EFFECTS OF THIOPHENE ON ACID CORROSION OF MILD STEEL

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ABSTRACT

The inhibition of the corrosion of mild steel in 0.1 M HCl solution by Thiophene from 303 K to 333 K at concentrations of 5×10^{-4} M, 1×10^{-4} M, 5×10^{-5}, 2×10^{-5} M and 1×10^{-5} M had been studied using weight loss technique, and findings revealed that the maximum inhibition efficiency observed was 59.98% at 5×10^{-4} M for 333 K. The compound acts as corrosion inhibitors in HCl solution through adsorption on the mild steel surface. The maximum heat of adsorption (Q) was 1.0297 KJ/mol whereas the average kinetic energy (Ea) was 20.0 KJ/mol. The weight loss data treated kinetically gave a first order type of mechanism. The results elucidate the effects of inhibitor concentration, temperature, dλ – Pλ interaction between the metal surface, the heteroatom of the inhibitor, and the electron charge densities on the heteroatoms of the Thiophene molecule.

INTRODUCTION

Steel is preferred in ship and bridge construction, riveting, bolting, etc., because of its excellent mechanical strength (Bebon, 2011). However, its proneness to corrosion is its greatest challenge. Industrial exercises like metal scale removal and cleaning, acid descaling, oil well acidizing and several others usually cause metal corrosion. These occur when the aggressive acid solutions come in contact with the metals. Before acid solution is used for any industrial process, it is customary to add metal corrosion inhibitors. The common metal corrosion inhibitors are organic with N, O, S, P and π electrons in their structure. (Xhanari and Finshar, 2016) and inorganic (nitrites, nitrates, phosphates, and lanthanides (Umoren and Solomon, 2017a).

At present, organic metal corrosion inhibitors demand is at 70%, while that of the inorganic counterpart is remarkably low due to their negative influence on the ecosystem (Umoren and Solomon, 2017b). However, inhibitors are usually effective only for a particular material in a certain environment (Barmatov *et al.,* 2015), but the corrosion environments are highly variable. Therefore, an inhibitor that works in one well may not work in another (Khodyrev *et al.,* 2011) such that it is necessary to continuously develop new formulas for different environment (Ibeawuchi, 2013). This study shall aid the understanding of corrosion mechanism and minimize corrosion problem.

MATERIALS AND METHOD

Materials and Metal Samples Preparation

Thiophene compound used in this experiment was of analytical grade and products of M and B limited, Dagenham, England. All the chemicals were procured from Sigma Aldrich and were used as purchased without further purification. Sheet of mild steel which was cut into 5×4 cm^2 coupons was supplied by Ken-Johnson Nig. Ltd, Uyo, Akwa Ibom State, Nigeria. The samples were mechanically abraded using different grit of emery papers (800 – 2000 grade). They were washed with distilled water, degreased with ethanol, rinsed in acetone and dried with warm air (Verma *et al.,* 2017) and then stored over calcium chloride in a desiccator.

Quantum Chemical Calculations

In this work, Quantum parameter calculations were conducted by the ArgusLab (tm) (Version 4.0). The calculations were conducted to simulate the effects of Thiophene molecules on acid

corrosion. Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) reveals the active sites of the molecules and are here discussed.

RESULTS AND DISCUSSION

Inhibitory actions of Thiophene**:**

The results obtained from the weight loss measurements of mild steel in 0.1 M solution containing different concentrations of Thiophene showed a general increase in weight loss with time of exposure. The decrease is due to the inhibitive effects of the inhibitor and these effects increase with increase in concentrations of the inhibitor. The values of inhibition efficiency, rate constant and half-life from weight loss measurements at different concentrations of the inhibitor after 7 days immersion at 303-333 K are summarized in Table 1. It is evident from this table that the inhibition efficiency (% I) increased with increasing inhibitor concentration, reaching a maximum of 59.98 % at 333 K for 5 x 10^{-4} M. This may be due to the adsorption of Thiophene onto the mild steel surface through non-bonding electron pairs of sulphur atoms as well as the π-electrons of the aromatic rings.

Table 1: Kinetic data for mild steel in 0.1 M HCl solution containing Thiophene

Inhibitor Conc. X 10^{-4}	Inhibition efficiency (%)				Rate Constant (day^{-1})				Half life (day)			
	303	313	323	333	303	313	323	333	303	313	323	333
5.0	20.17	32.10	43.72	59.98	0.106	0.076	0.074	0.067	6.539	9.118	9.403	10.37
1.0	-13.16	24.36	40.03	56.30	0.129	0.131	0.081	0.065	5.372	5.278	8.598	9.907
0.5	29.28	19.29	37.10	54.01	0.081	0.083	0.074	0.071	8.598	8.360	8.950	9.706
0.2	17.11	18.23	34.28	50.41	0.097	0.078	0.076	0.131	6.608	8.851	9.118	5.278
0.1	9.87	17.05	27.66	47.01	0.106	0.076	0.074	0.184	6.544	9.118	9.403	3.762

The high inhibitive performance of Thiophene suggests a higher bonding ability of the inhibitor to the mild steel surface. Similar observation had been reported elsewhere (Ahamad and Quraishi, 2010). Higher maximum inhibition efficiency (59.98 %) was obtained at 333 K for inhibitor concentration of 5.0 x 10^{-4} M. The inhibition efficiency followed a zigzag trend at 333 K, but at 313 K, 323 K and 333 K, a trend of increasing inhibition efficiency as a function of inhibitor concentration was observed. Ateya *et al*. (1981) observed that inhibition efficiency increases with increasing additive concentration. The difference in behaviour of inhibitor at these temperatures could be attributed to the nature of alignment of the inhibitor molecules on the mild steel surface, which is temperature controlled. A more uniform alignment of the inhibitor molecule was seen at 313 K, 323 K and 333 K than at 303 K, since at these higher temperatures, the inhibitive molecules are energized and tend to spread more evenly on the mild steel surface than at 30^3 K, and form a thin adsorbed layer on the mild steel surface. Since the efficiency of inhibitor increased with increase in temperature, it is also suggested that the mechanism of inhibition is probably due to the formation of a chemically absorbed thin layer by the additive on the mild steel surface.

The initial increase in corrosion by inhibitors could be associated with the duration for the stabilization of the inhibitors on the mild steel surface, during which time the mild steel remains unprotected and corrodes at a fast rate. At low inhibitor concentrations, the inhibitors tend to accelerate the corrosion of mild steel. This observation could be attributed to the insufficient amount of inhibitors on the surface of the mild steel, which is easily washed away during the corrosion process thereby exposing the mild steel to severe localized attack by the acid.

Effect of inhibitor concentration on surface area:

Within this range of inhibitor concentration and temperature, the inhibitor gives a monolayer adsorption over the surface of mild steel according to Langmuir adsorption isotherm as expressed by;

$$\frac{\theta}{1-\theta} \quad = \quad ACe^{-Q/RT}$$

Where, θ = Surface coverage

Q = Heat of adsorption

R = Universal gas constant

T = Temperature

C = Inhibitor concentration

This may, as well, interpret the adsorption kinetics of these inhibitors over mild steel surface during acid corrosion process. Plots of log θ/1-θ against 1/T at constant inhibitor concentration were linear over this range of concentration indicating that simple Langmuir adsorption isotherm is inadequate at all temperature range and concentrations (Fig. 1). The slopes of the linear portion of the plots are equal to –Q/2.303R from which the average heat of adsorption was calculated.
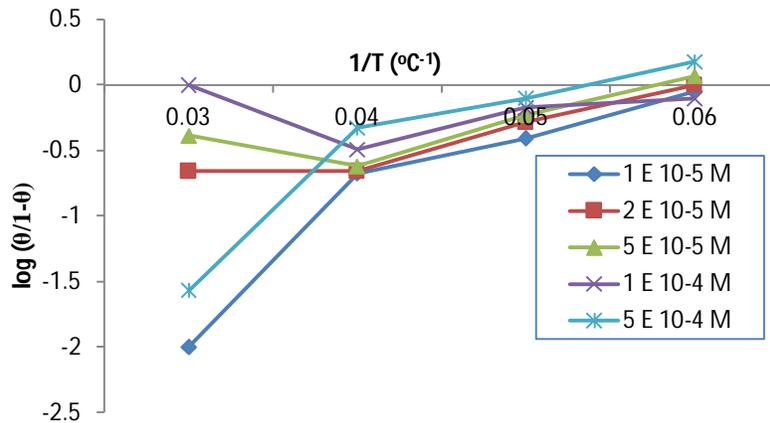

Figure 1: Plot of log θ/1-θ against 1/T at constant inhibitor concentration

Barrow (1983) distinguished between the two types of adsorption process. He stated that the heat of adsorption for physisorption was less than 40 KJ/mol; while it was greater than 80 KJ/mol for chemisorption. On the basis of this argument and the experimentally determined average activation energy value of 20.0 KJ/mol, and this ranges of value for heat of adsorption of 0.8635 - 1.4958 KJ/mol, the adsorption process favours physisorption. Hence, the inhibition increases with the rise in temperature at higher concentration (Table 2).

Table 2: Average activation energy and heat of adsorption at constant inhibitor concentration

Average activation energy, Ea (EJ/mol)			Heat of adsorption (Q) at constant inhibitor concentration (KJ/mol)
303 – 313 K	313 – 323 K	323 – 333 K	
-13.1	-11.7	20.0	0.8635
			1.4958
			1.4307
			1.0297

Proposed mechanism of action for the Thiophene molecule:

The Thiophene molecule is conjugated with various ring and heteroatoms (Fig. 2). The aromatic nature of this molecule and the charge densities on the ring atoms depend on the electronegativity of the heteroatoms and their participation in the extensively delocalized π – electron system. If the inhibition of this compound is thought to be due to the adsorption of this molecule on the metal surface through the dπ – pπ interactions, the π – electron charge densities on the heteroatoms, their electronegativity and electron affinities should play an important role during acid corrosion of mild steel (containing mainly iron) in the presence of the inhibitor. Thiophene molecule resembles benzene. The stable delocalized π - electron system of the molecule in acid solution causes a strong adsorption of the compound on the material and considerate inhibition

result. The adsorption of Thiophene also takes place through the lone pairs which are to form co - ordination bond with metal atom in mild steel.
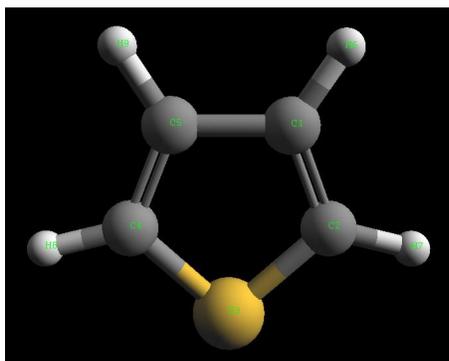

Figure 2: DFT-B3LYP Optimized Structure of Thiophene.

Quantum chemical studies**:**

The study of corrosion inhibition mechanism has been proven to be a powerful tool using quantum chemical calculations (Okafor *et al.*, 2010). Thus, in this work, quantum chemical calculation using DFT was employed to explain the experimental results obtained, and to further give insight into the inhibition action of Thiophene on the mild steel surface.

The calculated values of the quantum chemical parameters obtained using the Hartree-fock/ Density functional theory (HF-DFT) by Hamiltonian method with PM3 (NDDO) basis set of Minimal Valence Basis as STO 3G program are presented in Table 3.

Table 3: Quantum chemical parameters

E_{HOMO}	E_{LUMO}	Energy gap	Heat of formation	Dipole moment
-0.3514	-0.00730	0.3441	30.985	0.6586

The high value of dipole moment of Thiophene (Table 3) probably increases the adsorption between organic compound and metal surface (Li *et al*., 2009). The values of dipole moment indicate the possibility of adsorption of studied compound by electron donation to the unfilled orbital of iron. The electronic configuration of iron is [Ar] $4S^2 3d^6$, so 3d orbital is not fully filled with electrons.

The relation between inhibition efficiency of inhibitor and the calculated quantum chemical parameters like E_{HOMO}, E_{LUMO}, dipole moment and E_{LUMO} - E_{HOMO} (ΔE) were investigated. These parameters provide information about the reactive behaviour of molecules. The reactive ability of the inhibitor is considered to be closely related to their frontier molecular orbitals, the HOMO and LUMO (Obi-Egbedi and Obot, 2010). The highest occupied molecular orbital (HOMO) is usually the region of high electron density, therefore is often associated with the electron donating ability of the molecule to appropriate acceptor molecules with low-energy empty molecular orbital, and thus explains the adsorption on metallic surfaces by way of delocalized pairs of π - electrons. E_{LUMO}, the energy of the lowest unoccupied molecular orbital signifies the electron receiving tendency of a molecule. The optimized geometry of Thiophene is shown in Fig. 2. As we know, frontier orbital theory is useful in predicting the adsorption centres of the inhibitor responsible for the interaction with surface metal atoms. The HOMO and the LUMO population of Thiophene are shown in Figs. 3 and 4 respectively.

It could also be easily seen that the HOMO were distributed mainly around the ring and the sulphur atoms while the LUMO were distributed on the entire molecule. Moreover, the gap between the LUMO and HOMO energy levels of the molecule was another important factor considered. It has been reported that excellent corrosion inhibitors are usually those organic

compounds that do not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal (Obot *et al.,* 2010).
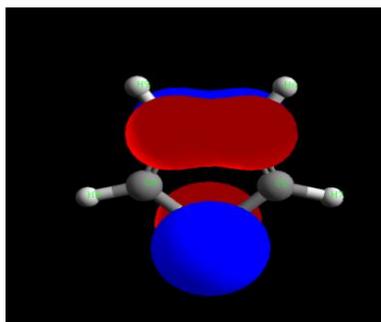

Figure 3: HOMO electronic density
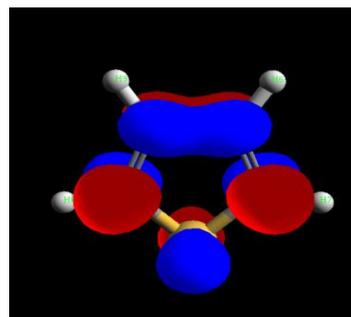of Thiophene molecule

Figure 4: LUMO electronic density
of Thiophene molecule

It is also well documented in literature that the higher the HOMO energy of the inhibitor, the greater its ability to donate electrons to unoccupied d - orbital of the metal, and the higher the corrosion inhibition efficiency. This shows that the Thiophene molecule has electron donating ability. This confirms the experimental results that interaction between Thiophene and mild steel is electrostatic in nature (physisorption). In addition, the lower the LUMO energy, the easier the acceptance of electrons from the metal surface, and as the LUMO – HOMO energy gap decreased, the efficiency of inhibitor improved (Obot *et al.*, 2010). Low values of the energy gap (ΔE) will provide good inhibition efficiencies, because the excitation energy to remove an electron from lest occupied orbital will be low (Gece, 2008). A molecule with a low energy gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is termed soft molecule (Dwivedi and Misra, 2010). Quantum chemical parameters listed in Table 3 indicate that Thiophene is an efficient inhibitor in HCl solution which corresponds to the experimental results. The Mulliken charge distribution of Thiophene is presented in Table 4. It has been reported that the more negative the atomic charges of the adsorbed centre, the easier the atom donates its electron to the unoccupied orbital of the metal (Xia *et al.*, 2008).

Table 4: Mulliken atomic charges for Thiophene

	Atom	Charge
1	C	- 0.2043
2	C	-0.4310
3	S	-0.3372
4	C	-0.4310
5	C	-0.2044
6	H	0.2175
7	H	0.2493
8	H	0.2493
9	H	0.2175

It is clear from Table 4 that sulphur and some carbons atoms carry negative charge centres which could offer electrons to the mild steel surface to form a coordinate bond. It could be readily observed that sulphur atoms and the double bonds had higher charge densities and might form the adsorption centres. Moreover, the adsorption of this compound on the anodic sites through lone pair of electrons on S atoms and through the π - electrons of Thiophene molecule will then reduce the anodic dissolution of mild steel (Obot *et al.*, 2009). The dipole moment is another important electronic parameter that results from non - uniform distribution of charges on the various atoms in a molecule. It is mainly used to study the intermolecular interactions involving the Van der Waals type dipole - dipole forces etc., because the larger the dipole moment, the stronger the intermolecular attraction (Dwivedi and Misra, 2010).

CONCLUSION

The organic compound inhibits the acid corrosion of mild steel to a remarkable degree. The maximum inhibition efficiencies of 59.98 % at the highest inhibitor concentration of 5×10^{-4} M suggest that the inhibition efficiency is proportional to the concentration of the additive. The kinetics of mild steel in HCl solution in both inhibited and uninhibited reactions confirms a first order type of mechanism. The inhibition process may be due to the physical adsorption of the heterocyclic compounds on the mild steel due to interaction between the additive and the mild steel surface. Quantum chemical calculations show that apart from Thiophene adsorbing as cationic species on the mild steel surface, it can also adsorb as molecular species using sulphur and cyclic carbons as its active centres.

REFERENCES

Ahamad, L. and Quraishi, M. A., (2010). Mebendazole: New and efficient corrosion inhibitor for mild steel in acid medium. *Corrosion Science*, 52: 651 – 656.

Ateya, B. G., El-Anadouli, B. E. And El-Nizamy, F. M. (1981). Corrosion inhibition behaviour of some thioamides on mild steel in sulphuric acid. Bull chem. Soc., 54, 31 – 57.

Barmatov, E., Hughes, T. and Nagl, M. (2015). The inhibition action of ammonium salts of O ,O – dialkyldithiophosphoric acid on carbon dioxide corrosion of mild steel. *Corrosion Science,* 5893: 1 – 14.

Barrow, G. M. (1983). Physical Chemistry, 4th Edn. New York: McGraw-Hill.

Bebon, H. (2011). *St37 Steel Plate.* www.steel-plate-sheet.com/steel-plate/D/N/St372.html. Accessed 2nd July, 2016.

Dwivedi, A. and Misra, N. (2010). Quantum chemical study of Etodolac (Lodine). Der Pharma Chei, 2(2), 58 – 65.

Gece, G. (2008). The use of quantum chemical methods in corrosion inhibitor studies. *Corrosion Science*, 50: 2981.

Ibeawuchi, I. (2013). Review applications to prevent corrosion reducing gas pipeline. International Journal of Chemistry, 1, 94 – 101.

Khodyrev, Y. P., Batyeva, E. S., Badeeva, E. K., Platova, E. V., Tiwari, L. and Sinyashin, O. G. (2011). The inhibition action of ammonium salts of O, O' – dialkyldithiophosphoric acid on carbon dioxide corrosion of mild steel. Corrosion Science, 53 (3), 976 – 983.

Li, X., Deng, S., Fu, H. and Li, T. (2009). Adsorption and inhibition effect of 6-b enzylaminopurine on cold rolled steel in 1.0 M HCl. *Electrochemical Acta*, 54: 4089 – 2992.

Obi-Egbedi, N. O. and Obot, I. B. (2010). Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by Ketoconazole: Experimental and theoretical investigation corrosion science, 52: 198 – 204.

Obot, I. B., Obi - Egbedi, N. O., Umoren, S. A. and Ebenso, E. E. (2010). Synergistic and antagonistic effects of anions and *Ipomoca invulcrata* as green corrosion inhibitor for aluminium dissolution in acidic medium. *International Journal Electrochemical Science*, 5: 994 – 1007.

Obot, I. B., Obi-Egbedi, N. O. and Umoren, S. A. (2009). Adsorption characteristics and corrosion inhibitive properties of Clotrimazole for aluminium corrosion in hydrochloric acid. *International Journal Electrochemical Science* 4(6): 863 – 877.

Umoren, S. A. & Solomon, M. M. (2017a). Synergistic corrosion inhibition effect of metal cations and mixtures of organic compounds: A review. *Journal of Environmental Chemical Engineering,* 5: 246 – 273.

Umoren, S. A. & Solomon, M. M. (2017b). Application of polymer composites and nano composites as corrosion inhibitors. In E. Hart (Ed.). Corrosion inhibitors, principles, mechanisms, and application. New York: Nova Science publishers Inc.

Verma, C., Chauhan, D. S. and Quraishi, M. A. (2017). Drugs as encironmentally benign corrosion inhibitors for ferrous and non ferrous materials in acid environment: an overview. Journal of materials and environmental sciences, 8(11), 4040 – 4051.

Xhanari, K. & Finsgar, M. (2016). Organic corrosion inhibitors for aluminium and its alloys in acid solutions: A review. *RSC Advances*, 6: 62833 – 62857.

Xia, S., Qiu, M. Yu, L., Liu, F. and Zhao, H. (2008). Molecular dynamics and density functional theory study on relationship between structure of Imidazole derivatives and inhibition performances, *Corrosion Science*, 50: 2021 – 2029.