Pressure Effect on Nitroglycerin Sorption inside Single-Wall Carbon Nanotubes: a Monte-Carlo Study

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Sorption of drugs in nano-scale materials such as single-wall carbon nanotubes is a very interesting research in nanomedicine. Nitroglycerin is one of drugs that can be used medically as a vasodilator to treat heart conditions. It is one of the oldest and most useful drugs for treating heart disease by shortening or even preventing attacks of angina pectoris. Nitroglycerin can be used to help destroy prostate cancer as well as being used as a heart medicine. Therefore, the study of capability of delivery of nitroglycerin as a drug may be useful in nano-scale medicine. We apply Monte Carlo simulations to predict the sorptivity of single-wall carbon nanotubes for nitroglycerin at room temperature and varying pressure. The isotherm diagrams for nitroglycerin sorption report to find mechanism of this fluid sorption in single-wall carbon nanotubes. The sorption isotherms show that nitroglycerin can diffuse inside the single-wall carbon nanotubes while their diameter is larger than 10 Å. Also, these results can be verified with energy sorption plots. The density field and the distribution energy diagram were prepared to verify the sorption isotherms of nitroglycerin inside single-wall carbon nanotubes.

Keywords: Grand canonical Monte-Carlo, Nitroglycerin, Sorption, Carbon nanotube

Introduction

Nitroglycerin (NG) also known as IUPAC name of 1,2,3-trinitroxypropane (See Fig. 1) is a heavy, colorless, oily, explosive liquid obtained by nitrating glycerol. It was the first practical explosive stronger than black powder and synthesized by chemist Ascanio Sobrero in 1847, working under TJ Pelouze at the University of Turin. Nitroglycerin has been used as an active ingredient in the manufacture of explosives. It is employed in the construction and demolition industries. Nitroglycerin is also used medically as a vasodilator to treat heart conditions, such as angina and chronic heart failure. It is one of the oldest and most useful drugs for treating heart disease by shortening or even preventing attacks of angina pectoris. Nitroglycerin can be used to help destroy prostate cancer as well as being used as a heart medicine. Therefore, the study of capability of delivery of nitroglycerin as a drug may be useful in nano-scale medicine. The aim of this paper is the investigation of nitroglycerin sorption inside single-wall carbon nanotubes (SWCNTs) to characterize the role of CNTs as Drug Delivery tools.

Drug delivery is the method of administering a pharmaceutical compound to achieve a therapeutic effect in humans or animals. Drug delivery technologies are patent protected formulation technologies that modify drug release profile, absorption, distribution and elimination for the benefit of improving product efficacy and safety, as
Ahadi et al.

well as patient convenience and compliance. Many different types of drug delivery systems are currently available. In the last years, many attempts have been shown the application of carbon nanotubes (CNTs) as a new alternative and efficient tool for transporting and translocating therapeutic molecules in drug delivery technology. These systems hold great potential in the field of nanobiotechnology and nanomedicine [1-3].

Fig. 1. The chemical structure of nitroglycerin. The red, white, gray and blue atoms are O, H, C and N respectively.

Sorption of drugs in nano-scale materials such as CNTs is a very interesting research in nanomedicine. To the best of our knowledge, the sorption of nitroglycerin in single-wall carbon nanotubes (SWCNT) does not consider. Here, we employ the theoretical approach in the field of thermodynamics to study this phenomenon. We apply the Monte-Carlo (MC) simulations [4] and illustrate the pressure effect on sorption of NG in SWCNTs at fixed temperature.

Simulation details

We carried out MC simulations to investigate the loading properties of molecular nitroglycerin in five SWCNTs that their physical properties are reported in Table 1.

It is assumed that the nanotubes have rigid structure and no geometry variation of the adsorbent is considered, since the induced geometric variation of nanotubes by nitroglycerins can be neglected at room temperature.

<table>
<thead>
<tr>
<th>Indices</th>
<th>Diameter (Å)</th>
</tr>
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<tbody>
<tr>
<td>(16,16)</td>
<td>21.696</td>
</tr>
<tr>
<td>(14,14)</td>
<td>18.984</td>
</tr>
<tr>
<td>(12,12)</td>
<td>16.272</td>
</tr>
<tr>
<td>(10,10)</td>
<td>13.56</td>
</tr>
<tr>
<td>(8,8)</td>
<td>10.848</td>
</tr>
</tbody>
</table>

In the MC simulation, the configurations are sampled from a grand canonical ensemble. The temperature, volume and chemical potential are kept constant during the simulation. The probability of a configuration, \( \rho_{\text{con}} \), in the grand canonical ensemble is given by:

\[
\rho_{\text{con}} = CF \left\{ N \right\}_{\text{con}} e^{-E_{\text{con}}/k_B T}
\]

where \( E_{\text{con}} \) is the total energy of configuration, \( \text{con} \). This is defined as:

\[
E_{\text{con}} = E_{\text{int}}^{\text{con}} + E_{\text{int}}^{\text{intra}} + U_{\text{con}}
\]

where the first term relates to the intermolecular energy between the sorbate molecules, the middle concern to the interaction energy between the sorbate molecules and the framework. The last one is the total intermolecular energy of the sorbate molecules. The set of sorbate loadings of all components in configuration \( \text{con} \) is denoted by \( \left\{ N \right\}_{\text{con}} \). For a single component, the function \( F(N) \) is given by:

\[
F = \left( \frac{f \nu / k_B T}{N!} \right)^N e^{-\mu_{\text{intra}} / k_B T} 
\]

where \( f \) is the fugacity, \( \mu_{\text{intra}} \) is the intermolecular chemical potential, and \( N \) is the loading of the component. Displacement, creation and deletion are three types of operations with equal probability that are performed in the MC simulation cell. The moves are repeated until the number of nitroglycerin molecules in the simulation cell comes to the equilibrium.

The molecular diameter for nitroglycerin molecule is about 11 Å that is very more than the C–C bond length in a carbon hexagon that is around 1.42 Å. The nanotube wall can screen fluid molecules, that is to say nitroglycerin molecules inside the tube cannot cross the tube walls.
Furthermore, periodic boundary conditions (PBC) are set at the open end of SWCNT during displacement.

In this research, each simulation consists of $5 \times 10^6$ GCMC moves. The first $2.5 \times 10^6$ moves were as equilibration and have been discarded, and last $2.5 \times 10^6$ moves have been used for calculating ensemble averages of thermodynamics parameters.

The potential models used are all of the spherical (12-6) Lennard-Jones pair potential for nitroglycerin in simulations is described by Eq. (4).

$$U_{ij} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

(4)

where $\varepsilon_{ij}$ and $\sigma_{ij}$ are the energy and length parameters in LJ potentials, and $r_{ij}$ denotes the distance between the centres of particles $i$ and $j$. In MC, the parameters $\varepsilon_{ij}$ and $\sigma_{ij}$ between different particles and the solid–fluid potentials were derived from the following Lorentz–Berthelot combining rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = \left( \sigma_i + \sigma_j \right)/2$$

(5)

It should be noted that in actual calculation, the spherical cut-off distance is set to a little smaller than the half of simulation cell in our study. Finally, the isotherms of nitroglycerin inside five SWCNTs at temperature 298 K and varying pressure illustrate the nitroglycerin adsorption behaviour in SWCNTs.

Results and discussion

This section illustrates the effects of pressure and pore size (nanotube diameter) at fixed nanotube length of 40 nm and fixed temperature of 298 K on sorption of pure nitroglycerin in SWCNTs by using MC simulations. Fig. 2 is the sorption isotherm of NGs inside the SWCNTs via pressure at different diameters. The unit of diameter is the angstrom. Fig. 2 shows that NG loading inside SWCNTs is an increasing function of pressure at fixed diameter. At high pressure, it seems the sorption of NG will be almost constant and increasing the pressure can not be affected on the loading of NG inside the SWCNTs. This figure emphasizes that in small diameter around 10 Å, we can not observe any sorption and loading of NG inside the tube. This takes places because of the large van der Waals diameter of NG that is about 11 Å. This causes that the NGs can diffuse inside the tube with diameter of bigger than 10 Å. Therefore the NGs storage capacity will be efficiently increased by the reasonable increase of the diameter. At fixed pressure the sorption of NG inside the SWCNTs increase while the diameter of tube increases.

![Fig. 2. Sorption isotherms of nitroglycerin in different SWCNTs at 298.](image-url)
Fig. 3. Calculated energy of nitroglycerin sorption at (kcal/mol) concern to (a) (16,16), (b) (14,14), (c) (12,12), (d) (10,10) SWCNTs.
Fig. 2 shows at low pressure of 2000 kPa the sorption of NGs inside the nanotubes are very considerable, but the slope of sorption isotherm after 2000 kPa decreases. Here, two effects are clear; the space effect and the molecular effect. The molecular effect is related to potential effect. The potential effect comes from the interactions of C–NG; however, the space effect comes from the space inside the CNTs. It means that the NGs storage capacity will be efficiently increased by the optimization of the two effects.

The next investigation is presented at Fig. 3. Fig. 3 indicates the energy of sorption for NGs inside the SWCNTs at the last 100000 steps. This figure clears that total energy of sorption for NGs inside the (16,16) SWCNTs is more than other nanotubes. It verifies the Fig. 2. In Fig. 3, also we can observe the analytical energy obtained from MC simulations. They show that the van der Waals potential interactions between NGs and the wall of tube are very closely about 2000 to 5000 kcal/mol that means with increasing the NGs loading this type of potential increases slowly. Although there is not electrostatic potential interactions between NGs and CNTs, the differences between intramolecular interactions and van der Waals potentials is governed by the NGs sorption. This is the same effect that we named as potential effect.

The energy distributions of NGs sorption inside SWCNTs are presented in Fig. 4. This figure illustrates that when the diameter of tube increases, the range of energy sorption also increases; consequently it causes the energy distribution diagram becomes wide. However the pick of P(E) (probability of energy) falls down slowly. Then, in small diameter, the energy distribution plot will be thinner and higher than large diameter. This behavior helps us to program for sorption of NGs inside the SWCNTs as well as other fluids such as hydrogen in CNTs by experimental procedures. Hence, experimental scientists can be managed the energy applying for the best achievement to nitroglycerin sorption inside the SWCNTs.
Ahadi et al.

Fig. 5 shows the fields that have been created on the SWCNT framework structures by showing the density of each NG component. This generates fields on the SWCNT framework structures by showing the intermolecular energy of each NG component. Fig. 5 is cross section view of SWCNTs and gives evidence to the previous figures especially Fig. 2. According to Fig. 5 we can understand the distribution of NGs inside the nanotubes. For example, NGs can be collected inside the (16,16) SWCNT more than (12,12) SWCNT. In fact, this figure proves the space effect has important role in sorption of NGs inside the SWCNTs.

Fig. 5. Density field of NGs sorption concern to (A) (16,16), (B) (14,14), (C) (12,12) SWCNTs.

Conclusion

We apply Monte Carlo simulations to predict the sorptivity of single-wall carbon nanotubes for nitroglycerin at room temperature and varying the pressure. The isotherm diagram for nitroglycerin sorption report to find the mechanism of this fluid sorption in single-wall carbon nanotubes. The sorption isotherms show that nitroglycerin can diffuse inside the single-wall carbon nanotubes while their diameter is larger than 10 Å. Also, these results can be verified with energy sorption plots. The density field and the distribution energy diagram prepare to prove the sorption isotherm of nitroglycerin inside single-wall carbon nanotubes.
Acknowledgements

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References