Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 7 (1) 1-6: Spring 2010
(J. Phys. Theor. Chem. IAU Iran)
ISSN: 1735-2126

Thermodynamics Study of Polychlorinated Biphenyls (PCBs) Passing through SWNT and Their Removal from Environment

L. Mahdavian[1,*]

[1] Department of Chemistry, Doroud Branch, Islamic Azad University, P.O. Box: 133, Doroud, Iran

Received February 2010, Accepted April 2010

ABSTRACT

Palychlorinated Biphenyls (PCBs) have been widely used in flame-retard products common in homes and the workplace, and subsequently. Polychlorinated biphenyls (PCBs) typify a class of highly toxic, stable aromatic pollutants. PCBs are recently being scrutinized for potential environment damage in groundwater and in the atmosphere. The elimination of chemical pollutants from a contaminated environment is one of the most important steps towards achieving the goal of environmental remediation.

Recent studies have used carbon nanotubes (CNTs) for adsorptioa of pullution in environment, which are significantly higher dioxin elimination efficiencies In this study, mechanism and interaction of single-walled carbon naatube (SWNT) for removal of PCBs are calculated by Gaussian program package. Inter SWNT; there are four situations for PCBs near SWNT (6, 6) with length of 1.54 nm that we calculated simulation of passing PCB through SWNT. The thermodynamics properties are catculated for passiag PCBs across from SWNT that their results are showed this method can use for removal PCBs in environmental and their interaction are low potential in SWNT middle. So there is a place for adsorption of PCBs into SWNT, PCBs trap in it. This passing is exothermic, spontaneous, and favorable.

Keywords: Palychlorinated biphenyls (PCBs); SWNT (single-walled carbon nanotube); Environment pollution; MNDO method; DFT

INTRODUCTION

PCBs were used for many different industrial purposes. including electrical industry and hydraulic fluids, casting wax, carbonless carbon paper, compressors, heat transfer systems, plasticizers, pigments, adhesives, liquid cooled electric motors, fluorescent light ballasts and etc. Bioremediation might be an effective, cost competitive and environment-friendly solution for remediation environment matrices contaminated by PCBs but it is still unsatisfactory, mostly for the limited biodegradation potential of bacteria involved in the processes [1]. Polychlorinated biphenyls (PCBs) are highly toxic priority pollutants widespread and they accumulate in the food chain and end up in human bodies when people consume animal and fish products [2-5]. Also, PCBs with large numbers of chlorines are more stable and thus resistant to biodegradation. The most highly favored PCBs tended to be the ones with large numbers from chlorine. These congeners are also proving to be the ones that present the greatest environment and health risks [6]. Activated carbons are widely used as the traditional adsorbents in Japan and Europe, for the elimination of dioxins from the gaseous emissions of waste incinerators [7]. The CNTs-based adsorbent column designed which was obtained by simply packing a stainless-steel tube with CNTs [8]. However, its potential for adsorptive applications seems to be restricted to the purification of polluted gas streams.

*Corresponding author. Mahdavian_leila@yahoo.com

Single-walled carbon nanotubes (SWNTs) have attracted great interest due to their unique electronic properties and nanometer size. Because of these unique properties, they have great potential candidates in many important applications such as nano-scale electronic devices, chemical sensors and field emitters [9-11].

Theoretical studies have confirmed the remarkable change in electronic properties of SWNT due to the detection and removed of gas molecules [12, 13]. SWNTs (single-walled carbon nanotubes) can be chiral or non chiral. The tubes are uniquely characterized by a pair of integers (n, a) that are components of the vector defining the direction in which the graphite sheet was rolled up in Fig. 1.

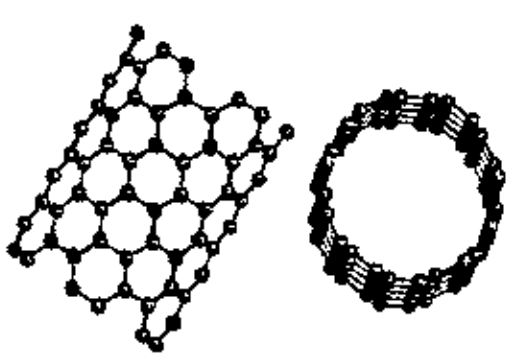

Fig. 1. Optimized configuration top-view and Side-view SWNT (6, 6).

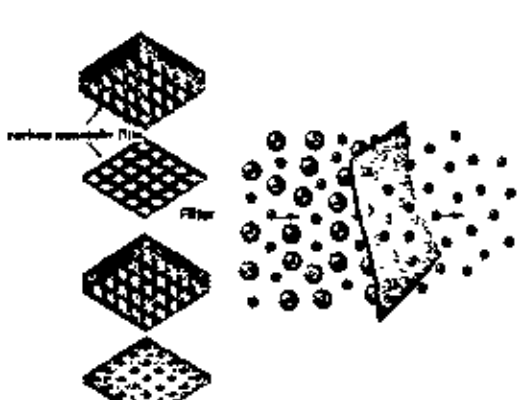

Fig. 2. Homogeneous two-phase separation by SWNT membrane.

In previous reported vapor sensors based on SWNT Field Effect Transistors (FETs), the structure of the FET sensor and the experimental geometric response are schematic [14]. Nanotubes have high capillarity properties and can pass or adsorb gases and liquids. The carbon nanotube membranes can be made by covering a silicone paper or metal catalyst particles; they are vertical row, which can be used as a compact package (Fig. 2). Then, the spaces between SWNT are filled with ceramic materials that durability of membrane increases.

In this work, interactions between gas molecular species and SWNTs are simulated and investigated. Exposing to gas molecules such as PCBs, the electrical resistance of a semi-conducting SWNT is found to dramatically increase or decrease. The PCB is neared to SWNT and is passing through it or is been adsorption on surface reduced to other produces, by this method is decreasing PCB's environmental damage. There are four situations for PCB beside SWNTs that are showed in Fig.3.

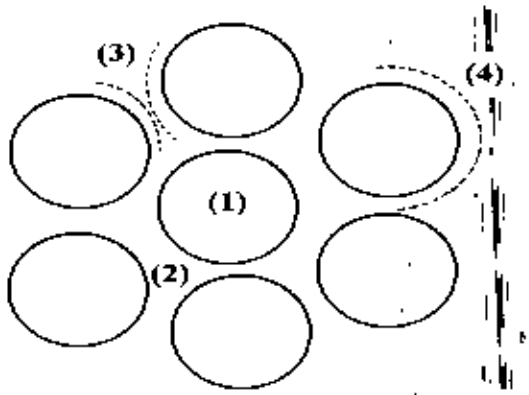

Fig. 3. The four situations for interaction PCB in SWNTs.

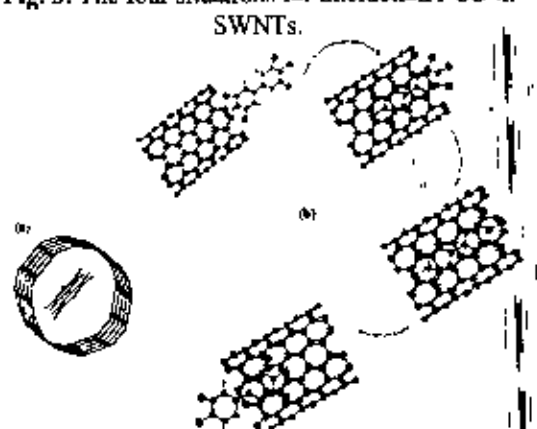

Fig. 4. Configuration (a) Top-view and (b): Side-view passing PCB across from SWNT in environmental.

The PCB molecules may pass through SWNT, adsorb on SWNT or convert to other product. For investigation and calculation the passing of PCB through SWNT, is neglected from other interaction in environmental and the passing of PCB through SWNT is simulated in

Fig.4. The uanutuhe sensors exhibit a fast response and a substantially higher sensitivity than that of existing solid-state sensors in 298K. Sensor reversihility is achieved hy slow recovery under cnvironmental conditions or by heating to high temperatures.

Interaction between PCBs molecules and SWNT is investigated by MNDO method in semi-empirical methods. We study the structural and tntal energy, thermodynamics properties of passing PCBs and SWNT in 298K. All tbe geometry optimization structures were carried nut using Gaussian program package. Density Functional Theory (DFT) optimized intermediates and their transient states. Tbc results show a sensitivity enhancement in resistance and capacitance when PCBs is passing through SWNT.

THEORETICAL

Synthesis of PCB isomers ond their properties

PCBs consist of a biphenyl (two henzene rings with a carhon to carbon bond hetween carbon 1 on onc ring and carbon 1' on the second ring) with a varying numher of chlorines. Symmetrical PCB isomers are synthesized in Fig.5. Chloraniline was treated with sodium nitrite to give thc corresponding diazonium derivativc, which was replaced hy iodine, followed by condensation [15]. The 3,4,5.3',4',5 - hexachlorobiphenyl isomers have thc melting points about 201°C, 300 retention times among and spectroscopic observations on K bands and ϵ values is 266 nm and 23.20M [16].

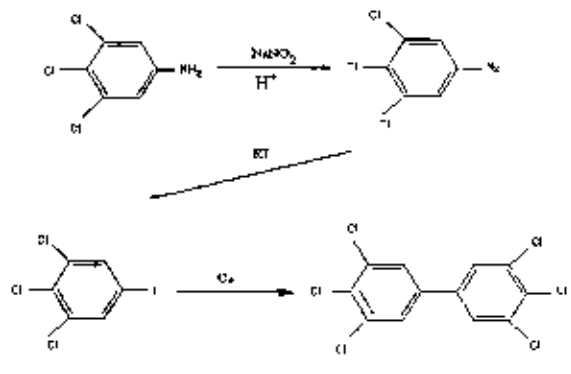

Fig. 5. Synthesis PCB, which it is the most toxic isomer for PCB structure.

The toxicity of a PCB is dependent not only upon the numher of chlorines present on the biphenyl structures, but also the positions of the chlorines. For instance congeners with chlorines in both para positinns (4 and 4') and at least 2 chlnrines at thc meta positinns (3, 5, 3', 5') are ennsidered to be "dioxin like" and are particularly tnxic [17]. When there is just 1 nr no suhstitution in the ortho positinn, the atoms of the cnngener are able to line up in a single plane (sometimes referred to as cnplanar). The planar or flat cnnfiguration is particularly tnxic. In this study, PCB is been simulation in Ball-and-stick models, then genmetry optimizations were perfnrmed using a B3LYP/6-31G** hy DFT methods.

COMPUTATIONAL METHODS

The geometry optimizations were performed using an all-electron linear combination of atomic orhital and the first-principles methodology. We used density functional theory (DFT) [18] with MNDD and IR-DFT methods hy the Gaussian program package. In this work, the B3LYP/6-31G level of theory was used for the optimizations of solids (3, 4, 5, 3`, 4`, 5`-hexachlorohiphenyl and C_{120} (6, 6)) [19].

The accuracy of semi-empirical quantum mechanics method depends on thc database used to parameterize the method. Configuration interaction (or electron correlation) improves energy calculations using CNDO, INDO, MINDO/3, MNDO, AM1, PM3, ZINDO/1, and ZINDO/S for these electron configurations. We can usc the information obtained from semi-empirical calculations to investigate many thermodynamics and kinetic aspects of chemical processes. Energies and geometries of molecules have clear relationships to chemical phenomena. The beat of formation is calculated for thcsc methods by subtracting atomic heats of formation from tbe binding energy. MNDO has been used widely to cateulate heats of formation. molecular geometries, dipole moments, ionization energies, electron affinities, and other properties [20, 21]. The interaction parameters between thc PCB molecules and SWNT structures were taken fnnn the study of nano-surfacc that the interactions between them were refined for this work in DFT calculatinns. Ball-and-stiek models of thc SWNT and PCB are

showed ia Fig.4. The electronic structure and the conductance properties are calculated for PCB passing through SWNT by DFT.

RESULTS

Polychlorinated biphenyls (PCBs) are persistent pollutants that are ubiquitous in the food chain, and detectable amounts are in the blood of almost every person in most populations that have been examined [22]. The suggestion is that water with PCBs can then passes through the precisely drilled sapphire nnzzle and separated into droplets of equal size on exiting the nozzle. These droplets passed through the electrostatic field between the aozzle and the ring electrode and acquired an electrostatic charge on their surfaces. Electrostatic repulsion forces dispersed the droplets as they fell into the SWNT hardening solution. In this manuscript, we simulated this interaction by computer programs of chemistry, so the thermodynamics properties nf PCBs passing through SWNT are calculated for them (table 1), which PCBs passed in-side to out-side in length nf tube by six stages.

Table 1. Thermodynamic propcnes nf interaction PCB-SWNT in 298K

Distance (nm)	G_{ele} (MJ/mol)	E_{ele} (V)	Dipole moment (D)	E_{bin} (MJ/mol)	H_f (MJ/mol)	RMS (kcal/mnlÅ)
0	-27886.35	-68.82	11580	7904.74	8001.09	4574
0.246	-29117.10	-71.85	10470	8146.11	8242.45	5011
0.493	-38783.19	-95.71	1.024	-82.45	13.90	83.30
0.739	-31706.70	-78.24	8570	8156.80	8253.15	4664
0.985	-32093.54	-79.20	8141	8486.03	8582.38	4946
1.584	-31353.04	-77.37	7230	7496.59	7592.93	4214
2.135	-27979.52	-69.05	11520	7929.76	8026.11	4691

With the objective to understand how the pattern and degree of chloriaation influence on the properties of the title molecules, a computational study on chlorinated biphenyls has hecn undertaken. The study includes conformational searches (and further refinement hy DFT) and the ah initio calculation of MNDD methods in semi empirical and the dipole moments for all the steps into nanotuhe. The most significant property is the MNDD, finding a good correlation hetween the MNDO and the suhstitution pattern on chlorinated hiphenyls. The most toxic congeners possess highly positive values of electrostatic potential on the aromatic rings and highly negative values of electrostatic potential on the chlorine atoms.

The PCB is passing through SWNT by six distances from in-side to out-side of length nanotuhe, which it is investigated by MNDO and its results are showed in Table 1. A current versus voltage curve recorded with a SWNT sample after time exposure to PCB showed up-fold conductance depletion. Exposure to PCB molecule increased the conductsnce of the SWNT sample, such as that in 0.493 nm distance, the E_{ele} is -95.71V, so it is increased until out-side nanotube. RMS gradient (kcal/mol Å) is different for passing of PCB in length of SWNT in 298K.

The G_{ele} (MJ/mol) for this passing has two minimum amounts in 0.493 and 0.985 nm of SWNT length. The dipole moment (D) in both ends of SWNT is at most amounts about 11550D and in 0.493 nm distance is the least quantity. These places of inter nanotuhe are snared PCB and can eliminate it in environment.

The total energy for this passing is showed in Fig. 6. The E_{total} is decreased in middle of leagth of nanotube, which this is a potential for entered PCB to SWNT For interaction between them, the heat of formation (enthalpy) is calculated in MNDO methods by suhtracting atomic heats of formation from the binding energy. The heat of formation and binding energy are fitted together for this interaction (Fig. 7). The least among of them is in 0.493nm length of SWNT (6,6) for the E_{bin} and H_f is ~-82.45 and 13.90 MJ/mol respectively, which is more than total energy.

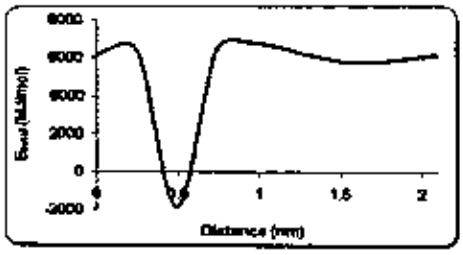

Fig. 6. The total energy (MJ/mol) of passing PCB across from SWNT.

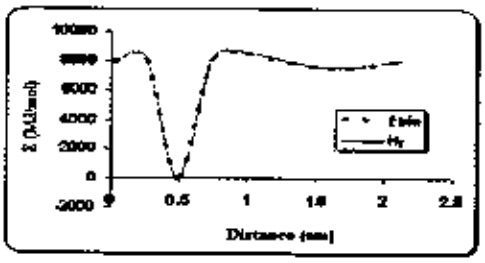

Fig. 7. The heat of formation and binding energy (MJ/mol) of passing PCB across from SWNT.

In the interactinn, we cnrrclate the sensor signals with the relative changes of the clcctrical resistance (Ω) sn wc have to coavcrt calculatioa data (in Table 1) to the eleetrieal resistanee (Ω) that shnwed in Fig. 8. The SWNT is an up hnle-doped semicnaductor, as can he glcaned from the current versus gate voltagc eurve shown in Fig. 8 (middle eurve), where the resistanee af the SWNT-PCB is ohserved to deerease.

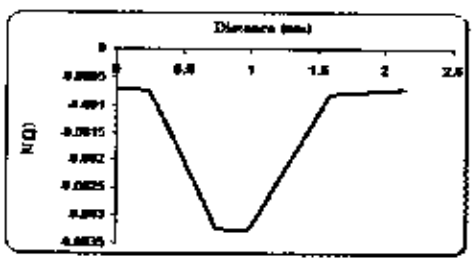

Fig. 8. The electronic resistanee (Ω) ealculated for passing PCB aeross from SWNT.

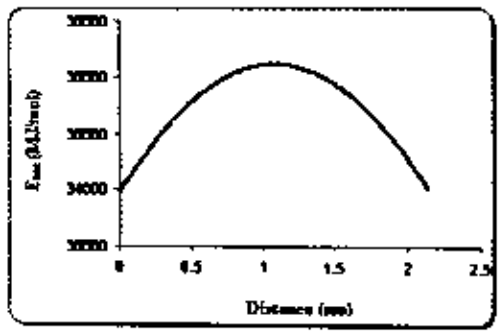

Fig. 9. The nuclear energy (MJ/mol) ealculated for passing PCB across from SWNT.

Band bending induced hy charged molecules causes the increase ar decrease in surface cnnductivity respnnsihle for thc gas responsc signal. The nuclear energy fnr PCB passing is observed in Fig. 9. It has maximum amount in the middle of thc tube, becausc all atoms nf SWNT applied nn PCB in the middle nf tube. The enthalpy difference fnr them is negative, whieh has exothermie interactinn and spnntaneous and PCB is separated from air-water in enviroment.

Thermndynamic parameters (ΔG_{ele}, ΔH_{ele}, and ΔS_{ele}) arc ealculated fnr the passing from top to middle and middle tn end of tuhe length, and the results distinguisbed that the nature of passing ta inter SWNT is exothermic, spontanenus and favorable in initial of tuhe, so it is endothermic in end. Aeeording to the values of electronie energy and enthalpy, the passing of PCB to inter SWNT is spontaneous and strong, that is sbowed in Table 2, so this methnd is suggested for removal fnr PCB in environment.

Table 2. Thermodynamic properties of interactioo PCB on the both end SWNT

Distance (nm)	ΔG_{ele} (MJ/mol)	ΔH_{ele} (MJ/mol)	ΔS_{ele} (MJ/mol)	lnK
0-0.493 (top to middle tube)	-10896.84	-7987.19	9.76	4.4×10^{6}
0.985-2.135 (Middle to end tube)	4114.01	-556.27	-15.67	-1.7×10^{6}

CONCULUSION

PCBs eampounds contain 209 eongeners. each of which is chlorinated to vorious degrees. These enmpounds are still detectable, eveo at the edge of the aretic and in the depths of the oceans.

After absorption, PCBs undergo little catalysis. They are highly lipophilic, accumulate in the liver and adipose tissue, and easily transfer to the embrya through the placenta and via breast milk. Thus, PCB contamiaatian is inheritable. At low doses, PCB might affect embryonic and neonatal devclopment. Braia devclopment seems to he particularly affected hy PCB.

The high thermal and chemical resistance of PCBs means that they dn not readily hreak down when exposed to heat or chemical treatment. The toxic congeaers possess coaformations with low dipole moments. a fact that may be linked to the ready accumulatioa on the adipose tissue. The results oa the geometry and electrostatic properties of chlorinated biphenyls caa be useful to rationalize their selective toxicities.

In waste and water pollution, there are some other coataminants, which they make trouhle for separated PCBs by SWNT, hut in this study, we neglected them and just calculated interaction betweea them.

Then for removal of PCBs in environment, we suggest using SWNT for it; SWNT is a good nano-filter for pollution in environment. For this wark, we choose armchair carhon nanotube (6,6) and is iavestigated PCB passing through it. The interaction betweea them is calculated by ab initio. A change in the potential of all atoms of inter surface of SWNT is observed passing result of PCB. These surface phases have different properties resulting in aliered molecule–surface interactions. In SWNT (6,6), there are two high potential places at 0.493 and 0.985 nm, respectively. These places of inter nanotube are saared PCB and can eliminate it in environment.

REFERENCES

[1] V. Tigmi, V. Prigione, S. Di Toro, F. Fava, and G. C Varese. *Micrab Cell Fact.* 8 (2009) 5.

[2] J. Kaiser. *Science*. 288 (2000) 1941.

[3] J. Kaiser. *Science*. 288 (2000) 1313.

[4] J. Borja, DM. Taleoa. J. Aurescaia, S. Gallardo. *Process Biochem*. 40 (2005)1999.

[5] GK. Vasilyeva, ER. Strijakova. *Micrabiolagy* 76 (2007) 639.

[6] W. Miyazaki, T. Iwasaki, A. Takeshita, Y. Kuroda, and N. Koibuchi. *J. Bia. Chem*, 279, 18 (2004) 18195.

[7] R. T. Yang, R. Q. Long, J. Padia, A. Takahashi and T. Takahashi. *Ind. Eng. Chem. Res.* 38 (1999) 2726.

[8] R. Q. Long and R. T. Yang, *J. Am. Chem. Sac* 123 (2001) 2058.

[9] J. Zhao, A. Buldum, J. Han, J.P. Lu. *Nanotechnalagy*. 13 (2002)195.

[10] Y. Cai, G. Jiang, J. Liu and Q. Zhou, *Anal. Chem.* 75 (2003) 2517.

[11] Y. Cai, G. Jiang, J. Liu aad Q. Zhou, *Anal. Chim. Acta*. 494 (2003) 149.

[12] Y. Doo Lee, W. S. Cho, S.I. Moon, Y.H. Lee. J. K. Kim, S. Nahm, B.K. Ju. *Chemical Physics Letters*. 433 (2006)105.

[13] R. G.Olmos and M. Iglesias *J. Chem. Eng. Data*, 53 (11) (2008) 2556.

[14] S. J. Kim., S. H. Lee., and C. J. Lee. *J. phys. D* 34, **2001**, 3505.

[15] S. Kawanishi, T. Mizutani and S. Sano. *Biochim. Biaphys Acta*. 540 (1978) 83.

[16] S. Sano, S. Kawanishi and Y. Seki. *Enviranmental health perspectives*. 59 (1985) 137.

[17] M. Okumura, T. Akita, M. Haruta, X. Wang, O. Kajikawa and O. Okada. *Appl. Catal. B*, 41 (2003) 43-52.

[18] P. Hohenberg, W. Kohn. *Phys. Rev.* 136 (1964) B864.

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

[20] M. J. S. Dewar and M. L. McKee. *J. Am. Chem. Soc*. 99 (1977) 5231.

[21] M. J. S. Dewar and W. Thiel. *J. Am. Chem. Sac*. 99 (1977) 4899.

[22] M. P. Longnecker, M. S. Wolff. B. C. Gladen, J. W. Brock, Ph. Grandjean, J. L. Jacobson. S. A Korrick, W. J. Rogan,. N. Weisglas-Kuperus, I. Hertz-Picciotto, P. Ayotte, P. Stewart, G. Winneke, M. J. Charles, S. W. Jacobson, É. Dewailly, E. R. Boersma. L. M. Altshul, B. Heinzow, J. J. Pagano, and A. A. Jensen. *Enviranmental Health Perspectives*.111 (1) (2003) 65.