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DFT Calculations on Corrosion Inhibition of Aluminum by Some Carbohydrates

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Authors' contributions

This work was carried out in collaboration between all authors. Author SMK designed the study, wrote the protocol and supervised the work. Authors GMAM and NMA carried out all theoretical work and performed the statistical analysis. Author SMK managed the analyses of the study. Author GMAM wrote the first draft of the manuscript. Author NMA managed the literature searches and edited the manuscript. All authors read and approved the final manuscript.

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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.

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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 are to be taken into account in the development of corrosion inhibitors are their toxicity and impact on environmental pollution.

Natural products were studied considerably as corrosion inhibitors of metals by using crude extract of different sources such as essentially pure products derived from animals or plants. So that, there has been a large number of research articles employing natural products as a green corrosion inhibitor [2,3].

Carbohydrates have been tried as corrosion inhibitors for different metal/electrolyte systems [4-7]. Ali-Shattle et al. [4a] have reported that sucrose has good inhibition efficiency towards iron in different mineral acids at a temperature of 25℃. Chakrabarty et al. [4b], studied the effect of carbohydrates on corrosion of aluminum in nitric acid at 35℃. 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. Maria and Mor have reported that saccharides have a moderate efficiency towards copper in nitric acid [5a]. Krishnan and Subramanyan [5b] showed that Glucose and sucrose showed good inhibitors for corrosion of aluminum in alkaline solution.

The aim of this paper was to give more theoretical insights to the glucose, fructose, lactose, maltose and sucrose in order to search a relationship between the molecular structure of these compounds and the corrosion inhibitions of aluminum. Also, this paper was to compare these calculated results with 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.

2. RESULTS AND DISCUSSION

The carbohydrate compounds under investigation and their structures are shown in Fig. 1, after optimization and with their HOMO-LUMO orbitals.

The energy of the frontier molecular orbitals, the energy gap (Δ *E*), the hardness (η), the softness (σ), The electrophililcity index (ω), the fraction of the electron transferred (Δ *N*), 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:

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

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

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

where μ represent the chemical potential and is assumed to be equal to the negative of electronegativity (*X*) [9]. ω is the electrophilicity index, which was proposed by Parr [9] 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, (Δ *N*), 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 [9]. The calculated results of the energies of frontier molecular orbitals for the inhibitors are given in Table 1.

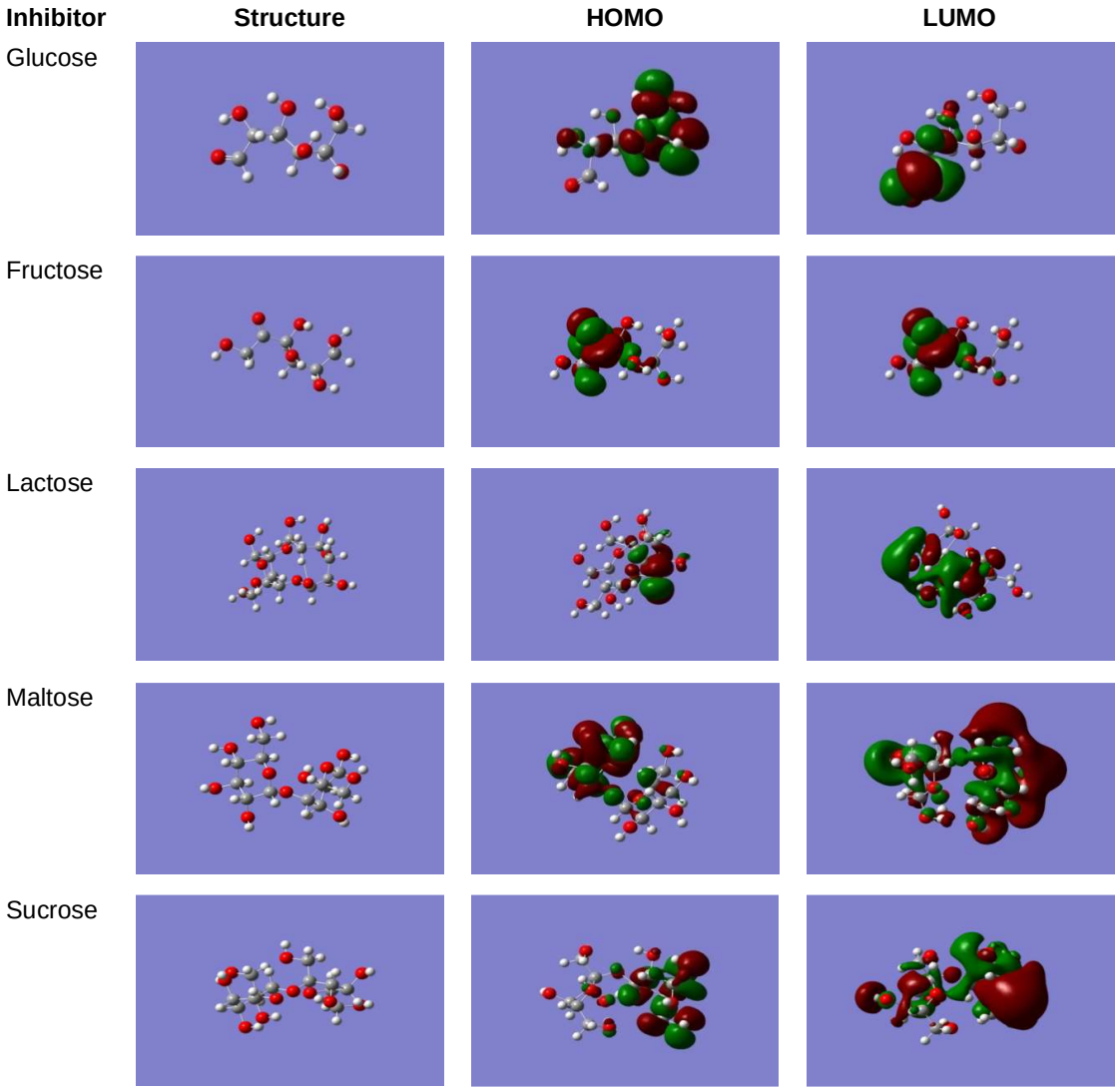

Fig. 1. Optimized structures of inhibitors with their HOMO and LUMO

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.

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

Inhibitors	$LUMO_{inhib}$ - $HOMO_{Al}$ (eV)	$LUMO_{Al}$ – $HOMO_{inhib}$ (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

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 $LUMO_{inh}$ – $HOMO_{Al}$ gap approximately fall between 4 to 5 eV.

Strong covalent bond can be expected only if the $LUMO_{inh}$ – $HOMO_{Fe}$ gap is approximately zero [15]. The interactions of Al with the inhibitors were found to be stronger than that of Fe [6] which may be due to the smaller energy gap ($E_{LUMO} - E_{HOMO}$) 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, $\Delta E_{gap} = (E_{LUMO} - E_{HOMO})$, 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 para-meters. 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.

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 and glucose have the larger values of electrophilicity than lactose, maltose and sucrose. This shows that the inhibitor with the highest value of softness is the best as it is more reactive than a hard molecule [21].

Table 3. The calculated quantum chemical parameters for the inhibitors

Quantum parameter	Glucose	Fructose	Lactose	Maltose	Sucrose
$E_{HOMO(ev)}$	- 6.8975	- 6.7299	- 4.4610	- 6.7906	- 6.5906
$E_{LUMO(eV)}$	- 1.6403	- 0.5208	0.0644	1.1249	1.0196
ΔE_{gap}	5.2572	6.2091	4.5254	7.9155	7.6102
I(ev)	6.8975	6.7299	4.4610	6.7906	6.5906
A(ev)	1.6403	0.5208	-0.0644	- 1.1249	- 1.0196
X(ev)	4.2689	3.6253	2.1983	2.8328	2.7855
ή(ev)	2.6286	3.1045	2.2627	3.9577	3.8051
σ	0.3804	0.3221	0.4419	0.2526	0.2628
∆N	-0.0980	-0.0353	0.1003	0.0279	0.0321
ω	3.4663	2.1167	0.9197	1.0138	1.0195

$X_{Al} = 3.2092$ $\eta_{Al} = 2.7764$

The fraction of electrons transferred (Δ*N*), was also calculated and tabulated in Table 3. Δ*N* 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 to 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 ∆G values for adsorption of the investigated carbohydrates on aluminum surface are calculated and given in Table 4.

Table 4. Calculated ∆G (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 ∆G 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 [22-25]. Generally, the ∆G 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 ∆G is in the range of -36.3228 to -97.5525kJmol^{-1}, while glucose and fructose give rise to the mechanism of chemisorption because ∆G in the range of -117.9524 to -132.1742 kJmol^{-1} [26].

For cathodic inhibitor, ∆G of glucose (-132.1742 kJmol^{-1}) is more negative than that of fructose (-117.9524 kJmol^{-1}) (Table 4) due to the interaction of (LUMO)inh –$(HOMO)_{Al}$ 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 (∆ N) and (*ω*) given in Table 3, where (∆ N) and (*ω*) values of glucose are greater than that of fructose, in good agreement with experimental work [4].

For anodic inhibitor, ∆G of lactose is more negative than that of maltose and sucrose because of strong interaction of $(LUMO)_{Al}$ - $(HOMO)_{inh}$ compared to that of maltose and sucrose (Table 2). Also the values of (∆ N) and (*ω*) 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.

3. CONCLUSION

i) All ∆G values are negative which indicate spontaneous adsorption process.
ii) The investigated carbohydrates show better interaction with aluminum than that with iron.
iii) It can be concluded that glucose and fructose could be a good inhibitor for aluminum followed by lactose, maltose and sucrose as it agrees with the experimental results.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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