

ELECTROCHEMICAL INVESTIGATION AND QUANTUM CHEMICAL EVALUATION OF 5-PHENYLISOXAZOLE OF MILD STEEL CORROSION IN HCl SOLUTIONS



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ABSTRACT

The inhibiting ability of 5-Phenylisoxazole for mild steel in 2 M HCl solutions has been studied using potentiodynamic polarization and quantum chemical techniques. For potentiodynamic polarization, the curves shifted towards lower current density in the presence of the inhibitor suggesting that the inhibitor retarded the corrosion process without changing the mechanism of the reaction. The polarization resistance (R_p) was determined with maximum inhibition efficiency (%) of 73.0 % in 10×10^{-4} M concentration of the inhibitor. Inhibition efficiency increases with increasing E_{HOMO} indicating that the molecule has tendency to donate electrons to the appropriate acceptor molecule with low energy empty molecular orbital; whereas low value of E_{LUMO} suggests that the molecule easily accepts electrons from donor molecules. Quantum chemical calculations were performed using Density Functional Theory (DFT). The energy gap (ΔE) was 8.63 eV.

INTRODUCTION

Mild steel is widely used in most of the chemical industries due to its low cost and availability. It is one of the most important metals used in different fields of industries, automobiles, engineering, submarine and others. However, this metal is severely affected due to environmental pollutants such as chlorate, sulphate, nitrate, and phosphate (Revie and Winston 2000). The economic aspects of corrosion are far greater than what most people realize. According to a 2001 report (Yadav *et al*, 2014), the cost of corrosion in the U.S. alone was \$276 billion per year. Of this, about \$121 billion was spent to control corrosion, leaving the difference of \$155 billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer the largest economic impact with motor vehicles and transportation being a close second.

Oil spills are a common events in Nigeria. 50% of oil spills occur due to pipeline and tanker accidents. Other causes include sabotage (28%) and oil production operations (21%) with 1% of the spills being accounted for by inadequate or non-functional production equipment. Corrosion of pipelines and tankers is as a result of the rupturing or leaking of old production infrastructures that often do not receive inspection and maintenance (Anderson, 2005). One reason corrosion accounts for such a high percentage of oil spills is the small size of the oilfields in the Niger Delta.

The choice of 5 - phenylisoxazole (P) as inhibitor for this work is due to the fact it has never been used as a mild steel corrosion inhibitor in acidi medium to the best of our knowledge, even though it possesses heteroatoms, is highly available, is cost effective and eco-friendly-essential requirements of corrosion inhibitors. This study was carried out in order to investigate the corrosion inhibition properties of 5 - phenylisoxazole (P) for mild steel in acidic medium as well as the possible formation of complexes with the metal ions, and on the metal surface.

MATERIALS AND METHOD

The electrochemical tests were conducted in a Model K0047 corrosion cell using a VERSASTAT 400 complete DC voltammetry and corrosion system with V3 Studio software. Graphite rod was used as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The

working electrode was immersed in the test solution for 30 minutes until a steady state open circuit potential E_{ocp} was obtained. A new specimen was used for each run. These studies were carried out in the potential range of ± 250 mV versus corrosion potential (E_{corr}). When a small potential drop (ΔE) was applied, a current flow (I) was calculated using Equation (1) Nnabuk *et al.*(2010):

$$\frac{\Delta E}{\Delta I} = R_p = \frac{\beta_a \times \beta_c}{2.303 \times I_{corr} \times (\beta_a \times \beta_c)} \quad (1)$$

In Equation (1), β_a and β_c are Tafel constants which can be obtained from a well-known Tafel plot for the system under consideration. The corrosion rate of the structure was calculated using corrosion current density I_{corr} . The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}). The inhibition efficiency (%) was calculated from the measured i_{corr} values (Roy and Sukul, 2015):

$$I(\%) = \left(\frac{I_{corr}^o - I_{corr}}{I_{corr}^o} \right) \times 100 \quad (2)$$

Where I_{corr}^o and I_{corr} are the corrosion current densities in the absence and presence of inhibitor respectively.

RESULTS AND DISCUSSION

Potentiodynamic Polarization Technique

Fig. 1 shows the potentiodynamic polarization curves for mild steel in 2 M HCl solutions with and without different concentrations of inhibitor at 303 K. The presence of inhibitor in the corrodent caused a remarkable decrease in the corrosion rate by shifting both anodic and cathodic curves to lower current densities. In other words, the inhibitor acted as a mixed-type inhibitor in HCl solutions.

The potentiodynamic polarization parameters including corrosion current densities (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c), anodic Tafel slope (b_a), and inhibition efficiency (%) are presented in Table 1. The polarization curves show that higher current density was observed in the anodic branch, and not in the cathodic branch. So, the effect was in the kinetics of anodic dissolution. The acid anion (Cl⁻) was first adsorbed on the steel surface to form the surface complexes in the anodic process, and the complexes desorbed from the surface (Cao, 1996).

Table 1 shows that i_{corr} decreased considerably in the presence of the inhibitor in the acid, and decreased with the increase of inhibitor concentration as previously reported by Lowmunkhong *et al.*(2010). In turn, inhibitive ability improved with the inhibitor concentration. In the HCl solutions, E_{corr} values do not alter significantly in the presence of the inhibitor. According to Cao (1996), the inhibition category belongs to geometric blocking effect. That is: the inhibition action manifests through the reduction of the reaction area on the surface of the corroding metal (Cao, 1996). The slight variation of both β_c and β_a suggests that the corrosion mechanism of steel does not change in the presence of the inhibitor. Similar finding has been reported by Lowmunkhong *et al.* (2010). The results also show that R_p values increased with concentration of the inhibitor as previously reported by Lowmunkhong *et al.* (2010). The percentage inhibition calculated from R_p values indicates that the inhibitor acted as a good inhibitor in acid medium.

Global Molecular Reactivity

The values of some quantum chemical parameters for the 5 - Phenylisoxazole computed with PM7 Hamiltonian in the MOPAC 2014 software using gas phase for all the molecules. The frontier molecular orbital energies (energy of the highest occupied molecular orbital (E_{HOMO}) and that of the lowest unoccupied molecular orbital (E_{LUMO}) are important parameters for defining the reactivity of a chemical species. A good correlation has been found between corrosion

inhibition efficiency and some quantum chemical parameters including ΔE , E_{HOMO} and E_{LUMO} . E_{HOMO} is associated with the disposition of the inhibitor molecule to donate electrons to an appropriate acceptor with an empty molecular orbital.

Table 1: Electrochemical parameters obtained from potentiodynamic polarization plots of mild steel immersed in 2 M HCl with different concentrations of the inhibitor.

Inhibitor	Conc.(M)	E_{corr} (V)	I_{corr} (A)	β_c (V dec ⁻¹)	β_a (V dec ⁻¹)	I (%)
P	0.0002	-0.4566	0.000188	0.2821	0.3835	62
	0.0001	-0.4579	0.000132	0.0375	1.2355	73

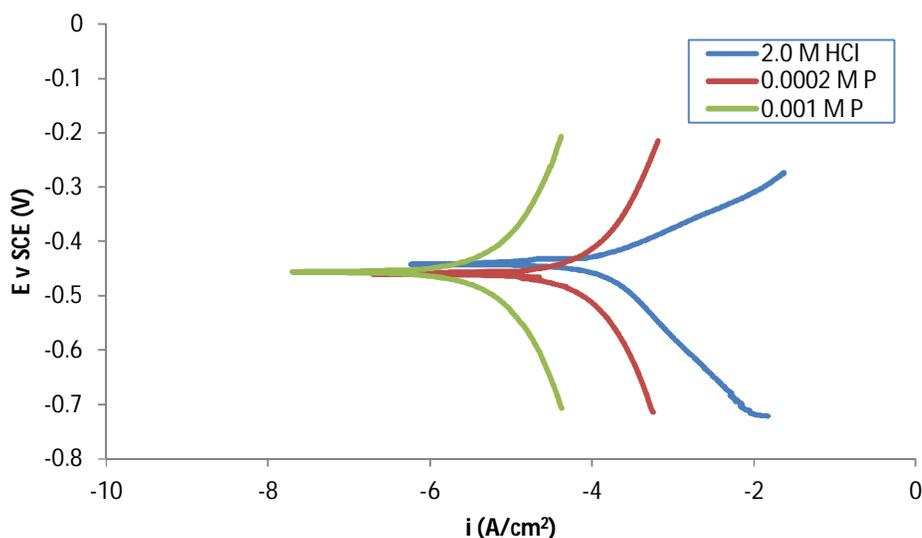


Figure 1: Polarization curve of mild steel in 2 M HCl with different concentrations of 5-Phenylisoxazole at 303 K

Therefore, an increase in the value of E_{HOMO} indicates the strength of adsorption and better inhibition efficiency. On the other hand, E_{LUMO} indicates the ability of the inhibitor molecule to accept electrons which implies that the inhibition efficiencies of the 5 - Phenylisoxazole were expected to increase with decreasing values of E_{LUMO} (Gao and Liang, 2007; Bentiss *et al.*, 2007). From the results obtained, it is observed that the values of E_{HOMO} are all less than those of E_{LUMO} , indicating strong adsorption arising from effective electronation of the iron empty orbital by the inhibitor molecule. It is assumed that after physical adsorption, chemisorption of organic molecules occurs due to chelation on metal surface by donation of electrons to unoccupied d orbital of the metal and the subsequent acceptance of the electrons from the d-orbital using antibonding molecular orbital. The formation of a feedback bond is usually characterized by the increasing values of E_{HOMO} and the decreasing values of E_{LUMO} which is proposed for the observed trend. The energy gap ($\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$) of an inhibitor is another parameter that can be used to predict the extent of corrosion inhibition. Larger values of the energy gap imply low reactivity to a chemical species. The energy gap, ΔE of inhibitor molecule P was 8.63 eV. Fig. 2 shows the distribution of HOMO and LUMO on the 5-Phenylisoxazole molecule with the observation that the distribution of HOMO and LUMO mainly located at benzene ring, nitrogen and oxygen atoms in substituent groups. This kind of distribution favours parallel adsorption of 5 - Phenylisoxazole onto the metal surface via two modes. One mode is that the inhibitor molecules donate electrons to unoccupied d orbital of Fe atom forming coordinate bond, and the

other mode is that the inhibitor molecules accept electrons from Fe atom to form back-donating bond. From the values of the ground state energy of the systems, the ionization energy (IE) of the 5 - Phenylisoxazole molecule was calculated using Equation 4 (Stoyanov, 2003):

$$IE = E_{(N-1)} - E_{(N)} \quad (4)$$

where $E_{(N-1)}$, $E_{(N)}$ are the ground state energies of the system with N - 1, N electrons respectively.

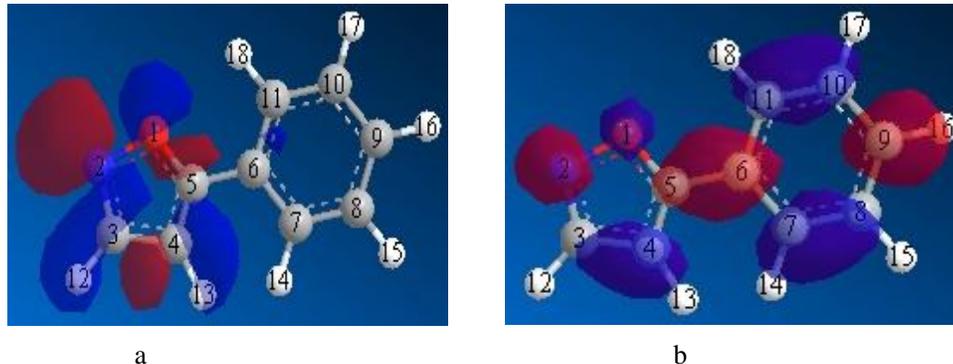


Figure 2 (a) and (b): HOMO and LUMO orbitals of 5 - Phenylisoxazole molecule

Calculated values of IE (for gas phase) are presented in Table 2. Values of IE calculated from Equation 12 can be compared with those obtained from semi-empirical calculations for both gas phase. Moreover, the expected trend for the variation of inhibition efficiencies is also consistent with the experimental results. The close similarity between the values of IE and E_{HOMO} can be explained as follows. Semiempirical calculations estimate ionization energy through the value of E_{HOMO} . Ionization energy measures the tendency toward loss of electrons. Therefore, IE is closely related to E_{HOMO} . In this case, two systems, Fe (in mild steel) and inhibitor are brought together. Hence, electrons will flow from the lower system with lower electronegativity (inhibitor) to the system with higher electronegativity until the chemical potential becomes equal. Based on decreasing value of IE, the trend for the variation of inhibition potentials of the studied inhibitor agrees with experimental findings.

This study on quantum chemical descriptors has been extended to include the total and electronic energies of the molecules. From the results, strong correlations exist between experimental inhibition efficiencies and the other quantum chemical parameters namely: E_{HOMO} , E_{LUMO} , $E_{LUMO} - E_{HOMO}$, and IE.

Table 2: PM7 Semi empirical parameters for 5-Phenylisoxazole molecule

Semi-empirical Parameters	5-PHENYLISOXAZOLE (P)
H_f (kCal/mol)	45.20
TE (eV)	-1679.25
EE (eV)	-8247.38
CCR (eV)	6568.14
Dipole (eV)	3.19
IE (eV)	9.51
E_{HOMO} (eV)	-9.51
E_{LUMO} (eV)	-0.88
E_{L-H} (eV)	8.63
Maximum IE %	66

H_f = Heat of formation, TE = Total energy, EE = Electronic energy, CCR = Core-core repulsion energy, IE = Ionization energy, log p = hydrophobicity

CONCLUSION AND RECOMMENDATION

In this work, 5 - Phenylisoxazole was effective in retarding the corrosion of mild steel in 2 M HCl solutions by adsorption of the organic molecule on the steel surface. The potentiodynamic polarization curves shifted towards lower current density in the presence of the inhibitor with well-defined Tafel regions suggesting that the inhibitor retarded the corrosion process without changing the mechanism of the corrosion as mixed type inhibitor (because the change in E_{corr} is less than 85 mV/SCE with respect to the blank). Corrosion current densities were calculated by extrapolation of the linear parts of these curves to the corresponding corrosion potential; and corrosion potential (E_{corr}), corrosion current densities (i_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) were determined with maximum value of inhibition efficiency of 73 % for 10×10^{-4} M concentration of the inhibitor. This study shows that quantum chemical parameters and local selectivity indices can be used to predict the direction of the inhibition reaction and sites for nucleophilic/electrophilic attack with respect to the inhibitor. The use of 5 - Phenylisoxazole as corrosion inhibitor is highly recommended

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