Molecular dynamics simulation of primary ammonium ions with different alkyl chains on the muscovite (001) surface

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ABSTRACT

Molecular dynamics simulations employing PCFF_phyllosilicate force field have been carried out to explore the adsorption of primary ammonium collectors on the muscovite (001) surface. The results show that primary ammonium ions coat the muscovite surface, they form a monolayer coating on the surface, irrespective of the alkyl chain length. By computing interaction energy between the ammonium ion and mica surface, we find that primary ammonium ions have the same interaction with the muscovite surface. Atomic density profiles for water molecules on muscovite surface are calculated, we reproduced an important conclusion with theoretical calculation that hydrophobic force for long alkyl chains is stronger than that for short chains. We find that ammonium ions form a relatively orientationally ordered structure with respect to the muscovite surface. The simulation reveals hydrogen bonds between head groups and bridging oxygen atoms are affected by water molecules around the head groups, however, the head groups still constrain themselves above the hexagonal ring of the muscovite surface.

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1. Introduction

As common-used collectors, amines have been widely used in the flotation of nonsulfide system, such as silicates (quartz (Li and De Bruyn, 1966; Novich and Ring, 1985; Takeda and Usui, 1987; Smith and Scott, 1990; Fuerstenau, 2005; Ata and Yates, 2006), muscovite (Herder et al., 1987; Nishimura et al., 1992, 2000), feldspar (Hanumantha Rao and Forssberg, 1997), lepidolite, kaolinite (Hu et al., 2003, 2005), illite (Zhong et al., 2008), pyrophyllite (Zhao et al., 2003)), metal oxides (bauxite (Wang et al., 2004), zirconia, goethite and corundum (Fuerstenau., 2005)), and sylvite (Monte and Oliveira, 2004; Cao et al., 2010). Significant progress has been made during the past several decades in delineating the physical chemistry of flotation systems through utilization of a number of experimental techniques (Fuerstenau., 2005), such as, Zeta Potential Measurement Analyzer, Contact Angle Meter, Fourier transform infrared spectroscopy (FTIR) (Hamid and Eric, 2006; Burdukova et al., 2009; Ejtemaei et al., 2013), and X-ray photoelectron spectroscopy (XPS) (Hamid and Eric, 2006). The attention to flotation test has always been concentrated on the flotation response. Many flotation results have been represented by illustrating the influence of the concentration of collector and pH on flotation recovery of minerals; the effect of collector on the mineral floatability has also been considered in the presence and absence of other collectors or ions. In fact, the microscopic structures of surfactants and water molecules adsorbed on mineral surface are crucial,

which cannot only reproduce the flotation process but also in turn can help to instruct the flotation. Even though, with the help of advanced equipment, we can obtain information involving the solid/liquid/gas interface, it is difficult to totally elucidate the detailed phenomenon only by virtue of one instrument, let alone the test economy.

Incomplete understanding of both surfactant adsorption and mineral flotation process has resulted in the inefficient introduction to flotation practice. Molecular dynamics simulation (MDS), which uses force fields to describe intra- and intermolecular interactions, has successfully explained experimental observations in flotation process (Wang et al., 2009; Rai et al., 2011) and can be employed to explore microscopy features including adsorption sites (Wang et al., 2005; Heinz et al., 2007; Argyris et al., 2008; Heinz, 2012), water/surfactant adsorption (Rai et al., 2011; Kerisit, 2011), and mineral wettability (Du and Miller, 2007; Argyris et al., 2011). The advantage of molecular dynamics simulation is that it can present not only the atomic level insight into the microstructure of the adsorption system but also provide the dynamic and thermodynamic information for the adsorption process.

Rai et al. (2011) studied adsorption mechanisms of oleate and dodecylammonium chloride molecules on two different mineral surfaces, that are the (110) and (001) faces of spodumene and jadeite, and computed the surface–surfactant interaction energies using molecular dynamics (MD) simulations. The conclusions drawn from purely theoretical computation matched remarkably well with experimental results. Considering Al-terminated and OH-terminated alumina surfaces, Argyris et al., 2011 assessed the structural and dynamic behavior of the first few hydration layers in contact with the substrates with CLAYFF force field (Cygan et al., 2004). Density profiles suggest water

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layering up to ~10 Å from the solid substrate, water exhibits bulk-like behavior at distances greater than ~10 Å from the substrate. Du and Miller (2007a) and 2007b) performed MD simulations using CLAYFF–DREIDING (Mayo et al., 1990) force field and confirmed that the hydrophobic chains of the cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) preferentially adsorb on the graphite and talc basal plane surface through hydrophobic interactions, as expected from the previous laboratory studies; the DTAB cationic surfactant adsorbs on the talc edge surface through electrostatic interactions. Wang et al. (2009) revealed states of adsorbed dodecylamine (DDA) on a silica surface as a function of pH by vibrational spectroscopy (SFVS, FTIR), contact angle measurements, and molecular dynamics (MD) simulations. The results showed that the state of adsorbed DDA at a silica surface varies significantly at different pH values.

PCFF_phyllosilicate force field was developed by Heinz et al. (2005) based on the PCFF (polymer consistent force field) (Accelrys, 2012) force field, which included accurate sheet silicate force field types. The force field has successfully reproduced the surface energies of many sheet silicate minerals, properties involving gauche conformation and X-ray diffraction patterns agreed very well with the experimental measurements (Fu and Heinz, 2010; Heinz et al., 2007). Because of its abundant and accurate force field types for minerals and organic molecules, it is very promising in the MD simulation of collector–mineral interface.

In this paper, molecular dynamics simulations are applied to investigate the adsorption of different primary ammonium ions on muscovite (001) surface. Muscovite is a prototypical silicate surface, it is a widely used research substrate which gains chemical formula of $KAl_2(Si_3Al)O_{10}(OH)_2$. It belongs to 2:1 layered silicate with respect to its structure which consists of an $[AlO_4]$ octahedral sheet sandwiched between two $[(Si,Al)O_4]$ tetrahedral sheets. Substitution of one Al for one of every four Si in the tetrahedral sheet causes a net negative structural charge which is compensated by positively charged ions K^+ ions. The isomorphic substitutions obey the Loewenstein's rule (Loewenstein, 1954).

In the previous work (Xu et al., 2013), we have studied the adsorption of ammonium ions and water molecules on the muscovite (001) surface with accurate PCFF_phyllosilicate force field, results showed that ammonium ions have thermodynamic advantages to resist the hydration layer sufficiently for effective flotation to occur. The interaction energy between the ammonium ion and the muscovite (001) surface was calculated by inspecting one adsorbed ammonium ion on the surface, without considering "aggregation effect" of the collector molecules.

PCFF force field provides reliable parameters for hydrocarbon chains (Fu and Heinz, 2010; Heinz et al., 2003), we run a series of molecular dynamics simulations by means of PCFF_phyllosilicate force field to elucidate the structure of $C_nH_{2n+1}NH_3^+$ in aqueous solution at the cleaved muscovite with regard to the influences of varying alkyl chain length (n = 4, 6, 8, 10, 12, 14, 16, 18). Subtle microscopic structures and physical properties are discussed, such as, interaction energy, atomic density profile, gauche conformation and order parameter. It is a new application for PCFF_phyllosilicate force field in flotation system, we believe that the analysis could promote the understanding of the adsorption of collector molecules on minerals.

2. Simulation details

2.1. Force field

Heinz et al. developed the PCFF_phyllosilicate force field with recent parameters for layered silicates based on polymer consistent force field (PCFF). The semi-empirical energy model for layered silicates takes surface energies accurately into account, and thus reproduces crystal structures, surface energies, and approximates vibrational frequencies of sheet silicates in very good agreement with experiment (Heinz et al., 2005).

In PCFF_phyllosilicate force field, the primary potential energy expression is consistent with the PCFF force field. For the mineral, only four contributions are considered, and the potential energy is given

$$E_{pot} = E_b + E_\theta + E_{coul} + E_{VDW} \tag{1}$$

$$E_{pot} = \sum_{ij bonded} \frac{1}{2} K_{r,ij}(r_{ij}-r_{0,ij})^2 + \sum_{ijk bonded} \frac{1}{2} K_{\theta,ijk}(\theta_{ijk}-\theta_{0,ijk})^2 + \frac{1}{4\pi\varepsilon_0\varepsilon_r} \sum_{\substack{ijk nonbonded \\ (1,3excl)}} \frac{q_i q_j}{r_{ij}} + \sum_{\substack{ijk nonbonded \\ (1,3excl)}} E_{0,ij}\left[2\left(\frac{r_{0,ij}}{r_{ij}}\right)^9 - 3\left(\frac{r_{0,ij}}{r_{ij}}\right)^6\right]$$

$$\tag{2}$$

E_{pot}, E_{vdW}, E_{col}, E_{bond} and E_{angle} are the total potential energy, a 9–6 nonbond potential with geometric combination rules, coulomb energy, quadratic bond stretching and quadratic angle bending contributions, respectively. K_r is the elastic constant, r is the instantaneous distance between the bonded atoms, and r_0 is the equilibrium distance between them. K_θ is the force constant. θ_0 and θ are the equilibrium and the instantaneous angles, respectively. $E_{0,ij}$ is equilibrium well depth. ε is relative dielectric constant, and q is the atom charge.

2.2. Models

Muscovite (Rothbauer, 1971) supercell (5 × 3 × 1) with Si → Al substitution pattern according to ^{29}Si NMR is used to obtain a double layer (001) surface by cleaving the (001) surface along the middle of the interlayer. After cleavage, each surface retains half of the interlayer K^+ ions.

The models of $C_nH_{2n+1}–NH_3^+$ in all-trans configuration, with chain lengths n = 4, 6, 8, 10, 12, 14, 16, 18 are optimized employing Forcite module (Accelrys, 2012) with the PCFF_phyllosilicate force field. Charge assignments for cationic collectors are from Heinz et al. (2005) and Heinz and Suter (2004). For NH_3 head groups, the assigned partial charges are −0.50 e for N, +0.4 e for each H, and +0.3 e distributed over the alpha CH_2 group (+0.05 e for H, the residual charge for C). For clarity, the atom charge distributions of $C_{12}H_{25}NH_3^+$ are shown in Fig. 1. The flexible SPC model is used for water.

The lattice charge on the muscovite supercell (5 × 3 × 1) is −15 e, 15 ammonium ions are added to consider its adsorption process on muscovite (001) surface. Different systems are constructed by "Amorphous Cell" module and "Build Layers" tools in Materials Studio. Details of cell components and the parameters are listed in Table 1.

Because ammonium ions adsorb on the muscovite surface by ion exchange mechanism, alkali metal ions on the surface are deleted in C_4–C_{18} systems, and all mica sheets are fixed. Results from first principle calculation (Odelius et al., 1997) and our MD simulation (Xu et al., 2013) showed that the ammonium ion prefers the $[Si_4Al_2]$ cavity not the $[Si_5Al_1]$ cavity, in order to save the computation time, all ammonium head groups are initially positioned above the $[Si_4Al_2]$ di-trigonal rings. Surface K^+ ions have been removed according to the same method from our previous study (Xu et al., 2014). The treatment can be found in the self-assembly study of alkylammonium chains on montmorillonite (Heinz et al., 2007). Na^+ and Cl^- ions are added to maintain an electrically neutral system.

2.3. Simulations

The built vacuum slab (thickness ca. 70–80 Å) is to eliminate the influence of period boundary conditions. The simulation cell dimension is set to approximately 26 × 27 × 112 Å for a × b × c and periodic boundary conditions are applied to the three dimensions, all energy expressions and inter-atomic interaction parameters are taken from the