

CORROSION INHIBITION PERFORMANCE OF *o* – VANILLIN AND *o* – VANILLIN HYDRAZONE ON MILD STEEL SURFACE: INSIGHT FROM FIRST-PRINCIPLES



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ABSTRACT

The adsorption properties of *ortho* – vanillin (OV) and *ortho*-vanillin hydrazone (OVH) for mild steel corrosion was investigated by quantum chemical calculations using Gaussian 09 program at B3LYP functional with 6-31G(d,p) basis set implemented within the framework of density functional theory (DFT). Some global reactivity parameters such as E_{HOMO} , the number of electrons transferred (Δn) and dipole moment (μ) followed the order: OVH > OV. The highest values of the electrophilic Fukui function (f) indicate that the most likely sites in OVH for adsorption on the iron surface include N14 (0.131790) > C13 (0.094542) > H8 (0.080241) while those in OV are O18 (0.158823) > C17 (0.150548) > H19 (0.104696). The equilibrium adsorption behavior of the molecules on Fe (110) surface was investigated using Quench Dynamics Simulation. The adsorption energy of Fe (110)/OVH was -95.56 kcal/mol while that of Fe (110)/OV was -91.72 kcal/mol, indicating that OVH had a stronger interaction on Fe (110) surface and is a better inhibitor of mild steel corrosion. This study confirms that OVH is a better inhibitor of mild steel corrosion than OV.

INTRODUCTION

Metals and alloys are used in the construction of various industrial and domestic appliances. Metallic structures and equipment corrode when in contact with aggressive environments. The use of corrosion inhibitors in protecting metals in such situations is very cost-effective (Abakedi and Moses, 2016). Effective corrosion inhibitors are organic compounds containing heteroatoms like N, S, O and P, multiple bonds or aromatic rings which can adsorb on a metal surface and decrease the corrosion rate (Ita *et al.*, 2007; Bentiss *et al.*, 2007; Yadav *et al.*, 2015). For decades, the inhibition efficiency of a compound had to be empirically tested. The use of computational methods as a predicting tool is assuming much prominence in chemical research nowadays. Theoretical methods such as quantum chemical studies and molecular dynamics simulation are very useful in studying the relationship between the molecular structure and corrosion inhibition properties of organic compounds (Khaled, 2008; Shahraki *et al.*, 2016; Rajendran *et al.*, 2016). Whereas quantum chemical studies relate the corrosion potentials of compounds to their quantum chemical parameters, molecular dynamics simulation studies the interaction of inhibitors with the metal surface.

The experimental data reported by Ita (2004) revealed that *ortho*-vanillin (OV) and *ortho*-vanillin hydrazone (OVH) inhibited the corrosion of mild steel in hydrochloric acid medium, with OVH exhibiting a higher inhibition efficiency by gravimetric measurements. The inhibition efficiencies of both compounds increased with increase in inhibitor concentration but decreased with increase in temperature. At 30 °C and at inhibitor concentration of 1×10^{-4} M, the inhibition efficiency followed the trend: OVH (90%) > OV (83%). The aim of this work is to evaluate the corrosion inhibition performance of OV and OVH on mild steel corrosion in acidic medium on quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap (ΔE), global hardness (η) global softness (σ), dipole moment (μ), electron affinity (A), ionization potential (I), electrophilicity index (ω) and the total energy (E). Molecular dynamics simulation is used in determining the adsorption sites in which the inhibitors adsorbed on the steel surface as well as

the adsorption energy involved. These shall be used in predicting the effectiveness of the compounds as corrosion inhibitors.

COMPUTATIONAL DETAILS

Quantum Chemical Calculations

Geometry optimization of the investigated compounds was performed using DFT with the Becke's three parameter exchange functional along with the Lee-Yang-Parr non local correlation functional (B3LYP) with 6-31G(d,p) basis set as implemented in Gaussian 09 program (Frisch *et al.*, 2009). The geometry optimization was done in gas phase and under no constraint. The molecular structures of the compounds are given in Figs. 1(a) and (b).

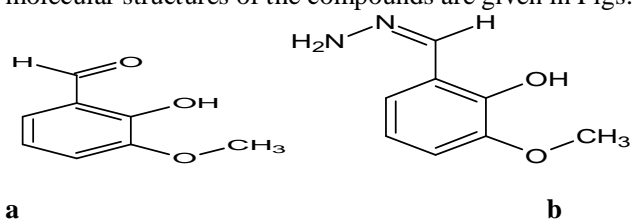


Figure 1: Molecular structure of (a) *ortho*-vanillin (OV); (b) *ortho*-vanillin hydrazone (OVH)

The ionization potential, electron affinity, electronegativity, global hardness, and number of electrons transferred were calculated using Equations 1 – 6 (Kabanda *et al.*, 2013; Rajendran *et al.*, 2016):

$$\text{Ionization potential (IP)} = - E_{\text{HOMO}} \quad (1)$$

$$\text{Electron affinity (EA)} = - E_{\text{LUMO}} \quad (2)$$

$$\text{Global electronegativity, } \chi = \left(\frac{\text{IP} + \text{EA}}{2} \right) \quad (3)$$

$$\text{Global hardness, } \eta = \left(\frac{\text{IP} - \text{EA}}{2} \right) \quad (4)$$

$$\text{Global electrophilicity index, } \omega = \frac{\chi^2}{2\eta} \quad (5)$$

$$\text{Number of electrons transferred, } \Delta n = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (6)$$

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule while η_{Fe} and η_{inh} are the absolute hardness of iron and the inhibitor molecule, respectively ($\chi_{\text{Fe}} = 7.0$ eV and $\eta_{\text{Fe}} = 0$).

Local reactivity analysis

The local reactivity of the compounds was analysed using condensed Fukui functions of the Dmol³ module implemented in Materials Studio developed by Dassault Systemes BIOVIA, with the generalized gradient approximation (GGA) functional obtainable within the density functional theory (DFT). The exchange-correlation functional of Perdew and Wang (PW91) was employed. The basis file of the double numerical basis set with polarization function (DNP) was set to 4.4 ensuring improved calculation accuracy.

Molecular dynamics simulation

Molecular dynamics simulation was performed to study the interaction between the inhibitor molecules and the metal surface. The Fe (body centered 3D cubic) crystal was obtained from BIOVIA Materials Studio database with lattice parameters $a = b = c = 2.8664$ Å and $\alpha = \beta = \gamma = 90^\circ$ belonging to m-3m crystal class. The cell and atomic positions were optimized using Forcite geometry optimization module utilizing Smart algorithm with convergence tolerance of energy, force and displacement, set to 1×10^{-4} kcal/mol, 5×10^{-3} kcal/mol/Å and 5×10^{-5} Å, respectively. The force field chosen for the optimization was the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS). The Fe (110) surface was cleaved from

the optimized Fe crystal. A 5 x 5 super cell was created from the cleaved surface and the surface was optimized with the same Forcite parameters used previously.

A vacuum slab of thickness 30 Å was built at a slab position of 0.00 Å from the cleaved surface. The OV and OVH molecules were docked on the slab surface. To obtain the global energy minimum, Quench molecular dynamics approach was employed to sample many different configurations. The surface atoms were allowed to relax while the rest of the atoms were constrained. Quench dynamics calculation was performed at 30 °C using NVE thermodynamic ensemble with a time step of 1.0 fs and a total simulation time of 5 ps. The lowest energy configuration corresponding to a global energy minimum was obtained and this configuration was used to perform single point energy calculations for the molecules and Fe(110) surface to obtain the interaction (adsorption) energy according to Equation. (7):

$$\text{Adsorption Energy} = E_{\text{Fe/Inh}} - (E_{\text{Inh}} + E_{\text{Fe}}) \quad (7)$$

where $E_{\text{Fe/Inh}}$ is the total energy of Fe(110) surface and adsorbed inhibitor, E_{Inh} is the energy of the inhibitor and E_{Fe} is the energy of the Fe(110) surface.

RESULTS AND DISCUSSION

Optimized Molecular Structures of the Studied Compounds

The molecular structures of the studied compounds *o*-vanillin and *o*-vanillin hydrazone were optimized using Density Functional Method at B3LYP/6-31G (d,p) level of theory in gas phase. The optimized structures of *o*-vanillin and *o*-vanillin hydrazone are shown in Fig. 2.

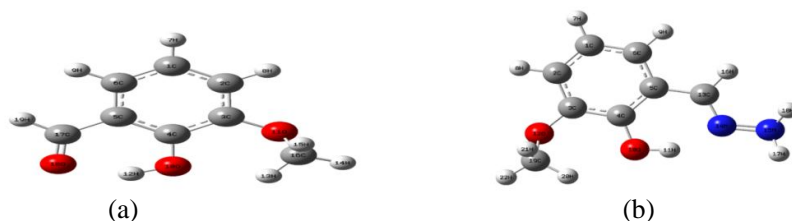


Figure 2: Optimized molecular structure using DFT/B3LYP/6-31G(d,p) basis set: (a) *o*-vanillin (b) *o*-vanillin hydrazone

Quantum Chemical Parameters

The calculated quantum chemical parameters of the compounds (OV and OVH) after geometry optimization are presented in Table 1.

The Frontier Molecular Orbitals (E_{HOMO} and E_{LUMO}) of OV and OVH are shown in Fig. 3. The energy of the HOMO provides information about the electron donating ability of the molecule. The molecule with the highest E_{HOMO} value often have the highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. The inhibitor does not only donate electron to the unoccupied d-orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feedback bond. The higher value of E_{HOMO} (-5.55007 eV) of OVH indicates the better inhibition efficiency than E_{HOMO} (-6.14519 eV) of OV. The energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) is an important parameter that signifies the reactivity of the inhibitor molecule towards the adsorption on the metal surface. Low values of the ΔE will give good inhibition efficiencies since the energy needed to remove an electron from the last occupied orbital will be low (Issa *et al.*, 2008). A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule.

Table 1: Quantum chemical parameters for inhibitor *o*-vanillin and *o*-vanillin hydrazone calculated using DFT/B3LYP/6-31G(d,p) basis set

Parameters	OV	OVH
Total Energy, E (a.u.)	-535.33512162	-570.78959817
Dipole Moment, μ (Debye)	2.5220	4.0539
E_{LUMO} (eV)	-1.92821	-1.03322
E_{HOMO} (eV)	-6.14519	-5.55007
Energy gap, ΔE (eV)	4.21698	4.51685
Ionization potential, IP (eV)	6.14519	5.55007
Electron affinity, A(eV)	1.92821	1.03322
Global Hardness, η (eV)	2.10849	2.25842
Global Softness, σ (eV)	0.47427	0.44278
Electrophilic Index, ω (eV)	3.86412	2.39877
Electronegativity, χ (eV)	4.03670	3.29 164
Number of electrons transferred, Δn	0.70270	0.82100

Table 1 reveals that OVH has a lower energy gap 0.47821 eV compared to that of OV inhibitor 4.21698 eV, indicating that OVH could have a better performance as corrosion inhibitor than OV.

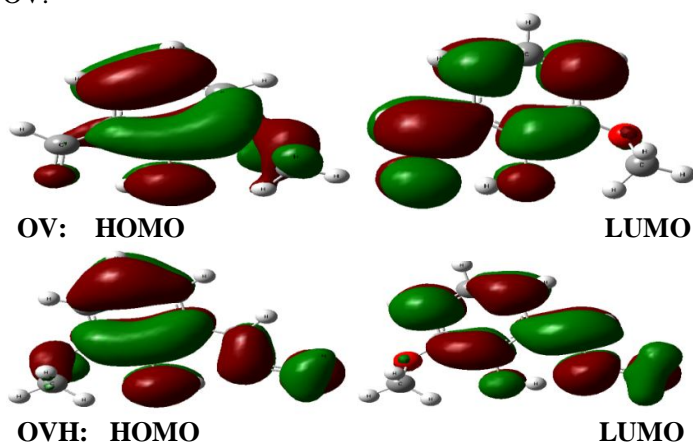


Figure 3: Frontier molecular orbital diagrams of OV and OVH using DFT/B3LYP/6-31G(d,p)

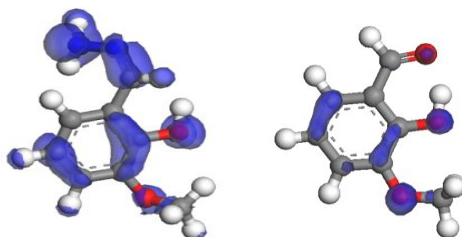
The dipole moment of a compound is a reflection of its polarity. There is no general consensus on the correlation between dipole moment and corrosion inhibition efficiency in literature. However, in this work, the dipole moment was found to follow the trend: 4.0539 Debye (OVH) > 2.5220 Debye (OV), which is in conformity with the reported experimental results.

The number of electrons transferred (Δn) was also calculated and tabulated in Table 1. Values of Δn reveal that the inhibition efficiency resulting from electron donation agrees with reports in literature that if $\Delta n < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of the inhibitors to donate electrons to the metal surface (Lukovits *et al.*, 2001). Hence, the highest fraction of electrons transferred is associated with the best inhibitor. Based on the number of electrons transferred, OVH was a better inhibitor than OV: OVH (0.82100 eV) > OV (0.70270 eV)

Ionization energy (IP) is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness, and vice versa. The lower ionization energy of OVH (5.55007 eV) indicates its high inhibition efficiency compared to that of OV (6.14519 eV).

Fukui Indices

Fig. 4 depicts the electrophilic Fukui centres of the studied molecules. These are reactive centres where the inhibitor molecules are likely to be attached to the metal surface. The highest value of the Fukui function (f) indicates the preferred site for electrophilic attack on the molecule. In OVH, the most likely sites for electrophilic attack are N14 (0.131790) > C13 (0.094542) > H8 (0.080241) while those in OV are O18 (0.158823) > C17 (0.150548) > H19 (0.104696).

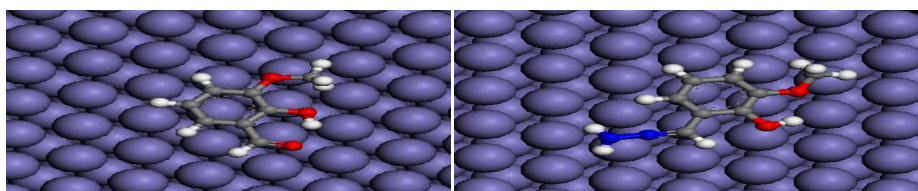


(a)(b)

Figure 4: Electrophilic Fukui centres for neutral molecules of (a) OVH and (b) OV in gas phase

Molecular Dynamics Simulation

The adsorption of OVH and OV on iron surface was simulated by modelling the interactions between the inhibitor molecules and Fe(110) crystal surface. Fig. 5 depicts the equilibrium configurations of the simulated systems. The adsorption energy of Fe(110)/OVH was -95.56 kcal/mol while that of Fe(110)/OV was -91.72 kcal/mol. The higher interaction energy of OVH indicates that it had a stronger interaction on Fe(110) surface and is a better inhibitor of corrosion of iron.



(a)

(b)

Figure 5: Equilibrium configurations of Fe(110)/inhibitor systems for (a) OV and (b) OVH

CONCLUSION AND RECOMMENDATION

The calculated quantum chemical parameters E_{HOMO} , dipole moment and fraction of electrons transferred support the corrosion inhibition efficiency of the compounds in the order: OVH > OV. The higher adsorption energy of Fe(110)/OVH over Fe(110)/OV further shows that OVH is

a better corrosion inhibitor than OV. Quantum chemical studies and Molecular Dynamics Simulation could be used to predict the inhibition efficiencies of compounds.

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