

Molecular design of carbon nanotubes for the separation of molecules

H. Takaba, M. Katagiri, M. Kubo, R. Vetrivel¹, A. Miyamoto*

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Sendai 980, Japan

Received 22 April 1994; accepted 25 June 1994

Abstract

Studies on the molecular dynamics (MD) simulation of the structure of a carbon nanotube and the dynamic behavior of benzene, alkylated benzenes and alkylated naphthalenes are reported. The results of our calculations indicate the possibility of the development of a carbon nanotube as potential material for selective adsorption and shape-selective separation. The carbon nanotubes behave as flexible porous material towards organic molecules. The carbon nanotubes can be useful in the separation of molecules with different sizes (isomers of monomethylnaphthalenes) and with different shapes (isomers of dimethylnaphthalenes) as demonstrated with a tube of 0.73 nm I.D.

Keywords: Carbon nanotube; Separation; Hydrocarbons; Dimethylnaphthalene; Molecular dynamics; Computer graphics

1. Introduction

Carbon materials possessing molecular sieve properties [1] have been reported for gas chromatographic and gas separation applications on a commercial scale. However, the recent discovery of molecular carbon structures such as C_{60} and related compounds [2] has provided impetus to search for newer applications of such materials. In the search for materials with interesting optoelectronic properties, studies on the self-assembly of covalent structures leading to the formation of supra-molecular complexes are aggressively pursued [3]. Such molecules have the additional advantages of transporting trapped molecules through cell membranes, behaving as nanoscale

reactors, forming one-dimensional quantum dots and two-dimensional quantum wires, etc. Recently, the incorporation of C_{60} molecules on a quantum scale [4] and large scale [5] inside the one-dimensional channel of VPI-5 has been demonstrated, leading to the possibility of materials with interesting optoelectronic properties.

A broader class of molecular clusters based on graphitic carbon, such as metallocarbohedrenes (Ti_8C_{12}), are reported, and the possibility of larger titanium-carbon clusters have been hinted at [6]. Iijima [7] described a polymorph of graphitic carbon with a novel shape, namely micro-tubular form, which was later characterized as polarizable “molecular straws”, capable of ingesting dipolar molecules [8] and even metallic particles [9]. More recently there have been many attempts at theoretical calculations to evaluate their magnetic and electronic properties [10–13]. However, because of the experimental difficulty in their isolation, the

* Corresponding author.

¹ On leave from the National Chemical Laboratory, Pune-411 008, India.

characterization remains a challenge. Transmission electron microscopic (TEM) [7] and scanning tunneling microscopic (STM) [14] studies revealed that the nanotubes exist as tightly packed bundles. Of late, new and remarkable structures of carbon nanotubes incorporating various metals have been reported [15,16]. The custom designing of these structures is thus possible as continuously packed sheets or radiating carbon nanotubes around LaC_2 and GdC_2 metal cores and as concentric tubes of graphitic carbon capped by fullerene-like domes.

Our aim was to design effective molecular sieves for the bulk separation of hydrocarbon molecules of industrial importance. In the present study, the results of MD simulations of the structure of carbon nanotubes and the dynamic behavior of various aromatic molecules diffusing into the nanotubes are reported.

2. Experimental

2.1. Method

The MD simulations were carried out using the Discover module of the commercial software package developed by Biosym Technologies (USA) in a Silicon Graphics-IRIS 4D/30 workstation. The motion of the nuclei on the potential energy surface of the system with energy $E(R)$ is described by Newton's equation of motion as follows:

$$\frac{dE}{dR} = m \frac{d^2R}{dt^2} \quad (1)$$

The MD code derives the solution to Eq. 1, using an empirical fit to the potential energy surface for the motion of all atoms in the system. This equation is numerically integrated using small ($\sim 10^{-15}$ s) time steps, producing a trajectory of the system. The empirical fit to the potential energy is performed using a suitable forcefield. We choose the consistent valence force field (CVFF) reported by Dauber-Osguthorpe et al. [17] which include parameters for a variety of functional groups. The algorithms for minimization and the functional forms of force fields used to evaluate the potential

energy are described in detail elsewhere [18]. The procedure includes finding the equilibrium structures and their relative energy values over a period of time. In all the calculations, static energy minimization was carried out prior to MD simulation. The interval of each MD simulation step was typically $2.0 \cdot 10^{-15}$ s, and the simulation was carried out typically for 5000 time steps. All calculations were carried out at 300 K using the NVT ensembles (constant number of particles, constant volume, constant temperature).

2.2. Model

The model of the carbon nanotube is generated by rolling a sheet of graphitic layer of dimensions $2.5 \text{ nm} \times 1.0 \text{ nm}$. This led to a open-ended tube containing nearly twelve hexagonal rings lengthwise and six hexagonal rings on the circumference. The inner diameter of the tube after accounting for the Van der Waals radii of carbons was 0.73 nm. The computer graphics (CG) pictures of the model in longitudinal and cross-sectional views are shown in Fig. 1a. The unsaturated valencies of the carbon atoms on the circumference are saturated by adding hydrogen atoms. The hydrogen atoms have charges of +0.1 and the carbon atoms to which they are attached have charges of -0.1, thus overall the carbon nanotube is a neutrally charged structure. The aromatics such as benzene, the three isomers of xylene and two typical isomers of methyl and dimethylnaphthalene were considered in their equilibrium configurations. Their minimum diameters [19] obtained from the CPK model CG pictures are shown in Table 1.

3. Results and discussion

Initially, the MD simulations were performed for the carbon nanotube in the absence of any molecules. Both the longitudinal and cross-sectional configurations of the carbon nanotube after 2000 time steps of simulation are shown in Fig. 1b. Rarely are any structural differences noticed during this simulation; hence the chemical validity of the model is established. Although

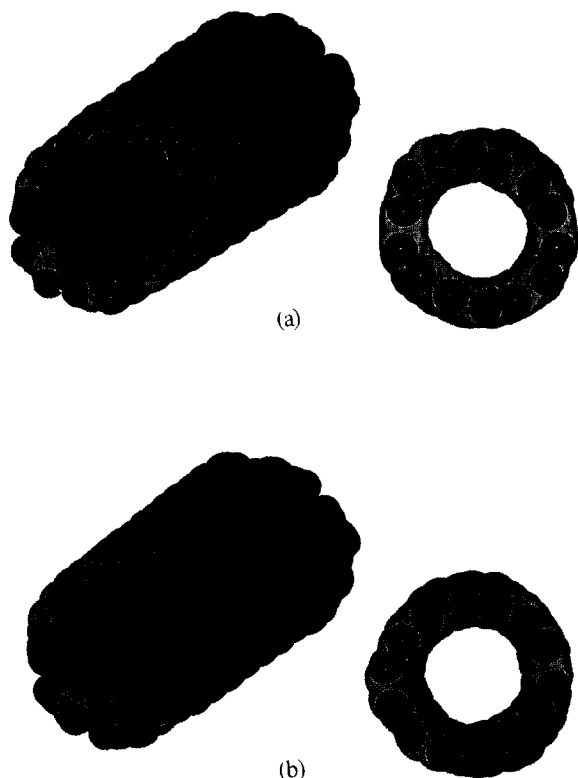


Fig. 1. CG picture of the longitudinal and cross-sectional views of the carbon nanotube model considered for simulation (a) at 0 steps and (b) after 2000 steps of MD simulation at 300 K.

Table 1
Dimensions for various molecules

Molecule	Width (nm)
Benzene	0.65
<i>p</i> -Xylene	0.65
<i>o</i> -Xylene	0.72
<i>m</i> -Xylene	0.73
2-Methylnaphthalene	0.71
1-Methylnaphthalene	0.81
2,6-Dimethylnaphthalene	0.72
2,7-Dimethylnaphthalene	0.71

concentric tubes with diameters in the range 2–7 nm were characterized [7] by electron microscopy, nanotubes with diameters less than 2 nm have also been observed [9]. Our results indicate that such smaller nanotubes are stable structures at 300 K, and their properties could be studied by simulation techniques.

3.1. Dynamics of benzene

Studies to simulate the dynamic behavior of benzene are carried out as the first step in the analysis of diffusion of various aromatics inside the carbon nanotube. Fig. 2 shows the CG picture of the configuration of the benzene molecule and carbon nanotube as observed during several steps of MD simulation at 300 K. The benzene molecule is placed above the tube opening, as shown in Fig. 2. In the initial 360 steps, the molecule was lingering around the mouth, changing its orientation all the time. When it obtains the correct orientation, it is ingested into the tube and makes a smooth sailing towards the other end of the tube. The variation of the potential energy of the system during the MD simulations is shown in Fig. 3. The system has a favorable energy when the molecule is inside the tube and it has to cross an activation energy barrier to enter or exit the tubes. This phenomenon was also observed during the dynamic animation of the various steps during the simulation. Benzene sailed towards the other end of the tube but instead of going out, it changed its direction of diffusion and again sailed into the tube. Thus the tube behaves like a “molecular straw” in pulling the molecules and keeping them in. The energy values shown in Fig. 3 could be used to obtain a qualitative estimate of the interaction energy between benzene and the carbon nanotube. However, because of the more generalized atom–atom potential model, much emphasis cannot be put on the absolute values. Quantum chemical calculations will be needed for the determination of realistic adsorption energy.

3.2. Dynamics of xylenes

We were interested in the dynamics of xylene molecules, where the separations of isomers are industrially important. Currently their isomerization-cum-separation is commercially carried out over zeolite molecular sieves [20]. Fig. 4 shows the salient results of the simulation of isomers of xylene in the carbon nanotube in terms of the CG pictures. It was observed that all these molecules could enter the tube and remain inside and that their overall dynamic behavior was similar to that

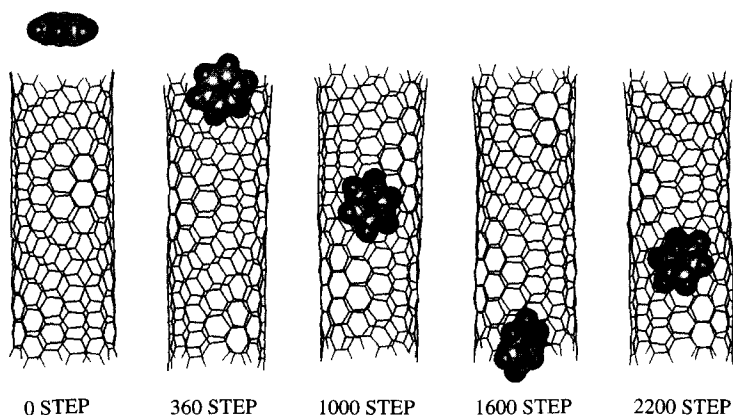


Fig. 2. Dynamic behavior of benzene at various time intervals during the simulation of the ingesting process into a carbon nanotube at 300 K.

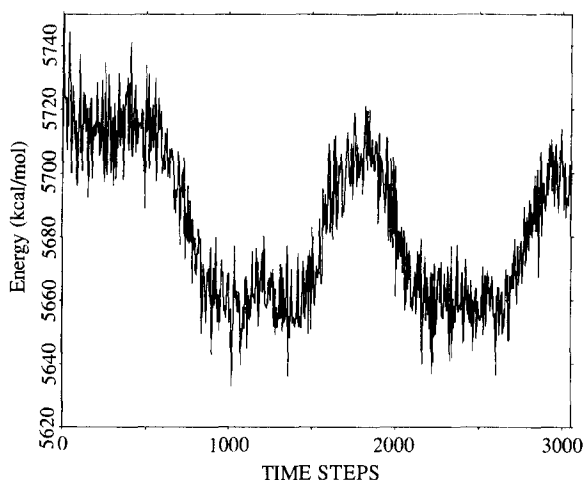


Fig. 3. Variation of the potential energy of the "carbon nanotube-benzene" system during the various time steps of MD simulation.

of the benzene molecule. The ingesting of all isomers inside the tube in spite of the differences of their dimensions was rather surprising. We analyzed the results of the calculation in more detail to understand this rather interesting phenomenon. The variations in the pore width, measured as the largest diameter of the tube near the ingesting molecule, during the ingesting of the molecules are studied. In Fig. 5, the pore width variations of the carbon nanotube during the diffusion of *o*-xylene are shown. This typical example indicates that there is widening of the pore due

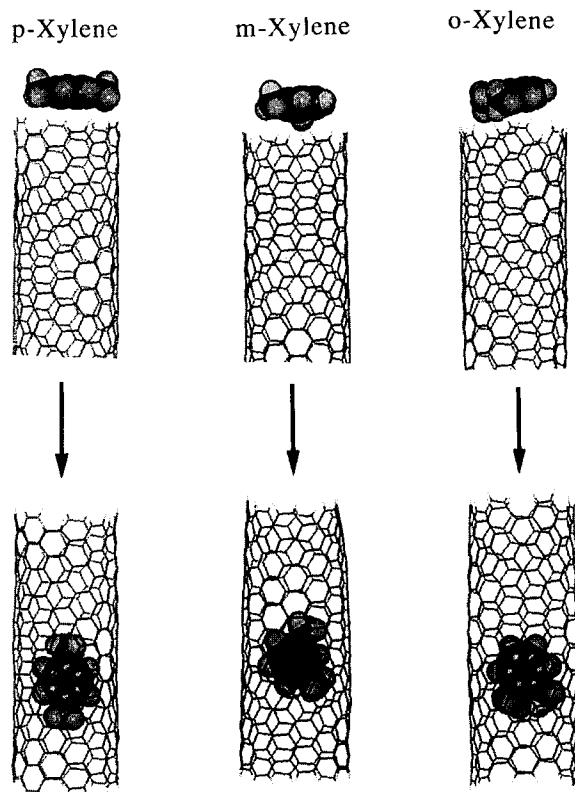


Fig. 4. Dynamic behavior of *p*-, *m*- and *o*-xylene molecules during the simulation of the ingesting process into a carbon nanotube at 300 K.

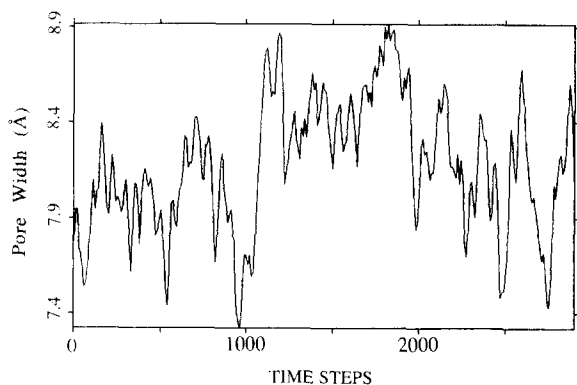


Fig. 5. Variation in the diameter of the pore during the ingesting process of *o*-xylene, indicating the flexibility of the carbon nanotube.

to the presence of the molecule. The tube itself is very flexible, since it can increase its diameter to the extent of ~ 0.15 nm. The widening of the pore was less during the ingesting of a smaller molecule, namely benzene, and the expansion was more close to the thermal vibrations.

3.3. Dynamics of mono- and dimethylnaphthalenes

The next step of our investigation was to study the behavior of still larger molecules, namely mono- and dimethylnaphthalenes. In this simulation study, we found that the carbon nanotubes exhibited an interesting molecular sieve property. The results of the simulation of the ingesting process of 1- and 2-methylnaphthalene at 300 K are shown in Figs. 6 and 7, respectively. It was observed that the smaller 2-methylnaphthalene could diffuse into the tube, while the larger 1-methylnaphthalene was unable to enter the mouth of the tube. Thus there seems to be a cut-off value of molecular diameters which can diffuse into it, in spite of its flexibility observed in the case of ingestion of xylenes.

2,6-Dimethylnaphthalene (DMN) is a valuable intermediate for the preparation of monomers to produce thermotropic liquid crystalline polymers, although nine other isomers of this compound with closely related dimensions are of no use to produce such engineering plastics. Liquid phase alkylation of naphthalene and monomethylnaph-

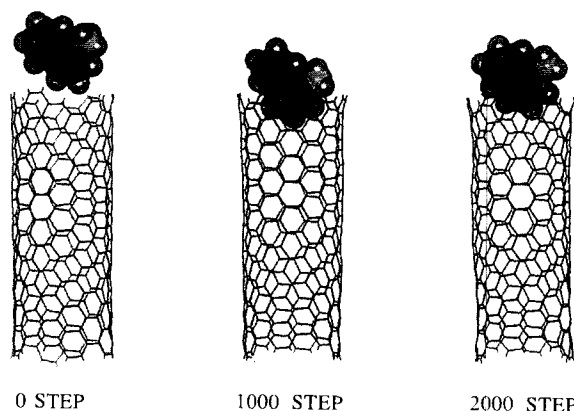


Fig. 6. Dynamic behavior of 1-methylnaphthalene at various time intervals during the simulation of the ingesting process into a carbon nanotube at 300 K.

thalene leads to the selective formation of 2,6- and 2,7-DMN isomers [21]. However, separation of these two isomers with almost the same dimensions is still a challenging task. The results of our simulations on the dynamic behavior of these two isomers inside the carbon nanotube indicate that they could serve as useful molecular sieves for this separation. The results of the simulation studies of 2,6-DMN during the various time steps at 300 K are shown in Fig. 8. It can be seen that the ingestion of the molecule takes place as in the case of benzene or xylenes. However, the same is not true in the case of 2,7-DMN, as can be seen in Fig. 9, where the results of simulation during the various time steps at 300 K are shown. The ingestion of 2,7-DMN did not occur, even after 5000 time steps. The molecule clearly faces a greater activation energy barrier and is unable to enter the mouth of the tube.

From our preliminary studies it can be concluded that the entry and diffusion of molecules into the carbon nanotube are occurring through specific orientations. The molecules always enter the tube with their narrowest end pointing in, which is the methyl group in the case of DMN. In the case of 2,6-DMN, when one of the methyl groups points into the tube, the molecule takes a linear orientation due to the *trans*-arrangement of the methyl groups. This orientation facilitates the entry of the molecule into the tube. On the con-

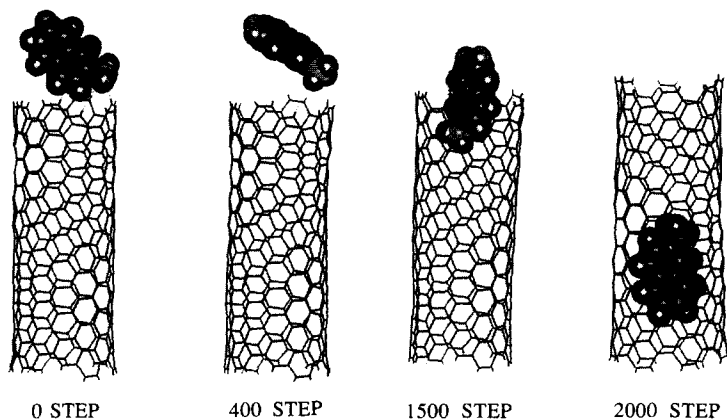


Fig. 7. Dynamic behavior of 2-methylnaphthalene at various time intervals during the simulation of the ingesting process into a carbon nanotube at 300 K.

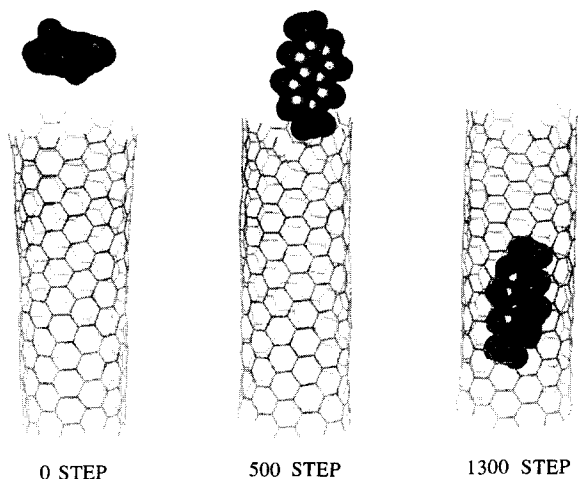


Fig. 8. Dynamic behavior of 2,6-dimethylnaphthalene at various time intervals during the simulation of the ingesting process into a carbon nanotube at 300 K.

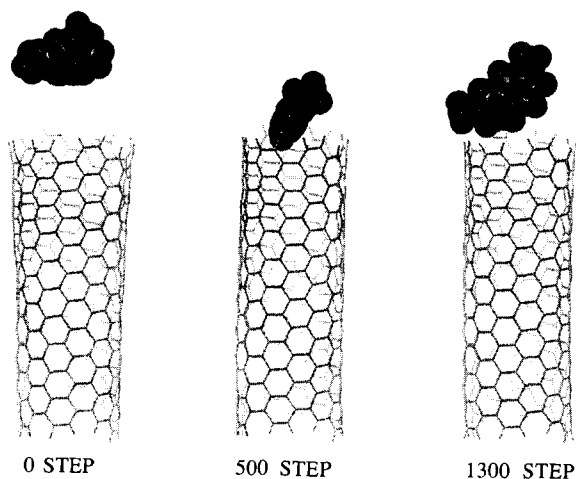


Fig. 9. Dynamic behavior of 2,7-dimethylnaphthalene at various time intervals during the simulation of the ingesting process into a carbon nanotube at 300 K.

trary, in the case of 2,7-DMN, the methyl groups have a *cis*-arrangement. When one of the methyl groups points into the tube, the other methyl group is colliding with the wall of the tube and, hence, prohibiting its entry. This phenomenon is qualitatively brought out from the CG pictures of the configurations after 500 steps in Figs. 8 and 9, respectively. These results indicate that the kinetic diameter of 2,7-DMN may be larger than that of 2,6-DMN.

4. Conclusions

We have demonstrated the application of MD simulation and CG technique to evaluate the usefulness of a new polymorph of graphite with novel shape, namely carbon nanotubes as molecular sieves. The salient outcome of our study could be summarized as follows. (i) The carbon nanotubes can uptake and ingest aromatic molecules; they have an attraction force to pull molecules and are flexible enough to incorporate fairly large mole-

cules. (ii) The carbon nanotubes of varying diameters can be chosen based on simulation studies to design efficient molecular sieves. (iii) The carbon nanotubes can be useful in the separation of molecules not only with different sizes (monomethylnaphthalenes) but also those with different shapes (dimethylnaphthalenes), as demonstrated with a tube of 0.73 nm I.D.

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