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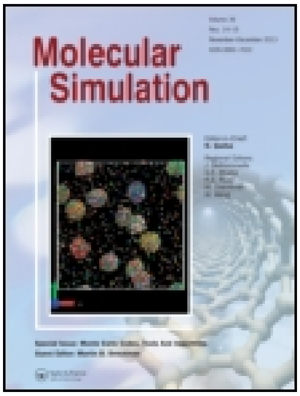

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Effect of chirality, length and diameter of carbon nanotubes on the adsorption of 20 amino acids: a molecular dynamics simulation study

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Effect of chirality, length and diameter of carbon nanotubes on the adsorption of 20 amino acids: a molecular dynamics simulation study

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We carried out molecular dynamics simulations to study the adsorption of all the 20 amino acids (AAs; aromatic, polar and non-polar) on the surface of chiral, zigzag and armchair single-walled carbon nanotubes. The adsorption was occurring in all systems. In the aromatic AAs, the $\pi-\pi$ stacking and the semi-hydrogen bond formation cause a strong interaction with the carbon nanotubes (CNTs). We also investigated the chirality, length and diameter dependencies on adsorption energies. We found that all AAs have more tendency to adsorption on the chiral and zigzag CNTs over the armchair. The results show that increasing both the diameter and the length causes the enhancement of the adsorption energy. But, the effect of the length is more than of the diameter. For example, the adsorption energy of Trp on the surface of CNT (4,1), with 2 nm length, is 20.4 kcal/mol. When the length of CNT becomes twice, the adsorption energy increases by 24 ± 0.3%. But by doubling the diameter, the adsorption energy increased only by 9.8 ± 0.25%.

Keywords: molecular dynamics simulation; carbon nanotubes; amino acids; adsorption

1. Introduction

Nanotechnology is being considered for use inside the human body at an increasing rate. To date, there are only a few clinically approved nanocarriers that incorporate molecules to selectively bind and target cancer cells.[1] The major goal of expanding nanocarrier drug delivery system (DDS) was to increase the therapeutic effect or reduce toxicity of active materials. The demands for new DDSs to improve the pharmacological forms while decreasing the toxicological effects of the delivered drugs have envisaged carbon nanotubes (CNTs).[2,3] In these days, after 36 years from the first synthesis of CNTs by Oberlin et al. [4] and 21 years from their detailed structural description by Iijima [5], CNTs have been developed from a matter of dreams to a real matter that has already found its application. CNTs have been investigated as absorbents for the thermal ablation of tumours,[6] as an *in vivo* glucose measurement means [7] and as *ex vivo* devices for the measurement of cholesterol concentration.[8,9] In general, CNTs display a great role for usefulness as delivery agents and sensors,[10,11] with very low toxic effects, perhaps due to their small size, stable structures and non-polar nature. It is quite obvious that due to their high surface area, they are powerful for adsorbing or conjugating with a broad variety of therapeutic molecules.[12] CNTs help the attached therapeutic molecule to perforate through the target cell to treat diseases. The needle-like shape of the CNTs enables them to penetrate cellular membranes and transport the carried therapeutic molecules to the cellular components.[13]

However, proteins are the functional units of life. Studies on the interaction of the nanoparticles and proteins may provide a key to conception of the basic question in nanotoxicology and nanopharmacology. There is an increasing penchant in the investigation of interaction between proteins and nanoparticles in recent years.[14,15] It has been found that some proteins could be encapsulated into the inner space of CNTs [16–18] or non-covalently bound to the sidewalls of CNTs.[19–21] As for the non-covalent binding proteins to the sidewall of CNTs, the processes consider the adsorption of these molecules on the CNT surfaces.[22,23] Many experiments with different methods were carried out for consideration of the adsorption of proteins on the CNT surfaces. These experiments excessively increased the understanding of the interaction between the protein and the CNT surfaces. The atomic details of the interactions taking place at the molecular level are unclear, due to the limitation of the experimental methods.[24] For example, the details of the function and conformation of proteins that are non-covalently absorbed onto the CNTs cannot be explored by these techniques. In addition, the dynamics of the adsorption process, which is essential in the biological applications of CNTs, is insignificantly understood via these methods. In any case, these branches of science are very important in understanding the environmental and biological activities of CNTs. Atomistic molecular simulation presents one of the most direct methods to investigate the atomic details of the adsorbate–adsorbent surface interactions. It could discover the dynamics at the molecular level and define the effect of surface chemistry on the adsorption behaviour of proteins.

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Understanding more details about these processes still needs more research. Since the proteins are built with the building blocks called amino acids (AAs), it seems that the investigation of the interaction between AAs and CNTs will be the key to guide understanding the interaction of complex proteins with CNTs. There are some theoretical studies on the interaction between CNTs and AAs. Roman et al. [25] investigated the adsorption of the simplest AA (Gly) on CNT (3,3) based on density functional theory (DFT). De Miranda Tomásio and Walsh [26] studied the geometries of Trp and His adsorbed on the surface of zigzag CNTs by AMOEBAPRO force field. Sun and Bu [27] studied the adsorption of Gly on the surface of zigzag CNTs by DFT method. Wang et al. [28] investigated the adsorption of only three aromatic AAs (Trp, Tyr and Phe) on the sidewall of chiral and armchair CNTs with different diameters, using DFT calculations.

As described earlier, in previous studies the quantum mechanical methods (most DFT method) were used for investigation of the AAs adsorption on the surface of CNTs. In these works, the solvent is not included and many of the investigations have been done in the gas phase. Therefore we wanted to simulate the systems that are very similar to the real biosystems. Consequently, we inserted water molecules as the solvent molecules in the simulation box. As the computational cost of the quantum mechanical methods (such as DFT) is much higher than the classical molecular dynamics (MD) simulation, we selected MD simulation. By using the MD method, we can simulate the solution systems for the longer periods of time than the previous works.

In this study, we used MD simulation to investigate the adsorption of the 20 AAs (aromatic, polar and non-polar AAs) on the surface of various types of single-walled carbon nanotubes (zigzag, chiral and armchair) with different diameters and lengths. We investigated the effect of AA structure, chirality, length and diameter of CNT on the value of adsorption energy.

2. Computational details

In this study, the GROMACS package (version 4.0.5) [29] was used for all simulations, with the OPLS/AA force field. [30] We prepared the structure files of the 20 AAs (from RCSB databank). The.pdb files for CNTs (with different diameters and lengths) were prepared by VMD software. [31] The parameters of CNTs are given in Table 1. The Morse potential was used to explain the bonds of the CNT and a cosine potential was used to describe the angles. In previous MD simulations, these parameters were used for the systems involving the CNTs in the presence of biomolecules, and were found to reproduce experimental results successfully.[32] The parameters of Lennard-Jones potential for the cross interactions between non-bonded atoms (e.g. CNT–AA and CNT–water) were obtained from the Lorentz–Berthelot combination rules as the others.[24] Particle mesh Ewald summation [33] was used to calculate the long-ranged electrostatic interactions for the separation of the direct and reciprocal space, with a cut-off distance of 12 Å. Periodic boundary conditions were applied for all simulations.

Table 1. The parameters of CNTs.

(n,m)	D (Å)	θ (°)	L (Å)
(3,3)	3.32	30.00	20
(4,4)	5.43	30.00	20
(5,5)	6.78	30.00	20
(8,8)	10.86	30.00	20
(5,0)	3.92	0.00	20
(7,0)	5.47	0.00	20
(10,0)	7.83	0.00	20
(14,0)	10.97	0.00	20
(4,1)	3.60	10.89	20
(5,2)	5.00	16.10	20
(8,2)	7.18	10.89	20
(10,5)	10.36	19.11	20

Notes: D, diameter; θ, chiral angle; L, length. (The values of θ and D for the CNTs with $L = 4$ nm is similar too.)

A time step of 1 fs was set. The OPLS simulations in aqueous solution typically use the TIP4P or TIP3P water model.[34] Since that TIP3P is a three-site model and is simpler than TIP4P model, we used TIP3P water model in all simulations. This water model is suitable for biomolecular simulations too. There were 570 water molecules in each simulation box to maintain a constant density of 1000 kg/m^3. During these MD simulations, the pressure was held at 1 atm using Parrinello–Rahman [35] coupling, and the temperature was maintained at 300 K using Berendsen thermostat.[36] For the computation of the adsorption energy, simulation boxes of the CNT–AA–water systems, the CNT–water systems and the AA–water systems were prepared. The CNT–AA–water systems were carried out with starting structures that the closest atom to the surface of CNT placed ~5 Å to ensure that there is enough space to contain several layers of water between the AAs and the CNT surface.[24,37]

Therefore, we calculated the energy of each of them. A 100,000-step energy minimisation of each system was carried out at first. Then, all of the systems underwent 5-ns MD runs until the RMSD and the total energy fluctuated around constant values. The interaction energy, E_{int}, for all the systems in MD simulations, is defined as follows:

$$E_{\text{int}} = E_{\text{CNT+AA}} - E_{\text{CNT}} - E_{\text{AA}}, \tag{1}$$

where E_{int} stands for the total interaction between the AA and the CNT surface, and $E_{\text{CNT+AA}}$, E_{CNT} and E_{AA} are the total energy of the CNT–AA complex in water, the potential energy of CNT in water and that of the AA in water, respectively. These data were derived from the preserved frames in the simulations by averaging the data for the last 200 ps. This method has been successfully applied to investigate the adsorption of proteins on inorganic material surfaces.[24]

3. Results and discussion

MD simulations show that the adsorption was occurring in all systems before 2 ns. The chemical structures of AAs affect the value of the adsorption energy. There is exactly the same trend in the adsorption of the AAs on the surface of CNTs. The values of adsorption energies are shown in Figure 1.

From these data, we observe a general trend that expresses the most adsorption belonging to aromatic structures and then to sulphur and polar and aliphatic AAs, respectively. Several factors such as hydrophobic and electrostatic effects may take part in this orientation. The non-polar aliphatic AAs such as Val adsorbs to the surface through the van der Waals attraction and the hydrophobic interaction. Because the carbon atoms in CNTs have no net charge, the charged and polar AAs can adsorb onto the surface through the van der Waals interaction too. About aromatic AAs, the $\pi-\pi$ interaction is a key factor that affects on the adsorption energy.[38–40] The experimental results also showed that peptides containing aromatic rings have the most affinity with CNTs.[41,42]

The comparison of the values between the adsorption energies of aromatic AAs and all the CNTs surfaces shows that the Trp–CNT has more adsorption energy than the other three aromatic AAs (Tyr, Phe and His). For more explanations, the structures of four aromatic AAs are shown in Figure 2. The positions of these aromatic AAs, before and after the equilibration, beside the CNT (4,1) ($L = 2\,\mathrm{nm}$), are shown in Figures 3–6. At first step, the rings of these AAs have been put in vertical situation to the rings of CNTs. In Figure 3, it is clear that the indole ring in the side chain of Trp has a stronger interaction with the CNT. During the MD simulation, the indole ring rotated completely and stood nearly parallel to the CNT's rings. The similar cases have been occurring in the other aromatic AAs. In other words, the aromatic rings of AAs (that put vertical to the CNT's rings) rotated around the CNT and selected the almost parallel position to the CNT's rings, finally. It seems that the $\pi-\pi$ stacking has an

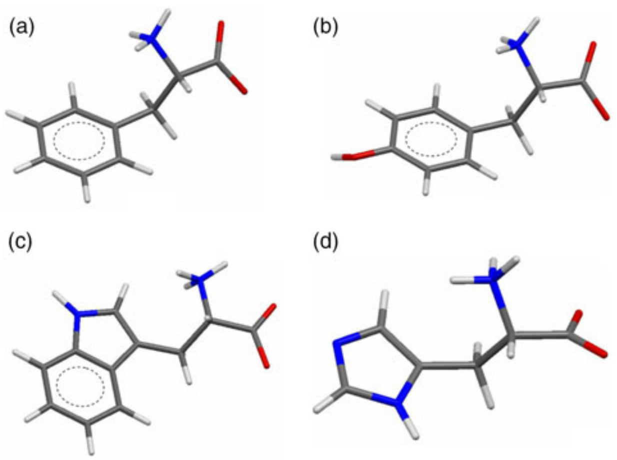

Figure 2. (Colour online) The oxygen atoms are shown by red capped sticks, nitrogen atoms by blue capped sticks and carbons by grey capped sticks. (a) In Phe, there is a benzene ring in the side chain, (b) Tyr has the —OH functional group instead of the hydrogen, (c) Trp has an indole ring and (d) His has an imidazole ring.

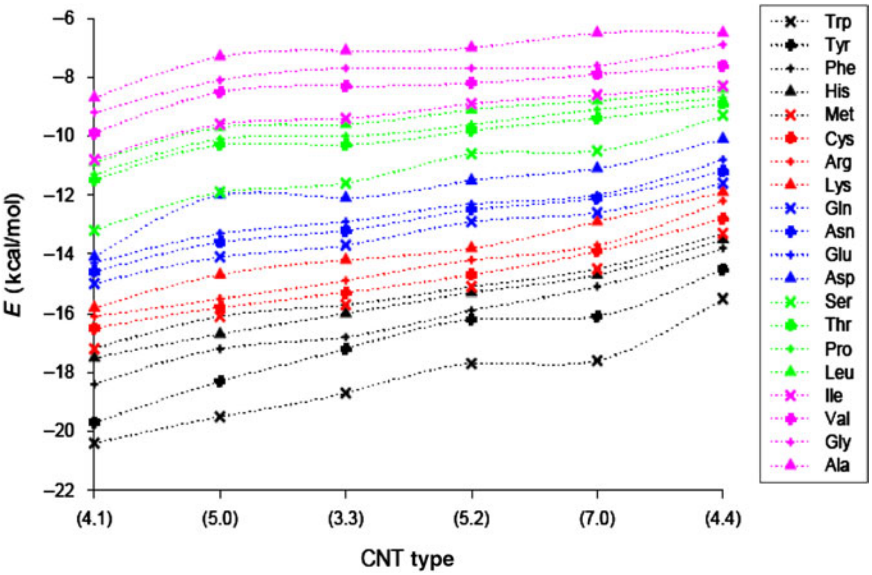

Figure 1. Adsorption energy of AAs on the surfaces of the CNTs ($L = 2\,\mathrm{nm}$).

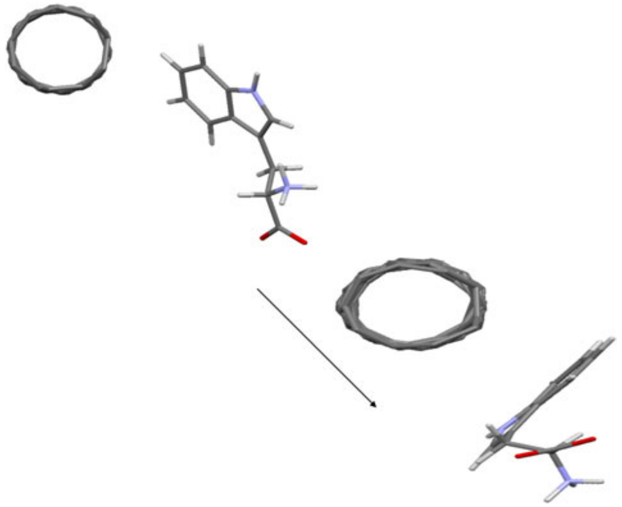

Figure 3. The position of Trp before and after the equilibration, beside the CNT (4,1) ($L = 2$ nm).

Figure 5. The position of Phe before and after the equilibration, beside the CNT (4,1) ($L = 2$ nm).

important role in the interaction of aromatic AAs with CNTs.

Then, the Tyr–CNT has larger adsorption energy than the Phe–CNT. It is because of the presence of —OH functional group that linked to the phenyl ring. In Figure 4, it is shown that the —OH group is oriented towards the CNT surface. Levitt and Perutz [43] reported that aromatic rings act as hydrogen bond acceptors. They showed that there is a significant interaction between a hydrogen bond donor and the centre of a benzene ring, which acts as a hydrogen bond acceptor. This interaction which is about half as strong as a normal hydrogen bond is expected to play a significant role in molecular associations. In interaction of Tyr and CNT, it seems that there are the similar conditions. The hydrogen atom of —OH group tends to be closer to the CNT ring that can play a semi-hydrogen bond acceptor. The tendency to the formation of a semi-hydrogen bond, in addition to the $\pi-\pi$ stacking of the aromatic ring of Tyr and CNT, causes that the adsorption energy of Tyr becomes more than Phe, which has no mentioned —OH group.

In aromatic AAs, His has the least value of the adsorption energy on the surface of CNTs. Considering that all hetrocycles have lower resonance energies than benzene, then His has less aromaticity than Phe (resonance energy of benzene is 36 kcal/mol and resonance energy of imidazole is 22 kcal/mol). The least aromaticity in His may cause a weak $\pi-\pi$ stacking and leads to the least adsorption energy rather than the other aromatic AAs. After aromatic group, the polar AAs have more adsorption

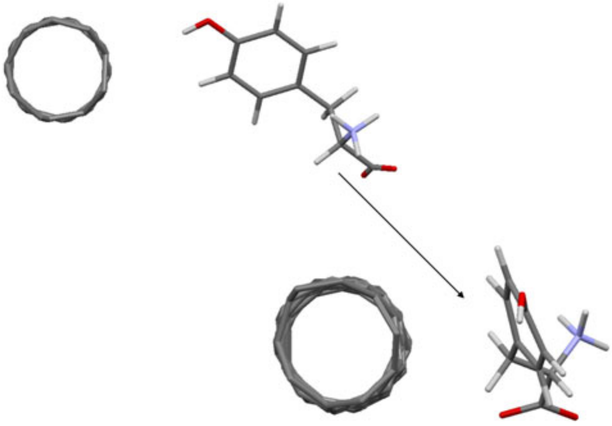

Figure 4. The position of Tyr before and after the equilibration, beside the CNT (4,1) ($L = 2$ nm).

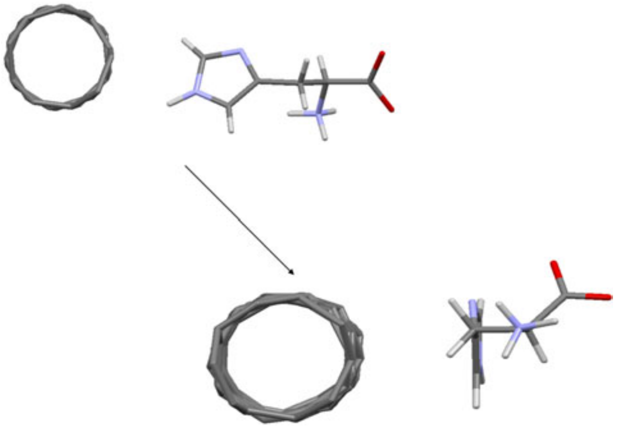

Figure 6. The position of His before and after the equilibration, beside the CNT (4,1) ($L = 2$ nm).

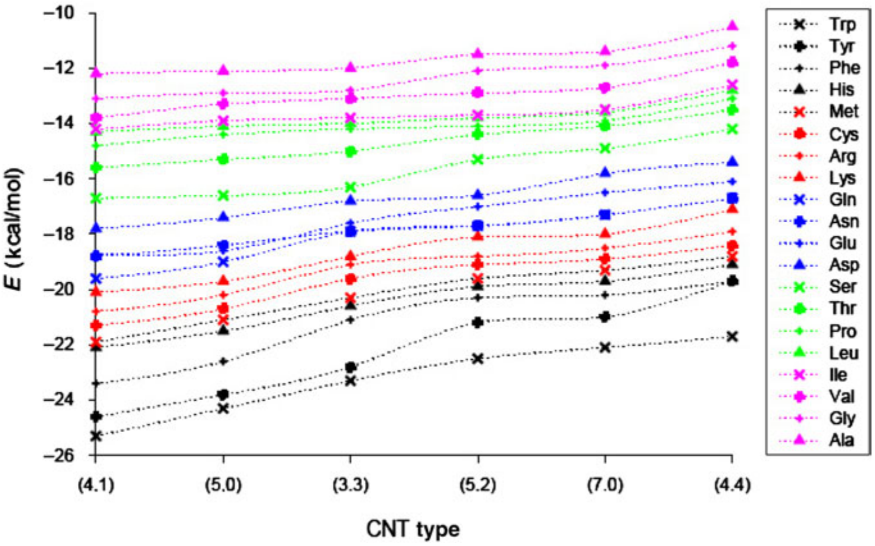

Figure 7. Adsorption energy of AAs on the surfaces of the CNTs ($L = 4\,\mathrm{nm}$).

energy on the surface of CNTs. In between, the molecules that have sulphur in their structures (Met and Cys) have more interaction with the CNT's surface. Then, the polar AAs that have a long branch of —CH_2— have been adsorbed. These proceedings can be explained by the electrostatic effects.

However, the type of CNTs (chiral, zigzag or armchair) influences the values of adsorption energies. Comparison between the adsorption energy of AAs on the surface of CNTs with the same length and diameter show that all AAs have more affinity for adsorption on the chiral and zigzag CNTs over the armchair CNTs. This phenomenon was reported by Wang et al. [28]. They investigated the adsorption of Trp and Tyr and Phe on the surface of zigzag and armchair CNTs using DFT calculations. They found that the AAs prefer adsorption onto the zigzag CNTs over the armchair CNTs of the same diameter. They did not explain the reason of these results. But, we focused on these observations and found that it is because of the less aromaticity of the armchair CNTs. We know that all armchair CNTs, basically, are metallic, and the zigzag and chiral CNTs are semiconductors. CNTs can be regarded as quasi-one-dimensional cylindrical aromatic macromolecules. Aihara [44] showed that both armchair and semiconducting CNTs are aromatic, although metallic nanotubes are less aromatic than semiconducting nanotubes. Therefore, it is clear that AAs prefer adsorption onto the CNTs that have more aromaticity. As a result, they form the more stable complexes with zigzag and chiral over the armchair CNTs.

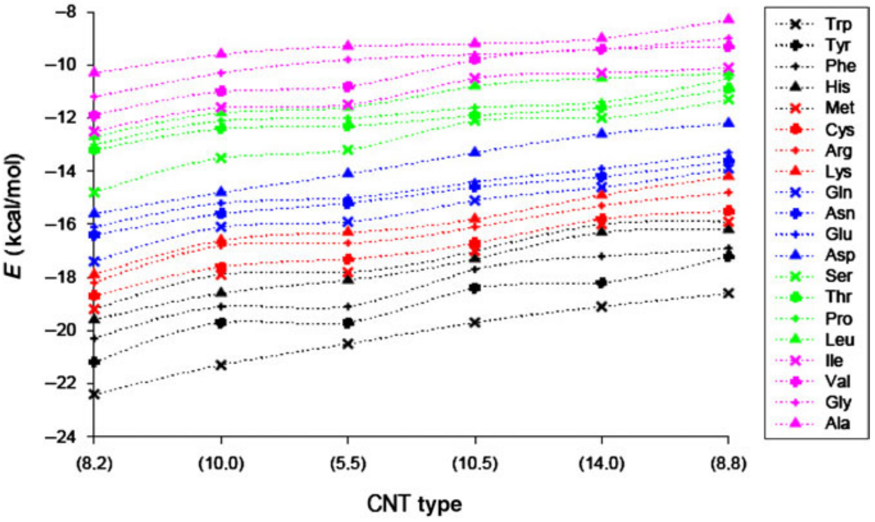

Figure 8. Adsorption energy of AAs on the surfaces of the CNTs ($L = 2\,\mathrm{nm}$).

Another factor that affects the values of the adsorption energies is the length of CNT. In all types of CNTs (zigzag, chiral and armchair), with the same diameter, the adsorption energy of AA on the CNT surface increases by the enhancement of the length of the CNT (Figure 3). Comparison between Figure 1 and Figure 7 shows that the longer length produces the larger surface of adsorbent. The larger surface adsorbent (that means the larger contact area between the AA and the CNT) causes to the strong interaction.

In addition, increasing the diameter of the CNTs has the same effect (Figure 4). As shown in Figure 8, by increasing the diameters of the CNTs, all AAs tend to adsorb better (compare the results of Figures 1 and 8). It is worthy to mention that the adsorbent surface also increases by diameter enhancement. But, the effect of increasing the length is more than the effect of increasing the diameter. For example, the adsorption energy of Trp on the surface of CNT (4,1), with 2 nm length, is 20.4 kcal/mol. When the length of CNT becomes twice (from 2 to 4 nm), the adsorption energy becomes 25.3 kcal/mol (24 ± 0.3% increased). But by doubling the diameter, the adsorption energy becomes 22.4 kcal/mol (9.8 ± 0.25% increased). These conditions have been observed in all systems (all AAs and on the all types of CNTs). As described earlier, when the length or the diameter of the CNT increases, the surface of adsorbent increased. Therefore, the adsorption energy is increased too. Considering that the side surface area (A) of a cylinder is $A = \pi DL$, it is obvious that there is a linear relationship between A and D, and also A and L. Therefore it is expected that both changes, doubling the diameter and the length of the CNT, have the same effects on the increased per cent of the adsorption energy, because by doubling the length or doubling the diameter, the side surface area becomes double. Thus, it is accepted that there is another reason for this case.

It is known that the armchair CNTs are metallic. But, chiral and zigzag CNTs have semiconductor properties. The analytical results show that the band gap of CNTs depends on both the diameter and the chirality.[45] The band gap of semiconductor CNTs depends inversely on its diameter. It can be described that when the diameter increases, the band gap decreases. Reduce in the band gap causes the semiconductor properties of CNT change to the metallic properties. Lu and Chen [46] reported that zigzag and chiral CNTs with small diameters have metallic properties (with finite gap). We can conclude that when the diameter of the CNT increased, the metallic properties increased too. As described previously, the metallic nanotubes have less aromaticity. Then, the increase in the diameter has two effects on the AAs adsorption. The first effect is the increase in the surface of adsorbent (CNT) that causes an increase in adsorption. The second effect is the increase in the metallic properties that causes reduction in the aromaticity of the CNT, and then reduction in the adsorption. Therefore, it can be expected that the effect of increasing the length be more than the effect of increasing the diameter.

4. Conclusion

For the first time, the adsorption of all the 20 AAs on the surface of chiral, zigzag and armchair CNTs was investigated by MD simulations. We simulated the systems in the solution state. We found that the adsorption was occurring in all systems before 2 ns. There is a general trend which expresses that the most adsorption belongs to aromatic, then the sulphur and then the polar and aliphatic AAs, respectively. Between the aromatic AAs (Trp, Tyr, Phe and His), Trp has a stronger interaction with the CNTs because of the presence of the indole ring. The Tyr–CNT has larger adsorption energy than the Phe–CNT. The —OH functional group that linked to the phenyl ring tends to be closer to the CNT's ring. It can play a semi-hydrogen bond acceptor. This semi-hydrogen bond formation in addition to the π–π stacking causes that the adsorption energy of Tyr becomes more than Phe. Meanwhile, His has the least value of the adsorption energy on the surface of CNTs, because His is a heterocycle molecule and has lower resonance energy than Phe.

The results show that all AAs have more affinity for adsorption on the chiral and zigzag CNTs over the armchair. We found that the less aromaticity of the armchair CNTs is its reason. We investigated the effect of increasing the length and the diameter of CNTs on the adsorption energy of AAs too. Data show that in all types of CNTs, as the same diameter, the adsorption energy of AAs increases by enhancing the length of the CNT. In addition, increasing the diameter of the CNTs, as the same length, has the same effect. But, the effect of increasing the length is more than the effect of increasing the diameter. It is known that the band gap of CNTs depends on both the diameter and the chirality. Since that the band gap of semiconductor CNTs depends inversely on its diameter, thus by increasing the diameter of CNT the metallic properties increase too. Therefore, the aromaticity of the CNT decreases. This factor can decrease the value of adsorption energy. So the effect of increasing the length on the adsorption energy is more than the effect of increasing the diameter.

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