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THEORETICAL STUDY OF STARCH AS A NOVEL SUBSTRATE FOR PbS

A. DE LEON[a*], R. RAMÍREZ-BON[b], S. J. CASTILLO[c]
[a]*Departamento de Ciencias Químico-Biológicas, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, Hermosillo, Sonora, México*
[c]*Departamento de Investigación en Física, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, Hermosillo, Sonora, México*

Starch is a natural product that has been utilized in the green synthesis of metals and semiconductors. In addition, it can aid in obtaining products with higher purity. However, the interactions involved between the metals and starch have not been studied previously. Computations have been performed at the MP2/lanl2dz level of theory for systems of Pb/PbS and the principal components of starch: amylose and amylopectin. Results show there is a favorable interaction for both polysaccharides and Pb/PbS, opening a window of possibilities of producing other chalcogenides with starch as a substrate.

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Keywords: PbS, amylose, amylopectin

1. Introduction

Starch is a natural semi-crystalline biopolymer constituted by two types of macromolecules: amylose and amylopectin. Most of the green plants produce starch in the form of granules with size between 2 and 100 mm, depending on the botanical origin. These granules are constituted by growth rings in alternating semi-crystalline and amorphous concentric spherical shells [1]. The highly branched amylopectine macromolecule is the origin of the semi-crystalline nature of starch [2]. Being a natural product it is considered a renewable, biodegradable, low cost and high availability biopolymer. It is an essential ingredient in the food industry with other applications in the papermaking, adhesives, bioplastics, etc. industries. In the last few years, starch has attracted an increasing interest for the green synthesis of metal [3-7] and semiconductor nanostructures [8-12]. In the case of metals, such as silver, starch plays the role of stabilizing agent avoiding the aggregation of nanoparticles during the chemical reduction synthesis process, which otherwise coalesce and aggregate due to their high surface energy. For this, starch is used together with a reducing agent for silver ions, such as glucose [4] or ascorbic acid [5], to convert them into silver atoms, which are the first nuclei centers for the formation of the metal nanoparticles. Although, in some papers [3,7], it is reported the dual role of starch as reducing and stabilizing agents in very simple synthesis processes of silver nanoparticles. Thus, the characteristics of starch make it a convenient alternative to replace conventional toxic reducing agents and organic solvents employed in the synthesis processes of metal nanoparticles. The interaction of starch with metal cations to support its use as reducing and stabilizing agent has been explained in very general terms. It is argued that the linear amylose and branched amylopectine macromolecules of starch and their modifications after hydrolization in aqueous solution, contain chemical groups capable of reducing and stabilizing metal nanoparticles [7].

Regarding the interaction of starch with heavy metals, some papers report the use of starch-based sorbents to remove heavy metals such as Cd, Cu, Pb, Zn, etc from aqueous solutions [13-14]. On the other hand, starch has also been used in the green synthesis of ZnO porous spheres [8], starch capped CdS nanoparticles [9-10], CdSe [11] and CdTe [12] nanostructures.

* Corresponding author: aneduarda@gmail.com

All these works show the great interaction capability between starch and heavy metals, although specific chemical interactions have not been yet studied. In this work our aim is to understand the interactions between Pb and starch and also to analyze the possibility of favorable interactions between PbS and starch. This should give us a hint on whether it can be used to produce other chalcogenides involving different metals.

2. Computational Methods

Ab initio quantum mechanical calculations were performed with the Gaussian 09 [9] program codes. Geometry optimizations and frequency computations were obtained with the Møller-Plesset second order perturbation theory (MP2) [10] in conjunction with the LANL2DZ [11] basis set. This method was selected based on the fact that it takes into account dispersion forces, which are the main interactions involved in the species studied. Hessian matrix elements were analyzed to identify which configurations are transition states and which are energy minima. Negative vibrational frequencies indicate a transition state, whereas positive vibrational frequencies depict energy minima. Global orbital cutoffs and tight convergence criteria were enforced to corroborate the energies obtained. Due to space limitation, we only illustrate the lowest energy configurations, although the number of energy minima configurations is greater. We present those with relative dissociation energies less than 20 kcal/mol to discuss only the most stable systems.

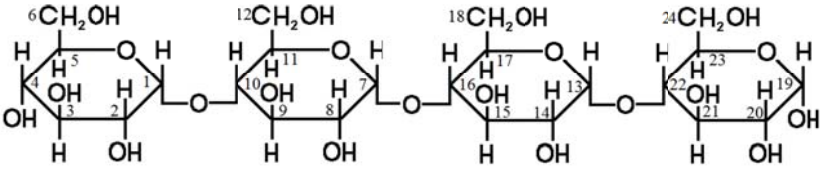
The van der Waals forces were quantified by calculating the dissociation energies (ΔE) as:

$$\Delta E = E_{polysac(Pb/PbS)} - E_{polysac} - E_{Pb/PbS}$$

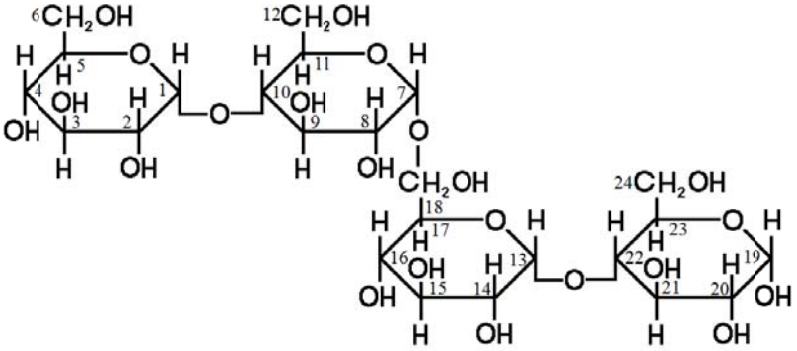
In other words, the dissociation energy is given by the energy of the system formed by the polysaccharide (amylose or amylopectin) and Pb or PbS minus the energy of each individual species. The values obtained quantify the strength of the interaction among the substances involved. In addition to dissociation energies, we list the relative dissociation energies to simplify the comparison between the systems. Global energy minima configurations have a value of 0.00 kcal/mol, while the rest of the systems have positive values. A higher positive value indicates a greater deviation from stability.

3. Results and discussion

Starch is mainly composed of amylose and amylopectin. Thus, we constructed the following set of systems: amylose-Pb, amylose-PbS, amylopectin-Pb and amylopectin PbS. Both amylose and amylopectin form a helical structure formed of n glucose subunits, which can be in the order of thousands. Therefore, we had to cut these polysaccharides to a smaller amount of subunits. We performed tests with a different number of subunits and realized that with more than four subunits, the tips of the polysaccharides tend to interact and form a ring. Since we know beforehand that the tips should not interact between them because they are linked to other glucose subunits, we decided to use only four subunits. Amylose was simulated as four glucose molecules all linked through α(1→4) glycosidic bonds, whereas amylopectin was simulated as four glucose molecules where the sequence of bonds is α(1→4), α(1→4), α(1→6), α(1→4), as it is pictured schematically on Fig. 1. Hydrogen atoms were attached to the tips of both polysaccharides with the purpose of reducing the reactivity on them.



Amylose



Amylopectin

Fig. 1. Scheme of amylose and amylopectin specia where only carbon atoms are numbered.

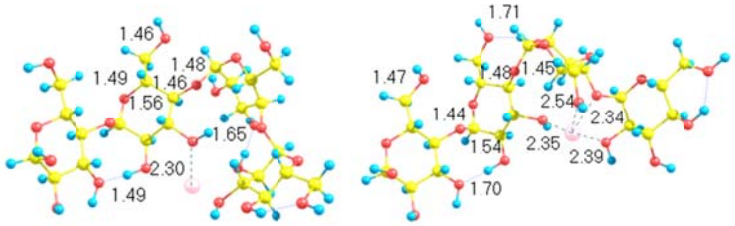
Fig. 2 illustrates the energy minima structures for amylose-Pb and amylose-PbS, while the most stable configurations for amylopectin-Pb and amylopectin-PbS are depicted on Fig. 3. Table 1 lists the relative dissociation energies with zero point corrections and HOMO-LUMO gaps. The obtained values of the individual gaps of Pb, PbS, amylose and amylpectin are of 11.37 eV, 4.07 eV, 6.74 eV and 6.68 eV, respectively.

The most stable structures for amylose-Pb pictured in this work were configurations 1 and 2 because the rest of the energy minima structures showed a considerable difference in dissociation energy. Structure 1 has a contact point between the oxygen attached to C15 and Pb with a distance of 2.30 Å and a HOMO-LUMO gap of 1.52 eV. In Structure 2, Pb interacts with the oxygens attached to C21, C18 and C15, with contact distances of 2.39 Å, 2.54 Å and 2.35 Å, respectively. In addition, Pb has a contact distance with the oxygen in between C22 and C13 that links two glucose subunits, with a value of 2.34 Å. These interactions twist the amylose molecule, causing it to destabilize with a relative dissociation energy of 10.88 kcal/mol and a HOMO-LUMO gap of 1.19 eV.

For amylose-PbS, more energy minima structures were found with relative dissociation energies closer to each other than for amylose-Pb. However, the presence of S tends to destabilize the structures, which can be confirmed with the higher values of dissociation energies of the amylose-PbS structures.

In structure 3, Pb interacts with the O attached to C2 with a contact distance of 2.47 Å, while S interacts with the hydrogen in the OH attached to C9 with a contact distance of 2.26 Å. Its relative dissociation energy is of 11.93 kcal/mol and a HOMO-LUMO gap of 3.92 eV. PbS in structure 4 interacts with the OH groups attached to C2 and C9 with contact distances of 2.56 Å and 2.88 Å between Pb and O, respectively and 2.47 Å between S and H. This interaction causes tension within the amylose molecule, and as a result, it has a higher relative dissociation energy with a value of 15.91 kcal/mol and a similar gap of 4.07 eV.

Amylose-Pb



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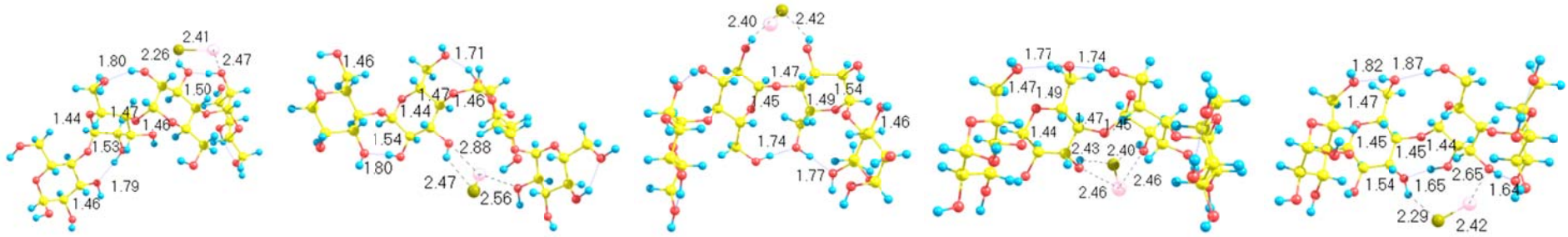
Amylopectin-Pb



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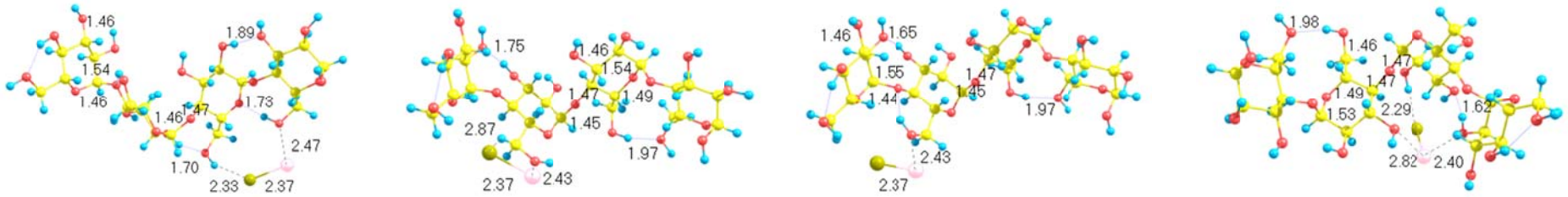

8 9 10 11

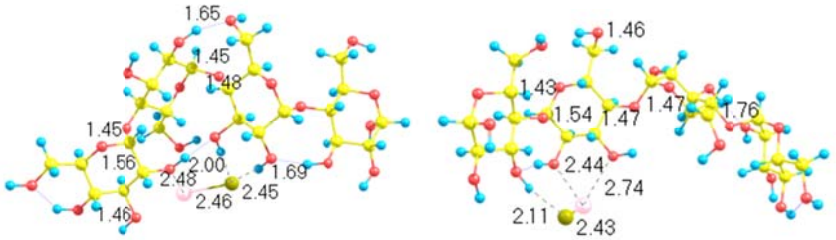

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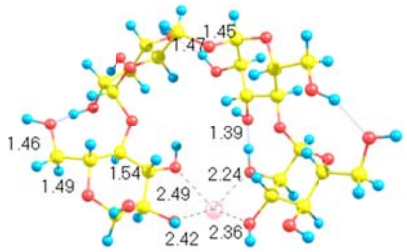
Fig. 2. Selected geometrical parameters of the systems amylose-Pb and amylopectin-Pb whereby bond lengths are in angstroms (Å).

Amylopectin-Pb



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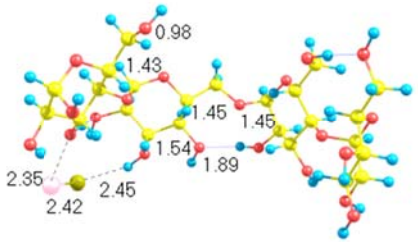
Amylopectin-PbS



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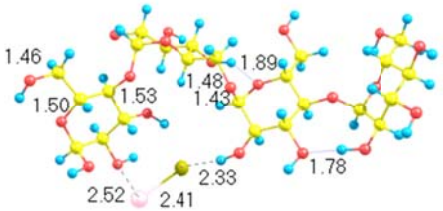

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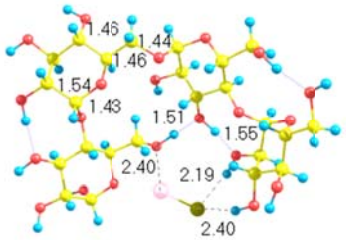

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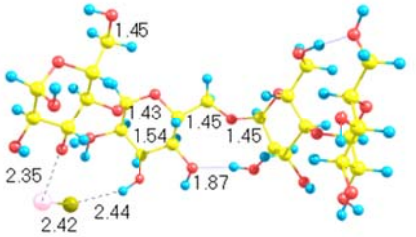

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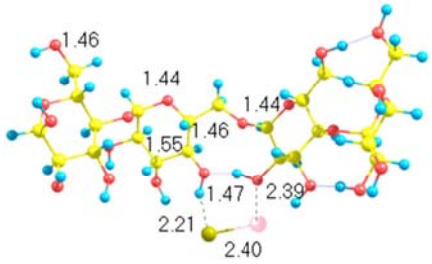

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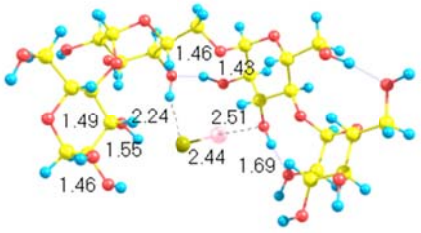

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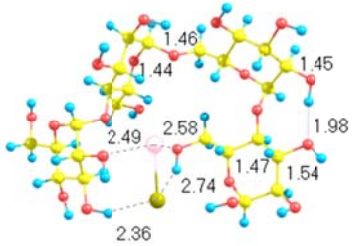

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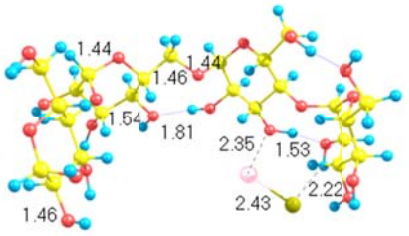

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Fig. 3. Selected geometrical parameters of the systems amylose-PbS and amylopectin-PbS whereby bond lengths are in angstroms (Å).

Table 1. MP2/LANL2DZ dissociation energies and relative dissociation energies with zero point corrections are listed under ΔE(0K) and ΔE_{rel}(0K) in kcal/mol. HOMO/LUMO Gaps are listed under GAP in eV.

System		ΔE(0K)	ΔE_{rel}(0K)	GAP
amylose-Pb	1	-247.58	0.00	1.52
	2	-236.71	10.88	1.19
amylose-PbS	3	-21.86	11.93	3.92
	4	-17.87	15.91	4.07
	5	-24.93	8.86	4.35
	6	-21.55	12.23	4.36
	7	-33.78	0.00	3.87
	8	-15.47	18.31	3.82
	9	-25.18	8.60	3.74
	10	-26.63	7.15	3.79
	11	-24.65	9.14	4.15
	12	-25.45	8.33	4.57
	13	-23.84	9.95	3.92
amylopectin-Pb	14	-233.66	0.00	3.63
amylopectin-	15	-13.72	16.48	3.70
PbS	16	-14.29	15.91	3.92
	17	-30.20	0.00	3.79
	18	-15.13	15.07	3.71
	19	-16.13	14.08	3.77
	20	-20.28	9.92	3.89
	21	-26.28	3.92	4.11
	22	-13.10	17.10	3.68

Structure 5 shows PbS interacting with the OH's linked to C8 and C15 with contact distances of 2.40 Å and 2.42 Å. The distortion caused by this interaction in the amylose species is small. Thus, the system is more stable than structures 3 and 4, with a relative dissociation energy of 8.86 kcal/mol and a HOMO-LUMO gap of 4.35 eV. Structure 6, however does constrain the spatial arrangement of amylose, causing tension within the molecule. This can be confirmed by the interaction between PbS and amylose. Pb interacts with the O's attached to C15 and C9, with contact distances of 2.46 Å while S interacts with the OH attached to C15 at a distance of 2.43 Å. This yields a relative dissociation energy of 12.23 kcal/mol and a gap of 4.35 eV. In contrast, PbS in structure 7 interacts with the oxygen attached to C9 via Pb at a distance of 2.65 Å and with the OH linked to C15. The presence of PbS enhances the stability of the system by interacting with groups that do not cause steric hindrance. Thus, this is the most stable structure for the PbS-amylose structures, with a band gap of 3.87 eV.

Structure 8 is the least stable of the PbS-amylose systems. S interacts with the OH group linked to C18 at a distance of 2.33 Å and Pb interacts with the OH group linked to C24. Both, C18 and C24 are the pending carbons of the glucose subunits. Therefore, the interaction with these groups yields tension within the amylose species and steric hindrance. This results in a higher relative dissociation energy of 18.31 kcal/mol with a gap of 3.82 eV. In contrast, configuration 9 depicts an interaction between Pb and the OH attached to C12, while S interacts with a H linked to C12. In other words, PbS interacts with atoms in the same pending group (of the second glucose subunit). Although there is steric hindrance, most of the amylose molecule remains unaffected and thus its dissociation energy is not high, with a value of 8.60 kcal/mol and a gap of 3.74 eV.

In configuration 11, PbS has interacts with three groups of OH's at distances of 2.82 Å, 2.29 Å and 2.40 Å. However, the presence of S causes repulsion with the O's nearby, which destabilizes the system to a relative dissociation energy of 9.14 kcal/mol and a gap of 3.79 eV. In structure 12, Pb interacts with C2 with a contact distance of 2.48 Å, while S interacts with two H's in the OH groups attached to C15 and C14 at 2.00 Å and 2.45 Å, respectively. This structure is slightly less stable than configuration 11 due to the fact that Pb only interacts with one O. Its values of relative dissociation energy and HOMO-LUMO gap are of 8.33 kcal/mol and 4.57 eV. In structure 13, S has a contact distance of 2.11 Å with the O linked to C21. Pb interacts with the O's attached to C15 and C14 at 2.44 Å and 2.74 Å. Anyhow, this causes the O's to be drawn closer together and repel each other, destabilizing the molecule. Its relative dissociation energy is of 9.95 kcal/mol and its gap, is of 4.57 eV.

Configuration 14 is the most stable system for the amylopectin-Pb systems. The rest of the systems had relative dissociation energies too far apart from it, with values higher than 20.00 kcal/mol. In this structure, Pb interacts with the O's linked to C20, C21, C2 and C3, with contact distances of 2.42 Å, 2.49 Å, 2.24 Å and 2.36 Å, respectively. Its HOMO-LUMO gap is of 3.63 eV, and its dissociation energy is of -233.66 kcal/mol, which is higher than that of the most stable system for amylose-Pb, with a value of -247.58 kcal/mol. This can be accounted for the torsion that the amylopectin species undergoes with an increased ammount of interactions with Pb.

Structures 15-22 are the energy minima configurations for the amylopectin-PbS systems. In these cases, the glycosidic bond α(1→6) causes the amylopectin species to have more degrees of freedom than amylose, and therefore, higher values of dissociation energy, in general. This means that the stability of amylopectin-PbS systems, unlike those of amylose-PbS, is favoured by the interaction of PbS with glucose subunits that are farther apart to reduce the degrees of freedom.

PbS in structure 15 only interacts with two glucose subunits, the O linked to C21 at 2.35 Å and the OH attached to C15 at 2.45 Å. The degrees of freedom are not reduced significantly, which leads to a relative dissociation energy of 16.48 kcal/mol, with a gap of 3.70 eV. Structure 16 interacts with the 2nd and 4th subunits, through the OH's linked to C20 and C8, at 2.52 Å and 2.33 Å, respectively. As the degrees of freedom are reduced, so is its dissociation energy. Its relative dissociation energy is of 15.91 kcal/mol and its gap is of 3.92 eV. Additional interactions between PbS and the amylopectin species reduce the degrees of freedom even more, with contact distances to OH's attached to C24, C2 and C3 at 2.40 Å, 2.19 Å and 2.40 Å, respectively. As a consequence, this is the most stable configuration of the amylopectin-PbS systems and has a gap of 3.79 eV.

Structure 18, similarly to structure 15 only interacts with two subunits close by through the OH's attached to C21 and C15 at 2.35 Å and 2.44 Å, respectively. This does not enable the dissociation energy to be reduced significantly and as a result has a relative dissociation energy of 15.07 kcal/mol and a gap of 3.71 eV. Structure 19 interacts with the 2nd and 3rd subunits, which is where the amylopectin molecule has a higher mobility through the α(1→6) bond. This helps the amylopectin species to adopt a more stable structure via the interaction between PbS and the OH's linked to C16 and C8 at 2.21 Å and 2.39 Å, respectively. Its relative dissociation energy is therefore lower than that of structure 18, with a value of 14.08 kcal/mol and a gap of 3.77 eV. Structure 20also shows an interaction between the 2nd and 3rd subunits, which aids in the stability of the system, via the OH's linked C14 and C9 AT 2.24 Å and 2.51 Å. This configuration is closer to the helix form amylopectin is known to have and thus is more stable than structure 19, with a relative dissociation energy of 9.92 kcal/mol and a gap of 3.89 eV.

Structure 21 shows PbS interacting with the 1st and 4th subunit, aiding in reducing the degrees of freedom and therefore its relative dissociation is one of the lowest, with a value of 3.92 kcal/mol and a gap of 4.11 eV. Pb interacts with the OH's linked to C2 and C24, at 2.49 Å and 2.58 Å; while S interacts with the OH's linked to C3 and C24 at 2.36 Å and 2.74 Å. Finally, structure 22 only interacts with the 1st and 2nd subunits though the OH's attached to C9 and C2 at 2.35 Å and 2.22 Å. This does not favor the system's stability and thus has one of the highest relative dissociation energy of this set of systems, with a value of 17.10 kcal/mol and a HOMO-LUMO gap of 3.68 eV.

4. Conclusions

Starch is proposed as a substrate for PbS. In order to understand the interactions between these specia, a theoretical study was performed. Energy minima structures were obtained for four set of structures: amylose-Pb, amylose-PbS, amylopectin-Pb and amylopectin-PbS.

For the first set of geometries, amylose-Pb, the most stable system is structure 1, which keeps the amylose molecule in a semi-circular configuration. This was expected, since both amylose and amylopectin are known to have a helical form. By adding PbS to amylose, more structures with relative dissociation energies close to each other were obtained. Nevertheless, the presence of S elevates the values of dissociation energy. In structure 7, steric hindrance is minimum, which can explain why it is the most stable structure for this set of configurations.

Amylopectin has an interesting characteristic. Its α(1→6) bond gives mobility to the molecule. Thus, the most stable structures were obtained by enhancing the interaction between farther apart subunits to keep a semi-circular geometry which is closer to the helical configuration it is know to have. The most stable structure for amylopectin-Pb is that in which Pb interacts with the 1st and 4th glucose subunits, reducing its dissociation energy. In the case of amylopectin-PbS, the most stable system is structure 17, in which PbS interacts with the 1st and 4th glucose subunit, drawing them close together in a spatial arrangement similar to a helical form.

The interesting results obtained in this work support the hypothesis that starch can be a substrate for PbS and gives us a hint that it can also be a substrate for other chalcogenides in which the metal interacts with oxygen, in a similar way in which the amylose and amylopectin molecules interacted with Pb. Our prospects are to confirm this experimentally and analyze this possibility with other metals.

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