Experimental and theoretical investigation of clotrimazole as corrosion inhibitor for aluminium in hydrochloric acid and effect of iodide ion addition

I.B. Obot[a,]*, N.O. Obi-Egbedi[b] S.A. Umoren[a]

[a]*Department of Chemistry, Faculty of Science, University of Uyo, Uyo, Nigeria*

[b]*Department of Chemistry, University of Ibadan, Ibadan, Nigeria*

Abstract

The corrosion and inhibition behavior of aluminium in hydrochloric acid in the presence of clotrimazole (CTM) and potassium iodide (KI) were investigated using weight loss method at 30 and 50 ^{o}C. It was found that the inhibition efficiency increased with CTM concentration but decreased with increase in temperature. A synergistic effect was observed between KI and CTM. The experimental results suggest that the presence of iodide ions in the solutions stabilized the adsorption of CTM molecules on the metal surfaces and, therefore improve the inhibition efficiency of CTM. 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}. To further explain the adsorptive behavior of the molecules on the aluminium surface, a semiempirical approach involving quantum chemical calculations using Spartan ’06 was undertaken. The HOMO and the LUMO electronic density of the molecule was used to explain the inhibiting mechanism. The most probable adsorption centers were found in the vicinity of the imidazole group.

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

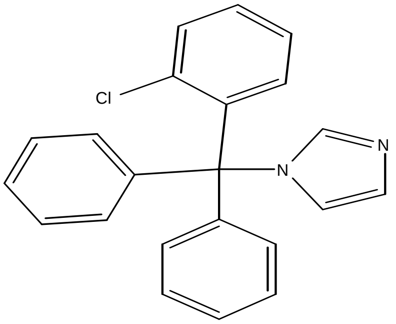
Introduction

The interaction between a material and its environment that results in a degradation of the physical and mechanical properties of that material is termed corrosion. Over the years, reductions in the rate of metal corrosion have been achieved in a number of ways. It involved controlling of the pH or ion concentration of solution or controlling the metal – solution interface. Control of this interface can be achieved through the addition of small amount of chemicals called inhibitors, that either form a barrier–like layer on the metal surface or stimulate film formation and by so doing retard or slow down the rate of metal dissolution[1].

Corrosion prevention and control in aggressive service environments has been effectively achieved by the use of corrosion inhibitors. Owing to stringent environmental regulations, organic compounds are replacing inorganic corrosion inhibitors especially heavy metals derivatives. Organic substances containing polar functions with N, S, or O in a conjugated system have been reported as effective inhibitors of metal corrosion [2-5]. Such compounds function by adherence to the metal surface through metal ions still in place in the lattice and thereby retard metal dissolution by virtue of adsorption. The polar function is usually regarded as the reaction centre for the adsorption process and the resulting adsorption film acts as a barrier isolating the metal surface from the corrodent. The nature of inhibitor adsorption depends on the number and types of adsorption sites on the metal surface as well as the type of interaction between the organic molecule and the metallic surface [6]. Interestingly, the efficiency of organic inhibitors in acidic solutions has been reported to be greatly enhanced on addition of halide salts to the solution [7-10].

Clotrimazole (CTM) is a non toxic, cheap and environmental friendly antifungal drug that is use in the treatment of fungal disease. It contains reactive centers like N atoms containing lone pairs of electrons and aromatic rings with delocalize π electron systems which can aid the adsorption onto metal surfaces. Furthermore, it has a high molecular weight (molecular weight- 344. 845 amu) and likely to effectively cover more surface area (due to adsorption) of the aluminium metal thus preventing corrosion from taking place.

The present study investigates the inhibitve effect of clotrimazole on the corrosion of aluminium in HCl under various experimental conditions using weight loss method. The influence of iodide ions on the adsorption and corrosion – inhibitive properties of CTM has also been studied in order to ascertain the specific mode (ionic or molecular) in which the compound exerts its inhibiting action. Also, activation parameters that govern metal corrosion in acidic media have been evaluated. Finally, quantum chemical calculations have been used to give further insight into the adsorption mechanism of the corrosion process.



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

Fig. 1 The chemical structure of clotrimazole (CTM)

Results and discussion

Weight loss measurements

Gravimetric measurements of aluminium subjected to the effect of acidic medium in the absence and presence of various concentrations of CTM and CTM + KI mixtures were made after 168 h of immersion at 30 and 50^o C respectively. The calculated values of corrosion rate (mg cm^{-2} h^{-1}), inhibition efficiency (% I) and surface coverage (θ) for aluminium corrosion in 0.1M HCl (blank) and in the presence of different concentrations of inhibitor (CTM) and 0.005M KI in combination with different concentrations of clotrimazole at 30 and 50^0 C are shown in Tables 1 and 2 respectively. The corrosion rate, inhibition efficiency, and surface coverage were evaluated using the following equations:

$$v = (m_1 - m_2)/St \qquad (1)$$

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 (1) is an average corrosion rate as no localized corrosion takes place.

$$(\%I) = (v_0 - v)/v_0 x 100 \qquad (2)$$

$$\theta = (v_0 - v)/v_0 \qquad (3)$$

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

Results shown in Tables 1 and 2, revealed that corrosion rates increase with increase in temperature for all the systems studied. In the presence of CTM, the corrosion rate was observed to reduce significantly indicating that clotrimazole actually inhibited the corrosion of aluminium in the acidic environment. Further reduction in corrosion rate was observed on addition of 0.005M KI to CTM. The reduction in corrosion rate of CTM alone and in combination with iodide was found to be concentration dependent. These results can be attributed to the fact that the rate of chemical reaction increases with increase in temperature, concentration and increase rate of diffusion [11].

Table 1. Corrosion parameters for aluminium in 0.1M HCl in the absence and presence of different concentrations of 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	68.2	0.68
	4 x 10^{-5}M	12.50	72.7	0.73
	6 x 10^{-5}M	10.41	77.3	0.77
	8 x 10^{-5}M	8.33	81.8	0.82
	1 x 10^{-4}M	4.16	90.9	0.91
50	Blank	312.50	-	-
	2x 10^{-5}M	237.50	24.0	0.24
	4 x 10^{-5}M	225.00	28.0	0.28
	6 x 10^{-5}M	214.58	31.3	0.31
	8 x 10^{-5}M	206.25	34.0	0.34
	1 x 10^{-4}M	200.00	36.0	0.36

Table 2. Corrosion parameters for aluminium in 0.1M HCl in the absence and presence of different concentrations of clotrimazole + 0.005M KI mixtures at different temperatures

Temperature (°C)	System/Concentration	Corrosion rate (mgcm^{-2}h^{-1}) x10^{-3}	(IE %)	θ
30	Blank	45.83	-	-
	KI (0.005M)	16.66	63.6	0.64
	2x 10^{-5}M + KI	12.50	72.5	0.73
	4 x 10^{-5}M + KI	10.41	77.2	0.77
	6 x 10^{-5}M + KI	8.33	81.9	0.82
	8 x 10^{-5}M + KI	6.25	86.4	0.86
	1 x 10^{-4}M + KI	2.08	95.5	0.96

50	Blank	312.50	-	-
	KI (0.005M)	127.08	16.6	0.17
	2x 10^{-5}M + KI	197.91	36.7	0.37
	4 x 10^{-5}M + KI	185.41	40.0	0.40
	6 x 10^{-5}M + KI	179.16	42.2	0.42
	8 x 10^{-5}M + KI	170.83	45.3	0.45
	1 x 10^{-4}M + KI	166.66	46.7	0.47

Inspection of Table 1 also revealed that inhibition efficiency increase with increase in concentration of the inhibitor and decrease with increase in temperature. Decrease in inhibition efficiency with increase in temperature may be attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal that may otherwise inhibit the reaction rate. According to Ferreira et al. [12], an increase in inhibition efficiency with decrease in temperature indicates inhibitor physisorption on the corroding metal surface while the reverse behavior implies chemisorptions. Similar observations have been reported elsewhere [13, 14]. It is also clear from Table 2 that inhibition efficiency synergistically increase on addition of 0.005M KI to clotrimazole at the studied temperatures.

Adsorption consideration

Inhibitor molecules are either physically or chemically adsorbed on a corroding metal surface, where the physisorbed molecules essentially retard metal dissolution by inhibiting the cathodic reaction whereas chemisorbed molecules inhibit the anodic reaction by reducing the inherent reactivity of the metal at the adsorption sites [10]. Thus, in order to properly understood the nature of adsorption, the values of surface coverage (θ) for the different systems at 30 and 50 ^{o}C have been used to explain the best adsorption isotherm to determine the adsorption process. Adsorption of organic adsorbate on the aluminium surface is regarded as substitutional adsorption process between the organic molecule in the aqueous phase (org_{aq}) and the water molecules adsorbed on the Al surface $(H_2O)_{ads}$ [7].

$$xH_2O_{ads} + Org_{sol} \leftrightarrow Org_{ads} + xH_2O_{sol} \qquad (4)$$

Where x is the size ratio, that is, the number of water molecules replaced by one organic molecule. Attempts were made to fit θ values to various isotherms including Frumkin, Langmuir, Flory-Huggins, Temkin, Freundlich and El-Awady kinetic/thermodynamics model. By far the best fit for the experimental data were the Langmuir isotherm and kinetic/thermodynamic model of El-Awady and correlation coefficient (R^2) values were used to determine the best fit isotherm.

The Langmuir isotherm is given by:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

The plot of C/θ versus C for clotrimazole and clotrimazole in combination with iodide ions are shown (Figs. 2a and 2b) to be linear with slope greater than unity (correlation > 0.9 (Table 3)). Though the linearity of the plot may be interpreted to suggest that the experimental data from CTM obey the Langmuir adsorption isotherm, the considerable deviation of the slope from unity shows that the isotherm cannot be strictly applied. Thus, deviation from unity is attributable to interactions between adsorbate species on the metal surface [15, 16] as well as changes in the adsorption heat with increasing surface coverage [17], factors that were not taken into consideration in the derivation of the isotherm. The adsorption behavior of CTM can be more appropriately represented by a modified Langmuir equation suggested by Villamil et al. [18] as follows:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{6}$$

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

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y\log C \tag{7}$$

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 are shown for clotrimazole and clotrimazole + KI mixtures in Figs 3a and 3b respectively. These plots 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 is given in Table 3. 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

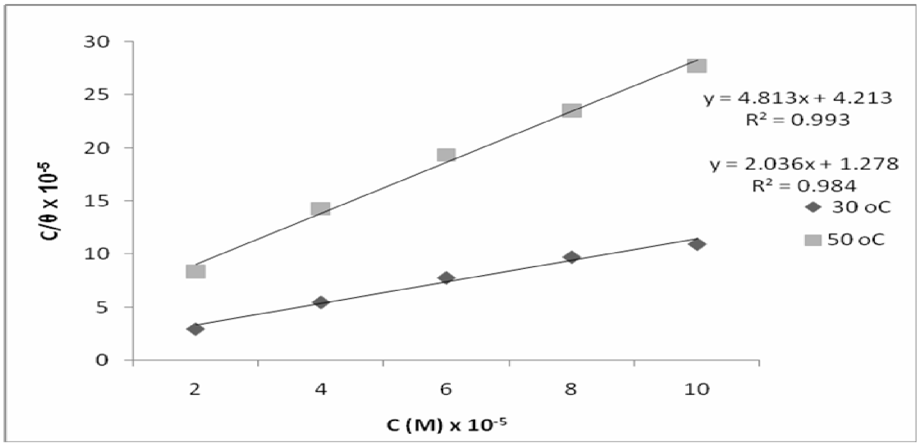


Fig. 2(a) Langmuir adsorption Isotherm plot for Clotrimazole at 30^{o}C and 50^{o}C

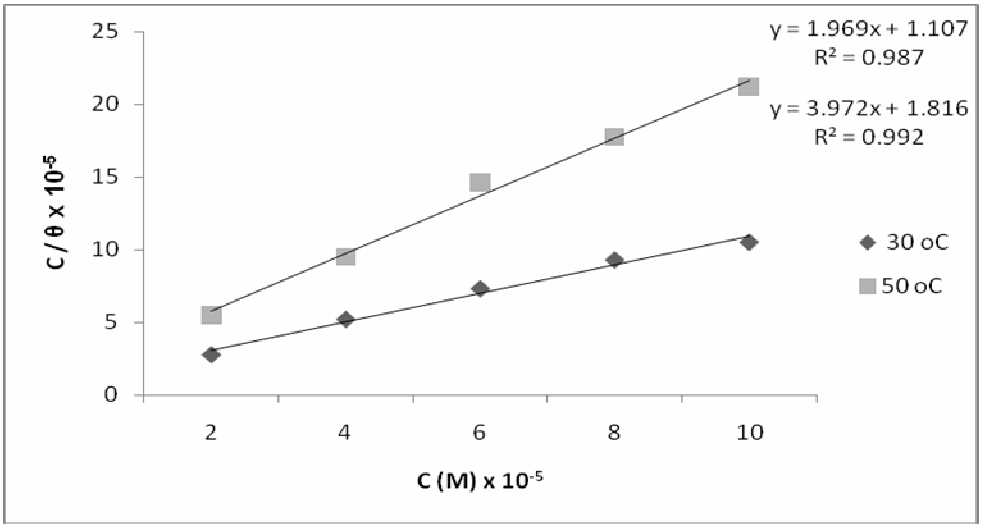


Fig. 2(b) Langmuir adsorption Isotherm plot for Clotrimazole + KI at 30^{o}C and 50^{o}C

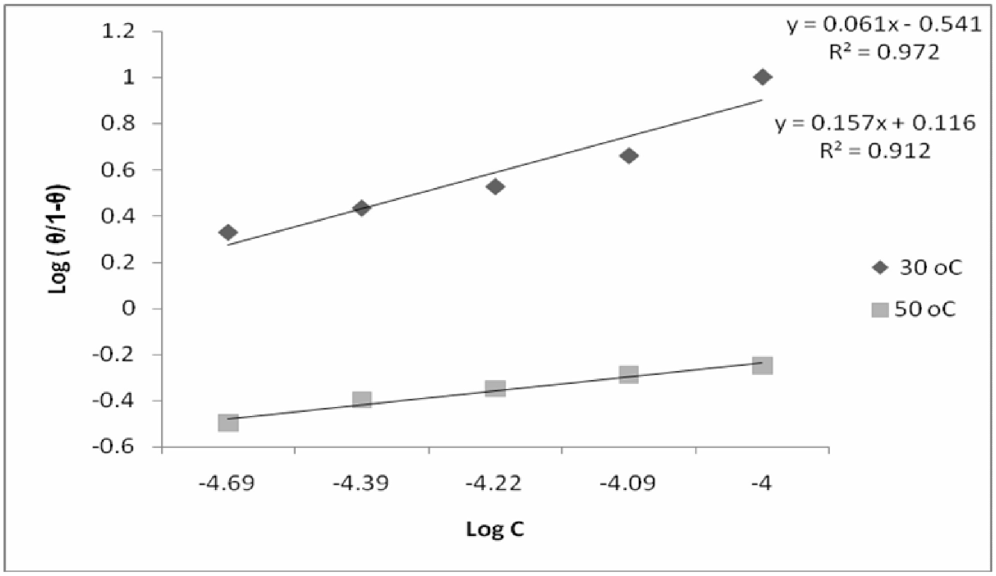


Fig. 3 (a) El-Awady et al. plot for Clotrimazole at 30^{o}C and 50^{o}C

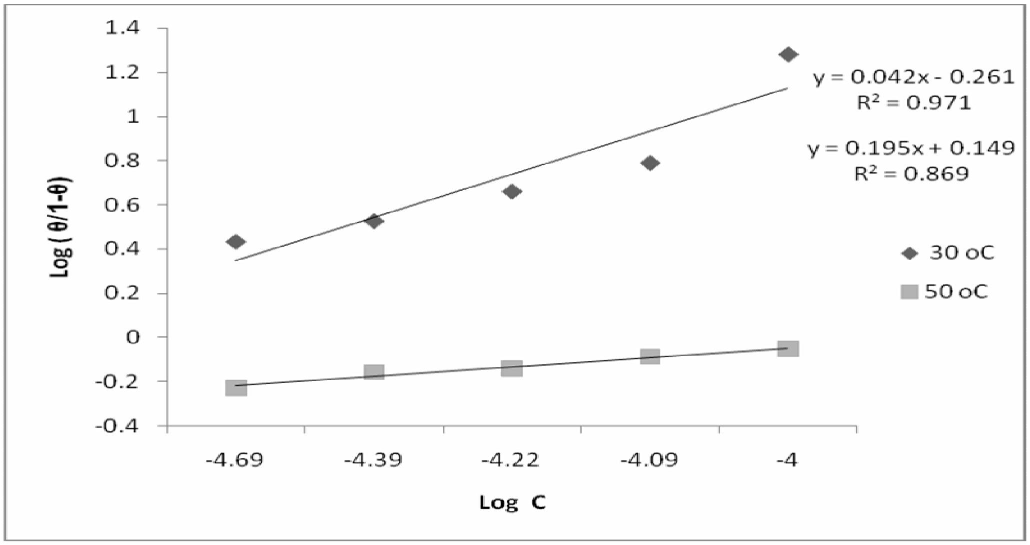


Fig. 3(b) El-Awady et al. plot for Clotrimazole + KI at 30^{o}C and 50

Kinetic/thermodynamic consideration

Kinetic assessment of the experimental data was also undertaken to further elucidate the inhibitor adsorption mechanism. The apparent activation energies (E_a) for aluminium corrosion in the absence and presence of CTM, CTM + iodide mixture were evaluated from Arrhenius equation (equation (8)):

$$\log\frac{v_2}{v_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{8}$$

where v_1 and v_2 are the corrosion rates at temperature T_1 and T_2, respectively. An estimate of heat of adsorption was obtained from the trend of surface coverage with temperature as follows [11]:

$$Q_{ads}=2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right)-\log\left(\frac{\theta_1}{1-\theta_1}\right)\right]x\left(\frac{T_{1X}T_2}{T_2-T_1}\right)kJmol^{-1} \tag{9}$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2. The calculated values for both parameters are given in Table 4.

Table 3. Calculated parameters from Langmuir and El-Awady Adsorption Isotherm

Inhibitor	Temperature (°C)	Langmuir Isotherm				El-Awady Isotherm			
		K_{ads}	ΔG^o_{ads}	Slope	R^2	K_{ads}	ΔG^o_{ads}	1/y	R^2
CTM	30	0.78	-8.49	2.036	0.984	1.31	-10.79	6.37	0.912
	50	0.24	-6.92	4.813	0.993	0.29	-7.44	16.39	0.972
CTM + KI	30	0.55	-8.62	3.972	0.992	1.41	-10.97	5.13	0.869
	50	0.40	-10.51	1.969	0.987	0.55	-9.17	23.81	0.971

Table 4. 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, clotrimazole + KI at 30-50 ^oC

System/concentration	E_a(kJmol^{-1})	Q_{ads} (kJmol^{-1})
Blank	78.27	-
2 x 10^{-5} M CTM	113.75	-77.57
4 x 10^{-5} M CTM	117.78	-78.89
6 x 10^{-5} M CTM	126.23	-81.77
8 x 10^{-5}M CTM	130.84	-88.73
1 x 10^{-4}M CTM	157.78	-117.59
2 x 10^{-5} M CTM + KI	112.62	-62.12
4 x 10^{-5} M CTM + KI	117.32	-64.00
6 x 10^{-5} M CTM + KI	125.02	-74.86
8 x 10^{-5} M CTM + KI	134.87	-82.08
1 x 10^{-5} M CTM + KI	178.61	-124.71

Increased activation energy in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower E_a in the presence of inhibitor suggest chemisorptions [13]. E_a values obtained for the blank, CTM and CTM + KI are presented in Table 4. It is seen that E_a values were higher in the presence of the additives compared to that in their absence. This supports the earlier proposed physisorption mechanism. Similar results have been reported in earlier publications. [7,14].

The calculated values of adsorption heat also confirm the earlier proposed inhibitor adsorption trend. Thus, it is clearly seen that in all cases, the Q_{ads} values were negative and ranged from -124.71kJ/mol to -62.12kJ/mol (Table 4). The negative Q_{ads} values show that the adsorption and hence inhibition efficiency decreased with rise in temperature also supporting physical adsorption mechanism [19].

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:

$$k_{ads} = \frac{1}{55.5}\exp\left[\frac{-\Delta G^{o}_{ads}}{RT}\right] \tag{10}$$

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^{o}_{ads}, which can characterize the interaction of adsorption molecules and metal surface, was calculated by equation (10). The negative values of ΔG^{o}_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface. Generally, the values of ΔG^{o}_{ads} around -20kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption) while those around -40kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorptions). The calculated ΔG^{o}_{ads} values were less negative than -20kJ/mol, (Table 3) indicating that the adsorption mechanism of clotrimazole on aluminium was physisorption.

Effect of iodide addition

It is generally accepted that the presence of halide ions in acidic media yields an enhancement of inhibition efficiency of some organic compounds. It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. The greater influence of the iodide ion is often attributed to its large ionic radius, high hydrophobicity, and low electronegativity, compared to the other halide ions [15]. Thus, the CTM + KI combination produced pronounced effects on the inhibition efficiency (95.46%) at 30 ^{o}C, compared to 90.90% obtained for CTM alone. The observed enhancement results from increase surface coverage arising from ion-pair interactions between I^- ions and CTM cations. According to Oguzie et al. [2], the ion pairs could be formed in the bulk solution and then adsorbed from the solution onto the metal surface as follows:

$$I^-_s + CTM^+_s \rightarrow (I^- - CTM^+)_s \tag{11}$$
$$(I^- - CTM^+)_s \rightarrow (I^- - CTM^+)_{ads} \tag{12}$$

On the other hand, ion-pair formation could result from initial contact adsorption of the iodide ions on the metal surface, which leads to a recharging of electrical double layer. The inhibitor is then drawn into the double layer by the adsorbed anions such that ion-pair formation occurs directly on the metal surface:

$$I^-_s \rightarrow I^-_{ads} \tag{13}$$
$$I^-_{ads} + CTM^+_s \rightarrow (I^- - CTM^+)_{ads} \tag{14}$$

Where I^-_s , CTM^+_s , and $(I^- - CTM^+)_s$ represent the iodide ion, inhibitor and ion pair, respectively, in the bulk of the solution, while I^-_{ads} , CTM^+_{ads} , and $(I^- - CTM^+)_{ads}$ refer to the same species in the adsorbed state. As suggested by Oguzie et al. [2], as well as other authors [20, 21], the ion- pair interactions occur via the second mechanism.

Attempt was also made in the present study to determine the nature of the observed enhancement of inhibition efficiency of CTM in the presence of iodide ions by determining the synergism parameter S_1, evaluated using the relationship given by Aramaki and Hackerman and reported elsewhere [7, 22]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \tag{15}$$

where I_{1+2}= (I_1 + I_2); I_1 = inhibition efficiency of the halides; I_2 = inhibition efficiency of clotrimazole; I`= measured inhibition efficiency for the clotrimazole in combination with iodide ions. S_1 approaches unity means that there is no interaction between CTM and iodide ions; $S_1 > 1$ points to synergistic effect and $S_1 < 1$ shows competitive adsorption. The calculated values of synergism parameter of 1.866 and 1.394 were obtained for the iodide at 30 and 50 ^{o}C respectively. The values are greater than unity, suggesting that the enhanced inhibition efficiency resulting from the combination of CTM and iodide is only due to synergism. Similar results have been reported elsewhere [7, 8]. Strong adsorption of iodide ions on the metal surface is responsible for the synergistic effect of iodide ions in combination with the cation of the inhibitor (CTM). The cation is then adsorbed by coulombic attraction on the metal surface where iodide ions are already adsorbed by chemisorptions. Stabilization of the adsorbed iodide ions with cations leads to a greater surface coverage and therefore greater inhibition.

Quantum chemical studies

Quantum chemical calculations have proved to be a very powerful tool for studying corrosion inhibition mechanism [23]. Table 5 shows the quantum chemical calculation parameters obtained by semi-empirical AM1 method with commercially available quantum chemical software SPARTAN'06 V112. These parameters are mainly the energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals, dipole moment (μ), and the heat of formation of clotrimazole.

E_{HOMO} is often associated with the electron donating ability of the molecule and inhibition efficiency increases with increasing E_{HOMO} values. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. It is evident from Table 5 that CTM 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 organic heterocyclic inhibitors [24]. 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.

The AM1 optimized geometry of the clotrimazole molecule is shown in Fig.4. The electron/orbital density distributions of HOMO and LUMO for CTM are expressed in Figs 5 and 6. For the HOMO (Fig.5), it is observed that the imidazole ring had larger electron density mainly concentrated on the N atoms and around the C atoms of the ring and were more feasible to bind with the empty-low lying orbital of Al; while for the LUMO (Fig. 6), the aromatic rings (π systems) had larger orbital density and could take priority of interaction with 3S orbital of Al. Both bindings strengthened interaction from the evidence of negative value of ΔG^{o}_{ads}.

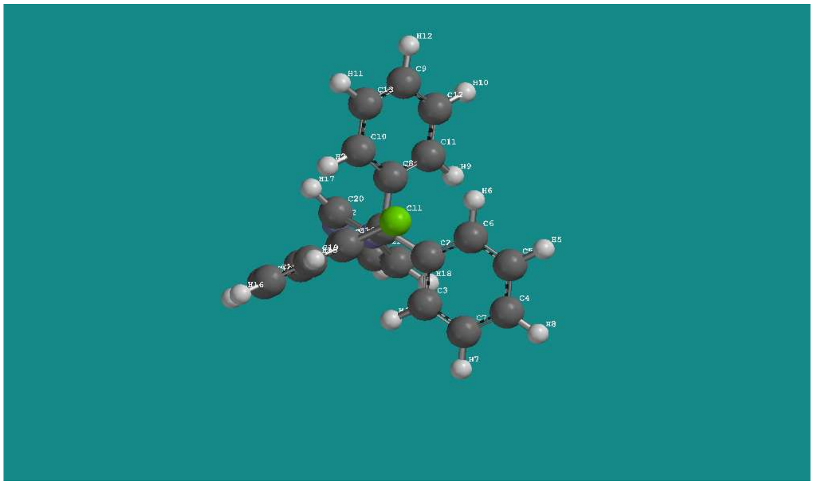


Fig. 4 An AM1 optimized geometry of clotrimazole molecule

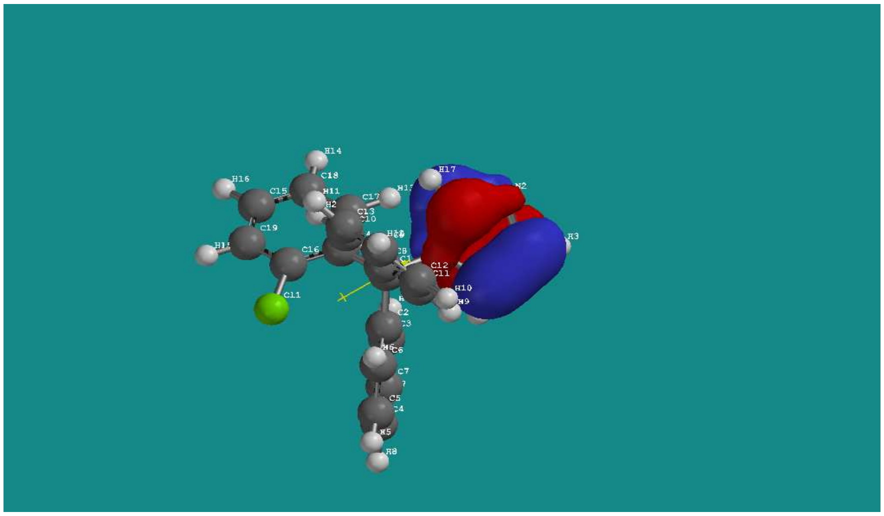


Fig. 5. HOMO electronic density of clotrimazole molecule showing electron rich centres around the imidazole ring (in red and blue colours)

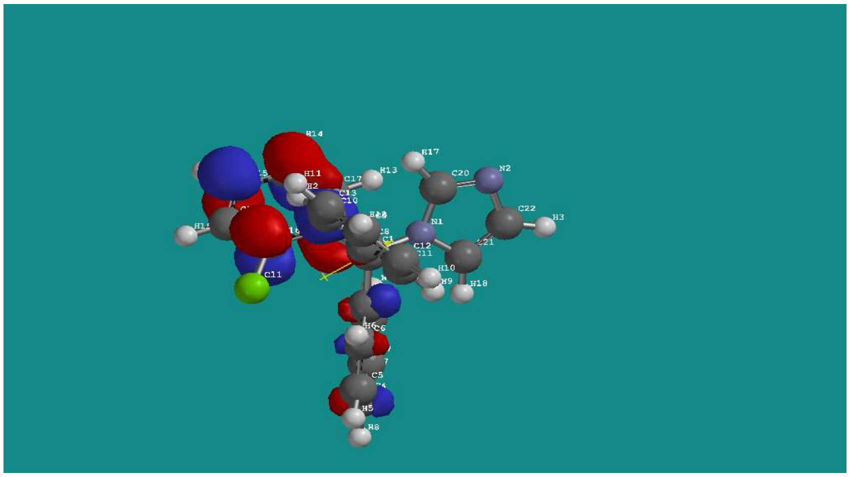


Fig. 6. LUMO electronic density of clotrimazole molecule. The plot is on ring containing the chlorine atom. This ring contains carbons C13, C14, C15, C16, C17, C18, and Cl atom (red and blue)

Table 5. Quantum parameters of clotrimazole obtained by Spartan'06

Quantum Parameter	μ (D)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} - E_{LUMO} (eV)	Heat of formation (kJ/mol)
Calculated value	3.68	-8.98	-0.14	8.84	659.03

Materials and Methods

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, and stored in moisture-free desiccators prior to use [10].

All reagents used were BDH analytical grade. They 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 x 10^{-5} – 1 x 10^{-4}. The halide salt, potassium iodide (KI, BDH) used was in the concentration range of 0.001 – 0.005M. However, 0.005M KI was used for the synergistic studies. In each experiment, the cleaned aluminium coupon was weighed and suspended with the aid of glass rod and hook in a beaker containing 500 ml acid solution. The coupon was then taken out of the test solution after 24 h progressively for 7 days (168h), washed in 70% nitric acid for 2 minutes to remove the corrosion products using bristle brush, 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.

AM1 (Austin model 1) is a semi-empirical method based on the neglect of differential diatomic overlap integral approximation. Specifically, it is a generalization of the modified neglect of diatomic differential overlap approximation. AM1 was developed by Michael Dewar and co-workers in 1985. AM1 is an attempt to improve the MNDO model (Modified neglect of differential overlap) by reducing the repulsion of atoms at close separation distances. The atomic core-atomic core terms in the MNDO equations were modified through the addition of off-center attractive and repulsive Gaussian functions. The complexity of the parameterization problem increased in AM1 as the number of parameters per atom increased from seven in MNDO to 13-16 per atom in AM1 .The quantum chemical calculation was performed using Spartan’06 V112 semi-empirical program [25]. AM1 semi-empirical method was employed to obtain the optimized geometry.

Conclusion

1. Clotrimazole (CTM) was found to be a good inhibitor of aluminium corrosion in acidic medium.
2. Then inhibition is due to adsorption of the inhibitor molecules on the aluminium surface and blocking the active sites.
3. Adsorption of the inhibitor follows the Langmuir adsorption isotherm and kinetic/thermodynamic model of El-Awady et al.
4. Inhibition efficiency increased with an increase in CTM concentration but decreased with rise in temperature.
5. Addition of iodide ions improved the inhibition efficiency of clotrimazole.
6. The presence of CTM increased the corrosion activation energy and the adsorption heats gave negatives values.
7. The free energy of adsorption indicates that the process was spontaneous.
8. Quantum chemical calculation revealed that the adsorption of clotrimazole was mainly concentrated around the imidazole ring.

References

[1] K.F. Khaled, Appl. *Surf. Sci*., **2006**, 252, 4120.
[2] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Corros. Sci*.**, 2009**, 51, 1868-1875.
[3] I.B. Obot, N.O. Obi-Egbedi, *Surf. Rev. Lett*., **2008,** 15(6), 903-910.
[4] I.B. Obot, N.O. Obi-Egbedi, *Colloids and surfaces A: Physicochem.Eng. Aspects,* **2008,** 330, 207-212.
[5] I.B. Obot, N.O. Obi-Egbedi, *Surf. Rev. Lett*., **2008,** 15(6), 903-910.
[6] L. Tang, X. Li, L. Li, G. Mu, G. Liu, *Surf. & Coat. Technol*., **2006**, 201 384.
[7] S.A. Umoren, E.E. Ebenso, *Mater. Chem. Phys.*, **2007**, 106, 387.
[8] S.A. Umoren, O. Ogbobe, E.E. Ebenso, *Bull. Electrochem*., **2006**, 22(4), 155.
[9] S.A. Umoren, O. Ogbobe, E.E. Ebenso, U.J. Ekpe, *Pigment Resin Technol*., **2006**, 35 (3) 284.

[10] E.E. Oguzie, E.E. Ebenso, *Pigment Resin Technol*., **2006**, 35 (1), 30.
[11] S.A. Umoren, I.B. Obot, E.E. Ebenso, P.C. Okafor, O. Ogbobe, E.E. Oguzie, *Anti-corros. Methods and Material,* **2006,** 53(5), 277.
[12] E.S. Ferreira, C. Giacomelli, F.C. Gicomelli, A. Spinelli, *Mater. Chem. Phys*., **2004,** 83(1) 129.
[13] A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros sci.*, **2003,** 45, 33
[14] E.E. Oguzie, *Corros Sci*, **2007**, 49, 1529.
[15] E.E. Oguzie, G. N. Onuoha, A.I. Onuchukwu, *Mater. Chem. Phys*., **2004,** 89, 305.
[16] C. Chakrabarty, M.M. Singh, P.N.S. Yadav, C.V. Agarwal, *Trans SAEST*, **1983**, 18, 15.
[17] E.E. Oguzie, B.N. Okolue, E.E. Ebenso, G.N. Onuoha, A.I. Onuchukwu, *Mater. Chem. Phys.*, **2004**, 87, 394.
[18] R.F.V. Villamil, P. Corio, J.C. Rubin, S.M.L. Agostinho, *J. Electroanal. Chem*.,**1999,** 472, 112.
[19] H.M. Bhajiwala, R.T. Vashi, *Bull. Electrochem*. **2001**, 17, 441.
[20] S.M.A Shibli, V.S. Saji, *Corros Sci*., **2007**, 47, 2213.
[21] G. Mu, X. Li, *J. Colloid Interface Sci*., **2005**, 289, 829.
[22] G.K. Gomma, *Mater. Chem. Phys*., **1998,** 54, 241.
[23] H. Ju, Y. Li, *Corros Sci*., **2007,** 49, 4185.
[24] G. Bereket, C. Ogretir, C. Ozsahim, *J. Mol. Struct. (THEOCHEM*), **2004**, 663, 173.
[25] Spartan,06 Wavefunction, Inc. Irvine, CA: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipehenko, S.V. Levehenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T.Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C.P. Hsu, G. Kedziora, R.Z. Khalliulin, P.Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I.Lotan, N. Nair, B.Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W.Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.,* **2006**, 8, 3172.