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Electrochemical Studies of Corrosion of Mild Steel Inhibition by Using Some Substituted Piperidin-4-Ones with Semicarbazone in an Acidic Medium

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ABSTRACT

The impact of r-2,c-6-diphenyl-t-3-methylpiperdin-4-ones with semicarbazone (01SC), r-2,c-6-diphenyl-N-methyl-t-3-ethylpiperdin-4-ones with semicarbazone (02SC) and r-2,c-6-diphenyl-t-3-ethylpiperdin-4-one with semicarbazone (03SC) on the corrosion inhibition nature of mild steel in 1N sulhuric acid is investigated by employing quantum chemical calculation, potentiodynamic polarization, weight loss method and AC impedance spectroscopy methods. The experimental result depicts that the percentage of inhibition efficiency (IE) increases with the rising inhibitor concentration of some alkyl (methyl, N-methyl ethyl, ethyl) substituted piperidin-4-ones with semicarbazone. The adsorption of inhibitor on the mild steel follows the Langmuir adsorption isotherm. The potentiodynamic polarization plots portray that substituted piperdin-4-ones with semicarbazone act as a mixed type character in acid medium. This is suspended by the impedance spectroscopy, which shows a change in the value of charge transfer resistance (Rct) and double layer capacitance (Cdl) indicating the adsorption of the some substituted piperidin-4-ones with semicarbazones on the mild steel surface. Quantum chemical estimations are utilizing Density Functional Theory to identify a transparent link exists that between the inhibiting effect of the inhibitor and the electronic properties of its fundamental constituent.

Keywords: Corrosion inhibitor, Mild steel, Adsorption, Impedance, Polarization, Quantum chemical calculations, Density functional theory

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INTRODUCTION

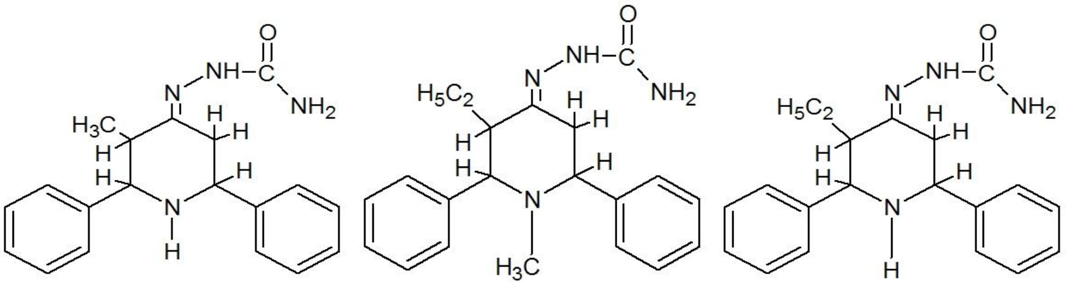
Almost 3% of the world's GDP is the annual cost of corrosion, because it has an impact upon the metallurgical, chemical, oil-industries and so on. In addition, governments and industries pay little attention to corrosion except in large risk areas such as aircraft and pipelines. Now, there is an opportunity for corrosion professionals to join together to educate the government, the industries, and the public. The growing importance in the sulfuric acid production has created the need for extracting data about on the corrosion resistance of mild steel to sulfuric acid attack. In particular, a significant effect also is the need to present certain organic compounds as corrosion inhibitors into the corrodent system of the mild steel to inhibit corrosion. Most of the well-known acid inhibitors contain organic compounds which include multiple bonds, nitrogen, oxygen and sulfur atoms and they have been confirmed to be the impressive inhibitors of the corrosion of mild steel in acidic media [1-5]. These organic compounds can adsorb onto the surface of the metal and arrest active surface of the metal sites, lowering the rate of corrosion [6]. The strength of the inhibitor layer on the metal surface determines the physicochemical characteristic feature of the molecule, which are connected to the existence of some functional groups, aromaticity, type of corrosive medium, steric effect, electronic density of the donors, the charge on the metal surface, the structure of the inhibitor, and the nature of the interaction between the p-orbitals of the inhibitor and the d-orbitals of mild steel [7]. The organic compounds with functional groups acquitting heteroatoms, which can give a lone pair of electrons, are quite beneficial as inhibitors for metal corrosion [8-15]. Piperidin-4-ones have been reported to inhibit corrosion of acid on mild steel [16].

The present study focuses on the inhibition efficiency of alkyl (methyl, N-methyl ethyl, ethyl) substituted r-2,c-6-diphenyl piperidin-4-ones with semicarbazone of corrosion in 1 N sulfuric acid on mild steel and to study the corrosion inhibition using the weight loss method, polarization techniques, AC impedance spectra and quantum chemical calculations is utilized in the present study.

MATERIALS AND METHODS

Synthesis of piperidin-4-one semicarbazones

The alkyl (methyl, N-methyl ethyl, ethyl) substituted 2,6-piperidin-4-one semicarbazones are prepared by the method of Baliah and Noller [17]. The products are re-crystallized from ethanol. Inhibitors were used in the present work 2,6-diphenyl-3-methyl piperdin-4-ones with semicarbazone (01SC), 2,6-diphenyl-N-methyl-3-ethyl piperdin-4-ones with semicarbazone (02SC) and 2,6-diphenyl-3-ethyl piperdin-4-one with semicarbazone (03SC).



(01SC) **(02SC)** **(03SC)**

Structure of the compounds

Preparation of the metal specimen

Mild steel specimens had composed of C: 0.07%, P: 0.008%, Mn: 0.34% and Fe balance. Mild steel specimens of the size 5 × 2.5 cm^2 used for the weight loss measurements. The working electrodes with an exposed area 0.5 cm^2 in the electrochemical measurements aggraded with emery paper grade 600-800 on test face, rinsed with double distilled water, degreased in ethyl alcohol and dried at room temperature. Before measurement the electrode was immersed in the test solution at open circuit potential (OCP) for 20 min to be sufficient to attain a stable state. All electrochemical measurements are carried out at 303K in a stationary condition. Each analysis was imitated at least three times to check the reproducibility.

Weight loss method

The mild steel samples in triplicate are immersed in 250 ml of the sulfuric acid solution having the inhibitor of some substituted piperidin-4-ones with semi carbazone for 1 h. The weight of the mild steel samples before and after immersion is determined. Thus, corrosion inhibition is then calculated by the following equation:

$$\text{Corrosion rate (in millimiles per year)} = 87.6 \times W / (D \times A \times T)$$

Where W=Weight loss (in milligram),
A=Area of exposure (in square centimeter),
D=Density (in gram per cubic centimeter)and
T= Time (in hours).
Inhibitor efficiency has been derived by using the equation below

$$\text{Inhibitor efficiency (\%)} = (W_0 - W_e / W_0) \times 100$$

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 performed in a glass cell with a volume of 100 ml. A saturated calomel electrode and a platinum electrode were used as a reference electrode and a counter electrode respectively. The mild steel electrode is then dropped into the test solution (uninhibited and inhibited solutions) for 10-15 min before electrochemical measurements.

Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization are performed in an electrochemical measurement unit (Model 1280 B Solartron, UK). The EIS measurements are made at corrosion potentials over a frequency range of 10 kHz to 0.01 Hz with signal amplitude of 10 mv. The Tafel polarization measurements are made after EIS for a potential range of -200 mv to +200 mv with respect to open circuit potential, at a scan rate of 1 mv/Sec. The I_{corr}, E_{corr}, R_t and C_{dl} values are obtained from the data using the corresponding "Corr view" and "Zview" software's. The inhibition efficiency from potentiodynamic polarization is calculated from the value I_{corr} by using the formula (18-19).

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

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 using the formula (16).

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

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

RESULTS AND DISCUSSION

Weight loss measurements

Table 1 provides the value of the inhibition efficiency; surface courage and corrosion rate with different concentration (0.2, 0.4 and 1.0) of some alkyl substituted piperidin-4-ones with semicarbazones [18-20] on mild steel in 1 N sulphuric acid have been evaluated by weight loss measurements at 303 K.

Table 1: Corrosion parametric quantity of Alkyl substituted piperidin-4-ones with semicarbazone on mild steel in 1 N H_2SO_4 from weight loss measurements

Name of the inhibitor and concentration (mM)		**Weight Loss (*gram*)**	**Corrosion Rate (milli miles per year)**	**Inhibition efficiency (%)**	**Surface Coverage (θ)**
Blank	-	0.0768	69.09	-	-
01SC	0.2	0.0167	15	78.28	0.7828
	0.4	0.015	13.48	80.49	0.8049
	1	0.0093	8.4	87.9	0.849
02SC	0.2	0.0174	15.63	77.37	0.7737
	0.4	0.0156	14.02	79.71	0.7971
	1	0.0123	11.05	84	0.84
03SC	0.2	0.0278	24.98	63.84	0.6384
	0.4	0.0231	20.75	69.96	0.6996
	1	0.0142	12.76	81.53	0.8153

The measurement of weight loss implies that the inhibition efficiency increases with an increase in inhibition concentration while the corrosion rate gets decreased. The optimum inhibition of these compounds is achieved even at low concentration. The effect of concentration of inhibitor on weight loss measurements reveals that the metal-loss gently decreases with the increasing inhibitor concentrations. The order of inhibition efficiencies of these inhibitors at 303 K is (01SC)>(02SC)>(03SC). Analysis of the inhibition efficiencies of inhibitors (01SC), (02SC) and (03SC) reveals that inhibition efficiency, decrease when it is substituted with various groups at 3-position of the piperidin-4-one ring. The noticed trend can be explained by because of the conformations of substituted piperidin-4-ones and steric hindrance caused by the substituent.

Potentiodynamic polarization measurements

From Table 2, it can be seen that as the inhibitor concentration increases, the I_{corr} value decreases and the inhibitor efficiency increases significantly and this indicates the inhibiting nature. The lowering corrosion rate in potentiodynamic polarization shows that the inhibitor absolutely operates on the mild steel metal surface. A deviation in the values of Tafel constant of b_a and b_c concludes the nature of the inhibitor. An increase in the b_c values in the concentration of the inhibitor is a characteristic phenomenon of a cathodic inhibitor, which reveals an increment in the energy barrier for proton discharge leading to less gas evolution. The variation of b_a and b_c values for the concentration of inhibitor in 1 N sulphuric acid are presented in Table 2. Analysis of the data reveals that b_a and b_c values do not change considerably with the concentration of some substituted Piperidin-4-ones with semicarbazone and slight variation is observed. The E_{corr} value shifts towards less negative side when the concentration of the inhibitor is increased. Thus, Alkyl substituted Piperidin-4-ones with semicarbazone may be considered as the mixed type inhibitors having more cathodic character. Figures 1-3 indicate the potentiodynamic polarization curves of mild steel for some alkyl substituted piperidin-4-ones of semicarbazone. The corrosion kinetic factors derived from these curves are presented in Table 2.

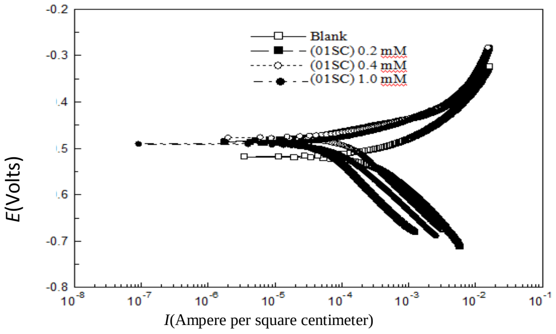


Figure 1: Potentiodynamic polarization graph for mild steel in 1 N H_2SO_4 in the absence and presence of (01SC)

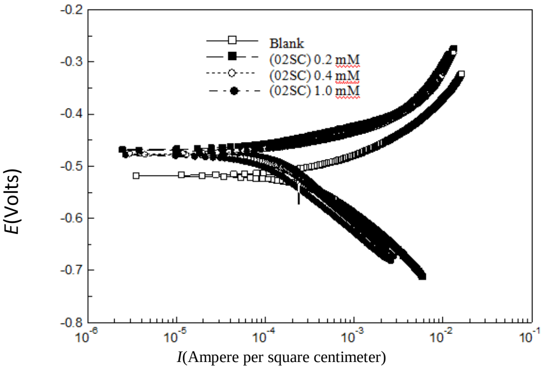


Figure 2: Potentiodynamic polarization graph for mild steel in 1 N H_2SO_4 in the absence and presence of (02SC)

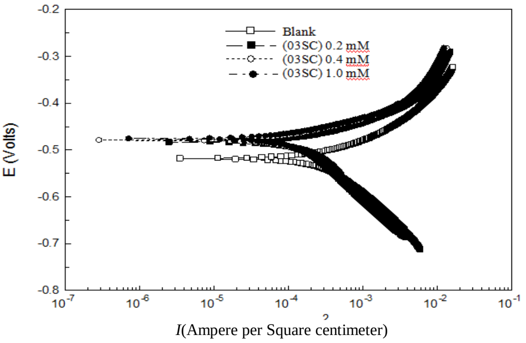


Figure 3: Potentiodynamic polarization graph for mild steel in 1N H_2SO_4 in the absence and presence of (03SC)

Table 2: Potentiodynamic polarization parametric quantity for the corrosion of mild steel in 1 N H_2SO_4 with and without Alkyl substituted piperidin-4-ones with semicarbazone

Name of the Inhibitor and concentration (mM)		**I_{corr} (in micro amper per cm2) x 10^{-2}**	**E_{corr} (milliVolts vs Saturated calomel electrode)**	**ba (milliVolts/Decade)**	**bc (milliVolts/Decade)**	**Corrosion Rate (milli miles per year)**	**Inhibition Efficiency (%)**
Blank		4.57	-524	120	-137	104.71	
01SC	0.2	0.69	-486	41	-122	15.81	84.90
	0.4	0.46	-482	36	-138	10.54	89.50
	1.0	0.24	-480	45	-138	5.50	94.75
02SC	0.2	1.30	-483	53	-143	29.79	71.55
	0.4	1.21	-497	71	-138	27.72	73.52
	1.0	1.07	-465	45	-135	24.52	76.59
03SC	0.2	1.81	-489	67	-153	41.47	60.39
	0.4	1.32	-481	61	-142	30.24	71.11
	1.0	1.27	-483	64	-144	29.10	72.21

AC impedance measurements

Nyquist graphs for mild steel in 1 N sulfuric acid for some alkyl substituted piperidin-4-ones of semicarbazone are exhibited in Figures 4-6. Table 3 provides the value charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency (IE) attained from the above graphs.

Table 3: Impedance parametric quantity for the corrosion of mild steel in 1 N H_2SO_4 with and without Alkyl substituted piperidin-4-ones with semicarbazone

Name of the inhibitor and concentration (mM)		**Weight Loss (gram)**	**Corrosion Rate (milli miles per year)**	**Inhibition efficiency (%)**	**Surface Coverage (θ)**
Blank		0.0768	69.09		
01SC	0.2	0.0167	15	78.28	0.7828
	0.4	0.015	13.48	80.49	0.8049
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	0.4	0.0156	14.02	79.71	0.7971
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	1	0.0142	12.76	81.53	0.8153

The data indicate that R_{ct} value gets increased with the increase in the concentration of inhibitor. The addition of inhibitor decreases the C_{dl} values because the absorption of inhibitors on the metal surface (increase in the surface courage of inhibitor). The impedance diagrams are nearly semicircular. The value of charge transfer resistance indicates the electron transfer across the interface. The presence of inhibitors tremendously increases the radius of the semicircular in the Nyquist plots.

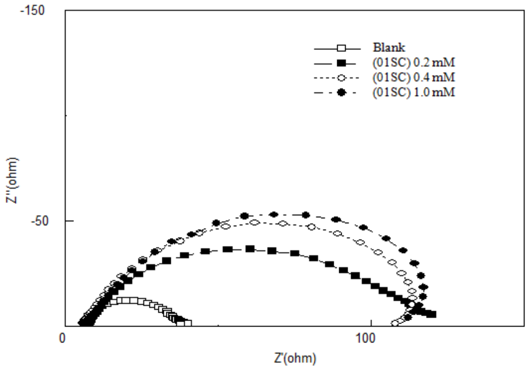


Figure 4: Nyquist graph of mild steel in 1 N H_2SO_4 in the absence and presence of (01SC)

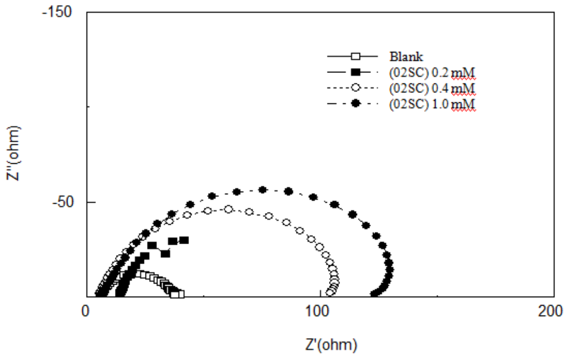


Figure 5: Nyquist group of mild steel in 1 N H_2SO_4 in the absence and presence of (02SC)

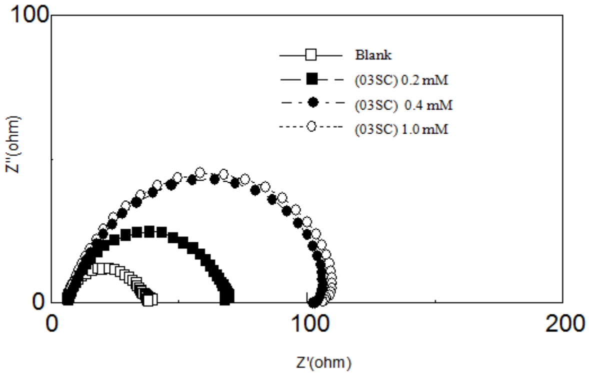


Figure 6: Nyquist graph of mild steel in 1 N H_2SO_4 in the absence and presence of (03SC)

Adsorption isotherm

Organic molecules help to inhibit corrosion as they are adsorbed on the metal-solution interface. The adsorption relies on the chemical structure of the inhibitor, temperature, chemical distribution of the solution, the character of the metal surface and electrochemical potential at the metal-solution integrates. The adsorption provides knowledge about the adsorbed inhibitor molecules and their cooperation with the metal surface. The values of surface coverage (θ) corresponding to different inhibitor concentrations (C) are used to obtain the best adsorption isotherm. The θ values have been estimated using the following relationships.

$$\theta=\frac{1-W_{inh}}{W}$$ (From weight loss measurements) and

$$\theta=\frac{1-C_{dl(inh)}}{C_{dl}}$$ (From impedance measurements)

The Langmuir adsorption isotherm is expressed as $\theta=\frac{K}{1+KC}$

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

A straight line with slope equal to unity should be obtained by plotting C/θ vs C when the experimental data follow Langmuir adsorption isotherm. In the present study Langmuir adsorption isotherm is observed throughout all the inhibitors on mild steel in 1 N sulfuric acid. Langmuir plots are presented in Figure 7 for which θ values are attained from weight loss measurements. Equilibrium adsorption constants are calculated from the Langmuir plot and shown in Table 4. The high value of *K* indicates that the inhibitor is firmly adsorbed on mild steel surface.

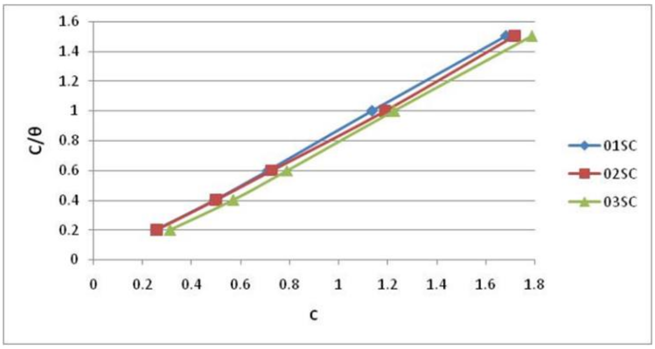


Figure 7: Langmuir isotherms for the adsorption of compounds [(01SC), (02SC) and (03SC)] on the surface of mild steel in 1 N H_2SO_4

Table 4: Equilibrium constants from Langmuir adsorption isotherms

Name of the inhibitors	***K***
01SC	20.65
02SC	19.87
03SC	9.34

The inhibitor utilized in the present study has two groups of anchoring sites, namely ring Nitrogen and semicarbazone group. Usually these types of compounds exist either in a boat or in a chair conformation. The Alkyl substituted Piperidin-4-ones with semicarbazone chair conformation is the preferred conformation as phenyl and alkyl substitutions are in equatorial orientations. The inhibition efficiency of the compounds is higher. The interaction of these compounds with metal surface could occur either through a carbonyl group or through ring nitrogen, but not through both of them 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 which is highly strained. Further, the less electro negativity of nitrogen than oxygen support, ring nitrogen to be the most inhibiting site [16]. The inhibition efficiency is further increased by converting carbonyl group into semicarbazone group. The involvement of either semicarbazone group or ring nitrogen is expected due to the presence of substitutes. The high inhibition may be due to the attraction between the nitrogen and the oxygen atom of semicarbazone and metal surface.

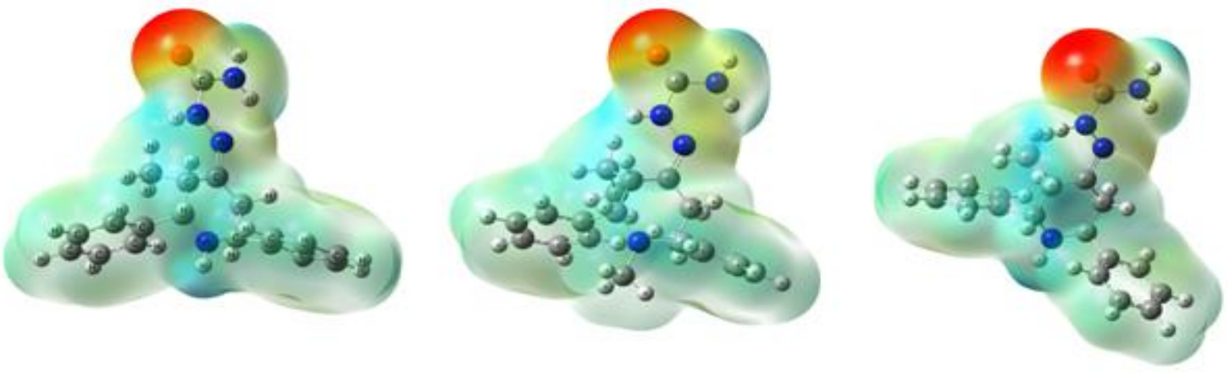
The result of the present study indicates that all the three corrosion monitoring techniques complement with each other. Determination of inhibition efficiency (IE) of the three different inhibitors shows the following trends (01SC)>(02SC)>(03SC)

Quantum chemical calculations

Quantum chemical estimations are shown from experimental results that it is likely to get a better performance with inhibitors as corrosion inhibitor. It has been expressed that the energy of the highest occupied molecular orbital (E_{HOMO}) regularly combined with the electron donating capability of the molecules. High values of E_{HOMO} express a tendency of the molecule to donate electrons to perform with acceptor molecules with low energy unfilled or empty molecular orbital. Correspondingly, the energy of the lowest unoccupied molecular orbital (E_{LUMO}) represents the intelligence of the molecule to the accept electrons. The lower value of E_{LUMO} proposes that the molecule receives electrons more probable.

The electronic properties like the 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 are observed through optimization. The optimized molecular structure of the inhibitor is given in Figure 8. The HOMO and LUMO surfaces for inhibitor are given in Figure 9. The electronic properties are given in Table 5.

Results reveal that the charge transfer from the inhibitor molecules occurs during the adsorption of the inhibitor molecules on the metal surface. When the chemisorption reaction takes place, one of the reacting species performs as an electron pair donor and another one performs as an electron pair acceptor [21]. Table 5 shows that the E_{HOMO} of inhibitors are almost the same. The results are in good understanding with the experiment. The energy gap is a significant parametric quantity as a behavior of reactivity of the inhibitor molecule in the direction of the adsorption on the metallic surface. As the energy gap (ΔE) lowers, the reactivity of the molecule increases, dominant to increase the percentage inhibition efficiency (IE) of the molecule. Lower values of the energy gap (ΔE) would be provided good inhibition efficiency because the energy required for the removal of an electron from the last occupied orbital would be low [22,23].

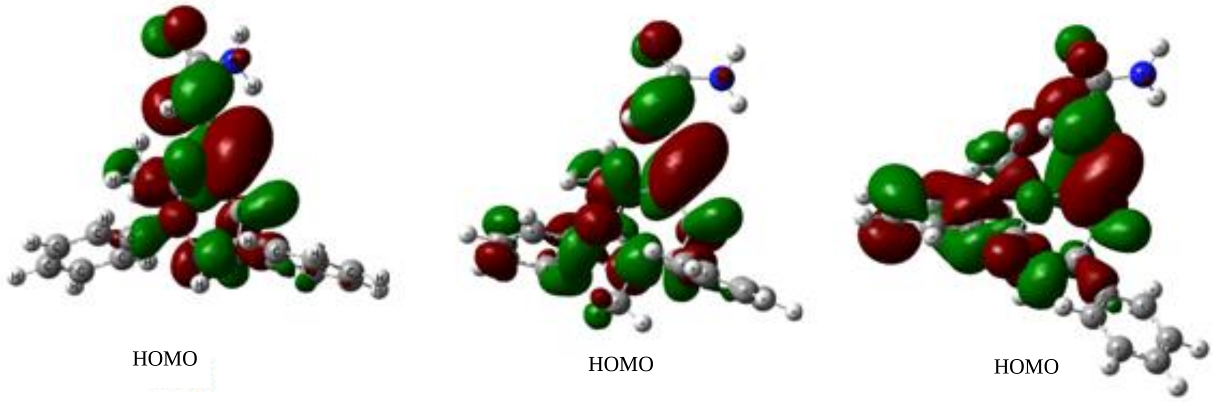


N-(amino-l2-methyl)nitrous amide compound with 3-methyl-4-methylene-2,6-diphenylpiperidine and l3-methane (1:1:1)

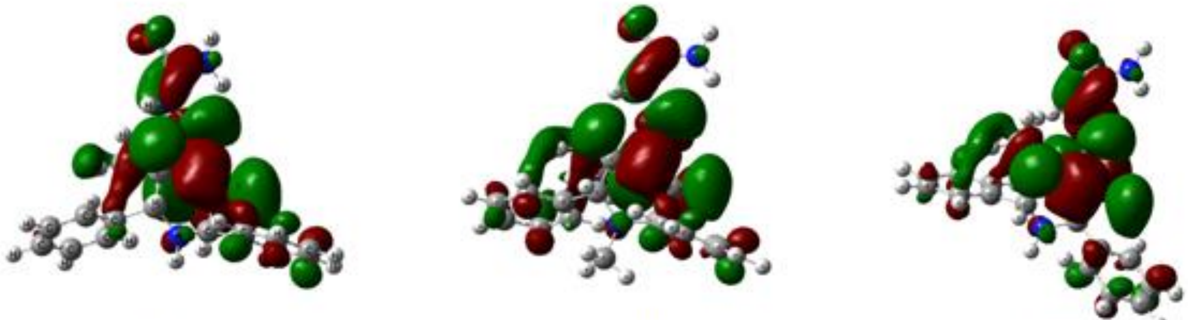
N-(amino-l2-methyl)nitrous amide compound with 1,3-dimethyl-4-methylene-2,6-diphenylpiperidine and 1l3-ethane (1:1:1)

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

Figure 8: Optimized molecular structure of the inhibitors



HOMO HOMO HOMO



LUMO LUMO LUMO

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

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

Figure 9: HOMO and LUMO surface of the inhibitors [(01SC, 02SC, and 03SC)]

Table 5: Quantum parameters of [(01SC),(02SC)and (03SC)]

Quantum chemical parameters	**01SC**	**02SC**	**03SC**
E_{HOMO}	-0.29990	-0.29664	-0.29780
E_{LOMO}	1.00014	1.09883	0.09802
$\Delta E = E_{LOMO} - E_{HOMO})$	0.40004	0.39154	0.39582
$I = -E_{HOMO}$ **(ev)**	0.29990	0.29664	0.29780
$A = -E_{LOMO}$	-0.10014	-0.09883	-0.09802
μ **(debye)**	5.8368	5.8178	5.6098

The dipole moment μ (Debye) is another valuable electronic parameter in quantum studies that results from non-uniformed sharing of charges on various atoms in the molecule. The high value of the dipole moment (μ) apparently increases the absorption between chemical compounds and metal surface [24]. The energy of the deformability grows respectively, with the increase in dipole moment μ (Debye) accomplishing the molecule easier to adsorb on the surface of metal. The inhibitor molecule volume also grows with the increase in Debye. This increases the approaching area between the molecule and the surface of mild steel and increasing the corrosion inhibition capability of inhibitors.

CONCLUSION

1) The corrosion inhibition nature of mild steel in 1 N sulphuric acid by some alkyl (methyl, N-methyl ethyl, ethyl) substituted 2,6-diphenyl piperidin-4-one with semicarbazone has been studied by quantum chemical calculation, weight loss method, AC impedance spectra and potentiodynamic polarization technique.

2) Alkyl substituted 2,6-diphenyl piperidin-4-one with semicarbazones exhibit maximum efficiency towards the inhibition of corrosion of mild steel in 1 N H_2SO_4 media. This is probably due the formation of a complex at lower concentrations due to adsorption.

3) The optimum inhibition efficiency of these compounds is achieved even at very low concentration. The rate of corrosion gets decreased with the increasing in inhibitor concentration.

4) The adsorption of some alkyl substituted 2,6-diphenyl piperidin-4-one with semicarbazones at mild steel in acid solution obeyed Langmuir adsorption isotherm model.

5) The deviation in Tafel constants b_a and b_c and E_{corr} values with the increase in the concentration of the inhibitors propose that these compounds function as a mixed type with more cathodic character. This was supported by the AC impedance spectra which showed a change in the charge transfer resistance and double layer capacitance indicating adsorption of inhibitors on the mild steel surface. The inhibitors adsorb to the mild steel surface mainly by chemisorption mechanism.

6) Even though these compounds contain ring nitrogen, the maximum inhibition is due to >N-NH-CO-NH_2

7) Computed quantum chemical properties such as HOMO-LUMO energy gap (ΔE) and dipole moment (μ) are found to be better correlated with the experimentally resolved inhibition efficiency.

8) Analysis of inhibition efficiency of the three different inhibitors shows the following trends. (01SC)>(02SC)>(03SC).

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