



Density functional theory study of α -Bromolauric acid adsorption on the α -quartz (101) surface



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ABSTRACT

Adsorption mechanism of collector α -Bromolauric acid ($\text{CH}_3(\text{CH}_2)_9\text{CHBrCOOH}$, α -BLA) on α -quartz (101) surface has been investigated by first-principles calculations based on density functional theory (DFT). The interaction energies of H_2O molecule, calcium ions (Ca^{2+}), hydroxyl ions (OH^-), calcium hydroxyl ions ($\text{Ca}(\text{OH})^+$), and α -BLA⁻ ions with α -quartz (101) surface were in the order of $\text{Ca}(\text{OH})^+ < \text{Ca}^{2+} < \text{OH}^- < \text{H}_2\text{O} < \alpha$ -BLA⁻. The results revealed that the collector α -BLA cannot adsorb on α -quartz (101) surface due to the hindrance of hydration shell of quartz surface, while $\text{Ca}(\text{OH})^+$ could repulse the hydration shell and consequently adsorb on quartz surface, which further leads to the adsorption of the collector α -BLA⁻ anions on $\text{Ca}(\text{OH})^+$ -activated quartz surface. Mulliken populations analysis of the external oxygen atom (O2) of quartz surface, calcium atom (Ca) of $\text{Ca}(\text{OH})^+$, and oxygen atom (O1) of collector α -BLA⁻ (-OH group) shows that the electron transfer between the Ca–O1 and Ca–O2 atoms. The overlap area of electron density between Ca–O1 and Ca–O2 atoms indicates strong interactions among the three atoms of Ca, O1, and O2, suggesting that $\text{Ca}(\text{OH})^+$ ions act as a bridge between the α -quartz (101) surface and the α -BLA collector.

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1. Introduction

Cationic/anionic reverse flotation has been considered as one of the most efficient technologies for the separation and concentration of iron containing minerals from iron ores (Cao et al., 2013; Vidyadhar et al., 2014; Weng et al., 2013). The flotation process utilizes the differences in physicochemical surface properties of iron containing minerals and gangue minerals. After the treatment with reagents, such differences in surface properties within the flotation pulp become apparent that the hydrophobic gangue mineral quartz particles are floated out to the water surface, while the iron oxides are kept depressed in pulp with the help of starches (Weng et al., 2013). The collector α -BLA has been proven to be an efficient collector with excellent collecting performance for flotation of quartz at a relatively low temperature, 15 °C. The pilot-scale tests for the reverse flotation of iron ores in China shown the collector could be used in a relatively low temperature to reduce non-renewable energy resources consumption and greenhouse gases emissions (Zhu et al., 2015). It is necessary to investigate and study the collector–mineral interfacial interactions so that the iron con-

taining minerals and gangue could be separated effectively, and the economic value of iron ore resources could be utilized fully.

Quartz is the major gangue mineral in iron ores. The adsorption mechanism of various collectors on quartz surface has been studied extensively by common traditional analysis methods, such as micro-flotation tests (Lima et al., 2013; Liu et al., 2015; Vidyadhar et al., 2014), adsorption capacity measurements, surface tension (Huang et al., 2014), atomic force microscope (AFM) (Ni and Liu, 2012), zeta-potentials measurements (Churaev et al., 2000; Ndlovu et al., 2011; Yang et al., 2014), Fourier transform infrared spectrum (FT-IR) analysis (Wang and Ren, 2005), X-ray photoelectron spectrum (XPS) analysis (Wang et al., 2014a; Zhang et al., 2014), and contact angle measurements (dos Santos and Oliveira, 2007) in the last several decades. Compared with these traditional methods, the new molecular simulation method is a useful complement to the experimental techniques involving density functional theory, molecular mechanics, and semi-empirical approaches that allows us to observe the atomic-scale phenomena and establish the favorable mineral–collector interaction configurations directly, which cannot be achieved in current experimental studies (Qin et al., 2013). Molecular simulation has great potential to provide an important insight into the flotation mechanism of reagent molecular on mineral surfaces, and to study

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the physical or chemical phenomena involved in the adsorption process.

Numerous workers have successfully used molecular simulation method in developing highly selective flotation collectors for quartz separation (Rath et al., 2014; Zhang et al., 2011) and explaining adsorption process of collectors on mineral surface (Liu et al., 2015; Tian et al., 2011; Wang et al., 2014b; Xu et al., 2013; von Oertzen and Skinner, 2005; von Oertzen et al., 2007). Rath et al. (2014) worked on the application of the DFT approach to design different carbon chain length amine collectors for quartz flotation. Wang et al. (2014a,b) employed molecular dynamic simulation to study the adsorption mechanism of dodecylamine on muscovite and quartz. Liu et al. (2015) investigated the structure–relativity relationship of dodecylamine, dodecyl-propyl ether amine and fatty amine molecules as flotation collectors for quartz in consideration of solvation effect. von Oertzen and co-workers used *ab initio* density functional and mixed functional calculations to investigate the electronic structure of pyrite (100) surfaces induced by fracture in comparison to that of bulk pyrite (von Oertzen and Skinner, 2005), and further to examine the stability of potential Cu surface sites and compared measured core-line binding energy (BE) shifts for the Cu-reacted surface with the corresponding charge distribution obtained from a Mulliken population analysis (von Oertzen et al., 2007).

However, several aspects related to molecular simulation haven't been studied or published. Firstly, there are a few researches on quartz structure simulation parameters convergence tests, which were necessary to be conducted for a more accurate and convenient expression to obtain an optimum quartz crystal geometry. Also, the convergence tests of quartz surface layer and vacuum thickness based on surface energy were little done for an optimal quartz surface slab, in consideration of computational limitation and simulation accuracy. Secondly, molecular simulations at present were mainly involving in the adsorption process of cationic collectors on quartz surface, while surface reactions between anionic collectors and various metallic ions (e.g. Ca^{2+} , Fe^{3+} , Fe^{2+} , and Mg^{2+} , etc.) activated-quartz mineral surfaces remain unsolved. Besides, the factors such as solvent water molecule, activation ions species as well as the deprotonation of the collector molecules in aqueous environment which could also influence the adsorption of the collectors onto quartz mineral surface were rarely considered (Liu et al., 2009; Ozkan et al., 2009; Potapova et al., 2011; Sayan, 2005).

In this work, the crystal optimization convergence tests were conducted to obtain an optimum quartz crystal geometry. Then, the accurate α -quartz (101) slab surface for later adsorption calculations was cleaved from the pre-optimized quartz bulk, in consideration of the slab surface layer and vacuum thickness. Subsequently, the exact adsorption mechanism of the new collector α -BLA on α -quartz (101) surface was investigated at a molecular level in the absence and presence of Ca(II), in conjunction with the results of quartz micro-flotation tests, zeta potential measurements and calcium ions species distribution diagram (Luo et al., 2015; Zhu et al., 2015). The study provides a comprehensive understanding on the possible interaction cases existing among the α -quartz (101), calcium and the α -BLA collector.

2. Computational details

DFT is a computational quantum mechanical modeling method used in physics, chemistry and materials science to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined. The periodic DFT calculations of the paper were performed with the Cambridge

serial total energy package (CASTEP), which is a first-principle pseudopotential method based on DFT using ultra-soft pseudopotentials (Vanderbilt, 1990) and a plane-wave (PW) expansion of the wave functions (Sun et al., 2005).

2.1. Crystal optimization of quartz

Crystal optimization convergence tests were conducted, in consideration of the essential parameter set such as exchange/correlation potential, kinetic cutoff energy, and Brillouin zone k -point, for an optimum quartz crystal geometry.

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately (Burke and Wagner, 2013). At present, generalized gradient approximation (GGA) and local density approximation (LDA) are widely applied in practice. LDA depends solely upon the value of the electronic density at each point in space, while GGA also takes into account the gradient of the density at the same coordinate (Perdew et al., 1996). Compared with LDA, gradient-corrected functional is more appropriate for adsorption energy calculations, so that several functions such as Perdew–Wang's 1991 (PW91), revised Perdew–Burke–Ernzerhof (RPBE), Perdew–Burke–Ernzerhof solids (PBE-SOL), Perdew–Burke–Ernzerhof (PBE), Wu–Cohen (WC) were developed under GGA framework. The optimized quartz lattice parameters were compared with the observed experimental values to verify the validity and rationality of the setting parameters.

2.2. Surface energy calculation

Surface energy (E_{surf}) is the index for measuring the thermodynamic stability of a given surface. A lower value indicates a more stable surface which can be used to represent the accurate surface structure (Hu et al., 2012). All surface slab surfaces obtained from the bulk quartz with the optimum unit cell volume were modeled by a super cell approach ($2 \times 1 \times 1$). For obtaining an accurate quartz slab surface, slab depth from 12.54 Å to 29.25 Å (1–6 layers of $2 \times 1 \times 1$ Si_3O_6 units) and vacuum thickness from 10 Å to 20 Å were considered with cutoff energy for the plane wave basis set fixed at 460 eV and Monkhorst–Pack mesh at $3 \times 4 \times 1$. The surface energy (E_{surf}) in a slab model (Dong et al., 2011) is calculated by Eq. (1).

$$E_{\text{surf}} = [E_{\text{slab}} - (N_{\text{slab}}/N_{\text{bulk}}) \cdot E_{\text{bulk}}]/(2A) \quad (1)$$

where E_{slab} and E_{bulk} are the total energies of the surface slab and the bulk unit cell, respectively; N_{slab} and N_{bulk} are the numbers of atoms contained in the slab and the bulk unit cells, respectively; A is the unit area of the surface; 2 denotes two surfaces along the z -axis in the surface slab.

2.3. Adsorption energy of adsorbate on quartz surface calculation

The relative affinity of interaction of the optimized quartz mineral surface and various adsorbates can be quantified in terms of the total adsorption energy (ΔE_{ads}) defined as the following Eq. (2) (Pradip et al., 2002; Radha and Navrotsky, 2014; Rai et al., 2011), and were performed using the CASTEP module.

$$\Delta E_{\text{ads}} = E_{\text{complex}} - (E_{\text{adsorbate}} + E_{\text{mineral}}) \quad (2)$$

where E_{complex} refers to the energy of the optimized adsorption configuration of the reagent and quartz, whereas $E_{\text{adsorbate}}$ and E_{mineral} refer to the total energy of the adsorbate and the cleavage quartz surface, respectively. A more negative value of ΔE_{ads} implies more exothermic adsorption, favorable and stronger interaction of the reagent on the mineral surface.

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