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Studies on Corrosion Inhibition Effect of o-Vanillin – Tryptophan Schiff Base on Low Carbon Steel in Acid Medium Using Density Functional Theory

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ABSTRACT

The inhibition effect of o-Vanillin – Tryptophan Schiff base (2- Hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid has been studied for low carbon steel corrosion inhibition in acid medium. The inhibition efficiency of Schiff base inhibitor was investigated using weight loss method and Density Function Theory (DFT/B3LYP-6-31G (d)) methods. The DFT studies reveals the corrosion control mechanism by the use of quantum chemical parameters such as EHOMO, ELUMO, Energy gap(ΔE), dipole moment (μ), electronegativity (χ), electrophilicity index (ω), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I) and the fraction of electrons transferred (ΔN) and the fraction of electron transferred (ΔN). The results explain that the Schiff base (2- Hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid is a new inhibitor for corrosion inhibition of low carbon steel in acid medium.

Key words: Low carbon steel, Schiff base, corrosion inhibitors, Weight loss,DFT

I. INTRODUCTION

Metal Corrosion is a main problem of developed industries. The use of corrosion inhibitors is one of the most useful methods to protect metals against corrosion. Organic compounds are most effective inhibitors containing electronegative functional groups and π-electrons in conjugated double bonds and triple bonds 1, 2.

Heterocyclic compounds containing nitrogen, oxygen, sulphur atoms, and multiple bonds in the molecules which are adsorbed on the metal surface3. Schiff base compounds are formed by the combination of an amine and a ketone/aldehyde. Due to the presence of a >C=N– group in the Schiff base is highly effective inhibitor4.

The aim of this work is to study the corrosion inhibition effects of the Schiff base o-vanillin-Tryptophan on low carbon steel in acid media by analysing the efficiency of inhibition theoretically using the Density Functional Theory (DFT) method5. Quantum Chemical methods have proven to be very useful in determining molecular structures and explaining electronic structures and reactivity.

II. MATERIALS AND METHODS

II.1 Preparation of the specimen and corrosive environment:

Low carbon steel sheets were degreased with trichloroethylene and polished using sand paper papers of various grades. This steel sheet was cut into a plates of size 4.0 x 2.0 x 0.19 cm for weight loss studies. The HCl solution of 5% (V / V), prepared using pure HCl and double distilled water was used as a corrosive environment.

II.2 Synthesis of Schiff Base Ligand (SB):

A mixture of alcoholic o-Vanillin (0.5N, 20 ml) and aqueous solution of L-Tryptophan (0.5N, 20ml) was heated under reflux for 5-6 hours at 60-65°C. The solution was concentrated till its volume is one fourth of its initial volume, allowed to stand overnight, yellow precipitate of Schiff base was obtained. The obtained precipitate was filtered, repeatedly washed with diethyl ether and dried to get pure Schiff base. This was used for further analysis.

II.3 Weight Loss study

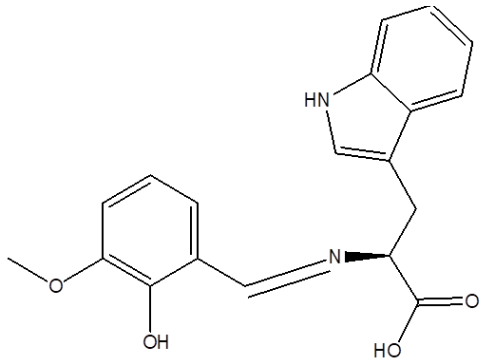
Polished and degreased low carbon steel specimens of size 4.0 x 2.0 x 0.19 cm were used for weight loss studies. Already weighed Low carbon steel plates were separately immersed in 100ml of the corrosive environment and 100ml each of the test solutions with 0.1, 0.2, 0.3, 0.4, 0.5g of the Schiff base for one hour. After the specified time, low carbon steel specimens were washed immediately with double distilled water, dried and weighed again. The same experiment was carried out at three different temperatures of 305, 310, and 315K respectively. From the measured weight loss data, the inhibition efficiency (IE) were calculated using the formula

$$IE\% = (W_0 - W_i) / W_0 \quad (1)$$

Where Wi& W0 are the weight loss values in the presence and absence of the inhibitor 6. All these data were tabulated

II.4 DFT Calculations:

The chemical and optimized structures of the compounds studied are given in Fig.1 and Fig.2.



2-hydroxy-3-methoxy benzaldehyde L-Tryptophan

2-hydroxy-3-methoxybenzylideneamino)-3-(1*H*-indol-3-yl)propanoic acid

Fig.1.Chemical structure of Schiff base

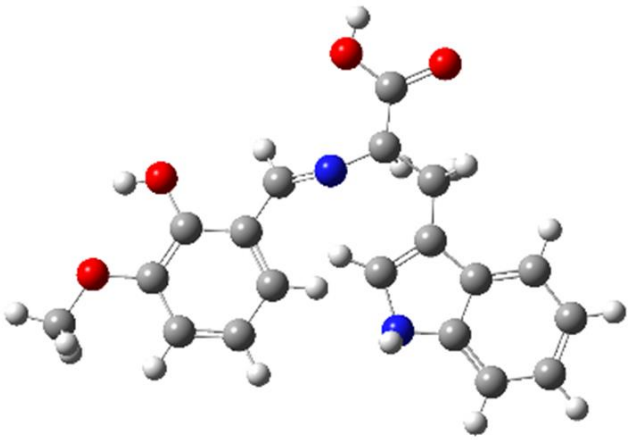


Fig.2. Optimised structure

All calculations were made by the Density Functional Theory method (DFT / B3LYP-6-31G (d)). The following quantum chemical parameters were calculated from the optimized structure obtained: the highest occupied molecular orbitals (EHOMO) and lowest unoccupied molecular orbitals (EHOMO), energy differences (ΔE) between EHOMO and ELUMO, dipole moment (μ), electronegativity (χ), the electrophilicity index (ω), electron affinity (A), global

hardness (η), global softness (σ), ionization potential (I) and the electron fraction transferred (ΔN). Ionization potential (*I*) and electron affinity (*A*) related to EHOMO and ELUMO as follows 7

I = -EHOMO (2)

A = -ELUMO (3)

ΔE=ELUMO -EHOMO (4)

The quantities absolute electronegativity (*χ*) and global hardness (*η*) are related to electron affinity (*A*) and ionization energy (*I*) as follows8

χ=(I+A)/2 (5)

η=(I-A)/2 (6)

Global chemical softness (σ), which describes the capacity of an atom or group of atoms to receive electrons9was estimated by using the equation:

σ=(1)/η=-(2)/(E_Homo-E_Lumo) (7)

According to Pearson the number of electrons transferred (Δ*N*) from the inhibitor molecule to the metal surface was calculated10as

ΔN=(χ_Fe-χ_Inh)/([2(η_Fe-η_Inh)]) (8)

Where χFe and χinh denote the absolute electronegativity of iron and inhibitor molecule, ηFe and ηinh denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χFe =7.0 eV and ηFe = 0, for calculating the number of electrons transferred.

Chemical reactivity parameter known as electrophilicity index (*ω*) is defined as11

ω= 〖μ/2η〗 ^2 (9)

According to this definition, this index measures the tendency of chemical species to receive electrons. Good nucleophile, more reactive, marked with a low value μ, ω and vice versa electrophiles are well marked with high value μ, ω. This new reactivity index measures stabilization in energy when the system acquires additional electronic costs ΔN from the environment.

III. RESULT AND DISCUSSION

III.1 Weight Loss Studies of o-Vanillin –Glutamine Schiff base.

The weight loss studies were carried out at different temperatures. From the experimental weight loss data, percentages of inhibition efficiencies were calculated and the results are shown in Table1 .From the table, it is clear that the extent of weight loss is found to be dependent on the inhibitor concentration. The IE increases with increase in concentration of the inhibitor as shown in Fig.4. Further it is also noted that at higher concentrations, the inhibition efficiency decreases with rise in temperature Fig.3.

Table.1.Weight loss data:

%Conc.of the inhibitor	Weight loss g			Inhibition Efficiency %		
	305 K	310 K	315 K	305 K	310 K	315 K
0	0.239	0.039	0.287	--	--	--
0.1	0.12	0.02	0.165	49	48	42
0.2	0.045	0.015	0.106	81	61	63
0.3	0.027	0.012	0.092	88	69	67
0.4	0.013	0.006	0.088	94	84	69
0.5	0.009	0.004	0.054	96	89	81

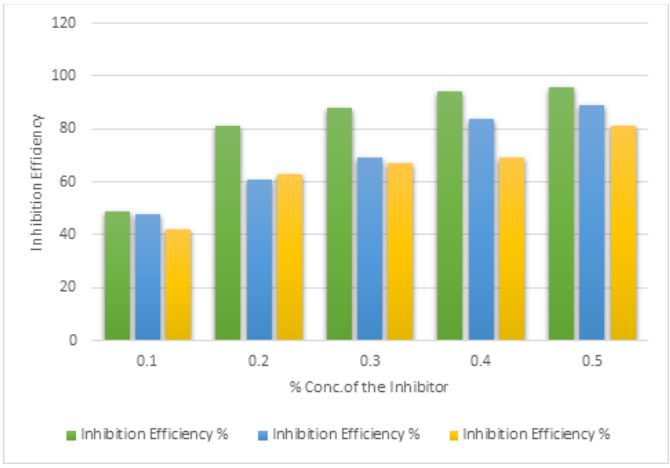


Fig.3. Effect of temperature on inhibition efficiency of Schiff bas

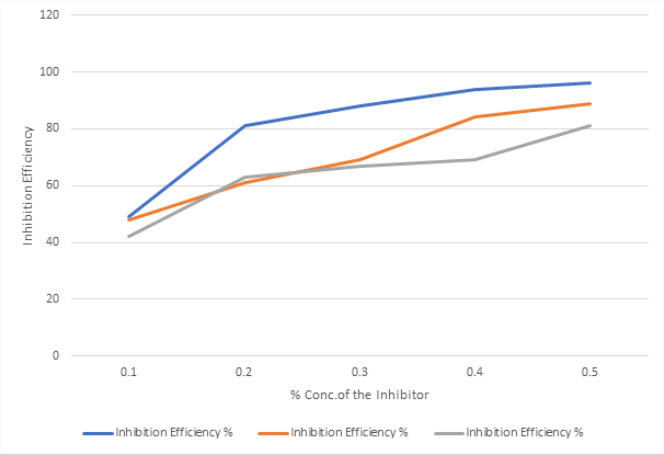


Fig.4. Plot between %IE against% concentration of Schiff base inhibitor

Table.2.Quantum Chemical Parameters

Quantum parameters	(2- Hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid
EHOMO (eV)	-5.0730
ELUMO (eV)	-2.4336
ΔE gap (eV)	2.6394
μ(debye)	-3.7533
I = -EHOMO	5.0730
A = -ELUMO	2.4336
χ=(I+A)/2	3.7533
η (I=-A)/2	1.3197
σ=(1)/η	0.7578
ΔN=(χ_Fe-χ_Inh) /[2(η_Fe-η_Inh)]	1.23
ω= 〖μ/2η〗 ^2	5.3373
Dipole moment	7.6328
Etotal	-1144.34

III.2 DFT Calculations:

To investigate the effect of structure on the inhibition mechanism and efficiency, theoretical calculations were performed. The Frontier molecular orbitals are shown in Fig-3, 4.The calculated quantum chemical parameters necessary for discussion on the reactivity of the studied compounds are presented in Table 1.

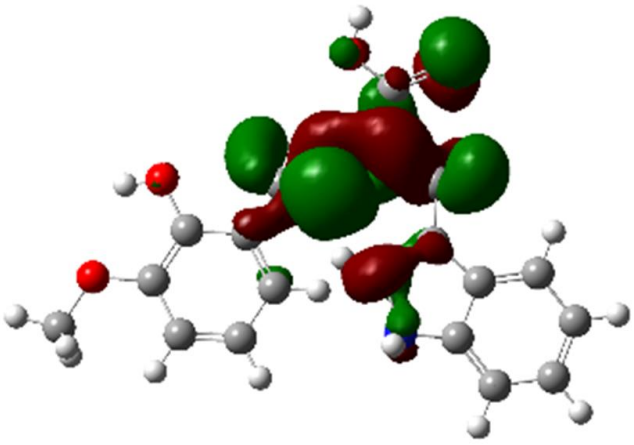


Fig.5.HOMO of Schiff base

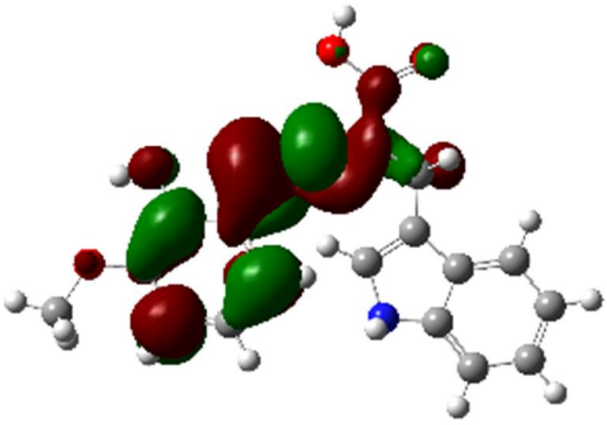


Fig.6. LUMO of Schiff base

Highest occupied molecular orbital energy (EHOMO) and lowest unoccupied molecular orbital energy (ELUMO) are popular quantum chemical parameters. EHOMO is related with the electron donating ability of the molecule. EHOMO values increased that the molecule has a tendency to donate electrons to appropriate acceptor molecules with empty molecular orbital of lower energy. Increasing the EHOMO values indicates that adsorption on the inhibitor on the metal surface and enhancing the inhibition efficiency 12. ELUMO indicates the ability of the molecules to accept electrons. The lower values of the ELUMO, the more probable it is that the molecule would accept electrons.

The energy gap between the EHOMO and ELUMO energy levels of the molecules is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. Decreases the ΔE values indicates that the reactivity of the molecule increases and increasing in the %IE of the molecule. Lower values of the energy difference will provide good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low 13.

The dipole moment (μ) results from non-uniform distribution of charges on the various atoms in the molecule. High dipole moment is required to ensure a better molecule adsorption on metal surfaces 14.
Ionization energy is an essential descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness 15.

Absolute hardness and softness are important parameters to measure the molecular stability and reactivity. It is evident that the chemical hardness generally indicates the resistance towards the distortion or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap. Normally, the inhibitor with the least value of global hardness is expected to have the highest inhibition efficiency 16.

The calculated fraction of electrons transferred, ΔN for (2- Hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid was carried out using Eqn. (7) by using the theoretical χ value of 7 eV/mol and η value of 0 eV/mol for iron. The values of ΔN showed inhibition effect resulting from electrons donation. If $\Delta N < 3.6$, the inhibition efficiency increased. The ΔN value of 1.23 shows, the inhibition efficiency increased with the increasing electron-donating ability at the metal surface.

IV. CONCLUSION

The corrosion inhibition effect of Schiff base inhibitor on corrosion of Low carbon steel in HCl acid medium increases on increasing the concentration of Schiff base and decreases with rise in temperature. The maximum inhibition efficiency of 96% was obtained with 0.5g Schiff base in 100 ml of 5% HCl acid. Quantum Chemical approaches of DFT method is used to find out the inhibition efficiency of (2-Hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid Schiff base. Quantum Chemical parameters such as EHOMO,ELUMO, Energy gap(ΔE),Chemical Hardness(η), Chemical Softness(σ), Electro negativity(χ), and the fraction of electron transferred (ΔN) calculations were performed using Density Functional Theory(DFT/B3LYP-6-31G(d)) methods. The results obtained from those parameters are in agreement with experimental data. The ΔN value of 1.23 shows the inhibition efficiency increased with increase in electron donating ability of metal surface. The results explain that the Schiff base (2- Hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid is a new inhibitor for corrosion inhibition of low carbon steel in acid medium.

V. ACKNOWLEDGEMENT

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