

Adsorption Characteristics and Corrosion Inhibitive Properties of Clotrimazole for Aluminium Corrosion in Hydrochloric Acid

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Clotrimazole (CTM) [1-[(2-chlorophenyl)-diphenyl-methyl]imidazole], an antifungal drug, was investigated as a corrosion inhibitor for aluminium in HCl using weight loss method. CTM inhibited the corrosion of aluminium in HCl. The inhibition efficiency increased with increase in the concentrations of CTM to reached 90.90% at 1×10^{-4} M, but decreased with increase in temperature. Phenomenon of physical adsorption is proposed for the inhibition and the process followed the Langmuir adsorption isotherm and kinetic / thermodynamic model of El-Awady et al. The mechanism of adsorption inhibition and type of adsorption isotherm were proposed from the trend of inhibition efficiency with temperature, E_a , ΔG_{ads} , and Q_{ads} . Quantum chemical calculations results show that CTM possesses a number of active centres concentrated mainly on the imidazole moiety of the molecule. The highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) were also found around the nitrogen atoms and the cyclic of the benzene rings.

Keywords: Clotrimazole, Aluminium, corrosion inhibition, adsorption isotherm, thermodynamics, quantum chemical studies, Austin Model 1 (AM1)

1. INTRODUCTION

An enormous breadth of engineering systems depends upon corrosion protection for their reliability, performance and safety. A recent cost of corrosion study estimated that in 2002, corrosion drained about 3.1% of the GDP from the US economy. On this basis, the direct economic loss from corrosion in US in 2004 was put at \$364 billion [1]. In this sense, corrosion is the largest continuing technical calamity of our time.

Among several methods used in combating corrosion problems, the use of chemical inhibitors remain the most cost effective and practical method. Therefore, the development of corrosion

inhibitors based on organic compounds containing nitrogen, sulphur and oxygen atoms are of growing interest in the field of corrosion and industrial chemistry as corrosion poses serious problem to the service lifetime of alloys used in industry [2]. However, the efficiency of these inhibitors depends on the nature and the state of the metallic surfaces, chemical composition and structure of the inhibitor. Furthermore, the stability of the adsorbed inhibitor films formed over the metal surface to protect the metal from corrosion depends on some physico-chemical properties of the molecule, related to its functional groups, aromaticity, the possible steric effects, electron density of donor atoms, type of corrosive medium and the nature of the interaction between the inhibitor and the metal surface [3-5].

The use of drugs as corrosion inhibitors for metals in different aggressive environments is not widely reported. Few reports exist in literature to date. These include the use of sulphur drugs [6,7], antimalarial drug [8] and analgesic drug [9] as efficient corrosion inhibitors for metals in various media. To the best of our knowledge, the use of antifungal drugs as corrosion inhibitor may not have been reported at all.

Recently, quantitative structure activity relationship (QSAR) has been a subject of intense interest in many disciplines of Chemistry. The development of semi-empirical quantum chemical calculations emphasizes the scientific approaches involved in the selection of inhibitors by correlating the experimental data with quantum-chemical properties. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), charges on reactive centre, dipole moment (μ) and conformations of molecules have been used to achieve the appropriate correlations.

In this paper, we report the use of clotrimazole (CTM) [1-[(2-chlorophenyl)-diphenylmethyl]imidazole] as an effective and efficient corrosion inhibitor for aluminium in HCl using weight loss method at 30 and 50 °C. Clotrimazole is a synthetic antifungal drug. The molecule is made up of three benzene ring of planar structure with delocalized π electrons (aromaticity), an imidazole ring containing delocalized π electrons and two (N) atoms with lone pairs of electrons which can serve as centres for adsorption. These factors favour the interaction of imidazole with metal. Moreover, the molecule is big enough (molecular mass- 344. 485) and likely to effectively cover more surface area (due to adsorption) of the aluminium metal. Furthermore, clotrimazole is very cheap, easily available, environmentally friendly and the most important, nontoxic. In view of these favourable characteristics, clotrimazole was chosen for the corrosion studies. Thermodynamics was used to properly characterize the mechanism of the corrosion process while the correlation of inhibition effect and molecular structure of clotrimazole was discussed to some extent using quantum chemical calculations.

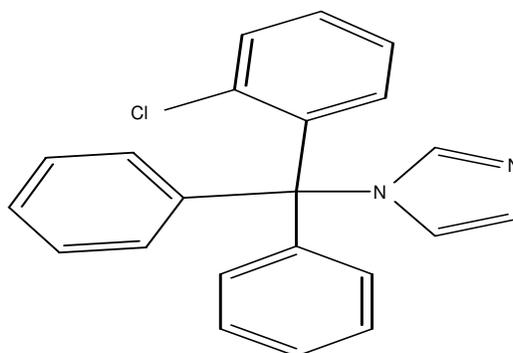
2. EXPERIMENTAL PART

Aluminium sheets of the type AA 1060 and purity 98.8% were used in this study. Each sheet was 0.14 cm in thickness was mechanically press-cut into coupons of dimension 5cm x 4cm. These coupons were used as cut without further polishing. They were however degreased in absolute ethanol, dried in acetone, weighed and stored in moisture-free desiccators prior to use [10].

All reagents used were BDH grade. These were used as sourced without further purification. An aqueous solution of 0.1 M HCl was used as a bank solution. Clotrimazole was added to the acid in

concentrations ranging from 2×10^{-5} – 1×10^{-4} M. Experiments were conducted in the test solutions for 24 h progressively for 168 h (7 days) at 30 and 50 °C, respectively. In each experiment, the cleaned aluminium coupon was weighed and suspended with the aid of glass rod and hook in a beaker containing 100ml acid solution. The coupon was then taken out of the test solution, rinsed with distilled water, dried and re-weighed. The weight loss was taken as the difference between the weight at a given time and the initial weight of the test coupon. The average weight loss for two determinations is reported in this study.

All the quantum chemical calculations were performed with SPARTAN'06 V112 semi-empirical program using AM1 method [11]. The following quantum chemical indices were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, dipole moment (μ), and atomic charges of clotrimazole.



1-[(2-chlorophenyl)-diphenyl-methyl]imidazole

Scheme 1. The chemical structure of clotrimazole (CTM)

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability [12]. Several authors have reported on comparable agreement between weight loss technique and other techniques of corrosion monitoring. These include polarization measurement [7,13-15], hydrogen evolution [16-19], thermometric technique [20,21] and electrochemical impedance spectroscopy [22,23].

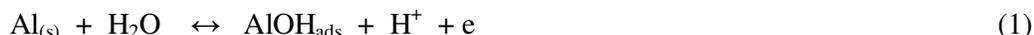
The corrosion rate of aluminium in the absence and presence of clotrimazole at 30 and 50 °C was studied using weight loss technique. Table 1 shows the calculated values of corrosion rate ($\text{mgcm}^{-2}\text{h}^{-1}$), inhibition efficiency (IE%) and the degree of surface coverage for aluminium dissolution in 0.1 M HCl in the absence and presence of clotrimazole. From the values obtained, it is clear that the corrosion rate of aluminium decreases in the presence of CTM when compared to the blank. The corrosion rate also decreases with increasing concentration of the CTM. This indicates that the CTM in

the solution inhibits the corrosion of aluminium in HCl and that the extent of corrosion inhibition depends on the amount of the CTM present. Furthermore, the corrosion rate is found to increase with increase in temperature with and without CTM. This can be attributed to the fact that the rate of chemical reaction increases with increase in temperature.

Table 1. Corrosion parameters for aluminium in 0.1M HCl in the absence and presence of different concentrations clotrimazole at different temperatures.

Temperature (°C)	System/Concentration	Corrosion rate (mgcm ⁻² h ⁻¹) x10 ⁻³	(IE %)	θ
30	Blank	45.83	-	-
	2x 10 ⁻⁵ M	14.58	68.18	0.68
	4 x 10 ⁻⁵ M	12.50	72.73	0.73
	6 x 10 ⁻⁵ M	10.41	77.27	0.77
	8 x 10 ⁻⁵ M	8.33	81.82	0.82
	1 x 10 ⁻⁴ M	4.16	90.90	0.91
50	Blank	312.50	-	-
	2x 10 ⁻⁵ M	237.50	24.00	0.24
	4 x 10 ⁻⁵ M	225.00	28.00	0.28
	6 x 10 ⁻⁵ M	214.58	31.33	0.31
	8 x 10 ⁻⁵ M	206.25	34.00	0.34
	1 x 10 ⁻⁴ M	200.00	36.00	0.36

Corrosion of Al in aqueous solution has been reported [24] to depend on the concentration of anions in solution. A general mechanism for the dissolution of Al metal would be similar to that reported by Oguzie et al. [10]



The controlling step in the metal dissolution is the complexation reaction between the hydrated cation and the anion present Eq. (3). In the presence of chloride ions the reaction will correspond to:



The soluble complex ion formed increases the metal dissolution rate which depends on the chloride concentration, this accounts for the observed increase in corrosion rate in HCl (blank) as compared to the presence of CTM.

The value of corrosion rate was calculated from the following equation [25].

$$v = (m_1 - m_2) / St \quad (6)$$

where m_1 is the mass of the Al coupon before immersion, m_2 the mass of the Al coupon after immersion, S is the total area of the Al coupon, t is the corrosion time and v is the corrosion rate. The calculated corrosion rate (v) in equation (6) is an average corrosion rate as no localized corrosion takes place.

From the corrosion rate, the percentage inhibition efficiency IE (%) and the degree of surface coverage (θ) were calculated using equations (7) and (8) respectively [26].

$$IE(\%) = (v_0 - v) / v_0 \times 100 \quad (7)$$

$$\theta = (v_0 - v) / v_0 \quad (8)$$

where v_0 and v are the corrosion rates of the Al coupon in 0.1M HCl in the absence and presence of CTM, respectively.

The values of inhibition efficiency ($IE\%$) obtained from weight loss method at different concentrations of CTM and at different temperatures (30 and 50 °C) are also shown in Table 1. It is seen from the table that IE (%) for CTM reaches a maximum value of 90.90% with the highest concentration of $1 \times 10^{-4}M$ at 30 °C. Also, inhibition efficiency increases with increase in the concentrations of CTM but decrease with increase in temperature. Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption mechanism and may be attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of Al metal that may otherwise inhibit the corrosion process. It may further be attributed to a possible shift of the adsorption-desorption equilibrium towards desorption of adsorbed inhibitor due to increased solution agitation. Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency. It has been postulated that inhibitors slow corrosion processes by (i) increasing the anodic or cathodic polarization behavior (Tafel slopes), (ii) reducing the movement or diffusion of ions to the metallic surface, and (iii) increasing the electrical resistance of the metallic surface. Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration.

3.2. Adsorption considerations

Adsorption depends mainly on the charge and nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent and other ionic species, temperature of corrosion reaction and on the electrochemical potential at solution-interface [27]. Adsorption of inhibitor involves the formation of two types of interaction responsible for bonding of inhibitor to a metal surface. The first one (physical adsorption) is weak undirected interaction and is due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of metal. The potential of zero charge plays an important role in the electrostatic adsorption process. The charge on metal surface can be expressed in terms of potential difference (Φ) between the corrosion potential (E_{corr}) and the potential of zero charge (E_{pzc}) of the metal ($\Phi = E_{corr} - E_{pzc}$). If Φ

is negative, adsorption of cations is favoured. On the contrary, the adsorption of anions is favourable if Φ is positive. The second type of interaction (adsorption) occurs when directed forces govern the interaction between the adsorbate and adsorbent. Chemical adsorption involves charge sharing or charge transfer from adsorbates to the metal surface atoms in order to form a coordinate type of bond. Chemical adsorption has a free energy of adsorption and activation energy higher than physical adsorption and, hence, usually it is irreversible [28].

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Frumkin, Hill de Boer, Parsons, Temkin, Flory-Huggins, Dhar-Flory-Huggins, Bockris-Swinkels and the recently formulated thermodynamic/kinetic model of El-Awady et al. [29-31]. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clues to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the H₂O molecule and the metal surface [32].

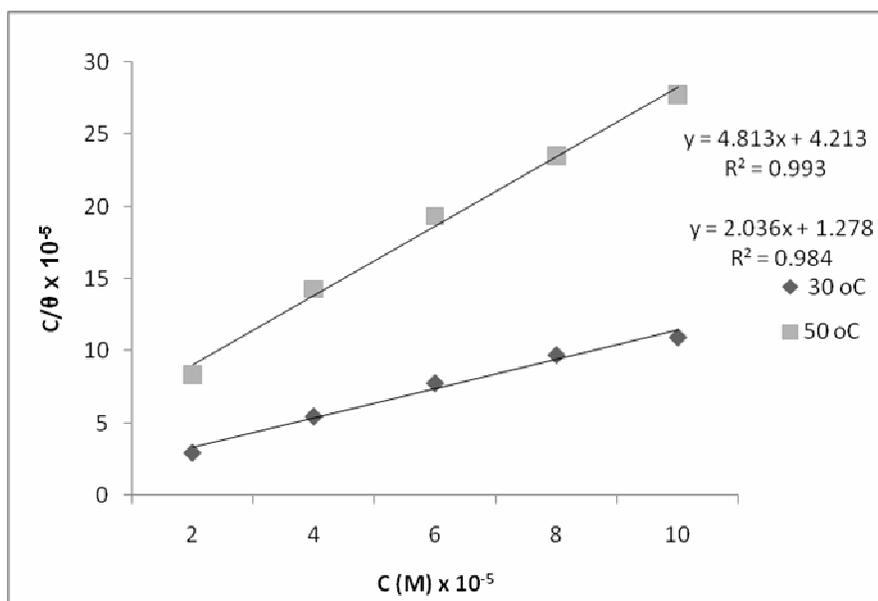


Figure 1. Langmuir adsorption Isotherm plot for Clotrimazole at 30°C and 50°C

In order to obtain the adsorption isotherm, the degree of surface coverage (θ) for various concentrations of the inhibitor has been calculated according to equ. (8). Langmuir isotherm was tested for its fit to the experimental data. Langmuir isotherm is given by

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (9)$$

Where θ is the degree of surface coverage, C the molar inhibitor concentration in the bulk solution and K_{ads} is the equilibrium constant of the process of adsorption. Though the plot of C/θ

versus C was linear (Fig.1) (correlation > 0.9), the deviation of the slopes from unity (Table 2) (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. Langmuir isotherm assumes that:

- The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate;
- ΔG_{ads}° is the same for all sites and it is independent of θ ;
- The adsorbates do not interact with one another, ie. there is no effect of lateral interaction of the adsorbates on ΔG_{ads}° [33].

Though the linearity of the Langmuir plot may be interpreted to suggest that the experimental data for CTM obey the Langmuir adsorption isotherm, the considerable deviation of the slope from unity shows that the isotherm cannot be strictly applied.

Table 2. Calculated parameters from Langmuir and El-Awady Adsorption Isotherm

Inhibitor	Temperature (°C)	Langmuir Isotherm				El-Awady Isotherm			
		K_{ads}	ΔG_{ads}°	Slope	R^2	K_{ads}	ΔG_{ads}°	1/y	R^2
	30	0.782	-8.497	2.036	0.984	1.306	-10.79	6.37	0.912
	50	0.237	-6.920	4.813	0.993	0.288	-7.44	16.39	0.972

Hence, the experimental data were fitted into the El-Awady's kinetic/thermodynamic model. The characteristics of the isotherm is given by

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y \log C \quad (10)$$

where C is the concentration of the CTM, θ is the degree of surface coverage, K_{ad} is the equilibrium constant of adsorption process and $K_{ad} = K^{1/y}$. In this model, the number of active sites y is included. Values of 1/y less than one imply multilayer adsorption, while 1/y greater than one suggests that a given inhibitor molecule occupies more than one active site. Curve fitting of the data to the thermodynamic-kinetic model is shown in Fig. 2. This plot gave straight lines which clearly show that the data fitted well to the isotherm. The values of 1/y and K_{ad} calculated from the El-Awady et al. model curve is given in Table 2. From the table the obtained values of 1/y is greater than one showing that a given CTM molecule occupies more than one active site (which may be due to the presence of two N atoms in CTM molecule together with several π electrons). It is also seen from the table that K_{ad} decreases with increase in temperature indicating that adsorption of CTM on the aluminium surface was unfavourable at higher temperatures.

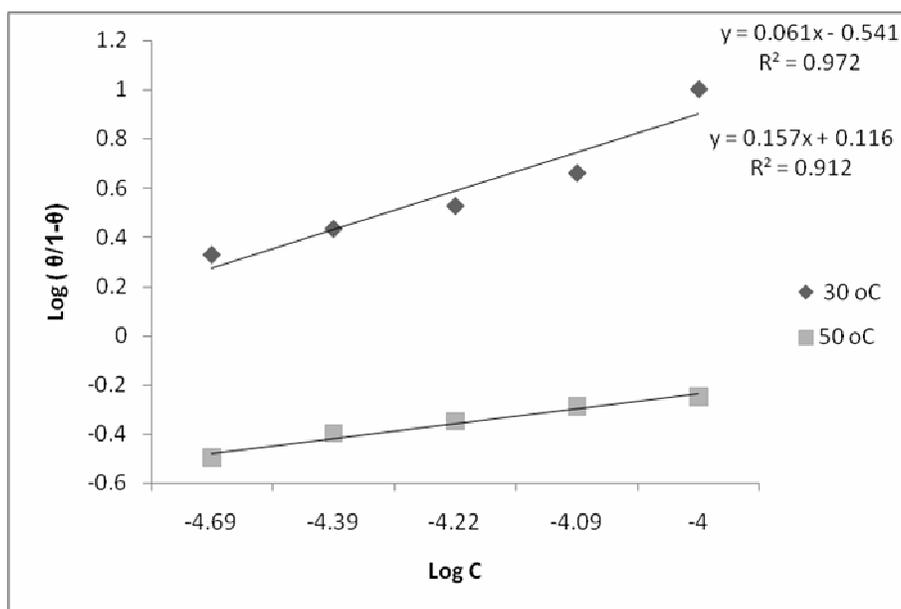


Figure 2. El-Awady et al. plot for Clotrimazole at 30°C and 50°C

3.3. Kinetic and thermodynamic considerations

The relationship between the temperature, percentage inhibition efficiency (IE %) of an inhibitor and the activation energy in the presence of an inhibitor was given as follows [12].

- Inhibitor whose IE (%) decreases with temperature increase. The value of activation energy (E_a) found is greater than that in the uninhibited solution.
- Inhibitors whose IE (%) does not change with temperature variation. The activation energy (E_a) does not change in the presence or absence of inhibitors.
- Inhibitors whose IE (%) increases with temperature increase. The value of activation energy (E_a) found is less than that in the uninhibited solution.

While the higher value of the activation energy (E_a) of the process in an inhibitor's presence when compared to that in its absence is attributed to its physical adsorption, its chemisorptions is pronounced in the opposite case [12].

In order to further support physical adsorption, the values of activation energy (E_a) were calculated with the help of Arrhenius equation [34].

$$\log \frac{v_2}{v_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (11)$$

Where v_1 and v_2 are the corrosion rates at temperature T_1 and T_2 , respectively. The values are presented in Table 3. The higher value of E_a in the presence of CTM compared to that in its absence

and the decrease of its IE% with temperature increase can be interpreted as an indication of physical adsorption. These results are in agreement with observations in earlier publications [34, 35].

Table 3. Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for Al dissolution in 0.1M HCl in the absence and presence of clotrimazole at 30-50 °C

System/concentration	E_a (kJmol ⁻¹)	Q_{ads} (kJmol ⁻¹)
Blank	78.27	-
2 x 10 ⁻⁵ M	113.75	-77.57
4 x 10 ⁻⁵ M	117.78	-78.89
6 x 10 ⁻⁵ M	126.23	-81.77
8 x 10 ⁻⁵ M	130.84	-88.73
1 x 10 ⁻⁴ M	157.78	-117.59

An estimate of heat of adsorption was obtained for the trend of surface coverage with temperature as follows [36].

$$Q_{ads} = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \left(\frac{T_1 T_2}{T_2 - T_1} \right) \text{kJmol}^{-1} \quad (12)$$

Where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 .

The calculated values for Q_{ads} is presented in Table 3. According to Bhajiwala and Vashi [36], negative Q_{ads} values imply that inhibitor adsorption and hence efficiency decreases at high temperature while positive values suggest increased efficiency at high temperature. From Table 3, it is evident that in all cases the values of Q_{ads} are negative and ranges from -77.579 kJ/mol to -117.587 kJ/mol. This is in support of the earlier proposed physisorption mechanism.

The equilibrium constant for the adsorption process from Langmuir and Kinetic/thermodynamic isotherm model of El-Awady et al. is related to the standard free energy of adsorption by the expression:

$$k_{ads} = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{ads}^o}{RT} \right] \quad (13)$$

where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar. The standard free energy of adsorption, ΔG_{ads}^o , which can characterize the interaction of adsorption molecules and metal surface, was calculated by equation (13). The negative values of ΔG_{ads}^o ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface. Generally, the values of ΔG_{ads}^o around -20kJ/mol or lower are consistent with physisorption, while those around -40kJ/mol or higher involve chemisorptions [37]. The values of ΔG_{ads}^o for CTM is given in Table 2 and these values indicate that CTM molecules are

physisorbed onto Al surface. The adsorption is enhanced by the presence of two N atoms with lone pairs of electrons and the delocalized π electrons in the inhibitor molecules that makes it adsorbed electrostatically on the metal surface forming insoluble stable films on the metal surface thus decreasing metal dissolution.

3.4. Quantum chemical studies

Generally speaking, it is unusual to include quantum chemical calculation in corrosion investigation. However, quantum chemical calculation has obvious advantages compared with existing methods for synthesis and selection of corrosion inhibitors. This approach is not restricted closely to related compound, as is often the case with group theoretical, topological and others, and it makes interpretation of quantitative structure-activity relationships more straightforward. In addition, the results of quantum chemical calculations could be obtained without laboratory measurements, thus saving time and equipment, alleviating safety and disposal concerns [38]. Besides, the correlations between inhibition efficiency and molecular parameters can be used for pre-selection of new inhibitors, which are, at the moment, taken essentially from empirical knowledge [39]. These facts have made quantum chemical calculations to be a very powerful tool for studying corrosion inhibition mechanism.

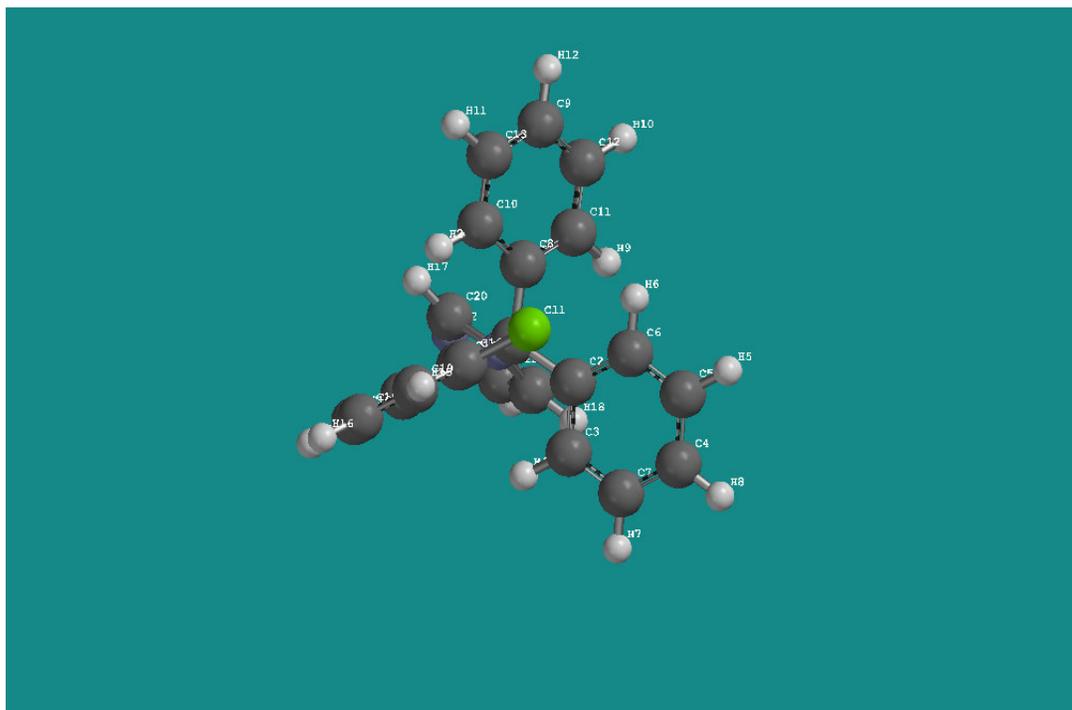


Figure 3. An optimized geometry of clotrimazole molecule.

The quantum chemical parameters of clotrimazole were calculated and listed in Table 4. The AM1 optimized geometry of CTM is shown in Fig 3. Information about the adsorption centres

showing the calculated total partial atomic charges (TPAC) in clotrimazole molecule is presented in Table 5.

Table 4. Quantum parameters of clotrimazole obtained by Spartan'06

Quantum Parameter	μ (D)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)	Heat of formation (kJ/mol)	CPK Area (\AA^2)
Calculated value	3.68	-8.98	-0.14	8.84	659.03	342.94

Table 5. The charge density of the clotrimazole molecule

No.	Atom	Charge	No.	Atom	Charge
1	C	0.235744	13	C	-0.134406
2	C	-0.094225	14	C	-0.133827
3	C	-0.115420	15	C	-0.083147
4	C	-0.116304	16	C	-0.116072
5	C	-0.136024	17	C	-0.046919
6	C	-0.099339	18	C	-0.115119
7	C	-0.135078	19	C	-0.131024
8	C	-0.098161	20	C	-0.131375
9	C	-0.116300	21	C	-0.102003
10	C	-0.106938	22	C	-0.157190
12	C	-0.107577	23	C	-0.185988
			24	N1	-0.168241
			25	N2	-0.142024

Frontier orbital theory was useful in predicting the adsorption centres of the inhibitor molecule responsible for the interaction with surface metal atoms [13, 15]. Thus, HOMO and LUMO properties of CTM were plotted as shown in Figures 4 and 5. It could be easily found that the frontier orbital were distributed around the heterocycle mainly. It is evident from Table 4 that clotrimazole showed a relatively higher value of HOMO energy and a lower value of LUMO energy, which was in favour of bonding with metal surface, compared with some other organic heterocyclic inhibitors [39]. As E_{HOMO} is often associated with the electron donating ability of the molecule, high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule with low energy and empty molecular orbital. The electronic configuration of Al is $1S^2 2S^2 2P^6 3S^2 3P^1$. The incompletely filled 3P orbital of Al could bond with HOMO of clotrimazole while the filled 3S orbital of it could interact with LUMO of CTM.

From the values of the atomic charge density (Table 5), it can be concluded that the negative charge is concentrated on the N atoms and around the C atoms of the imidazole ring. Accordingly,

CTM molecule can be adsorbed on the Al surface (positive charged) leading to the corrosion inhibition action.

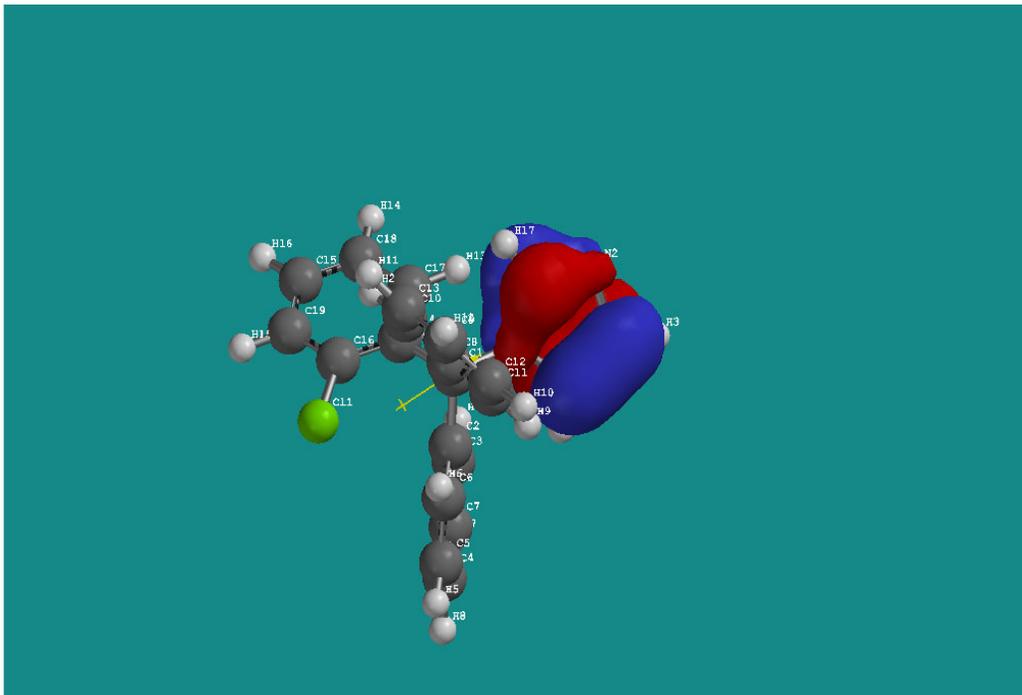


Figure 4. HOMO energy density of clotrimazole molecule showing electron rich centres around the imidazole ring (in red and blue colours)

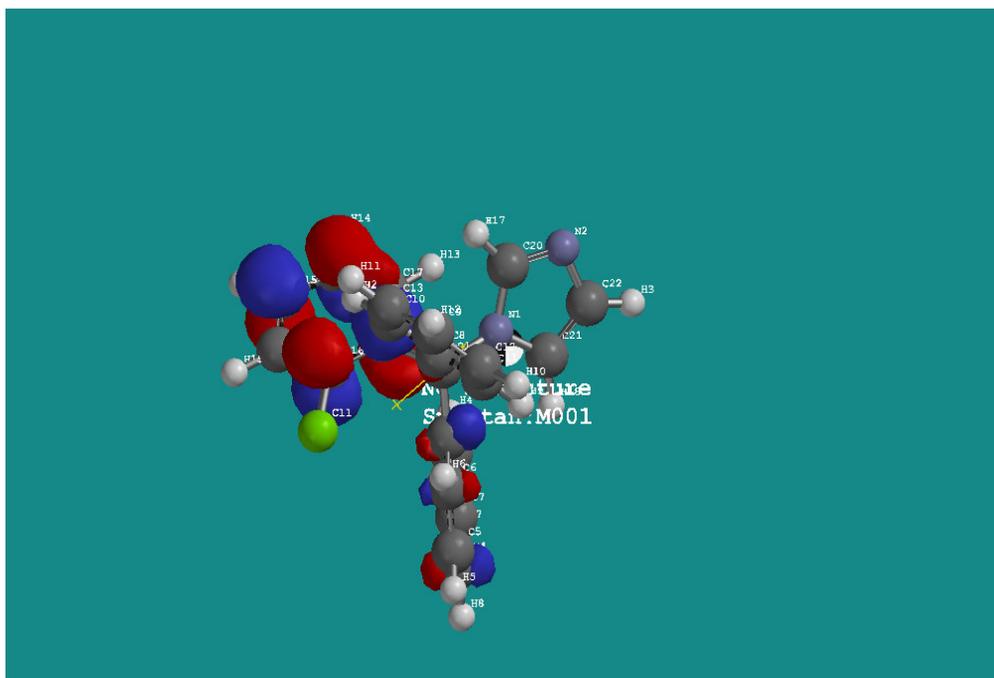


Figure 5. LUMO energy density of clotrimazole molecule. The plot is on ring containing the chlorine atom. This ring contains carbons C13, C14, C15, C16, C17, C18, and Cl atom (red and blue)

From the foregoing, it is clear that more than one adsorbed site could be obtained from one molecule of CTM. It is also proved by the Langmuir and El-Awady adsorption isotherm plots, which indicate a multi-centre adsorption on Al surface. The parameter $1/y$ from the El-Awady plot and the deviation of the slope of the Langmuir isotherm from unity suggested that there is more than one active site having influence on the adsorption for one inhibitor molecule. This result is in good agreement with quantum chemical calculations.

Another important factor is that the molecular weight of CTM (344.485) is larger than other common inhibitors [13, 40]. So enough molecular weight also should be taken into consideration when evaluating a new inhibitor.

3.5. Mechanism of inhibition of corrosion by clotrimazole

The inhibition efficiency of clotrimazole (CTM) against the corrosion of Al in 0.1 M HCl can be explain on the basis of the number of adsorption sites, their charge density, molecular size and mode of interaction with the metal surface [41]. As noted earlier, the proceeding of physical adsorption requires the presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair electrons. However, the compound reported is an organic base which can be protonated in an acid medium, predominantly affecting the nitrogen atoms in the imidazole ring. Thus, they become cations, existing in equilibrium with the corresponding molecular form



The protonated CTM, however, could be attached to the Al surface by means of electrostatic interaction between Cl^- and protonated CTM since the Al surface has positive charges in the acid medium [42]. This could further be explained based on the assumption that in the presence of Cl^- , the negatively charged Cl^- would attach to positively charged surface. When CTM adsorbs on the Al surface, electrostatic interaction takes place by partial transference of electrons from the polar atom (N atoms and the delocalized π electrons around the imidazole ring) of CTM to the metal surface. Similar mechanism has been proposed by Tang et al [14].

4. CONCLUSIONS

The following main conclusions are drawn from the present study:

- Clotrimazole (CTM) was found to be a good inhibitor of aluminium corrosion in acidic medium.
- The inhibition efficiency increases with inhibitor concentration to attain a value of 90.9% ($1 \times 10^{-4}\text{M}$) at 30 °C.

- Inhibition efficiency increased with an increase in CTM concentration but decreased with rise in temperature.
- The presence of CTM increased the corrosion activation energy and the adsorption heats gave negatives values.
- The free energy of adsorption indicates that the process was spontaneous.
- Quantum chemical calculation revealed that the adsorption of clotrimazole was mainly concentrated around the imidazole ring.

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