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Quantum Chemical Studies on the Inhibition Mechanism of *Ficus carica, FC* and *Vitellaria paradoxa, VP* Leaf Extracts

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ABSTRACT

The use of *Ficus carica* (FC) and *Vitellaria paradoxa* (VP) as corrosion inhibitors using weight loss measurements at 303, 313, 323 and 333 K has been reported. In this present study, quantum chemical studies using the molecular-modelling program hyperchem are employed to give an insight into the mechanism of inhibition of FC and VP. The quantum chemical parameters obtained in this study include Energy of highest occupied molecular orbital, E_{HOMO} (eV), energy of lowest unoccupied molecular orbital, E_{LUMO} (eV), energy gap, $E_{L\text{-}H}$, (eV), dipole moment, (D) absolute electronegativity, hardness, ionization potential, and electron affinity. The values of quantum chemical descriptors obtained reveal that both FC and VP inhibited the corrosion of aluminium but FC shows better performance. The presence of alkaloids, glycosides, saponins and tannins (having –C=O, C-OH, C=C, OH -CH_3, etc groups) was found to have contributed greatly to the inhibition process by interacting with the aluminium surface.

1. Introduction

Aluminium is one of the most important and widely used metals in the transport, construction, packaging and electrical sectors. It is pertinent to note that aluminium is prone to corrosion due to its negative standard potential of -1.66 V [1]. The susceptibility of Al to attack is observed in oil well acidizing, pickling, cleaning and descaling operations where the metal is exposed to hydrochloric or sulphuric acid once the protective oxide layer is destroyed.

It has been observed that aluminium and its alloys deteriorate due to corrosion in different environments (acidic or alkaline). Different organisations and industries therefore spend huge sum of money in combating corrosion of their engine parts, pipe lines etc. The need to research into the field of corrosion inhibition using less expensive, environmentally friendly inhibitors has therefore become expedient.

Different synthetic organic inhibitors are used for Al alloys, other metals and alloys in various aggressive media [2]. Most of these organic inhibitors are nitrogen, oxygen or sulphur containing compounds. Inorganic compounds and their derivatives have also been reported as inhibitors for metals/alloys in aqueous solutions. The experimental performance of some Schiff bases for mild steel corrosion has also been studied [3-6]. These synthetic organic, inorganic, dyes etc., compounds used as corrosion inhibitors are expensive, toxic, and hazardous to health. It has become important therefore, to source for cheap, non-hazardous and environmentally friendly inhibitors for the protection of metals/alloys against corrosion. Many authors [7-12] have investigated the possible substitute for these costly, toxic and environmentally non-friendly chemicals used as corrosion inhibitors for metals/alloys in acid/alkaline media from naturally occurring substances of plant origin.

Common fig (*Ficus carica*) is a small tree native to South West Asia. This edible fig is widely grown for its fruit and is commercially produced in the United States of America. This tree is also found in some parts of Northern Nigeria with Adamawa State inclusive. Several therapeutic effects such as hypoglycaemia [13], hypotriglyceridemia, and hypocholestrolemia [14-15], have been reported for different parts of *Ficus carica*. The presence of alkaloids, flavonoids, and tannins in *Ficus carica* leaf extracts has prompted the need for its selection as corrosion inhibitor This is because in addition to heteroatom in alkaloids and flavonoids which are the major adsorption centres, tannins exhibit a dual corrosion retarding action via: Formation of a protective oxide film and tannate as the anodic sites of the corroded surface [16].

Although the use of *Ficus carica* and *Vitellaria paradoxa* as corrosion inhibitors has been reported by Onen *et al*., Onen and Jacob [1,17], the use of Quantum chemical studies to give an insight into the mechanism of inhibition of FC and VP has not been reported. The present study is therefore aimed at evaluating the Quantum chemical properties of these inhibitors – *Ficus carica* and *Vitellaria paradoxa* (VP) leaves extract on the corrosion of Aluminium in HCl at 303 K 313 K, 323 K, and 333K respectively using weight loss method and Quantum chemical studies. This area of research is primarily significant due to the fact that natural products are environmentally friendly and ecologically acceptable.

In the present investigation, the inhibitive effect has been evaluated of methanolic leaf extracts of *Ficus carica* and *Vitellaria paradoxa* and has worked as green inhibitor, which is non-toxic and biodegradable. The investigation is carried out using weight loss method and quantum chemical study to evaluate the corrosion inhibition potential of *Ficus carica* at 303 K, 313 K, 323 K and 333 K respectively. Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition. Quantum chemical calculations have proved to be a very powerful tool for studying the mechanism [18].

Several attempts have also been made to predict corrosion inhibition efficiency with a number of individual parameters obtained via various quantum chemical methods as a tool for studying corrosion inhibitors [18]. These trials were aimed at finding possible correlations between corrosion inhibition efficiency and a number of quantum chemical properties/ descriptions such as dipole moment, Energy of highest Occupied Molecular Orbitals (E_{HOMO}), Energy of Lowest unoccupied Molecular Orbitals (E_{LUMO}), the difference (L_{UMO}- $_{HOMO}$), electronegativity, Mulliken charges as well as some structural parameters.

2. Experimental Methods

The molecular-modelling program, hyperchem is used for all the quantum chemical studies reported in this study. The following parameters Energy of highest occupied molecular orbital, E_{HOMO} (eV), energy of lowest unoccupied molecular orbital, E_{LUMO} (eV), energy gap, $E_{L\text{-}H}$ (eV), dipole moment, (D) absolute electronegativity, hardness, ionization potential, and electron affinity were determined with the hyperchem program using the semi empirical method, Complete Neglect of Differential Overlap (CNDO) [18].

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3. Results and Discussion

The quantum chemical parameters of the studied compounds (FC and VP) are presented in Table 1. These are: energy of highest occupied molecular orbital, E_{HOMO} (eV), energy of lowest unoccupied molecular orbital, E_{LUMO} (eV), energy gap, E_{L-H}, (eV), dipole moment, (D) absolute electronegativity, Hardness, Ionization potential, and Electron affinity. It has been found in previous works that a good correlation between corrosion inhibition efficiency and E_{HOMO} exist. Similar relations were found between corrosion inhibition efficiency and $\Delta E = E_{LUMO}-E_{HOMO}$ [17-19]. There are also, certain Quantum-chemical parameters that can be related to metal-inhibitor interactions.

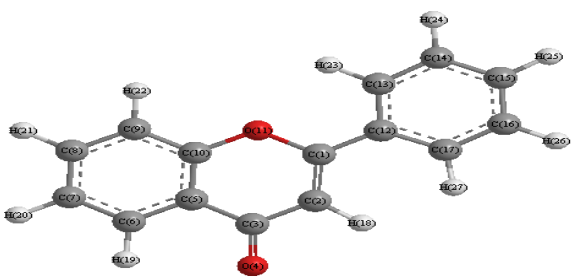
Table 1 Quantum-chemical parameters for the phyto-constituents in the inhibitors

Quantum-chemical parameters	Salicin	Tannic acid	Flavone	Ursane
Dipole moment	12.32	2.74	3.76	8.44
Total Energy (kJmol^{-1})	-503.74	-477.07	-307.54	-764.70
E_{HOMO} (eV)	-9.28	-10.30	-9.77	-11.06
E_{LUMO} (eV)	-10.15	0.022	1.87	-10.70
Energy gap, E_{L-H} (eV)	-0.87	12.17	9.79	0.36
Electronegativity (χ)	0.44	-6.09	-4.90	-0.18
Hardness (η)	-0.44	6.09	4.90	0.18
Ionization potential, I (eV)	9.28	10.30	9.77	11.06
Electron Affinity, A (eV)	10.15	-1.87	-0.022	10.70

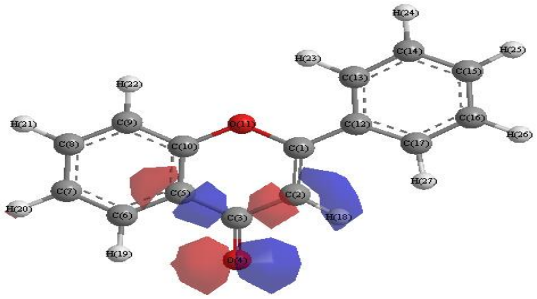
Among these, we can mention the energy of HOMO that is often associated with the electronic donating ability of a molecule. Therefore, an increase in the values of E_{HOMO} can facilitate the adsorption and therefore the inhibition efficiency by indicating the disposition of the molecule to donate orbital electrons to an appropriate acceptor with empty molecular orbitals. The energy of LUMO on the other hand indicates the ability of the molecule to accept electrons. The lower the value of E_{LUMO}, the more probable it is that the molecules accept electrons. In the same way, low values of the energy gap, $\Delta E = E_{LUMO}-E_{HOMO}$ will render good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low.

Increasing values of dipole moments have been reported to facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. From Table 1, it is evident that salicin (FC) has the highest value of dipole moment. Several authors have stated that inhibition efficiency increases with increasing values of dipole moments. Furthermore, it could also be seen from Table 1 that salicin (FC) has the smaller energy gap ($\Delta E = E_{LUMO}-E_{HOMO}$) as compared to other molecules. This indicates that salicin molecule can easily transfer an electron from HOMO level to LUMO level. According to Quantum-chemical results, and the experimentally found inhibition efficiencies, it can be affirmed that *Ficus carica* (FC) has more potency to get adsorbed on aluminium/brass surface than *Vitellaria paradoxa*. The ionization potential (I) and the electron affinity (A) can be calculated by application of the Koopmans' theorem. This theorem establishes a relation between the energies of the HOMO and the LUMO and the ionization potential and the electron affinity respectively. Although there exist no formal proof of this theorem within density functional theory (DFT), its validity is generally accepted. The obtained values of I and A were considered for the calculation of the electronegativity and global hardness. Electron affinity (A) and ionization potential (I) are related in turn to E_{HOMO} and E_{LUMO} using the following equation.

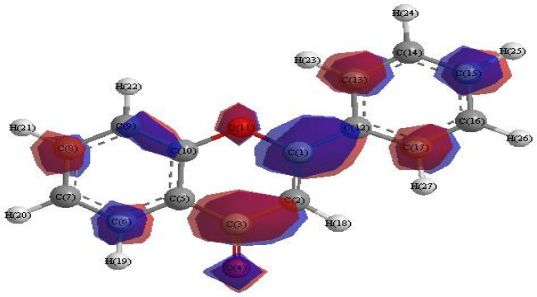
Fig. 1a shows the optimized structure of flavone which is a phyto-constituent of FC. In Figs. 1b and c, the higher occupied molecular orbital (HOMO) and the lower unoccupied molecular orbital (LUMO) for flavone are respectively displayed. Fig. 2a pictures the optimized structure of Tannic acid in FC while Figs. 2b and c respectively display the higher occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) for tannic acid. In Fig. 3a, the optimized structure of US is shown. Figs. 3b and c respectively show the HOMO LUMO diagrams of US.



a) Optimized structure of flavone; a phyto-constituent of FC

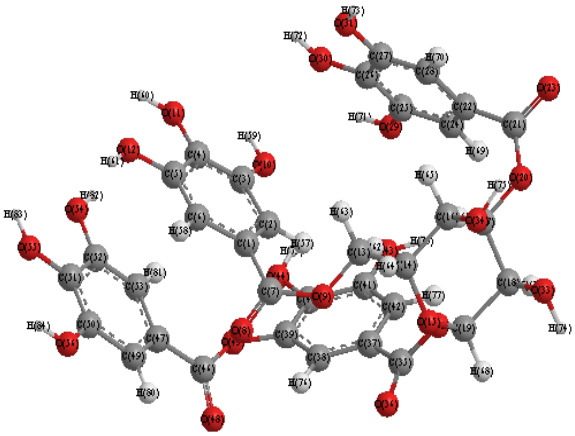


b) Higher occupied molecular orbital (HOMO) for flavone

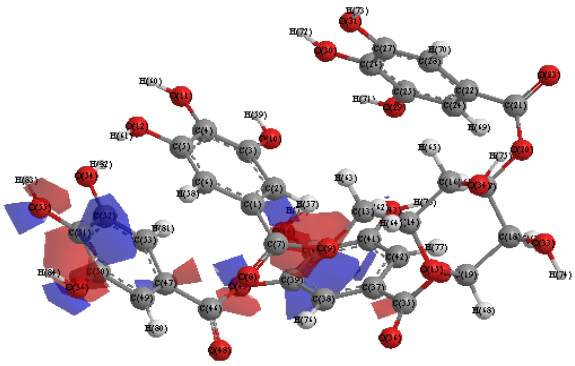


c) Lower unoccupied molecular orbital (LUMO)

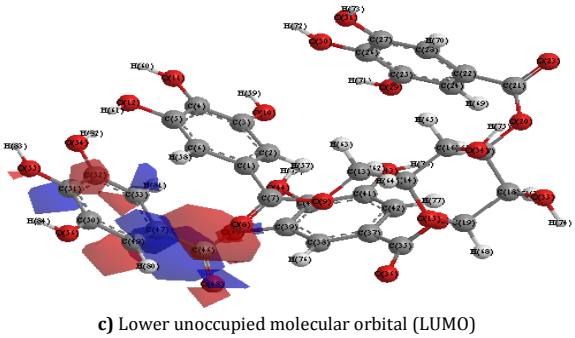
Fig. 1 Optimized structures of flavone



a) Optimized structure of tannic acid in FC



b) Higher occupied molecular orbital (HOMO) for tannic acid



c) Lower unoccupied molecular orbital (LUMO)

Fig. 2 Optimized structures of tannic acid

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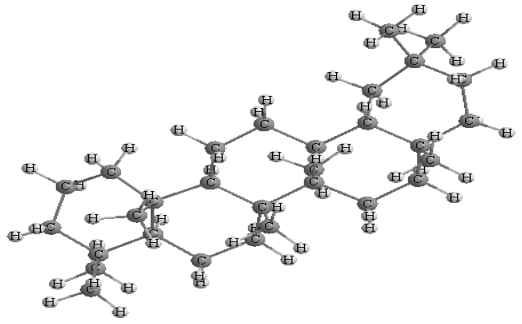
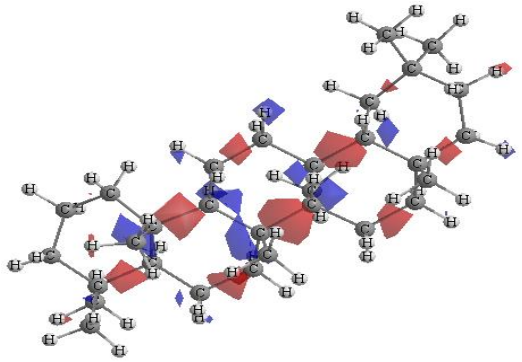
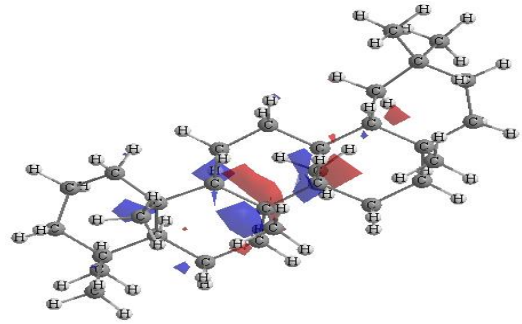


a) Optimized structure of US



b) HOMO diagram of US



c) LUMO diagram of US

Fig. 3 Optimized structres of Ursane

4. Conclusion

The study shows that both inhibitors (FC and VP) investigated inhibit the acid corrosion of aluminium with inhibition efficiency (%I) increasing with concentration but decreasing with temperature. On the basis of Ea values, both FC and VP obey the mechanism of physisorption, as seen from the experimentally observed increase in inhibition efficiency (%I) with decrease in temperature. The inhibition efficiency increases with increase in additive concentration and decreases with increase in temperature in the order: VP < FC. Quantum chemical treatment of the result also reveals that both FC and VP inhibited the corrosion of aluminium but FC inhibited better.

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