



Research paper

Adsorption of alkylamine cations on montmorillonite (001) surface: A density functional theory study

Chenliang Peng^a, Yihang Zhong^b, Fanfei Min^{c,*}^a Institute of Engineering and Research, Jiangxi University of Science and Technology, Ganzhou 341000, China^b Department of architectural and surveying & mapping engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China^c Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China

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ABSTRACT

Hydrophobic aggregation in cationic surfactant dispersion is an effective method for the dewatering of clay-rich tailing. The effect of head groups type and alkyl chain length on the adsorption of alkylamine cations on montmorillonite (001) surface was investigated by density functional theory (DFT), sedimentation and measurement of contact angle and adsorption quantity. The results showed that the strongest active sites were located above the six-membered oxygen ring (SOR) of montmorillonite layer, around the H atoms on N atom in the head group for alkyl primary amine (C_nPA^+), secondary amine (C_nSA^+), tertiary amine (C_nTA^+) cations and around H atoms in the $-CH_3$ groups for quaternary amine (C_nQA^+) cation. The alkylamine cations interacted with surfaces by electrostatic attraction and hydrogen bonding where PA^+ , SA^+ , and TA^+ cations formed three, two and one $N-H_n \cdots O_s$ hydrogen bonds with the montmorillonite (001) surface, respectively, while QA^+ cations formed non-traditional $C-H_c \cdots O_s$ hydrogen bonds. The adsorption energies of C_n alkylamine cations decreased with the increasing substitution degree of $-CH_3$ groups to H_n atoms in the head group. Moreover, the adsorption energies increased with the n increasing from 12 to 16, but changed slightly when beyond 16. The experimental results were consistent with the theoretically calculated results.

1. Introduction

Clay minerals, a group of phyllosilicates (e.g., kaolinite, montmorillonite, illite, etc), are widely used in ceramics, plastics, coatings, paper, rubber and cosmetics and other industrial products (Sposito 1999; Uddin 2008). However, as the common gangue minerals in mineral processing, clay minerals bring adverse effects in tailing dewatering because they can form stable dispersion that settle very slowly to prevent efficient water recovery in the absence of reagents (Ndllovu et al. 2013; Wang et al. 2014; Harris et al. 2015). In this case, hydrophobic aggregation is an effective method to promote tailing dewatering. It is based on the selective adsorption of surfactants on the desired mineral surface. The adsorbed surfactants render the clay mineral hydrophobic. The particles easily form aggregates which settle fast under gravity and hence are effectively separated from water phase (Ren et al. 2008; Song et al. 2000; Min et al. 2014). Long chain alkyl amine with 12–18 carbon atoms in alkyl chain (C_{12-18}), can be used as the hydrophobic modifier of clay minerals. For example, cationic surfactants such as dodecylamine (Hu et al. 2013) and cetyltrimethyl ammonium (Zhang et al. 2008) were proved to be effective surfactants

for the hydrophobic aggregation of kaolinite.

The phenomena, involving the intensity of adsorption, the orientation of the adsorbed species, and the nature of the adsorbed layer, can affect the process of tailing dewatering. Therefore, it is very important to understand the interaction model and mechanism of hydrophobic modifiers with mineral surfaces at a micro-level. The adsorption mechanism of long-chain alkylamines on mineral surfaces was investigated using atomic force microscopy (AFM) (Zhang et al. 2007; Xie et al. 2016), zeta potential measurement (Nishimura et al. 2000; Chen et al. 2017), contact angle measurement (Wang et al. 2016; Shen et al. 2017), adsorption measurement (Wang et al. 2016; Xu et al. 2016) and spectroscopic methods (e.g., Fourier Transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS)) (Chernyshova et al. 2000; Jin et al. 2016; Sahoo et al. 2016). These studies showed that the factors, such as the type of head groups, the length of alkyl chain length, reagent concentration and solution pH, have an important effect on the adsorption behavior of alkylamines. Under the acidic condition, long-chain alkylamines primarily exist in the cationic form and are adsorbed at the negatively charged silicate surface mainly through electrostatic interaction when below the critical micelle concentration

* Corresponding author.

E-mail address: ffmin@aust.edu.cn (F. Min).

(CMC). The interaction selectivity and intensity of alkylamines on mineral relate to the type of head groups to a great extent. The growth of chain length would somewhat increase the adsorption strength at surface, and enhance the effect of mineral flotation. Recently, molecular modeling has opened a new door for exploring the complex chemical structure and reaction of adsorbate on the surface, which can avoid the limitation of the resolution of experimental analysis and the interference to the target system. Molecular modeling involves molecular mechanics, semi-empirical approaches and density functional theory (DFT) method, among which DFT method has a very extensive application in many fields (Liu et al. 2013; Wang et al. 2015; Han et al. 2016; Zhang et al. 2016). (Y. Chen and J. Chen 2010, J. Chen et al., 2010, 2013) and Long et al. (2016) used DFT method to explain the interaction mechanism of reagent with surface in flotation of sulfide ores as well as the effect of lattice defect and surface hydration on the adsorption of xanthate and thiophosphates collectors. Liu et al. (2015) investigated the structure-reactivity relationship of dodecylamine and its derivatives as flotation collectors for quartz using DFT method. Their calculations indicated that the molecular form of alkylamines hardly formed covalent bond with the silicon atom of surfaces while the cationic form was easily adsorbed on the quartz surface through electrostatic attraction. Rath et al. (2014) studied the interaction of alkylamine collectors with C_{12-18} chain length and the ether and ester derivatives with the quartz surface using DFT methods, finding that among the collectors, the ester amines had the strongest adsorption strength.

Montmorillonite (Mt) is a kind of high-swelling clay mineral commonly encountered in waste tailings, which can easily exfoliate to smaller particles in aqueous dispersion due to the strong hydration of surface, resulting in the highest stability among the clay minerals (Peng et al. 2016, 2017). And as the hydrophobic modifier, alkylamine cations are classified as primary amine cation (C_nPA^+), secondary amine cation (C_nSA^+), tertiary amine cation (C_nTA^+) and quaternary amine cation (C_nQA^+) on the basis of degree of substitution of $-CH_3$ groups to H atoms on N atoms in the polar head groups, where C_n denotes the number of carbon atoms in non-polar alkyl chain. Therefore, the objective of the present investigation is to understand the adsorption mechanism of these four types of alkylamines cations on montmorillonite (001) surface (the main surface of montmorillonite) as well the effect of the alkyl chain length using DFT calculation combined with experiments. The active sites of alkylamines cations and surface, the structure and energy characteristics of adsorption geometries were calculated and discussed in the paper, and the calculated results were compared with the results of experiments such as sedimentation test, contact angle and adsorption quantity.

2. Experiments and methods

2.1. Computational detail

Because there was no available experimental atomic coordinate, the initial model of montmorillonite was derived from pyrophyllite structure through the replacement of Al^{3+} by Mg^{2+} in the octahedral sheet which was sandwiched between two SiO_4 tetrahedral sheets. The optimized cell parameters of pyrophyllite bulk were: $a = 5.19 \text{ \AA}$, $b = 9.01 \text{ \AA}$, $c = 9.50 \text{ \AA}$, $\alpha = 91.02^\circ$, $\beta = 101.79^\circ$, $\gamma = 89.84^\circ$. Lattice vectors a , b and c were within the error of 1.6% compared to the experimental values of 5.16 \AA , 8.96 \AA and 9.35 \AA , respectively (Wardle and Brindley 1972). Then the optimized bulk structure was used to create the structure of montmorillonite with the unit-cell formula of $Na_{0.5}Al_{3.5}Mg_{0.5}Si_8O_{20}(OH)_4$, where the negative charge was neutralized by Na^+ in the interlayer space. To represent the montmorillonite surface, a periodically repeated slab was constructed by cleaving the bulk unit cell at the (001) plane because it is the most predominant plane for montmorillonite. The $2a \times b \times c$ supercell was created to calculate the adsorption of C_1 alkyl amine cations on Mt. (001) surface (Fig. 1a)

while a larger $2a \times 2b \times c$ supercell was used when the adsorption of C_{12-18} long-chain alkylamine cations was investigated (Fig. 1b). A vacuum of 30 \AA was added on the surface along the c -axis to minimize the artificial interference from adjacent layer. The structure diagrams of C_nPA^+ , C_nSA^+ , C_nTA^+ and C_nQA^+ are showed in Fig. 2. From C_nPA^+ to C_nQA^+ , the substitution number of $-CH_3$ to the H atom on N increases from 0 to 3. Because the structure and properties of the polar groups significantly affect the selectivity and intensity of the adsorption of surfactant on clay mineral surface, the non-polar alkyl carbon chain was initially reduced to $-CH_3$ group ($n = 1$) to focus on the adsorption mechanism of different types of alkylamine cations, and then C_{12-18} alkylamine cations were used to proceed with the effect of alkyl chain length. All reagent ions were created in a periodic cell of $30 \times 30 \times 60 \text{ \AA}^3$. The initial structures of the reagent-mineral complex were created by placing the optimized reagent cations on the optimized mineral surfaces with the head groups of the reagent being oriented toward surfaces.

The density functional theory (DFT) calculation was implemented in the DMol³ program using the generalized gradient approximation (GGA) density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) functional (Perdew et al. 1996). Physical wave functions are expanded in terms of numerical basis sets in DMol³ codes to produce highly accurate results while keeping the computation cost low. The double numerical basis set with polarization functions on hydrogen atoms (DNP), which is comparable with the 6-31G** basis set, was used in the work (Delley 1990). The core electrons were treated with All Electron which provides no special treatment of cores and all electrons are included in the calculation. Grimme dispersion correction was added to the DFT calculation (Grimme 2006). The Brillouin zone sampling by Monkhorst-Pack schemes was restricted to Γ -point due to the large size of the supercell (Monkhorst and Pack 1976). A Fermi smearing of 0.005 Ha (1 Ha = 27.211 eV) and a global orbital cutoff of 4.5 \AA were employed. The stopping criterion for the SCF loop was 1×10^{-5} eV/atom. The convergence thresholds of geometry optimizations were 4×10^{-3} Ha/ \AA for the maximum atomic force, 5×10^{-3} \AA for the maximum atomic displacement, and 2×10^{-5} Ha for the total energy. The effect of water on the adsorption was studied with the aid of Conductor-like Screening Model (COSMO) (Klamt and Schüürmann 1993) as implemented in DMol³ program where the solvent is treated as a dielectric continuum. The COSMO is a considerable simplification of the continuum solvation model without significant loss of accuracy. With water (permittivity ≈ 78.4), a very good accuracy is achieved.

The frontier orbital theory is used to predict the active sites of montmorillonite surface and alkylamine cations which account for where and how the alkylamine cations are adsorbed on surface. Based on the frontier orbital theory, the additional electrons would occupy the lowest unoccupied molecular orbital (LUMO), whereas upon ionization electrons would be removed from the highest occupied molecular orbital (HOMO) in the chemical reaction (Fukui 1982). In general, the interaction between frontier orbitals can be divided to two types: the one is that the electrons transfer from HOMO of surface to LUMO of reagent where the HOMO-LUMO energy gap is denoted ΔE_1 ; the other is that the electrons transfer from HOMO of reagent to LUMO of surface where the HOMO-LUMO energy gap is denoted ΔE_2 . The effective interaction between two frontier orbitals should meet three principles: energy closing, maximum orbital overlap and symmetry matching. When the latter two principles are met, the smaller the HOMO-LUMO energy gap, the stronger the interaction between the reagent and the surface (Musa et al. 2010; Saikia and Deka 2011). The smaller one between ΔE_1 and ΔE_2 indicates the type of the interaction between frontier orbitals.

The different adsorption configurations of the reagents on montmorillonite (001) surfaces were investigated, where only the most stable configurations were further analyzed. The adsorption energy E_{ads} of the reagents on montmorillonite surface was computed as following

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