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Investigation of the nanotubes-H_2O complex by molecular mechanics and semi empirical methods

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ABSTRACT

In this study, a three-component BBNT-MWCNT-SWCNT nanotubes with water as the inter-nanotube guest were investigated as well as single wall and multi wall nanotubes in which terminal carbons were substituted by oxygen and nitrogen using thermodynamic and molecular calculation methods. Molecular computational methods were conducted by molecular dynamics methods such as Monte Carlo with OPLS force field at 6 different temperatures (249, 298, 302, 306, 310 and 314 K) and semi-empirical methods using PM3 method. The best temperature for comparison was 298 K. The temperature of 310 K (human body temperature) was also investigated for biological and medical applications. We investigated different energies such as potential and kinetic as well as total energy in 10 steps at 10-nm scale. All the positions of complexes were optimized by semi-empirical and molecular mechanics methods in which total energy and atomic force were minimized. For all shapes of SWNT and BBNT, a decrease was observed in the slope and SWCNT exhibited the most stable state at 310 and 298 K. The lowest potential energy was observed at 310 K. Potential energy of SWCNT showed a decreasing trend relative to MWCNT. Therefore, carbon nanotubes can be used as a drug carrier at body temperature.

Keywords: *nanotubes-H_2O, Molecular mechanics, Semi empirical, nanotube SWCNT, MWCNT and BNNT and H_2O*

1. INTRODUCTION

Use of Carbon nanotubes (CNTs) as mediators has attracted increasing attention in recent years and in comparing with traditional ones, they've shown up some advantages such as unique structure, incredible strength and fascinating electronic properties, high surface area, stability, high thermal conductivity, and fascinating physicochemical properties enable covalent and noncovalent introduction of several pharmaceutically related entities[1,2].

CNTs can have strong links with different functional groups to transfer several moieties together for targeting, imaging, and therapy [3].

This structural property, topology the size of nanotubes are the reasons of making them exciting in compared with the parent, planar graphite-related structures, such as are for example found in carbon fibers [4].

Among two main types of CNTs, single-walled nanotubes which made of single graphite sheet seamlessly wrapped into a cylindrical tube [5] have exclusivity for studying fundamental properties in one-dimensional electronic systems with revolutionary ability of many aspects of Nano/molecular electronics [6] and because of what is mentioned above about CNTs properties that are more remarkable in SWNTs, this kind of nanotubes are more popular [7].

Spectroscopic measurements showed one-dimensional singularities in the SWNT can exhibit either metallic or semiconducting properties, depending on the orientation of the lattice. Zig-zag and armchair carbon nanotubes exhibit metallic properties, while chiral nanotubes can be either semiconducting or metallic depending upon the difference between the n and m units. [5]

The second form of the main CNTs is Multi-walled nanotubes (MWNTs) Which consist of a set of nanotubes that are usually in the form of tree rings [5]. That can be as few as 2, or as many as 100 plus walls and their diameters may be as great as 50nm as opposed to 0.7 - 2.0 nm [7].

The electronic properties of the MWNTs and SWNTs are rather similar and this is because of the weak molecular bonds between their cylinders. Mercantile access to MWNTs is less problematic. Hyperion Catalysis International, Inc., introduced MWNTs in multitone quantities in the early 1990s [5]. With considering the fact of non-polarity of CNTs and comparatively hydrophobic structure, water spontaneously can fill them [8]. The capability of carbon nanotubes (CNTs) to transport water such fast has led to a huge recent interest in CNT-based nanofluidics [9, 10].

For getting to know the concept of filling mechanism, we should have understood the solvent's polarity, ion concentration, and the van der Waals forces between the water and the CNT. The presence of water in CNT can produce less chemical potential and fill the CNT. This characteristic is used by van der Waals forces between the water and the membrane walls to absorb water molecules into the CNT [11]. Simulations of a CNT with small diameter (~0.8-nm diameter) covered in water showed that a small reduction of the van der Waals attraction between water and the carbon atoms persuade drying of the previously water-filled pore [12,13].

For what we mention above abut delivery fluid by CNTs, it'll use in nanofluidic devices such as separation membranes [14] and Nano pumps [9,15].

Nowadays, the most common method for desalinating water is 'reverse osmosis' in which salty water is put under high pressure

to force it through semipermeable membranes that allow the passage of water but block ions but with further improvements we still looking for making this technology widespread [14] and The something surprising is found in simulation studies was, water can enter narrow hydrophobic channels such as the interior of carbon nanotubes (CNTs) [16] so has been confirmed experimentally [17] to open the door to the entry of CNTs into membranes to form smooth pores for the target of desalination[14]. Studies on transferring water and ion through CNTs have given a range of pore size which shows that water molecules are passing rapidly but this is not the case with a series of ions [18] and also selective ions with different pore radius [19].

The effect of an electric field on the water in CNTs is also related to nanotechnology-based applications such as Nano pumping and desalination, the applied electric field changes the balance state toward the condition in which water molecules filling CNT [9,20]. A similar result has been displayed in larger CNTs, where the occupancy of water molecules in the CNTs increases with an electric field, implying a priority of water to fill the CNTs [9,21].

While it is all for the non-polar nature of the CNTs which supposed to make them suitable for use in desalination membranes, simulations have also suggested that non-carbonic nanotube forms such as boron nitride may also be suitable [14,22]. Boron nitride nanotubes (BNNTs) are a polymorphism of nitride, they are known as structural analogs of CNTs [23]. They were experimentally discovered in 1995[24]. They are structurally similar to nanotubes, with the difference that carbon atoms are relatively substituted by nitrogen and boron atoms. Since carbon nanotubes can be metal or semiconductor according to the rolling direction and radius, however, the properties of BN nanotubes are very distinct and they are electrical insulators with a bandgap of ~5.5 eV, free of the tube chirality and morphology [25]. Moreover, a graphitic carbon structure thermally and chemically is much more unstable than a layered BN structure [26,27]. They have unique physicochemical properties such as high hydrophobicity, heat and electrical insulation, resistance to oxidation, and hydrogen storage capacity and which make it possible to use them in the medicine target and biomedical applications including drug delivery [28].

All well-established techniques of production carbon nanotubes, such as arc-discharge [29], laser ablation [30], and chemical vapor deposition [31], are used for bulk-production of BN nanotubes at a tens of grams scale [32].

BN nanotubes can also be produced by ball-mill of amorphous boron, mixed with a catalyst (iron powder), under NH3 atmosphere. Subsequent annealing at ~1100 °C in nitrogen flow transforms most of the product into BN [33,34]. Eventually, a high-temperature high-pressure method is also suitable for BN nanotube synthesis. Since the charge distribution is asymmetric in B–N bonds in BNNTs compare with the C–C bonds in CNTs, electronic structures of the BNNTs are rather different from the CNTs. [35].

2. EXPERIMENTAL SECTION

In this study molecular mechanic (MM) and quantum mechanics (QM) methods for the purpose of calculating thermodynamic properties, vibrational frequencies, charges distribution, temperature affects and quantum mechanics equation for ten molecules attached by H2O such as two forms of 3.3.8 and 5.5.10 of SWCNTs, MWCNTs, BNTs and four carbon replaced SWCNTs were used(FIG1). Therefore HyperChem.8.0.8 Software for Molecular mechanic calculations and semi empirical methods were purposed. Computing of molecular changes by using the combination of methods such as QM/MM have done. At first in MM calculations, the 3D structure of the molecule by PDB format which opened via HyperChem.8.0.8 software that is a sophisticated molecular modeling environment that is popular for its flexibility and 3D incarnation, molecular and quantum mechanics calculations then Mont Carlo which is theatrical computation were done [36]. Energy parameters (potential, total and kinetic energy) Simulations by Mont Carlo method is included, OPLs force field in different temperatures such as 294,298, 302,306, 310,314 kelvin degree at 100 steps [37].

In the next step vibrational analysis which is better to be described via quantum mechanical methods, were applied via semi empirical methods [37]. Remarkable energy in these methods is total and binding energy, isolated atomic energy, electronic energy, core–core interaction and heat of formation in parameterized model number 3 PM3 Methods. PM3 which gave lower average errors in comparison with AM1 is adequate to study carbon systems mainly for the enthalpies of formation [37, 38].

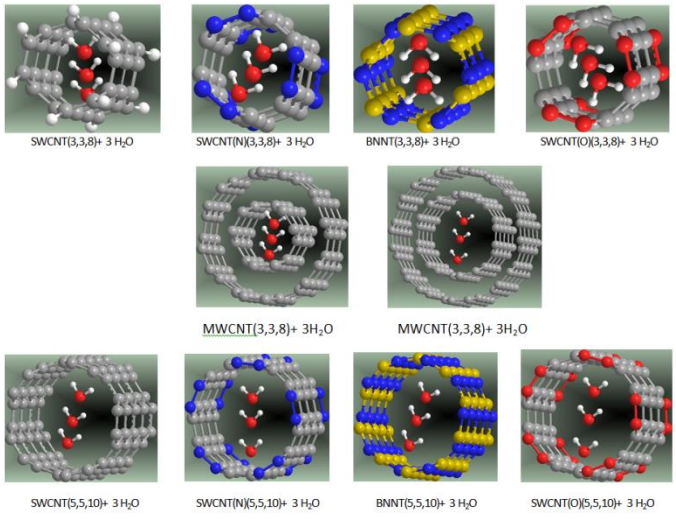

Figure 1. Nanotube-H_2O complex.

3. RESULTS SECTION

In this study, all the results were obtained by Monte Carlo and semi-empirical methods. Studies showed that the atoms were connected to each other by forces. In these calculations, the optimized energy in which the molecules have the most stable

state was found. In Monte Carlo method, OPLS force field is the only investigated force field. OPLS has been developed for proteins and nucleic acids.

Bond potentials can be nonbonding such as Van der Waals and electrostatic forces which were more significant at 298 and 310 K.

6 different temperatures (294, 298, 302, 306, 310 and 314 K) were considered as shown in Table (2).

Potential energy of (8, 3, 3) and (10, 5, 5) nanotubes at 310 and 298 K is shown in Fig 1 for cases where water fills the nanotubes. A considerable decrease can be seen in the last stage. This decline was more significant for (5, 5, 10) BBNT which was about 210.551 Kcal/mol.

As shown for BBNT (5, 5, 10) and MWCNT (5, 5, 10) (Fig 1), optimal potential energy can be observed at 298 K (193.1068 and 2277.299 kcal/moll, respectively).

Comparing two types of SWCNT at 310, smaller diameter and shorter length SWCNT (3, 3, 8) exhibited higher potential energy compared to SWCNT (5, 5, 10) (having larger diameter and longer length) (about 772.4152 kcal/moll).

Compared to MWCNT (5, 5, 10), MWCNT (3, 3, 8) (Table 2) possessed lower energy at 298 and 310 K (2277.922 versus 1396.648 kcal/moll and 1415.198 versus 444.511 kcal/moll, respectively).

Based on Tables 1 and 2, the potential energy of SWCNT (3, 3, 8) and MWCNT (3, 3, 8) at 298 and 310 K was 764.1095 and 1396.658 **kcal/moll, respectively. The minimum kinetic energy** at 298 K was for SWCNT (3, 3, 8) and BBNT (3, 3, 8) (50.63199 kcal/moll) and the highest value was recorded for MWCNT (5, 5, 10) (256.7114 kcal/moll).

Energy parameters of SWCNT (5, 5, 10) were decreased during calculations; by progress of steps at 298 and 310, it further decreased. The trend was completely opposite for SWCNT (3, 3, 8).

In terms of total energy, for both shapes of BBNT and SWCNT and at various temperature ranges, lower energy was observed. Comparing the beginning with the end, a decrease can be seen in the slope.

For SWCNT (3,3,8) and at 310 and 298 K, the structure in which the terminal carbons were replaced by nitrogen showed lower energy in comparison with its counterpart possessing oxygen substitution at the 100th stage (743.2592 Vs. 723.554 kcal / moll) (Table 2).

For SWCNT (5, 5, 10) (Tables 1 and 2) and at 310 and 298 K, nitrogen stabilized the nanotube compared to (3, 3, 8) (272.8046 and 44.511 kcal / moll, respectively). Total energy of SWCNT with oxygen inlet was lower than the one possessing nitrogen inlet (for both(3 , 3, 8) and (5,5,10) types); and the energy was about(-272.8 kcal / moll) .

All atomic coordinates were optimized using semi-empirical calculations in which the total energy and atomic forces were minimized.

Total energy, bonding energy, isolation atomic energy, electronic energy, core-core interactions and formation heat of various types of nanotubes (SWCNT (3,3,8),) ،SWCNT(5.5.10) BBNT(3.3.8) ،BBNT(5.5.10) ،MWCNT(3.3.8) ،MWCNT (5.5.10)) were optimized.

The calculation parameters of the semi-empirical method are shown in Fig 2 in which the total energy and bonding energies were equal to r2=0.94; separation energy was r2=0.88, formation energy was calculated as r2=0.94, electronic energy was r2=0.90, core-core interaction was r2=0.92. In OPLS method, the optimal total energy was for SWCNT (5, 5, 10) which was about (-260100.9547 kcal/mol)

Figure 1. The lowest potential energy of Nanotubes+ H_2O by Monte-Carlo simulation using OPLS method at 294-314 K.

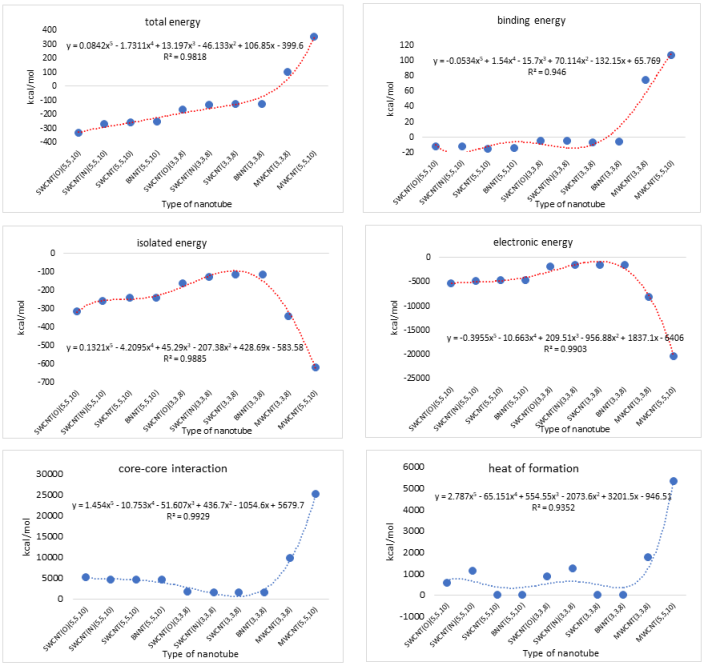

Figure 2. Optimized parameters of total energy, binding energy, isolated atomic energy, electronic energy, core–core interaction and heat of formation (Kcal/mol) for Nanotubes+ $3H_2O$ by PM3 method (polynomial).

Minimum electrical energy was -20364.51 which was for MWCNT (5, 5, 10).

Table1. The lowest potential energy of Nanotubes+ H_2O by Monte-Carlo simulation using OPLS method at 294-314 K.

TEMP	SWCNT (3,3,8)	MWCNT (3,3,8)	BNNT (3,3,8)	SWCNT (5,5,10)	MWCNT (5,5,10)	BNNT (5,5,10)	SWCNT(N) (3,3,8)	SWCNT(O) (3,3,8)	SWCNT(N) (5,5,10)	SWCNT(O) (5,5,10)
294	744.8256	1406.719	336.5988	272.4914	2293.564	207.214	740.052	765.5814	441.4456	400.2895
298	746.1095	1396.648	335.4615	286.3998	2277.922	193.1068	723.554	743.2529	446.8608	392.9672
302	758.0886	1403.759	335.5069	271.8185	2287.241	206.2883	725.6473	758.7219	426.3297	390.2453
306	768.7688	1391.954	322.7015	278.479	2292.148	213.6638	735.3131	763.7204	423.2307	412.2269
310	772.4152	1415.198	334.6676	272.8046	2289.292	210.5517	726.9049	754.4257	444.511	395.1455
314	772.3817	1408.609	339.6946	278.323	2298.301	215.7248	749.1508	752.7252	424.8171	428.953

Table2. Optimized parameters of total energy, binding energy, isolated atomic energy, electronic energy, core–core interaction and heat of formation (Kcal/mol) for Nanotubes+ H2O using PM3 method.

Energy (Kcal/mol)	SWCNT(3,3,8)	SWCNT(5,5,10)	BNNT(3,3,8)	BNNT(5,5,10)	MWCNT(3,3,8)	MWCNT(5,5,10)
total energy	-125.65	-260.1	-123.91	-256.3	1400.23	4648.36
binding energy	-7.03	-15.93	-6.28	-14.26	1741.56	5271.54
isolated energy	-118.62	-244.16	-117.63	-242.03	-341.32	-623.17
electronic energy	-1596.44	-4828.02	-1585.54	-4800.63	-8226.31	-20364.51
core-core interaction	1470.78	4567.92	1461.62	4544.33	9626.55	25012.88
heat of formation	0.935	0.646	-0.27	-1.86	1765.13	5314.41

Energy (Kcal/mol)	SWCNT(3,3,8),N	SWCNT(3,3,8),O	SWCNT(5,5,10),N	SWCNT(5,5,10),O
total energy	-133.28	-169.467	-272.8	-333.05
binding energy	-5.44	-5.16	-13.27	-12.77
isolated energy	-127.84	-164.29	-259.52	-320.281
electronic energy	-1620.63	-1843.41	-4871.6	-5385.11
core-core interaction	1487.34	1673.94	4598.8	5052.05
heat of formation	1206.26	835.2	1111.49	542.22

4. CONCLUSIONS

When water is placed in the center of the SWCNT, the complex is stable with minimum potential energy as shown for all the mentioned temperatures.

The important point is higher stability at 310 and 298 K. The temperature of 310 K is of crucial importance for medical applications.

In comparison with other temperatures, potential energy trend changed in 298 and 310 K. Moreover, they showed decreasing trend in comparison with other temperatures.

The second investigated parameter was total energy which showed lowest values for (5, 5, 10) SWCNT relative to MWCNT.

Core-core interaction is one of the important parameters; it possessed a significant value in MWCNT (5, 5, 10) while its minimum values were observed for SWCNT (3, 3, 8) BBNT (3, 3, 8) R2=0.99.

Bonding energy was the third investigated parameter which was lower in SWCNT compared to MWCNT. Finally, changes in the length of nanotubes, temperature and atomic structure will induce variations in their potential energy trend. Regarding stability of SWCNT at 298 and 310 K, it can be applied as a pattern for drug carrying applications.

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