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Molecular dynamics simulation study of the interaction of mixed cationic/anionic surfactants with muscovite

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ABSTRACT

Molecular dynamics simulations were performed to investigate the adsorption of dodecylamine (DDAH), oleate (NaOL) and the mixture of the two ions on a muscovite surface in an aqueous solution. The results indicate that DDAH molecules absorb on the muscovite surface by electrostatic interactions and hydrogen bonding. In contrast, NaOL molecules cannot independently adsorb on the muscovite surface. A micelle structure of DDAH and NaOL molecules forms on the muscovite surface. The DDAH molecules are determined to play a dominant role in the adsorption of the mixed surfactants on the muscovite surface, while the NaOL molecules co-adsorb with the DDAH molecules. Sodium ions also play an important role in the adsorption of the mixed surfactants. This paper may provide a template for studying the adsorption configuration and mechanism of mixed surfactants on mineral surfaces.

1. Introduction

Muscovite has demonstrated great potential for applications in cosmetics, construction and metallurgy due to the excellent dielectric properties and high thermal stability of this material [1,2]. Moreover, this material is an important carrier for certain rare metals, including vanadium, titanium, and lithium [3]. Muscovite is often associated with quartz, feldspar and iron oxide in nature [4]. In the past decades, the flotation technique has been demonstrated as an effective strategy for the purification of muscovite [5–7]. Traditionally, the flotation process is performed using long-chain amine surfactants and sulfuric acid in strongly acidic conditions (pH <3). However, the strong acid pulp from the flotation process is likely to cause environmental pollution and corrosion of the flotation equipment. Moreover, this method is always accompanied by large amounts of foam in the presence of slime, which inevitably deteriorates the flotation indexes [8].

Compared with a single surfactant, mixed anionic/cationic surfactants provide better flotation performance in muscovite processing due to synergistic effects in solid–liquid systems [1,9]. In recent years, an increased amount of effort has been devoted for investigating the adsorption mechanism of mixed anionic/cationic surfactants on muscovite. Xu et al. used dodecylamine and sodium oleate as mixed surfactants for the flotation of muscovite. Zeta potential measurements and pyrene fluorescence tests demonstrated the co-adsorption of the mixed surfactants on muscovite [9]. This co-adsorption mechanism was also confirmed by another group using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and qualitative tests [1,10,11]. However, these studies investigated the adsorption mechanism mainly by experimental methods, which become incompetent when studying microscopic phenomenon of mixed surfactant molecules on mineral surfaces.

Molecular dynamics (MD) simulations are a valuable tool to study surfactant adsorption on solid surfaces at the microscopic level [12]. Moreover, MD simulation can elucidate the dynamic characteristics of the adsorption process [13]. Du et al. used MD simulations to describe the state of dodecyl trimethyl ammonium bromide (DTAB) on a talc surface, and revealed that the negatively charged bromide ions behave similar to bridges that join the surfactant to the edge of the talc surface and create a hydrophobic surface state [14]. Heinz et al. studied the structure and dynamics of octadecyl ammonium on montmorillonite, and these authors found that the ammonium head groups were hydrogen-bonded to cavities on the montmorillonite surface [15]. To the best of our knowledge, no studies reported the use of MD simulations to investigate the adsorption mechanism of cationic/anionic surfactant mixtures on minerals.

In this work, MD simulations were used to study the adsorption mechanisms of cationic, anionic, and mixed cationic/anionic

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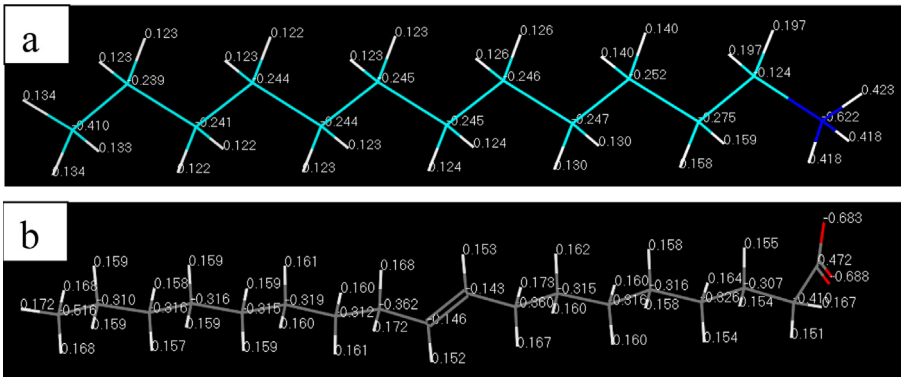

Fig. 1. The optimized models (a: DDAH; b: OL). The color representation is as follows: red, oxygen atoms; white, hydrogen atoms; blue, nitrogen atoms; light blue, carbon atoms of DDAH; and gray, carbon atoms of OL. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

surfactants on a muscovite (0 0 1) surface. The cationic and anionic surfactants that we selected were dodecylamine hydrochloride (DDAH) and sodium oleate (NaOL), respectively. The adsorption mode of the surfactants (DDAH, NaOL, or their mixture) on the muscovite surface was determined. The density profiles of these surfactants were determined to elucidate the interaction between the surfactants and muscovite surface.

2. Computational details

2.1. Forcefield

In this paper, the phyllosilicate force field embedded in the polymer-consistent force field (PCFF_phyllosilicates) was adopted throughout the simulation. This force field has provided reasonably accurate results for both phyllosilicates and hydrocarbon chains, such as atomic charges, cell parameters, and surface energies. In addition, this force field has been successfully used for modeling various clay minerals [16–18]. The flexible SPC model was applied to simulate the water molecules. In previous studies, this force field performed well in for computing the structure of muscovite, montmorillonite and pyrophyllite [12,15,17,19].

In the PCFF_phyllosilicates force field, the potential energy can be expressed as [12,16,17]:

$$E_{total} = E_{bonds} + E_{angles} + E_{non\text{-}bond} \quad (1)$$

The non-bond interaction term ($E_{non\text{-}bond}$) is expressed as:

$$E_{non\text{-}bond} = \frac{1}{4\pi\varepsilon_0\varepsilon_r}\sum_{i>j}\frac{q_i q_j}{r_{ij}} + \sum_{i>j}E_{ij}\left[2\left(\frac{r_{ij}^0}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}^0}{r_{ij}}\right)^6\right] \quad (2)$$

where the first term represents the electrostatics interactions and the second term is the van der Waals force. The parameters ε and r are, respectively, the minimum of the potential and the equilibrium distance between the bonded atoms, E_{ij} is the equilibrium well depth, and r^0 is the equilibrium distance between these atoms.

2.2. Models

Muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$) belongs to the group of 2:1 layer silicates and consists of an [AlO_6] octahedral sheet sandwiched between two [(Si, Al)O_4] tetrahedral sheets. The monoclinic C2/c 2M1 muscovite crystal structure was used as the initial input structure for our MD simulations [20]. The experimental lattice optimizations are $a = 5.20$ Å, $b = 8.99$ Å, $c = 20.03$ Å, $\alpha = 90^\circ$, $\beta = 94.50^\circ$ and $\gamma = 90.00^\circ$ [21,22]. The muscovite surface was built by cleaving the structure along the (0 0 1) plane at the middle of the interlayer space. Alkyl ammonium head groups were found to adsorb on the muscovite surface by an ion-exchange mechanism [12,15,16]. Therefore, potassium metal ions on the surface were not considered in this study, and the initial configuration was prepared with the DDAH head groups pointed to the solid surface at the location of the previously mentioned potassium ions, while same number

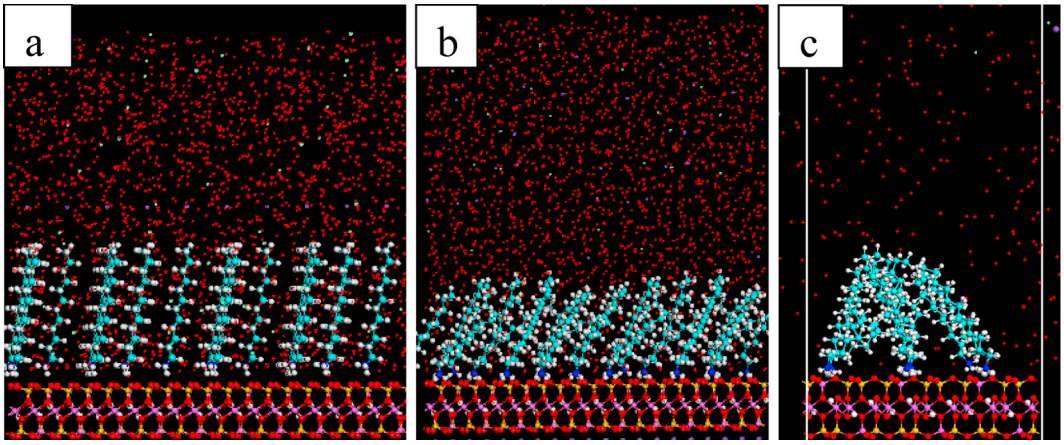

Fig. 2. MD simulation snapshot of 12 DDAH molecules near the muscovite surface. The snapshots are taken after 2 ns at the apparent equilibrium state. The color representation is as follows: red, oxygen atoms; white, hydrogen atoms; blue, nitrogen atoms; light blue, carbon atoms of DDAH; pink, alumina atoms; purple, sodium atoms; and green, chloride atoms. For clarity, the hydrogen atoms of the water molecules are not shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)