COMPUTER MODELING OF CHITOSAN ADSORPTION ON A CARBON NANOTUBE

J.T. Azimov[1],
J.T.Azimov[2]
[1]. The Academy of the Armed Forces of the Republic of Uzbekistan, Tashkent 100023, Uzbekistan, str. Parkent
[2]. Tashkent University of Information technologies named after Muhammad al-Khorazmi, Tashkent 100084, Uzbekistan, Amir Temur Avenue 108.

Annotation

Molecular Dynamics (MD) simulation results for the adsorption process of chitosan oligomer on a carbon nanotube (CNT) are presented. Ab initio DFT calculations are employed to obtain optimal geometric parameters and atomic charge distribution of the chitosan monomer and dimer. Then by means of classic molecular dynamics the binding energy of a chitosan molecule with CNT calculated. It is found that character of the interaction between a chitosan molecule and CNT is non-specific.

Keywords: carbon nanotube, chitosan, adsorption, molecular dynamics.

INTRODUCTION

The properties of polymer solutions and their interaction with carbon nanotubes (CNTs) have been intensively studied over the past decade [1—3]. This is due to that polymers (especially charged) are good stabilizers for microemulsions and suspensions and therefore have been widely used in practice. For example, in the preparation of both aqueous and organic solutions of CNTs the non-covalent functionalization of CNTs by surfactants or bioactive polymers is being widely applied [2, 3]. Chitosan is of special interest among these biopolymers because it is a kind of polysaccharides and has a number of properties that are uniquely appropriate for nanotechnology [4]. On the other hand, polymers are the building material for living organisms and therefore they are important objects in biology and biophysics. Most proteins and nucleic acids are charged, and their electrostatic field affects the properties of membranes. Due to the presence of long-range Coulomb forces the properties of charged polymers and their interaction with other objects have been poorly studied as compared to neutral polymers. Moreover, counterion condensation and screening effect hinder the theoretical consideration of such systems. In this case, it seems reasonable to employ the molecular dynamics method because it enables the study and analysis of the structure and dynamics of polymer molecules under different conditions.

Thus, the aim of this work is to study the structural and energetic properties of CNT - chitosan complexes by means of the molecular dynamics method.

MOLECULAR DYNAMICS SIMULATION

A polymer interacts with nanotubes in different ways: by physical (processes induced by van der Waals forces, dipolar interactions, or weak hydrogen bonds) or chemical adsorption. The non-covalent interaction of nanotubes with a macro molecule is very weak; in the case of chemisorption, the efficiency of this interaction is determined by the number of polar groups of the adsorbed polymer on a surface unit regardless of the macro molecule shape. Not only the presence in the polymer of definite functional groups is important here, but also their intensive interaction with surface atoms of the nanotube, e.g., as electron donors. In this work, we studied the physical adsorption of a chitosan molecule on the nanotube. The structure of the chitosan molecule and its electron density distribution

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were determined quantum chemically using the GAUSSIAN03 code [5]. The structure of the molecule was optimized by the B3LYP method [6] in different combinations of basis sets (6-31G**, 6-31++G**). Interaction parameters and partial charges used in the work are given in Fig. 4 and Table 1. Interactions between water molecules, the chitosan molecule, and CNT are calculated by the pair potential V_{ij} represented as the sum of Coulomb and Lennard—Jones potentials

$$V_{ij}(r_{ij}) = V_{ij}^{\mathrm{el}}(r_{ij}) + V_{ij}^{\mathrm{LJ}}(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \qquad (1)$$

where q_i and q_j are the charges of i and j atoms; r_{ij} is the distance between the atoms. Parameters □ (the van der Waals diameter) and ε (the depth of the potential well V^{LJ}) are found from the experimental data on neutron scattering or solvation energy. For pair interactions of the atoms the parameters were calculated by the Lorentz—Berthelot formula

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \qquad (2)$$

The chemical structure of chitosan is shown in Fig. 1. A large number of amino groups in the chitosan molecule determine its property of binding hydrogen ions and acquiring an excess of positive charge, therefore chitosan is a perfect cation exchanger.

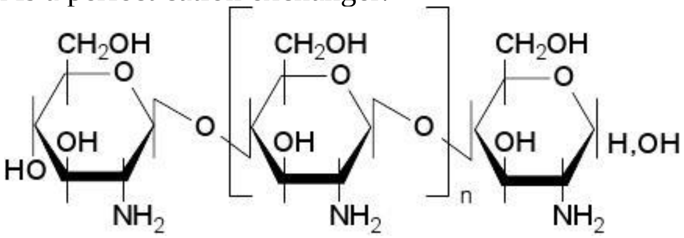

Fig.1. Chemical structure of chitosan.

The structural and energy properties of the chitosan molecule and the nanotube were studied by classical molecular dynamics using the GROMACS 4.0 program [6]. Six chitosan oligomers consisting of eight monomers were selected as chitosan molecules. In order to analyze the effect of chitosan molecules on the energy spectrum of CNT we considered a nanotube of chirality (11,0). The 16.78 Å-long CNT with a diameter of 8.5 Å was placed at the center of a cubic box with dimensions 30×30×30 Å, and the chitosan molecules were located near the nanotubes at a distance of 8—10 Å from the lone passing through the center of the nanotube. After this the cubic box was filled with water molecules that were previously relaxed to the equilibrium state. Since the chitosan molecule is protonated and has a positive charge, negative Cl^- ions were added to neutralize the system. In the calculations of the energy of dissolved water molecules we used an improved simple point-charged (SPC/E) model that well describes the structural and thermodynamic properties of pure water in a wide range of temperatures and pressures. The length of the covalent bond between oxygen and hydrogen atoms was fixed at 1.0 Å, and the bond angle was 109.47°, so that the geometry of the SPC/E model for water was a rigid structure with partial charges of –0.8476e for the oxygen atom and +0.4238e for hydrogen. Lennard—Jones interaction parameters were determined by the Lorentz—Berthelot rule. The calculations were carried out at constant pressure and temperature with the Berendsen barostat and thermostat algorithm in a cubic box filled with 3000 water molecules (Fig 2).

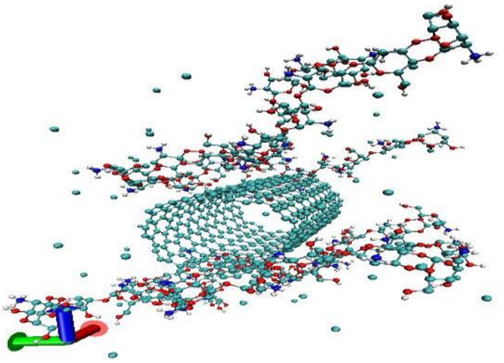

Fig 2. Complex of CNT and chitosan.

Because of cylindrical symmetry and the screening effect of the external electric fields of nanotubes, the partial charge on the carbon atoms in nanotubes is close to zero [7, 8]. Therefore, in the works examining the properties of nanotubes and their interaction with other compounds by the classical molecular dynamics method, the carbon atoms of nanotubes are modeled as neutral particles interacting with other atoms through the Lennard—Jones potential, and electrostatic interactions are not taken into account. Indeed, the quantum chemical calculations have shown that all CNTs have a dipole moment only with open ends, and consequently only the first two carbon atoms at the ends of the tube have a dipole moment, and then starting from the third atom of the nanotubes and up to the middle the exponential decline of the charge distribution is observed [9]. A monolayer nanotube can acquire a dipole moment only as a result of deformation, chemical adsorption, and other atoms (such as hydrogen or fluorine) on carbon atoms and its open ends. Some models involve the electrostatic interaction between the partial charges of water molecules and the quadruple moment of carbon atoms in the nanotube. However, as shown in [10], owing to the quadruple moment and the effects of molecular adsorption on the nanotube surfaces the contribution of the electrostatic interaction to the energy of the system is insignificant, and as a rule, it is possible to neglect its value.

Thus, the carbon atoms of the nanotube were modeled as neutral particles, and the interaction parameters in the Lennard—Jones potential for the CNT atoms were taken from [11] (Table 1).

Tabl 1. Atomic Interaction Parameters for the Lennard—Jones Potential

Atom	□, Å	□, kJ/mol	Atom	□, Å	□, kJ/mol
O (water)	3,166	0,6502	O (chitosan)	2,7099	0,5858
H (water)	0,000	0,000	C (chitosan)	3,5999	0,3180
Cl	4,4	0,54	H (chitosan)	2,4200	0,1255
N (chitosan)	3,04	0,29	C (CNT)	3,85	0,44

Equations of motion were solved by the Verlet algorithm with a time step of 1 fs. Long-range Coulomb forces were calculated by means of the Ewald method with an accuracy of 1×10^{-6}, and all intermolecular interactions inside the box were calculated inside a sphere with the radius $R_{\text{cutoff}} = 9$ Å. The equilibrium state of the system was reached in 50 ps, and this procedure was repeated for each system before the calculation of thermodynamic parameters.

RESULTS AND DISCUSSION

We have obtained the equilibrium configurations of the monomer and dimer of the chitosan molecule. The reliability of the results was proved by the calculation of the vibrational spectra (Fig. 3) of chitosana molecules and a comparison with the experimental data [4].

As seen from Fig. 3, the intensity of vibrations has a maximum at 1100 cm^{-1}, which well coincides with the experimental vibrational frequency of the C—O—C bond (1070 cm^{-1}) and the intensity maximum. Other characteristic vibrational frequencies at 1366 (1390), 1453 (1430), 1674 (1600), 2960 (2950), and 3542 (3490) also well describe the vibrational levels of the chitosan molecule (experimental values are given in parentheses).

Calculation results for the charge distribution of the chitosan molecule are presented in Fig. 4. It is seen that amide groups N (–0.89150e) have a high negative charge compared to the OH group.

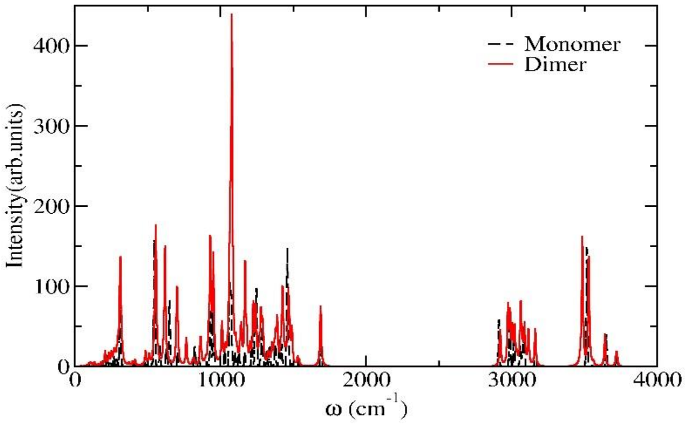

Fig. 3. Vibrational spectra of the chitosan molecule for the monomer (dashed lines) and the dimer (solid lines).

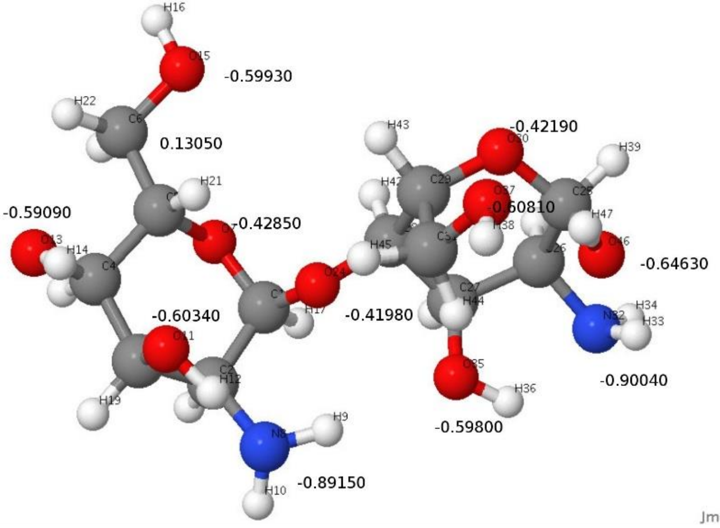

Fig. 4. Dimer of the chitosan molecule with atomic charge distribution (charges are given in elementary charge units).

Fig. 5 depicts the radial distribution functions of the O atom from the CH_2OH (*a*) group and the N atom of the chitosan amino group (*b*) with CNT. The results show that CNT mainly interacts with two chitosan groups: oxygen from the CH_2OH group and nitrogen from the amino group. The equilibrium distance between CNT and oxygen is ~5 Å, and that between CNT and nitrogen is ~6 Å.

The radial distribution changes noticeably with temperature for the interaction of CNT with nitrogen, namely: as the temperature decreases there appear two equilibrium distances of 6 Å and 10 Å.

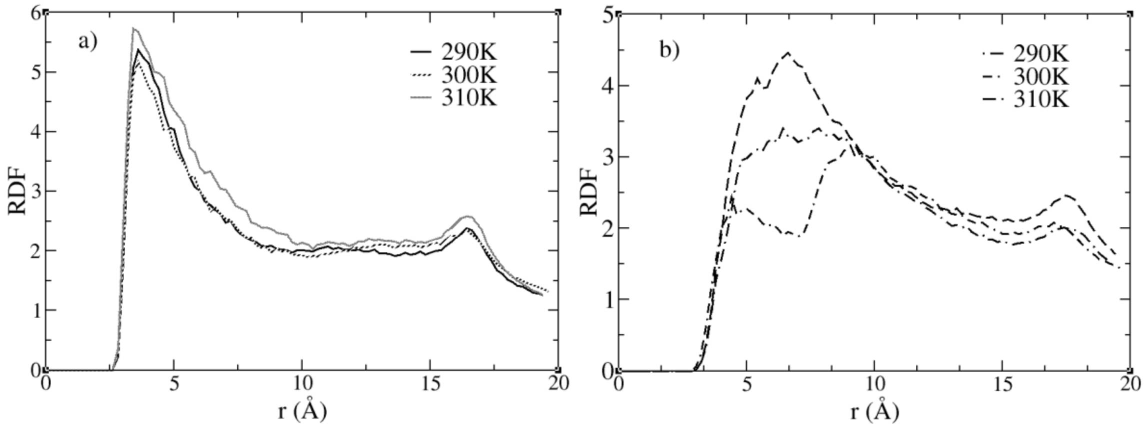

Fig. 5. Radial distribution functions of the O atom from the CH_2OH group (a) and the N atom of chitosan (b) in the interaction with CNT.

As is known, CNTs are hydrophobic and an increase in the hydrophobic effect is observed with an increase in epy temperature, as a result of which the polymer molecule is attracted to the nanotube. As the temperature decreases, it is more preferable for the chitosan molecule to stay in the aqueous environment rather than on the nanotube surface. In fact, the attraction having an ion-induced dipole character is always inversely proportional to the relative permittivity of the medium (water, in our case). As is known, water permittivity determined by orientational polarizability is expressed through the Langevin function L(x) as follows:

$$\varepsilon = 1 + \frac{Np}{\varepsilon_0 E}\mathrm{L}(x), \tag{3}$$

where p is the dipole moment of one water molecule; N is the number of water molecules in a unit volume; E is the external field (in our case, this is the field between the chitosan ion and the induced dipole of CNT); $x = pE/kT$ [12]. As seen from this expression, the permittivity increases with a decrease in the temperature. Physically this means that as the temperature decreases, the dipoles of the environment become ordered, which can be expressed as a decrease in the entropy of the dipole system. Some authors (Mott and Gurnei) interpret this as a change in the entropy barrier with temperature. The permittivity growth with a decrease in the temperature weakens the attraction between chitosan and CNT.

Using the simulation results based on energy parameters, we calculated the binding energy between CNT and the chitosan molecule. To this end, we used the following calculation algorithm.

The total energy of the system is defined as the sum of all total energies of separate components (chitosan, CNT, water, ions) and pair interactions between these components, i.e.

$$E_{tot} = E^{chit} + E^{CNT} + E^{water} + E^{ion} + E^{chit/CNT} + E^{chit/water} + E^{chit/ion} + E^{CNT/water} + \\ + E^{CNT/ion} + E^{water/ion} \tag{4}$$

The binding energy of CNT and chitosan can be considered to be an exception from the system of water and ions. The corresponding ensemble CNT+chitosan is constructed by excluding chlorine ions and water molecules of the optimized conformation from the global system, and the corresponding energy $E^{\mathrm{CNT/chit}}$ is calculated from the total energy without subsequent minimization. Then from this ensemble chitosan is removed and the corresponding energy E^{CNT} of isolated CNT is calculated. Then CNT is removed from the CNT+chitosan ensemble, and the corresponding energy of chitosan E^{chit} is calculated. Hence, the binding energy between the polymeric matrix and CNT can be calculated by the following expression:

$$E_{bind}^{CNT/chit} = -E^{chit/CNT} = E^{chit} + E^{CNT} - E^{CNT/chit} \qquad (5)$$

Total energies of chitosan, CNT, and the CNT+chitosan complex and the binding energy of chitosan with CNT, calculated based on equation (5), are given below.

$E^{\text{CNT/chit}}$, kJ/mol	E^{CNT}, kJ/mol	E^{chit}, kJ/mol	$E_{bind}^{CNT/chit}$, kJ/mol
$2{,}23996 \cdot 10^4$	$2{,}09742 \cdot 10^3$	$2{,}08216 \cdot 10^4$	500

The average binding energy of one chitosan molecule with CNT is 500 kJ/mol:6 ≈ 5 eV:6 ≈ ≈ 0.83 eV. Taking into account that in the chitosan monomer two groups (hydroxyl and amino) interact with CNT, then judging by the binding energy value it is possible to say that the intermolecular interaction between chitosan and CNT has the non-specific character.

Thus, in this work, the adsorption process of the chitosan molecule on CNT is modeled using molecular dynamics method. Based on the calculated total energies of the solution+chitosan+CNT system, we calculated the binding energy of the chitosan monomer and CNT by stepwise exclusion of separate components from the global system, which turned out to be 0.83 eV. As the results on the temperature dependence of the radial distribution function of the и chitosan molecule show, at low temperatures the attraction of chitosan to the nanotube decreases. As the temperature decreases, the aqueous environment becomes more preferable for the chitosan molecule rather than the nanotube surface. This gives evidence of an entropy character of the adsorption of the polymer molecule on the nanotube surface.

REFERENCES

1. P. Harris, *Carbon Nanotubes and Related Structures*: *New Materials for the Twenty First Century*, Cambridge University Press, Cambridge (2001).
2. *Vaisman L.* // Adv. Colloid Interface Sci. – 2006. – **128-130**. – P. 37.
3. *Ozaki T.* // Phys. Rev. B. – 2003. – **67**. – P. 155108.
4. S.Sh. Rashidova and R.Yu. Milusheva, *Chitin and Chitosan Bombyx mori*, FAN, Tashkent (2009).
5. *Frisch J., Trucks G.W., Schlegel et al.* GAUSSIAN 03, Rev. A.7. – Pittsburg: Gaussian, Inc., 2003.
6. *Van der Spoel D., van Buuren A.R., Apol E., Meulenhoff P.J., Tielemann D.P., Sijbers A.L.T.M., Hess B., Feenstra K.A., van Drunen R., Lindahl E., Berendsen H.J.C.* Gromacs User Manual, version 3.1.1. – University of Groningen: Groningen, The Netherlands, 2002; www.gromacs.org.
7. *Hansong Cheng, Alan C. Cooper, Guido P. Pez, Milen K. Kostov, Pamela Piotrowski, Steven J. Stuart* // J. Phys. Chem. B. – 2005. – **109**. – P. 3780 – 3786.
8. *Werder T., Walther J.H., Jaffe R.L., Halicioglu T., Koumoutsakos P.* // J. Phys. Chem. B. – 2003. – **107**. – P. 1345 – 1352.
9. *Deyu Lu, Yan Li, Umberto Ravaioli, Klaus Schulten* // J. Phys. Chem. B. – 2005. – **109**. – P. 11461 – 11467.
10. *Walther J.H., Jaffe R., Halicioglu T., Koumoutsakos P.* // J. Phys. Chem. B. – 2001. – **105**. – P. 9980 – 9987.
11. *Rapp A.K., Casewit C.J., Colwell K.S., Goddard III W.A., Skiff W.M.* // J. Amer. Chem. Soc. – 1992. – **114**, N 25. – P. 10024 – 10035.
12. *C. Kittel*, *Introduction to Solid State Physics*, 4th Ed., Wiley, New York (1971).