape is observed for mild steel in acidic media. As in previous studies [40-41], the parallel results were detected in EIS data. The EIS results and equivalent circuit were presented in Figs. 5 and 6, respectively**.**

It is the diameter of Nyquist plot shows the difference in real impedance at lower and higher frequencies. The CPE is the constant phase element which is used in place of double layer capacitance (C_{dl}) to give non-ideal capacitive behavior [42]. In Fig. 5, Nyquist plots for mild steel in 1 M HCl solution with, and without different concentrations of the 1,4-benzothiazine derivative (P1) were seen. The Nyquist plots were detected as one part of a semicircle.

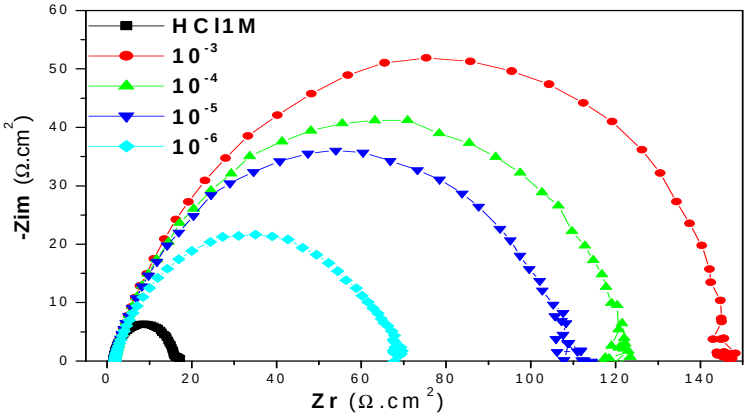


Figure 5: Nyquist plot at different concentrations of 1,4-benzothiazine derivative (P1) in 1M HCl solution

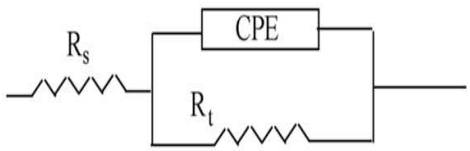


Figure 6: Electrical equivalent circuit model used for the modeling metal/solution

Results obtained show that R_t increases and C_{dl} tends to decrease when the concentration of inhibitor increases. A decrease in the Cdl values, which can result from a decrease in the local dielectric constant and/or an increase in the

thickness of the electrical double layer, suggests that the 1,4-benzothiazine derivative (P1) function by adsorption at the metal solution/interface [43-44].

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

Inhibitor	Concentration (M)	R_t (Ω cm^2)	R_b (Ω cm^2)	C (µf/cm^2)	η (%)
1M HCl	-	14.57	1.37	200	--
1, 4-benzothiazine (P1)	10^{-6}	69	1.53	94.12	79
	10^{-5}	108	1.68	73.62	87
	10^{-4}	122	1.67	67.47	88
	10^{-3}	148	1.68	64.83	90

3.4. Adsorption isotherm

The interactions of 1,4-benzothiazine derivative (P1) inhibitor and the mild steel surface can be examined by the adsorption isotherm. The degree of surface coverage values (θ) for various concentrations of the inhibitors in the solution have been estimated from the different techniques measurements. Suitable adsorption isotherm was obtained, using these calculated values. The linear relationships of C/θ versus C, as shown in Fig 7, suggest that the adsorption of 1,4-benzothiazine derivative (P1) on the mild steel obeyed the Langmuir adsorption isotherm. This isotherm can be represented as [45]:

$$C/\theta = 1/K_{ads} + C \qquad (5)$$

$$\Theta = E/100 \qquad (6)$$

The degree of surface coverage of each inhibitor at a given concentration can be calculated using the above equation (6). The strong correlation (R^2=0.99) of the Langmuir adsorption isotherm for Caffeine was observed. Fig.7. depicts the graph of the Langmuir adsorption isotherm for the studied compound.

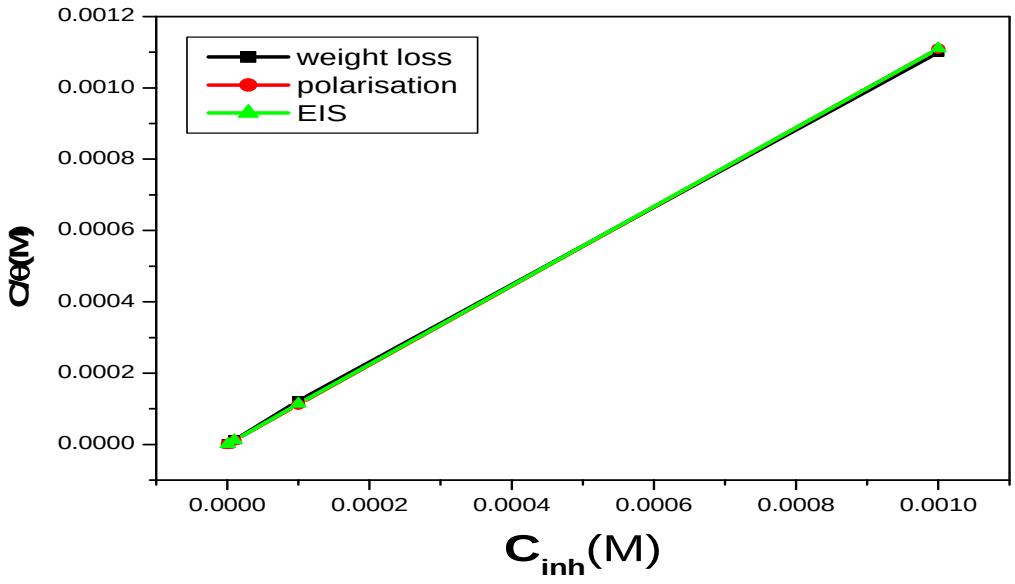


Figure 7: Experimental results at 308 K according to the Langmuir adsorption isotherm for 1,4-benzothiazine derivative (P1) by various methods

3.5. Theoretical calculations

Quantum chemical calculations were performed to investigate the effect of structural electronic parameters on the inhibition efficiency of inhibitor. Previous studies confirmed the fact that, in aqueous acidic solution, these types of compound get protonated and exist as neutral molecule or in the form of cation. The studied compound may absorb on the metal surface in the form of neutral molecule or in the form of protonated molecule. Geometric and electronic structure of the inhibitor was calculated by the complete geometrical optimization in their neutral and protonated form. The obtained molecular structure and HOMO and LUMO orbitals of the neutral inhibitor molecule by DFT/B3LYP/6-31G(d, p) [46] obtained from the DFT calculations are given in Figs. 8 and 9.

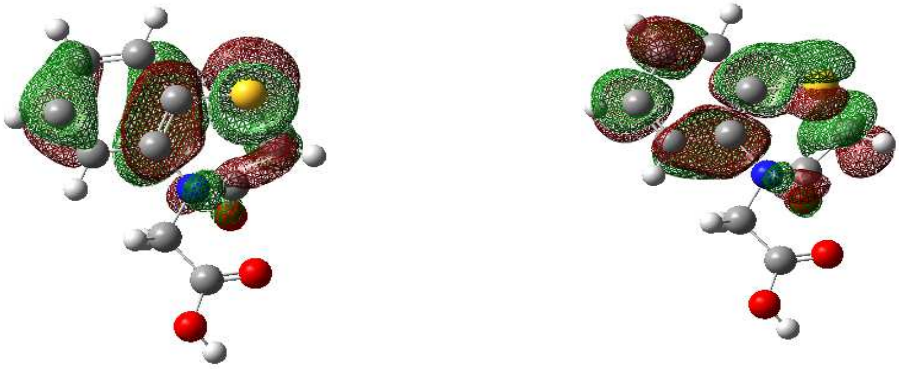


Figure 8: Calculated HOMO and LUMO molecular orbitals of the studied molecule neutral form

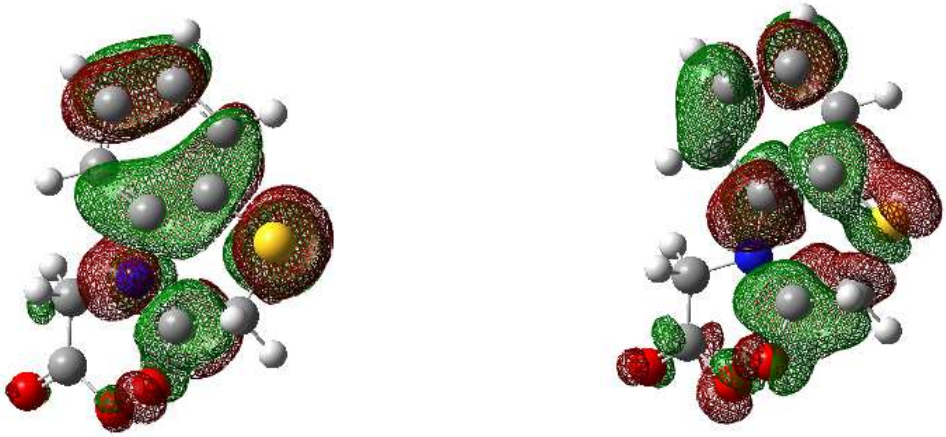


Figure 9: Calculated HOMO and LUMO molecular orbitals of the studied molecule protonated form

Quantum chemical parameters are obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the energies of HOMO (E_{HOMO}), energy of LUMO (E_{LUMO}), energy gap (ΔE) and dipole moment (μ)are shown in Table 4.

Table 4. Calculated quantum chemical parameters of the studied compound

Quantum parameters	Neutral	Protonated
E HOMO (eV)	**-0.31898**	**-0.31055**
E LUMO (eV)	**-0.01268**	**-0.01854**
ΔEgap (eV)	**0.30630**	**0.29201**
μ (debye)	**3.2058**	**4.3656**

The energy of HOMO is often associated with the electron-donating ability of a molecule. Therefore, the energy of LUMO indicates the ability of the molecule to accept electrons [47]. So, the calculations show that the compound protonated, has the highest LUMO level and lowest HOMO. On the other hand, when we examine the obtained values of gap energies, the results obtained show that the compound protonated has a small value of DE gap. This parameter provides a measure for the stability of the formed complex on the metal surface. Even in the literature the correlation between ΔE gap and inhibition efficiency is often cited [48].

The most widely used quantity to describe the polarity is the dipole moment of the molecule [49]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of the charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule, the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments. The calculations show that the benzothiazine derivative neutral has the lowest value of dipole moment. Indeed, the inhibition efficiency decreases with increasing dipole moment [50].

CONCLUSION

The following conclusions are drawn:
➢ The 1,4-benzothiazine derivative (P1) inhibit the corrosion of steel in 1 M HCl solution. The inhibition efficiency increases with the inhibitor concentration.
➢ Inhibitor act essentially as mixed type inhibitor.
➢ The adsorption of inhibitor on the steel surface from 1 M HCl solution follows the Langmuir adsorption isotherm.
➢ The inhibition efficiency of organic compound decrease in the temperature range 308–353 K.
➢ Through the quantum chemical calculations, we have shown that the calculated parameters are correlated with the experimental results,

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