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# The effect of 3-cyclohexylamino-propionitrile and aminocyclohexane on the behaviour steel in HCl solution

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## ABSTRACT

*Inhibitory effect of some new synthesized and analyzed aminocyclohexane compounds, namely, 3-cyclohexylamino-propionitrile (P1) and aminocyclohexane (P2) respectively; on corrosion of steel in 1M HCl solution has been studied using weight loss measurements and electrochemical technique polarization methods. The results obtained reveal that these compounds are efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration and reaches 90 % for P1 at* $10^{-3}$ *M. Potentiodynamic polarisation studies clearly reveal that P1 and P2 acts cathodic inhibitors without change of the mechanism of hydrogen evolution. The temperature effect on the corrosion behaviour of iron in 1 M HCl without and with the inhibitors at* $10^{-3}$ *M was studied in the temperature range from 313 to 353 K. Significant correlations are obtained between inhibition efficiency with the calculated chemical indexes, indicating that variation of inhibition with structure of the inhibitor may be explained in terms of electronic properties. The inhibitors were adsorbed on the iron surface according to the Langmuir adsorption isotherm model at different temperature. From the adsorption isotherm some thermodynamic data for the adsorption process (K and* $\Delta G°_{ads}$*) are calculated and discussed.*

***Key words***: *Amine, Cyclohexane, Inhibition, Corrosion, Iron, Acid.*

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## INTRODUCTION

Corrosion is natural and inevitable, but it can be minimized and delayed. To truly understand the cost of not implementing sound corrosion practices, consider a study conducted by the U.S. Federal Highway Administration (FHWA) and National Association of Corrosion Engineers (NACE). The study estimates the annual direct cost of metallic corrosion to the U.S. economy is 3.1% of the gross domestic product (GDP) or approximately $300 billion. Beyond the huge direct outlay of funds to repair and/or replace corroded bridges, facilities, and architectural steel, there are costs associated with accidents caused by corroded structures, needless consumption of natural resources to constantly repair and maintain infrastructure, and lost productivity when delays cause traffic jams or lost opportunity. Depending on which market sector (industrial, infrastructure, commercial, etc.) is being considered, these indirect costs may be as high as five to ten times the direct cost. The study also states avoidable corrosion accounts for about one third of the total corrosion costs and concludes “these costs could be reduced by broader application of corrosion-resistant materials and the application of the best corrosion-related technical practices.”

The cost of corrosion has been reported from many studies also to be in the order of 1 to 5 per cent of GNP for any country. Chemical acid cleaning, acid descaling and pickling processes are widely used in industrial processes to remove corrosion scales from metallic surface in high concentrated HCl media at elevated temperature up to 60 °C. Corrosion never stops but its scope and severity can be lessened [1-15]. In a sense, the use of inhibitors is one of the best known methods of corrosion protection.

A corrosion inhibitor is a chemical compound which is designed to protect a metal or alloy from corrosion. While corrosion inhibitors will not halt or completely prevent corrosion, they can reduce the rate at which corrosion occurs, and block early corrosion damage. A wide variety of chemicals can be used for this purpose, although many are toxic, and must therefore be used with care to protect the environment. One form of corrosion inhibitor is a compound added to a fluid such as a fuel or lubricant. In this case, the corrosion inhibitor travels with the fluid, providing protection to the systems the fluid moves through. Commonly, it forms a thin film which prevents reactions between compounds in the fluid and systems such as pipes. This type of corrosion inhibitor may be blended into the fluid continuously, or added periodically to maintain a protective film.

Corrosion inhibitors can also be sprayed or painted on to create a thin layer which will provide protection from corrosion. Many people do this on a regular basis when they oil locks and hinges to prevent them from rusting and to keep them moving smoothly. The thin layer of oil acts as a corrosion inhibitor to prevent oxidation, so that rusting cannot occur. In order to work effectively, the surface needs to be clean when the chemical is applied, as otherwise corrosive reactions can take place underneath the corrosion inhibitor.

The use of Inhibitors is the one of the most practical methods to protect metals against acid solution attack. Organic compounds containing electronegative functional groups and π-electron in triple or conjugated double bonds are usually goods inhibitors. Heteroatom's as sulfur, phosphorus, nitrogen and oxygen as well as aromatic ring in their structure are the major adsorption centres [16-26] . The effect of organic nitrogen, sulfur compounds on the corrosion behaviour of iron and steel in acidic solution has been well documentation in our laboratories. It was shown that the protective properties of such compound depend upon their ability to reductive corrosion rate and are enhanced at higher electron densities around the sulfur and nitrogen atom [3, 5, 20, 21, 27-29].

The selection of suitable inhibitor depends on its chemical structure, on concentration, on the nature of the metal and on the type of acid. In acid environment, the inhibitor acts generally by chemisorptions and/or physical adsorption at the metal surface. To be effective, an inhibitor must be also displace water molecules from the metal's surface and interact with anodic and cathodic reaction sites to retard the oxidation and/or reduction corrosion reaction. So, the inhibition efficiency of organic compounds depends on the structure of inhibitor, the characteristics of the environment in which acts and the mode of interaction with the metal surface [4, 6]. Numerous works in our laboratory have been devoted to the corrosion inhibiting effect of aqueous soluble heterocyclic organic compounds on metallic materials. Heterocyclic organic compounds containing nitrogen, sulfur have been proved to perform as very good inhibitors for the corrosion of metals in acidic solutions [9, 10, 12-14, 18].

In the present work, we aimed at investigating the corrosion inhibition of steel in 1M HCl by 3-cyclohexylamino-propionitrile (P1) and aminocyclohexane (P2) and to observe any relation between molecule structure and their inhibitive action. The behaviour of steel in 1M HCl without and with inhibitor is studied by Weight loss tests and electrochemical techniques measurements.

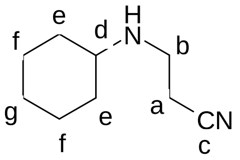
## MATERIALS AND METHODS

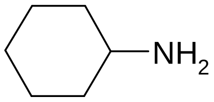
### 2. Experimental details.

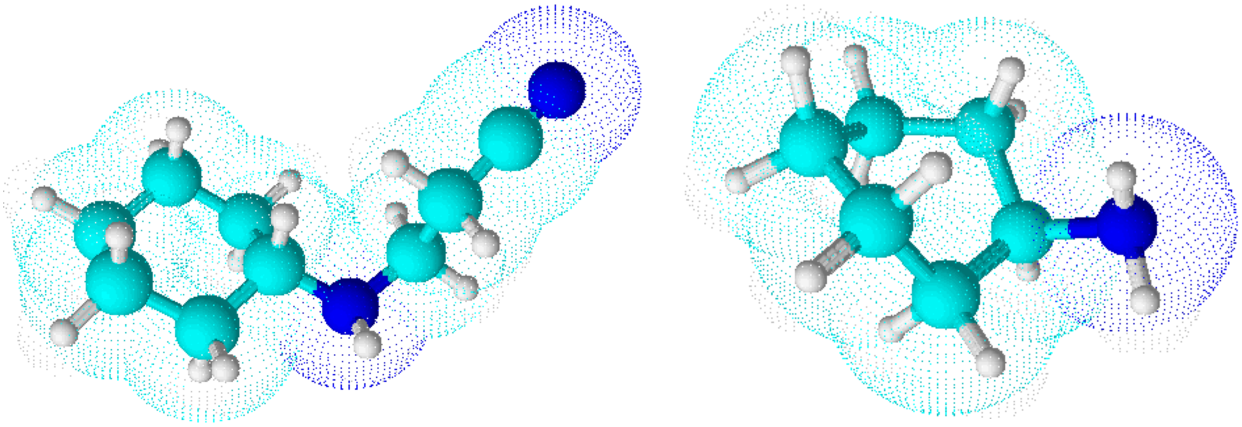
### 2.1. Inhibitors

Schema.1. shows the molecular formula of the investigated. The aminocyclohexane (P2) is a commercial product and analytical. The 3-cyclohexylamino-propionitrile (P1) is synthesis and analyzed by 1H NMR, 13C NMR and IR. RMN 1H (300 MHz, CDCl3): δ=2.88-2,95 (CH2-CH2-CN,2H, t (J= 11.73)) ; 2,36-2,50 (CH2-CN,2H, t (J= 6.5) et 0.93-1,86 (C6H11,6H, m (J= 19.56)). RMN 13C (CDCl3, 75 MHz): δ=118.82 (c); 55.95 (d); 42.05 (b); 32.31-36.7 (e); 26.35 (g); 24.82-25.94 (f) and 19.08 (a)

The synthesis of P1 following the procedure follows: a solution of cyclohexylamine (0.2016 mmol, 3 g) was cooled to 0 ° C then (0.2016 mmol, 1.06 g) of acrylonitrile cold and stirred for 24 hours in the absence of light. We obtain yellowish oil with an 85% yield







**3-cyclohexylamino-propionitrile (P1)** **Aminocyclohexane (P2)**

***Scheme 1: the molecular structure of P1 and P2***

### 2.2. Gravimetric and electrochemical measurements

Prior to all measurements, the steel samples, were polished with different emery paper up to 1000 grade, washed thoroughly with bi-distilled water degreased and dried with acetone.

The aggressive solution (1M HCl) was prepared by dilution of Analytical Grad 37% HCl with bi-distilled water. Steel samples of the following weight percentage composition 0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron are used. The specimens used in the chemical investigations are in the form of strips of dimensions 2cm×1cm×0.2cm.

Electrochemical measurements are carried out in a conventional three-electrode cylindrical glass cell. The working electrode, in the form of a disc cut from steel, has a geometric area of $1cm^2$. A saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrode, respectively. The temperature is thermostatically controlled at 308K. The polarisation curves are recorded with the electrochemical system (Tacussel) which included a digital potentiostat model Voltalab PGZ 100 computer at $E_{cor}$ after immersion in solution, at a scan rate of 1mV/s. The test solution is deaerated for 30 min in the cell with pure nitrogen. Gas bubbling is maintained throughout the experiments.

All calculations are performed using Argus Lab 2.0, Chem3D Ultra 8.0 and Gaussian 98 package software's. The following quantum chemical indices are considered: the energy of the highest occupied molecular orbital ($E_{HOMO}$), the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), $\Delta = E_{HOMO} - E_{LUMO}$, total charge density calculated by extended Huckel, and the dipole moment ($\mu$).

## RESULTS AND DISCUSSION

### 3.1. Weight loss tests

The effect of added of 3-cyclohexylamino-propionitrile (P1) and aminocyclohexane (P2) compounds at different concentrations on the corrosion of steel in de-aerated 1M HCl solution was studied by weight-loss at 308 k after 6 hours of immersion period. Inhibition efficiency (E %) was calculated as follows:

$$E_w\% = \left(1-\frac{W_{cor}}{W^{o}_{cor}}\right).100 \qquad (1)$$

$W_{cor}°$ and $W_{cor}$ are the corrosion rates of iron samples in the absence and presence of the organic compound, respectively.

The results of weight loss of pure iron in 1M HCl with and without 3-cyclohexylamino-propionitrile (P1) and aminocyclohexane (P2) compounds at various concentrations are given in table (1). The results given in table (1) show that it clears that for each compounds tested, the iron corrosion rate values decrease when the concentration of (P1) and (P2) compounds increases.

The inhibiting action is more pronounced with Acid 3-cyclohexylamino-propionitrile (P1), and its inhibition efficiency attains the maximum value of 90.2% at $10^{-3}$M. It was shown that the protective properties of such compounds depend upon their ability to reductive corrosion rate and are enhanced at higher electron densities around the nitrogen atoms

**Table 1: Gravimetric results of steel corrosion in 1MHCl without and with addition of P1 and P2 at different concentration.**

| Inhibitor | Concentration (M) | W (mg.cm$^{2}$.h$^{-1}$) | E % |
|---|---|---|---|
| | Blank | 1.439 | - |
| **P1** | **$10^{-6}$** | 0.284 | 47.8 |
| | **$10^{-5}$** | 0.504 | 65.0 |
| | **5 x $10^{-5}$** | 0.325 | 77.4 |
| | **$10^{-4}$** | 0.310 | 78.4 |
| | **5 x $10^{-4}$** | 0.219 | 84.7 |
| | **$10^{-3}$** | 0.141 | 90.2 |
| P2 | **$10^{-6}$** | 0.752 | 47.7 |
| | **$10^{-5}$** | 0.496 | 65.5 |
| | **5 x $10^{-5}$** | 0.450 | 86.7 |
| | **$10^{-4}$** | 0.380 | 73.6 |
| | **5 x $10^{-4}$** | 0.248 | 82.8 |
| | **$10^{-3}$** | 0.202 | 85.9 |

It is interest to note that, the inhibiting effect of P1 compound can be attributed to their adsorption at the metal solution interface; the adsorption is owing to the presence more active centre (several nitrogen atoms and a great deal of $\pi$-electrons of rings ) for adsorption. They reported that the nitrogen atoms are the adsorption centres for their interaction with the metal surface and these compounds are usually good inhibitors [19, 30].

### 3.2. Polarization measurements

Evaluation of E (%) can also be performed through electrochemical experiments which consist of the determination of intensity/potential curves. Various corrosion kinetic parameters such as corrosion current ($I_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slope ($b_c$) derived from the polarization curves (Figure.1) and inhibition efficiencies ($E_I$%) of 3-cyclohexylamino-propionitrile (P1) and aminocyclohexane (P2) compounds studied are given in Table 2. In the case of polarization method, the inhibition efficiency (EI %) is determined by the relation :

$$E_I\% = \left(1 - \frac{I_{corr}}{I^{o}_{corr}}\right).100 \qquad (2)$$

$I_{corr}$ and $I^0_{corr}$ are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

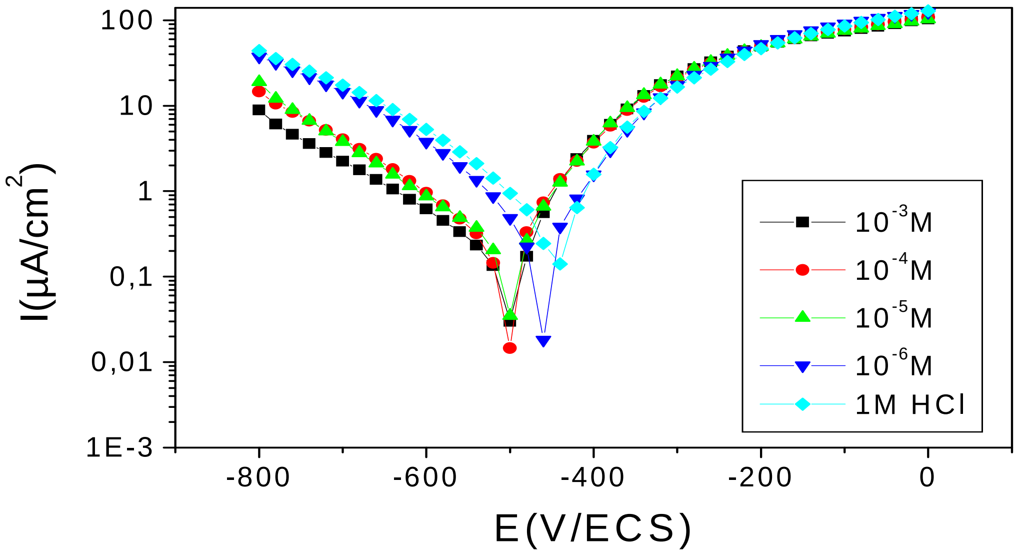


**Figure 1. Typical polarisation curves of steel in 1 M HCl for various concentrations of P1.**

Figure. 1 shows the influence of P1 on the polarisation curves for the steel electrode in 1M HCl. It is observed that the addition of the compound studied shifts the cathodic polarization curves to lower current density. In cathodic domain a large linearity plots indicating that the reduction of hydrogen ion is activation control. Cathodic portions rise to parallel Tafel lines indicating that the presence of compound tested does not modify the mechanism of the hydrogen reduction [3-5, 31]. This results in values: slope ($b_c$) is slightly modified relative to the blank ($b_c$). Values of associated electrochemical parameters and corresponding inhibition efficiencies (E%) are given in Table 2. The Tafel. But in the anodic domain a slight effect is observed. The decrease in corrosion rate is associated with a shift of only cathodic branches of the polarization curves towards lower current densities with a non modification in $E_{corr}$. In the anodic range (Figure.2), the polarization curves showed also an increase of over voltage near the corrosion potential

**Table 2: Potentiodynamic polarization parameters for the corrosion of mild steel in 1M HCl at different P1 compound studied**

| Concentration | $E_{corr}$ (mV) | $b_c$ (mV/ dec) | $I_{corr}$ (μA/cm$^2$) | E% |
|---|---|---|---|---|
| Blank | -474 | 177 | 947 | - |
| $10^{-6}$M | -487 | 169 | 573 | 41 |
| $10^{-5}$M | -544 | 160 | 356 | 63 |
| $10^{-4}$M | -533 | 158 | 231 | 76 |
| $10^{-3}$M | -502 | 165 | 122 | 87 |

For an overvoltage higher than –350 mV/SCE, the presence of inhibitors does not change the current-vs-potential characteristics. This fact means that the inhibition mode of P1 depends upon electrode potential. It seems that the presence of the three inhibitors does not change the current versus potential characteristics. This suggests that this compound acts essentially as a cathodic inhibitor [9, 10, 32-35].

### 3.3. 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. In order to study the effect of temperature on the corrosion inhibition of mild steel in the acid medium and to determine the activation energy of the corrosion process, Gravimetric measurements are taken at various temperatures (313-353 K) in the presence and absence of 3-cyclohexylamino-propionitrile (P1) at $10^{-3}$ M at 1h. The corresponding results are given in Table 3. We note that the corrosion rate increases with the rise of temperature both in inhibited and uninhibited acids. Figure 3 shows Arrhenius plots for steel corrosion rate. The apparent activation energies can be determined by the relation:

$$\begin{aligned} \ln W &= \frac{-E_a}{RT} + \ln A \\ \ln W' &= \frac{-E'_a}{RT} + \ln A \end{aligned} \qquad (3)$$

$E'_a$ and $E_a$ are the apparent activation corrosion energies with and without 3-cyclohexylamino-propionitrile (P1)**,** R is the universal gas constant, T is the absolute temperature and A is the pre-exponential factor [6, 19, 34, 36-38].

**Table 3: Corrosion rates and inhibition efficiency of steel in 1M HCl in presence and absence of P1 at $10^{-3}$M at different temperatures.**

| Temperature (K) | Concentration (M) | W (mg/cm$^2$.h) | %E | θ |
|---|---|---|---|---|
| 313 | Blank | 2.604 | - | - |
| | $10^{-4}$ | 0.574 | 78 | 0.78 |
| | $5\times10^{-4}$ | 0.270 | 89 | 0.89 |
| | $10^{-3}$ | 0.215 | 92 | 0.92 |
| 323 | Blank | 4.834 | - | - |
| | $10^{-4}$ | 1.398 | 71 | 0.71 |
| | $5\times10^{-4}$ | 0.509 | 89 | 0.89 |
| | $10^{-3}$ | 0.473 | 90 | 0.90 |
| 333 | Blank | 8.7815 | - | - |
| | $10^{-4}$ | 3.138 | 64 | 0.64 |
| | $5\times10^{-4}$ | 1.625 | 81 | 0.81 |
| | $10^{-3}$ | 1.439 | 83 | 0.83 |
| 343 | Blank | 13.235 | - | - |
| | $10^{-4}$ | 6.995 | 47 | 0.47 |
| | $5\times10^{-4}$ | 5.344 | 59 | 0.59 |
| | $10^{-3}$ | 4.773 | 64 | 0.64 |
| 353 | Blank | 26.552 | - | - |
| | $10^{-4}$ | 15.404 | 42 | 0.42 |
| | $5\times10^{-4}$ | 12.315 | 53 | 0.53 |
| | $10^{-3}$ | 9.654 | 63 | 0.63 |

We note that the corrosion rate increased with increasing temperature both in uninhibited and inhibited acids and the values of effectiveness decreases with increasing of temperature (Table 3).

The linear regression plots between ln(W) and 1000/T are presented in Figure.2. The calculated activation energies, $E_a$, and pre-exponential factors, A, at different concentrations of the inhibitor are collected in Table 3. The change of the values of the apparent activation energies may be explained by the modification of the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [2-4, 39, 40].

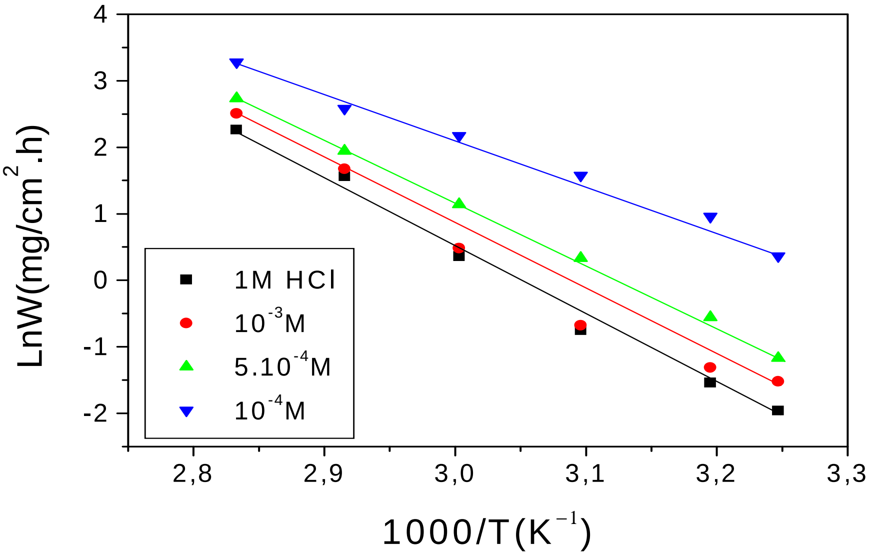


**Figure 2. Typical Arrhenius plots for logW vs. 1/T for steel in 1 M HCl at different concentrations of P1.**

The apparent activation energy $E_a$ for the corrosion process in uninhibited and inhibited acids for steel is evaluated from slopes of Arrhenius plots (Figure. 2). Literature [1-15, 41] discussed the variation of the apparent activation energy $E_a$ in the presence and absence of inhibitor. Higher values for $E_a$ were found in the presence of inhibitors. Other studies [42, 43] showed that in the presence of inhibitor the apparent activation energy was lower than that in the absence of inhibitor. However, in our study, $E_a$ increases with increasing the P1 concentration, and all values of $E_a$ were higher than that in the absence of P1 compound. This type of inhibitor retards corrosion at ordinary temperatures but inhibition is diminished at elevated temperature.

Arrhenius law predicts that corrosion rate increases with the temperature and Ea and A may vary with temperature (Eq. 1). The obtained values seem that A and Ea increase continuously with the inhibitor's concentration. It's observed that the Ea value is increased in the presence of inhibitor that indicates the poorer performance of the compound at higher temperatures. The addition of inhibitor modified the values of the apparent activation energies; this modification may be attributed to the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules. The lower value of the activation energy of the process in a P1 inhibitor's presence when compared to that in its absence is attributed to its chemisorptions while the opposite is the case with physical adsorption. This type of inhibitor retards corrosion at ordinary temperatures but inhibition is diminished at elevated temperature.

Other kinetic data (enthalpy and entropy of corrosion process) are accessible using the alternative formulation of Arrhenius equation eq (3) and transition state equation eq (4) [12, 13, 15, 44, 45]:

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^o}{R}\right)\exp\left(-\frac{\Delta H_a^o}{RT}\right) \qquad (4)$$

Where h is planks constant, N is Avogadro's number, $\Delta S_a^\circ$ and $\Delta H_a^\circ$ are the entropy and enthalpy of activation, respectively. Plots of ln (W/T) vs. the reciprocal of temperature show straight lines with a slope equal to $(-\Delta H_a^\circ/R)$ and an intercept of $(\ln R/Nh + \Delta S_a^\circ/R)$. The values of $\Delta H_a^\circ$ and $\Delta S_a^\circ$ are also presented in Table 4.

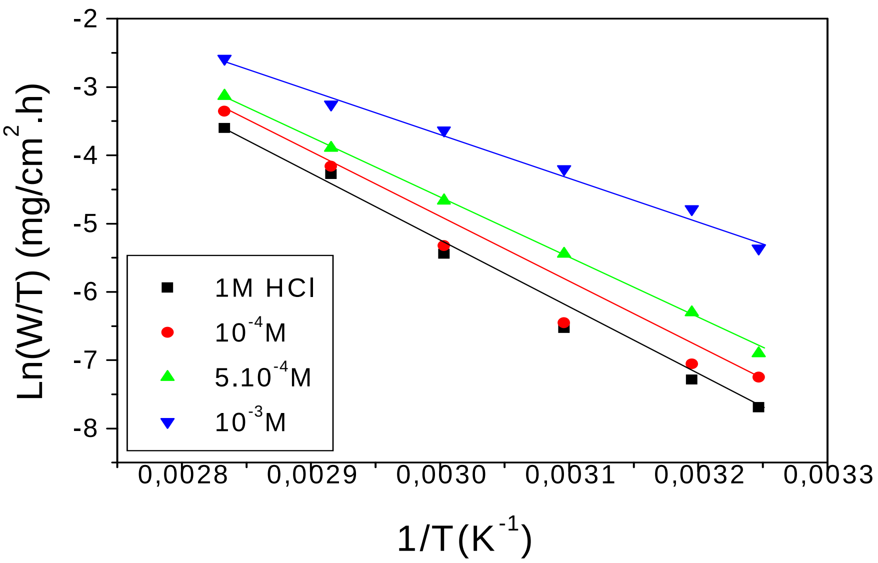


**Figure 3. The relation between log (*W* / *T*) vs. 1 / *T* for steel at different concentrations of P1.**

The positive signs of ΔH* reflect the endothermic nature of the steel dissolution process. The values of $E_a$ and ΔH* enhance with an increase in the concentration of P1 suggesting that the energy barrier of corrosion reaction increases as the concentration of P1 is increased. This means that the corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of $E_a$ as the concentration of the inhibitor becomes greater [40]. Inspection of the kinetic data obtained in Table.4 shows that all parameters of corrosion process increases with the inhibitor concentration. In the present study, it could be found that the ΔS* increase with the increase in concentration of P1, and passes from the -13.3 at $10^{-4}$M to 13.0 J $mol^{-1}$ at $10^{-3}$M, furthermore, we notice as the ΔS* changes its sign from negative to positive as a result of possible change in the mechanism of the corrosion process and in disordering takes place on going from reactants to the activated complex. The obtained result was similar to the author's previous outcome [16, 46-48].

**Table 4. Activation parameters of the dissolution of steel in 1 M HCl in the absence and presence of P1**

| C(M) | $E_a$ (kJ/mol) | $\Delta H^{\circ}_a$ (kJ/mol) | $\Delta S^{\circ}_a$ (J/mol.K) | $E_a$-$\Delta H^{\circ}_a$ (kJ/mol) |
|---|---|---|---|---|
| Blank | 52.5 | 55.0 | -70.6 | 2.7 |
| $10^{-4}$ | 74.3 | 77.0 | -13.3 | 2.7 |
| 5 $10^{-4}$ | 81.6 | 84.4 | 4.6 | 2.7 |
| $10^{-3}$ | 85.0 | 87.7 | 13.0 | 2.7 |

The increase of *Ea* and $\Delta H^{\circ}_a$ with an increase in the P1 concentration (Figure.2 .3) suggests that the energy barrier of corrosion reaction increases with the inhibitor's concentration. The higher activation energy in the inhibitor's presence further supports the proposed physisorption mechanism. Unchanged or lower values of Ea in inhibited systems compared to the blank to be indicative of chemisorptions mechanism, while higher values of Ea suggest a physical adsorption mechanism. This type of inhibitors retards the corrosion process [19, 34, 40, 49-53].

In this work, P1 compound tested contain a chain between aminocyclohexane and N atom, cyano group contains the main active centres of molecule and cycle ring. The presence of free electron pair in the nitrogen atom favours the adsorption of inhibitor. It apparent from the results that the molecular structure of this compound that the essential affect of the corrosion inhibition [51, 54-56].

The inhibitory effect of these compounds studied can be also interpreted by formation of a stable film on the metal surface. The formation of a stable film on the metal surface through chemisorptions is tested and reported [13, 14, 19, 34]. It is found that an adsorbed film is formed on mild steel surface which is responsible for the inhibition of corrosion in the acid. The protective activity of the adsorbed film in the acid solution is retained for a period of time when specimens, dipped in inhibited acid, are transferred to fresh acid without inhibitor.

P1 is the best inhibitor among the compounds tested. That is expected to due to the existence of cyano group and the recover effect of grouping by organic chain. This observation clearly proves that the inhibition is due to the formation of an insoluble stable film from the process of chemisorptions on the metal surface.

### 3.3. Thermodynamic parameters and adsorption isotherm.

Attempts were made to fit values of θ to many isotherm including Langmuir, Temkin, Frumkin and Freundlich. The organic compound seems that follows well the Langmuir adsorption isotherm written in the rearranged form:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \text{with } K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \qquad (5)$$

Where *C* is the concentration of inhibitor, *K* is the adsorptive equilibrium constant; *θ* is the surface coverage and the standard adsorption free energy ($\Delta G_{ads}$).

The relationship between C/θ and C presents linear behaviour at all temperatures studied (Figure. 4) with slopes equal to unity.

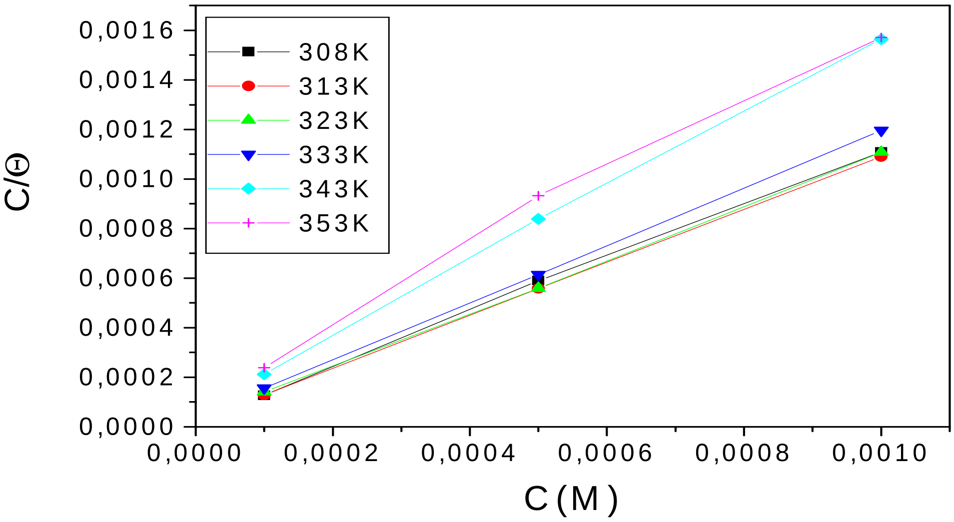


**Figure 4. Fitting Langmuir's adsorption isotherm model for P1 in 1 M HCl at different temperatures.**

To get more adsorption enthalpy, $\Delta H^{\circ}_{ads}$, the Van't Hoff equation was used [27]:

$$\ln(K) = -\frac{\Delta H^{\circ}_{ads}}{RT} + Constant \qquad (6)$$

The straight line obtained between ln(K) and 1/T , which is equal to that estimated by the Gibbs–Helmholtz equation, expressed by:

$$\left[\frac{\partial(\Delta G^{\circ}_{ads}/T)}{\partial T}\right]_P = -\frac{\Delta H^{\circ}_{ads}}{T^2} \qquad (7)$$

and written in the following equation.

$$\frac{\Delta G^{\circ}_{ads}}{T} = \frac{\Delta H^{\circ}_{ads}}{T} + A \qquad (8)$$

The standard adsorption entropy $\Delta S^{\circ}_{ads}$ may be deduced using the thermodynamic basic equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \qquad (9)$$

All the obtained thermodynamic parameters are shown in Table 3. The negative values of $\Delta G^{\circ}_{ads}$ for P1 indicate the spontaneous of the adsorption of P1 and stability of the adsorbed layer on the Steel surface [9, 10, 57, 58].

**Table 5. Thermodynamic data for studied P1 from experimental adsorption isotherm.**

| Temperature (K) | $\Delta G^\circ_{ads}$ (kJ mol$^{-1}$) | $\Delta H^\circ_{ads}$ (kJ mol$^{-1}$) | $\Delta S^\circ_{ads}$ (J mol$^{-1}$K$^{-1}$) |
|---|---|---|---|
| 308 | -37,12 | -31.9 | 17 |
| 313 | -38,35 | -31.9 | 20.48 |
| 323 | -38,90 | -31.94 | 21.55 |
| 333 | -39,30 | -31.94 | 22.09 |
| 343 | -38,70 | -31.94 | 19.69 |
| 353 | -38,11 | -31.94 | 17.46 |

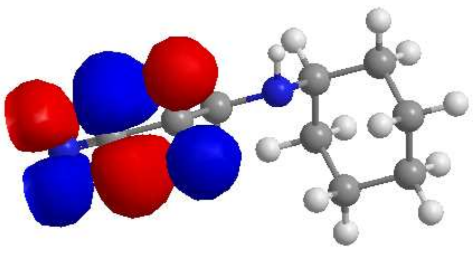
The values of thermodynamic parameters for the adsorption of inhibitors can provide valuable information about the mechanism of corrosion inhibition. More negative value, $\Delta G^\circ_{ads\ and}$ $\Delta H^\circ_{ads}$ designates that inhibitor is strongly adsorbed on the Steel surface. The negative values of $\Delta H^\circ_{ads}$ also show that the adsorption of inhibitor is an exothermic process [20]. It assumed that an exothermic process is attributed to either physical or chemical adsorption but endothermic process corresponds solely to chemisorptions. In an exothermic process, physisorption is distinguished from chemisorptions, generally, values of $\Delta G^\circ_{ads}$ up to -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption) while those around -40 kJ mol$^{-1}$ or higher are associated with chemisorptions as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorptions) [5, 7, 34]. In this study; the standard adsorption heat between -37.12 kJmol$^{-1}$ and 38.11 kJmol$^{-1}$, indicating, therefore, that the adsorption mechanism of the P1 on steel in 1.0 M HCl solution was typical of chemisorptions (Table 5).The possible mechanisms for chemisorptions can be attributed to the donation $\pi$-electron by the rings, and the presence of nitrogen atoms in structure molecule as reactive centres [3-6, 12-14].

Finally, we show this change the inhibition by: first with the organic chain that is long for P1 than P2, this ensures an important recovery of metal surface. Other hand the existence of two active adsorption sites in the structure of P1 [12-14] permitted to reinforce this interaction.

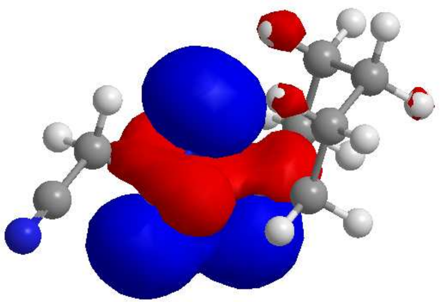
### 3.9. Theoretical calculations

The calculated quantum chemical indices ($E_{HOMO}$ = energy of the highest occupied molecular orbital, $E_{LUMO}$ = energy of the lowest unoccupied molecular orbital) of the three inhibitors are shown in Table 8. Inhibition efficiency increases with increasing values of $E_{HOMO}$ [1, 16, 23, 59].

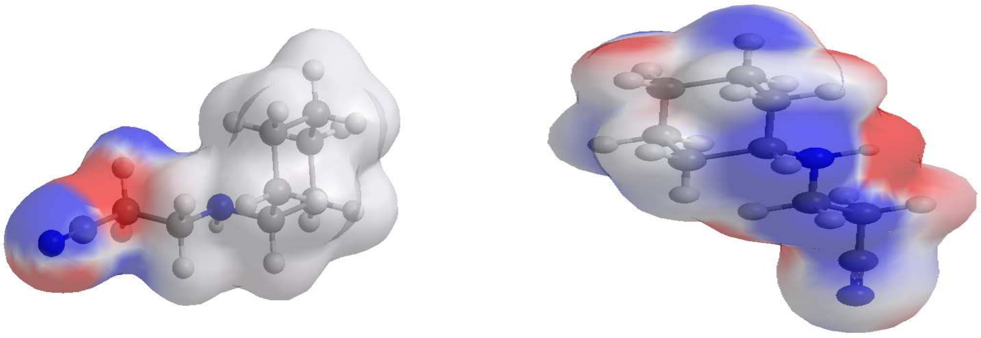
In order to correlate some quantum chemical parameters with experimental inhibition efficiencies of P1 and P2 were obtained. This may be explained by the fact that the inhibition efficiency in this case is not strictly governed by the electronic properties. The reactive ability of the inhibitor is considered to be closely related to their frontier molecular orbitals, the HOMO and LUMO. A typical electron density distribution of HOMO and LUMO for P1 and P2 are shown in schema.2. The results seem to indicate that charge transfer from the inhibitor takes place during the adsorption on the metal surface. Increasing values of the $E_{HOMO}$ may facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. However, the difference $\Delta E = E_{HOMO} - E_{LUMO}$ is a negative number, whereas the coefficient of ΔE is positive, indicating that smaller absolute value of ΔE, and therefore, a low excitation energy to move an electron from the highest occupied molecular orbital will cause higher inhibition efficiency. This means that the band gap energy value (Figure. 5) is more favourable for P1 than P2 to explain percentage of the inhibition efficiency.



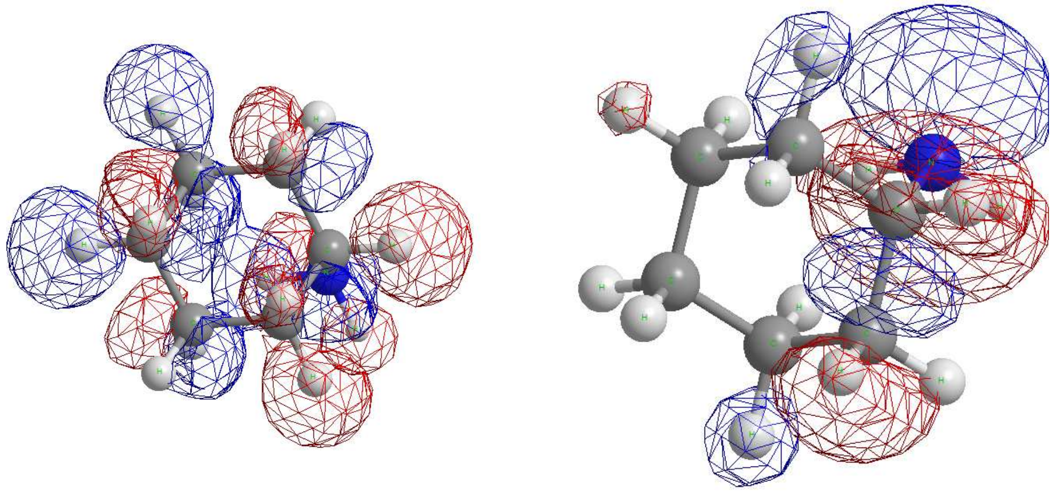
**LUMO of P1**



**Homo for P1**



**LUMO and charge density surface of P2** **Homo charge density surface for P2**



**LUMO of P2** **LUMO of P2**

**Schema 2. The frontier molecular orbital density distributions (HOMO and LUMO) along the P1 and P2.**

**Table 6. Total charge density surface and calculated by Gaussian program**

| Compounds | N(7) | N(12) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $\Delta E$ (eV) |
|---|---|---|---|---|---|
| **P1** | -0.208 | -0.383 | -10.275817 | 5.732889 | -38.73603 |
| **P2** | -0.299 | - | -11.325343 | 28.460213 | -39.78555 |

Table 6. indicates that for compound P1, N(7) and N(12) have negative charges and consequently they are the centres of the adsorption phenomenon; but for P2 have only N(17) have negative charge [1, 16, 23, 59-63].

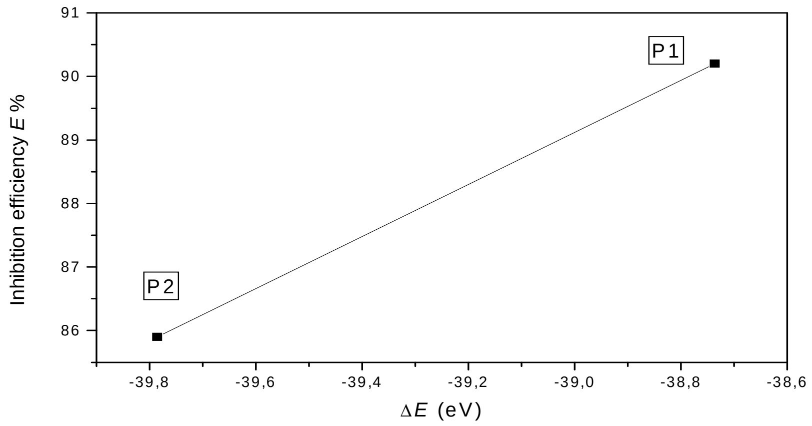
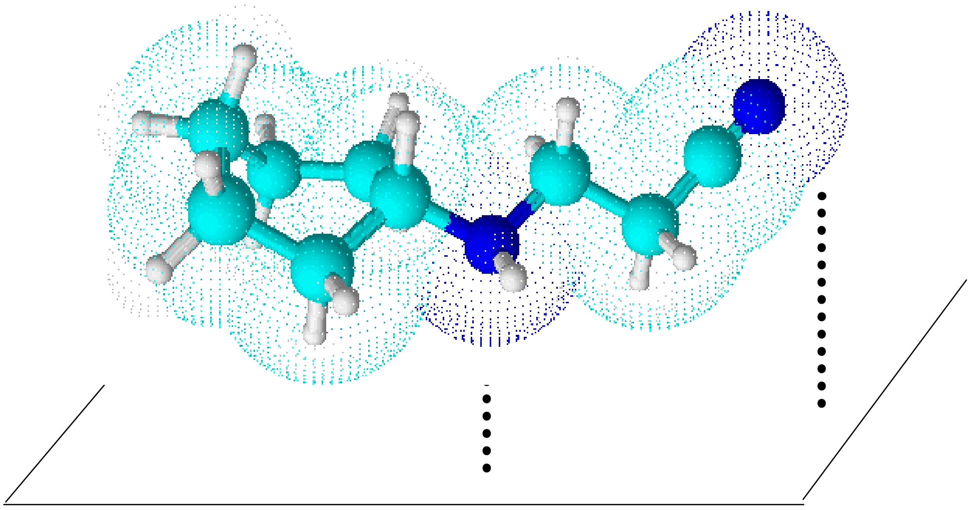


**Figure. 5. Correlation of energies difference Δ*E* with percent inhibition P1 and P2.**

The findings obtained by the experimental study and the calculation of the total charge density surface of inhibitor P1 may suggest the adsorption mode as below (Scheme 3).



**Scheme 3. Schematic representation of the mode of P1 adsorption.**

Due to the geometry configuration, the repartition of the HOMO density is preferentially localized on one part of amine function for both molecules. The steel may transfer electron to P1 on both nitrogen to form a stable steel complex, improving therefore the corrosion resistance of mild steel in 1 M HCl medium. It is reported that excellent inhibition corrosion properties are usually obtained using organic compounds that not only offer electrons to unoccupied orbital's of the metal but also accept free electrons from the metal by using their anti-bond orbital's. This fact proves that the feedback bonds are formed between d orbital's of steel and inhibitor molecules. Forming of feedback bonds increases the chemical adsorption of inhibitor molecules on the steel surface and so increases the inhibition efficiency. Therefore, this could lead to the conclusion that the strongest feedback bonds are formed in the case of P1. Moreover the band gap ($\Delta E$) between the HOMO and LUMO energy levels of the molecules is another important factor that should be considered [1, 23, 61-63].

According to the results listed in Table 6, we note a smaller absolute value of $\Delta E$ (-38.74 eV) is found for P1 and higher inhibition efficiency. This conclusion is in good agreement with experimental results (Table1,2) with the theoretical calculations (Table.6)

## CONCLUSION

From the above results and discussion, the following conclusions are drawn:

1. The type molecules have been low-cost and stable corrosion inhibitors.
2. Their inhibition efficiency (E%) increases with the concentration for all inhibitors.
3. The inhibitory efficiency is dependent of inhibitors structure of P1 and P2.
4. P1 containing cyano group, as usually excellent inhibitor and its inhibition efficiency attain 90.2% since $10^{-3}$M.
5. The inhibition efficiency of P1 is temperature dependent and the addition of P1 and their addition lead to an increase of the activation energy of the corrosion process.
6. The adsorption of the P1 on the steel surface in molar hydrochloric acid obeys to the Langmuir adsorption isotherm model.
7. High $E_{HOMO}$ and low energy gap ($E_{HOMO} - E_{LUMO}$) explain the best inhibition efficiency of P1
8. The results obtained from weight loss, potentiodynamic polarization are in good agreement

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