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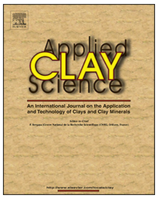

Research paper

Complexation of quinone species on 2:1 dioctahedral phyllosilicate surfaces

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ABSTRACT

Aiming at the complexation mechanisms of quinone species on clay minerals, we carried out systematic first-principles molecular dynamics simulations by taking 1,4-benzoquinone and its reduced form including semiquinone and hydroquinone as model molecules. The structures and desorption free energies of quinone complexes on both basal surface and edge surfaces ((010) and (110)) were investigated. The pKas of semiquinone and hydroquinone on edge surfaces were also calculated. Results show that semiquinone and hydroquinone can form inner-sphere complexes on edge surfaces, while benzoquinone cannot replace water ligand of edge Al. In contrast, the three quinone species did not form inner-sphere complexes on interlayer surfaces. The pH dependence of semiquinone and hydroquinone complexation was discussed based on the calculated pKas. Complexation of quinone groups onto clay minerals was weak compared with carboxylic groups in natural organic matters (NOM). The microscopic structures and thermodynamic data obtained in the present research can help understand the interactions between NOM and clay minerals in geological environment and provide primary information for developing molecular level clay mineral-NOM models.

1. Introduction

The interactions between natural organic matters (NOM) and clay minerals are of paramount importance in many geochemical, environmental, and biological processes (Greathouse et al., 2014) such as petroleum generation (Johns, 1979; Liu and Gonzalez, 2000; Geatches et al., 2010; Wu et al., 2012; Yuan et al., 2013), carbon sequestration (Wagai et al., 2008; Keil and Mayer, 2014), retention of organic and inorganic contaminants (Hizal and Apak, 2006; Polubesova and Chefetz, 2014), and uptake of plant nutrients (Sparks, 2003). NOM are the organic compounds excluding the biomass, undecayed and partially decomposed plant and animal tissues (Stevenson, 1994; Sparks, 2003). NOM consist of nonhumic and humic substances (HS). Nonhumic compounds are easily decomposed by microorganisms (Sparks, 2003) while HS is stabilized to degradation by binding with metal ions and clay minerals (Baldock and Skjemstad, 2000; Sparks, 2003; Curry et al., 2007). Carboxyl and quinone groups are the most important groups in NOM. According to Sparks (2003), the main acidic groups in NOM are carboxyl and smaller amounts of phenolic OH and quinone groups. On the other hand, quinone groups play a vital role in the formation of HS as suggested by the polyphenol HS genesis theory (Tipping, 2002; Sparks, 2003) and are responsible for the redox properties of NOM (Lovley et al., 1996; Scott et al., 1998; Struyk and Sposito, 2001; Fimmen et al., 2007; Macalady and Walton-Day, 2011). Studies suggested that the contents of quinones in NOM have profound influence on their properties, such as the cation solubility (Rashid, 1972) and the ability to reduce or oxidize organic and inorganic contaminants (Struyk and Sposito, 2001; Gu and Chen, 2003; Kappler and Haderlein, 2003; Cory and McKnight, 2005).

Clay minerals hold two types of surfaces: basal surfaces and edge surfaces (Schoonheydt and Johnston, 2013). Basal surfaces consist of siloxanes whose reactivity depends on the charge distributions (Sposito et al., 1999) and do not show pH-dependent properties (Schoonheydt and Johnston, 2013). Clay mineral frameworks are usually negatively charged due to the isomorphic substitutions in octahedral and tetrahedral sheets (Brigatti et al., 2006). Alkali and alkali earth cations like Ca^{2+}, Na^{+} are present in interlayer region to compensate the negative charges (Chiou and Rutherford, 1997). Edge surfaces have pH-dependent groups such as silanol and aluminol, which are responsible for the variable charges and acid-base properties of clay minerals (Lagaly, 2006). It was also proposed that edge surfaces serve as catalysts in the formation of HS from quinone species (Wang and Huang, 1989).

Various models were developed to represent the NOM, such as the DOM model (Schulten, 1999; Sutton et al., 2005), TNB (Sein et al., 1999) model, Stevenson model (Stevenson, 1994; Kubicki and Apitz, 1999), VSOMM (Sündermann et al., 2015) and Leenheer model (Leenheer et al., 1998; Kubicki and Apitz, 1999). Molecular dynamics simulations using these models provided quantitative insights into the structures, energetics and dynamics of NOM (Greathouse et al., 2014; Orsi, 2014) in aqueous solutions (Alvarez-Puebla et al., 2004; Xu et al.,

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2006; Kalinichev and Kirkpatrick, 2007; Aristilde and Sposito, 2010; Aquino et al., 2011; Kalinichev et al., 2011; Petrov et al., 2017) and in interlayer region of clay minerals (Sutton and Sposito, 2006). For example, Iskrenova-Tchoukova et al. (2010) studied the complexation of the TNB model with Na^+, Mg^{2+}, and Ca^{2+} in aqueous solution and found that the aggregation of NOM can occur in the presence of Ca^{2+} easier than Na^+ and Mg^{2+}. By simulating the aggregation process, it was found that the size of the aggregates increased with increasing pH due to the increased intermolecular repulsive interactions (Alvarez-Puebla and Garrido, 2005). Sutton and Sposito (2006) performed simulations to identify the interaction between NOM and basal surfaces of clay minerals with DOM model and rigid mineral framework, and they ascribed the stabilization of thus formed organo-mineral systems to the direct hydrophobic and hydrogen bonding interactions. However, to our knowledge, the atomistic-level information of the interactions between quinone groups and edge surfaces are still lacking.

In previous studies, by using first-principles molecular dynamics (FPMD) techniques, we investigated the structures of the interface between edge surfaces and water (Liu et al., 2012a; Liu et al., 2012b), and the pKas of different edge groups (Liu et al., 2014, 2015). These studies overall provide a quantitative basis for understanding the surfaces complexation and acid-base chemistry of clay minerals. In recent contribution (Liu et al., 2017), we explored the complexation of carboxyl group on edge surfaces and basal surfaces. The pH dependence of carboxyl complexation was revealed by integrating the pKas and desorption free energies (Liu et al., 2017).

The objective of this study is to reveal the interactions between quinone groups and clay mineral surfaces. The redox potential for 1,4-benzoquinone (Q) and its reduced form such as semiquinone ($QH^{\cdot}$) and hydroquinone (QH_2) couples are in the range of redox potentials given for HS (~0.2 V for Q/QH_2 couple in the range from −0.9 to 1.0 V) (Sparks, 2003; Bauer et al., 2007) and can therefore be taken as the model molecules for quinoid moieties in NOM. In this study, we investigated the complexation of quinone species on both edge surfaces and basal surface of 2:1 type clay minerals by taking Q, $Q^{\cdot-}$, and QH^- as model molecules. We calculated the desorption free energies of Q, $Q^{\cdot-}$, and QH^- from the edge and basal surfaces. The pKas of $QH^{\cdot}$ and QH^- adsorbed on edge surfaces were computed. Together with previous work of carboxyl (Liu et al., 2017), we derived the binding characteristics between clay minerals and NOM, which provide invaluable information for developing molecular-level clay mineral-NOM models and facilitate the interpretation of experimental results.

2. Method

2.1. Models

2.1.1. Edge surfaces

The edge models, including (010) and (110) surfaces, were taken from previous studies (Liu et al., 2012a, 2013). No isomorphic substitution was imposed. There are two unit cells in the edge surface models (Fig. 1). Following previous studies (Liu et al., 2008, 2017), quinone species replaced the water coordinated to the outermost octahedral Al atom on both (010) (Fig. 1A) and (110) (Fig. 1B) surface, Q, $Q^{\cdot-}$, and QH^- were selected as model molecules. One proton of hydroquinone was removed so that one oxygen atom can directly bond with Al. The pKa of semiquinone is 4.1 (Huynh and Meyer, 2007) thus the deprotonated form is the main species under common conditions, so the deprotonated form for semiquinone was adopted in present simulations. The edge models were placed in 3D periodically repeated orthorhombic boxes with a solution region of 12 Å (1 Å = 1.0 × 10^{-10} m). 33 water molecules were placed in the solution region, approximately reproducing the density of bulk water at the ambient conditions. The solution regions were extended to 24 Å with 71 water molecules in the pKa calculations of $QH^{\cdot}$ and QH^- systems (Fig. 1D).

2.1.2. Interlayer surface

The Ca^{2+}-smectites were selected as model systems in interlayer surfaces simulations. The swelling behaviors of smectites have been characterized by both experiments and simulations (Tamura et al., 2000; Ferrage et al., 2005; Zhang et al., 2014). In the case of Ca^{2+}-smectites, bilayer hydrate is the most favorable hydration state (Zhang et al., 2014). In this study, the bilayer hydrate with a basal spacing of 15.0 Å was adopted in the interlayer. The interlayer system consisted of 2 × 2 × 1 unit cells (Fig. 1C) which contained two isomorphic substitutions of Mg for Al in the octahedral sheet with one Ca^{2+} as the counterion. 34 water molecules were inserted in the interlayer region.

2.2. FPMD details

Born-Oppenheimer molecular dynamics (BOMD) simulations were carried out using CP2K/QUICKSTEP package (Vandevondele et al., 2005; Hutter et al., 2014) where the electronic structures were calculated with density functional theory (DFT). Within the dual basis set GPW (Gaussian and Plane Wave) density functional scheme (Lippert et al., 1997) as implemented in QUICKSTEP, a double-ζ with polarization (DZVP) Gaussian-type orbital basis was employed and the plane-wave basis were expanded to 280 Ry to represent the electron density. The Goedecker-Teter-Hutter pseudopotentials were used to represent the core electronic states (Goedecker et al., 1995) and Perdew–Burke–Ernzerhof functional was utilized to account for the exchange-correlation (Perdew et al., 1996). Van der Waals interactions were taken into account by including the DFT-D3 dispersion corrections (Grimme et al., 2010). Wave functions were optimized to a tolerance of 1.0e-6 using an orbital transformation method (Vandevondele and Hutter, 2003). Radical systems (i.e. systems containing $QH^{\cdot}$ and $Q^{\cdot-}$) were calculated with spin-polarized DFT in the doublet state.

The simulations were propagated in the NVT ensemble with a time step of 0.5 fs (1 fs = 1.0 × 10^{-15} s). The temperature was controlled at 330 K with the Nosé-Hoover chain thermostat. This temperature was used to avoid the glassy behavior of liquid water at a lower temperature (Vandevondele et al., 2004). The simulation time of each BOMD (i.e. free energy calculation and pKa calculation) was over 10 ps (1 ps = 1.0 × 10^{-12} s) and the equilibration time was at least 2 ps.

2.3. Constrained MD method

The desorption free energy changes (*ΔF*) were obtained by integrating the mean force (*f*) along the reaction coordinates (*X*) according to the thermodynamic integration relation (Sprik, 1998; Sprik and Ciccotti, 1998):

$$\Delta F(X) = -\int_{X_0}^{X} f(X')\mathrm{d}X' \quad (1)$$

In this study, the distance between octahedral Al or interlayer Ca^{2+} and O atom of quinone species was selected as the reaction coordinate to represent the bond breaking process. It should be mentioned here that the desorption free energies of quinone species from basal surface were actually the free energy changes between inner- and outer-sphere complexes with Ca^{2+}. The mean forces were obtained through a series of constrained FPMD simulations.

2.4. pKa calculation

The pKa values of $QH^{\cdot}$ and QH^- adsorbed on edge surfaces were calculated via the half-reaction scheme of the vertical energy gap method (Sulpizi and Sprik, 2008; Cheng et al., 2009; Costanzo et al., 2011; Cheng and Sprik, 2012). In this approach, the proton of the acid site (labeled as AH) is gradually transformed into a classical particle with no charge, the so-called “dummy atom” as indicated in Fig. 1D. The free energy change in this transformation is calculated with the