RESEARCH ARTICLE OPEN ACCESS

Theoretical Studies on Corrosion Inhibition Effect of Coumarin and its Derivatives against Metals using Computational Methods

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Abstract:

Quantum chemical calculations were performed on Coumarin and its derivatives to determine corrosion inhibition properties using Parameterized Model7 (PM7). E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ) and other parameters including global hardness (η), global softness (S), absolute electro negativity (χ), and electrophilicity index (ω) from inhibitor molecule to the metallic atom were determined. Results illustrate that adsorption of inhibitor onto metal surface would preferentially be through heteroatoms of molecules. Theoretical calculations on compounds show that Scopoletin and Coumarin possess efficient corrosion inhibition property on metals.

Keywords — **Corrosion inhibition, Quantum chemical calculations, Parameterized model, Coumarin, Scopoletin.**

I. INTRODUCTION

Inhibitors are chemical compounds added to corrosive environment with aim of adsorbing on the metal surface and reducing corrosion rate. Most of the organic compounds used as corrosion inhibitors have heteroatoms and electron rich groups in their molecular structures.

Inhibitors have ability to modify entire surface of corroding metal. Adsorption of inhibitor on metal surface is a complex mechanism involving a number of factors such as nature of metal, environment, electrochemical potential at metal interface and nature of the inhibitor [1].

Developments in software, contribute to use of computational methods to extend in various fields [2]-[6], one of which is the application of quantum chemical calculations (QCCs) in the corrosion inhibition studies [7]-[14]. By performing QCCs calculations, it could be possible to characterize molecular structure of organic inhibitors by calculated electronic and geometrical parameters and analyse inhibition mechanism and interactions of inhibitors.

Aim of present study was to investigate effect of inhibitor structure on inhibition efficiencies and to obtain information on inhibition mechanism using computational analysis.

II. MATERIALS AND METHODS

A. Molecular Structures

Structures of Coumarin, Xanthyletin, Esculetin, 4-hydroxy coumarin, Angelicin, Scopoletin, Seselin, Warfarin and 7-hydroxy coumarin were obtained from literature for computational analysis.

3-Dimensional (3D) structures were retrieved from structural database and was optimized (Fig. 1) and taken as input file for the quantum chemical studies.

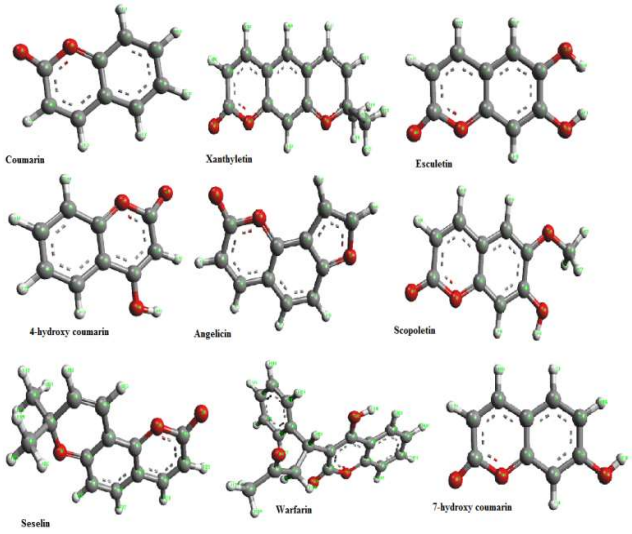

Fig.1 3-Dimensional structures of the Coumarin and its derivatives.

B. Softwares

The computational analysis of molecular structures of Coumarin and its derivatives were done by MOPAC2016 [15] software using PM7 method. The name of software package was derived from Molecular Orbital PACkage. MOPAC2016 can perform calculations on small molecules and enzymes using PM7, PM6, PM3, AM1, MNDO, and RM1. PM3 or Parameterized Model number 3, based on semi-empirical method for the quantum calculation of molecular electronic structure in computational chemistry [16].

PM7 was parameterized using experimental and high-level ab initio reference data, augmented by a new type of reference data intended to better define the structure of parameter space [15]. MOPAC2016 software based on PM7 method was employed for analysis. Mulliken atomic charges were performed with the semi-empirical Parametric Method 3 (PM3) parameterization. Positive and negative regions in HOMO and LUMO orbitals of compounds were computed using ArgusLab 4.0.1[17].

C. Quantum Chemical Calculations

Molecular properties like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), global reactivity parameters such as chemical hardness (η), chemical potential (μ) and electrophilicity index (ω) were obtained to analyze reactivity of the inhibitor molecules. Chemical potential is negative of electronegativity (18). Electronegativity is measure of power of an electron or group of atoms to attract electrons towards it [19].

$$\mu = -\chi \quad (1)$$

Molecular properties related to the reactivity and selectivity of the inhibitors like ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and softness (σ), were estimated according to Koopman's theorem [20] which relates to the energy of HOMO and LUMO. Ionization potential is the amount of energy required to remove an electron from a molecule. Lower the ionization potential, easier to remove an electron from a molecule. High Ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules [21]. Ionization potential (I) can be related to the energy of the E_{HOMO} through the equation:

$$I = -E_{HOMO} \quad (2)$$

Electron affinity (A) can be related to E_{LUMO} through the equation:

$$A = -E_{LUMO} \quad (3)$$

Electronegativity (χ) and global hardness (η) can be determined from the values of I and A. The chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electro cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has the least tendency to react while a soft molecule has high tendency to react. A hard molecule has a large energy gap and soft molecule has a small energy [45]. Absolute electronegativity (χ) and absolute chemical hardness (η) of the inhibitor molecule can be given [22] as,

$$\chi = \frac{I+A}{2} \quad (4)$$

$$\eta = \frac{I-A}{2} \quad (5)$$

Electron polarizability, also called as chemical softness (σ) is the measure of the capacity of an atom or group of atoms to receive electrons [23], was estimated by using the equation:

$$\sigma = \frac{1}{\eta} \quad (6)$$

Electrophilicity values gives information on the nucleophilic or elecrophilic nature of the molecule. A high electrophilic value informs that the molecule has a high tendency to act as an electrophile while a low value of electrophilicity informs that the molecule has a high tendency to act as a nucleophile [24]. The absolute electrophilicity index (ω) [25] can be calculated by the equation

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

According to the definition, this index measures the propensity of chemical species to accept electrons. Mulliken population analysis determines the nucleophilic and electrophilic reaction centers in the compounds.

III. RESULTS AND DISCUSSIONS

D. Quantum Chemical Parameters

Quantum chemical methods have been proved to be a very powerful tool for studying inhibition of corrosion of metals [26]. The structures are sketched with ACD chemsketch and structural geometries were optimized to obtain a stable structure. The HOMO density distribution and LUMO density distribution for molecules were executed using MOPAC2016 with PM7 method. Positive and negative regions on HOMO and LUMO orbitals of the molecules were computed using ArgusLab 4.0.1 (Fig. 2 and Fig. 3).

Examination of E_{HOMO} and E_{LUMO} are important so as to find the electronic properties of the compounds theoretically using PM3. The positive and negative phases of the orbital are represented by two colours, the blue regions represent an increase in electron density and the red region represents a decrease in electron density [27].

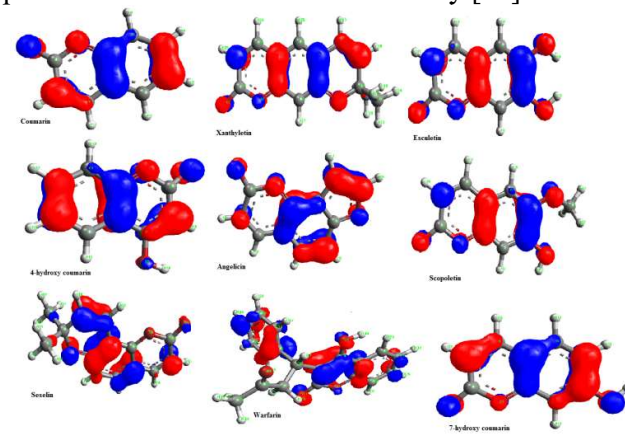

Fig. 2 HOMO orbitals of Coumarin and its derivatives

E_{HOMO} measures electron donating ability of a compound to an appropriate acceptor molecule with low-energy empty molecular orbital. An inhibitor with higher HOMO energy can easily provide electrons for metallic substrate to adsorb on its surface [28]-[30]. Electrophilic attacks were shown to correlate with atomic sites having high density of the HOMO orbital, whereas nucleophilic attacks correlated well with atomic sites having high density of the LUMO orbital (Kunichi Fukui was awarded the Nobel prize in chemistry in 1981 for developing this concept) [31],[32].

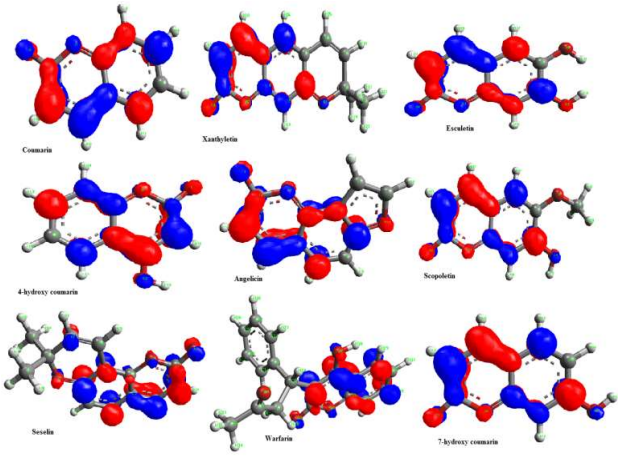

Fig.3 LUMO orbitals of Coumarin and its derivatives

E_{LUMO} reveals tendency of a molecule to receive electrons. A molecule with lower LUMO energy would be a better electron acceptor from a donor molecule [33], [28]-[30]. It has been reported that inhibitor molecules can be adsorbed not only by donating electrons from their HOMO orbitals of Fe, but also by receiving electrons from metals to their LUMO molecular orbitals leading to create a feedback bond [28]-[30]. Energy gap ΔE, is an important parameter as a function of reactivity of inhibitor molecule towards adsorption on metallic surface. As ΔE decreases, reactivity of molecule increases, leading to increase of inhibitor efficiencies [34].

TABLE 1.
QUANTUM CHEMICAL PARAMETERS FOR COUMARIN AND ITS DERIVATIVES USING PM7

S. No.	Compounds	E_{HOMO} eV	E_{LUMO} eV	Energy Gap eV
1.	Coumarin	-9.236	-1.415	7.821
2.	4-hydroxy coumarin	-9.701	-1.282	8.419
3.	Angelicin	-9.072	-1.195	7.877

4.	Esculetin	-9.263	-1.279	7.984
5.	7-hydroxy coumarin	-9.702	-1.281	8.421
6.	Scopoletin	-9.071	-1.221	7.850
7.	Seselin	-9.254	-1.123	8.131
8.	Warfarin	-9.364	-1.131	8.233
9.	Xanthyletin	-9.187	-1.231	7.956

The molecule with highest E_{HOMO} value has highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [35]. From results of quantum chemical calculations, it was evident that Scopoletin had highest value of E_{HOMO} -9.071 (eV) and would be better adsorbed on metal surface and be a best corrosion inhibitor. Energy gap (ΔE) provides information about overall reactivity of a molecule. As ΔE decreases, reactivity of molecule increases leading to increase in inhibition efficiency of molecule [34]. Low values of ΔE gap will render good inhibition efficiencies since energy to remove an electron from last occupied orbital will be minimized [36].

From the quantum chemical study, tendency for (ΔE) values follows the order Coumarin < Scopoletin < Angelicin < Xanthyletin < Esculetin < Seselin < Warfarin < 4 - hydroxy coumarin < 7-hydroxy coumarin, which suggests that Scopoletin had good reactivity in comparison to other compounds and would therefore likely interact strongly with metal surface and act as good inhibitor. Mulliken population analysis is mostly used for calculation of charge distribution in a molecule [37]. These numerical quantities are easy to obtain and could provide at least a qualitative understanding of structure and reactivity of molecule [38]. Quantum chemical parameters obtained from theoretical calculations which are responsible for inhibition efficiency of compounds such as dipole moment (μ), electro negativity (χ), electron affinity (EA), global hardness (η), softness (S), ionization energy (IE) and electrophilicity (ω) are shown in Table 2 and Table 3.

TABLE 2.
QUANTUM CHEMICAL PARAMETERS OF COUMARIN AND ITS DERIVATIVES

S.No.	Compounds	IE	EA	χ
1.	Coumarin	9.236	1.415	5.326
2.	4 - hydroxy coumarin	9.701	1.282	5.492
3.	Angelicin	9.072	1.195	5.133
4.	Esculetin	9.263	1.279	5.271
5.	7-hydroxy coumarin	9.702	1.281	5.491
6.	Scopoletin	9.071	1.221	5.146
7.	Seselin	9.254	1.123	5.188
8.	Warfarin	9.364	1.131	5.248
9.	Xanthyletin	9.187	1.231	5.209

TABLE 3.
QUANTUM CHEMICAL PARAMETERS OF COUMARIN AND ITS DERIVATIVES

S.No	Compounds	η	S	μ	ω
1.	Coumarin	3.911	0.256	-5.326	3.626
2.	4 - hydroxy coumarin	4.21	0.238	-5.492	3.582
3.	Angelicin	3.938	0.254	-5.133	3.345
4.	Esculetin	3.992	0.25	-5.271	3.48
5.	7-hydroxy coumarin	4.21	0.238	-5.491	3.581
6.	Scopoletin	3.925	0.255	-5.146	3.373
7.	Seselin	4.065	0.246	-5.188	3.311
8.	Warfarin	4.117	0.243	-5.248	3.345
9.	Xanthyletin	3.978	0.251	-5.209	3.41

High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of atoms and molecules [39]. Low ionization energy 9.071(eV) of Scopoletin indicates high inhibition efficiency.

Absolute hardness and softness are important properties to measure molecular stability and reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap [40]. For simplest transfer of electron, adsorption could occur at part of molecule where softness (S), which is a local property, has a highest value [41]. Scopoletin with softness value of 0.255 has highest inhibition efficiency.

Scopoletin with low hardness value 3.925 (eV) compared with other compounds have a low energy gap. Normally, inhibitor with least value of global hardness can be expected to have highest inhibition efficiency [42].

E. Mulliken charge distribution of Scopoletin and Coumarin

Mulliken charge distribution of Scopoletin and Coumarin are presented in Table 4. More negative the atomic charges of adsorbed centre, more easily atom donates its electron to unoccupied orbital of the metal [43]. The inhibition efficiency of inhibitors under study depends on presence of electronegative atoms in their molecular structure.

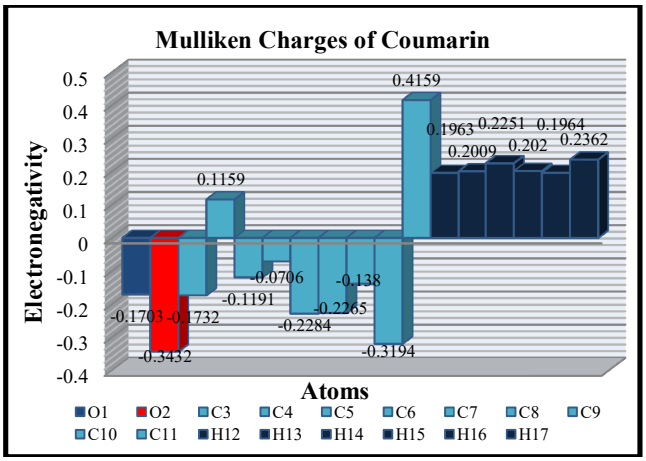

Fig. 4 Mulliken Charge Density Plot of Scopoletin Molecule

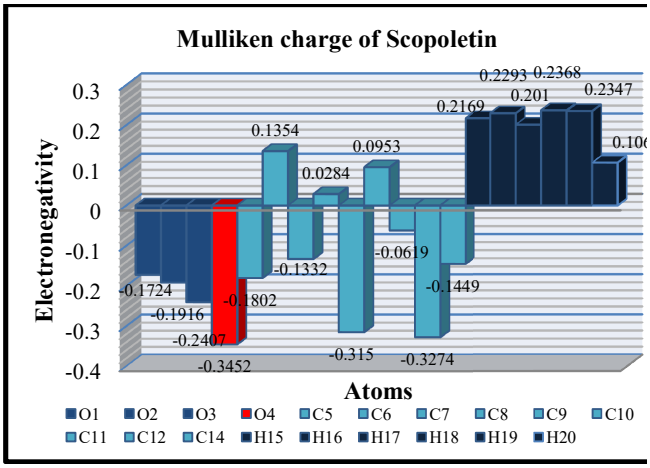

Fig. 5 Mulliken charge density plot of Coumarin molecule

TABLE 4.

MULLIKEN CHARGE DENSITY OF SCOPOLETIN AND COUMARIN MOLECULES

Scopoletin		Coumarin	
O1	-0.1724	O1	-0.1703
O2	-0.1916	O2	-0.3432
O3	-0.2407	C3	-0.1732
O4	-0.3452	C4	0.1159
C5	-0.1802	C5	-0.1191
C6	0.1354	C6	-0.0706
C7	-0.1332	C7	-0.2284
C8	0.0284	C8	-0.2265
C9	-0.315	C9	-0.138
C10	0.0953	C10	-0.3194
C11	-0.0619	C11	0.4159
C12	-0.3274	H12	0.1963
C13	0.418	H13	0.2009
C14	-0.1449	H14	0.2251
H15	0.2169	H15	0.202
H16	0.2293	H16	0.1964
H17	0.201	H17	0.2362
H18	0.2368		
H19	0.2347		
H20	0.1066		
H21	0.1017		
H22	0.1083		

The calculated Mulliken charges showed that there was more than one active center in molecules. It could be readily observed that oxygen and some carbon atoms have high charge densities. Scopoletin and Coumarin has more electronegative O4 and O2 with charges -0.3452 and -0.3432 that shows due to more electron-donating nature of the atoms (Fig. 4 and Fig. 5). The regions of highest electron density are generally the sites to which electrophiles can attack [44]. O and C atoms were the active centers that possess strong ability of bonding to the metal surface.

Some carbon atoms carry positive charges, which are sites to which nucleophiles can attack. O4, C9, C12 and O2, C10 in Scopoletin and Coumarin are most liable sites for electrophilic attacks as they possess highest values of negative charge (Table 4).

C13 and C11 in Scopoletin and Coumarin are the most liable sites for nucleophilic attacks with highest positive charge. Therefore, Scopoletin and Coumarin can accept electrons from metal through these atoms and hence these compounds could serve as good corrosion inhibitor against metal surface protection.

IV. CONCLUSIONS

Quantum chemical calculations presented virtually compiled fundamental results on properties that cannot be calculated in laboratory. From obtained results using Semi-empirical PM3 and PM7 calculations, inhibition efficiency of studied compounds investigated leads to the following conclusions:

- Based on energy gap values, the reactivity trend followed Coumarin < Scopoletin < Angelicin < Xanthyletin < Esculetin < Seselin < Warfarin < 4 - hydroxy coumarin < 7-hydroxy coumarin.
- Among the analyzed derivatives of Coumarin, Scopoletin and Coumarin was found to have highest inhibitive reactivity in comparison to the other compounds.
- Scopoletin had highest inhibition efficiency because it possessed highest E_{HOMO} energy in comparison with the other derivatives and it was more capable of offering electrons.
- The parameters like hardness (η), softness (S), dipole moment (μ), electron affinity (EA) ionization potential (IE) and electro negativity (χ) confirmed the inhibition efficiency of Scopoletin.
- Mulliken population analysis demonstrated O4 and O2 with charges -0.3452 and -0.3432 in Scopoletin and Coumarin showing nucleophilic and electrophilic reactive centers. The analysis of HOMO, LUMO, and partial atomic charges suggested that these centres would be preferred for nucleophilic or electrophilic attack.

Quantum chemical analysis showed that Scopoletin and Coumarin could serve as effective corrosion inhibitor against metal that could be proved further with experimental studies to establish these candidates as eco friendly corrosion inhibitors.

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