Computational Investigations on Curcumin and Demethoxycurcumin as Corrosion Inhibitors: A Comparative Analysis

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***Abstract*—Inhibition performance and adsorption behaviour of Curcumin and Demethoxycurcumin on metals were studied by quantum chemical calculations – a method very valuable in determining molecular structure and to study reactivity of compounds. Quantum chemical methods have become common practice to carry out virtual determinations in corrosion inhibition studies. Quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, HOMO–LUMO energy gap and electronic density are virtually identified. Structure and activity of compounds, including those not yet synthesized, can be readily screened, employing computational methodology with help of set of mathematical equations that are capable of representing accurately the chemical phenomenon under study.**

Present study elucidates inhibition efficiency of Curcumin and its derivative. Research was performed using quantum chemical calculations by means of MOPAC 2016 with PM7 method to find correlation between molecular structure of compound and its behaviour as corrosion inhibitors. Results showed that compounds inhibit corrosion of metals significantly.

***IndexTerms*— Quantum chemical parameters, Curcumin, MOPAC, Demethoxycurcumin**

I. INTRODUCTION

Metals are extensively used in industries and get corroded when exposed to different industrial environments. Acid solutions are widely used in industry as pickling agents, acid cleaning and oil well acidizing, etc. Use of corrosion inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [Trabanelli, 1991]. Well-known acid inhibitors are chemical compounds containing nitrogen, sulphur, oxygen with aromatic and heterocyclic rings through which they are adsorbed on the metal surface [Yadav et al., 2012]. Development of computational modeling of compounds would help to understand the mechanism of inhibitor action, their adsorption patterns, and inhibitor-metal surface interface which in turn aid the development of designer inhibitors. Theoretical prediction of efficiency of corrosion inhibitors has become very popular in parallel with progress in computational hardware and development of efficient algorithms which assisted routine development of molecular quantum mechanical calculations [Domenicano, 1992]. Quantum-chemistry computations have been widely used to study reaction mechanisms and to interpret experimental results of compounds virtually. This is an useful approach to explore mechanisms of reaction in the molecule and its electronic structure levels [Wang et al., 1999]. Structure and electronic parameters can be achieved by using computational methodologies of quantum chemistry with MOPAC2016.

II. MATERIALS AND METHODS

Structures of compounds

Molecular structures of Curcumin, and Demethoxycurcumin were obtained from literature for computational analysis. 3-Dimensional (3D) structures were retrieved from structural database and were geometrically optimized (Fig. 1) and used as input file for quantum chemical studies.

Quantum chemical study

Quantum chemical calculations were carried out by using semi-empirical PM7 which is highly reliable for calculating physical properties of molecules from MOPAC2016. 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 quantum calculation of molecular electronic structure in computational chemistry [Stewart, 1989]. PM7 was parameterized using experimental and high-level ab initio reference data, augmented by a new type of reference data intended to better define structure of parameter space [Stewart, 2013].

Geometry optimization of the structure was performed using Argus Lab (Mark, 2003). Mulliken atomic charges were performed with semi-empirical Parametric Method 3 (PM3) parameterization. Positive and negative regions in HOMO and LUMO orbitals of compounds were computed using Argus Lab 4.0.1 [Thompson, 2004].

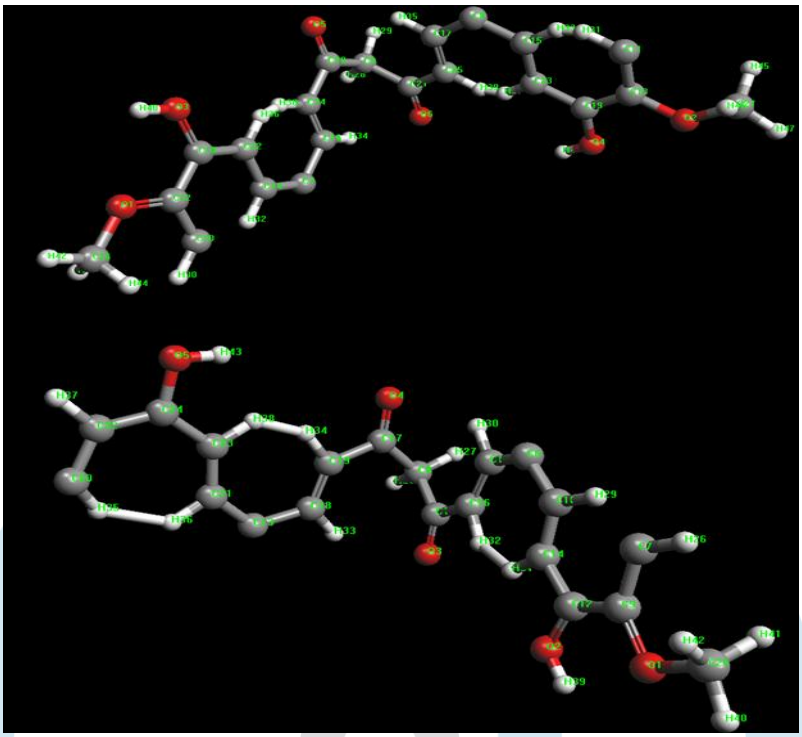

Figure.1. Chemical structures of Curcumin and Demethoxycurcumin

Chemical parameters

Quantum parameters: 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 analyse reactivity of inhibitor molecules. Chemical potential is negative of electronegativity (Parr, 1989). Electronegativity is measure of power of an electron or group of atoms to attract electrons towards it [Pauling, 1960].

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

Molecular properties related to reactivity and selectivity of inhibitors like ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and softness (σ), were estimated according to Koopman's theorem [Koopmans, 1933] which relates to 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 is to remove an electron from a molecule. High Ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of atoms and molecules [Pearson, 1986]. Ionization potential (I) can be related to energy of 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. Chemical hardness fundamentally signifies the resistance towards deformation or polarization of electro cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has 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 [Pearson, 1986]. Absolute electronegativity (χ) and absolute chemical hardness (η) of the inhibitor molecule can be given [Parr and Pearson, 1983] as,

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

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

Electron polarizability, also called as chemical softness (σ) is a measure of capacity of an atom or group of atoms to receive electrons [Senet, 1997], was estimated by using the equation:

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

Electrophilicity values gives information on nucleophilic or electrophilic nature of 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 [Kalaiselvi et al., 2014]. The absolute electrophilicity index (ω) [Parr et al., 1999] can be calculated by the equation

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

According to the definition, this index measures the propensity of chemical species to accept electrons.

Mulliken Population Analysis

Mulliken charges arise from Mulliken population analysis [Mulliken , 1955; Csizmadia and Enriz, 2001] and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbitals molecular orbital method, and are routinely used as variables in linear regression (QSAR) procedures [Leach, 2001; Ohlinger et al., 2009]. Mulliken population analysis determines the nucleophilic and electrophilic reaction centers in the compounds. Local charges such as Mulliken charges are generated from Argus Lab using PM3 parameterized method.

III. RESULTS AND DISCUSSIONS

Quantum chemical analysis

Structures are sketched with ACD chemsketch and structural geometries were optimized to obtain a stable structure. HOMO and LUMO for Curcumin and Demethoxycurcumin were generated using MOPAC2016 with PM7 method. Positive and negative regions on HOMO and LUMO orbitals of the compounds were computed using Argus Lab 4.0.1 (Fig. 2 and Fig. 3).

Examination of E_{HOMO} and E_{LUMO} are 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 [Laxmi, 2014].

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 [Soltani et al., 2012; Adnani et al., 2013; Morad and Kamal, 2006]. 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) [Laxmi, 2016]. Quantum chemical parameters obtained from theoretical calculations which are responsible for inhibition efficiency of compounds such as E_{HOMO}, E_{LUMO}, ΔE, dipole moment (μ), electro negativity (χ), electron affinity (EA), global hardness (η), softness (S), ionization energy (IE) and electrophilicity (ω) are shown in Table 1

Table 1. Quantum Chemical Parameters for Curcumin and Demethoxycurcumin using PM7

S. No.	Chemical parameters	Curcumin	Demethoxy curcumin
1.	E_{HOMO} (eV)	-9.387	-9.973
2.	E_{LUMO}(eV)	-0.396	-0.541
3.	ΔE (eV)	8.991	9.433
4.	IE (eV)	9.387	9.973
5.	EA (eV)	0.396	0.541
6.	χ (eV)	4.892	5.257
7.	η (eV)	4.496	4.717
8.	S	0.2224	0.212
9.	μ	-4.892	-5.257
10.	ω	2.661	2.929

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 [Awad et al., 2010]. The molecule with highest E_{HOMO} value has highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [Gece and Bilgin, 2009][Kavitha and Gunavathy, 2014].

From results of quantum chemical calculations, it was evident that Curcumin had highest value of E_{HOMO} -9.387 (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 [Awad et al., 2010]. Low values of ΔE gap will render good inhibition efficiencies since energy to remove an electron from last occupied orbital will be minimized [Akalezi et al., 2012].

From the quantum chemical study, tendency for (ΔE) values follows the order Curcumin < Demethoxycurcumin, which suggests that Curcumin had good reactivity in comparison to Demethoxycurcumin 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 [Murrell et al., 1985]. These numerical quantities are easy to obtain and could provide at least a qualitative understanding of structure and reactivity of molecule [Gruber and Buss, 1989].

High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules [Chakraborty et al., 2010]. The low ionization energy 9.387 (eV) of Curcumin indicates the 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 [Obi-Egbedi et al., 2011]. For simplest transfer of electron, adsorption could occur at part of molecule where softness (S), which is a local property, has a highest value [Hasanov et al., 2007]. Curcumin with softness value of 0.2224 has highest inhibition efficiency.

Curcumin with low hardness value 4.496 (eV) have a low energy gap. Normally, inhibitor with least value of global hardness can be expected to have highest inhibition efficiency [Ebenso et al., 2010].

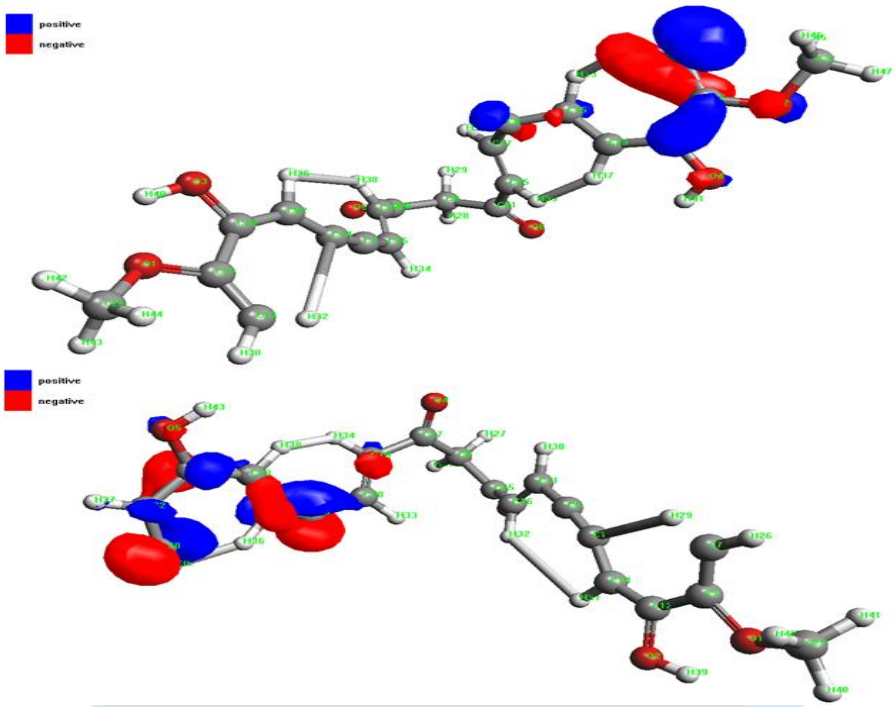

Figure. 2 HOMO orbitals of Curcumin and Demethoxycurcumin

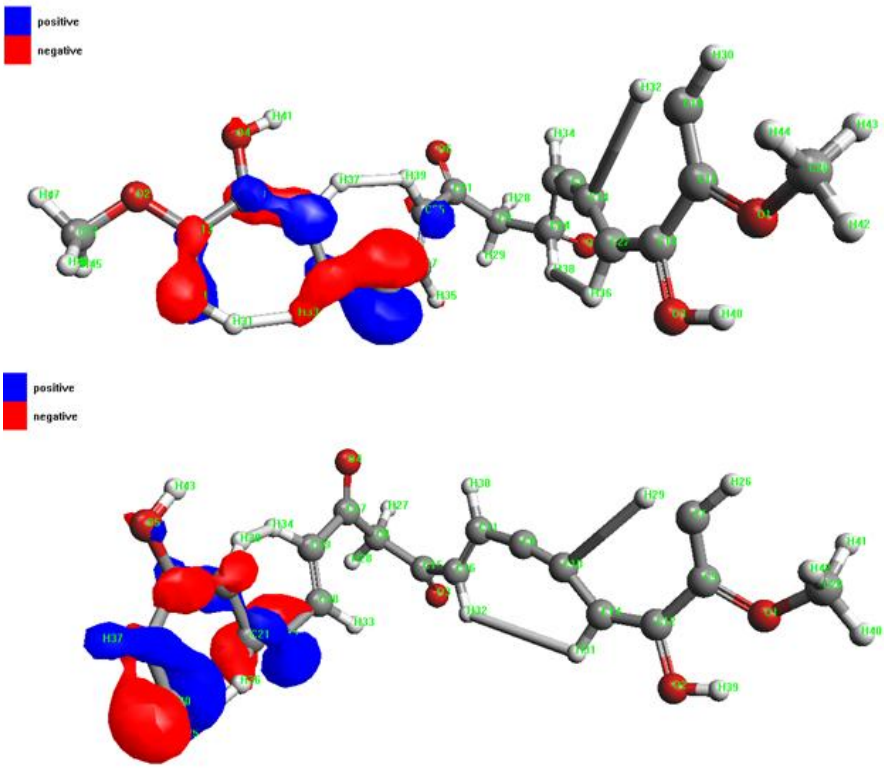

Figure. 3 LUMO orbitals of Curcumin and Demethoxycurcumin

Mulliken charge distribution of Curcumin and Demethoxycurcumin

Mulliken charge distribution of Curcumin and Demethoxycurcumin are presented in Table 2. More negative the atomic charges of adsorbed centre, more easily the atom donates its electron to unoccupied orbital of the metal [Xia et al., 2008]. Inhibition efficiency of inhibitors under study depends on presence of electronegative atoms in their molecular structure.

Table 2. Mulliken Charge Density of Curcumin and Demethoxycurcumin

Curcumin		Curcumin		Demethoxycurcumin		Demethoxycurcumin	
Atoms	**Charge**	**Atoms**	**Charge**	**Atoms**	**Charge**	**Atoms**	**Charge**
O1	-0.2464	**C25**	-0.3107	**O1**	-0.2523	**C25**	-0.1207
O2	-0.1946	**C26**	-0.124	**O2**	-0.2651	**C26**	0.1901
O3	-0.2745	**C27**	-0.1328	**O3**	-0.3312	**C27**	0.1731
O4	-0.1935	**H28**	0.1898	**O4**	-0.3344	**H28**	0.1783
O5	-0.313	**H29**	0.1653	**O5**	-0.2303	**H29**	0.2094
O6	-0.31	**H30**	0.1889	**C6**	-0.191	**H30**	0.209
C7	-0.199	**H31**	0.0232	**C7**	-0.3883	**H31**	0.2122
C8	0.1454	**H32**	0.2051	**C8**	-0.374	**H32**	0.2165
C9	-0.3725	**H33**	0.2661	**C9**	0.0413	**H33**	0.2145
C10	-0.3848	**H34**	0.2025	**C10**	-0.0672	**H34**	0.2032
C11	-0.1064	**H35**	0.2404	**C11**	0.007	**H35**	0.2872
C12	0.0503	**H36**	0.2171	**C12**	0.1221	**H36**	0.2118
C13	-0.1475	**H37**	0.1918	**C13**	-0.1317	**H37**	0.2478
C14	-0.0492	**H38**	0.2261	**C14**	-0.179	**H38**	0.2225
C15	-0.2251	**H39**	0.2083	**C15**	0.352	**H39**	0.2515
C16	0.0003	**H40**	0.255	**C16**	-0.3365	**H40**	0.1149
C17	-0.2389	**H41**	0.2279	**C17**	0.3697	**H41**	0.0992
C18	0.1222	**H42**	0.1087	**C18**	-0.0715	**H42**	0.1014
C19	0.1985	**H43**	0.1000	**C19**	-0.3757	**H43**	0.2307
C20	0.3524	**H44**	0.1043	**C20**	-0.2396		
C21	0.3487	**H45**	0.1088	**C21**	-0.2116		
C22	-0.1862	**H46**	0.1054	**C22**	-0.1702		
C23	-0.3048	**H47**	0.0977	**C23**	-0.2461		
C24	-0.3367			**C24**	0.0506		

Calculated Mulliken charges showed that there was more than one active centre in molecules. The more negative atomic charges of the adsorbed centre, the more easily the atom donates its electron to the unoccupied orbital of the metal [Fu et al., 2010]. It could be readily observed that oxygen and some carbon atoms have high charge densities. Curcumin has more electronegative C10, C9 and O5 with charges -0.3848, -0.3725 and -0.3130 that shows due to more electron-donating nature of the atoms. Demethoxycurcumin has more electronegative C7, C19 and O4 with charges -0.3883, -0.3757and -0.3344 that liable to electrophile attack. The regions of highest electron density are generally the sites to which electrophiles can attack [Musa et al., 2010]. O and C atoms were the active centres that possess strong ability of bonding to the metal surface.

Some carbon atoms carry positive charges, which are sites to which nucleophiles can attack [Elazhary et al., 2016]. C20 and C21 in Curcumin are the most liable sites for nucleophilic attacks with highest positive charge. Therefore, Curcumin can accept electrons from metal through these atoms and hence could serve as good corrosion inhibitor against metal surface protection.

IV. CONCLUSIONS

Theoretical analysis with computational software has rendered insight of quantum properties that cannot be calculated in laboratory. From calculations using Semi-empirical PM3 and PM7 methods, inhibition efficiency of studied compounds investigated leads to the following conclusions:

- Based on energy gap values, the reactivity trend followed Curcumin < Demethoxycurcumin.
- Among the two compounds, Curcumin was found to have highest inhibitive reactivity.
- Curcumin had highest inhibition efficiency because it possessed highest E_{HOMO} energy and more capable of offering electrons.
- Parameters like hardness (η), softness (S), dipole moment (μ), electron affinity (EA) ionization potential (IE) and electronegativity (χ) confirmed the inhibition efficiency of Curcumin.
- Mulliken population analysis demonstrated Curcumin showing nucleophilic and electrophilic reactive centres. Analysis of HOMO, LUMO, and partial atomic charges suggested that these centres would be preferred for nucleophilic or electrophilic attack.

Theoretical studies showed that Curcumin could serve as effective corrosion inhibitor against metals and in-depth analysis of same with experimental studies will prove curcumin to be candidate compound for development of efficient corrosion inhibitor.

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