A Theoretical Study of Carbohydrates as Corrosion Inhibitors of Iron

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In memoriam of Prof A. Klemm

The inhibitive effect of fructose, glucose, lactose, maltose, and sucrose against the iron corrosion is investigated using density functional theory at the B3LYP/6-31 G level (d) to search the relation between the molecular structure and corrosion inhibition. The electronic properties such as the energy of the highest occupied molecular orbital (HOMO), the energy of lowest unoccupied orbital (LUMO), the energy gap (LUMO–HOMO), quantum chemical parameters such as hardness, softness, the fraction of the electron transferred, and the electrophilicity index are reported. The inhibition efficiency of the investigated carbohydrates follows the trend: maltose < sucrose < lactose < fructose < glucose.

Key words: Iron; Inhibitors; Corrosion; Carbohydrates; DFT.

1. Introduction

The corrosion of metal surfaces is a phenomenon that leads to great economic losses in industry: one of the most efficient alternatives to protect metals is the use of inhibitors that are adsorbed on the metallic surface and slow down the cathodic as well as the anodic processes of dissolution of the metal [1]. The inhibition of steel corrosion in acidic media by organic inhibitors has been studied in considerable details [2 – 8]. The most efficient inhibitors are organic compounds that have π bonds and heteroatoms (sulfur, nitrogen, oxygen). These compounds adsorb on the metal surface and block the active sites thereby reducing the corrosion process [9 – 11]. The inhibition effect mainly depends on the physico-chemical and electronic properties of the organic inhibitor which relate to its functional groups, the electron density of the donor atoms, and the orbital character of the donating atoms [12]. The inhibition mechanism is generally explained by the formation of a physical and/or chemically adsorbed film on the metal surface [13]. The inhibition efficiency of an inhibitor depends on the characteristics of the environment, the nature of the metal surface, the structure of the inhibitor, and the formation of metallic complexes [14]. Many organic inhibitors have been used on different metals, such as xanthene [15, 16], triazoles [17], imidazoline [18],
pyrrolidinnoles [19], triphenyltin2-thiophene carboxylate [20], pyrazole [21], and tetrazole [22].

A number of carbohydrates have been tried as corrosion inhibitors for different metals [23 – 27]. Ali-Shattle et al. have recently reported that sucrose has a good inhibition efficiency towards iron (Libyan steel) in different mineral acids in the concentration range (0.01 – 1.5 M) at a temperature of 25 °C [23]. Chakrabarty et al. studied the effect of carbohydrates on corrosion of aluminum in nitric acid at 35 °C. Lactose is found to be the most efficient followed by fructose and glucose. Sucrose showed a very poor inhibitive effect at low concentration [24]. Maria and Mor have reported that saccarides have a moderate efficiency towards copper in nitric acid [25]. Glucose and sucrose have been successfully used as inhibitors for corrosion of aluminum in sodium hydroxide solution [26, 27].

The paper aims to give a more theoretical insight in to the effect of carbohydrates as corrosion inhibitors of iron using density functional theory (DFT) and the quantum chemical parameters that can be obtained from these calculations.

2. Computational

B3LYP, a version of the DFT method, using Becke's three-parameter functional (B3) and including a mix-
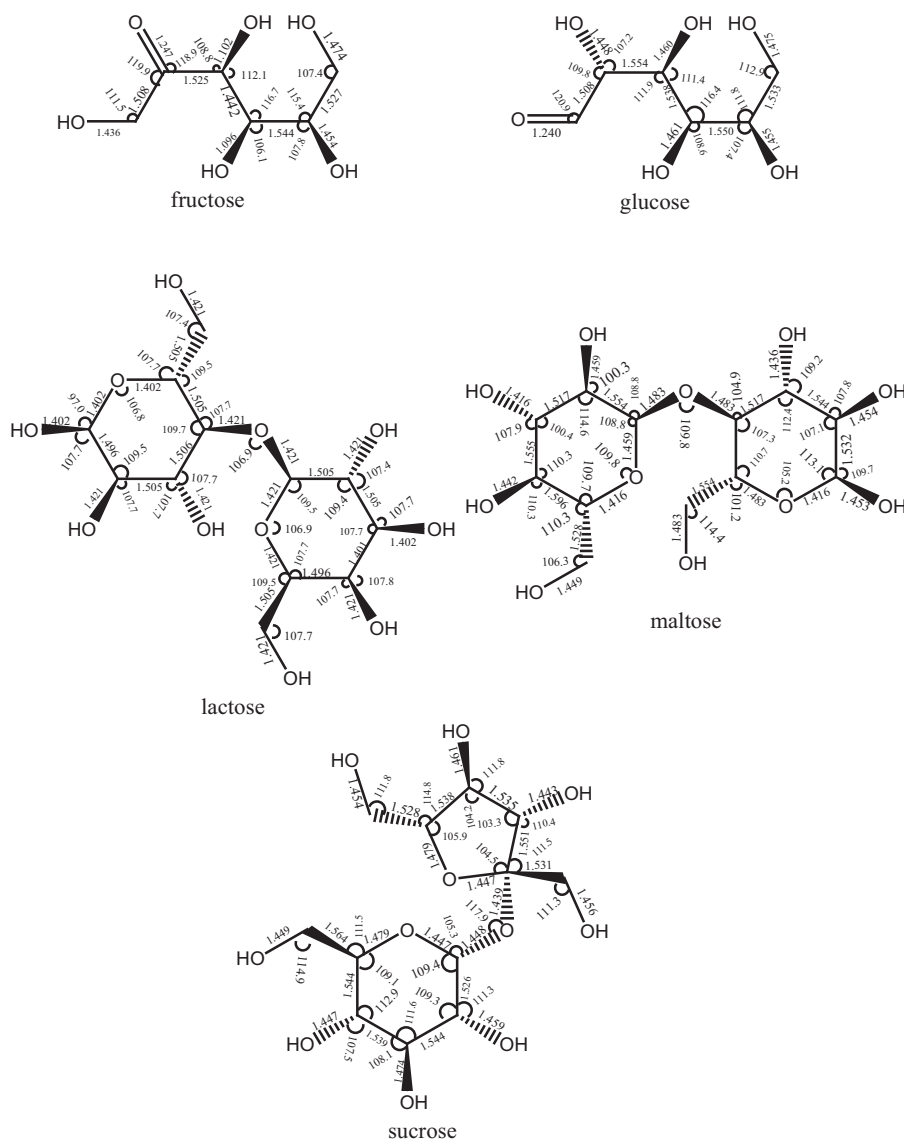
Scheme 1. Optimized geometry of the carbohydrates. Bond lengths are in Ångstrom and angles in degrees.

ture of Hartree–Fock (HF) with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP), was used in this work. The geometry of all carbohydrates under investigation was determined by optimizing all geometrical variables without any symmetrical constraints at the B3LYP/6-31G (d) level of theory [28, 29]. No imaginary frequencies were found, indicating minimal energy structures. The effect of a solvent (water) was taken into consideration using self-consistent reaction field

Table 1. Comparison between bond lengths in Ångstrom for fructose and glucose with the ones (calculated) at the DFT BLYP/DZVP level of theory [30].

Bond Distance	Fructose	Glucose
C−C (CH$_2$O)	1.527 (1.529)[a]	1.533 (1.537)[a]
C−H	1.111 (1.110)[a]	1.113 (1.120)[a]
O−H	0.983 (0.987)[a]	0.980 (0.984)[a]
C−O	1.436 (1.428)[a]	1.448 (1.454)[a]
C=O	1.247 (1.243)[a]	1.240 (1.235)[a]

[a]From [30].

Table 2. Calculated HOMO–LUMO energies of the inhibitors by the DFT method.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)
Fe	− 7.9024[a]	− 0.1510[a]
Fructose	− 7.2894	− 1.5741
Glucose	− 7.0094	− 2.1489
Lactose	− 5.2689	− 0.7548
Maltose	− 6.8439	0.6960
Sucrose	− 6.6521	0.3540

[a]From [40].

(SCRF) methods to perform calculations in aqueous solution.

3. Results and Discussion

The carbohydrate compounds under investigation are fructose, glucose, lactose, maltose, and sucrose. The optimized molecular structures of these compounds are given in Scheme 1. The geometrical parameters for the fructose and glucose (Scheme 1) indicate that there are similarities in the structure which is in agreement with recent work on the analysis of the structure and vibrational spectra of the glucose and fructose by Ibrahim et al. [30], using BLYP/DZVP level. They found that both molecules are not linear and show similarities in bond lengths and vibrational modes. The bond lengths for fructose and glucose calculated by Ibrahim et al. [30], given in Table 1, agree with the present work.

The energy of the frontier molecular orbitals, i.e. E_{HOMO} and E_{LUMO}, the energy gap ΔE, the hardness η, the softness σ, the fraction of the electron transferred ΔN, and the electrophililcity index ω were calculated for these compounds. According to molecular orbital theory [31], E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential I and the electron affinity A, respectively, by the following relations:

$$I = -E_{\text{HOMO}} \text{ and } A = -E_{\text{LUMO}}.$$

The absolute electronegativity X, the absolute hardness η of the inhibitor, the softness σ and the electrophilicity index ω are given by [32]

$$X = \left(\frac{I+A}{2}\right), \ \eta = \left(\frac{I-A}{2}\right), \ \sigma = \frac{1}{\eta}, \ \omega = \frac{\mu^2}{2\eta},$$

where μ represent the chemical potential and is assumed to be equal to the negative of the electronegativity X [32]. ω is the electrophilicity index, which was proposed by Parr et al. [33, 34] as a measure of the electrophilic power of a molecule.

When two systems, metal and inhibitor, are brought together, electrons will flow from lower X (inhibitor) to higher X (metal) until the chemical potentials become equal. The obtained values of X and η are used to calculate the fraction of the electron transferred, ΔN, from the inhibitor to the metallic surface as follows [35]:

$$\Delta N = \frac{X_{\text{metal}} - X_{\text{inh}}}{2(\eta_{\text{metal}} + \eta_{\text{inh}})},$$

where X_{metal} and X_{inh} denote the absolute electronegativity of metal and inhibitor, respectively, and η_{metal} and η_{inh} denote the absolute hardness of metal and inhibitor, respectively. The difference in eleceronegativity drives the electron transfer, and the sum of the hardness parameters acts as resistance [32].

The calculated results of the energies of frontier molecular orbitals for the inhibitors are given in Table 2.

According to the frontier molecular orbital (FMO) theory, the chemical reactivity is a function of the interaction between the HOMO and LUMO levels of the reacting species [36, 37] E_{HOMO} is a quantum chemical parameter which is associated with the electron donating ability of the molecule. A high value of E_{HOMO} is likely to indicate a tendency of the molecule to donate electrons to the appropriate acceptor molecule of low empty molecular orbital energy [38]. The energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electrons [39]; so the lower the value of E_{LUMO}, the more the molecule accepts electrons. Thus the binding ability of the inhibitor to the metal surface increases with increasing HOMO and decreasing LUMO energy values. The energies of HOMO and LUMO [40] for iron were compared to the values calculated for the carbohydrate compounds to determine the type of the interaction. LUMO–HOMO gaps for the interaction iron–inhibitors are given in

Table 3. HOMO–LUMO gap interaction of iron-inhibitor by the DFT method.

Inhibitors	$\text{LUMO}_{\text{inh}} - \text{HOMO}_{\text{Fe}}$ (eV)	$\text{LUMO}_{\text{Fe}} - \text{HOMO}_{\text{inh}}$ (eV)
Fructose	6.3283	7.1384
Glucose	5.7535	6.8584
Lactose	7.1476	5.1179
Maltose	8.5984	6.6929
Sucrose	8.2564	6.5011

Table 4. Calculated quantum chemical parameters for the inhibitors.

Quantum parameter	Fructose	Glucose	Lactose	Maltose	Sucrose
E_{HUMO} (eV)	−7.2894	−7.0094	−5.2689	−6.8439	−6.6521
E_{LUMO} (eV)	−1.5741	−2.1489	−0.7548	0.6960	0.3540
ΔE_{gap}	5.7153	4.8605	4.5141	7.5399	7.0061
I (eV)	7.2894	7.0094	5.2689	6.8439	6.6521
A (eV)	1.5741	2.1489	0.7548	−0.6960	−0.3540
X (eV)	4.4317	4.5791	3.0118	3.0739	3.1490
η (eV)	2.8576	2.4302	2.2570	3.7699	3.5030
σ	0.3499	0.4115	0.4430	0.2652	0.2854
ΔN	0.0300	0.0438	0.0827	0.0623	0.0624
ω	3.4364	4.3140	2.0095	1.2532	1.4154

$X_{Fe} = 4.0267$, $\eta_{Fe} = 3.8757$

Table 3, and all computed quantum chemical parameters are given in Table 4.

From Table 3, it can be seen that iron will act as a Lewis base while the inhibitors fructose and glucose act as a Lewis acids. So iron will utilize the HOMO orbital to initiate the reaction with the LUMO orbital of the fructose and glucose. The interaction will have a certain amount of ionic character because the values of the $LUMO_{inh}$–$HOMO_{Fe}$ gap approximately fall between 5 and 6 eV.

A strong covalent bond can be expected only if the $LUMO_{inh}$–$HOMO_{Fe}$ gap is approximately zero [41, 42]. However, the inhibitors lactose, maltose, and sucrose act as a base and iron acts as acid (Table 3). Thus fructose and glucose act as cathodic inhibitors while lactose, maltose, and sucrose act as anodic inhibitors.

The separation energy, $\Delta E_{gap} = (E_{LUMO} - E_{HOMO})$, is an important parameter (Table 4) and it is a function of the reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE_{gap} decreases, the reactivity of the molecule increases leading to an increase of the inhibitor efficiencies [43]. The effectiveness of the carbohydrate compounds under investigation as inhibitors has been further addressed by evaluating the global reactivity parameters. The electronegativity X, the global chemical hardness η, the global softness σ, the fraction ΔN of electrons transferred from the inhibitor to iron, and the electrophilicity ω are tabulated in Table 4.

The bonding tendencies of the inhibitors towards the metal atom can be discussed in terms of the Hard-Soft-Acid–Base (HSAB) and the frontier-controlled interaction concepts [44, 45]. The general rule suggested by the principle of HSAB is that hard acids prefer to co-ordinate to hard bases and soft acids prefer to co-ordinate to soft bases. Metal atoms are known as

soft acids [15]. Hard molecules have a high HOMO–LUMO gap and soft molecules have a small HOMO–LUMO gap [46], and thus soft bases inhibitors are the most effective ones for metals [43]. So, fructose, glucose, and lactose which have the lowest energy gap and the highest softness are expected to have the largest inhibition efficiency as compared to maltose and sucrose [23, 24]. This could also be confirmed by calculating another quantum chemical parameter, σ, which measures the softness of the molecule and so its reactivity. From Table 4, it can be observed that fructose, glucose, and lactose have larger σ values than maltose and sucrose. Table 4 also presents the hardness values η obtained for the carbohydrates. We note that maltose and sucrose have larger hardness values than fructose, glucose, and lactose, which is the reverse of what was obtained for softness. This shows that the inhibitor with the smallest value of global hardness (hence the highest value of global softness) is the best. This is because a soft molecule is more reactive than a hard molecule [47].

The fraction ΔN of electrons transferred from the inhibitor to the iron was also calculated and tabulated in Table 4. It is found that the donation of electrons by lactose, maltose, and sucrose to the iron is higher than that of fructose and glucose; this is because they have many donor atoms that can donate electrons to the iron (anodic inhibitors).

The electrophilicity index ω shows the ability of the inhibitor molecules to accept electrons from iron (Table 4). It can be seen that glucose and fructose exhibit the highest value of electrophilicity as compared to those of lactose, sucrose, and maltose, which confirms their high capacity to accept electrons. This is because of the low E_{LUMO} of glucose ($E_{LUMO} = -2.1489$ eV) and fructose ($E_{LUMO} = -1.5741$ eV) compared to that

of lactose, maltose, and sucrose [39], i. e. iron acts as Lewis base while glucose and fructose act as Lewis acids (cathodic inhibitor). Thus, the unoccupied d orbitals of the iron atoms can accept electrons from the inhibitor molecule to form a coordinate bond. Also the inhibitor molecule can accept electrons from the iron atom with its anti-bonding π-orbitals to form back-donating bonds. These donation and back-donation processes strengthen the adsorption of glucose and fructose onto the iron surface and increase the inhibition efficiency [47]. This agrees with the recent experimental work of Ali-Shattle et al. [23] on iron (Libyan steel), indicating that sucrose is a good inhibitor for iron because of its decomposing into glucose and fructose.

4. Conclusion

We conclude that glucose and fructose can be a good inhibitor for iron and to a lesser extent lactose, sucrose, and maltose. In fact, upon addition of sucrose as inhibitor to iron, it will decompose into glucose and fructose. Sucrose will therefore be a good effective inhibitor and even the remaining sucrose has certain inhibition efficiency. This agrees with the recently published experimental work [23]. Also sucrose is cheap and safe to use. This study, thus displays a good correlation between theoretical and experimental data which confirms the reliability of the DFT method to study the inhibition of corrosion of metal surfaces.

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