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Adsorption and Inhibition Behavior of Purine based Drugs on Mild Steel Corrosion in Hydrochloric Acid Solution: DFT Study

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Abstract- The adsorption behavior of three purine based chemical medicines (drugs) namely, 2-amino-9-((2-hydroxyethoxy)methyl)-3H-purin-6(9H)-one (Acyclovir; Acy), ((1S,4R)-4-(2-amino-6-(cyclopropylamino)-9H-purin-9-yl)cyclopent-2-en-1-yl)methanol (Abacavir; Aba) and (R)-(((1-(6-amino-9H-purin-9-yl)propan-2-yl)oxy)methyl)phosphonic acid (Tenofovir; Ten) on mild steel corrosion in acidic solution has been investigated using DFT based quantum chemical calculations. An attempt has been made to established correlation between experimentally determined inhibition efficiency and DFT based quantum chemical calculations. Several computational parameters such as energies of highest occupied and lowest unoccupied frontier molecular orbitals (E_{HOMO} and E_{LUMO}), energy band gap (ΔE), electronegativity (χ), global harness (η) and global softness (σ), fraction of electron transfer (ΔN), and dipole moment (μ) were derived in order to describe the relative adsorption tendency of these drugs on the mild steel surface. Among the tested drugs, abacavir exhibited

the maximum adsorption tendency. The adsorption tendency of these drugs follows the order: abacavir>acyclovir>tenofovir. The DFT based quantum chemical calculations was carried out for neutral as well as protonated forms of the drug molecules.

Keywords- DFT study, Corrosion inhibition, Frontier molecular orbitals, Drug molecules, Adsorption behavior, Theoretical parameters

1. INTRODUCTION

1.1. General introduction

The corrosion prevention of mild steel is highly desirable because it is major constructional material in various industries including food, petroleum, transportation and chemical industries because of its high mechanical straight and relatively low price [1-3]. Generally, the isolation of pure iron from its ores requires some cleaning processes like acid descaling and acid pickling during which loss of metal occurs due to corrosion. Therefore, these cleaning processes require some external additives known as corrosion inhibitors, in order to retard the metallic dissolution. Among the available methods, use of organic inhibitors is first line of defense against metallic corrosion. These organic inhibitors adsorb onto the metallic surface through their π- and non-bonding electrons of multiple (double and triple) bonds and heteroatoms (such as N, O, S, P) and thereby form protective film that isolates metal from corrosive environment and protects from corrosion [1-4]. The heteroatoms exist in the form of polar functional groups such as $–NO_2$, -OH, $-OCH_3$, -COOH, $-COOC_2H_5$, $-NH_2$ etc. that can act as adsorption centers during metal-inhibitor interactions. Recently, several classes of organic compounds such as thiazoles derivatives, sulphonamides, thiophene Schiff's bases, semicarbazones and thiocarbazones, phenothiazine derivatives, dihydroquinazolinone, thioamides, thiophene derivatives, pyridinthiourea, phenanthrothiadiazole dioxide, Phenyl-substituted amino Thiadiazoles, pyridine-pyrazole, mercaptothiadiazole derivatives, diphenylbenzoquinoxaline, benzoylthiourea derivatives, blue tetrazolium aminomercaptothiadiazole, and phenoxyoxopentanes etc. have investigated as effective corrosion inhibitors for metallic corrosion in several electrolytic media [1-11].

The growing level of ecological awareness and severe environmental legislations in the last few decades restrict the use of synthetic organic inhibitors as they are generally synthesized by toxic and expensive starting materials [12-14]. Their synthesis is not only costly and time consuming but also results into release of environmentally malignant chemicals into the surrounding environment. Therefore, there is increasing demands of inhibitors that can be derived from natural and biological resources [12-14]. In this course, use of plant extracts and chemical medicines (drugs) have gained significant advancement because of their natural origin, non-toxic nature and negligible adverse effect on the environment. Several drugs molecules Metformin [15], Clotrimazole and Fluconazole [16], Ampicillin, Cloxacillin, Flucloxacillin and Amoxycillin [17], Fluconazole [18], Enalapril

maleate, Atenolol and Etilefrine hydrochloride [19] etc. have been investigated earlier as effective corrosion inhibitors for variety of metals and alloys in different electrolytic media.

1.2. DFT as tool for corrosion study

Traditionally, inhibition performance of inhibitors is primarily determined by experimental methods such as gravimetric, electrochemical impedance spectroscopy (EIS) and electrochemical potentiodynamic (Tafel) polarization methods. However, these experimental methods are non-cost effective and time consuming as they need use of several chemical and instruments and also require even several days for their completion [20-25]. One of the greatest drawbacks of the traditional experimental techniques is that these instrumental techniques often did not provide any solid mechanistic information [22-24]. Recently, computational simulations, particularly, DFT based quantum chemical (QC) calculations, molecular dynamics (MD) and Monte Carlo (MC) simulations have emerged as significant tools to explore the interactions of the organic inhibitors and metallic surfaces [20-25]. The DFT calculations is one of the most significant software based techniques as it gives several vital parameters such as energy of highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (E_{LUMO}), energy band gap (ΔE; E_{LUMO}-E_{HOMO}), electronegativity (χ), global hardness (η) and global softness (S), fraction of electron transfer (ΔN) and dipole moment (λ) etc. in the terms of which chemical reactivity and adsorption behavior of any compound can be predicted even for a molecule which cannot synthesized or prior to its synthesis [22-25].

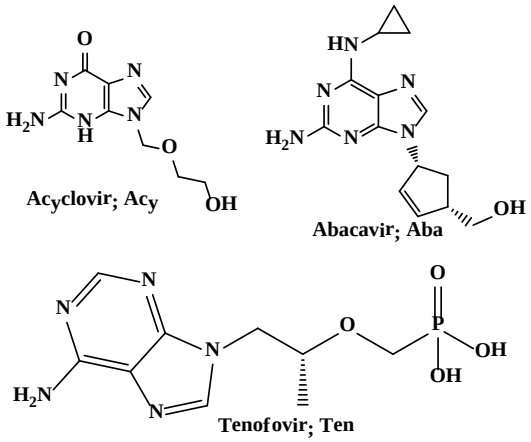

Fig. 1. Chemical structures of Acyclovir (Acy), Abacavir (Aba) and Tenofovir (Ten)

The aim of present analysis is to study the adsorption behavior of three pharmaceutically active (drugs) molecules namely, 2-amino-9-((2-hydroxyethoxy)methyl)-3H-purin-6(9H)-one (Acyclovir), ((1S,4R)-4-(2-amino-6-(cyclopropylamino)-9H-purin-9-yl)cyclopent-2-en-1-yl)methanol (Abacavir) and (R)-(((1-(6-amino-9H-purin-9-yl)propan-2-

yl)oxy)methyl)phosphonic acid (Tenofovir) (Fig. 1), on mild steel corrosion in hydrochloric acid solution using DFT based quantum chemical calculations. Several theoretical parameters such as E_{HOMO}, E_{LUMO}, ΔE, χ, η, σ, ΔN and μ were derived for these drug molecules in order to explain their relative order of effectiveness. The inhibition effect of acyclovir and abacavir using weight loss and electrochemical methods have been investigated by Verma and coworkers [26,27]. These authors found that acyclovir (2-amin-1,9-dihydro-9-((2-hydroxyethoxy)methyl)-6H-purin-6-one) and abacavir ((4-(2-amino-6-(cyclopropylamino)-9Hpurin-9-yl)cyclopent-2-enyl) methanol sulphate) exhibited maximum inhibition efficiencies of 92% and 97.7% at 500 ppm and 400 ppm respectively.

On the basis of the experimental results it can be concluded that abacavir is a better corrosion inhibitor for mild steel corrosion in 1 M hydrochloric acid solution as compared to the acyclovir. The inhibition effect of tenofovir (Tenofovir disproxil fumarate) for zinc and mild steel corrosion in acidic solution have been reported by by Hebbar et al. [28,29]. In our present study we described the adsorption behavior of these drug molecules on the mild steel surface in hydrochloric acid solution using DFT based quantum chemical calculations. The section of these compounds is based on the fact that all of these compounds are purine based and differ from each other only in the nature of different substituents. The DFT gives good insight about the effect of different substituents on the inhibition behavior of purine based corrosion inhibitors. Therefore, the finding of present study will be useful for designing of purine based corrosion inhibitors, because literature survey reveals that purine based compounds act as efficient corrosion inhibitors.

1.3. DFT based chemical reactivity descriptors

The adsorption behavior of organic compounds on the metal surface can be correlated with their chemical reactivity. DFT study provides several theoretical parameters that provide direct relationship between chemical reactivity and adsorption behavior of any particular molecule over the metallic surface. Some common DFT based parameters are:

1.3.1. Frontier molecular orbitals

The energies of highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}) are two most important parameters for describing the chemical reactivity and adsorption behavior of organic chemical [30-32]. A good correlation has been found between chemical reactivity (and adsorption tendency) and the value of E_{HOMO}. The value of E_{HOMO} is often related with electron donating tendency of the organic (inhibitor) molecule [31-34]. The electron donating consideration is important while describing the adsorption of inhibitor molecule on the metal surface as it is well established that adsorption of the organic inhibitors on the metallic surface occurs via donor-acceptor interactions between non-bonding and pi-electrons of inhibitor molecules and vacant d-orbitals of surface

metallic atoms [31,35]. A high value of E_{HOMO} for an inhibitor indicates its high electron donating ability to the acceptor molecule having low energy empty molecular orbital. Among a series of organic compounds, increasing values of E_{HOMO} indicates the increased electron donating tendency as well as increased inhibition performance [30-35]. The value of E_{LUMO} is related with the electron accepting ability of the organic (inhibitor) molecule from appropriate donor molecule (d-orbital of metal). An organic (inhibitor) molecule with lower value of E_{LUMO} behaves as good electron acceptor [31-33,35]. According to the Koopmans theorem, negative of the ionization potential (I) is approximated as E_{HOMO}, whereas negative of the E_{LUMO} is approximated as electron affinity (A) [35-37]:

$$I = -E_{HOMO} \quad (1)$$

$$A = E_{LUMO} \quad (2)$$

1.3.2. Energy band gap (ΔE; E_{LUMO}-E_{HOMO})

This is most important secondary parameter derived by subtracting the value of E_{HOMO} from E_{LUMO} (E_{LUMO}- E_{HOMO}) in order to describes the chemical reactivity (adsorption behavior) of the organic species [31,35]. Generally, a higher value of ΔE suggests lower chemical reactivity and vice versa. A lower energy gap between E_{HOMO} and E_{LUMO} implies that transfer of electrons from highly energetic HOMO (highest occupied molecular orbital) to lower energetic LUMO requires low energy that will leads to the high chemical reactivity and high electron transfer ability of the species. Therefore, among a given series of inhibitors, the inhibition performance increases with decreasing values of ΔE or increasing chemical reactivity [31,33,35].

1.3.3. Electronegativity (χ) and chemical potential

DFT study also provides some global molecular properties like electronegativity (χ) and chemical potential (μ) that in turn provide good insight about chemical reactivity [35,38]. An N-electronic molecular system having total molecular energy E and external potential v(r); the chemical potential (μ) can be defined as first derivative of the total energy (E_{total}) with respect to N at constant v(r) [35,38,39]:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \quad (3)$$

Moreover, in general term, the negative of the electronegativity (χ) is chemical potential (μ) [35,39]:

$$\chi = -\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \quad (4)$$

On assuming a quadratic association between the total energy (E_{total}) and total electronic component (N) in a finite difference approximation, according to the earlier work reported by Iczkowski and Margrave, equation 4 can be written as follows [35,40]:

$$\chi = -\mu = \left(\frac{I + A}{2} \right) \tag{5}$$

$$\chi = -\left(\frac{E_{LUMO} + E_{HOMO}}{2} \right) \tag{6}$$

In the above equation, I and A represent ionization potential and electron affinity, respectively. The derivation of electronegativity with help of energies of E_{HOMO} and E_{LUMO} gives Mulliken principal of electronegativity. The Mulliken electronegativity can be further supported by Sanderson's principal of electronegativity equalization, which specified that the electronegativity of any molecule formed by association of two or more atoms, has the intermediate value of the electronegativities of all combining atoms [41]. It is important to note that a higher value of electronegativity implies the lower electron donating tendency of the chemical species. Among a given series of organic compounds, the electron transfer thereby adsorption tendency increases with decreasing value of electronegativity [42,43].

1.3.4. Global hardness and Softness

The global hardness (η) of a chemical species for N-electronic system having chemical potential μ and total energy E_{total} can be represented by following relationship [44-46]:

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N} \right)_{v(r)} = \frac{1}{2}\left(\frac{\partial^2 \mu}{\partial N^2} \right)_{v(r)} \tag{7}$$

The value of hardness derived above is a global quantity and frequently termed as "absolute hardness" that emphasizes that this value calculated for a molecule in some environment may be different from its value derived for isolated molecule. The reciprocal of the global hardness is often called "global softness" (S) [35,44-46]:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} \tag{8}$$

According to Janak's theorem as well as valance state probable model, the global hardness can be approximated in terms of energies of frontier molecular orbitals (HOMO and LUMO) [35,44-46]:

$$\eta = \frac{I - A}{2} = -\left(\frac{E_{LUMO} + E_{HOMO}}{2} \right) \tag{9}$$

1.3.5. Fraction of electron transfer

It has been well established that during metal-inhibitor bonding, firstly, organic inhibitors transfer their non-bonding and π-electrons into the d-orbital of the surface iron atoms by a process known as donation. The magnitude of electrons transfer from inhibitor to metal can be derived using Pearson formula [33,35,44-46]:

$$\Delta N = \frac{\chi_M - \chi_{inh}}{\left[2\left(\eta_M + \eta_{inh}\right)\right]} \quad (10)$$

In the above equation, χ_{inh} and χ_M represent absolute electronegativities of inhibitor and metal, respectively. The η_{inh} and η_M represent the absolute hardness of inhibitor and metal, respectively. According to Pearson, when two or more reacting species having different electronegativity interact with each other, the continuous flow of electrons takes place from lower electronegative species (inhibitor) to the species having higher electronegativity (iron), until the chemical potential of both the species become equal [47]. For calculation of fraction of electrons transfer from inhibitors (drug molecules) to metal in present study, values of the electronegative (χ) and global hardness (η) of bulk iron has been taken as 7 eV and 0 (η_{Fe}= 0), respectively. It is important to mention that the ΔN value does not indicates the exact number of electron transfer form inhibitor to metal but it gives information about the extent of electrons to be transferred from inhibitors molecules to metallic surface [35,46].

1.3.6. Dipole moment

Dipole moment (λ) is measure of polarity of the polar covalent bond which is generally defined as the charges of two atoms bonded by polar covalent bond and distance between them. Dipole moment is a vector quantity which magnitude can be derived as [48,49]:

$$\lambda = qR$$

Where, q denotes the charge and R represents the distance between bonding atoms. Although, coulomb meter (Cm) is the SI unit, however, Debye, named after Peter Debye pioneer working in the field of dipole moments of molecules, is the most common unit for the measurement of dipole moment. One Debye is equal to 3.33564×10^{-30} Cm. Dipole moment derived from Gaussian software reflects the global quantity rather than the dipole moment of a single bond. Both positive and negative trends of inhibition efficiency with dipole moment have been reported. A higher value of dipole moment suggests that molecule under investigation has strong tendency of polarization. The increase in inhibition performance on increasing dipole moment of organic inhibitors in any given series is attributed due to increase in the surface area of the molecules due to increase in the polarizability of the molecules.

2. COMPUTATIONAL DETAILS

Density functional theory (DFT) is one of the most frequently used ab initio approaches for modeling of molecules, clusters and solids in their ground state.

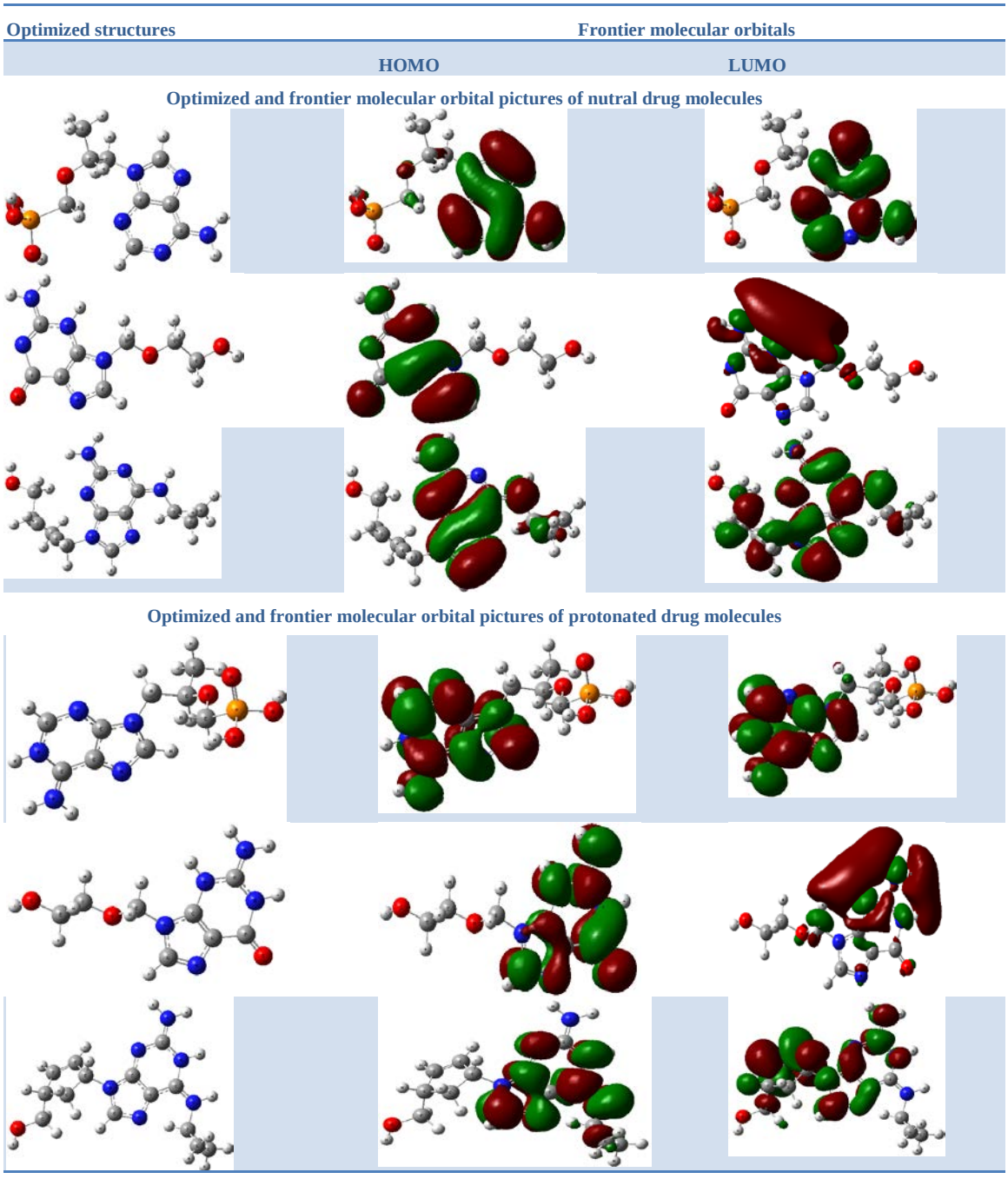

Fig. 2. Optimized and frontier molecular orbital pictures of nutral and protonated forms of investigated drug molecules

In the present study DFT calculations was carried out using the Gaussian 09 program [50-53]. The complete geometric optimization was carried out using 6-311G++(d,p) basis sets,

while the exchange-correlation was performed by hybrid B3LYP functional. The 6-311G++(d,p) basis set gives accurate geometries and electronic properties for a variety of organic compounds [50,53]. Unlike to single electron wave function, DFT emphases on electron density ρ(r) which itself is a gauss of all informations related to the ground state of the molecule (atom).

3. RESULTS AND DISCUSSIONS

Tral and protonated forms of drug molecules under taken in the present investigation and their frontier electron distribution pictures are shown in Fig. 2 and several theoretical indices are given in Table 1. It can be seen from the optimized structures side chains attached to the purine rings of Abacavir, Acyclovir and Tenofovir are non-planer to the purine rings that might cause some steric hindrance or repulsion during metal-inhibitors interactions. This repulsion may affect the distribution of HOMO and LUMO. From optimized structures it can be seen in Tenofovir bulky side chain causes substantial steric repulsion those results into fewer delocalization of HOMO and LUMO of Tenofovir purine moiety as compared to Abacavir and Acyclovir. As stated earlier, the high value of E_{HOMO} indicates the high electron donating and thereby high adsorption tendency [31-35]. From the results depicted in Table 1 it can be seen that the values of E_{HOMO} for studied drugs follows the order: aba>acy>ten, which is in accordance to the order of inhibition efficiency obtained by experimental methods like weight loss and electrochemical methods. From the frontier molecular electron distribution pictures it can be seen that HOMO is mainly localized over entire purine moiety for all investigated drug molecules. However, for abacavir the HOMO is also distributed over the cyclopropylamino moiety (Fig. 2) that resulted into higher adsorption tendency of the abacavir as compared to two remaining drug molecules where HOMO is strictly distributed only around purine moiety.

Although, the values of E_{LUMO} did not follow any regular trend, however from the frontier molecular electron distribution it is clear that LUMO is distributed almost entire part of the Abacavir molecules which indicates that almost whole part of molecules molecule accept electrons from the metal surface during metal-inhibitor interactions that results into highest adsorption tendency of abacavir among the studied drug molecules, while in remaining two drug molecules LUMO is localized only over some part of the molecules [31-33]. The value of energy band gap (ΔE; E_{LUMO}-E_{HOMO}) is another important chemical reactivity gauss. An inhibitor with low value of ΔE is associated with high chemical reactivity and thereby high adsorption ability. In the present study values of ΔE obeyed the order: ten (0.19377)>acy (0.18406)>aba (.18129) that is just converse and in well support to the order of experimental inhibition performance.

Table 1. Quantum chemical calculations parameters derived for neutral and protonated form of investigated drugs

Parameters → / **Drug** ↓	E_{HOMO}	E_{LUMO}	ΔE	χ	η	S	ΔN	μ	%
	Parameters for neutral form of drugs								
Ten	-0.2330	-0.0393	0.1937	0.1361	0.0968	10.32	0.6247	7.671	92%
Acy	-0.2137	-0.0297	0.1840	0.1217	0.0920	10.86	0.7362	13.094	---
Aba	-0.1835	-0.0022	0.1813	0.0928	0.0812	11.03	0.9066	1.323	97.7%
	Parameters for protonated form of drugs								
Ten-H+	-0.0678	-0.0227	0.0451	0.0453	0.0225	44.316	4.6962	9.58	---
Acy-H+	-0.0339	0.0076	0.0416	0.0131	0.0208	48.053	5.8643	11.26	---
Aba-H+	-0.0242	0.0024	0.0266	0.0108	0.0133	74.990	9.2377	5.64	---

The values of electronegativity (χ) can also be applied to explain the adsorption behavior of these drugs over mild steel [40,45]. Generally, an inhibitor with lower value of electronegativity is more potent to transfer its electron to the d-orbital of the metal during metal-inhibitor interaction as compared to inhibitor molecule with high value of electronegativity. In our present study, values of global electronegativity follow the order: aba<acy<ten, which is in supports to the experimental determined inhibition efficiency [35,37,40]. The global hardness and softness are two other secondary parameters that have been widely used to describe the adsorption of organic inhibitors on the metallic surface. Generally, an inhibitor with low value of hardness and high value of softness is associated with high chemical reactivity and thereby high adsorption tendency and vice versa [35,44-46]. The values of these two parameters are also in accordance with the experimentally obtained efficiency order. Lastly, the relative adsorption ability of these drug molecules on the mild steel surface was determined by values of electron transfer. The values of fraction of transfer follow the order: aba (0.9066)>acy(0.7362)>ten (0.6247) [35,48,49]. The highest value of ΔN for abacavir indicates that it has maximum electron transferring and adsorption ability among the studied drug molecules [45,46].

Both positive and negative orders of inhibition performance with the values of dipole moment have been reported. However, in our present study values of dipole moment did not follows any regular order. Generally, organic corrosion inhibitors having heteroatoms in their chemical structures exist in cationic or protonated forms. Therefore, in the present study DFT study was also carried out for protonated form of drug molecules. The trends of theoretical parameters derived for protonated form of drug molecules are similar as obtained for neutral form of inhibitors. The increasing values of E_{HOMO} on going Ten to Aba indicate that electron donating ability of the drug molecules are increasing in the same sequence. The values of

E_{LUMO} did not show any regular trends. The values of ΔE follow the order: Aba<Acy<Ten which indicates that Aba is most reactive and best corrosion inhibitors among the tested molecules. Electronegativity values for studied drugs molecules are also followed the same trend which is in consistence with experimentally determined inhibition efficiency. The values of hardness and softness also satisfied the experimental inhibition efficiency order. Lastly, dipole moment values for investigated drugs molecules did not showed any regular trend.

4. CONCLUSION

In the present investigation, an attempts has been made to established the adsorption behavior of three purine based chemical medicines (drugs) namely, 2-amino-9-((2-hydroxyethoxy)methyl)-3H-purin-6(9H)-one (Acyclovir; Acy), ((1S,4R)-4-(2-amino-6-(cyclopropylamino)-9H-purin-9-yl)cyclopent-2-en-1-yl)methanol (Abacavir; Aba) and (R)-(((1-(6-amino-9H-purin-9-yl)propan-2-yl)oxy)methyl)phosphonic acid (Tenofovir; Ten) on mild steel surface have been investigated using DFT based quantum chemical calculations. It is observed that studied drugs are acted as efficient adsorbates for mild steel surface in hydrochloric acid solution. A good correlation has been observed between earlier experimentally and theoretically determined inhibition efficiency. On the basis of several theoretical parameters it was concluded that among the studied drug molecules, abacavir exhibited the maximum inhibition efficiency, while tenofovir is minimum. The inhibition efficiencies of the studied drug molecules follow the order: Abacavir > Acyclovir > Tenofovir. The theoretical parameters derived for neutral and cationic forms of the drug molecules follow the same trends of adsorption tendency.

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