Corrosion and Quantum Studies of Alkyl Substituted Piperidin-4-Ones with Thiosemicarbazone on Mild Steel in an Acidic Medium

V. Shanmuga Priya[1*], C. Uma Rani[1], V. Balachandran[2], S. Velrani[3]

[1*]Department of Chemistry, Govt. Arts College, Salem, India.
[2]Department of Physics, Arignar Anna Govt. Arts College, Musiri, India.
[3]Department of Chemistry, Kamaraj College, Tuticorin, India.

Abstract: The acid corrosion inhibition technique of mild-steel in 1N sulfuric acid by a part of alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazone has been observed by quantum chemical calculations, electrochemical AC impedance measurements, weight loss process and potentiodynamic polarization studies. Results show that substituted γ-2,c-6-diphenyl piperidin-4-ones with thiosemicarbazone act as perfect corrosion inhibitors and their inhibition efficiency increase with the addition of inhibitors. The potentiodynamic polarization curves pointed the studied inhibitors are mixed type of character and cathodic nature in 1 N H_2SO_4 media. The impedance spectroscopy shows a change in the value of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) indicating the adsorption of the some substituted piperidin-4-ones with thiosemicarbazones on the mild steel surface. For all the three types of alkyl substituted 2,6-diphenyl pipieridin-4-one with thiosemicarbazone, the inhibition efficiency raised to increment in the inhibitor concentration and the performance of the three inhibitors are 01TS> 02TS> 03TS. The adsorption of the alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazone on the mild-steel metallic surface pursued the Langmuir's adsorption isotherm. Quantum chemical calculations were executed by adopting density functional theory (DFT) to conclude whether a clear link exists among the inhibiting outcome of the inhibitor and the electronic characteristics of its main fundamentals.

Key Words: Sulfuric acid; Mild-Steel; Inhibitor; Impedance; Polarization.

1. Introduction

Sulfuric acid and hydrochloric acid are mineral acid with extensive applications in different industrial areas. Acid pickling of metals to discharge superficial oxides is one among the largest beneficial industrial application for sulfuric acid. Some other valuable applications include acid descaling, acidizing of oil-wells and acid cleaning. Corrosion inhibitors are frequently needed in this process to minimize the dissolution rate of metallic elements. Mild-steel is an economical metallic material with superior mechanical properties which is extensively utilized in industry. Hence, it is fundamental to find appropriate inhibitors for control of mild-steel metallic corrosion in sulfuric acid solutions. Many organic compounds a specially those containing unsaturated double bonds and triple bonds, electronegative atoms (sulfur, nitrogen and oxygen) and aromatic rings have proposed as productive organic inhibitors for mild-steel metallic corrosion in acid media [1-5]. These compounds may get adsorbed onto the metal surface and hinder active surface sites. This causes a lower in the rate of corrosion [6]. The establishment of the inhibitor coating on the metal surface decides the physicochemical type of the molecule, which is lead by the presence of some functional groups, aromaticity, nature and character of corrosive medium, steric effects, electronic density of the donors, the charge on the metal facial, the skeleton of the inhibitor and the type of the synergy between the p-orbitals of the inhibitor and the d-orbitals of the mild-steel [7]. The compounds with functional groups acquitting heteroatoms are capable of contributing to a lone pair of electrons, which are helpful mainly as organic inhibitors for metal corrosion [8-15]. The inhibition character of the Schiff base compounds against corrosion metals has been extensively stated in the literature. The Schiff bases are ketone and aldehyde like organic compounds where the carbonyl (C=O) functional group has been alternated by imine (C=N) group. The Schiff base compounds can be conveniently synthesized at high purities through a forthright synthetic procedure using quietly inexpensive materials. These compounds have important characteristics such as antitumor, antimicrobial,

antiviral and antifungal properties and are used for plant growth regulation. Piperidin-4-ones have been stated to inhibit mild-steel of acid corrosion [16]. The present effort involves the research of the corrosion inhibition efficiency of the alkyl substituted 2,6-diphenyl piperidin-4-ones with thiosemicarbazone on mild-steel inhibition of corrosion in 1 N sulfuric acid. To examine the inhibition of corrosion adopting the weight loss process, electrochemical AC impedance spectra and potentiodynamic polarization approach. The quantum parameters calculation helps us to determine the molecular structure, the chemical and physical form of bonding and HOMO-LUMO energy gap (ΔE). The occurrence of an electron crowd in the aromatic ring and the electronegative nitrogen or sulfur is likely to cause higher adsorption of the compound on the mild-steel metallic surface, which can direct to effective inhibition.
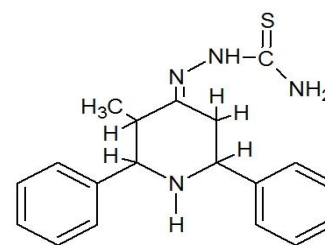
2. Materials and Methods

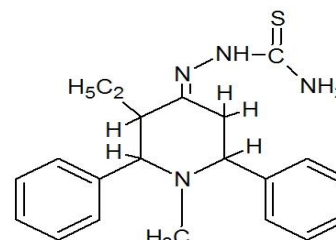### Synthesis of Alkyl Substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazones

The alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazone are processed by that of Noller and Baliah [4, 17 and 20] and re-crystallized from ethanol. The inhibitors utilized in this present analysis are (01TS) - Thiosemicarbazone of γ-2, c-6-diphenyl-t-3-methyl piperidin-4-one, (02TS) - Thiosemicarbazone of γ-2,c-6-diphenyl-t-3-ethyl-N-methyl piperidin-4-one, (03TS)- Thiosemicarbazone of γ-2, c-6-diphenyl-t-3-ethyl piperidin-4-one as shown in the Fig. 1.

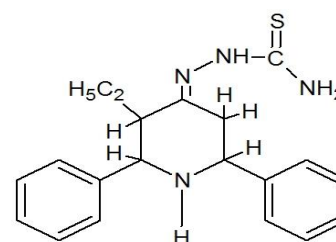### Preparation of the mild-steel specimen

Below mention composition of mild-steel specimens has been utilized during the present work. Silicon 0.07%, Phosphorous 0.008%, Manganese 0.35% and Carbon 0.07%. The mild-steel specimen of 5×2.5 cm^2 is polished with emery papers and it is degreased with trichloroethylene. The same has been utilized in the weight loss process.

(01TS)

(02TS)

(03TS)
Fig. 1 Structure of the inhibitors.

Weight loss method

The mild-steel specimens are suspended in triplicate in 250 ml of the sulfuric acid with the inhibitor (alkyl substituted 2,6-diphenyl piperidin-4-ones with thiosemicarbazone) for one hr. The weight of the mild-steel specimens previous immersion and after immersion is calculated. Then the corrosion inhibition is measured by applying the following equation.

Corrosion rate (in ml/year) = $87.6 \times W / (D \times A \times T)$ (1)

Where A = Area of exposure (in square centimeters), D = Density (in gram per cubic centimeter), W = Weight loss (in milligram) and T = Time (in hours).

Inhibitor efficiency (IE) has been derived by utilizing the coming equation

Inhibitor efficiency (%) = $(W_0 - W_e / W_0) \times 100$ (2)

Where W_0 is the weight loss without inhibitor and also W_e are the weight loss with an inhibitor.

Electrochemical measurements

Electrochemical measurements are built in a glass cell with a volume of 100 *ml*. A saturated calomel electrode and a platinum electrode are utilized as a reference electrode and a counter electrode correspondingly. The mild-steel electrode is located inside the test solution (uninhibited and inhibited solutions) for 10-15 minutes previously the electrochemical measurements.

Electrochemical AC impedance spectroscopy (EIS) and Tafel polarization are performed in an electrochemical measurement unit (Model 1280 B Solartron, UK). The EIS measurements are built at corrosion potentials accomplished a frequency spectrum of 10 kHz to 0.01 Hz with signal amplitude of 10 mv. The Tafel polarization measurements are made later EIS for a potential range of -200 mv to +200 mv with relative to open circuit potential, at a scan rate of 1 mv/Sec. The I_{corr}, E_{corr}, R_t and C_{dl} values are received from the data using the corresponding "Corr view" and "Zview" software's. The metallic corrosion inhibition efficiency (IE) arising out of potentiodynamic polarization is computed from the value I_{corr} by using the formula [18-20].

$$\text{Inhibition efficiency} \ (\%) = \frac{I_{corr(blank)} - I_{corr \ (inh)}}{I_{corr \ (blank)}} \times 100 \qquad (3)$$

Where $I_{corr \ (blank)}$ is the corrosion current in the absence of inhibitor and $I_{corr \ (Inh)}$ is the corrosion current in the presence of inhibitors. The inhibition efficiency from electrochemical impedance measurements was calculated utilizing the formula [16,20].

$$\text{Inhibition efficiency} \ (\%) = \frac{R_{t(inh)} - R_{t(blank)}}{R_{t(inh)}} \times 100 \qquad (4)$$

Where $R_{t \ (blank)}$ is the charger transfer resistance in the absence of inhibitor and $R_{t \ (Inh)}$ is the charge transfer resistance in the presence of inhibitors.

3. Results and Discussion

Weight loss process

Table 1 delivers the standards of the inhibition efficiency and corrosion rate with different concentration (0.2, 0.4 and 1.0) of few alkyl substituted 2,6-diphenylpiperidin-4-ones

with thiosemicarbazone [21] on mild-steel corrosion in 1 N sulfuric acid media have been computed by a weight loss process at 303 K.

Table 1 Corrosion parametric quantity of Alkyl substituted 2,6-diphenyl piperidin-4-ones with thiosemicarbazone on mild-steel in 1 N sulfuric acid from weight loss measurements (303K).

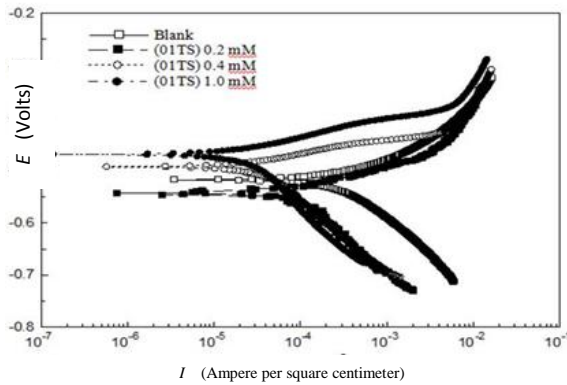| Name of the inhibitor and concentration		Weight Loss (*gram*)	Corrosion Rate (milli miles per year)	Inhibition efficiency (%)	Surface Coverage (θ)
Blank		0.0890	79.96		
01TS	0.2	0.0177	15.9	80.11	0.8011
	0.4	0.0091	8.2	89.78	0.8978
	1	0.0014	1.26	98.43	0.9843
02TS	0.2	0.0233	20.93	73.82	0.7382
	0.4	0.0172	15.45	80.67	0.8067
	1	0.0061	5.48	93.15	0.9315
03TS	0.2	0.0245	22.01	72.47	0.7247
	0.4	0.0179	16.08	79.89	0.7989
	1	0.0094	8.45	89.44	0.8944

The weight loss process indicates the inhibition efficiency (IE) raises with an increment in inhibition concentration and also the corrosion rate of the inhibitor decreases than to blank solution, it conveys that the alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazones react as a corrosion inhibitor. The surface courage (θ) of the corrosion inhibition raised to raise in the different concentration of the inhibitor. The optimum inhibition efficiency of these compounds achieved even at very low concentration. The effect of concentration of alkyl substituted 2,6-diphenyl piperindin-4-one with thiosemicarbazones on weight loss processes disclose that the metal-loss gently lowered with rising inhibitor concentrations. The structure of inhibition efficiencies (IE) of these inhibitors at 303 K is (01TS) > (02TS) > (03TS). Examination of the inhibition efficiencies of inhibitors (01TS), (02TS) and (03TS) explains that inhibition efficiency, decrease when it is substituted with various groups at 3-position of the piperidin-4-one ring. This tendency can be suggested by the conformations of substituted piperidin-4-ones and steric hindrance formed by the substitutes [20].

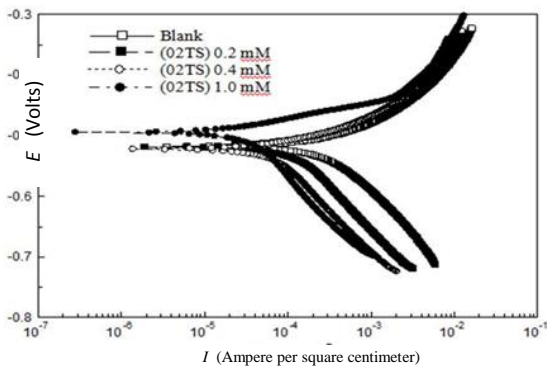**Potentiodynamic polarization method**

Fig. 2 to 4 indicates the potentiodynamic polarization plots of the alkyl substituted 2,6-

diphenyl piperidin-4-ones of thiosemicarbazone in 1N sulfuric acid at different concentrations at 303K. The kinetic parameters of inhibition of corrosion acquired from these plots are disclosed in Table 2.

Fig. 2 Potentiodynamic polarization graph for mild-steel in 1 N sulfuric acid in the before and after addition of (01TS).

Fig. 3 Potentiodynamic polarization graph for mild-steel in 1 N sulfuric acid in the before and after addition of (02TS).

Fig. 4 Potentiodynamic polarization graph for mild-steel in 1 N sulfuric acid in the before and after addition of (03TS).
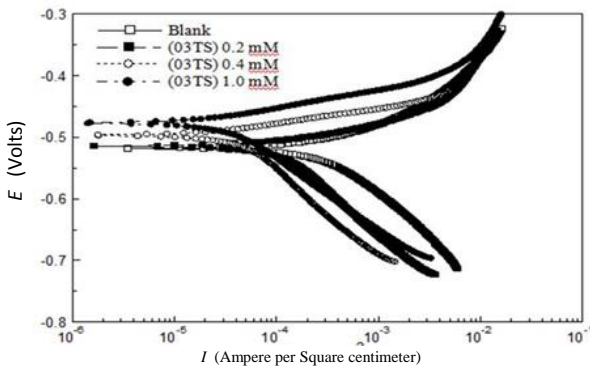
Table 2 Potentiodynamic polarization parametric quantity of the mild-steel in 1 N sulfuric acid with and without Alkyl substituted piperidin-4-ones with thiosemicarbazone

Name of the Inhibitor and concentration		I_{corr} (µA/cm²) ×10⁻²	E_{corr} (mV vs Saturated calomel electrode)	ba (mV/decade)	bc (mV/decade)	Corrosion Rate (ml/year)	Inhibition Efficiency (%)
Blank		4.57	-524	120	-137	104.71	
01TS	0.2	0.69	-547	46	-147	15.81	84.90
	0.4	0.35	-498	39	-131	8.02	92.34
	1.0	0.26	-469	35	-122	5.96	94.31
02TS	0.2	1.30	-533	79	-136	29.79	71.55
	0.4	0.48	-532	55	-133	11.00	89.50
	1.0	0.31	-495	32	-135	7.10	93.22
03TS	0.2	1.07	-525	48	-139	24.52	76.57
	0.4	0.46	-494	30	-140	10.54	89.93
	1.0	0.39	-478	35	-116	8.94	91.47

From Table 2, it can identify that as the inhibitor concentration increases, the I_{corr} value reduces and the inhibitor efficiency increases apparently and this shows the inhibiting character of the inhibitor. The least corrosion rate in potentiodynamic polarization examination exhibit that the inhibitor has definitely performed on the mild-steel metal surface. A distinction in the values of Tafel constant of b_a and b_c concluded the character of the inhibitor. An increment in the b_c values in the concentration of the organic inhibitor is a typical aspect of a cathodic inhibitor, which reveals a higher in the energy barrier for proton discharge prominent to less gas evolution. The variation of b_a and b_c values in the several concentrations of inhibitor in 1 N sulfuric acid are presented in Table 2. Examination of the results exposes that b_a and b_c values do not shift appreciably with the concentration of Alkyl substituted Piperidin-4-ones with thiosemicarbazone and slight variation is observed. The E_{corr} value shifts in the direction of less negative region when the concentration of the inhibitor is improved. This is associated to enhanced inhibitor adsorption on the mild-steel metallic surface. Thus, some alkyl substituted 2,6-diphenyl Piperidin-4-ones with thiosemicarbazone may be measured as a mixed type character of organic inhibitors having more cathodic character.

AC impedance method

Nyquist graphs for mild-steel metallic corrosion inhibition in 1 N sulfuric acid for alkyl substituted 2,6-diphenyl piperidin-4-ones of thiosemicarbazone exhibited in the Fig. 6 to 8. The Impedance range of the Nyquist plots is described by fitting the experimental data to a simple equivalent circuit model as exposed in Fig. 5. It exists of the solution resistance (R_s) and the double layer capacitance (C_{dl}) which is organized in parallel to the charge transfer resistance (R_{ct}) [12 and 4]. Table 3 provides the significance of double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}) and inhibition efficiency.
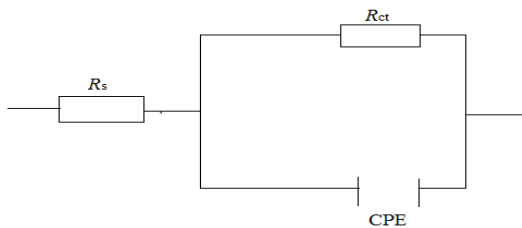

Fig. 5 Equivalent circuit model for fitting impedance spectra.

The Charge transfer resistance R_{ct} values are determined from the variation in impedance at low and high frequencies. The R_{ct} value is a determined of electron transfer over the surface of mild-steel, that is inversely proportional to the rate of the corrosion. The double layer capacitance C_{dl} is estimated at the frequency f_{max} at which the imaginary component of the impedance is maximal using the equation [18,4,20].
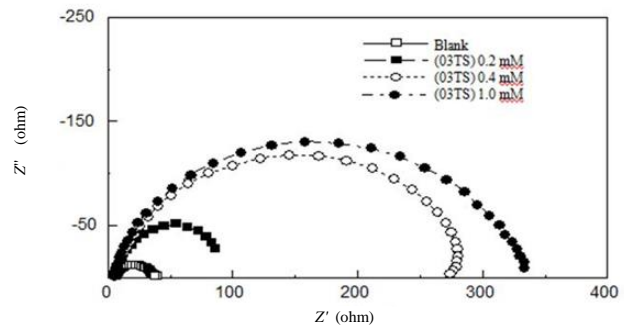
$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad (5)$$
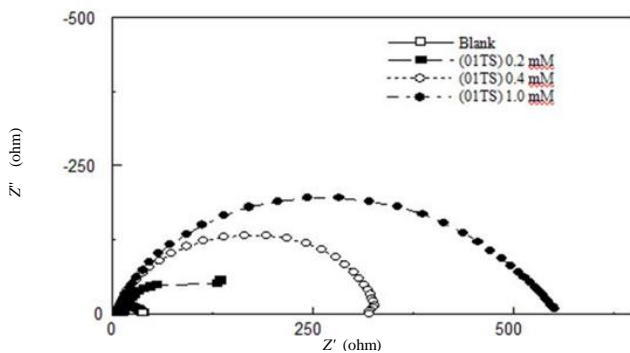
Fig. 6 Nyquist graph of mild-steel corrosion in 1 N sulfuric acid in the absence and presence of (01TS).
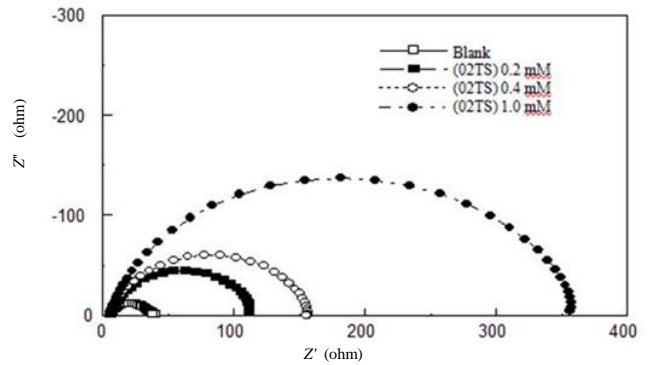
Fig. 7 Nyquist graph of mild-steel corrosion in 1 N sulfuric acid in the absence and presence of (02TS).

Fig. 8 Nyquist graph of mild-steel corrosion in 1 N sulfuric acid in the absence and presence of (03TS).

The data from Table 3 shows that R_{ct} value rises with a rise in concentration of inhibitor. The addition of inhibitor decreases the C_{dl} values, because the absorption of inhibitors on the metal surface (expansion in the surface courage of inhibitor). The impedance diagrams are almost semi-circular, illustrate that the corrosion of mild-steel is chiefly inhibited by a charge transfer method, and the existence of inhibitor does not influence the dissolution mechanism of mild-steel [1,3 and 4]. The data on inhibition efficiency attained from impedance measurements are good agreements with the weight loss process and potentiodynamic polarization measurements.

The inhibitor using in the present research has two groups of anchoring sites, namely ring Nitrogen and thiosemicarbazone group. Usually, these types of compounds exist either in a boat or in chair conformation. The Alkyl substituted 2,6-diphenyl Piperidin-4-ones with thiosemicarbazone chair conformation is the preferred conformation as phenyl and alkyl substitutions are in equatorial orientations. The inhibition efficiency of these compounds is higher. The interaction of these compounds with mild metal surface could appear either over a

carbonyl group or through ring nitrogen, but not over both of carbonyl group or nitrogen as they are in para position to one another. The simultaneous participation of both the groups is ruled out, because it would be possible only through the attainment of boat conformation that is highly strained. Further, the less electro negativity of nitrogen than sulfur support, ring nitrogen to be the inhibiting site [16, 20]. The inhibition efficiency is further increased by converting carbonyl group to thiosemicarbazone group. Here we also expect the involvement of either thiosemicarbazone group or ring nitrogen because of the presence of substitutes. The high inhibition may be on account of the attraction between nitrogen and sulfur atom of thiosemicarbazone and metal surface. The present investigation indicates that all the three corrosion monitoring techniques complement with each other. Analysis of inhibition efficiency of the three different inhibitors shows the following trends: (01TS) > (02TS) > (03TS).

Table 3 Impedance parametric quantity of the mild-steel in 1 N sulfuric acid with and without Alkyl substituted piperidin-4-ones with thiosemicarbazone

Name of the inhibitor and concentration		R_{ct} (ohms)	C_{dl} (μ faraday)	Inhibition efficiency (%)
Blank			32.13	0.14	
01TS	0.2	167.75	0.19	80.85
	0.4	332.28	0.10	90.33
	1.0	541.12	0.17	94.06
02TS	0.2	107.52	0.48	70.12
	0.4	161.49	0.15	80.10
	1.0	356.79	0.11	90.99
03TS	0.2	89.82	0.17	64.29
	0.4	257.06	0.83	87.50
	1.0	341.22	0.71	90.58

Adsorption isotherm

Organic molecules are helping to inhibit corrosion as they adsorbed on the metal-solution integrates. The adsorption anticipate on the chemical sharing of the solution, chemical skeleton of the inhibitor, temperature, the environment of the metal surface, and electrochemical potential at the metal-solution integrates. The adsorption procedure provides awareness about the adsorbed molecules themselves in addition to their cooperation with the metal surface. The standards of surface coverage (θ) equivalent to several

concentrations of an inhibitor (C) are utilized to attain the finest adsorption isotherm. The θ values have been computed using the following relationships

$$\theta = \frac{1 - W_{inh}}{W} \quad (6)$$

(From weight loss process) and

$$\theta = \frac{1 - C_{dl(inh)}}{C_{dl}} \quad (7)$$

(From impedance method)

The Langmuir adsorption isotherm is indicated as

$$\theta = \frac{K}{1 + KC} \quad (8)$$

Where C is the concentration and K is the equilibrium constant for the adsorption procedure. The above equation might be modified as $\frac{C}{\theta} = \frac{1}{K} + C$

A straight line with slope equal to unit is obtained when plotting C/θ vs C when the experimental data follow Langmuir adsorption isotherm. The existing study Langmuir adsorption isotherm was observed throughout all the inhibitors on mild-steel in 1 N sulfuric acid. Langmuir plots are disclosed in Fig. 9 for which θ values are attained from weight loss measurements. Equilibrium adsorption constants are intended from the Langmuir plot and specified in Table 4. The high value of K communicates that the inhibitor is firmly adsorbed on mild-steel metallic surfaces.
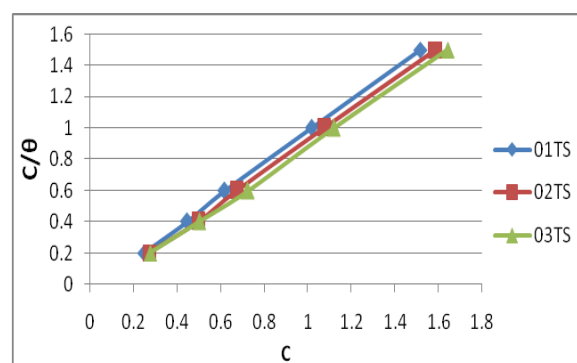
Fig. 9 Plot of C/θ vs C for mild steel in 1N sulfuric acid medium containing various concentrations of inhibitors.
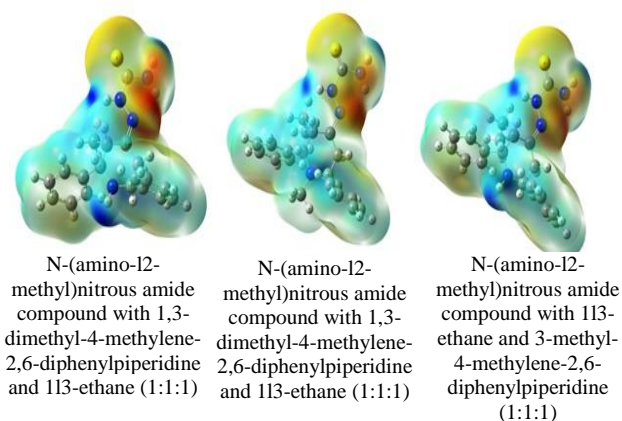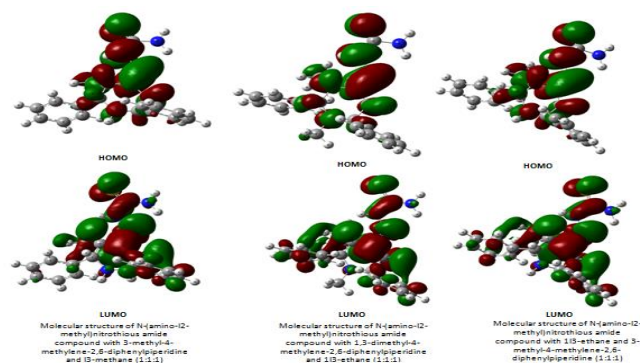
Table 4 Equilibrium constants from Langmuir adsorption isotherms.

Name of the inhibitor	K
01TS	20.66
02TS	13.05
03TS	12.50

Quantum chemical calculations

Quantum chemical estimations were shown from experimental results that it is possible to receive a better performance with inhibitors as a corrosion organic inhibitor. It had been expressed that the energy of highest occupied molecular orbital (E_{HOMO}) regularly pooled with the electron donating ability of the molecules. Greater values of E_{HOMO} mark a type of the molecule to donate electrons to perform with acceptor molecules with empty molecular orbital or low energy unfilled. Accordingly, the energy of lowest unoccupied molecular orbital (E_{LUMO}) shows the intelligence of the molecule to accept electrons. The least value of E_{LUMO} suggests the molecule accepts electrons more possible.

The electronic characteristics like energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (E) between E_{HOMO} and E_{LUMO} on the backbone atoms observed by optimization. The optimized molecular skeleton of inhibitor was given in Fig. 10. The HOMO and LUMO surfaces for inhibitor given in Fig. 11. The electronic properties are detailed in Table 4.

N-(amino-l2-methyl)nitrous amide compound with 1,3-dimethyl-4-methylene-2,6-diphenylpiperidine and l3-ethane (1:1:1)

N-(amino-l2-methyl)nitrous amide compound with 1,3-dimethyl-4-methylene-2,6-diphenylpiperidine and l3-ethane (1:1:1)

N-(amino-l2-methyl)nitrous amide compound with 1l3-ethane and 3-methyl-4-methylene-2,6-diphenylpiperidine (1:1:1)

Fig. 10 Optimized molecular structure of the inhibitors.

Fig. 11 HOMO and LUMO surface of the inhibitors(01TS, 02TS and 03TS).

The results seem to reveal that, charge transmission from the molecules of inhibitor takes place during the adsorption of the inhibitor molecules to the metal surface. When the chemisorption reaction appears, one among the reacting species perform as an electron pair donor and the rest as an electron pair acceptor [22]. It is clear from Table 5 illustrates that the E_{HOMO} of inhibitors are almost the same. The conclusions are in excellent concurrent with that of the experimental values. The energy gap ($ΔE$) is a valuable parametric quantity as a function of inhibitor molecule reactivity in the direction of the adsorption on the metal face [20]. As the energy gap ($ΔE$) decreases, the reactivity of the molecule rises, dominant to rise in the percentage (%) of inhibition efficiency (IE) of the molecule. The least value of the energy gap ($ΔE$) will be supported a enhanced inhibition efficiency, because the energy essential for the rejection of an electron from the finally occupied orbital will be low [23].

Table 5 Quantum parameters of (01TS), (02TS) and (03TS).

Quantum chemical parameters	01TS	02TS	03TS
E_{HOMO}	-0.28202	-0.28038	-0.28200
E_{LUMO}	0.10952	0.10774	0.10712
$ΔE=(E_{LUMO} - E_{HOMO})$	0.39154	0.38812	0.38912
$I= -E_{HOMO}$ (ev)	0.28202	0.28038	0.28200
$A= -E_{LUMO}$	-0.10952	-0.10774	-0.10712
$μ$ (Debye)	3.5729	3.4763	3.2728

The dipole moment $μ$ (Debye) is a further value electronic parameter in quantum chemical calculation studies that analysis from non uniformed sharing of charges on the a mixture of

atoms in the molecule. The larger values of the dipole moment (μ), possibly increases the absorption between chemical compounds and metal surface [24]. The energy of the deformability increases respectively, with the rise of dipole moment μ (Debye) developing the molecule easier to adsorb on the mild-steel metal surface. The inhibitor molecules volume further rises with the increase of Debye. This increases the approaching area surrounded by the molecule and the surface of the mild-steel in extension to the corrosion inhibition capability of inhibitors.

4. Conclusion

The inhibition nature of mild-steel metal in 1 N sulfuric acid by alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazone has been examined by quantum chemical calculation, AC impedance spectroscopy, weight loss process and potentiodynamic polarization method.The alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazones present greatest efficiency towards inhibition of corrosion of mild-steel in 1 N H_2SO_4 medium. This has possibly induced by the progress of a complex on the mild-steel metal surface at lower concentrations because adsorption on the surface. The higher value corrosion inhibition efficiency (IE) of these inhibitor compounds gained even at very low concentration of the inhibitor. The rate of corrosion inhibition gets decreased with the increment in the inhibitor concentration. The adsorption of a number of alkyl substituted 2, 6-diphenyl piperidin-4-one with thiosemicarbazones at mild-steel corrosion in acid solution (1 N H_2SO_4) pursued the Langmuir adsorption isotherm model. The deviation of Tafel constants b_a and b_c and E_{corr} values with the rise in inhibitor concentration suggest that these compounds perform as an inhibitor of mixed characteristics with more cathodic character. This is attested by the electrochemical AC impedance spectroscopy, which shows a transform in the charge transfer resistance and double layer capacitance signifying the inhibitors adsorption on the mild-steel surface. The some alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazone adsorb to the mild-steel surface mainly by chemisorption mechanism. Even though these compounds containing ring nitrogen, the ultimate inhibition efficiency (IE) are due to >N-NH-CS-NH$_2$. Computed quantum chemical characteristics such as HOMO-LUMO energy gap (ΔE) and dipole moment (μ) were formed in good correlation with experimentally resolved corrosion inhibition efficiency. Analysis of inhibition efficiency of the three distinctive inhibitors displays the successive trends. (01TS) > (02TS) > (03TS).

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