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Electrostatic interactions in the process of trapping of molecules into nanochannels

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Resumen

La adición de moléculas a materiales que presentan nanocanales puede llevar a la obtención de nuevos materiales con propiedades inesperadas. Tal es el caso del azul maya, constituido por paligorskita (Sacalum) y un tinte azul de origen vegetal. Hasta el momento no hay una base experimental que indique cual es el colorante exacto que da el color característico al azul maya, por lo que se ha propuesto una mezcla de índigo y dehidroindigo. Con base únicamente en interacciones electrostáticas proponemos que es el dehidroindigo el tinte que se encuentra atrapado en los nanocanales de la paligorskita.

Palabras claves: nanocanales, paligorskita, indigo, dehidroindigo, interacción dipolar.

Abstract

The trapping of molecules into nanochannels can give us a new material with unexpected properties. Such is the case of Maya blue, made up of palygorskite (Sacalum) and a blue dye, which is extracted from a plant. Because experiments give no evidence of which dye is the one that give the color to the Maya blue, a mixture of indigo and dehydroindigo has been proposed. Based only in electrostatic interactions, we propose that only dehydroindigo is the one that can be trapped by palygorskite nanochannels.

Keywords: nanochannels, palygorskite, indigo, dehydroindigo, dipolar interaction

1. Introduction

In nature there exists a special kind of materials known as fibrous clays. Some of them are used as adsorbents [1]. The main property of fibrous clays is that present a double array, which, when is combined, form channels. These channels had dimensions in the nanoscale domain. In our case we are interested in particular in palygorskite, that present both an octahedral and tetrahedral structures. Among others applications, palygorskite is used in pottery, as food, and even as a medicine. Its structure is well known, as its composition for the case of the clay founded in the Yucatán Peninsula (México)[2].

In Mexico, beside the applications mentioned above, palygorskite, known also as Sacalum, is used in making of Maya blue. This material shows awesome properties, one is that is acid resistant [3]. On the other hand, the second ingredient of Maya blue is well not characterized. First investigations assume that indigo is the other component. But, experimental evidence shows that dehydroindigo, indigo without two hydrogen atoms, is actually the dye that is in the Maya blue [4]. The controversy still remains because there are no arguments in which one can be discarded.

A classical molecular dynamics simulation for Maya blue has been performed, but the work is related only to equilibrium positions of indigo into the palygorskite nanochannel [5]. Also, several *ab initio* calculations have been reported, but all of them consider the indigo or dehydroindigo already inside the nanochannel [6]. The question about if the dye, whatever it is, can be inserted into the nanochannel remain.

Using density functional theory is possible to compute any local multiple potential for a specific region in a molecule. This kind of calculations were performed both indigo and dehydroindigo up to dipolar potential. As we found, big differences in this potential allows us argue why dehydroindigo is the dye that is into paligorskite instead of indigo.

2. Calculations

In order to obtain the properties of molecules, indigo and dehydroindigo, we use the density functional theory (DFT),.in particular, Car-Parinello Molecular Dynamics (CPMD-3.13.2) program [7] installed in the Laboratorio de Supercómputo of the UAEMex. The software capabilities are summarized in [8].

The positions for the palygorskite were obtained from those given by Asencio et. al. [9], and for the dyes an optimization of geometry was used to obtain they structures. The pseudopotentials used for the calculations were BLYP [10]. The reason for this choice is that is available to all elements, both clay and dyes. Beside, actually we are looking for a

description of the system, not give a fully description, which will be later on.

The difference between indigo and dehydroindigo is a couple of hydrogen atoms attached to nitrogen as can be seen in the following figures. To obtain local dipoles in the dyes, a separation of molecules in three regions was made. The first one is the half of the molecules, between the middle of the molecule and one of its ends. Looking at the figures below the ends are to the right and left of them. The other two regions cover the pentagon and the hexagon. These regions can be identified with no ambiguity in the figures 1 and 2.

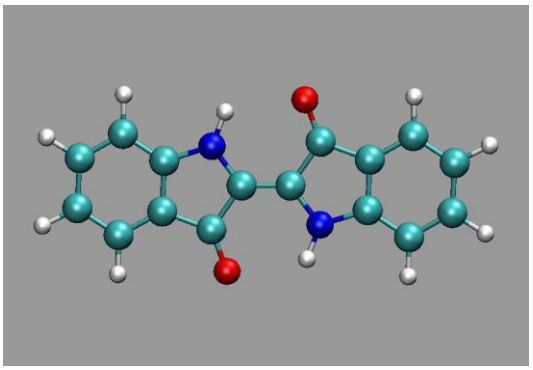

Figure 1. Indigo molecule obtained from a geometry optimization. Hydrogen atoms are shown in white, nitrogen in dark blue, oxygen in red, and the other are carbon atoms.

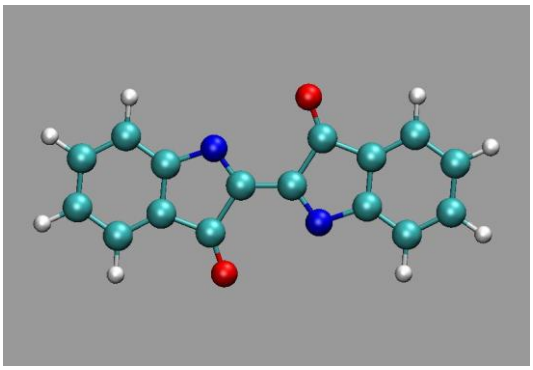

Figure 2. Dehydroindigo molecule obtained from a geometry optimization. The color notation is the same as the previous figure.

Dipolar moments are calculated in a straight way. Once that the electronic density is obtained from DFT the definition of dipolar moment [11] is applied to the desire region to obtain it.

3. Results

Once the structures and electrostatic properties for palygorskite and dyes are obtained, we look for an explanation about the possible interactions in the composite. First we say something about the results on the properties computed for each kind of system. In the case of the palygorskite, it is possible to see that the negative potential is given near the octahedral structure which, by the way, is the principal part [12] because the main interactions in our systems take place in this region. Actually, the presence of water molecules makes the zero potential surface shifts to the center or the palygorskite's channel, as can be seen in the figures (3) and (4).

The equipotential surfaces for negative values collapse to the center of the channel. Because of the symmetry, this gives an indication why any of the dyes are in equilibrium when classical molecular dynamics is made for the system.

On the hand, when local dipoles of indigo and dehydroindigo are compared, great differences are founded. If the middle of both molecules is now considered, the value of the dipole for indigo is almost twice that those for dehydroindigo. However, is located almost in the same point, about the center of the line shared by the pentagon and hexagon, which makes a similarity. Dipole direction shows another difference. For indigo, it points away from nitrogen, meantime for dehydroindigo it points away from the center of the molecule parallel to its axis. This dipole actually no has relevance because, as we will see, the principal contribution comes from a smaller part of the molecules, mainly for indigo.
Hexagon structures are almost the same and present similar dipolar moments. Actually, its contribution is in the sense to shift the center of dipole for the half of the molecule. The main part comes from the pentagonal region. Once again, for dehydroindigo it points away to the center of molecule parallel to the molecular axis, meantime the dipolar moment of the indigo is center near the center of the pentagon and pointed away to the oxygen atom. The numerical value of the later is about four times than the former.

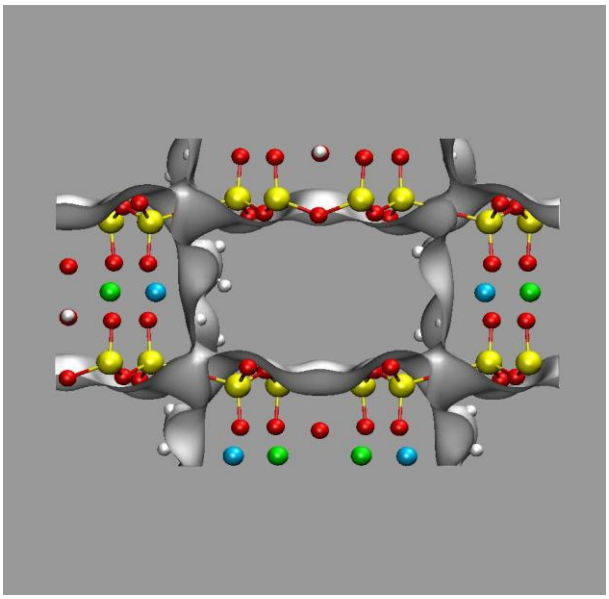

Figure 3. Neutral equipotential surface for palygorskite. Water molecules are included in this case to show its contribution. Silica is represented in yellow, oxygen atoms in red, magnesium atoms in green, aluminum in blue, and hydrogen in white.

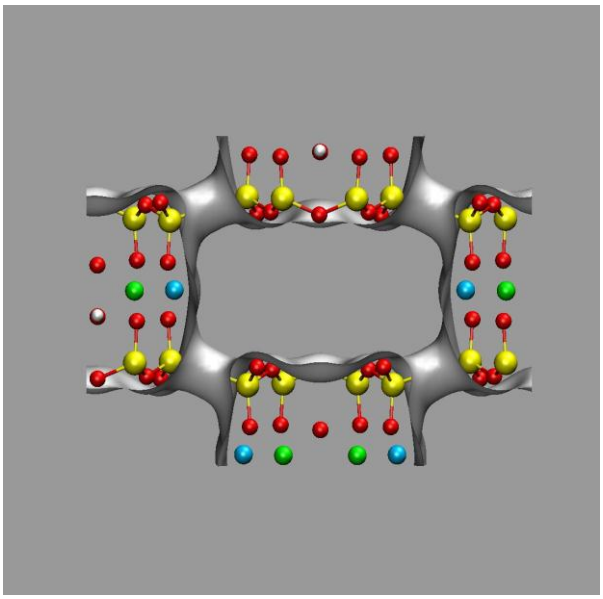

Figure 4. Neutral equipotential surface for palygorskite with no water molecules. The colors of the atoms is the same as the previous figure. When comparison is

The magnitude of this local dipole in indigo is strong enough to align water molecules around the oxygen. This can be confirmed if a classical molecular dynamics, with the appropriate charge distribution, is performed. This is not the case for dehydroindigo, in which there is no any align. Water is very important because is used in the making of Maya blue.

When the dimensions of the paligorskite's channel is compared with those of the molecules, it is possible realize that there is one possible way to insert the dye in the channel. This is when the channel axis and the molecule axis are parallel. But if we consider that indigo has several water molecules stick to it, the insertion process is harder than the dehydroindigo case because of the water shield attached to it. This is one reason why we consider that is not possible to have indigo into the palygorskite's channels.

In the case that indigo can be inside the channel, there is another factor that must be takes it into account, water molecules that are already in the channel. There is a competition between the dipolar moments of the clay and the indigo, to align those water molecules in opposite directions. If we consider that all models consider that nitrogen

bond to the octahedral structure, the shield of water molecules prevent that this occurs.

For dehydroindigo this is not the case. The dipolar moment is almost parallel to the molecular axes, and there is no alignment of water molecules that prevent the insertion into the channels. Besides, the nitrogen now can react with the octahedral structure because the double ligand with one of the carbon atoms. On the contrary to the indigo case, we can have not only one nitrogen atom attached to the palygorskite wall, but two. Indigotin is an unstable dye, which correspond to a mirror reflection of indigo. Local dipoles and thermal agitation makes that indigotin goes into indigo. The equivalent case for dehydroindigo is different. The dipolar interaction can be overcome for the thermal agitation making that dehydroindigo can be transform into “dehydroindigotin” with no effort. If this is the case for our system, we will have two nitrogen atoms that can be attached to the channel.

4. Conclusions

Taking only electric interactions into account, we argue that dehydroindigo is the dye that gives the characteristic color to the Maya blue. Besides, the acid resistance can be considered as the result of the attached of two, instead of one, nitrogen atoms to the walls of the palygorskite channels. *Ab initio* molecular dynamics must be performed to validate the above conclusions.

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