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Removes MTBE from air-water and transfer it from environment by single-wall carbon nanotube (SWNT): Ab initio

L.Mahdavian[1,*], M.Raouf[2]

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

[2]Islamic Azad University Doroud Branch, P.O. Box: 133. Doroud. (IRAN)

E-mail : Leila_mahdavian@yahoo.com

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ABSTRACT

Through its extensive use as a fuel oxygenate, methyl tert-butyl ether (MTBE) is found nearly ubiquitously throughout the environment. MTBE, a widely used gasoline additive, is recently being scrutinized for potential environmental damage in groundwater and in the atmosphere.

Select SWNT were shown to effectively remove methyl tert-butyl ether from air-water. There are four situations for MTBE near by SWNT that we have investigated passing it across from SWNT. The properties thermodynamic are calculated for passing MTBE across from SWNT that its results are showed this method, is endothermic, spontaneous, and favorable.

KEYWORDS

MTBE (methyl tert-butyl ether);
SWNT (Single wall carbon nantube);
Pollution environment;
MNDO method;
DFT.

INTRODUCTION

The increasing use of fuel oxygenates, including methyl tert-butyl ether (MTBE), has, during the last decade, raised concern over their environmental occurrence, fate and potential effects. Methyl tert-butyl ether (MTBE) belongs to a class of oxygen-containing compounds added to gasoline for incrassation octane to reduce certain pollutants and pollutant precursors in automobile exhaust by promoting a more complete combustion of the fuel.

Many publications relating to sources and transport[1,2], toxicity[3], transport processes and fates[4] have been published. Environmental levels of fuel oxygenates have increased following their introduction and wide use.

The major concern about MTBE (and other oxygenate compounds) is focused on their occurrence in groundwater and drinking water supplies. In MTBE, the use of oxygenates as octane enhancers, principally in replacement of alkyl-lead compounds.

Many processes will govern exchange of MTBE between surface waters and the atmosphere. As a major process in removing MTBE from aquatic systems, atmospheric behavior and fates of the compound are clearly important[5]. Air–water exchange appears to be the major process in the removal of MTBE from the estuarine and coastal waters. CNT, however, is likely to contribute to removal (albeit to a lesser extent)[6].

Single wall carbon nanotubes (SWNTs) have attracted great interest due to their unique electronic properties and nanometer size. Because of these unique properties, they are great potential candidates in many important applications such as nanoscale electronic devices, chemical sensors and field emitters. The effect of gas adsorption on the electrical resistance of a CNT has received great attraction because of fast response, good sensitivity of chemical environment gases and low operating temperature[7]. Theoretical studies have confirmed the remarkable change in electronic properties

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of CNT due to the detection and removed of gas molecules[8,9]. Most molecules are known to be an electron-acceptor such as O_2 or an electron donor such as MTBE and H_2O displaying relatively small charge transfer between adsorbed molecules weakly on the CNT wall or passing them inter CNT. SWNT re used for investigation for detection and removed MTBE in air-water.

Interaction between MTBE molecules and SWNT is investigated using MNDO method by semi-empirical methods. We study the structural, total energy, thermodynamic properties of passing MTBE and SWNT in room temperature. All the geometry optimization structures were carried out using GUSSIAN A7 program package. Density Functional Theory (DFT) optimized intermediates and transient states of them. The results show a sensitivity enhancement in resistance and capacitance when MTBE is passing across SWNT.

THE COMPUTATIONAL METHODS

The geometry optimizations were performed using an all-electron linear combination of atomic orbital and the first-principles methodology we used is based on density functional theory (DFT)[10] as implemented in the MNDO and IR-DFT methods by the Gaussian program package. We made use of the B3LYP/6-31G level for the optimizations of solids[11].

The accuracy of semi-empirical quantum mechanics method depends on the 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 use the information obtained from semi-empirical calculations to investigate many thermodynamic and kinetic aspects of chemical processes. Energies and geometries of molecules have clear relationships to chemical phenomena. The heat of formation is calculated for these methods by subtracting atomic heats of formation from the binding energy. MNDO has been used widely to calculate heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities, and other properties[12,13].

The interaction parameters between the MTBE molecules and SWNT structures were taken from the study of nano-surface that the interactions between them were refined for this work in DFT calculations.

Ball-and-stick models of the SWNT and MTBE are showed in Figure 1. The electronic structure and the conductance properties calculated for passing MTBE across from SWNT by DFT.

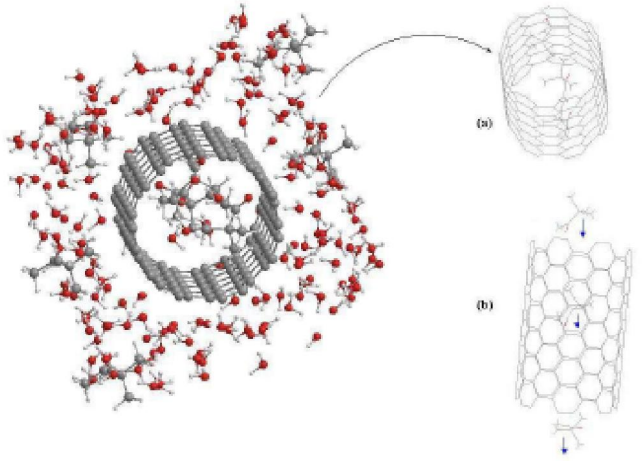

Figure 1 : Configuration top-view and side-view passing MTBE across from SWNT in air-water

RESULTS

Gasoline and heating oil travel through pipelines and are also distributed by truck to above ground and underground storage tanks. Underground storage tank leaks and spills provide major sources of MTBE in environment. In addition, people store gasoline in cars, boats, planes, lawn mowers, chain saws, generators, and off-road vehicles. Therefore, farm and residential releases, car accidents, spills, boats, and storm water run off also release gasoline into the environment. MTBE moves quickly through soil, dissolves easily in water, and takes longer to break down than some other chemicals. Drinking water with MTBE levels of 20 to 40 "parts per billion" (acceptable taste and odor) would probably not pose health risks. MTBE at 20 ppb in water is about the same as one drop in 500 gallons of water.

We have used SWNT for removed MTBE in environment. There are four situations for MTBE near by SWNTs that it is showed in Figure 2.

In this work, the first situation is investigated for MTBE. The effects of MTBE passing across from SWCNT were shown at TABLE 1 that MTBE by six stages passed in-side to out-side in length tube.

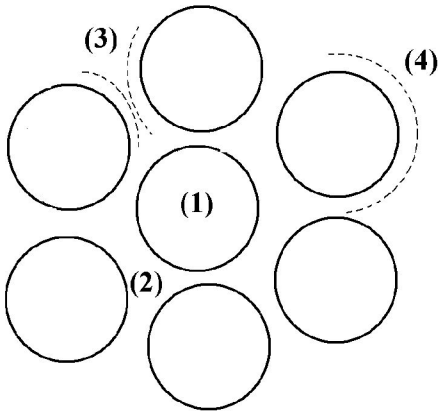

Figure 2: The four situations for interaction MTBE in SWNTs

To understand the effects MTBE in SWCNT, the properties thermodynamic calculated by MNDO methods in semi-empirical quantum with Gaussian program package.

The heat of formation is calculated for MNDO methods by subtracting atomic heats of formation from the binding energy. MNDO has been used widely to calculate heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities, and other properties.

The total energy (MJ/mol) for this passing has two minimum amounts in 4.92 and 12.31 nm of SWNT, which dipole moment (D) of them is the least quantity in these distances. These places inter tube are snared MTBE and can eliminate it in air- water. The enthalpy difference for them is -15513.41 MJ/mol, which is interaction exothermic and spontaneous and MTBE is separated from air- water. RMS gradient (MJ/mol·Å) is different for passing of MTBE in length SWNT in 298K.

In the interaction, correlate the sensor signals with the relative changes of the electrical resistance (Ω) so we have to convert calculation data (in TABLE 1) to the electrical resistance (Ω) that showed in Figure 3.

TABLE 1 : The properties thermodynamic of interaction MTBE – SWNT in 298K

The passing of MTBE across from SWNT in air- water								
Distance (nm)	**E_{total} MJ/mol**	**Dipole moment (D)**	**RMS MJ/mol·Å**	**E_{bin} MJ/mol**	**H_f MJ/mol**	**E_{ele} MJ/mol**	**E_{nuc} MJ/mol**	**E(V)**
0	13149.17	1.53×10^4	20.43	15387.99	15525.80	-55020	56280	-135.77
4.92	-2364.25	1.85	0.23	-125.42	12.39	-59640	57120	-147.17
7.38	12401.10	1.44×10^4	20.66	14639.93	14777.74	-45360	57960	-111.93
9.85	11400.69	1.41×10^4	20.09	13639.51	13777.32	-46620	57540	-115.04
12.31	-2364.43	0.50	0.24	-125.61	12.20	-60060	57960	-148.21
14.77	13104.34	1.48×10^4	20.78	15343.16	15480.97	-44100	57120	-108.83

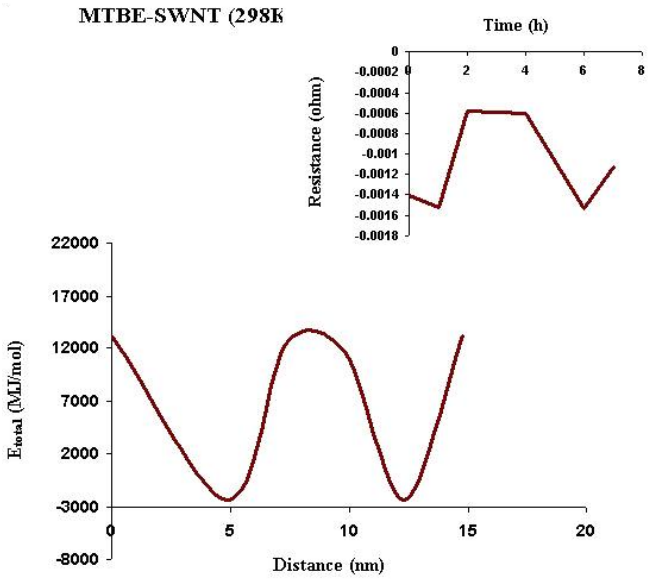

Figure 3 : The total energy (MJ/mol) and resistance (Ω) for passing MTBE across from SWNT

A current versus voltage curve recorded with a SWNT sample after time exposure to MTBE showed up-fold conductance depletion. Exposure to MTBE molecules decreased the conductance of the SWNT sample.

The SWNT is an up hole-doped semiconductor, as can be gleaned from the current versus gate voltage curve shown in Figure 3 (middle curve), where the resistance of the SWNT is observed to increase.

Thermodynamic parameters (ΔG, ΔH, and ΔS) for the passing process were calculated, and the results suggest that the nature of adsorption is endothermic, spontaneous, and favorable. According to the values of electronic energy and enthalpy, the passing of MTBE in the both end tube is weak that is showed in TABLE 2.

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TABLE 2 : The properties thermodynamic of interaction MTBE on the both end SWNT

Interaction	ΔG (MJ/mol)	ΔH (MJ/mol)	ΔS (MJ/K.mol)
MTBE-SWNT	10920	-44.83	36.80

CONCLUSION

The MTBE use began in the 1970's to replace lead in gasoline. After 1995, many metropolitan areas of the country with smog problems also added MTBE to gasoline because it helps to reduce harmful emissions from automobile exhaust. MTBE moves quickly through soil, dissolves easily in water, and takes longer to break down than some other chemicals.

We effort to use SWNT for decrease MTBE in air-water, because the SWNT is snared or adsorption it on wall and impossible it is converted to CO_2 and H_2O. The results in TABLE 2 are confirming this topic.

The prominent peak is corresponding to increasing distances (nm) passing of MTBE thorough SWNT at 298K until middle tube that is depended to electric properties SWNT.

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