

Original Research Article

DFT Calculations on Corrosion Inhibition of Aluminum by Some Carbohydrates

Abstract

We have performed a DFT calculations on glucose, fructose, lactose, maltose and sucrose as corrosion inhibitors of aluminum with complete optimization of geometries using B3LYP/6-31 G level (d, p) to find a relation between the molecular structure and corrosion inhibition. Frontier orbitals and quantum parameters together with calculated thermodynamic function ΔG for adsorption of the inhibitors on aluminum are reported. Glucose and fructose are found to be the most efficient, followed by lactose and maltose. Sucrose shows poor inhibitive effect.

Keywords: Aluminum, DFT, Carbohydrates, Inhibitors, Corrosion

1. Introduction

Aluminum has a large number of applications as an alloyed or pure metal and also enters valuable electrical industrial applications because of its negative value of standard electrode potential [1]. In recent years, owing to the growing interest towards the protection of the environment and the hazardous effects of using chemicals, the traditional approach of corrosion inhibitors has gradually changed. Aspects to be taken into account in the development of corrosion inhibitors are their toxicity and impact on environmental pollution.

Natural products have been studied extensively as corrosion inhibitors both in product mixtures extracted from natural sources such as plants or essentially pure products derived from animals or plants. There has been a large number of research articles employing green corrosion inhibitors [2, 3].

Carbohydrates have been tried as corrosion inhibitors for different metal/electrolyte systems [4-7]. Ali-Shattle *et al.* have reported that sucrose has good inhibition efficiency towards iron in different mineral acids at a temperature of 25 °C [4a]. Chakrabarty *et al.*, studied the effect of carbohydrates on corrosion of aluminum in nitric acid at 35 °C. Glucose is a better inhibitor than fructose. Lactose is found to be the most efficient than sucrose. Sucrose showed a

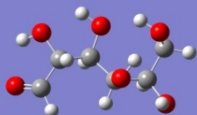
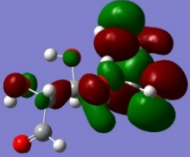
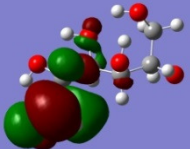
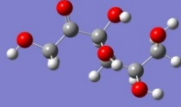
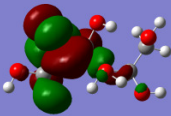
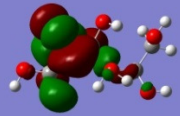
very poor inhibitive effect at low concentration [4b]. Maria and More have reported that saccharides have a moderate efficiency towards copper in nitric acid [5a]. Glucose and sucrose show good inhibitors for corrosion of aluminum [5b, 5c].

The aim of this paper is to give more theoretical insight to the glucose, fructose, lactose, maltose and sucrose in order to search a relation between the molecular structure of these compounds and the corrosion inhibitions of Aluminum. Also, to compare these calculated results with the previous work on the corrosion inhibition of iron [6].

Density functional theory DFT/B3LYP (G 09, Revision A.09) [7] calculations, and the quantum parameters that can be obtained from these calculations together with calculated Gibbs function ΔG for adsorption of the inhibitors on aluminum were used in this work.

1. Results and Discussion

The carbohydrate compounds under investigation are glucose, fructose, lactose, maltose and sucrose are shown in Fig. 1, after optimization, together with their HOM and LUMO orbitals.

Inhibitor	Structure	HOMO	LUMO
Glucose			
Fructose			

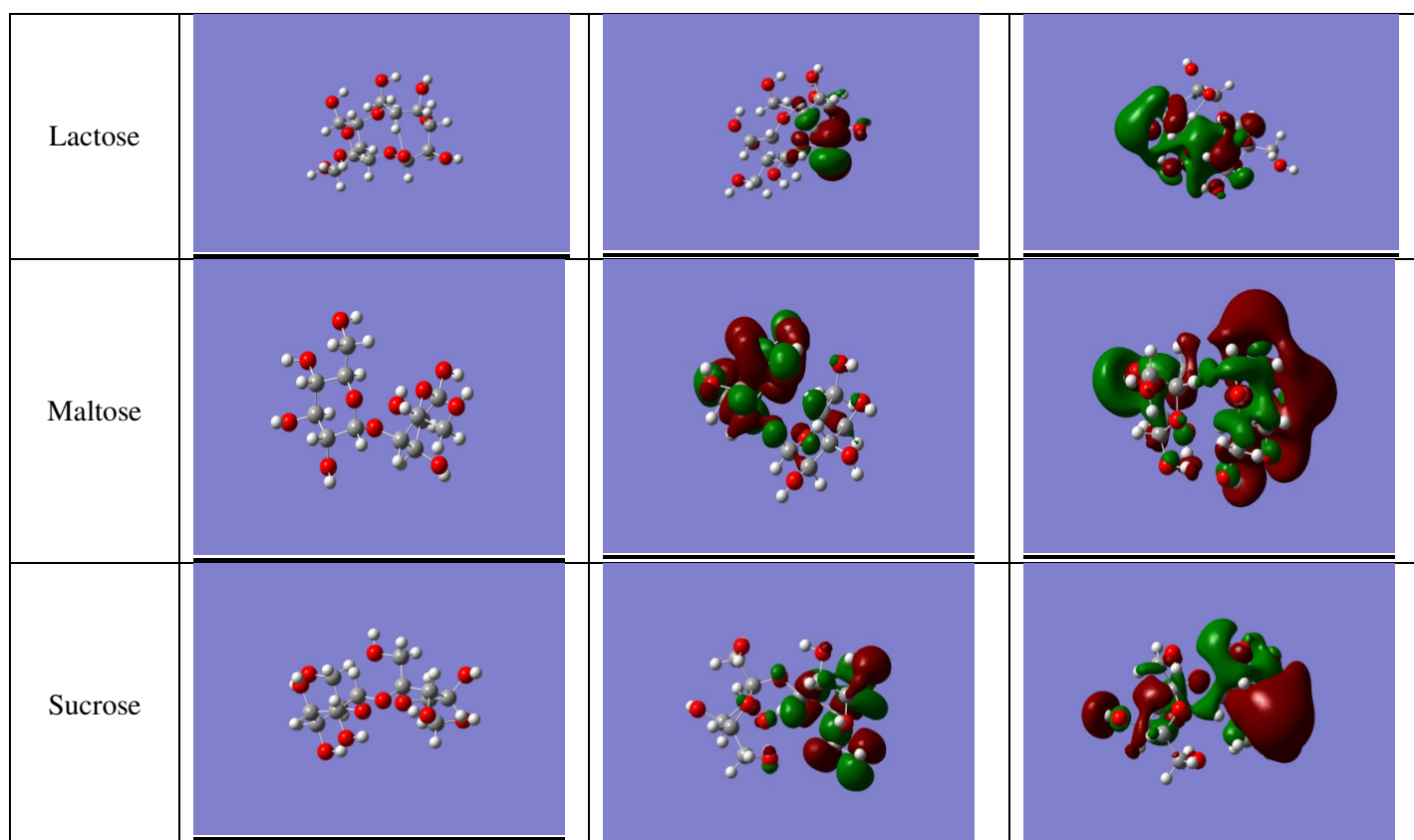


Figure 1: Optimized structures of inhibitors with their HOMO and LUMO

The energy of the frontier molecular orbitals, the energy gap (ΔE), the hardness (η), the softness (σ). The electrophilicity index (ω), the fraction of the electron transferred (ΔN), together with the ΔG of adsorption of inhibitors on aluminum were calculated for these compounds. According to molecular orbital theory [8], the E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A) respectively:

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

The absolute electronegativity (X), the absolute hardness (η) of the inhibitor, the softness (σ) and the electrophilicity index (ω) are given by [9a]:

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

where μ represent the chemical potential and is assumed to be equal to the negative of electronegativity (X) [9b]. ω is the electrophilicity index, which was proposed by Parr [9b] 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 metallic surface as follow [10]:

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

where X_{metal} and X_{inh} denote the absolute electronegativity of metal and the inhibitor, respectively, η_{metal} and η_{inh} denote the absolute hardness of metal and the inhibitor, respectively. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as resistance [9a]. The calculated results of the energies of frontier molecular orbitals for the inhibitors are given in Table 1.

Table 1. The calculated (HOMO-LUMO) energies of the inhibitors by DFT method

compounds	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$
Al	-5.9857 ^a	-0.4328 ^a
Glucose	-6.8975	-1.6403
Fructose	-6.7299	-0.5208
Lactose	-4.4610	0.0644
Maltose	-6.7906	1.1249
Sucrose	-6.5906	1.0196

^a From Ref. [14]

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 [11]. E_{HOMO} is associated with the electron donating ability of the molecule. A high value of E_{HOMO} indicates a tendency of the molecule to donate electrons to the appropriate acceptor molecule of

low empty molecular orbital energy [12]. The energy of the lowest unoccupied molecular orbital, E_{LUMO} , indicates the ability of the molecule to accept electron [13]; 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 [14] for aluminum were compared to the values calculated for the carbohydrate compounds to determine the type of the interaction. LUMO-HOMO gaps for the interaction aluminum-inhibitors are given in Table 2, and all computed quantum chemical parameters are given in Table 3.

From Table 2, it can be seen that aluminum will act as a Lewis base while the inhibitors glucose and fructose act as a Lewis acid. So aluminum will utilize the HOMO orbital to initiate the reaction with LUMO orbital of the glucose and fructose. The interaction will have a certain amount of ionic character because the values of $\text{LUMO}_{\text{inh}} - \text{HOMO}_{\text{Fe}}$ gap approximately fall between 4 and 5 eV.

Table 2. HOMO-LUMO gap interaction of Al with the inhibitors.

Inhibitors	$\text{LUMO}_{\text{inh}} - \text{HOMO}_{\text{Al}}$ (eV)	$\text{LUMO}_{\text{Al}} - \text{HOMO}_{\text{inh}}$ (eV)
Glucose	4.3454	6.4647
Fructose	5.4649	6.2971
Lactose	6.0501	4.0282
Maltose	7.1106	6.3578
Sucrose	7.0053	6.1578

Strong covalent bond can be expected only if the $\text{LUMO}_{\text{inh}} - \text{HOMO}_{\text{Fe}}$ gap is approximately zero [15]. The interactions of Al with the inhibitors were found to be stronger than that of Fe [6]; may be due to the smaller energy gap of Al (5.5529 eV) as compared to that of Fe (7.7514 eV). The inhibitors lactose, maltose and sucrose act as a Lewis base and aluminum acts as Lewis acid (Table 2). Thus fructose and glucose act as cathodic inhibitors while lactose, maltose and sucrose act as anodic inhibitors.

The separation energy, $\Delta E_{\text{gap}} = (E_{\text{LUMO}} - E_{\text{HOMO}})$, is an important parameter (Table 3) and it is a function of the reactivity of the inhibitor molecule towards the adsorption on metallic surface. As energy gap (ΔE_{gap}) decreases, the reactivity of the molecule increases leading to an

increase of the inhibitor efficiencies [16]. The effectiveness of the carbohydrate compounds under investigation as inhibitors has been further addressed by evaluating the reactivity parameters. The electronegativity, X , the chemical hardness, η , the softness, σ , the fraction of electrons transferred, ΔN , and the electrophilicity, ω , are tabulated in Table 3.

Table 3. The calculated quantum chemical parameters for the inhibitors

Quantum parameter	Glucose	Fructose	Lactose	Maltose	Sucrose
$E_{\text{HOMO(eV)}}$	- 6.8975	- 6.7299	- 4.4610	- 6.7906	- 6.5906
$E_{\text{LUMO(eV)}}$	- 1.6403	- 0.5208	0.0644	1.1249	1.0196
ΔE_{gap}	5.2572	6.2091	4.5254	7.9155	7.6102
$I(\text{eV})$	6.8975	6.7299	4.4610	6.7906	6.5906
$A(\text{eV})$	1.6403	0.5208	-0.0644	- 1.1249	- 1.0196
$\chi(\text{eV})$	4.2689	3.6253	2.1983	2.8328	2.7855
$\eta(\text{eV})$	2.6286	3.1045	2.2627	3.9577	3.8051
σ	0.3804	0.3221	0.4419	0.2526	0.2628
ΔN	-0.0980	-0.0353	0.1003	0.0279	0.0321
ω	3.4663	2.1167	0.9197	1.0138	1.0195
$X_{\text{Al}} = 3.2092 \quad \eta_{\text{Al}} = 2.7764$					

The bonding tendencies of the inhibitors towards the metal atom can be discussed in terms of the HSAB (Hard-Soft-Acid-Base) and the frontier-controlled interaction concepts [17, 18]. 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 [19]. Hard molecules have a high HOMO–LUMO gap and soft molecules have a small HOMO–LUMO gap [20], and thus soft bases inhibitors are the most effective ones for metals [16]. 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. 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 3, it can be observed that fructose, glucose and lactose have the larger values than maltose and sucrose. This shows that the inhibitor

with the highest value of softness is the best. This is because a soft molecule is more reactive than a hard molecule [21].

The fraction of electrons transferred (ΔN), was also calculated and tabulated in Table 3. ΔN values of fructose, glucose and lactose are greater than that of maltose and sucrose. The electrophilicity index, (ω), shows the ability of the inhibitor molecules to accept electrons from aluminum (Table 3). It can be seen that fructose and glucose 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 and fructose compared to that of lactose, maltose and sucrose. i.e. aluminum acts as Lewis base while fructose and glucose act as Lewis acids (cathodic inhibitor).

The ΔG values for adsorption of the investigated carbohydrates on aluminum surface are calculated and given in Table 4.

Table 4. Calculated ΔG (kJmol^{-1}) values of the investigated inhibitors.

Inhibitors	Cathodic Inhibitors	Anodic Inhibitors
Glucose	-102.2561	
Fructose	-40.1539	
Lactose		-97.5525
Maltose		-36.3228
Sucrose		-40.8873

All ΔG values are negative indicating spontaneous process especially glucose and fructose. The difference between physisorption and chemisorption lies in the magnitude of Gibbs free energy changes [22-26]. Generally, the ΔG value is in the range of 0 to -40 kJmol^{-1} for physical adsorption and -80 to -400 kJmol^{-1} for chemical adsorption. The suggested mechanism for lactose, maltose and sucrose is physical adsorption because ΔG is in the range of -36.3228 to $-97.5525 \text{ kJmol}^{-1}$, while glucose and fructose give rise to the mechanism of chemisorption because ΔG in the range of -117.9524 to $-132.1742 \text{ kJmol}^{-1}$ [26].

For cathodic inhibitor, ΔG of glucose ($-132.1742 \text{ kJmol}^{-1}$) is more negative than that of fructose ($-117.9524 \text{ kJmol}^{-1}$) (Table 4) due to the interaction of $(\text{LUMO})_{\text{inh}} - (\text{HOMO})_{\text{Al}}$ of glucose (3.836 eV) is stronger than that of fructose (4.4116 eV) as shown in Table 2. This, also agrees with calculated values of (ΔN) and (ϵ) given in Table 3, where (ΔN) and (ϵ) values of glucose are greater than that of fructose, in good agreement with experimental work [4b].

For anodic inhibitor, ΔG of lactose is more negative than that of maltose and sucrose because strong interaction of $(\text{LUMO})_{\text{Al}} - (\text{HOMO})_{\text{inh}}$ compared to that of maltose and sucrose (Table 2). Also the values of (ΔN) and (ϵ) are greater than that of maltose and sucrose (Table 3) which agrees with experimental work [4b]. Therefore, the inhibition efficiency follows the trend: glucose > fructose > lactose > maltose > sucrose.

Conclusion

All ΔG values are negative indicate spontaneous adsorption process. The investigated carbohydrates show good interaction with aluminum better than that with iron. Also it can be concluded that glucose and fructose could be a good inhibitor for aluminum followed by lactose, maltose and sucrose. This agrees with the experimental results.

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