



Full Length Article

Chlorinated paraffins wrapping of carbon nanotubes: A theoretical investigation

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ABSTRACT

How nanomaterials interact with pollutants is the central for understanding their environmental behavior and practical application. In this work, molecular dynamics (MD) and density functional theoretical (DFT) methods were used to investigate the influence of carbon chain length, degree of chlorination, chain configuration, and chirality of chlorinated paraffin (CP) and diameter of single-walled carbon nanotubes (SWNTs) on the interaction between CPs and SWNTs. The simulation results demonstrated that CP chain length and chlorination degree played considerably important roles in determining interaction strength between SWNTs and CPs. The interaction energies increased with increasing chain length and chlorination degree. The chirality of SWNT exerted negligible influence on the interaction energy between SWNTs and CPs. On the contrary, interaction energy increased with increasing radius of SWNTs due to the surface curvatures. This result was rationalized by considering the decrease in SWNT curvature with increasing radius, which resulted in plane-like CNT wall. The negligible influence of CP chain configurations was attributed to relative flexibility of CP carbon chains, which can wrap on tubes through conformational changes with low-energy barriers. MD results indicated that CPs could adsorb on SWNT surface rapidly in aqueous environment. Charge transfer and electronic density results indicated that the interaction between CPs and SWNTs was physisorption in nature. This work provides fundamental information regarding SWNTs as sorbents for CPs extraction and adsorptive removal from environmental water system.

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1. Introduction

Nanomaterials possess designable structures and tunable physical, chemical, and electrical properties [1], which enable development of new technologies for addressing environmental challenges [2]. Application of nanomaterials in the field of environmental science and technology drew special interest in the past decades [3]. The most widely explored nanomaterials include carbonaceous nanostructure materials [4], mainly comprising fullerene [5], carbon nanotube (CNT) [6], and graphene [7]. With their considerably large surface areas and excellent adsorption capacities, these materials were successfully explored as adsorbents for removal of polycyclic aromatic hydrocarbons, dyes, heavy metal ions, and antibiotics from various environmental systems [8–13].

Chlorinated paraffins (CPs) constitute a group of complex mixtures, which are formed by radical chlorination of *n*-alkanes in

the presence of UV–vis irradiation or heating [14]. Degree of chlorination of CPs varies from 30% to 70% (by mass content) [15]. Commercial CPs are divided into short-chain CPs (SCCPs, C_{10–13}), medium-chain CPs (C_{14–17}), and long-chain CPs (C_{>18}) [16]. CPs were extensively used for several decades as additives in metal working industry (71% of total use) and as plasticizers and flame retardants (10%) in plastics, paints (9%), and sealants (5%) due to their stability, viscosity, flame resistance, and low vapor pressure [14–16]. In consequence of their wide application and improper disposal, CPs, especially SCCPs, are widely detected in a variety of environmental and biological matrices [17–20]. The European Union has included SCCPs on their list of *priority hazards substances* in the field of water policy because of their considerable bioaccumulation and toxicity [21–25].

The nature of the interaction between nanomaterials and pollutants is important for understanding their environmental behavior and practical application. Despite the various applications of carbon-based nanomaterials in the remove of pollutants, the detail adsorption process of CPs on the carbon nanotube surface is still not well understood. On the other hand, due to the complex of CPs standards and limitation of experiments to study their adsorp-

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tion and interactions, computational simulations have become as an efficient way to study the adsorption process [26,27]. To the best of our knowledge, no theoretical investigation of the interaction mechanism between CPs and CNT was reported.

The present work investigated adsorption of typical CPs on CNT surface by density functional theory (DFT) and molecular dynamic (MD) method. The effects of structural parameters, including chain length, chlorination degree (Cl%), and chain configuration of CPs, on adsorption were systemically investigated. Effects of chirality and diameter of CNTs were also considered. This work aims to provide fundamental information regarding CNTs as sorbents for CP extraction and adsorptive removal from environmental water system.

2. Computational details

2.1. MD simulation

Materials Studio developed by Accelrys Inc. was used for all the calculation. Force-field computations were conducted using condensed-phase optimization molecular potentials for atomistic simulation studies (COMPASS) module in the Materials Studio software. COMPASS is a parameterized, tested, and validated first ab initio force-field [28,29], which enables accurate prediction of various gas-phase and condensed-phase properties of common organic and inorganic materials [30–32]. For non-bonded interactions, the Ewald method was used to calculate electrostatic interaction [33]. Atom-based methods were selected to calculate van der Waals energy with 12.5 Å cutoff. For each case study, MD simulation was performed with sufficient duration to observe several cycles of thermal vibration. Interval of each MD simulation step was typically 1 fs. All calculations were carried out at the initial temperature of 298 K, with a constant number of particles, constant volume, and constant temperature ensembles.

2.2. DFT simulation

Electronic properties of CP adsorption systems were investigated by DFT method. Periodic DFT calculations were carried out by using DMol³ package in the Materials Studio [34–36]. Exchange-correlation energy was calculated with generalized gradient approximation using the form of function proposed by Perdew and Wang (PW91) [37–40]. Calculations were based on double-numeric quality with polarization function basis set using the convergence criterion of 10⁻⁵ a.u. on energy and maximum force of 0.002 Ha Å⁻¹. Self-consistent field procedure was carried out with a convergence criterion of 10⁻⁶ a.u. on energy. A (4 × 4 × 4) Monkhorst-Pack k-point grid sampling in the reciprocal space was used in calculations [41]. A Fermi smearing of 0.005 Hartree and a real-space cutoff of 5.2 Å were also used.

3. Results and discussion

3.1. Molecular models

CPs with C₁₀–C₁₇, C₂₀, and C₂₄ were selected as target analytes to investigate chain-length effect. A total of 4–10 chlorine atoms were used for each CP chain to analyze effects of chlorination degree. Four different molecular models of C₁₀Cl₄ were constructed to analyze effects of carbon chain configurations. With a diameter of 13.56 Å and length of 196.76 Å, single-walled NTs (SWNTs) (10, 10) were selected as adsorbent. Unsaturated boundary effect was prevented by adding hydrogen atoms at the ends of SWNTs. Each C–C bond length measured 1.42 Å, and each C–H bond length spanned 1.14 Å. Electronic structures of carbon atoms in SWNT models exhibited

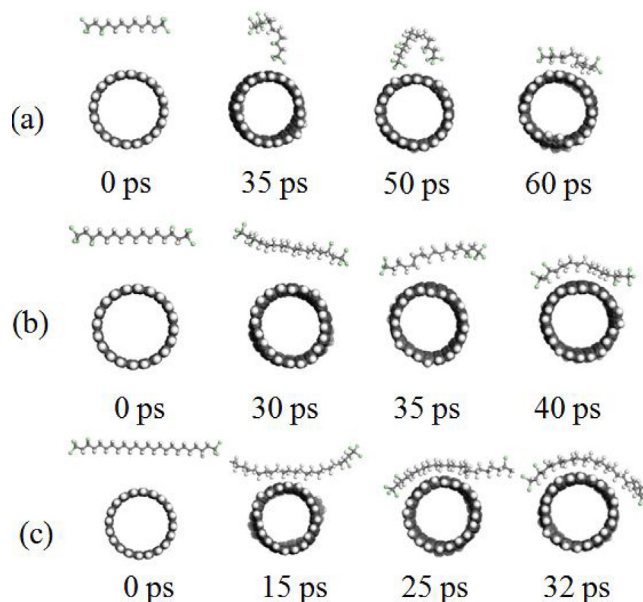


Fig. 1. MD simulation snapshots of SWNT-C₁₂Cl₈, SWNT-C₁₆Cl₈, and SWNT-C₂₄Cl₈ systems.

sp² hybridization. Hydrogen atoms possessed a charge of +0.1268 e. Carbon atoms connected to hydrogen atoms showed charges measuring −0.1268 e. Thus, neutrally charged SWNTs were constructed.

Dynamic wrapping behavior of CP chains can also be illustrated by tracking interaction energies of SWNT–CP molecules during the period for wrapping simulation. To evaluate the interaction between CPs and SWNTs, interaction energy is defined as follows [42]:

$$\Delta E = E_{total} - (E_{SWNT} + E_{CP}) \quad (1)$$

where E_{total} corresponds to total potential energy of the composite, and E_{SWNT} and E_{CP} represent potential energies of isolated CNT and CP, respectively.

3.2. Effects of CP chain length and degree of chlorination

Fig. 1 shows images of adsorption of three CP congeners (C₁₂Cl₈, C₁₆Cl₈, and C₂₄Cl₈) on SWNTs at different time steps of simulation. All three molecular chains were initially placed near the middle of SWNTs at a distance of 8.5 Å. After a relatively short simulation time, CP congeners stretched and moved to cover SWNT (10, 10) surface. Fig. 2(a) shows the interaction energy between SWNTs and CPs (C₁₂Cl₈, C₁₆Cl₈ and C₂₄Cl₈) during wrapping. Interaction energy increased until attainment of system equilibrium. Interaction energies between SWNT (10, 10) and C₁₂Cl₈, C₁₆Cl₈, and C₂₄Cl₈ measured −25, −29, and −39 kcal/mol, respectively. These results suggested that interaction energy between SWNTs and CPs increased with increasing CP chain length. Fig. 2(b) shows interaction energies between SWNT (10, 10) and C_mCl_n (m=10–17, 20, 24; n=4–10). For CPs which possessed the same chlorine atoms, interaction energy between SWNT (10, 10) and C_mCl_n increased with increasing CP chain length. Interaction energies ranged from −16.82 kcal/mol to −32.80 kcal/mol for C_mCl_n (m=10–17, 20, 24; n=4) molecules. C₁₀Cl₄ and C₂₄Cl₄ exhibited the lowest and highest interaction energies, respectively. As shown in Fig. 2(b), the chlorination degree of CPs can influence the interaction between CPs and SWNTs. C₁₀Cl_n (n=4–10) were used to determine the effect of degree of chlorination on interaction of CPs and SWNTs. Interaction energies ranged from −16.82 kcal/mol to −24.58 kcal/mol for C₁₀Cl_n (n=4–10). C₁₀Cl₄ and C₁₀Cl₁₀ showed the lowest and high-

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