Flotation and adsorption of muscovite using mixed cationic–nonionic surfactants as collector

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ABSTRACT

The performance of the mixed dodecylamine chloride (DDA)/octanol (OCT) surfactants on muscovite flotation was investigated using flotation tests, and their adsorption mechanisms on muscovite and air/water interface were clarified using contact angle measurement, surface tension and molecular dynamics (MD) simulations. The flotation results indicate that the recovery of muscovite rapidly decreases when the pH increases in the presence of only DDA, whereas the recovery of muscovite is high (>77%) over a wide range of pH in the presence of the mixed DDA/OCT surfactants with a ratio of 2/1. Contact angle measurements further confirm that the mixture displays a stronger collecting power than DDA and is a superior collector for the muscovite flotation. The surface tensions of DDA, OCT and their mixture indicate that the mixture is more efficient than DDA at decreasing the air–water interfacial tension and exhibits much better surface activities. MD simulations show that the mixture interacts with the muscovite mainly through electrostatic attraction and hydrogen-bonding. DDA ion is dominant in the interaction between the mixture and muscovite. OCT molecules are co-adsorbed onto the muscovite through the hydrogen-bond interaction and hydrophobic association with DDA ions. Compared with DDA, a well-compacted monolayer is formed on the muscovite surface in the presence of mixed surfactants, indicating a much stronger hydrophobic character of muscovite.

1. Introduction

As a widely used process in mineral separation, froth flotation exhibits exciting advantages, such as superior separation efficiency and cost effectiveness [1]. By adsorbing the appropriate collectors, mineral particles can be hydrophobic and attach to bubbles. Mixed surfactants are frequently used as collectors in flotation practice because they may often behave synergistically and exhibit better surface properties than the corresponding single surfactants [2,3]. In the muscovite–biotite flotation system, the use of a mixture of differently structured anionic sodium oleate and cationic dodecylamine hydrochloride as collectors enhances the flotation recovery and selectivity [2]. Selective feldspar flotation from quartz in mixed alkyl diamine/sulfonate collectors at pH 2 can be achieved in practice [4,5]. Mixtures of collectors, such as xanthate and dodecylamine, have been widely used for many years in sulfide flotation [6,7].

Among various surfactant combinations, mixed cationic–nonionic surfactants are of great interest because of their strong synergistic effects on the interfacial properties and spontaneous vesicle formation behavior in aqueous phases [8–10]. As the nonionic surfactant component, alcohols are the most common co-surfactants at their low concentration [11]. Many studies have been conducted on mixed micellar systems that consist of cationic and nonionic surfactants [12–17]. The results show that the mixed surfactant systems often show synergistic behavior, which results in a much lower critical micelle concentration (CMC), better efficiency in reducing the surface tension of water and better wetting, solubilizing and foaming. With respect to the adsorption of mixed cationic–nonionic surfactants at mineral surfaces, the adsorption of nonionic surfactant is enhanced in the presence of cationic surfactants on, for instance, alumina, silica, and kaolinite; almost all reporters found the co-adsorption of the mixed surfactants at the mineral surfaces, and a highly compact mixed monolayer of cationic and nonionic surfactants is formed at the mineral surfaces [18–21].

There are comprehensive studies on the interaction between cationic–nonionic surfactants in aqueous systems, but there are limited studies concerning the adsorption of mixed surfactants at the mineral surfaces, which should be contributed because the underlying mechanisms of the synergistic behavior remain not well-understood. Meanwhile, there is a lack of microscopic understanding of the behavior of mixed surfactants at the interfaces. Molecular-level information is necessary to achieve the desired understanding. Compared with experimental methods, computer simulations can directly provide microscopic details [22]. In recent years, molecular dynamics simulation has been used most extensively to study

single surfactants at the mineral surfaces at a molecular level. However, studies on the mixtures of nonionic and ionic surfactants are limited.

As a representative silicate mineral, muscovite is of significant interest because of its excellent dielectric properties and high thermal stability. Therefore, the muscovite surface chemistry/physics is of particular interest to mineral-processing engineers. In this study, the flotation performance of binary cationic/nonionic surfactant mixtures on muscovite was investigated. We used dodecylamine (DDA) as the cationic surfactant and octanol (OCT) as the nonionic surfactants because they are widely used in industrial applications. Computational calculations were used to obtain information on the adsorption mechanism of the mixed cationic and nonionic surfactants on the muscovite to elucidate the adsorptive characteristics of the mixed cationic/nonionic surfactant toward the muscovite. The study provides physical insight into the microscopic adsorption mechanism for reservoir muscovite surface.

2. Experiment

2.1. Materials and reagents

The muscovite sample was obtained from Hebei province in China. The sample was crushed, hand-selected, and ground in a porcelain mill with agate ball. The ground sample screened out the $-74 + 38$ μm fractions for the flotation experiments. Contact angle measurements were taken for the rock mineral samples, which were provided by the Emsdiasum Company of America.

The cationic surfactant DDA and nonionic surfactants octanol (OCT) with an analytical purity of 99.9% were purchased from Sinopharm Chemical Reagent Co., Ltd. H_2SO_4 and NaOH were used to adjust the pH, and deionized water was used in all experiments.

2.2. Flotation experiments

Flotation tests were conducted using an XFG5-35 flotation machine with a spindle speed of 1600 r/min. The reagents were added in the following order: (a) H_2SO_4 or NaOH conditioning for 2 min; (b) surfactant conditioning for 3 min, followed by a flotation collection period of 3 min. The products and tailings were weighed separately after filtration and drying and used to calculate the recovery.

2.3. Contact angle measurements

The contact angles of muscovite before and after treatment with surfactants were measured using the MiniLab ILMS (GBX, France). Freshly cleaved surfaces were obtained by peeling the top sheet of the mineral sample using a double-sided adhesive tape. The sample was immersed for 30 min in a beaker containing surfactant solution at a desired concentration. Subsequently, the sample was washed three times with deionized water and dried with nitrogen. The deionized water was dropped onto the muscovite surface using a special syringe, and the static contact angle was measured. During the measurement, the volume of the water drop should remain suitable and stable to avoid gravitational effects on the contact angle. The measurements were repeated at least four times by settling other drops at different sample locations. Each contact angle data point presented in this paper was the average value of at least three measurements.

2.4. Surface tension measurements

The surface tension of aqueous solutions that contained surfactants was measured using a Kruss K10 automatic tensiometer (Krüss GmbH, Germany) with a platinum plate, which was burned after washing in alcohol flame to completely remove the adsorbed surfactants before each measurement. The temperature was held constant at room temperature (25.0 °C). In all cases, more than three successive measurements were performed.

2.5. Computational details

2.5.1. Forcefield

The PCFF-PHYLLOSILICATE force field was applied for all simulations. This force field was developed by Heinz et al. and can be thoroughly evaluated. The atomic charges, cell parameters and surface energies are consistent with experiment [23,24]. Moreover, the PCFF-PHYLLOSILICATE force field includes reliable parameters for hydrocarbon chains; therefore, it can be used in organic molecules [25]. In previous studies, the force field also performed well in computing the structure of muscovite, montmorillonite and pyrophyllite [23,24,26,27]. In the PCFF-PHYLLOSILICATE force field, the potential energy can be expressed as [24,26,28]:

$$E_{total} = E_{bonds} + E_{angles} + E_{non-bond}. \tag{1}$$

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

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

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

2.5.2. Model

The monoclinic C2/c 2M1 muscovite crystal structure was used in our MD simulations [29]. The potential parameters of muscovite in the simulation are listed in Table 1 [23]. The crystal parameters optimized using the PCFF-PHYLLOSILICATE force field are listed in Table 2. The calculated lattice parameters are reasonably consistent with the available experimental data. The model of the muscovite surface was built by cleaving the muscovite structure along the (0 0 1) surface at the middle of the interlayer space. Supercell modes of muscovite (25.86 × 26.89 × 99.30 Å) were chosen for the simulation study.

According to the flotation solution chemistry, there is DDA in either ionized form in the acid solution or molecular form in the strong alkaline solution [30]. The OCT molecule is not easily hydrolyzed. Therefore, DDAs are described as $C_{12}NH_3$ at low pH and a mixture of both at intermediate pH values. The atomic structure models of the DDA ion, DDA molecule and OCT molecule are shown in Fig. 1. The water–water interactions were modeled using the simple point charge (SPC) potential. The atomic charges of the DDA and OCT molecules were derived from the density-functional theory calculation.

2.5.3. Simulation method

All simulations were conducted using the Materials Studio 6.0 package. The MD simulations were run at the constant-volume and -temperature (NVT) canonical ensemble. The temperature was controlled at 298 K using a Hoover–Nose thermostat. Periodic boundary condition was applied in all directions. The Nose–Hoover thermostat

Table 1
Potential parameters of muscovite in the simulation.

Atoms	Charge (e)	r^0 (pm)	E_0 (kcal/mol)
K	+1.0	410	0.20
Si^{surface}	+1.1	420	0.035
Al^{surface}	+0.8	450	0.035
Al^{octahedral}	+1.45	450	0.035
O^{surface}	−0.55	380	0.015
O^{apical}	−0.758	380	0.015
O^{hydroxyl}	−0.683	380	0.015
H^{hydroxyl}	+0.20	109.8	0.013