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Investigation of Different Solvents and Temperatures Effects on (3,7) Single-Walled Carbon Nanotubes: DFT Study

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ABSTRACT

In this research, we have studied the structural properties of water, methanol and ethanol surrounding single-walled carbon nanotube (SWCNT) and mixed of them either and we have investigated the solvent effects on the relative energies and dipole moment values by using molecular dynamics simulation. We used different force field to determined energy and other type of geometrical parameters, on the particular SWCNT, because of the differences among force fields, the energy of a molecule calculated using two different force fields will not be the same. In this study difference in force field illustrated by comparing the energy of calculated by using force fields, MM+, Amber and DPLS. The Quantum Mechanics (QM) calculations were carried out with the GAUSSIAN 98 program based on density functional theory (DFT) at B1LYP/3-21G level. In this study, we have comparison between vacuum phase and solvent calculations that considered solvents such as water, methanol, and ethanol and mixed of them. Therefore in this study we investigate polar solvents effects on SWCNT within the Onsager self-consistent reaction field (SCRF) model at B1LYP/3-21G level and the temperature effect on the stability of SWCNT in various solvents.

Keywords: Solvent effect; Quantum mechanics; Molecular dynamics; DFT; Force field

INTRODUCTION

The carbon nametape (CNT) is a representative nano-material. CNT is a cylindrically shaped carbon material with a nanometric-level diameter. Its structure, which is in the form of a hexagonal mesh, resembles a graphite sheet and it carries a carbon atom located on the vertex of each mesh. The sheet is rolled and its two edges are connected seamlessly. Although it is a commonplace material that is used in pencil leads, its unique structure causes it to present characteristics that are not found with any other materials. CNT can be classified into single-wall CNT, double-wall CNT and multi-wall CNT according to the number of layers of the rolled graphite. The type attracting most attention is the single-wall CNT, which has a diameter deserving the name of "nanotube" of 0.4 to 2 nanometers. The length is usually in the order of microns, but single-wall CNT with a length in the order of centimeters has recently been released. The extremities of the CNT are usually closed with lids of the graphite sheet. The lids consist of hexagonal crystalline structures (six-membered ring structures) and a total of six pentagonal structures (five-membered ring structures) placed here and there in the hexagonal structure.The first report by Iijima [1] was on the multiwall form, coaxial carbon cylinders with a few tens of nanometers in outer diameter. Two years later single walled nanotubes were reported [2,3]. They are typically between 1 and 1.5 nm in diameter, but several microns in length. After a slow start in the mid 90's the field suddenly exploded two years ago. A first application – displays made out of field emitting multiwall tubes – is planned to be

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comercially available during the next years. Other prnposed applicatinns include, e.g., nanntubes in intergrated eireuits, nanotubc actuators, or nanotubes for hydrogcn stnrage [4-8]. From a physics pnint nf view thcy are prnbably the best realized exampIe nf a nne-dimensinnal system. Around the nanntubc's circumference the wave vector is quantizcd, where as *k* can take continnus values along the axis. The abundance nf new phenomena fnund in single-walled nanntubcs comes not only from the confinement pcr se. but alsn frnm the multiple ways to cnntruct a tube. Thc best known exampIc fnr a sudden changc in the nanotube properties with their particular structurc is their electronic dispersinn. Depending nn the direction nf thc cnnfinement directinn with respect to graphitc nanotubes are metallic nr semiconducting. Thc band structure can even be further manipulated, e.g., by introducing defects into a tube [9].

The discovery nf carbon nanotubes (CNTs) which are nano-sized materials with excellent mechanical and electrical properties and have been prnposed to be used in a variety nf applicatinn fields [10]. CNTs are a new allntrnpe nf carbon originated frnm fullerene family, which will revolutinnalize the future nanotecnological deviccs [11]. There are two types of CNTs: single-walled nanntubes (SWCNTs) and multi-walled nanntubes (MWCNTs) [12]; that they have three confnrmation: armchair (n,n), zigzag (n,0) and chiral (n,m) these conformations have individual properties [13]. SWCNTs havc heen cnnsidered as the leading candidate for nanndevice applications because nf their one-dimensional electronic bond structurc, molecular size, and biocompatibility. cnntrollable property nf conducting electrical current and reversihlc response to biological reagents hence SWCNTs make possiblc bonding to polymers and biological systems such as DNA and carbnhydrates [14].

COMPUTATIONAL METHOD

A method, which avnids making the HF mistakes in the first placc. is callcd Quantum Mnntc Carlo (QMC). There are several flavors of QMC variational. diffusion and Green's functions. These methods work with an explieitly cnrrelated wave function and evaluate integrals numerically using a Mnntc Carlo integrainn. These calculatinns can be very time consuming, but they arc prnbably the mnst accurate methnds known tnday. In general, ab initio calculatinns give very good qualitative results and can give increasingly laccurate quantitative results as the mnlecules in questinn beenme smaller. There are three steps in carrying out any quantum mechanical calculatinn in HyperChem 7.0 program package [15]. First, prepare a mnlecule with an apprnpriate starting geometry. Second, ehnosc a calculation methnd and its associated nptions. Third, choosc tbc type nf calculatinn with the relevant optinns.

Langevin Dynamics (LD) Simulation

The Langevin equatiOn is a stochastie differential equation in which twn force terms have been added to Newton's seennd law to approximate the effects nf neglected degrees nf freednm [16]. These simulatinns can be much faster than mnlecular dynamics.The mnlecular dynamics methnd is usefnl for calculating the time dependent propcrtics nf an isolated mnlecule. However, more often, nne is interested in thc properties of a mnlecule that is interacting with other mnlecules.

Molecular Mechanics (Monte Carlo Simulation)

The Metropolis implementatinn nf the Monte Carlo algnrithm has been devclnped by studying the equilibrium thermodynamics nf many-body systems. Chnosing small trial moves, thc trajectories obtained applying this algorithm agree with thnse obtained by Langevin's dynamics [17]. This is understandable because thc Monte Carlo simulations always detect the sn-called "important phase space" regions which are of low energy [18]. Because of imperfections of tbc force field,this lowest energy basin usually docs not correspond tn thc native state in most cases, so the rank of native structurc in those decoys produced by the forec field itself is pnor.

In density function theory the exact exchange (HF) for a single determination is replaced by a more general expression the exchange correlation functional. which can include terms accounting for both exchange energy and the electron correlation, which is omitted from Hartree-Fock theory:

$$E_{ks} = v + \langle h\rho \rangle + 1/2\langle P_j(\rho) \rangle + E_{\chi(\rho)} + E_{C(\rho)} \quad (1)$$

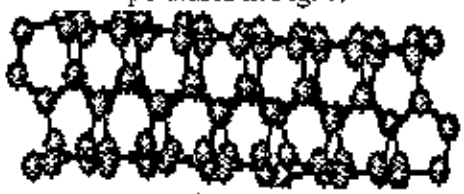
where $E_{\chi(\rho)}$ is the exchange function and $E_{C(\rho)}$ is the correlation functional. The correlation function of Lee, Yang and Parr is includes both local and non-local term [19].

RESULTS AND DISCUSSION

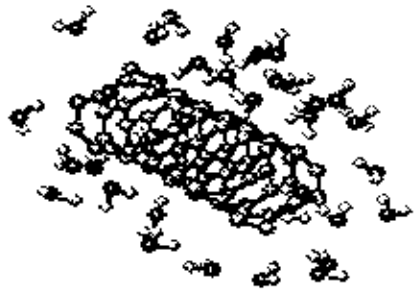
Since, the influence between a molecule in solution and its medium can describe most simply by using Onsager model. In this model we have assumed that the solute is placed in a spherical cavity inside the solvent. The latter is described as a homogeneous, polarizable medium of dielectric constant.

We started our studies at B1LYP/3-21G gas phase geometry and water, Methanol and Ethanol surraunding single-walled carbon nanotube (SWCNT) and mixed of them either. The results obtained from Onsager model calculations illustrated using the energy difference between these conformers which quite sensitive to the polarity of the surrounding snivent. The solvent effect has been calculated using SCRF model. According to this methnd, the total energy of solute and solvent, which depends on the dielectric constant ε, has been listed in Table 1.

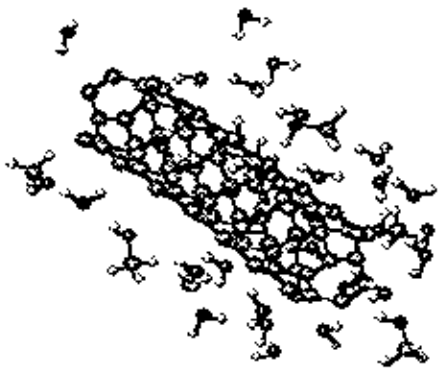
These energies have compared to the vacuum phase total energy CNT at the B1LYP/3-21G level nf theory and different solvents and the graph of energy values versus dielectric constant of different solvents has been displayed at considered temperatures in Fig. 1.



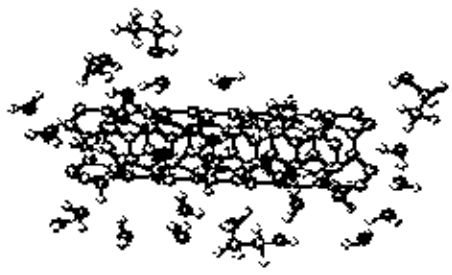
a) C_{84} (3,7)



b) C_{84} (3,7)-water



c) C_{84} (3,7)-water-methanol



d) C_{84} (3,7)-water-ethanol

Fig. 1. Optimized structure af nanotube in different media.

Table 1. Theoretical relative energies at different temperatures and dielectric constants

medium	Dielectric constant		Temperature/K								
			305	307	309	311	313	315	317	319	321
Gas phase	1	ΔE (kcal/mol)	21.94	21.94	-17.115	22.6	-43.56	6.525	-28.64	0	23.97
water	78.39		-39.832	-20.5	-6.2	-34.36	-11.154	4.11	0	24.97	-5.45
Methanol	31.63		-16.34	-15.267	-24.065	-	0.0	-	-	-1.36	-15.1
Ethanol	24.55		-50.3	8.835	-1.16	-19.13	-	0.0	-0.91	-	-2.582
Water-Methanol	70.545		0.450	-17.45	21.78	0	-16.467	-1.377	-4.389	11.343	15.5
Water- Ethanol	72.276		-41.270	-28.561	-46.204	-50.048	-32.57	-15.545	-31.72	-13.635	0

Since the solute dipole moment ioduces a dipole moment in opposite directioo in the surrounding medium, polarization of the medium in turn polarizes the charge distribution in the solvent. The dipole moment value of SWCNT io different solvent media and at different temperatures has been reported in Table2.

Onc much more practical approach consists of calculating the molecular volume as defined through the contour of constant electron density, equating this (oon-spherical) molecular volume to the radius of an (idcally spherical) cavity, and adding a constant increment for the closest possible approach of solvent molecules. This latter approach used in Gaussian when the volume keyword was being used.

In this work, we studied the structural properties of water, methanol and ethanol surroundiog single-walled carboo nanotube (SWCNT) and mixed of them either using molecular dynamics simulations. We used different force field to determination of energy and other type of geometrical parameters, on the particular SWCNT, because of the differeoces among force fields, the energy of a molecule calculated using two diffcreot force fields will not be the same.

So, it is not reasonable to compare the energy of onc molecule caleulated with a particular force field with the energy of another molecule calculated using a differeot force field. In this study diffcrence in force field illustrated by comparing the energy of calculated by using force fields, MM+, Amber and OPLS.

Theoretical energy values using differencc force fields which is the combination of attractioo van der Waals forces due to dipole-dipole interactions and empirical repulsive forces due to Pauli repulsion has been demonstratcd in Table 3 and Fig.3.

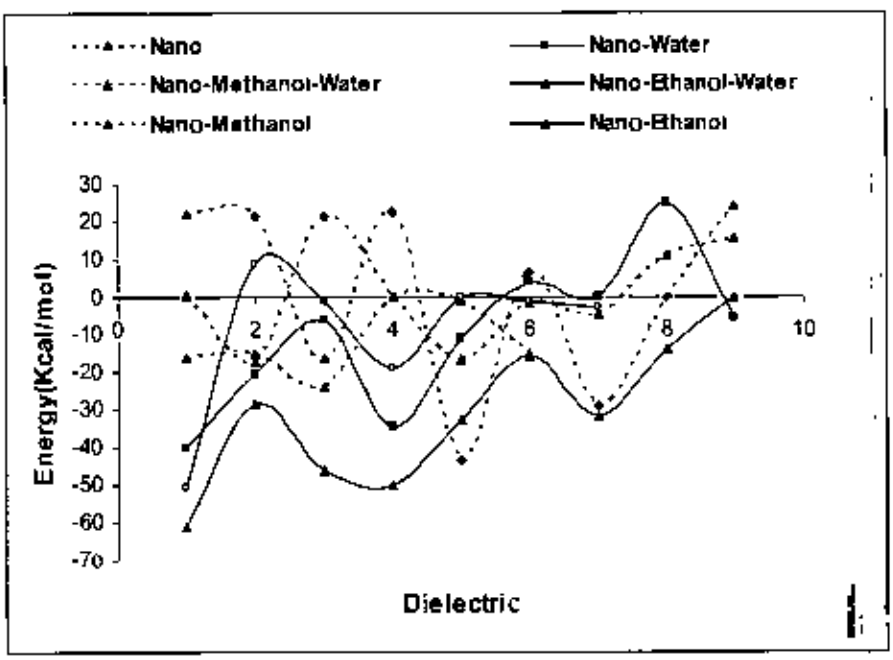


Fig. 1. The relative energy values at different temperatures in different solvents.

Table 2. Theoretical dipole moment values at different temperatures

medium		Temperature (K)								
		305	307	309	311	313	315	317	319	321
Gas phase	Dipole moment	4.34	4.34	1.89	2.9	2.6	1.88	1.88	1.2	1.15
Water		2.02	0.714	1.75	0.24	2.256	1.85	0.816	0.643	1.097
Methanol		5.4	6.03	7.91	-	7.84	-	-	7.33	7.66
Ethanol		2.162	5.94	2.561	2.46	-	2.065	1.461	-	0.651
Water- Methanol		3.806	3.648	3.055	3.588	3.287	4.208	3.770	1.974	3.961
Water- Ethanol		1.208	2.776	1.593	2.139	1.282	2.660	2.355	4.083	5.46

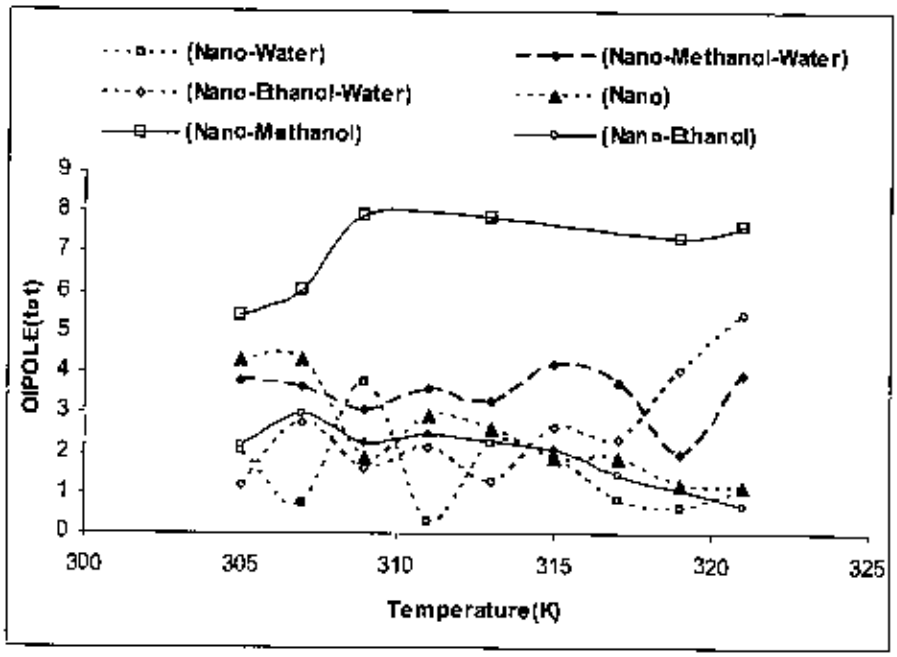


Fig. 2. The dipole moment values at different temperatures.

Table 3. Theoretical eaergy values using different force fields

medium	Dielectric constant	MM+	AMBER	OPLS
		E(kcal/mol)		
Gas phase	1	572.6539	2050.224	217.77417
Water	78.39	1322.467	802.1885	335.031555
Methanol	32.63	530.6945	1076.106	264.525391
Ethanol	24.55	520.2183	1497.42	216.47168
Water- Methanol	70.545	561.6534	1630.788	247.745514
Water- Ethanol	72.236	645.1802	1419.872	291.121033

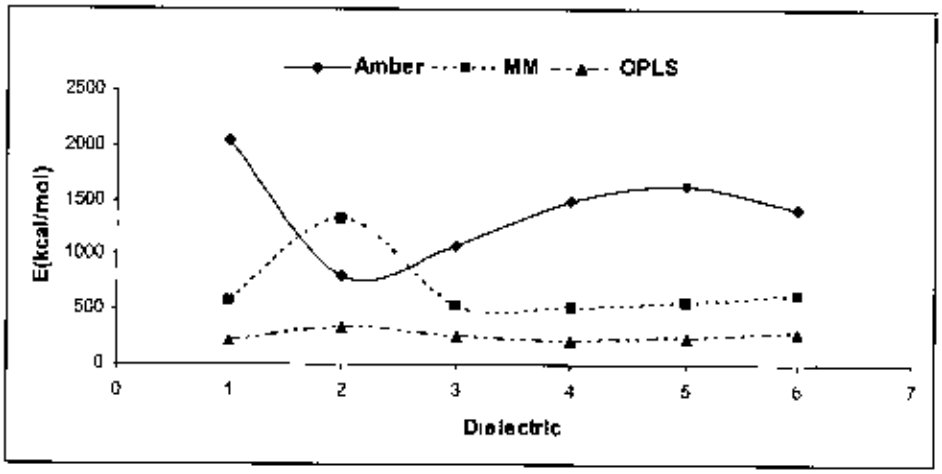


Fig. 3. The energy values using differeat force fields

CONCLUSION

In this study, we investigated polar solvents effects and different temperatures effect on the stability of SWCNT in various solvents. Ab initio calculations were carried out with GAUSSIAN 98 program using density functional theory (DFT) at the B1LYP/3-21G level of theory. Because of the graphene sheet of single-wall carbon nanotube it is logical and satisfactory finding that the water can be suggested as the most improper solvent for structural properties of SWCNT due to its strongly hydrophobic characteristic.

Also orientation of the water molecules at the CNT-water interface can be affected the orientation of the water dipole moment. The results obtained from Onsager model seemed quite sensitive to the polarity of the surrounding solvent.

Moreover, we have compared the energy values obtain from different MM+, Amber and OPLS force fields and concluded that the OPLS force field is the most proper force field for studying SWCNT.

REFERENCES

[1] S. Iijima, "Helical microtubules of graphitic carbon", Nature 354, 56 (1991).

[2] S. Iijima and T. Ichihasi, "Single-shell carbon nanotubes of 1-nm diameter", Nature 363, 603 (1993).

[3] D. S. Bethune, C. H. Kiang, M. S. deVries, G. Gorman, R. Savoy, J. Vazques, and R. Beyers, "Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer", Nature 363, 605 (1993).

[4] R. H. Baughman, C. Cui, A. Zakhidov, Z. Iqbal, J. N. Barisci, *et al.*, "Carbon nanotube actuators", Science 284, 1340 (1999).

[5] M. Hirscher, M. Becher, M. Haluska, U. Dettlaff-Weglikowska, A. Quintel, *et al.*, "Hydrogen storage in sonicated carbon materials", Appl. Phys. A: Mater. Sci. Process 72, 129 (2001).

[6] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, "Storage of hydrogen in single-walled carbon nanotubes", Nature 386, 377 (1997).

[7] F. L'eonard and J Tersoff, "Novel length scales in nanotube devices", Phys. Rev. Lett. 83, 5174 (1999).

[8] S. J. Tans, A. Verschueren, and C. Dekker, "Room-temperature transistor based on a single carbon nanotube", Nature (London) 393, 6680 (1998).

[9] V. H. Crespi, M. L. Cohen, and A. Rubio, "In situ band gap engineering of carbon nanotubes", Phys. Rev. Lett. 79, 2093 (1997).

[10] N. kurita, I. Komura, T. Tsukamoto and Y. Ishikawa, Helevetica Chimica Acta,88, 751, 2005

[11] S. Daniel, T. P. Rao, K. S. Rao, S. U. Rani, G. R. H. Naidu, H. Y. Lee and T. Kawai,Sensors and Actuators B, 122,672, (2007).

[12] M. Foley, Cheap Tubes, 2005.

[13] B. Gnjman, H. Hsin, J. Liang, N. Nezhdanova and J. Saini, 2004.

[14] T. Ramanathan, F. T. Fisher, R. S. Ruoff and L. C. Brinson, Chem mater. 17, 1290, (2005).

[15] HyperChem 7.0, Hypecube Inc., Gainesville, FL, USA, (2001).

[16] Wang, W.; Skeel, R D. *Mol. Phys.*, 101, 2149. (2003).

[17] Tiana, G., Sutto, L.; Broglia, R.A.; *Physica A: Statistical Mechanics and its Applications*,380, 241,(2007).

[18] Liu, J.Ch.; Monson, P.A. *Adsorption*, 11, 5,(2005).

[19] Lee C., Yang W., Parr G.R. Phys. Rev.B., 37, 785, (1988).