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Molecular dynamics simulations on the interactions of low molecular weight natural organic acids with C_{60}

Qian Sun [a,b], Hong-Bin Xie [b], Jingwen Chen [b,*], Xuehua Li [b], Zhuang Wang [b], Lianxi Sheng [a,*]

[a] *State Environmental Protection Key Laboratory of Wetland Ecology and Vegetation Restoration, College of Urban and Environmental Sciences, Northeast Normal University, Changchun 130024, PR China*

[b] *Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, PR China*

HIGHLIGHTS

- ▶ The interactions of LOAs with C_{60} are simulated by molecular dynamics.
- ▶ The interactions of LOAs with C_{60} in aqueous and gaseous phase were considered.
- ▶ The interactions between both neutral and ionic LOAs with C_{60} were simulated.
- ▶ Models were built to predict and interpret the interactions of LOAs with C_{60}.

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ABSTRACT

As an important part of dissolved organic matter (DOM), low molecular weight organic acids (LOAs) may play a key role in the process for DOM stabilizing carbon nanomaterials (e.g. C_{60}) suspensions in aquatic environment. In addition, both LOAs and C_{60} have been detected in the troposphere and therefore have a chance to interact with each other in the gaseous phase. However, the mechanism for LOAs–C_{60} interactions and their environmental implications need further investigations. In this study, molecular dynamics (MD) simulation was employed to investigate the interactions between both neutral and ionic LOAs with C_{60} in vacuum and water. The results showed that the adsorptions of all LOAs on C_{60} are favorable, and the aromatic acids have stronger interactions with C_{60} than the aliphatic acids in vacuum and water. The interaction energies (E_{int}) of the LOA anions with C_{60} were weaker than those of their corresponding neutral LOA molecules. The models were also developed to predict and interpret E_{int} based on the results from MD simulations. Dispersion, induction and hydrophobic interactions were found to be the dominating factor in E_{int}. These findings indicate that cost-efficient MD simulation can be employed as an important tool to predict the adsorption behavior of LOAs on carbon nanomaterials.

1. Introduction

As carbon nanomaterials (CNMs) are widely used in areas such as electronic, material, biomedical and environmental applications, they can be inevitably released into the environment (Godwin et al., 2009; Petersen et al., 2011). It is of importance to understand the behavior and fate of CNMs in the gaseous and aqueous environment, for the purpose of their ecological risk assessment (Klaine et al., 2008; Wiesner et al., 2009). Most CNMs, including fullerene (C_{60}), carbon nanotubes (CNTs) and graphene, are hydrophobic, and tend to aggregate in water (Jafvert and Kulkarni, 2008). However, CNMs are able to form water-stable aggregates due to hydraulic stirring (Brant et al., 2005; Ma and Bouchard, 2009) or their interactions with dissolved organic matters (DOMs) (Hyung and Kim, 2008; Xie et al., 2008) and/or surfactants (Ramakanth and Patnaik, 2008). Of particular importance are their interactions with DOM, which is believed to alter their surface properties, and drive their fate in water (Lin and Xing, 2008).

DOM is a mixture of chemically complex polyelectrolytes with varying molecular weights (Lankes et al., 2008). The interaction mechanism between DOM and CNMs is closely related with the characteristics of DOM. Most experimental studies focused on the interactions of CNMs with DOM mixtures extracted from natural waters or commercially available DOMs (Chen and Elimelech, 2007; Hyung and Kim, 2008; Xie et al., 2008; O'Driscoll et al., 2010; Saleh et al., 2010), among which high molecular weight organic acids are dominant. Lin and Xing (2008) employed tannic

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* Corresponding authors. Tel.: +86 411 84706269 (J. Chen), tel.: +86 431 85099797 (L. Sheng).

E-mail addresses: jwchen@dlut.edu.cn (J. Chen), shenglx@nenu.edu.cn (L. Sheng).

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acid with a molecular weight of 1701 as a model DOM to study the stabilization effects of DOM on CNTs. Low molecular weight organic acids (LOAs) produced mainly from the decomposition of plant and animal residues are an important part of DOM and have simpler molecular structures (Strobel, 2001). LOAs may also interact with CNMs to effect CNMs stabilization in natural waters. For example, Wang et al. (2011) found gallic acid could interact with C_{60} and enhanced the water solubility of C_{60} by density functional theory (DFT) calculation. However, the information on the interactions of other LOAs with CNMs is limited. It is worth mentioning that both LOAs and CNMs have been detected in the troposphere (Kitanovski et al., 2011; Sanchís et al., 2012) and therefore have a chance to interact with each other. Thus, it is necessary to understand the interactions between LOAs and CNMs not only in aqueous phase but also in gaseous phase.

Moreover, due to the difficulties encountered in experimental observations, and the mixture nature of DOMs in the aquatic environment, the structure of DOM–CNM complexes and their implications are largely unknown. Molecular modeling may provide valuable morphology and mechanism information on the interactions and compensate the deficiency encountered in the experimental observations. To date, various molecular modeling, e.g. quantum mechanics (QM) (Michalkova et al., 2011), molecular dynamics (MD) (Raffaini and Ganazzoli, 2004) and Monte Carlo (MC) (Jiang et al., 2004) have been employed to simulate the adsorption of chemical species on CNMs. Generally, QM is more time-consuming for large systems than the classical mechanics like MD and MC, as QM considers electronic motions. MD not only describes static properties of a system, but also characterizes dynamics processes (Leach, 2001).

It was the purpose of this study to investigate the interactions of different LOAs with C_{60}, using MD method. C_{60} was selected as a representative CNM as it has a well-defined structure. The adsorption of LOAs on C_{60} was simulated by MD in vacuum and water phases, respectively. The radial distribution function (RDF) $g(r)$ (Chandler, 1987) of LOAs and interaction energy (E_{int}) between LOAs and C_{60}, were calculated to understand the mechanism of interactions and evaluate the stability of the LOA–C_{60} complexes. Based on the mechanism understanding, quantitative predictive models on E_{int} involving quantum chemical parameters were developed using partial least squares (PLS) regression analysis.

2. Methods

2.1. MD simulation

Nine naturally occurring aliphatic and aromatic LOAs (Fig. 1) were selected as model for LOAs in the simulation. All the simulations were carried out in a box with 3-D periodic boundary conditions. The dimensions of the simulation boxes were $a = b = c = 20$ Å, $\alpha = \beta = \gamma = 90°$. The length of the simulation box in each direction was large enough so that the interactions between one C_{60} and the periodic images of C_{60} in adjacent boxes could be ignored (Wang et al., 2005). A target organic acid was initially placed beside C_{60} to start the simulation.

A high quality general force field COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) was adopted in the simulation. COMPASS is an *ab initio* force field that can enable accurate and simultaneous prediction of gas phase and condensed phase properties for a broad range of molecules (Rigby et al., 1997; Sun, 1998; Yang et al., 2000). The potential function in the COMPASS force field includes valence and nonbond terms. The valence terms represent bond, angle, torsion angle, and out-of-plane angle interactions, and the cross-coupling bond–bond, bond-angle, and bond-torsion interactions. Nonbond terms include van der Waals and electrostatic interactions. The Columbic function and the 9–6 type Lennard–Jones potential function (Sun, 1998) with a cutoff distance of 9.5 Å (Lin and Blankschtein, 2010), were employed to calculate the electrostatic and van der Waals interactions, respectively.

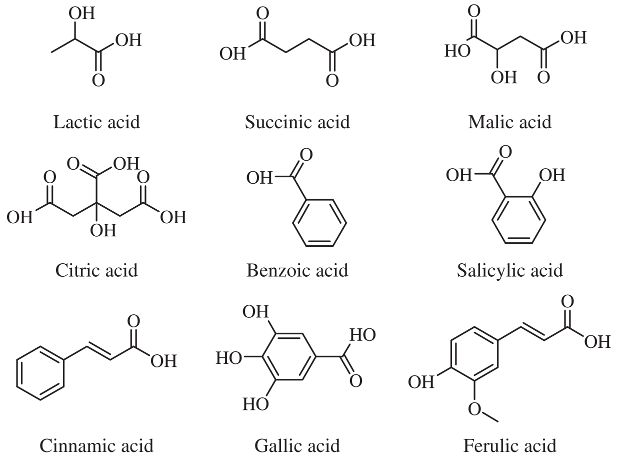

Fig. 1. Molecular structures of 9 LOAs.

Before the simulation, the total energy was minimized by the steepest descent and the conjugate gradient methods successively. The canonical (NVT) ensemble that means the number of particles (N), the volume (V) and temperature (T) of each system in the ensemble are constant was used in the simulation. The duration of simulation was 100 ps and time step was 1 fs. To ensure that 100 ps simulation is long enough to make the systems reach equilibrium, interaction energies (E_{int}) from100 ps and 1 ns simulations were calculated and compared (Table S1). The generated trajectory documents were used in the subsequent analysis. The simulation temperature (298 K) was controlled by the Andersen thermostat with relaxation time of 0.1 ps (Andersen, 1980). The dielectric constants were set at 1 and 78 to mimic gaseous and aqueous (298 K) conditions, respectively, as was done in the study of Raffaini and Ganazzoli (2004). To obtain more reliable results, three 100 ps trajectories were run for each system; particle momenta were sampled from the Maxwell distribution at the inverse temperature. All the simulations were performed with the Materials Studio software package (Ver. 4.4).

2.2. Radial distribution function and interaction energy

The radial distribution function (RDF) that describes the density variation of microscopic particles (atoms or molecules) as a function of the distance from one particular particle (Chandler, 1987), was employed to characterize the LOA–C_{60} complex. The formula of RDF is:

$$g(r) = \frac{dN}{\rho 4\pi r^2} \tag{1}$$

where $g(r)$ is the RDF, dN is the number of particles at a distance between r and $r + dr$ from a given target particle, ρ is the density of the system.

The interaction energy (E_{int}) is used to measure the stability of the LOA–C_{60} complexes. The greater the absolute E_{int}, the more stability of the LOA–C_{60} complexes. E_{int} was calculated by:

$$E_{\text{int}} = E_{\text{tot}} - (E_{C_{60}} + E_{\text{LOA}}) \tag{2}$$

where E_{tot} stands for the potential energy for the LOA–C_{60} system in equilibrium, $E_{C_{60}}$ and E_{LOA} are single point energies of the C_{60} and LOA based on the geometries which are obtained by stripping the