A computational study of two hexitol borates as corrosion inhibitors for steel

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Abstract

Herein we investigated computationally the inhibition characteristics of sodium sorbitol borate and sodium mannitol borate on steel corrosion in aqueous media using density functional theory (DFT). To further our understanding of the role of energetic parameters on inhibition by these compounds, quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), and energy gap (ΔE) have been calculated at the B3LYP/6-311++G(d,p) basis set. The results of theoretical calculations confirm the experimental findings on the superiority of sodium sorbitol borate to protect the corrosion of steel in aqueous media compared to sodium mannitol borate.

Keywords: *corrosion, inhibitor, steel, sodium sorbitol borate, sodium mannitol borate, density functional theory.*

Introduction

Carbon steel is used for general purpose in neutral (such as water lines), in alkaline (such as boiler circuits), and in somewhat acidic environments. Corrosion by such environments is accentuated by high fluid velocity and turbulence. This is controlled by design and, if feasible and permissible, by addition of corrosion inhibitors [1–3]. The use of some prolific compounds such as chromates, phosphates, nitrites *etc.* for corrosion protection was hampered by the fact that they caused several negative effects on the environment [4].

The very nature of the reversible binding between boron acids and alcohols has been exploited in many different ways and encouraged widespread agreement on the use of some salts of boron coordination compounds as corrosion inhibitors, where ligands are polyhydroxy organic acids or sugar alcohols (polyols or polyhydric alcohols) [5]. Polyols are saccharide derivatives obtained by replacing an aldehyde group with a hydroxyl group, and classified as hydrogenated monosaccharides (*e.g.*, sorbitol, mannitol, *etc.*) and disaccharides (isomalt, maltitol, *etc.*) [6]. In addition, borax and some other alkali metal borates are present in mixtures that exhibit inhibition activity by forming buffer solutions in a basic environment. Such mixtures showing the inhibition activity of salts of boron-

coordinating compounds containing polyhydroxy organic acids or polyols (sorbitol, mannitol, pentaerythritol *etc.*) as ligand have also been preferred in recent years. The most important reason for this is the lack of toxic properties of such coordination compounds [7].

In this context, Ignash *et al.* [8] synthesized sodium mannitol borate and sodium sorbitol borate (Figure 1) by reacting some polyols, *i.e.* D-mannitol and D-sorbitol, with sodium tetraborate. They reported that the inhibition activity of these compounds, measured using gravimetric methods, was up to be 94% for corrosion of steel in the aqueous solutions.
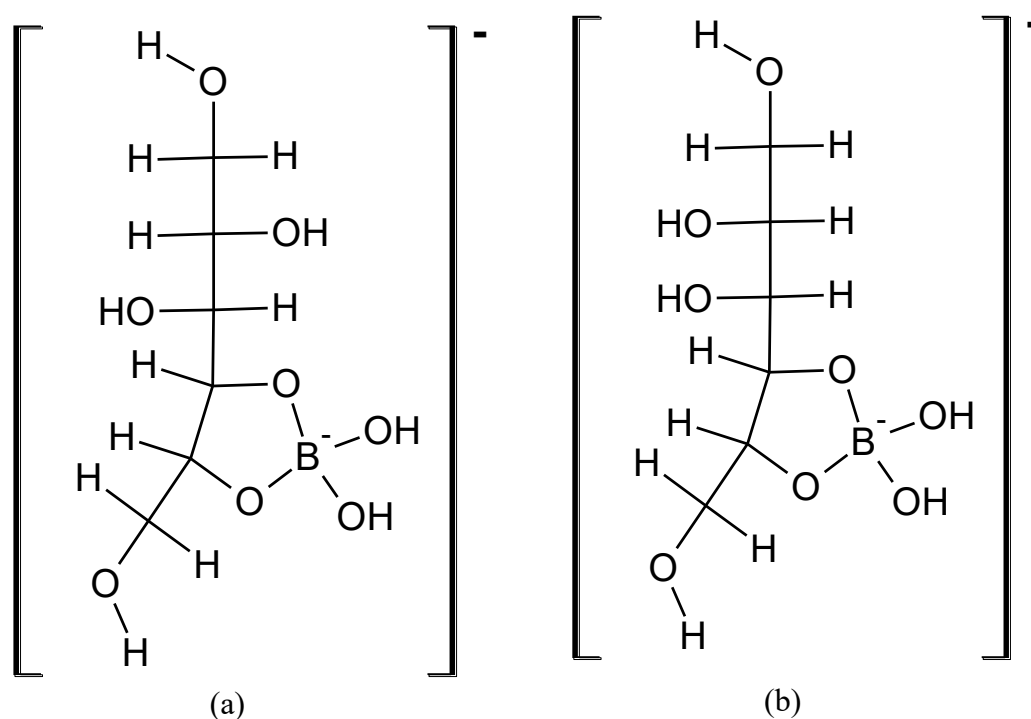

Figure 1. Molecular structure of (a) sorbitol and (b) mannitol borates.

Although much has been learned from this experimental study, an explanation from a theoretical perspective for the justification of the inhibition effects of these molecules needs to be held alongside an explicit conclusion about the underlying inhibition mechanism. Prompted by the successful application of theoretical calculations in corrosion inhibitor research [9], this paper is a further contribution to gain a better understanding of the inhibition effects of rutin and artesunate through a density functional theory (DFT) based approach. This approach allows an accurate calculation of a number of physical and chemical properties, some of which can either be compared directly to experiment or are complimentary to it [10–13].

Computational

All quantum mechanical calculations have been achieved using the Gaussian09 package [14]. Geometries of all the investigated systems (Figure 2) were optimized at the density functional theory level using the B3LYP functional (combination of exchange from Becke's three parameter hybrid exchange functional (B3) with the dynamical correlation functional of Lee, Yang and Parr (LYP)). The triple-zeta quality basis set with polarization and diffuse functions denoted 6-311G+(d,p) has been used. The bulk solvent effects have been included through the Integral Equation Formalism version of the Polarizable Continuum Model (IEF-PCM). In the study, the electronic properties of the inhibitors were investigated by calculating the effects of the frontier molecular orbital energies, the energy differences ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) between the lowest free molecular orbital (LUMO) and the highest filled molecular orbital (HOMO), and the dipole moment.
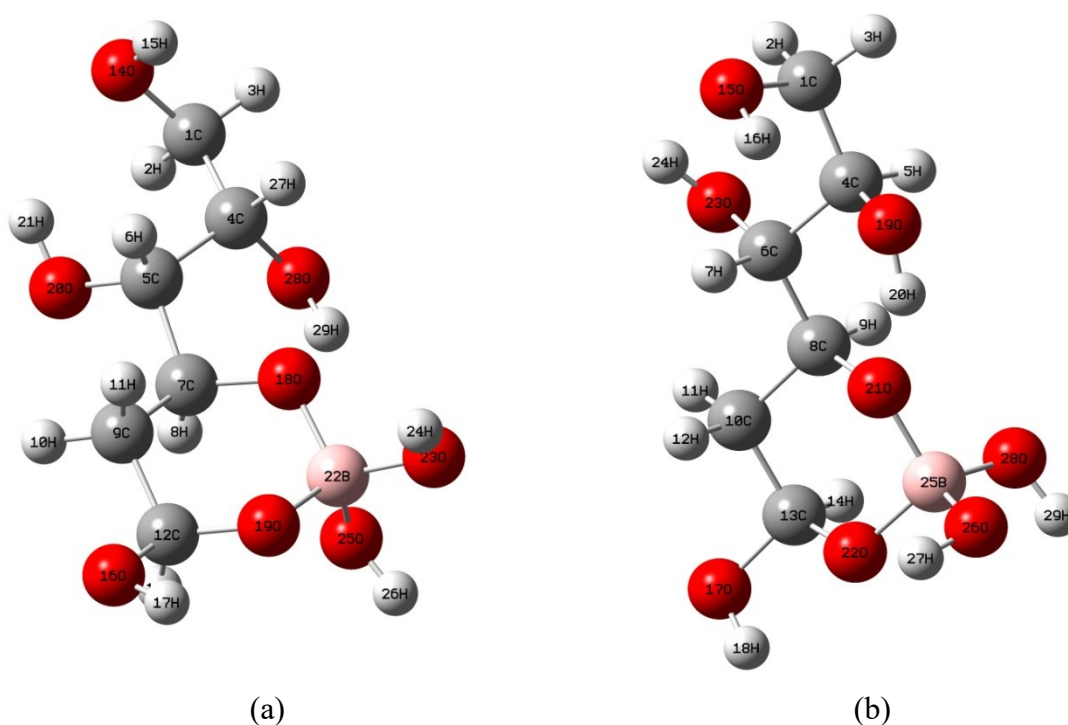

(a)   (b)

Figure 2. Optimized structures of (a) mannitol borate and (b) sorbitol borate compounds.

Results and Discussion

The inhibition effect of inhibitor compound is normally ascribed to adsorption of the molecule on metal surface. Adsorption of a molecule on a metal surface occurs through the formation of new electron orbitals between a molecule and a metal. If molecules adsorb at solid surfaces, this can occur either by chemical or by physical bonding. Chemisorption is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. On the other hand, physisorption is adsorption in which the forces involved are intermolecular forces of the same kind, and do

not involve a significant change in the electronic orbital patterns of the species involved. For molecular adsorption, both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) interactions often are of comparable strength. The corresponding molecular orbital energies allow one to estimate stability and reactivity of the studied molecules. Commonly, the atom which contributes more to the HOMO should have the stronger ability for detaching electrons, whereas, the atom which occupies the main component of the lowest unoccupied molecular orbital (LUMO) should be easier to gain electrons. Reportedly, excellent corrosion inhibitors are usually those organic compounds that not only offer electrons to the unoccupied orbital of the metal, but also accept free electrons from the metal [9].

A high value of the HOMO energy corresponds to copious donation of electrons to congruent molecules with low energy, empty molecular orbitals. Increasing values of E_{HOMO} lead to an increment in adsorption and exalts the efficiency of inhibition. The energy of the LUMO indicates the ability of the molecule to accept electrons. The lower is the value of E_{LUMO}, the more probable it is that the molecule would accept electrons. Accordingly, lower values of the energy difference (ΔE) will render good inhibition efficiency, because a large gap indicates that it is difficult to add electrons to a high LUMO and remove electrons from a deep HOMO [10–13]. Another property that makes ΔE an important chemical descriptor is the large range of energies associated with this parameter. With such a large range, small errors in the calculated ΔE are less significant. On the basis of these explanations, it is useful to compare the electronic properties.

Before the comparison of such electronic properties, it would be useful to validate the optimized geometries of the compounds. For this purpose, some selected geometric parameters of mannitol borate are compared with those only available for the crystal structure of *D*-mannitol obtained by X-ray diffraction analysis [15]. With a range of approximately 1.46–1.50 Å, the O–B bond of mannitol borate is slightly longer than typical O–O single bonds (1.48 Å). Consistent with experimental C–O bonds (1.42–1.45 Å), the C–O distances of mannitol lie in the range of 1.40–1.44 Å. It appears that the 7C–18O–22B and 12C–19O–22B angles (115.95° and 116.65°) are longer than the C–C–O angles (109.9(6)° and 108.7(6)°) of *D*-mannitol. On the other hand, the comparison of 7C–18O–22B–25O and 12C–19O–22B–23O dihedral angle distributions (73.03° and 167.49°) with refined values of *D*-mannitol (59.01° and 176.47°) yields small differences. In spite of the differences, calculated geometric parameters represent a good approximation and provide a starting point to calculate other parameters, such as the energies of the frontier molecular orbitals.

Figure 3 shows the shapes of HOMO and LUMO for the investigated molecules. It is discovered from the figure that the HOMO of sodium mannitol borate is mainly located on the O atoms of C–O and B–O single bonds, whereas the LUMO of sodium mannitol borate is primarily composed of carbon and oxygen atoms. For sodium sorbitol borate the HOMO is similar, however, the LUMO is apportioned over the longitudinal carbon–oxygen atoms, as well as boron–oxygen atoms.
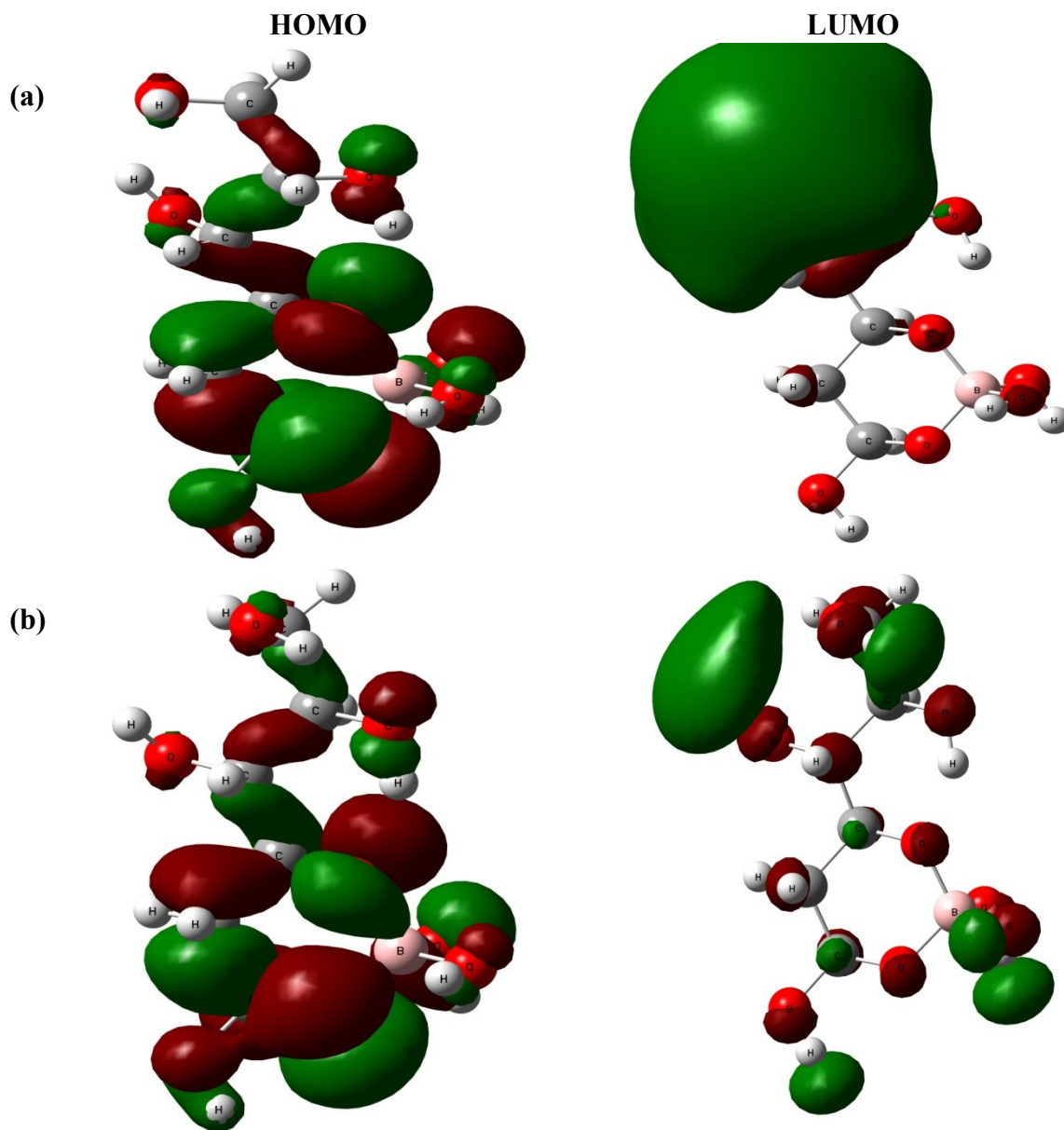
Figure 3. Frontier molecular orbitals for (a) mannitol borate and (b) sorbitol borate.

Certain quantum chemical parameters related to these molecular electronic structures, such as E_{HOMO}, E_{LUMO}, and $\Delta E = E_{LUMO} - E_{HOMO}$, have been used for the sake of comparison in Table 1. The results for E_{HOMO}, E_{LUMO} and ΔE yield that sodium sorbitol borate molecule prevails for the inhibitory action compared to sodium mannitol borate. These results also supported by the global reactivity parameters. In Table 1, global properties obtained by the frontier molecular orbital energies according to Koopmans theorem [16] are also listed. The ionization potential (I) and electron affinity (A) are given by:

$$I = -E_{HOMO} \tag{1}$$

$$A = -E_{LUMO} \tag{2}$$

In numerical applications, chemical potential μ and hardness η are commonly expressed on the basis of finite difference approximations in terms of the ionization potential I and the electron affinity A:

$$-\mu = \tfrac{1}{2}\,(I + A) = \chi \tag{3}$$

$$\eta = \tfrac{1}{2}\,(I - A) \tag{4}$$

where in Eq. 3 μ is the chemical potential and χ is the electronegativity. The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale and effectively is the power of a system to soak up electrons. The electrophilicity index ω can be expressed by:

$$\omega = \mu^2/\,2\eta \tag{5}$$

Global softness is defined as:

$$\sigma = 1\,/\,\eta \tag{6}$$

It is noted from Table 1 that the hardness of the molecules follows the order sodium mannitol borate < sodium sorbitol borate, which is the reverse of that obtained for softness. This shows that sodium sorbitol borate with the least value of global hardness (hence the highest value of global softness) is the best and *vice versa*. This is because a soft molecule is more reactive than a hard molecule. It is also important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some centre and is going to back-donate a certain amount of charge through the same centre or another one. To describe the energy change associated with these two processes, the second order simple charge transfer formula was regarded as a two-parameter expression, in which the donation and back-donation processes are differentiated through the use of the values of the chemical potential for each case, while the hardness is fixed to the value of $\mu = (\mu^+ - \mu^-)$ in both situations. Thus, according to the simple charge transfer model of Gómez *et al.* [17], "when a molecule receives a certain amount of charge, ΔN^+

$$\Delta E^+ = \mu^+ \Delta N^+ + \tfrac{1}{2}\eta(\Delta N^+)^2 \tag{7}$$

while when a molecule back-donates a certain amount of charge, ΔN^-, then:

$$\Delta E^- = \mu^- \Delta N^- + \tfrac{1}{2}\eta(\Delta N^-)^2 \tag{8}$$

If the total energy change is approximated by the sum of the contributions of Eqs. 7 and 8, and assuming that the amount of charge back-donation is equal to the amount of charge received, $\Delta N^- = -\Delta N^+$, then

$$\Delta E_T = \Delta E^+ + \Delta E^- = (\mu^+ - \mu^-)\,\Delta N^+ + \eta(\Delta N^+)^2 \tag{9}$$

The most favourable situation corresponds to the case when the total energy change becomes a minimum with respect to ΔN^+, which implies that $\Delta N^+ = -(\mu^+ - \mu^-)\,/\,2\eta$ and that";

$$\Delta E_T = -(\mu^+ - \mu^-)^2\,/\,4\eta = -\eta/4 \tag{10}$$

The data in Table 1 indicate that $\eta > 0$, $\Delta E_T < 0$. This result implies that the charge transfer to a molecule followed by back-donation from the molecule is energetically favourable. However, it is important to note that Eq. 9 does not predict that a back-donation process is going to occur; it only establishes that if both processes occur, the energy change is directly proportional to the hardness of the molecule.

During the interaction of the inhibitor molecule with bulk metal, electrons flow from the lower electronegativity molecule to the higher electronegativity metal until the chemical potential becomes equalized.

The fraction of the transferred electron, ΔN, was estimated according to Pearson [18];

$$\Delta N = \frac{\chi_m - \chi_i}{2(\eta_m + \eta_i)} \tag{11}$$

where the indices *m* and *i* refer to metal atom and inhibitor molecule, respectively. The fraction of transferred electron given in the table is calculated for Fe metal, and the experimental work function of iron (4.5 eV) [19] was employed for electronegativity, and a global hardness of zero was used due to the $I = A$ approximation for a bulk iron. If $\Delta N <$ 3.6, the inhibition efficiency increases by increasing electron-donating ability of these molecules to donate electrons to the metal surface [7]. Sodium sorbitol borate has the largest fraction of transferred electron to the iron metal, closely followed by sodium mannitol borate, in agreement with the above ordering supported by electronic parameters. The fit of the calculated dipole moments with the experimental dipole moments is also of the same accuracy, considering the values for aqueous phase. The dipole moment of sodium sorbitol borate is found to be slightly higher than that of mannitol borate, which probably increases its adsorption on the metal surface.

Conclusions

Based on the obtained data, a correlation could be established between DFT calculations between parameters related to the electronic structure of the two environmentally friendly compounds, namely sodium sorbitol borate and mannitol borate, and their corrosion inhibition properties. Comparing the theoretical and experimental data, the reliability of the B3LYP/6-311++G(d,p) method used in this study has been confirmed. The theoretical results confirm that sorbitol borate is superior to mannitol borate in the prevention of steel corrosion in aqueous media as supporting experimental data. The compromise between global reactivity parameters calculated for both gas and aqueous phase and electronic parameters also supports these findings.

Table 1. Global reactivity indexes (in eV): hardness, η, chemical potentials for electrodonating, μ^{-}, and electroaccepting, μ^{+}, processes, electrodonating power, ω^{-}, electroaccepting power, ω^{+}, net electrophilicity, $\Delta\omega^{\pm}$, and the calculated quantum chemical descriptors at the B3LYP/6-311G+(d,p) basis set in gas and aqueous phases.

Inhibitor	Phase[a]	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (E_L–E_H) (eV)	μ (D)	χ	η	ΔN	η	μ^{-}	μ^{+}	ω^{-}	ω^{+}	$\Delta\omega^{\pm}$	IE% [b]
Mannitol borate	G	–2.837	2.144	4.981	4.414	0.73	2.49	0.79	4.07	0.88	4.94	0.07	2.99	3.06	90.0
	A	–6.545	–0.196	6.349	6.877	3.37	3.44	0.19	4.10	0.90	5.00	0.09	3.05	3.14	
Sorbitol borate	G	–2.743	1.771	4.514	5.801	0.49	2.90	0.72	3.92	4.98	1.01	3.14	0.11	3.25	94.1
	A	–6.515	–0.262	6.253	7.961	3.39	3.98	0.16	3.97	5.04	1.06	3.19	0.14	3.33	

[a] G – gas phase ($\varepsilon = 1.0$), A – aqueous phase ($\varepsilon = 78.5$).
[b] Ref. [8].

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