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Flotation and adsorption of mixed cationic/anionic collectors on muscovite mica

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ABSTRACT

The adsorption of dodecylamine acetate (DAA), sodium oleate (NaOL) and DAA–NaOL mixtures on muscovite mica were investigated through flotation tests, zeta potential measurements, and pyrene fluorescence tests. The results show that the muscovite mica has a negative charge over the pH range 2–12. The muscovite mica did not float in the presence of NaOL alone. However, the recovery of muscovite mica ranged from ca. 80% (at pH 2) to 50% (at pH 11) using DDA alone. In the presence of mixed DAA–NaOL, recovery ranged from ca. 80% (at pH 2) to 90% (at pH 11). The individual cationic collectors DAA can be adsorbed strongly onto the muscovite mica, but no significant adsorption of anionic collectors NaOL can be detected by zeta potential measurements. In the mixed systems, the adsorption of both the cationic and anionic collectors are enhanced due to co-adsorption. The presence of NaOL in the mixture decreases the electrostatic head–head repulsion between the surface and ammonium ions and increases the lateral tail–tail hydrophobic bonds. Molecular dynamics (MD) simulations were conducted to further investigate the adsorption of DDA, NaOL, and DAA–NaOL on the (001) basal planes of muscovite using Materials Studio 5.0 program. The conclusions drawn from theoretical computations are in good agreement with experimental results.

1. Introduction

Muscovite mica has the general composition $KAl_2(AlSi_3O_{10})(OH)_2$, and its theoretical composition is 11.8%K_2O, 45.2%SiO_2, 38.5%Al_2O_3, and 4.5%H_2O. Micas have a layered lattice type structure composed of two silica tetrahedral sheets with a central octahedral sheet. In the case of muscovite mica, this central layer is dioctahedral, with only two-thirds of the possible octahedral positions being filled (Bailey, 1984). Aluminium substitution for one in every four silicon sites in the siloxane sheets leads to a negative layer charge. The charge balance of the siloxane plane is provided by interlayer cations which, in the case of muscovite, are potassium. Muscovite mica exhibits perfect cleavage along the (001) (siloxane) plane, which exposes interlayer potassium ions. In aqueous suspensions, the potassium ions readily enter into solution, leading to the development of a net negative charge on the siloxane plane. Thus, the surface of the muscovite mica is negatively charged at all pH > 1 (Nishimura et al., 1992).

Due to the negative charge surface over the whole pH range of 2–12, the muscovite mica would not be expected to respond to anionic collectors in the absence of an activator. Conversely, the mineral is readily recovered using cationic collectors, such as amines. At pH values greater than 5, many silicates are negatively charged. This means that selective separation of muscovite mica from these minerals, using a cationic collector, may not be possible (Nakazawa et al., 1988).

There are a number of processes where the mixtures of dissimilar surfactants have shown better properties than the individual components and there is strong interest in the behavior of mixed surfactant systems in recent years. The interactions between two surfactants in solution and at the air/liquid interface have been studied (Hanumantha Rao and Forssberg, 1997; Vidyadhar and Hanumantha Rao, 2007; Zhang and Somasundaran, 2006). In general, the physicochemical properties of a mixed monolayer does not obey the additive rule. Such a non-additive behavior is designated as synergism (Hua and Rosen, 1982; Von Rybinski et al., 1987).

Although the adsorption of a single surfactant at the solid–liquid interface has been studied thoroughly, few studies exist for the case of adsorption in mixed surfactant solutions. The use of mixed cationic/anionic collectors for enhanced flotation and selectivity has only recently been recognized (Hosseini and Forssberg, 2007; Vidyadhar and Hanumantha Rao, 2007; Vidyadhar et al., 2012). However, the adsorption mechanism of mixed cationic/anionic collectors in flotation processes is still largely unidentified.

The objective of this work is to understand the underlying adsorption mechanism of the mixture of cationic DAA and anionic NaOL collectors in muscovite mica flotation. Flotation tests,

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zeta-potential measurements, and fluorescence spectroscopic tests were undertaken. Results are discussed using molecular dynamics (MD) simulation to verify experimental results using theoretical computations. This study focused on elucidating the role of mixed cationic/anionic collectors systems in muscovite mica flotation.

2. Materials and methods

2.1. Materials

Muscovite mica, obtained from Lingshou of Hebei province (China), were crushed by a hammer and ground in a procelain mill. And −0.074 mm fractions were used in the experiments. X-ray fluorescence spectrometer (XRF) (Table 1) and X-ray diffraction (XRD) (Fig. 1) were used to study chemical and mineral compositions. The results showed the purity of the muscovite to be roughly 90%.

DAA and NaOL of analytical grade from Tianjin Damao Chemical Reagent Factory were used as collectors. DAA–NaOL were prepared by the mixing DAA with NaOL together, and the mixture were freshly prepared just before using with needs in order to avoid precipitation. Pyrene was from Sigma–Aldrich (Shanghai) Trading Co., Ltd., China. Pyrene was recrystallized twice using anhydrous ethanol. KCl of analytical purity was used as background electrolyte solution. Solutions of HCl and NaOH were used to adjust the pH of the system. Double distilled water was used in all tests. All reagents are listed in Table 2.

2.2. Flotation

Microflotation tests were carried out in a 40 ml hitch groove flotation cell (Fig. 2) (Liu et al., 2010). Mineral particles prepared (2 g) were placed in a plexiglass cell, and then filled with distilled water. HCl or NaOH were added for adjustment pH. After adding the desired amount of reagents, the suspension was agitated for 3 min. Flotation was conducted for 4 min. The froth products and tails were weighed respectively after filtration and drying, and the recovery was calculated based on the weight of the products.

2.3. Zeta-potential measurements

A suspension containing 0.1 wt.% mineral particles grounded to −5 μm in an agate mortar was prepared in the 1×10^{-3} mol/L KCl solution, and conditioned by magnetic stirring for 5 min. After settling for 10 min, the supernatant of dilute fine particle suspension was taken for zeta potential measurement.

The zeta-potentials were measured using a Malvern Zetasizer Nano ZS90 (England) equipped with a rectangular electrophoresis cell. The conductivity and pH of the suspension were monitored continuously during the measurement and the environmental temperature was maintained at 22 °C.

2.4. Pyrene fluorescence tests

Samples for fluorescence measurements were prepared by mixing pyrene stock solution with surfactant and mineral pulp, and allowed to stand for 2 h to equilibrate. The pyrene steady-state emission spectra in the suspension was obtained using a hitachi F-4500 fluorescence spectrophotometer. The excitation wave length of pyrene was 335 nm. The pyrene stock solution was prepared by dissolving pyrene in hot water until saturation, then cooling to 25 °C, and filtering. The concentration of pyrene in the solution was determined to be 6.53×10^{-7} mol/L (Mathias et al., 2001).

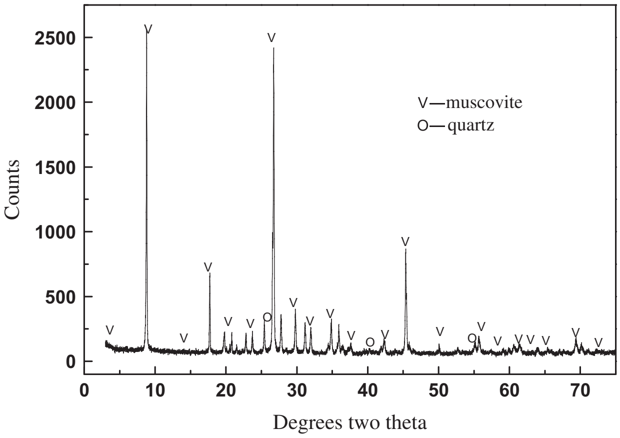

Fig. 1. X-ray diffraction patterns of muscovite.

2.5. Molecular dynamics (MD) simulations

All calculations were performed in the framework of the MD, using the Material Studio 5.0 (MS) package. Firstly, CASTEP module included in MS software was adopted to optimize the crystal structure of muscovite mica. By comparing different parameters to be optimized, the best optimization parameters are as follows: a function was GGA + PBESOL, *k*-point set was $3 * 3 * 4$, SCF tolerance was 1.0×10^{-6} eV/atom, use custom energy cutoff was 340 eV. Other parameters were default settings. The lattice optimization results are $a = 5.202$, $b = 9.037$, $c = 20.160$, $\alpha = 90°$, $\beta = 95.417°$, $\gamma = 90°$. Then, a 2D periodic surface cell is created from the unit cell of the mineral at the cleavage plane (001) and then optimized in this same way.

Secondly, the DAA, NaOL, DAA–NaOL molecule was optimized using DMol3 module.The optimization parameters are as follows: Quality was medium, Functional was LDA + PWC. A symmetry calculated was opened. According to molecule charged situation, charge was chosen, DAA was + l, NaOL was −1, DAA–NaOL was 0.

Finally, Discover module was employd to calculate adsorption energies. DAA, NaOL and DAA–NaOL are as adsorbate, muscovite mica is as adsorbent. First of all, the geometry optimization of the system of reagent–muscovite mica was conducted using Smart Minimizer in pcff force field. MD simulations were run using a canonical ensemble (NVT) at 298 K with the time step of 1 fs. Total run length was 10 ps. Ewald summation method corrected was employed for calculating both electrostatic and van der Waals forces (Pradip et al., 2002). Finally, the interaction energy could be calculated using the following equation (Pradip et al., 2002; Rai et al., 2011):

$$\Delta E = E_{\text{complex}} - (E_{\text{surface}} + E_{\text{reagent}}) \tag{2-1}$$

where E_{complex} is the total energy of the optimized reagent–muscovite mica complex, E_{reagent}, E_{surface} is the summation of single point energies of the free reagent and muscovite surface. The more

Table 1
Chemical composition of muscovite mica wt.%.

Composition	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O	Loss
Muscovite	80.98	0.78	0.29	2.84	0.01	0.046	0.007	0.025	14.06	14.5