

Kinetics, Molecular Dynamics and Adsorption Behaviour of Pyridine on Mild Steel in 0.1M HCl Solution

Ekerete Boekom¹, Kufre E. Essien², V. F. Ekpo¹ and Anne Obot¹

¹Department of Chemistry, University of Uyo, P.M.B 1017, Uyo, Akwa Ibom State, Nigeria

²Department of Chemistry, Akwa Ibom State University, P.M.B. 1167, Ikot Akpaden, Mkpato Enin

ARTICLE INFO

Article history:

Received: 14 February 2020;

Received in revised form:

12 May 2020;

Accepted: 22 May 2020;

Keywords

Corrosion,
Pyridine,
Mild Steel.

ABSTRACT

The inhibition of the corrosion of mild steel in 0.1 M HCl solution by Pyridine from 303K to 333K at concentrations of 5×10^{-4} M, 1×10^{-4} M, 5×10^{-5} M, 2×10^{-5} M and 1×10^{-5} M was studied using gravimetric technique. The maximum inhibition efficiency of 70 % at 5×10^{-4} M for 333 K was observed. The compound acted as corrosion inhibitor in 0.1 M 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 elucidated the effects of inhibitor concentration, temperature, $d\lambda - P\lambda$ interaction between the metal surface, the heteroatom of the inhibitor, and the electron charge densities on the heteroatoms of the Pyridine molecule. The adsorption of the inhibitor on the metal surface obeyed Temkin adsorption isotherm. Quantum chemical calculations using Hartree-fock Density Functional Theory by Hamiltonian method was employed with PM3 (NDDO) basic set of minimal valence basis as STO3G Program.

© 2020 Elixir All rights reserved.

1.0 Introduction

The demand for Iron and its alloys in industries is on the increase owing to its superior mechanical strength in comparison with other metals (Strickland, 1923). It is preferred in ship and bridge construction, riveting, bolting, and several others where high mechanical strength is required (Bebon, 2011). However, steel proneness to corrosion is one of the greatest challenges in industries (Solomon *et al.*, 2017). During industrial exercises like metal scale removal and cleaning, acid descaling, oil well acidizing, aggressive acid solutions come in direct contact with metals. These industrial exercises cause corrosion of metals. It is customary that for any industrial process, corrosion inhibitors be added to acid solution before use, to inhibit metal corrosion (Solomon *et al.*, 2018). Organic compounds (those with N, O, S, P and π – electrons in their structure) (Xhanari and Finsgar, 2016) and inorganic compounds (nitrites, nitrates, phosphates and lanthanides) (Umoren and Solomon, 2017a) are the common acid corrosion inhibitors. Organic metal corrosion inhibitor demand stood at 70 %, while that of the inorganic counterpart is remarkably low (Umoren and Solomon, 2017b) due to their negative influence on the ecosystem. This work was designed to examine the inhibition ability of Pyridine. The investigation was done using gravimetric and quantum chemical techniques.

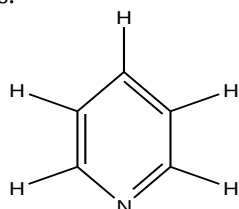


Figure 1. Chemical structure of Pyridine (C₅H₅N)

2.0 Experimental Details

2.1 Materials and Metal Samples Preparation

Pyridine compound used in this experiment was of analytical grade and product of M and B limited, Dagenham, England. All other chemicals were procured from Sigma Aldrich and were used as purchased. The metal sheet obtained from Ken Johnson Engineering Company, Uyo, Nigeria was cut into 5 x 4 cm coupons for gravimetric experiments. The samples were mechanically abraded using different grit of emery papers (#800 – #2000 grade). Thereafter, 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 prior to use (Solomon *et al.*, 2018).

2.2 Gravimetric Investigations

The specimens were suspended in a reaction vessel containing 100 ml of studied solution (acid solution without and with different concentrations of Pyridine). Before the samples were introduced into the reaction system, the initial weight was recorded. After immersion time in the solution, the specimens were removed, washed with distilled water, then with acetone, and finally dried with warm air (Solomon *et al.*, 2017; Solomon and Umoren, 2016; Verma *et al.*, 2017). The new weight of the samples was recorded. Weight loss (g) was computed as the difference between the initial and the final weights. Values of corrosion rate (ρ), surface coverage (θ) and inhibition efficiency (%) were computed using weight loss data (Obot *et al.*, 2011).

$$\text{Corrosion rate } (\rho) = \frac{\text{Weight loss } (\Delta W)}{\text{Area of mild steel } (A) \times \text{Immersion time } (t)} \quad (1)$$

$$\text{Surface coverage } (\theta) = \frac{\rho_1 - \rho_2}{\rho_1} \quad (2)$$

$$\text{Inhibition efficiency (\%)} = \frac{\rho_1 - \rho_2}{\rho_1} \times 100 \quad (3)$$

Where, ρ_1 and ρ_2 are the corrosion rates of the mild steel in 0.1 M HCl (Blank) in the absence and presence of inhibitor respectively.

2.3 Quantum Chemical Calculations

In this work, Quantum parameter calculations were conducted by the Parameterized Model Three (PM3) Semiempirical using ArgusLab (tm) (Version 4.0) software. The calculations were to simulate the effects of Pyridine molecules on acid corrosion. Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) revealed the active sites of the molecules and are here discussed.

3.0 Results and Discussion

3.1 Gravimetric measurements

The dissolution pattern of mild steel in 0.1 M HCl solution without and with Pyridine was studied. The gravimetric method is considered the “gold standard” for corrosion assessment because of its simplicity (Anupama *et al.*, 2016). It requires a reasonable immersion time during measurement. The parameters such as corrosion rate, surface coverage (mpy) and Inhibition efficiency (%) obtained from the weight loss method are listed in table 1. The table shows that the corrosion rate of the metal was reduced in acid solution containing various concentrations of Pyridine as reported by Solomon *et al.* (2017). This indicated that the mixture effectively protected the metal surface against corrosive attack in the acid solution. Again, the effectiveness of the Pyridine affirmed the larger surface coverage value (0.70) and higher inhibition efficiency of 70% for 5×10^{-4} M at 333 K. From table 1, it can be seen that corrosion rate, surface coverage and inhibition efficiency values were higher at 333 K. The higher values of weight loss and corrosion rate at 333 K may be attributed to intensified molecular thermal motion as reported by Arukalam (2014); while those of surface coverage and inhibition efficiency may be attributed to a shift in the adsorption – desorption equilibrium toward adsorption (Solomon *et al.*, 2010; Solomon and Umoren, 2016). A more compact and rigid film capable of effective corrosion inhibition was formed on the metal surface at high temperature than at low temperature.

The values of inhibition efficiency from gravimetric measurements for different concentrations of the inhibitor after 7 days immersion at 303-333 K are summarized in table 1. It is evident from the table that the inhibition efficiency (%) increased with increasing inhibitor concentration, reaching a maximum of 70 % at 333 K for 5×10^{-4} M. This may be due to the adsorption of Pyridine onto the mild steel surface through non-bonding electron pairs of nitrogen atom, as well as the π -electrons of the aromatic rings. The high inhibitive performance of Pyridine suggests a higher bonding ability of

the inhibitor to the mild steel surface. Similar observation had been reported by Ahamad and Quraishi (2010). The inhibition efficiency followed a zigzag trend at 303 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 molecules was seen at 313 K, 323 K and 333 K than at 303 K, since at these higher temperatures, the inhibitive molecules were energized and tended to spread more evenly on the mild steel surface than at 303 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 was 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 the mild steel remained unprotected and corrodes at a fast rate. This observation could be attributed to the insufficient amount of inhibitors on the surface of the mild steel, which was easily washed away during the corrosion process, thereby exposing the mild steel to severe localized attack by the acid.

3.2 Adsorption Considerations

Organic inhibitors are known to retard metal corrosion by an adsorption mechanism whereby the inhibitor molecules gradually substitute the adsorbed water molecules on the metal surface (Liu *et al.*, 2014; Mourya *et al.*, 2016; Solomon and Umoren, 2016). Organic molecules can be covalently (Chemisorption) or electrovalently (Physisorption) bonded on a metal surface or both (Solmaz *et al.*, 2008; Verma *et al.*, 2017; Yadav *et al.*, 2016). The influence on the type of adsorption that prevails over the other in a metal surface may be due to certain factors such as the chemical composition of the inhibitor and corrosive solution, electronic properties of the inhibitor molecule and the temperature of the aggressive medium (Tao *et al.*, 2012). It is a well known fact that low temperatures favour physical adsorption because of the low heat of adsorption, while elevated temperatures favour chemical adsorption owing to its stronger adsorption energy compared to physisorption (Tao *et al.*, 2012; Liu *et al.*, 2015). The mode of interaction between inhibitor molecules and metal surface can be gained through the use of the adsorption isotherm. To further understand the mode of adsorption of pyridine on mild steel surface in 0.1 M HCl solution, surface coverage values (Table 2) were fitted into various adsorption isotherms including Langmuir, El-Awady, Temkin, Frundlich, and Frumkin adsorption isotherms. Normally, the

Table 1. Kinetic data for mild steel in 0.1 M HCl solution containing pyridine

Inhibitor Conc (M). $\times 10^{-4}$	Corrosion rate				Surface Coverage (mpy)				Inhibition efficiency (%)			
	303	313	323	333	303	313	323	333	303	313	323	333
Blank	0.0299	0.1497	0.1313	0.3132	-	-	-	-	-	-	-	-
0.1	0.0263	0.1200	0.0775	0.1410	0.1217	20.37	41.29	55.21	12.17	20.37	41.29	55.21
0.2	0.0248	0.117	0.0748	0.119	0.1351	0.2195	0.4315	0.6181	13.51	21.95	43.15	61.81
0.5	0.0213	0.114	0.0722	0.116	0.1743	0.2401	0.4501	0.6321	17.43	24.01	45.01	63.21
1.0	0.0197	0.1048	0.0670	0.103	0.3355	0.3025	0.4891	0.6681	33.55	30.25	48.91	66.81
5.0	0.0193	0.0898	0.0591	0.0940	0.3521	0.4034	0.5481	0.6977	35.21	40.34	54.81	70.00

isotherm with the best fit to the data is adjudged by the value of the linear regression coefficient (R^2) (Solomon *et al.*, 2010; Akalezi *et al.*, 2012; Umoren and Ekanem, 2010). For a perfect fit, $R^2 = 1$.

The adsorption of Pyridine molecule onto mild steel surface followed Temkin isotherm with the form given in Equation 1 (Temkin and Pyzhev, 1940; Aharoni and Ungarish, 1977):

$$\exp(f\theta) = K_{\text{ads}} C_{\text{inh}} \quad (4)$$

Where, C_{inh} = concentration of Pyridine, θ = degree of surface coverage, f = heterogeneous factor of the metal surface describing the molecular interactions in the adsorption layer. K_{ads} = Equilibrium constant of adsorption-desorption process which usually defined the strength of the bond between adsorbate and adsorbent (Xia *et al.*, 2015; Zheng *et al.*, 2015). Straight lines graph were obtained by plotting θ versus $\ln C$ (Figure 2), and Temkin adsorption parameters (Table 2) were calculated. It is clear from the table that, the values of f were less than 0 ($f < 0$) indicating that attraction occurred between the adsorbate and the adsorbent (Obot *et al.*, 2011). The values of K_{ads} which denotes the strength between adsorbate and adsorbent are very low indicating weak interaction. Therefore, the electrostatic interaction (Physisorption) between the inhibitor molecules existing as cation prevails over molecular interaction which often results in strong interactions (Chemisorption).

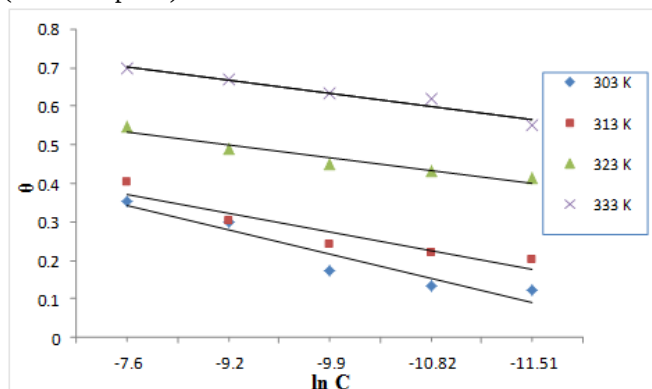


Figure 2. Temkin adsorption isotherm θ versus $\ln C$ for mild steel in 0.1 M HCl solution containing different concentrations of Pyridine

The adsorption equilibrium constant K_{ads} is related to the Standard free energy of adsorption (ΔG_{ads}^0) according to equation 2 (Roy and Sukul, 2015):

$$K_{\text{ads}} = \frac{1}{55.5} \exp \left(\frac{-\Delta G_{\text{ads}}^0}{RT} \right) \quad (5)$$

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. Calculated values of ΔG_{ads} are given in Table 4. From the table, the values of ΔG_{ads} are negative reflecting the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface (Obot *et al.*, 2011; Solomon and Umoren, 2016). Generally, values of ΔG_{ads} up to -20 kJ/mol are consistent with electrostatic interactions between the charged molecules and the metal (physisorption), while those around -40 kJ/mol or higher are associated with chemisorption as a result of sharing or transferring of electrons from organic molecules to the metal surface to form a coordinate type of bond (Zou *et al.*, 2014; Obot *et al.*, 2011). It is clear from table 4 that the values of ΔG_{ads} are between -6.15 kJ/mol and -48.64 kJ/mol suggesting

mixed adsorption: physisorption and chemisorption (Yuce *et al.*, 2016; Yadav *et al.*, 2016; Mobin and Khan, 2014; Solomon and Umoren, 2015; Solomon *et al.*, 2017).

Table 2. Adsorption parameters from Temkin isotherm for mild steel coupons in 0.1 M HCl solution containing different concentrations at 303-333 K

Inhibitor	T(K)	R^2	f	K_{ads}	$-\Delta G(\text{kJ})$
Pyridine	303	0.9157	-15.97	1.57×10^{-3}	6.15
	313	0.8743	-20.75	1.69×10^{-4}	11.63
	323	0.9326	-30.49	3.34×10^{-8}	35.44
	333	0.9555	-29.33	4.23×10^{-10}	48.64

The values of enthalpy of activation, ΔH and entropy of activation, ΔS were obtained from the transition state equation (Abboud *et al.*, 2007; Obot *et al.*, 2011).

$$\rho = \left(\frac{RT}{Nh} \right) \exp \left(\frac{\Delta S}{R} \right) \exp \left(\frac{-\Delta H}{RT} \right) \quad (6)$$

Where, ρ is the corrosion rate, h is the Planck's constant ($6.6261 \times 10^{-34} \text{ Js}$), N is the Avogadro's number ($6.02252 \times 10^{23} \text{ mol}^{-1}$), T is the absolute temperature and R is the Universal gas constant. A straight line graph was obtained by plotting $\log(\rho/T)$ versus $1/T$ (Figure 2) with slope of $(-\Delta H/3.03R)$ and an intercept of $[\log(R/Nh) + (\Delta S/2.303R)]$.

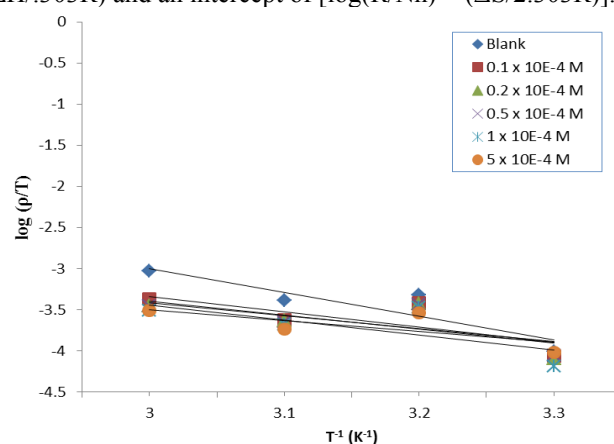


Figure 3. Transition state plot as $\log(\rho/T)$ versus $1/T$ for mild steel in 0.1 M HCl containing different concentrations of Pyridine

Values of ΔH and ΔS were computed and listed in table 4. From the table, it is shown that the values of ΔH for the dissolution reaction of mild steel in 0.1 M HCl in the presence of Pyridine are higher ($2.56 - 3.82 \text{ kJ/mol}$) than that in the absence of pyridine (5.50 kJ/mol). The positive sign of ΔH shows the endothermic nature of the solution process suggesting that the dissolution of mild steel is slow (Abboud *et al.*, 2007; Guan *et al.*, 2004; Obot *et al.*, 2011).

Table 3. Average Activation Energy and Heat of Adsorption at Constant Inhibitor Concentration

Average activation energy, E_a (kJ/mol)			Heat of adsorption (Q) at constant inhibitor concentration (KJ/mol)
303 – 313 K	313 – 323 K	323 – 333 K	
37.2	45.6	34.5	0.9972
			1.3357
			1.5651
			1.7125

The average activation energy for the dissolution of mild steel in 0.1 M HCl solution between 303 – 313 K, 313 – 323 K and 323 – 333 K were found to be 37.2, 45.6 and 34.5 kJ/mol, respectively. From thermodynamics point of view, two types of adsorption process had been distinguished (Zaferani and Shishesaz, 2014): physisorption in which the

activation energy is less than 40 kJ/mol and chemisorption, where activation energy is greater than 40 kJ/mol. On the basis of the experimentally determined activation energy values, the addition of this compound was considered chemisorption and therefore, as the temperature was raised, the adsorption of this compound on the surface of metal was improved (El-Etre, 2006).

Barrow (1983) distinguished between the two types of adsorption processes. 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 favoured physisorption. Hence, the inhibition increased with the rise in temperature at higher concentration.

Table 4. Thermodynamic parameters for mild steel containing different concentrations of Pyridine

Concentration (M) $\times 10^{-4}$	ΔH (kJ/mol)	ΔS (J/molK ⁻¹)
Blank	5.50	-249.71
0.1	3.82	-209.40
0.2	3.54	-210.71
0.5	3.32	-211.33
1.0	3.76	-211.40
5.0	2.56	-214.34

Entropy of activation, ΔS values were negative both in the uninhibited and inhibited systems. This indicates that the inhibitor molecules freely moving in the bulk solution were adsorbed in an orderly fashion onto the mild steel surface, resulting in an increase in entropy. This also implies that activated complex in the rate determining step represents an association rather than a dissolution step, meaning that a decrease in disordering takes place on going from reactants to the activated complex (Herrag *et al.*, 2010).

3.3 Proposed Mechanism of Action for the Pyridine Molecule

The Pyridine molecule is conjugated with benzene ring and heteroatom. 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 $d\pi$ - π 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. Pyridine molecule resembles benzene. The stable delocalized π -electron system of the molecule in acid solution caused a strong adsorption of the compound on the material and considerate inhibition result. The adsorption of Pyridine also takes place through the lone pairs which are to form co-ordination bond with metal atom in mild steel.

3.4 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 Pyridine on the mild steel surface.

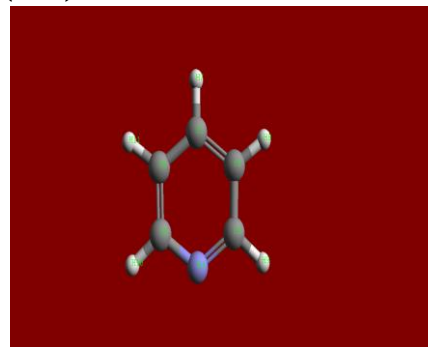


Figure 4. Optimized structure of Pyridine

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 5. 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 was 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 Pyridine is shown in Fig. 1. 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 Pyridine are shown in Figures 2 and 3 respectively.

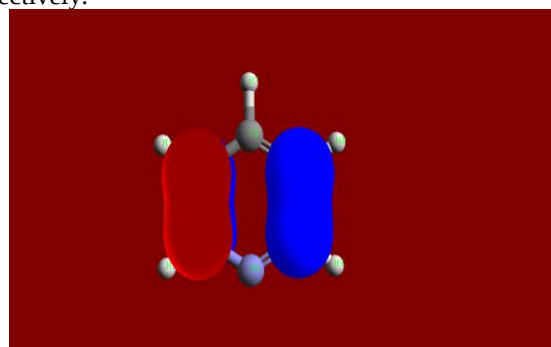


Figure 5. HOMO electronic density of Pyridine molecule

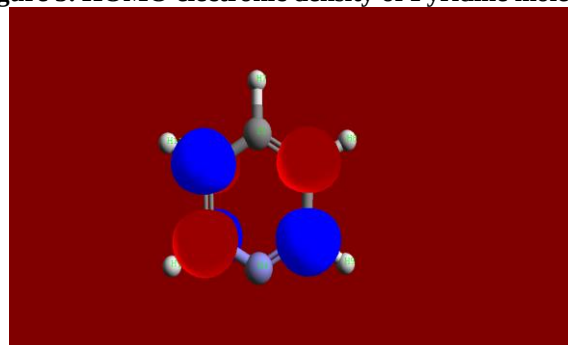


Figure 6. LUMO electronic density of Pyridine molecule

It could also be easily seen that the HOMO were distributed mainly around the ring and the Nitrogen atom, 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). 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 Pyridine molecule has electron donating ability. This confirms the experimental results that interaction between Pyridine 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 least 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).

Table 5. Quantum Chemical Parameters of Pyridine

E_{HOMO}	E_{LUMO}	Energy gap	Heat of formation	Dipole moment
-0.3685	-0.001822	0.3666	31.1367	1.9812

Quantum chemical parameters listed in Table 5 indicate that Pyridine is an efficient inhibitor in HCl solution which corresponds to the experimental results. The Mulliken charge distribution of Pyridine is presented in Table 6. 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 6. Mulliken atomic charges for Pyridine

	Atom	Charge
1	C	-0.1560
2	C	-0.2473
3	C	-0.1432
4	N	-0.0858
5	C	-0.1432
6	C	-0.2473
7	H	0.1969
8	H	0.2089
9	H	0.2041
10	H	0.2041
11	H	0.2089

It is clear from Table 6 that Nitrogen and some carbon 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 Nitrogen atom 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 N atoms and through the π - electrons of Pyridine 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 because the larger the dipole moment, the stronger the intermolecular attraction (Dwivedi and Misra, 2010).

The high value of dipole moment of Pyridine (Table 5) increased 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 $[\text{Ar}] 4\text{S}^2 3\text{d}^6$, so 3d orbital is not fully filled with electrons.

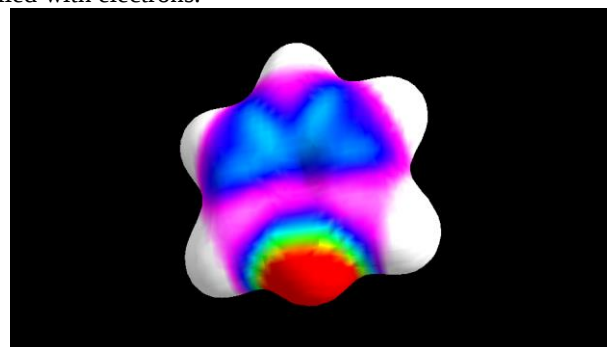


Figure 7. Electrostatic potential-mapped density of Pyridine

3.5 Molecular Electrostatic Potential (MEP)

It is a very useful descriptor in understanding the reactive sites of a molecule (Scrocco and Tomasi, 1978; Luque *et al.*, 1993; Udhayakala, 2015). In the present study the MEP was calculated at the PM3 optimized geometry. The MEP also displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading, and is very useful in research of molecular structure with its physiochemical property relationship (Murray and Sen, 1996; Alkorta and Perez, 1996). Different values of the electrostatic potential are represented by different colours. In most of the MEP, the maximum negative region which is the preferred site for electrophile attack indicates as red color, while the maximum positive region indicated by blue colour is the preferred site for nucleophilic attack. Potential increases in the order red < Orange < Yellow < Green < blue. As can be seen from the MEP of the Pyridine (Figure 6), the negative potentials are over the electronegative Nitrogen atom and the regions having the most positive potential mapped of Pyridine is given in Figure 7.

Conclusion

The organic compound inhibited the acid corrosion of mild steel to a remarkable degree. The maximum inhibition efficiencies of 70 % 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 was due to the physical adsorption of the heterocyclic compound on the mild steel from interaction between the additive and mild steel surface. Quantum chemical calculations show that apart from Pyridine adsorbing as cationic species on the mild steel surface, it can also adsorb as molecular species using Nitrogen 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.
- Alhaffar, M. T., Umoren, S. A., Obot, I. B. & Ali, S. A. (2018). Isoxazolidine derivatives as corrosion inhibitors for

low carbon steel in HCl solution: experimental, theoretical and effect of KI studies. *Royal Society of Chemistry*, 8: 1764 – 1777.

Anupama, K. K., Ramya, K., Joseph, A. (2016). Electrochemical and Computational aspects of surface interaction and corrosion inhibition of mild steel in hydrochloric acid by *Phyllanthus amarus* leaf extract (PAE). *Journal Molecular Liquid*, 216, 146 – 155.

Arukalam, I. O. (2014). Durability and Synergistic effects of KI on the acid corrosion inhibition of mild steel by hydroxypropyl methylcellulose. *Carbohydrate polymer*. 112, 291 – 299.

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.

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

Finsgar, M. and Jackson, J. (2014). Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review. *Corrosion Science*, 86: 17 – 41.

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

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

Liu, D., Qiu, Y. B., Tomoe, Y., Bando, K. & Guo, X. P. (2011). Interaction of inhibitors with corrosion scale formed on N80 steel in CO₂- saturated NaCl solution. *Material. Corrosion*, 62: 1153 – 1158.

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 *Ipomoea 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.

Okafor, P. C., Ebenso, E. E. and Ekpe, U. J. (2010). *Azadirachta indica* extracts as corrosion inhibitors for mild steel in acid medium. *International Journal of Electrochemical Science*, 5: 978 – 984.

Ozturk, S., Yildirim, A., Cetin, M. & Tavasli, M. (2014). Synthesis of quaternary, long-chain N-Alkyl Amides and their corrosion inhibition in acidic media. *Journal of Surfactants Detergents*, 17: 471 – 481.

Popoola, L. T., Grema, A. S., Latinwo, G. K., Gutti, B. and Balogun, A. S. (2013). Corrosion problems during oil and gas production and its mitigation. *International Journal Industrial Chemistry*, 4: 1 – 15.

Rihan, R., Shawabkeh, R. & Al - baker, N. (2014). The effect of two Amine - based corrosion inhibitors in improving the corrosion resistance of carbon steel in sea water. *Journal of Material Engineering Performance*, 23: 693 – 699.

Udhayakala, P. (2015). A theoretical evaluation on quinoxaline derivatives as corrosion inhibitors on mild steel. *Der Pharma Chemica*, 7(11): 177 – 185.

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.

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.