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Ab-Initio and DFT Calculations on Some Inorganic Inhibitors Computaional Study on Inorganic Corrosion Inhibitors

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ABSTRACT: Some electronic structure descriptors are calculated by using HF and MP2 which are ab-initio methods and B3LYP method with SDD, SDDALL, CEP-4G, CEP-31G, CEP-121G and QZVP basis sets in vacuo and water for CO_3^{2-}, HCO_3^-, H_2CO_3, SO_4^{2-}, HSO_4^-, H_2SO_4, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4 which are used as inorganic corrosion inhibitors. In a summary, MP2/SDDALL level in water is found as the best level. The active sites of these inhibitors are determined by natural bond orbital (NBO) charge analyses, molecular orbital character analysis, proton affinity of mentioned inhibitors and Fukui functions. According to the fraction of electrons transferred, the inhibition efficiency ranking is found as $CO_3^{2-} > PO_4^{3-} > HPO_4^{2-} > HCO_3^- > SO_4^{2-} > H_2PO_4^- > H_2CO_3 > HSO_4^- > H_3PO_4 > H_2SO_4$ in MP2/SDDALL level in water.

Keywords *– Inorganic Compounds, Ab initio and DFT calculations, Computational Techniques, Corrosion Inhibitors.*

1. Introduction

Corrosion is significant process for environment and causes great economic loss for industry and laboratory. This chemical process is a spontaneous and corrosion mechanism/prevention has been receiving great attractions [Davies and Burstein,1980; Machin and Mann, 1982; Nagiub and Mansfeld, 2001; Christov and Popova, 2004; Okafor et al., 2009; Herrag et al., 2010]. Some molecules which are both inorganic and organic molecules have been used as corrosion inhibitors [Doğru Mert et al., 2011; Sayin and Karakaş, 2013; Yuan et al., 2013; Torres et al., 2014]. Their efficiencies or rankings against different metal in different are have been report in many studies. Many mechanisms have been used to explain the corrosion mechanism. The first step, inhibitors are adsorbed to the metallic bulk [Abd El Rehima et al., 2010; Sayin and Karakaş; 2013].

Great economic losses have been performing in learning properties of the inhibitors. However, computational chemistry methods can provide to learn the inhibition efficiency ranking without experimental studies. These investigations prevent the economic, chemical and time losses. There are many experimental studies on inhibition efficiency of inorganic inhibitors [Robertson et al., 1951; Zhao and Zuo; 2002; Ilevbare and Burstein, 2003; Salghi et al., 2004; Foad El-Sherbi, 2006; Foad El-Sherbi et al., 2006; Moutarlier et al., 2008; de Lima-Neto et al., 2008; Samiento-Bustos et al., 2008; Naderi et al., 2009; Samiento-Bustos et al., 2009; Majine et al., 2012; Vishnudevan et al., 2012; Loto, 2012; Loto and Popoola, 2012; Ortiz et al., 2013]. Four experimental studies are selected to explain the inhibition efficiency ranking as theoretically. The first experimental study has been performed by

Rodríguez et al. in 2013 [Ortiz et al., 2013]. Inhibition efficiencies of sulphate, carbonate, hydrogen carbonate and carbonic acid have been investigated against Alloy 22 in 0.1 M and 1 M NaCl solution. In their study, inhibition efficiency of sulphate and carbonate anions has been observed. The second and third experimental studies have been performed by Touir et al. in 2012 and Attar et al. in 2009 [Naderi et al., 2009; Majine et al., 2012], respectively. According to report of Touir and co-workers, phosphate glasses have been used as corrosion inhibitor against mild steel in 1 M HCl solution. As for the report of Attar et al., zinc phosphate has been used as corrosion inhibitors against mild steel in 3.5% NaCl solution. The last study has been performed by Hammouti and co-workers in 2004 [Salghi et al., 2004]. In these studies, hydrogen phosphate ion has been used as inhibitors against Al 3003 and Al 6063 in carbonate solution. In these studies, some inorganic inhibitors have been used but there is not any inhibition efficiency value. Additionally, mentioned inhibitors have not been studied together as experimentally.

Some electronic structure descriptors about corrosion inhibition efficiency have been successfully performed to explain the moleculer properties of different kind of inhibitors [Costa and Lluch, 1984; Bereket et al., 2001; Khalil, 2003; Kandemirli and Sagdinc, 2007; Awad et al., 2010]. In this study, carbonic acid (H_2CO_3), hydrogen carbonate (HCO_3^-), carbonate (CO_3^{2-}), sulphate (SO_4^{2-}), hydrogen sulphate (HSO_4^-), sulphuric acid (H_2SO_4), phosphate (PO_4^{3-}), hydrogen phosphate (HPO_4^{2-}), dihydrogen phosphate ($H_2PO_4^-$) and phosphoric acid (H_3PO_4) are selected to determine the inhibition efficiency ranking toward iron metal. The highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap (E_{GAP}), sum of total negative charges of heteroatoms (TNC), hardness (η), softness (σ), electrophilicity index (ω), nucleophilicity index (N), molar volume (MV) and the fraction of electron transfer to metal surface (ΔN) are calculated by using three methods (HF, DFT and MP2) with six basis sets (SDD, SDDALL, CEP-4G, CEP-31G, CEP-121G and QZVP) in vacuo and water. The most appropriate method and basis set are selected as MP2/SDDALL in water. The inhibition efficiency ranking of mentioned inhibitors are obtained towards iron metal.

2. Computational Method

The input files of inorganic molecules used as corrosion inhibitors were prepared with GaussView 5.0.8 [Dennington II et al., 2009]. Numerical calculations were carried out by using Gaussian 09 IA32W Revision-A.02 [Frisch et al., 2009] and Gaussian 09 AML64L-Revision-C.01 [Frisch et al., 2009]. The whole inhibitors were optimized at HF, B3LYP, MP2 methods with SDD [Zhang et al., 2002], SDDALL [Ramirez-Solis et al., 2012], CEP-4G [Stevens et al., 1984; Stevens et al., 1992; Cundari and Stevens, 1993], CEP-31G [Stevens et al., 1984; Stevens et al., 1992; Cundari and Stevens, 1993], CEP-121G [Stevens et al., 1984; Stevens et al., 1992; Cundari and Stevens, 1993], QZVP [Weigend and Ahlrichs, 2005] basis set in vacuo and aqua. HF and MP2 are ab-initio methods. The Hartree-Fock (HF) method for the total interacting system is taken as the zero-order approximation. The second-order Moller-Plesset theory can be a choice by the perturbational inclusion of electron pair–pair interactions. The B3LYP is hybrid DFT method and combination of exchange and correlation functional [Lee et al., 1988; Becke, 1993]. The effective core potential (ECP) was used in basis sets calculation except SDDALL.

The interactions of solute-solvent were taken into account by the integral equation formalism polarizable continuum model (IEFPCM). All inhibitors were fully optimized in vacuo and water. No imaginary frequency was obtained in vibrational frequencies. Some electronic structure descriptors (E_{GAP}, TNC, η, σ, N, ω and ΔN) were obtained with Eq. (1-7), respectively [Kohn and Sham, 1965; Jesudason et al., 2009; Masoud et al., 2010; Gökce and Bahçeli, 2011; Arivazhagan and Meenakshi, 2011; MAsoud et al., 2011; Arivazhagan and Subhasini; 2012],

$$E_{GAP} = E_{LUMO} - E_{HOMO} \tag{1}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{2}$$

$$\sigma = \frac{1}{\eta} \tag{3}$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \tag{4}$$

$$\omega = \frac{\chi^2}{2\eta} \tag{5}$$

$$N = \frac{1}{\omega} \tag{6}$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh.}}{[2(\eta_{Fe} + \eta_{inh.})]} \tag{7}$$

using a theoretical value, χ_{Fe} = 7.0 eV/mol and value of η_{Fe} = 0 eV/mol for iron bulk, because mentioned bulks are softer than metallic atoms.

3. Results and Discussion

3.1. Non-protonated inhibitors

Inorganic corrosion inhibitors are fully optimized with different methods and basis sets in both phase. Electronic structure descriptors are calculated for each level. Optimized structures of mentioned inorganic molecules which are non-protonated inhibitors are represented in Figure 1.

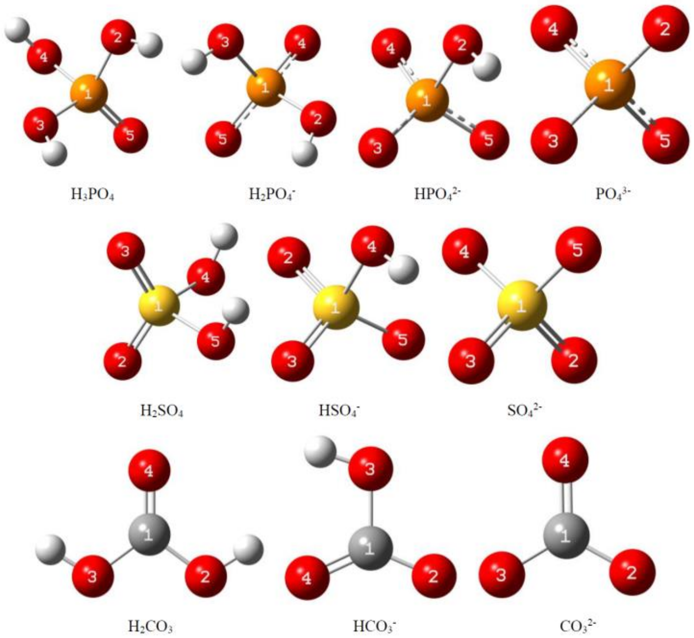


Fig. 1. The optimized structure of non-protonated inhibitors at MP2/SDDALL level in water.

Some electronic structure descriptors at MP2/SDDALL level are given in Table 1 for vacuo and water (aqua). The same electronic structure descriptors at other levels are given in supplementary materials.

Table 1. Electronic structure descriptors with MP2/SDDALL level in for non-protonated inhibitors

	$E_{HOMO}{}^{a}$	$E_{LUMO}{}^{a}$	$E_{GAP}{}^{a}$	η^{a}	σ^{b}	ω	N	TNC^{c}	MV^{d}	ΔN
Vacuo										
H_2SO_4	-14.103	0.230	14.334	7.167	0.140	3.357	0.298	-3.282	51.417	0.004
HSO_4^-	-7.959	5.372	13.331	6.666	0.150	0.125	7.968	-3.682	54.565	0.428
SO_4^{2-}	-1.858	9.171	11.028	5.514	0.181	1.212	0.825	-4.116	55.352	0.966
H_2CO_3	-13.569	3.312	16.882	8.441	0.118	1.558	0.642	-2.334	41.102	0.111
HCO_3^-	-5.921	8.614	14.535	7.268	0.138	0.125	8.013	-2.696	38.922	0.574
CO_3^{2-}	0.888	14.348	13.460	6.730	0.149	4.311	0.232	-3.192	42.295	1.086
H_3PO_4	-13.394	2.298	15.692	7.846	0.127	1.961	0.510	-4.244	53.296	0.093
$H_2PO_4^-$	-7.235	7.496	14.731	7.365	0.136	0.001	1.682	-4.523	63.270	0.484
HPO_4^{2-}	-1.347	11.932	13.280	6.640	0.151	2.109	0.474	-4.940	68.880	0.926
PO_4^{3-}	4.110	16.913	12.803	6.402	0.156	8.630	0.116	-5.436	72.932	1.368
Aqua										
H_2SO_4	-14.093	0.524	14.616	7.308	0.137	3.149	0.318	-3.388	58.237	0.015
HSO_4^-	-12.635	1.928	14.564	7.282	0.137	1.968	0.508	-3.753	56.139	0.113
SO_4^{2-}	-11.213	2.353	13.565	6.783	0.147	1.447	0.691	-4.144	54.302	0.189
H_2CO_3	-13.619	3.782	17.402	8.701	0.115	1.390	0.719	-2.409	38.374	0.120
HCO_3^-	-11.089	4.570	15.659	7.830	0.128	0.679	1.474	-2.751	43.872	0.239
CO_3^{2-}	-9.336	5.211	14.548	7.274	0.137	0.292	3.420	-3.188	48.094	0.339
H_3PO_4	-13.490	2.437	15.927	7.963	0.126	1.917	0.522	-4.351	52.049	0.093
$H_2PO_4^-$	-11.868	3.638	15.506	7.753	0.129	1.092	0.916	-4.642	55.478	0.186
HPO_4^{2-}	-10.529	4.327	14.856	7.428	0.135	0.647	1.545	-5.027	65.140	0.262
PO_4^{3-}	-9.497	4.941	14.438	7.219	0.139	0.359	2.783	-5.472	62.023	0.327

^{a} in eV, ^{b} in eV^{-1}, ^{c} in e^{-}, ^{d} in cm^{3} mol^{-1}

Carbonate, hydrogen carbonate, carbonic acid and sulphate have been studied by Ortiz and co-workers [Ortiz et al., 2013]. There are a lot of experimental studies to determine inhibition efficiencies or inhibition efficiencies ranking of mentioned inhibitor. Investigated inhibitors have not been studied together as experimentally. The inhibition efficiency rankings of studied compounds are expected as follows,

$SO_4^{2-} > HSO_4^- > H_2SO_4$
$CO_3^{2-} > HCO_3^- > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^- > H_3PO_4$

The agreements are examined between electronic structure descriptors and the above ranking. The better results are obtained at MP2/SDDALL level in vacuo and water. Additionally, the results in water are more appropriate than those of in vacuo. Therefore, MP2/SDDALL level in water is taken into consideration for other calculations.

Theoretical inhibition efficiency ranking can be obtained by using electronic structure descriptors. E_{HOMO} is an electronic structure descriptor and higher value of E_{HOMO} indicates the tendency of electron transfer to appropriate acceptor molecule. If E_{HOMO} is decisive for the inhibitor properties, the inhibition efficiency ranking of studied compounds should be:

$SO_4^{2-} > HSO_4^{-} > H_2SO_4$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-} > H_3PO_4$

There is a consistency between ranking of E_{HOMO} at MP2/SDDALL level in water and expected ranking. The second ranking is compatible with experimental results by Ortiz et al. in 2013 [Ortiz et al., 2013]. The energy gap between HOMO and LUMO is significant parameter to determine the theoretical inhibition efficiency [Özbek et al., 2013]. The energy gap is related with softness and hardness. The smaller value E_{GAP} means the more efficient [Özcan et al., 2004; Musa et al., 2012; Zhang et al., 2012]. According to the E_{GAP} value, the ranking of inhibitors should be:

$SO_4^{2-} > HSO_4^{-} > H_2SO_4$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-} > H_3PO_4$

There is a good agreement between E_{GAP} ranking and expected ranking. Other parameters are hardness and softness to determine the inhibition efficiency ranking. The coordination tendencies of the inhibitor towards the metal surface can be debated with HSAB (hard-soft-acid-base) approximation [Li et al., 2009]. According to this approximation, hard/soft acid prefer to coordinate to hard/soft bases. Hard and soft molecule has a big and small E_{GAP}, respectively. [Fujioka et al., 1996; Koch, 2005]. Inhibitors classified as soft bases can form deposits of stable salts or complexes with soft acids such as metallic bulk for repairing defect on metal surface or preventing the corrosion [Fujioka et al., 1996]. Soft bases are to be most effective for metallic bulks. Because metallic bulk is softer than a metal atom [Alexander and Moccari, 1993]. According to softness values, ranking should be:

$SO_4^{2-} > HSO_4^{-} \approx H_2SO_4$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-} > H_3PO_4$

A consistency is obtained between parameter rankings and expected ranking. The other significant parameters are ω and N. The electrophilicity index related with electron accepting of inhibitors [Obi-Egbedi et al., 2011]. Nucleophilicity index shows the ability of inhibitors to give electrons. The inhibition efficiency increases with increasing the N value or decreasing the ω value. According to the N and ω, efficiency ranking is as follows:

$SO_4^{2-} > HSO_4^{-} > H_2SO_4$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-} > H_3PO_4$

The good agreement is obtained according to the above ranking. Inorganic and organic corrosion inhibitors adsorp to metal surface. Total negative charge (TNC) analysis of natural bond orbital (NBO) has been mainly used to predict the adsorption regions of the inhibitors [Gao and Liang, 2007; Assaf et al., 2007; Allam, 2007 Roque et al., 2008; Gece, 2008; Boston et al 2012]. Total negative charges (TNC) of oxygen atoms are calculated. The higher value of TNC implies that the adsorption of inhibitor increases [Bereket et al., 2003; Issa et al., 2008]. According to this information, the ranking should be:

$SO_4^{2-} > HSO_4^{-} > H_2SO_4$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-} > H_3PO_4$

A consistency is found between TNC values and expected ranking. Another parameter is molar volume used to foresee the inhibition efficiency ranking. The anti-corrosion efficiency increases with increasing of molecular volume. Because it is expected that contact area between inhibitor and surface increases with increasing of molar volume. According to the molar volume, the inhibitor efficiency ranking should be:

$H_2SO_4 > HSO_4^{-} > SO_4^{2-}$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$HPO_4^{2-} > PO_4^{3-} > H_2PO_4^{-} > H_3PO_4$

There is not a consistency between molar volume and expected ranking. As for the ΔN, its values show that the inhibition efficiency increases with increasing of ΔN values [Musa et al., 2012]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability to the metal surface and order by which the ability of these inhibitors to donate electrons to the metal surface increase is:

$SO_4^{2-} > HSO_4^{-} > H_2SO_4$
$CO_3^{2-} > HCO_3^{-} > H_2CO_3$
$PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-} > H_3PO_4$

The values of ΔN indicate tendencies of anti-corrosion efficiency. ΔN values can be identified the number of electrons leaving the donor and entering the acceptor molecule. The expression “electron-donating ability” is more adequate than “number of transferred electrons” [Zhang et al., 2012]. The agreement is obtained between ranking of ΔN values and expected ranking. General inhibition ranking of inhibitors can be said by using ΔN values. Coordinate covalent bond forms by transferring electrons from inhibitors. Therefore, there is a correct proportion between ΔN and coordinate-covalent bond strength.

The general inhibition rankings should be as follows:

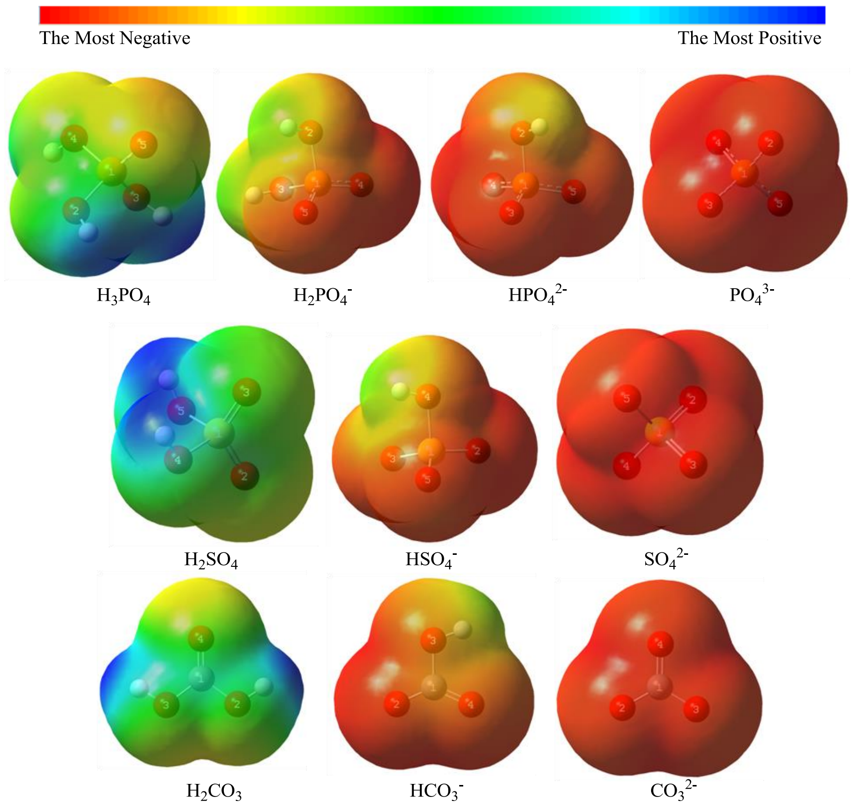
$CO_3^{2-} > PO_4^{3-} > HPO_4^{2-} > HCO_3^{-} > SO_4^{2-} > H_2PO_4^{-} > H_2CO_3 > HSO_4^{-} > H_3PO_4 > H_2SO_4$ (ΔN)

$CO_3^{2-} > PO_4^{3-} > HPO_4^{2-} > HCO_3^{-} > SO_4^{2-} > H_2PO_4^{-} > HSO_4^{-} > H_3PO_4 > H_2CO_3 > H_2SO_4$ (E_{HOMO})

These two rankings are compatible with each other except H_2CO_3.

3.2. NBO Charges, Proton Affinity and Molecular Orbital Analysis

The electronic charge, proton affinity (PA) and molecular orbital (MO) character analyses of heteroatom are significant to determination of active sites. Additionally, molecular electrostatic potential (MEP) maps indicate that which heteroatom is more active. The MEP maps of inorganic inhibitors are given in Fig. 2.



H_3PO_4 $H_2PO_4^-$ HPO_4^{2-} PO_4^{3-}

H_2SO_4 HSO_4^- SO_4^{2-}

H_2CO_3 HCO_3^- CO_3^{2-}

Figure 2. MEP maps of non-protanted inhibitors at MP2/SDDALL level in water.

The negative sites of inhibitors can be easily seen from MEP maps. The proton affinities, molecular orbital (MO) characters and NBO charges of oxygen atoms are given in Table 2 except the oxygen atoms which are bonded with hydrogen atom. The PA and MO characters are calculated with Eq. (8-10) [Sayin and Karakaş; 2013a, b].

$$PA = H_{pro} - [H_{inh.} + H_{H^+}] \tag{8}$$

$$H_{H^+} = H_{H_3O^+} - H_{H_2O} \tag{9}$$

$$\%Contribution = \frac{n^2}{\Sigma n^2} x100 \tag{10}$$

where n, $H_{inh.}$, H_{pro} and H_H^+ are the coefficient of atomic orbital, the enthalpy of inhibitors, protonated inhibitors and H^+ cation, respectively.

According to the Table 2, NBO charges of donor atoms of each molecule are close to each other. Therefore, the active site cannot be determined with NBO charges. The PA is mainly negative value and the protonation is generally exothermic process. For H_2CO_3 and H_3PO_4, the protonation must be done from O(4) and O(5), respectively. For H_2SO_4, the protonation can be done from O(3) atom. Because MO% of O(3) is bigger than O(2). For HSO_4^-, O(3) and O(4) donor atoms can be used for the protonation. In addition to this result, NBO charges is close to each other and proton affinity and MO% of O(3) and O(5) is bigger than O(2). As for the SO_4^{2-}, the protonation can be done from any one of donor atoms. The NBO charges, PA and MO% is same value in this inhibitor. For HCO_3^-, the NBO charge of O(4) is more negative than O(2) and the MO% is close to each other. Therefore, O(2) can be selected for protonation. The NBO charges and PA of each donor atom is same value for CO_3^{2-}. But MO% values of O(2) and O(4) in carbonate are bigger than O(3). The protonation can be done from O(2) or O(4). For dihydrogen phosphate, O(4) can be used for protonation. Because it has more negative PA and big MO%. For HPO_4^{2-}, the protonation can be done from O(3). Because, MO% of O(3) and O(5) is bigger than O(4) and NBO charges of O(3) is more negative than O(5). As for the phosphate, the protonation can be done any donor atom.

Table 2. NBO charges, PA, MO% of non-protonated inhibitors at MP2/SDDALL level in water

Inhibitors	Donor Atoms	NBO Charge	Proton Affinity (a.u.)	MO%
H_2SO_4	O(2)	-0.854	0.029	20.360
	O(3)	-0.852	0.028	34.920
HSO_4^-	O(2)	-0.943	-0.015	6.770
	O(3)	-0.942	-0.016	25.270
	O(5)	-0.942	-0.016	25.270
SO_4^{2-}	O(2)	-1.036	-0.056	21.970
	O(3)	-1.036	-0.056	21.970
	O(4)	-1.036	-0.056	21.970
	O(5)	-1.036	-0.056	21.970
H_2CO_3	O(4)	-0.769	-0.022	25.880
HCO_3^-	O(2)	-0.912	-0.044	50.230
	O(4)	-0.931	-0.044	49.740
CO_3^{2-}	O(2)	-1.063	-0.095	33.380
	O(3)	-1.063	-0.095	33.240
	O(4)	-1.064	-0.095	33.280
H_3PO_4	O(5)	-1.122	0.003	73.410
$H_2PO_4^-$	O(4)	-1.208	-0.039	49.150
	O(5)	-1.212	-0.033	47.240
HPO_4^{2-}	O(3)	-1.293	-0.072	33.790
	O(4)	-1.293	-0.072	32.420
	O(5)	-1.291	-0.072	33.790
PO_4^{3-}	O(2)	-1.368	-0.101	25.000
	O(3)	-1.368	-0.101	25.000
	O(4)	-1.368	-0.101	25.000
	O(5)	-1.368	-0.101	25.000

3.3. Local Molecular Reactivity

The other electronic structure descriptor is the condensed Fukui functions. These parameters inform about the active regions in a molecule [Kabanda et al., 2012; Adnani et al., 2013]. For a system of N electrons, single point calculations are done at the same level of theory for corresponding N+1 and N-1 electron systems. Fukui functions are calculated using the following Eq. (11-13) and represented in Table 3.

$$f_k^+ = P_k(N+1) - P_k(N) \tag{11}$$

$$f_k^- = P_k(N) - P_k(N-1) \tag{12}$$

$$f_k^0 = \frac{P_k(N+1) - P_k(N-1)}{2} \tag{13}$$

According to Fukui functions, the more negative value of donor atom means that more active. If so, the active site can be determined by determination the more negative value of f_k^+, f_k^- and f_k^0. The natural population analysis of N-1, N and N+1 system correspond $P_k(N-1)$, $P_k(N)$ and $P_k(N+1)$, respectively.

The agreements are found between Fukui functions and Section 3.2 except $H_2PO_4^-$ and HPO_4^{2-}. For these inhibitors, NBO charges, PA and MO% values in Table 2 are close to each other. According to these results, the determination of active region is very difficult. But the active site is clearly seen by results of Fukui functions. As a result, the active sites are O(5) atoms for $H_2PO_4^-$ and HPO_4^{2-}.

Table 3. The Fukui functions of non-protonated inhibitors at MP2/SDDALL level in water

Inhibitors	Donor Atoms	$P_k(N+1)$	$P_k(N)$	$P_k(N-1)$	f_k^+	f_k^-	f_k^0
H_2SO_4	O(2)	8.416	8.854	9.014	-0.438	-0.160	-0.299
	O(3)	8.404	8.852	9.037	-0.448	-0.185	-0.317
HSO_4^-	O(2)	8.825	8.930	9.097	-0.105	-0.167	-0.136
	O(3)	8.500	8.953	9.109	-0.453	-0.156	-0.305
	O(5)	8.500	8.953	9.109	-0.453	-0.156	-0.305
SO_4^{2-}	O(2)	8.712	9.036	9.253	-0.324	-0.217	-0.271
	O(3)	8.712	9.036	9.253	-0.324	-0.217	-0.271
	O(4)	8.712	9.036	9.253	-0.324	-0.217	-0.271
	O(5)	8.712	9.036	9.253	-0.324	-0.217	-0.271
H_2CO_3	O(4)	8.072	8.770	9.080	-0.698	-0.310	-0.504
HCO_3^-	O(2)	8.743	8.997	9.187	-0.254	-0.190	-0.222
	O(4)	8.187	8.882	9.195	-0.695	-0.313	-0.504
CO_3^{2-}	O(2)	8.729	9.102	9.347	-0.373	-0.245	-0.309
	O(3)	8.729	9.102	9.347	-0.373	-0.245	-0.309
	O(4)	8.729	8.972	9.347	-0.243	-0.375	-0.309
H_3PO_4	O(5)	8.366	9.113	9.287	-0.747	-0.174	-0.461
$H_2PO_4^-$	O(4)	9.064	9.208	9.352	-0.144	-0.144	-0.144
	O(5)	8.446	9.212	9.370	-0.766	-0.158	-0.462
HPO_4^{2-}	O(3)	8.963	9.298	9.318	-0.335	-0.020	-0.177
	O(4)	8.959	9.285	9.322	-0.326	-0.037	-0.181
	O(5)	8.963	9.298	9.374	-0.335	-0.076	-0.205
PO_4^{3-}	O(2)	9.100	9.369	9.544	-0.269	-0.175	-0.222
	O(3)	9.100	9.369	9.544	-0.269	-0.175	-0.222
	O(4)	9.100	9.369	9.544	-0.269	-0.175	-0.222
	O(5)	9.100	9.369	9.544	-0.269	-0.175	-0.222

3.4. The protonated inhibitors

Inorganic inhibitors are protonated from oxygen atoms which are explained in section 3.2 and 3.3. Some electronic structure descriptors of protonated inhibitors are calculated at MP2/SDDALL in water. These parameters are given in Table 4.

Table 4. Electronic structure descriptors with MP2/SDDALL level in water for protonated inhibitors

Inhibitors	E_{HOMO}^a	E_{LUMO}^a	E_{GAP}^a	η^a	σ^b	ω	N
$H_3SO_4^+$	-15.472	-0.860	14.612	7.306	0.137	4.564	0.219
H_2SO4	-14.082	0.566	14.648	7.324	0.137	3.118	0.321
HSO_4^-	-12.592	1.928	14.520	7.260	0.138	1.958	0.511
$H_3CO_3^+$	-16.715	1.675	18.389	9.195	0.109	3.075	0.325
H_2CO_3	-13.683	3.821	17.504	8.752	0.114	1.389	0.720
HCO_3^-	-11.089	4.570	15.659	7.830	0.128	0.679	1.474
$H_4PO_4^+$	-10.536	4.360	14.895	7.448	0.134	0.640	1.562
H_3PO_4	-11.821	3.675	15.496	7.748	0.129	1.070	0.934
$H_2PO_4^-$	-13.597	2.276	15.873	7.937	0.126	2.019	0.495
HPO_4^{2-}	-16.101	0.974	17.075	8.538	0.117	3.350	0.299

[a] in eV and [b] in eV^{-1}

The results in Table 1 and Table 4 show that electronic structure descriptors are different each other. According to the results in non-protonated inhibitors, the values of E_{HOMO}, E_{LUMO}, σ decrease in protonated inhibitors while the values of E_{GAP}, η, ω, N increase in protonated inhibitors.

4. Conclusion

The highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap (E_{GAP}), sum of total NBO negative charge (TNC), hardness (η), softness (σ) and molecular volume (MV) are calculated for oxyanions. These parameters are correlated with expected inhibition rankings. The best correlation with these rankings is obtained in MP2/SDDALL level in water. The atomic charges, proton affinities, molecular orbital character analyses and Fukui functions are considered for determining the donor atom which is coordinating to proton. According to these parameters, mentioned inhibitors are protonated from the most appropriate atom. As a results, ten electronic structure descriptors are calculated for determining the ranking of inhibition efficiencies. All parameters are in a good agreement with expected rankings except MV. As theoretically, the inhibition efficiency ranking is found as $CO_3^{2-} > PO_4^{3-} > HPO_4^{2-} > HCO_3^{-} > SO_4^{2-} > H_2PO_4^{-} > H_2CO_3 > HSO_4^{-} > H_3PO_4 > H_2SO_4$.

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