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Computer Simulation of Sorption Interactions of L-Arginine and L-Lysine with Carbon Nanotubes

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Abstract

Carbon nanotubes (CNTs) are a new class of nanomaterials with a high potential for different technological applications. The prospects of using them in biomedicine is associated with the ability of CNTs to cross the cell's membrane without being impaired, which determines the significance of the study of the interactions of CNTs with biologically active substances, especially amino acids. This work presents a computer simulation of the structure and characteristics of arginine (lysine) – single-wall carbon nanotube (CNT) systems using the B3LYP/6-31G(d,p) density functional theory with GD3 dispersion correction. We calculated the energies of adsorption, dipole moments, total charge on the amino acid and nanotube atoms, and the smallest distances from the amino acid atoms to the CNT. Taking into account the dispersion correction, which is almost absent in scientific literature, allows more accurate calculations of the energies of adsorption of amino acids on CNT to be obtained as compared to the existing calculations due to the high polarizability of CNTs. We considered scenarios with the amino acid position on the open end and on the external and internal lateral surfaces of the CNT. The calculated series of adsorption energies satisfies the conditions $E_{end} > E_{inside} > E_{lateral}$. This is due to the fact that when the amino acid is placed on the external lateral surface of a CNT the sorbate interacts with a part of the lateral surface of the tube. When it is placed inside the CNT the sorbate interacts with the whole surface through van der Waals forces and when the sorbate is placed on the end of the sorbent a covalent bond is formed between them. The formation of the covalent bond on the open end of the CNT is due to the higher electron density near the ends of the nanotube as compared to the external and internal lateral surfaces of the tube. An explanation is given of the mechanisms of adsorption and enhancement of the antibacterial action of the CNT functionalised by arginine and lysine, as compared to nonfunctionalised CNTs.

Keywords: carbon nanotubes, amino acids, computer simulation, adsorption.

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1. Introduction

Carbon nanotubes (CNTs) are one of the most widely studied nanomaterials due to their unique physicochemical properties and wide range of possible technological applications in biomedicine, nanoelectronics, and material science [1–7]. The unique sorption, electronic, and optic properties of CNTs as well as their size and mechanical strength make nanotubes a critical material for biotechnologies such as the development of targeted drug delivery platforms, tissue engineering, and next-generation biosensors [8–11]. To take advantage of the unique properties of CNTs in biotechnologies it is necessary to understand the nature of the immobilisation of biomolecules on CNTs [12–18]. One of the methods for the immobilisation of biological molecules on CNTs is adsorption, and amino acids (AA) are an elementary unit of many biomolecules. Thus, the interaction between CNTs and AAs is important for understanding the mechanism of the interaction of nanotubes with biomolecules. The goal of this work was to identify the features of sorption interactions of L-Arginine and L-Lysine with single-wall carbon nanotubes in aqueous solutions.

2. Experimental

2.1 Computer-aided experiments

A chiral nanotube (6,6) with open ends and a length 13.53 Å was used as the model of a carbon nanotube in a computer simulation of amino acid adsorption on CNTs. Using these nanotubes we studied the adsorption of the main amino acids of L-Lysine [HOOCCH(NH$_2$)(CH$_2$)$_4$NH$_2$] and L-Arginine [NH-C(NH$_2$)NH(CH$_2$)$_3$CH(NH$_2$)-COOH] from an aqueous solution with pH ~ 7. With this pH value, both acids are mainly in the form of cation (Fig.1), which was taken into account while constructing an initial structural model of the sorbate.

The cations of amino acid were positioned in the initial structures in three different ways: on the open end of the CNT, on the lateral surface of the CNT, and inside the CNT.
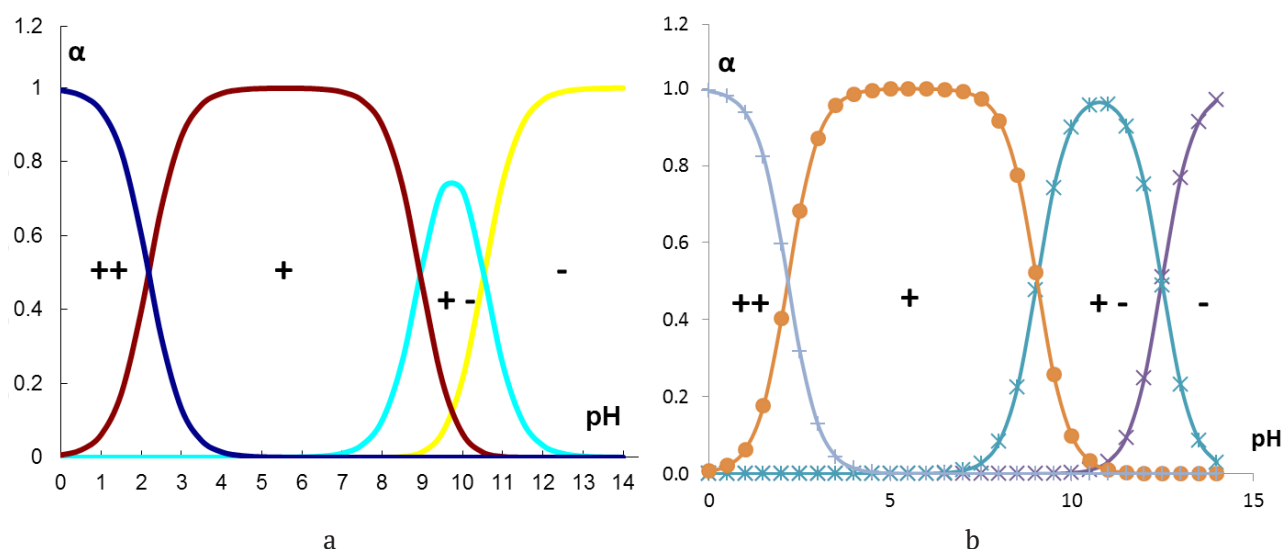
The aqueous environment was taken into account using the method of solvation of polarisation continuum (PCM) [19].

The structures were optimised using the Gaussian 09 program [20, 21] and the B3LYP/6-31G(d,p) method with GD3 dispersion correction [22]. As CNTs have high polarisation, taking into account the dispersion correction allows obtaining more accurate energies of amino acids sorption on CNTs. The adsorption energies were calculated using the following formula:

$$E^{ads} = E^{sorbate} + E^{CNT} - E^{sorbate + CNT}, \qquad (1)$$

E^{ads} is the adsorption energy, $E^{sorbate}$ is the energy of the particle whose sorption is being studied, E^{CNT} is the energy of the carbon nanotube.

The consideration of dispersion corrections means adding an additive term into the expression of energy of the atomic-molecular system

Fig. 1. Change in the content of ionic forms of lysine (a) and arginine (b) depending on the pH of the solution at a temperature of 293 K

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}, \tag{2}$$

where E_{DFT} is the energy of the system calculated using the calculation model of the density functional theory (DFT) B3LYP/ 6-31G(d,p), E_{disp} is the empirical dispersion correction. As for the quantum-chemical calculation, the GD3 method [22] takes into account the scaling and damping fitting the values of the specified series of dispersion energy

$$E_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \tag{3}$$

in the form of

$$E_{\text{disp}} = -\sum_{n=6,8} s_n \sum_{i,j>i}^{N_{\text{at}}} \frac{C_n^{ij}}{\left(R_{ij}\right)^n} f_{\text{damp}}, \tag{4}$$

$$f_{\text{damp}}\left(R_{ij}\right) = \frac{1}{1 + 6(R_{ij}/(s_{r,n} R_0^{ij})^{-\alpha_n}}. \tag{5}$$

Here the dispersion coefficients C_n^{ij} for each pair of atoms i and j were obtained as the geometric average of the elementary table values summarised by all the intercore distances. These coefficients are modulated using the damping function f_{damp}. The fitting parameters for the B3LYP functional are $s_6 = 1.0000$, $s_8 = 1.7030$, $s_{r,6} = 1.2610$.

3. Results and discussion

Several optimised structures were obtained for each of the CNT+AA systems when placing the amino acid on the open end of the CNT, on the lateral surface of the CNT, and inside the CNT. The structures of the optimised systems with the greatest energy of adsorption, their dipole moments (*d*, Debye), total charges on the atoms of the amino acid and CNTs, adsorption energies (E_{ads}, kcal/mol), and the smallest distances from the oxygen and nitrogen atoms of the amino acid cation to the carbon atom of the nanotube (R_{CO1}, R_{CO2}, R_{CN1}, R_{CN2}, Å) are presented in Tables 1 (lysine) and 2 (arginine).
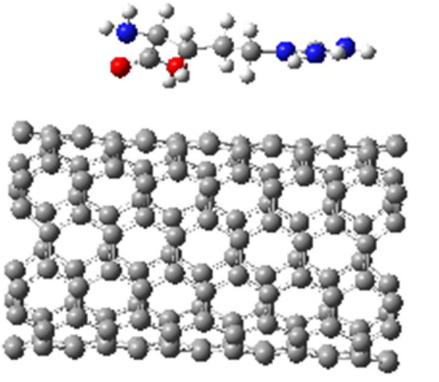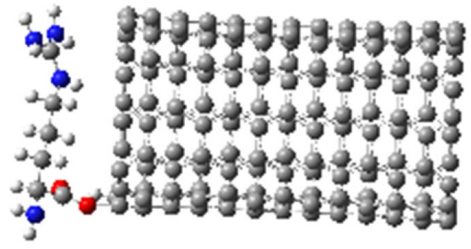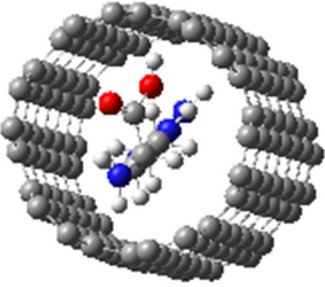
The series of adsorption energies on the CNT for both amino acids satisfies the condition $E_{\text{end}} > E_{\text{inside}} > E_{\text{lateral}}$. The value of the dipole moment of the amino acid – CNT system is within the range from 13.38 to 42.74 D (arginine) and within the range from 9.01 to 13.83 D (lysine). The values of the charges on the atoms of amino acid and CNT (q_{AA} and q_{CNT}) (Tables 1, 2) indicate an insignificant transfer of the charge from the amino acid to the nanotube. Thus, a complex with the transfer of the charge over the course of adsorption is not formed, and there is no donor-acceptor sorbent-sorbate interaction.

The values of the distances from the atom O (N) of the amino acid to the atom C of the nanotube allow drawing a conclusion about the method of fixing the amino acid on the CNT. Their values R_{CO2} = 1.38 Å (arginine on the end of the CNT, Table 1) and R_{CN1} = 1.50 Å (lysine on the end of the CNT) show that there is covalent bond between the atoms of oxygen (nitrogen) of the amino acid and the carbon atom of the nanotube as the sum of the covalent radii approximates the length of the covalent bond between the corresponding atoms. The highest adsorption energy of the amino acid is conditional on the end of the CNT (E_{end}). The formation of the covalent bond on the open end of the CNT is due to the higher electron density near the ends of the nanotube as compared to the external and internal lateral surfaces of the tube. It is associated with the fact that on the end of the open CNT each carbon atom has two neighbouring atoms and forms triple and single bonds –C≡C– [23, 24], while the inside carbon atoms form one and a half bonds with three neighbouring atoms C. The triple bond on the end of the nanotube breaks when a cation of amino acid is attached, which ensures the formation of the sorbent-sorbate covalent bond in this case.

The lowest values of the distances from the atoms of oxygen (nitrogen) of the amino acid to the carbon atom when attaching the sorbate on the external and internal lateral surfaces of the sorbent are within the range of 3.2–3.4 Å. This value is significantly greater than the sum of the corresponding covalent radii, which is indicative of the absence of the sorbent-sorbate covalent bond in case of the amino acid sorption by the lateral surface of the CNT. The absence of the covalent bond and donor-acceptor interaction in this case shows that the adsorption is conditioned by the van der Waals forces. The $E_{\text{inside}} > E_{\text{lateral}}$ ratio is determined by the fact that when placing the amino acid on the external lateral surface the sorbate is connected to the half of the lateral surface of the tube, and when placing it inside the CNT it is connected to the whole surface

Table 1. Structure, dipole moment (*d*, Debye), Mulliken charges on AA and CNTs, adsorption energy (E_{ads}, kcal/mol), the smallest distances from the oxygen and nitrogen atoms of the arginine cation to the carbon atom of the nanotube (R_{CO1}, R_{CO2}, R_{CN1}, R_{CN2})

No	Visualisation of the optimised structure	*d*, D	q_{AA} q_{CNT}	E_{ads}, kcal/mol	R_{CO1}, R_{CO2}, Å	R_{CN1} R_{CN2} R_{CN3} R_{CN4}, Å
Arginine cation on the lateral surface of a CNT						
1		36.25	0.97 0.03	19.02	3.24 3.25	4.17 3.38 3.46 3.41
Arginine cation on the open end of a CNT						
2		42.74	0.99 0.01	91.15	1.38 2.83	4.33 4.56 3.20 3.24
Arginine cation inside a CNT						
3		13.38	0.93 0.07	35.21	3.03 2.72	3.19 4.15 3.47 3.47

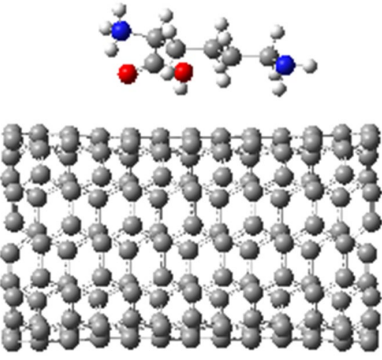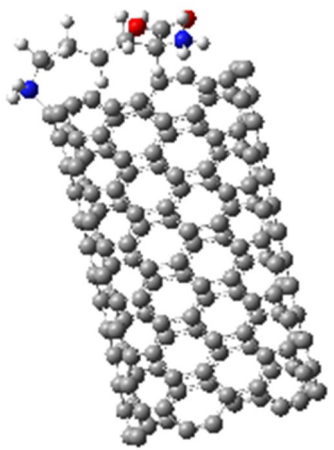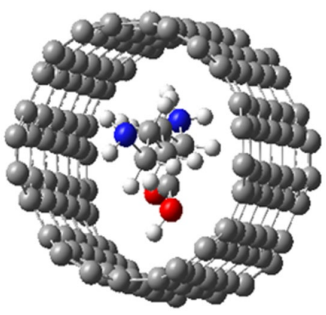of the tube, which results in a greater value of adsorption energy.

According to the reported data, multilayer CNTs functionalised by arginine and lysine have greater antibacterial activity against various bacteria [25]. In accordance with the calculated total charges on the atoms of amino acids and CNTs obtained in this work (column 4 of the Tables 1, 2), the enhancement of antibacterial activity of the CNTs functionalised by arginine and lysine (in the form of a cation in solution), as compared to nonfunctionalised CNTs, is due to the presence of a positive charge on the amino acid and the nanotube. This positive charge makes the adsorption of bacteria with the negative charge of the surface more effective.

4. Conclusions

1. The quantum-chemical calculation of structural and electrical properties of the

Table 2. Structure, dipole moment (d, Debye), Mulliken charges on AA and CNTs, adsorption energy (E_{ads}, kcal/mol), the smallest distances from the oxygen and nitrogen atoms of the lysine cation to the carbon atom of the nanotube (R_{CO1}, R_{CO2}, R_{CN1}, R_{CN2}

No	Visualisation of the optimised structure	d, D	q_{AA} q_{CNT}	E_{ads}, kcal/mol	R_{CO1}, R_{CO2}, Å	R_{CN1} R_{CN2}, Å
	Lysine cation on the lateral surface of a CNT					
4.		34.93	0.95 0.05	15.71	4.35 4.03	3.61 3.33
	Lysine cation on the end of a CNT					
5.		48.70	0.97 0.03	49.89	3.19 3.21	1.50 3.20
	Lysine cation inside a CNT					
6.		12.51	0.92 0.08	32.31	3.31 3.27	3.39 3.35

L-Lysine (L-Arginine) – chiral single-wall carbon nanotube (6,6) systems was conducted with the open ends in the aqueous solution with pH = 7 for three positions of sorbate: on the external lateral surface, on the end, and inside the CNT.

2. The row of adsorption energies of amino acids on the CNT satisfies the condition $E_{end} > E_{inside} > E_{lateral}$. A covalent bond is formed between the sorbent and the sorbate on the open end of the tube, and the amino acid is attached to the lateral surface through the van der Waals interactions.

4. The value of the dipole moment of the amino acid – CNT system is within the range

from 13.38 to 42.74 D (arginine) and within the range from 9.01 to 13.83 D (lysine). The charge transfer from the amino acid to the nanotube in the course of adsorption is insignificant (0.01 - 0.08e), which indicates the absence of the donor-acceptor interaction between the sorbent and the sorbate.

3. The enhancement of antibacterial activity of the CNTs functionalised by arginine and lysine, as compared to nonfunctionalised CNTs, found in the reported data, is due to the presence of a positive charge on the amino acid and the nanotube. As a result, the value of adsorption is higher on the functionalised CNTs for bacteria with a negative charge.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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