J. Chem. Soc. Nigeria, Vol. 47, No. 4, pp 852 – 864 [2022]

ELECTROCHEMICAL AND COMPUTATIONAL STUDY OF CORROSION INHIBITION OF MILD STEEL USING *CEFUROXIME* DRUG AS AN INHIBITOR.

B. A. Abiola[*], C. E. Gimba[1],G.A.Shallangwa,Y. A Dallatu[1], M. E. Ikpi[2],

[1]Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.
[2]Corrosion and Electrochemistry Research Laboratory, Department of Pure and Applied Chemistry, University of Calabar, P.M.B. 1115, Calabar-Nigeria.
Corresponding author-Email: bamigbolaabiola@ yahoo.com. 07039621425

ABSTRACT

The corrosion inhibition behavior of *cefuroxim*e was investigated on mild steel in 2 M H_2SO_4 solution using electron impedance spectroscopy measurement and Quantum chemical studies. The inhibitive effects of the studied compound increase with increasing concentration and the study revealed that cefuroxime is a mixed-type corrosion inhibitor and the Quantum chemical studies corroborate experimental results.

***Keywords*:** Corrosion Inhibition, EIS, *cefuroxime,* and Adsorption

INTRODUCTION

One of the most important problems facing the steel industry is metallic corrosion.Corrosion is an electrochemical process that involves the transfer of electrons between a metal surface and an aqueous solution. Corrosion of metals has caused huge economic losses involving billions of dollars each year in many industries. The international measure of prevention, application, and economics of corrosion technology (IMPACT) estimated the world global cost of corrosion to be $2.5 trillion which is equivalent to 3.4% of Gross Domestic Product GDP. The IMPACT found that the introduction of corrosion prevention could result in global savings between 15-35% of the cost damage. Therefore, control measures or procedures need to be implemented to reduce or inhibit corrosion thereby prolonging the life span of metals.

Several approaches have been suggested and implemented to protect metal against corrosion. One of the approaches is the use of corrosion inhibitors which is one of the best methods of controlling corrosion[1]. Most of the corrosion inhibitors used are toxic, expensive, and difficult to come by. Thus, researchers have focused on the useof eco-friendly compounds, that could be obtained conveniently and contain electronegative atoms such as Nitrogen, Sulphur,and Oxygen in the relatively long carbon chain compounds.

Presently a few nontoxic organic compounds such as *Azithromycin,*[2]; *Amoxicillin* [3]; *Cefixime*[4]; *Ciprofloxacin*[5] *Amoldipine*[6] have been reported as corrosion inhibitors, Nonetheless, there still need for research on other organic compounds to be used as inhibitors in industrial applications. The objectives of this study are to investigate the inhibitory action of

ISSN 0795 - 22066

Cefuroxime as a corrosion inhibitor for mild steel in 2 M H_2SO_4 solution using electrochemical experiments and Computational methods [7]

EXPERIMENTAL DETAILS

Inhibitor

Cefuroxime is an antibiotic drugthat is usedto treat skin, ear, throat infections, and gonorrhea disease. Is under the class of cephalosporin

The IUPAC nomenclature of the drug is 1-acetyloxyethyl(6R,7R)-3-(carboxyloxymethyl)-7-[(2E)-2-(furan-2-yl)-2-methoxyiminoacety] ami-no]-8-oxo-5-thia-1-azabicyclo {4, 2, 0}oct-2-ene-2-carboxylate.

With molecular formula $C_{16}H_{16}N_4O_8S$ and molecular weight of 361.368 g/mol. It has the chemical structure as shown in the Figure below.

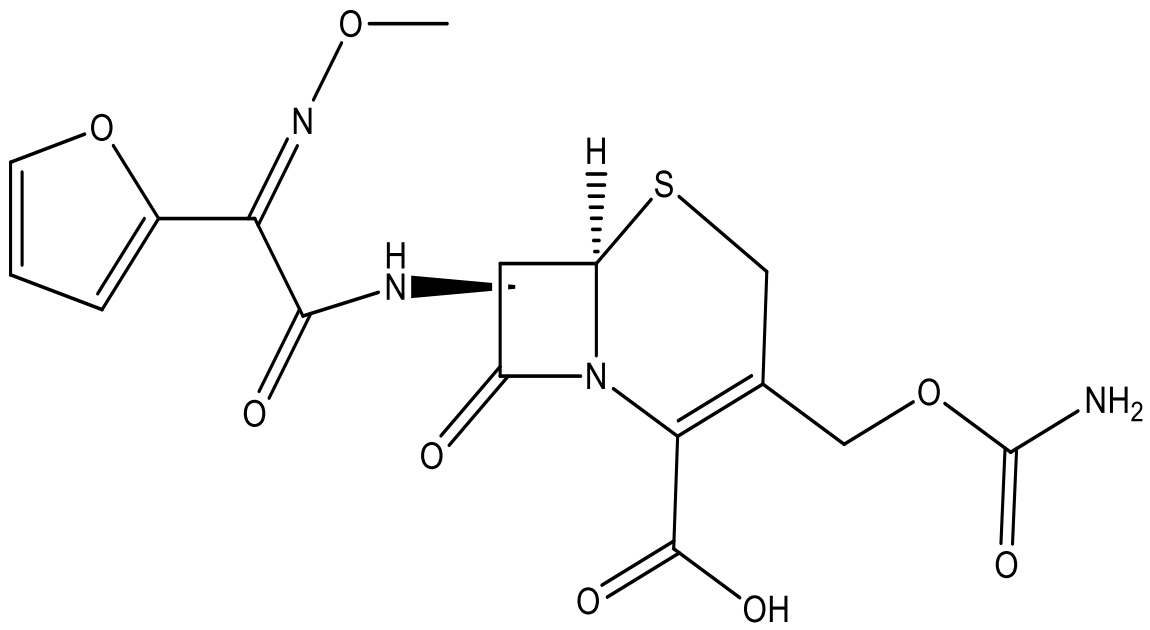


Figure 1: **Chemical Structure of *Cefuroxime* Drug.**

The Powder form of *cefuroxime* was obtained from Fidson Pharmaceutical company, Ogun State, Nigeria, and sold under the trade name "*Ciproflax*" Different concentrations of the drug were prepared by dissolving appropriate quantities of the powder from the mass of the drug sample [8].

Corrosion medium

The corrosive solution of 2 M H_2SO_4 was prepared from reagent grade of H_2SO_4 dilution

ISSN 0795 - 22066

using doubly distilled water. The concentration of the solution ranges from 100 ppm to 500 ppm.

Mild Steel Specimen

Mild Steel with 98% of Fe was used for the investigation and this was obtained from a flat metal sheet which was mechanically press cut into square coupons of about 1cm × 1cm and used in the electrochemical experiment as a working electrode. The coupons were used after polishing with 600 t0 900 grit emery papers. They were degreased in acetone and washed with distilled water and finally dried.

Electrochemical Studies

EIS Studies

The electron Impedance Spectroscopy (EIS) experiment was carried out using a conventional three-electrode electrochemical cell assembly. A freshly polished mild steel specimen with an exposed surface area of 1cm × 2cm was used as a working electrode and a saturated calomel electrode (SCE) as a reference electrode. The measurements were performed using Gamry Electrochemical Analyzer at 303K and Nyquist curves were recorded by changing the electrode potential E_{corr} automatically with a scan rate of 0.5 mVs^{-1} from a low potential -0.25 to + 0.6. Before each run, the working electrode was immersed in the test solution for 30 minutes to obtain a steady state. The corrosion rate of the metal was calculated through corrosion current density I_{corr}. The electrochemical impedance parameters obtained from the impedance spectra were solution resistance (R_{st}), charge capacitance (R_{ct}), corresponding double layer (c_{dl}), and inhibition efficiency (IE).

Polarization Studies

The effect of inhibitors on mild steel anodic and cathodic polarization curves in 2 M H_2SO_4 solution was investigated, and the polarization curves obtained are given in Figure 3 at 303 K. The linear region of the polarization curves was used to compute the values of cathodic (βc) and anodic (βa) Tafel slopes. The intersection of the linear parts of the anodic and cathodic curves with the open-circuit corrosion potential gave the corrosion current density (I_{corr}), (E_{corr}). Table 5 shows the corrosion parameters obtained from these curves, including corrosion potential (E_{corr}), anodic Tafel slope (a), cathodic Tafel slope (c), corrosion current density (I_{corr}), and percentage inhibition efficiency (percent). The results showed that raising the inhibitor concentration resulted in a decrease in corrosion current density and an increase in inhibition efficiency (η %), indicating that inhibitor molecules adsorbed to the mild steel surface to create a protective coating[9]. The presence of an inhibitor causes a change in E_{corr} values when compared to the E_{corr} value when no inhibitor is present.

Computational Details

Quantum Chemical Calculation details

Quantum chemical calculations were carried out with the aid of Spartan 14.0 software suit. The

ISSN 0795 - 22066

structure of *Cefuroxime* was used as the representative structure for computational studies. The initial structures were refined with self-consistent field theory (SCF). The Optimized structures obtained from SCF calculations were later optimized by Density Functional Theory DFT which involvesBacke's three Parameter hybrid functional and Lee-Yang-Paar Correlation functional (B3LYP). Quantum chemical parameters include the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), and the energy Gab ($\Delta E = E_{LUMO} - E_{HOMO}$) and dipole moment μ were recorded.

RESULTS AND DISCUSSIONS

EIS studies

The Nyquist plots for mild steel obtained at mild steel interface with and without the different concentrations of*cefuroxime* at 303 K are shown in Figure 2. The existence of a depressed semicircle with its center below the axis (Z') in Nyquist plots in Figure 2 for both inhibitors suggests the non-homogeneity and roughness of the mild steel surface[10]. The EIS spectra of all tests were analyzed using the equivalent circuit shown in Figure 3, which is a parallel combination of the charge transfer resistance (*R*ct) and the constant phase element (CPE), which are in series with the solution resistance (*R*s). This type of electrochemical equivalent circuit was reported previously to model the iron/acid interface[11]. Constant phase element (CPE) is introduced instead of pure double layer capacitance to give a more accurate fit as the double layer at the interface does not behave as an ideal capacitor.

ISSN 0795 - 22066

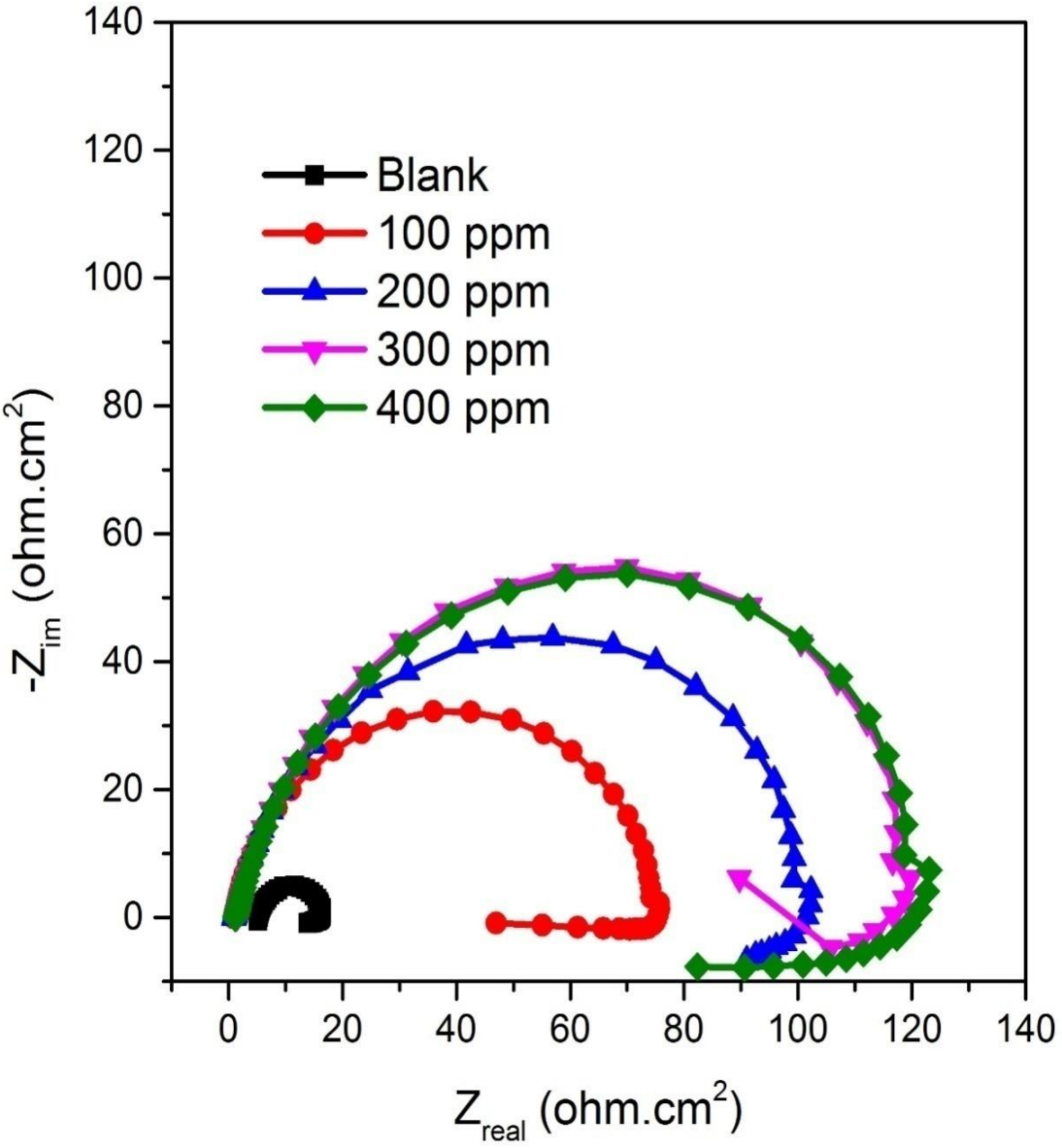


Figure 2. Nyquist plot for mild steel in 2M H_2SO_4,In the absence and presence of different concentrations of Inhibitor at 303 K.

ISSN 0795 - 22066

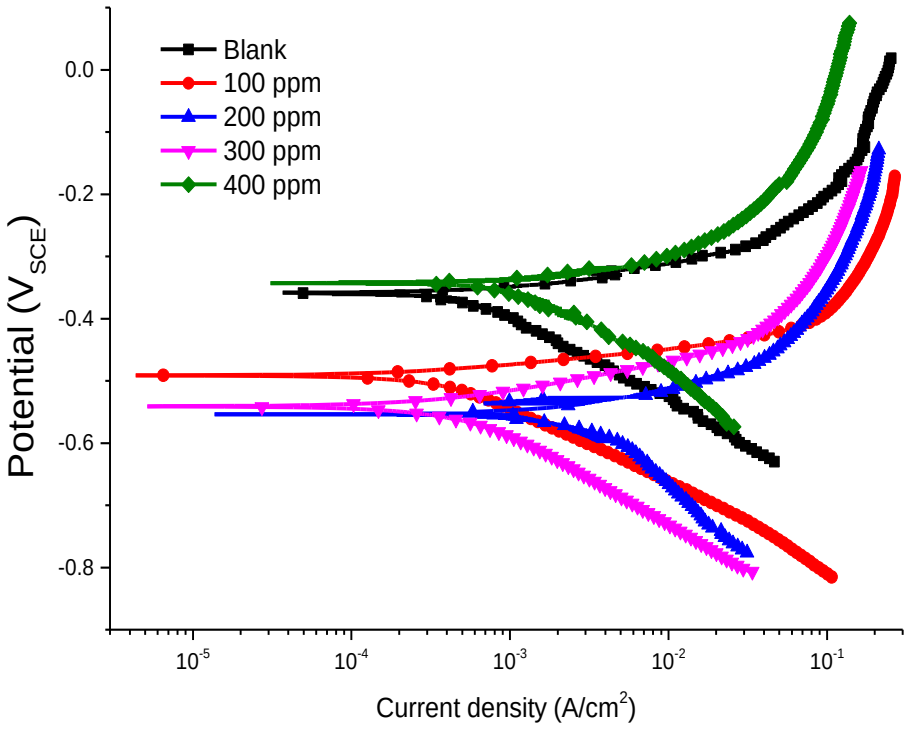


Figure 3. Polarization curves of the corrosion of mild steel in 2 M H_2SO_4 solution in the absence and presence of *Cefuroxime* at 303 K.

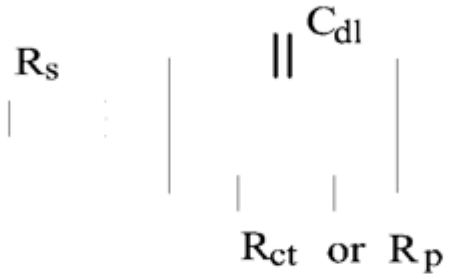


Figure 4: The equivalent circuit used to fit the EIS experimental data.

ISSN 0795 - 22066

The electrochemical parameters such as solution resistance, charge transfer resistance andC_{dl} constantsare obtained from fitting the experimental data of Nyquist plots in the equivalent circuit shown in Figure. 3 are presented in Table 1.

Table 1. Electrochemical impedance parameters for mild steel in H_2SO_4 solution in the absence and presence of inhibitor at the different concentrations at 303K.

Inhibitor	Conc(ppm)	R_{st}(Ωcm^2)	R_{ct} (Ωcm^2)	C_{dl}(µcm^{-2})	IE%
	Blank	5.20	13.97	143	-
	100	0.39	11.1	17.95	25
	200	0.81	152.1	16.52	90
	300	0.96	269.5	14.74	94
	400	2.34	521.1	1.90	97

Table 2. Potentiodynamic parameters for mild steel in H_2SO_4 solution in the absence and presence of inhibitor at the different concentrations at 303K.

Inhibitor	Concentration (ppm)	$-E_{corr}$ (mV/SCE)	I_{corr} (µAcm^2)	βa (mV/dec^1)	β_C (mV/dec^1)	η (%)
Cefuroxime	Blank	359	1150	56.3	369	–
	100	320	586	54.0	65.3	49
	200	506	541	53.8	179	53
	300	424	64	194.1	1.00	94
	400	347	18	32.9	90.0	98

The data shown in Table 1 reveal that the value of R_{ct} increases with the addition of inhibitors as compared to the blank solution, the increase in R_{ct} value is attributed to the formation of a protective film at the metal/solution interface. The C_{dl} value decreases on increasing the concentration of both the inhibitors, indicating the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface[12]Table 2 shows the corrosion parameters obtained from these curves, including corrosion potential (E_{corr}), anodic Tafel slope (a), cathodic Tafel slope (c),

ISSN 0795 - 22066

corrosion current density (I_{corr}), and percentage inhibition efficiency (percent). The results showed that raising the inhibitor concentration resulted in a decrease in corrosion current density and an increase in inhibition efficiency (η %), indicating that inhibitor molecules adsorb to the mild steel surface to create a protective coating[13]. The presence of an inhibitor causes a change in E_{corr} values when compared to the E_{corr} value when no inhibitor is present.

3. 1. Quantum Chemical Calculations

Quantum chemical calculations were carried out to investigate the adsorption and inhibition mechanism of the studied compound[14]. Figure.4 shows complete geometric optimization of the studied inhibitor. The HOMO and LUMO (frontier molecular Orbital) present in the *Cefuroxime* compound are shown in Figure. 5.

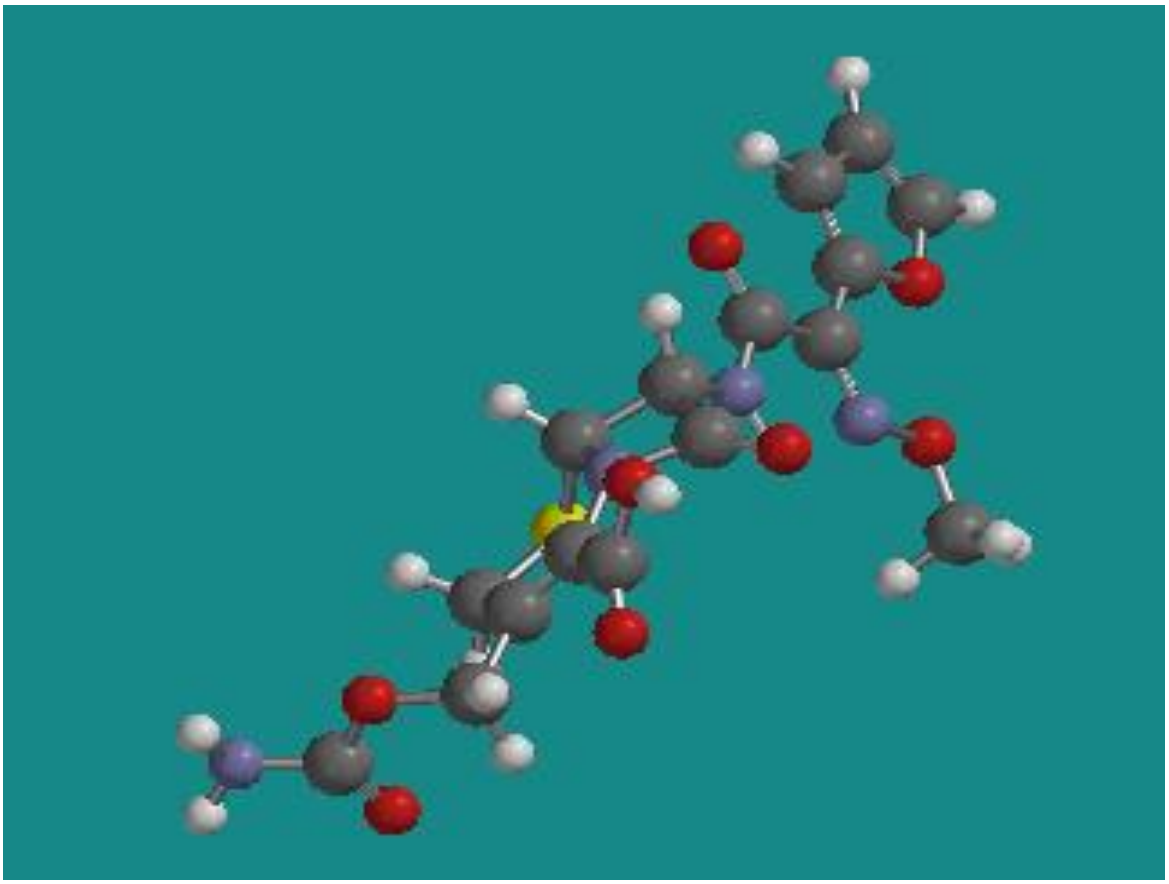


Figure 4. Optimized structure of the studied molecule Cefuroxime

ISSN 0795 - 22066

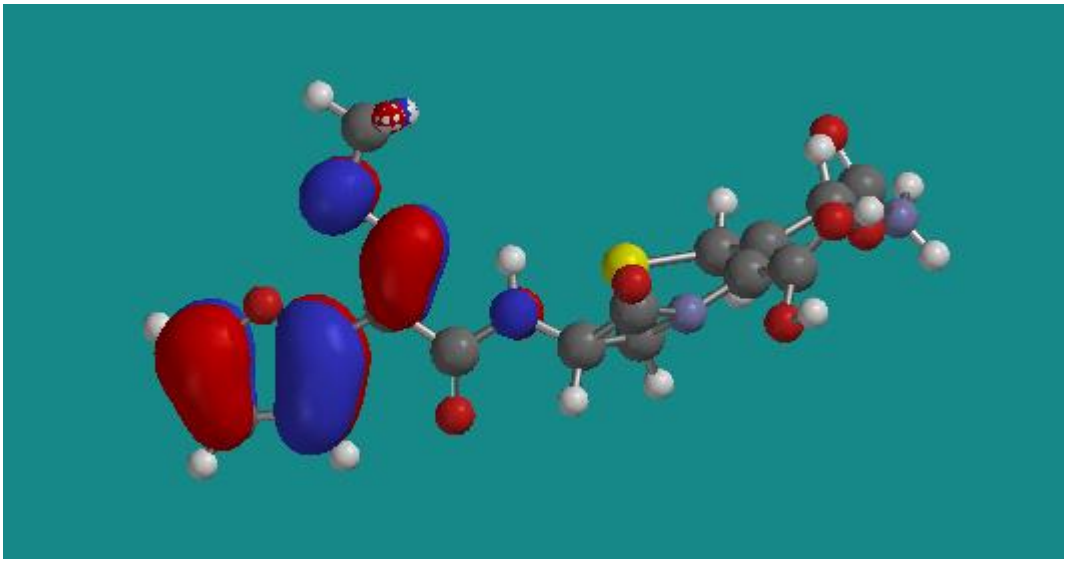
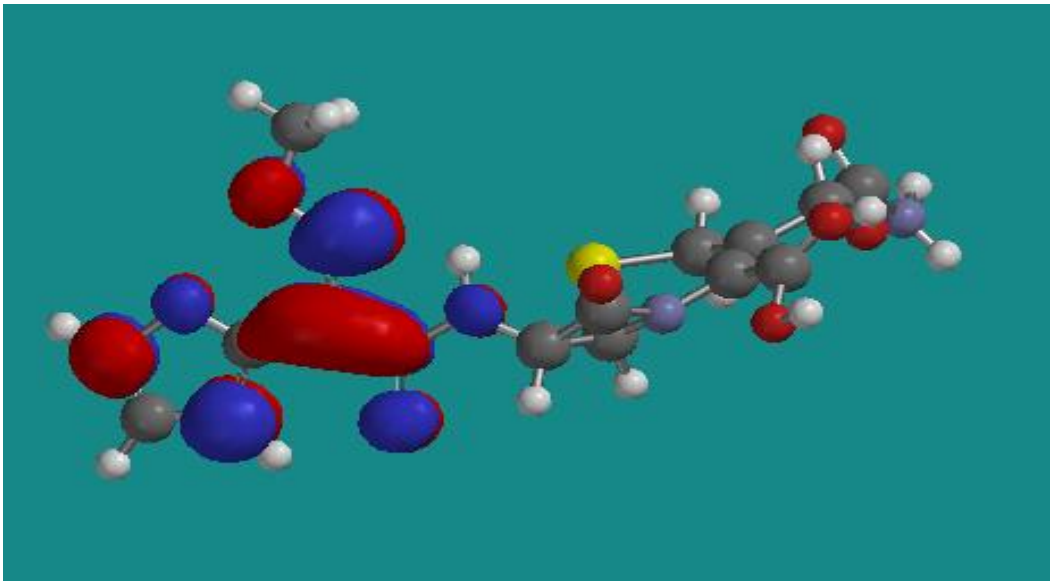


Figure 5a: Schematic Representation of the HOMO of molecular Orbital structure of *Cefuroxime*.



LUMO

Figure 5b. **Schematic Representation of the LUMO of molecular Orbital structure of *Cefuroxime*.**

ISSN 0795 - 22066

To understand the nature of the interaction of the compound with the metal surface is to focus on the composite index that directly controls the electronic interaction of the inhibitor molecules with the metal surface. The index includes E_{HOMO}, E_{LUMO}, ΔE, and dipole moment μ. Etc. listed in Table 2[15].

Table 3. Calculated Quantum Parameters for cefuroxime

E_{HOMO}(ev)	ELUMO (ev)	ΔE (ev)	M (debyes)
-5.91	-1.69	-4.22	3.33

.

E_{HOMO} is often connected with the electron-donating ability of a molecule, the higher energy value of E_{HOMO} revealed the ability of the molecule to donate an electron to an empty molecular orbital. Thus, an increase in E_{HOMO} value facilitates adsorption or inhibition. Therefore, the energy of LUMO shows the capability of the molecule to accept electrons, the lower the value of E_{LUMO} the more likely the molecule to accept electrons. The lower the value of the energy gap (ΔE), the higher the inhibition efficiency because the energy to remove an electron from the last occupied orbital will be low. And the higher value of dipole moment (μ) favorsthe accumulation of the inhibitor on the surface layer [16]. The adsorption of the inhibitor on the Fe surface takes nearly parallel to the surface to maximize its contact with the surface as shown in Figure 6.

ISSN 0795 - 22066

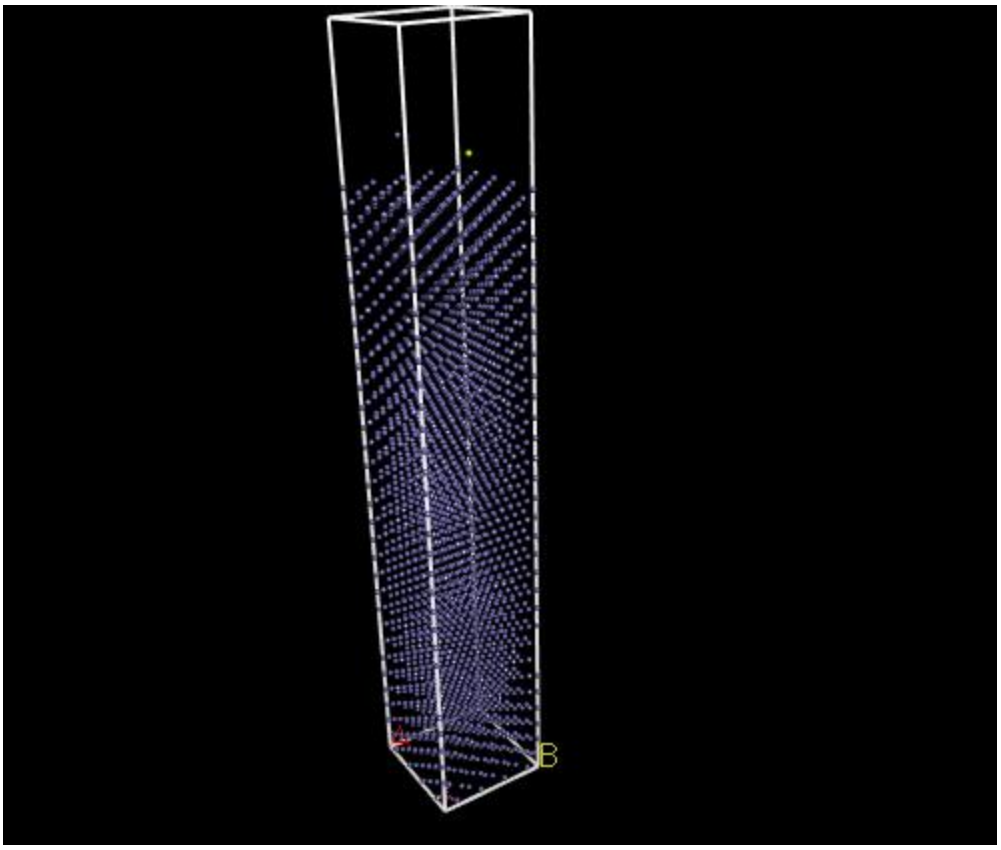


Figure 6. The adsorption of the inhibitor on the Fe surface.

CONCLUSIONS

The *cefuroxime* inhibitor act as a good corrosion inhibitor for mild steel in 2 M H_2SO_4 solution and EIS measurements showed that charge transfer resistance (R_{ct}) increases and double layer capacitance (C_{dl}) decreased in presence of inhibitors which suggested the adsorption of the inhibitor molecules on the surface of mild steel.

Polarizationmeasurementsrevealedthatthein hibitorwasofmixedtypeasboththeanodicand cathodic processes were hindered.

Lastly, theoretical parameters obtained by DFT calculations correlate with the results of *cefuroxime*obtained by experimental studies.

REFERENCES

[1] S. A. Umoren, I. B. Obot, A. Madhankumar, and Z. M. Gasem, "Performance evaluation of pectin as ecofriendly corrosion inhibitor for X60 pipeline steel in acid medium: Experimental and theoretical approaches," *Carbohydrate Polymers*, vol. 124, pp. 280–291, Jun. 2015, doi: 10.1016/J.CARBPOL.2015.02.036.

[2] A. S. Fouda, F. S. Mohamed, and M. W. El-Sherbeni, "Experimental and computational study of levofloxacin as corrosion inhibitor for carbon steel in acidic media," *World News of Natural Sciences*, vol. 09, no. 2, Jun. 2017, doi: 10.1007/S40735-016-0039-Y.

ISSN 0795 - 22066

[3] M. E. Ikpi, F. E. Abeng, and O. E. Obono, "Adsorption and thermodynamic studies for corrosion inhibition of API 5L X-52 steel in 2 M HCl solution by moxifloxacin," *World News of Natural Sciences*, vol. 09, 2017, Accessed: Aug. 22, 2022. [Online]. Available: www.worldnewsnaturalsciences.com

[4] I. Naqvi, A. Saleemi, S. N.-Int. J. Electrochem. Sci, and undefined 2011, "Cefixime: a drug as efficient corrosion inhibitor for mild steel in acidic media. Electrochemical and thermodynamic studies," *academia.edu*, vol. 6, pp. 146–161, 2011, Accessed: Aug. 22, 2022. [Online]. Available: https://www.academia.edu/download/7540243/6010146.pdf

[5] I. Akpan, N. O.-C. and P. E. Research, and undefined 2014, "Electrochemical investigation of the inhibitory action of Ciprofloxacin Drugs on the acid corrosion of mild steel," *core.ac.uk*, vol. 26, 2014, Accessed: Aug. 22, 2022. [Online]. Available: https://core.ac.uk/download/pdf/234688995.pdf

[6] I. A. Akpan and ---N O Offiong, "Electrochemical Study of the Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Amlodipine Drug," *International Journal of Chemistry and Materials Research*, vol. 2, no. 3, pp. 23–29, Mar. 2014, Accessed: Aug. 22, 2022. [Online]. Available: https://archive.conscientiabeam.com/index.php/64/article/view/1827

[7] K. Rokosz, T. Hryniewicz, Dudek, D. Matýsek, J. Valíček, and M. Harničárová, "SEM and EDS Analysis of Surface Layer Formed on Titanium After Plasma Electrolytic Oxidation in H3PO4 with the Addition of Cu(NO3)2," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 8, pp. 7814–7817, Aug. 2016, doi: 10.1166/JNN.2016.12558.

[8] I. A. Akpan and ---N O Offiong, "Electrochemical Study of the Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Amlodipine Drug," *International Journal of Chemistry and Materials Research*, vol. 2, no. 3, pp. 23–29, Mar. 2014, Accessed: Aug. 22, 2022. [Online]. Available: https://archive.conscientiabeam.com/index.php/64/article/view/1827

[9] N. D. Nam, P. van Hien, N. T. Hoai, and V. T. H. Thu, "A study on the mixed corrosion inhibitor with a dominant cathodic inhibitor for mild steel in aqueous chloride solution," *J Taiwan Inst Chem Eng*, vol. 91, pp. 556–569, Oct. 2018, doi: 10.1016/J.JTICE.2018.06.007.

[10] M. Yadav, T. K. Sarkar, and T. Purkait, "Studies on Adsorption and Corrosion Inhibitive Properties of Indoline Compounds on N80 Steel in Hydrochloric Acid," *Journal of Materials Engineering and Performance 2015 24:12*, vol. 24, no. 12, pp. 4975–4984, Oct. 2015, doi: 10.1007/S11665-015-1765-X.

[11] M. Yadav, T. K. Sarkar, and T. Purkait, "Amino acid compounds as eco-friendly corrosion inhibitor for N80 steel in HCl solution: Electrochemical and theoretical approaches," *Journal of Molecular Liquids*, vol. 212, pp. 731–738, Dec. 2015, doi: 10.1016/J.MOLLIQ.2015.10.021.

[12] F. Bentiss, M. Traisnel, and M. Lagrenee, "Influence of 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole on corrosion inhibition of mild steel in acidic media," *Journal of Applied Electrochemistry 2001 31:1*, vol. 31, no. 1, pp. 41–48, 2001, doi: 10.1023/A:1004141309795.

[13] N. D. Nam, P. van Hien, N. T. Hoai, and V. T. H. Thu, "A study on the mixed corrosion inhibitor with a dominant cathodic inhibitor for mild steel in aqueous chloride solution,"

ISSN 0795 - 22066

J Taiwan Inst Chem Eng, vol. 91, pp. 556–569, Oct. 2018, doi: 10.1016/J.JTICE.2018.06.007.

[14] I. Danaee, O. Ghasemi, G. R. Rashed, M. RashvandAvei, and M. H. Maddahy, "Effect of hydroxyl group position on adsorption behavior and corrosion inhibition of hydroxybenzaldehyde Schiff bases: Electrochemical and quantum calculations," *Journal of Molecular Structure*, vol. 1035, pp. 247–259, Mar. 2013, doi: 10.1016/J.MOLSTRUC.2012.11.013.

[15] A. S. Fouda, F. S. Mohamed, and M. W. El-Sherbeni, "Experimental and computational study of levofloxacin as corrosion inhibitor for carbon steel in acidic media," *World News of Natural Sciences*, vol. 09, no. 2, Jun. 2017, doi: 10.1007/S40735-016-0039-Y.

[16] J. Bhawsar, P. K. Jain, and P. Jain, "Experimental and computational studies of Nicotiana tabacum leaves extract as green corrosion inhibitor for mild steel in acidic medium," *Alexandria Engineering Journal*, vol. 54, no. 3, pp. 769–775, Sep. 2015, doi: 10.1016/J.AEJ.2015.03.022.

ISSN 0795 - 22066