

Adsorption mechanism of mixed cationic/anionic collectors in feldspar-quartz flotation system

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Abstract

The adsorption mechanism of mixed cationic alkyl diamine and anionic sulfonate/oleate collectors at acidic pH values was investigated on microcline and quartz minerals through Hallimond flotation, electrokinetic and diffuse reflectance FTIR studies. In the presence of anionic collectors, neither of the minerals responded to flotation but the diamine flotation of the minerals was observed to be pH and concentration dependent. The presence of sulfonate enhanced the diamine flotation of the minerals by its co-adsorption. The difference in surface charge between the minerals at pH 2 was found to be the basis for preferential feldspar flotation from quartz in mixed diamine/sulfonate collectors. The infrared spectra revealed no adsorption of sulfonate collector when used alone but displayed its co-adsorption as diamine–sulfonate complex when used with diamine. The presence of sulfonate increased the diamine adsorption due to a decrease in the electrostatic head–head repulsion between the adjacent surface ammonium ions and thereby increasing the lateral tail–tail hydrophobic bonds. The mole ratio of diamine/sulfonate was found to be an important factor in the orientation of alkyl chains and thus the flotation response of minerals. The increase in sulfonate concentration beyond diamine concentration leads to the formation of soluble 1:2 diamine–sulfonate complex or precipitate and the adsorption of these species decreased the flotation since the alkyl chains are in chaotic orientation with a conceivable number of head groups directing towards the solution phase.

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1. Introduction

The feldspar is the most abundant mineral group in the world, forming around 60% of the earth's crust, and is found in igneous, metamorphic and sedimentary deposits in most countries [1]. They are used in the production of glass, ceramics and in polymer, paper and paint industries as fillers and extenders. Silica is often associated with the feldspars, as quartz in pegmatic deposits and silica sand in feldspathic sand deposits. They are generally processed by wet methods, and froth flotation and magnetic separation are used to remove accessory minerals from feldspars. Traditionally, the feldspars are floated from quartz using a cationic collector and hydrofluoric acid (HF) as an activator for them in highly acidic conditions. The use of HF

is no longer acceptable due to environmental and health hazards, and the search for a new reagent scheme without fluoride ions is under serious attention for the last two decades. The subject of feldspar flotation in the presence and absence of fluoride ions was reviewed in 1995 [2].

Although there are a number of processes where the mixtures of dissimilar surfactants showed better properties than the individual components alone, the use of mixed cationic/anionic/non-ionic collectors for effective flotation and selectivity was recognised only lately [3–7]. A HF free flotation process using a mixture of cationic and anionic collectors for the separation of feldspar from quartz was described by Katayanagi [8] and this process was reported to be applied in industrial practice [9]. The mixed collectors were composed of cationic alkyltrimethylene diamine and anionic petroleum sulfonate. A similar reagent scheme consisting of a combined cationic–anionic collector, N-tallow-1,3-propylene diamine/dioleate, was also applied successfully on feldspar ores [10,11]. Several other studies with-

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out involving fluoride ions are limited to either single mineral flotation or artificial mixtures [12–15]. There are no detailed fundamental investigations to elucidate the role of mixed collectors in selective feldspar flotation besides the studies reported on mixed surfactants adsorption on other mineral systems [16–18].

The objective of the present investigation is to understand the underlying adsorption mechanism of the mixture of cationic alkyl diamine and anionic sulfonate/oleate collectors in the preferential feldspar flotation from quartz. The Hallimond flotation, zeta-potential and diffuse reflectance FTIR studies using pure microcline and quartz minerals have been carried out. In this paper, the results of these investigations are discussed and the role of mixed collectors in selective feldspar flotation is delineated.

2. Experimental

2.1. Materials

The pure crystalline microcline and quartz mineral samples purchased from Gregory, Bottley & Lloyd Ltd., UK were used in the investigations. The minerals were crushed to ~ 3 mm size and ground in an agate mortar. The products were wet-sieved to obtain size fractions of $-150 + 38 \mu\text{m}$ and $-38 \mu\text{m}$. A portion of the $-38 \mu\text{m}$ material was further ground and micro-sieved in an ultrasonic bath to obtain $-5 \mu\text{m}$ size fraction. The coarser fraction ($-150 + 38 \mu\text{m}$) was employed in Hallimond flotation tests and the finer fraction was used in zeta-potential and FTIR studies.

2.2. Reagents

The cationic diamine collector used was the tallow-1,3-diaminopropane (Duomeen T) supplied by Akzo Nobel, Sweden. A molecular weight of 330 g/mol of diamine specified by the manufacturer was used in the preparation of required concentrations of diamine solutions. The diamine was dissolved in dilute HCl. The anionic collectors of sodium dodecyl sulfonate and sodium oleate were procured from Fluka and Riedel-De Haen, respectively. Analar grade HCl and NaOH were used for pH adjustment.

2.3. Hallimond flotation tests

The Hallimond flotation tests of single mineral recovery were carried out as a function of pH, collector concentration and ratio of cationic/anionic collectors using a flotation cell of 100 ml capacity. About 1 g of the mineral was first conditioned separately at the desired pH and reagent conditions in a 100 ml volumetric flask for a predetermined time (5 min) and then transferred into the Hallimond tube. The flotation was performed for 1 min at constant agitation and aeration rate of 8 ml/min. When the tests were performed in mixed cationic/anionic collectors, the mineral was conditioned in a solution containing both the reagents at a specified concentration ratio.

2.4. Zeta-potential measurements

The zeta-potentials were measured using a Laser Zee Meter (Pen Kem Inc., model 501) equipped with video system employing a rectangular flat cell. 1.0 g/l mineral suspension was prepared in 10^{-3} KNO₃ electrolyte solutions, conditioned for 1 h at room temperature (22 °C) in the presence of predetermined concentration of reagents and pH. The pH of the suspension at the time of measurement was reported in the results.

2.5. Diffuse reflectance FTIR measurements

Exactly 0.1 g of the mineral powder ($\sim 5 \mu\text{m}$) was conditioned in an Erlenmeyer flask containing 100 ml collector solution at a specified pH and concentration for 60 min. After equilibration, the suspension was filtered through millipore filter paper (pore size $0.22 \mu\text{m}$) and the solids were air-dried overnight at room temperature before recording the DRIFT infrared spectrum. When the mineral was treated in the presence of mixed collectors, the solution contained a predetermined concentration ratio of the collectors before the addition of solids.

The spectra were obtained with a Perkin-Elmer 2000 spectrometer equipped with its own diffuse reflectance attachment. Typical spectrum was an average of 200 scans measured at 4 cm^{-1} resolution with a narrow band liquid nitrogen cooled MCT detector. The samples were prepared by dispersing 25 mg of the air-dried sample in 125 mg of KBr. The absorbance units were defined by the decimal logarithm of the ratio of pure finely powdered KBr reflectance to the sample one. The atmospheric water was always subtracted from the sample spectrum. The area under the alkyl chain bands was measured with the facility available within spectral manipulation software.

3. Results and discussion

3.1. Hallimond flotation studies

Although the objective of the present study is to delineate the underlying mechanism of mixed cationic/anionic collectors in preferential feldspar flotation from quartz, the flotation response of the minerals independently with cationic and anionic collectors is first assessed. Fig. 1 shows the flotation responses of microcline and quartz as a function of pH with cationic diamine, anionic sulfonate and oleate collectors, respectively. The recoveries are presented at 1×10^{-5} and 5×10^{-5} M initial diamine concentrations. At lower diamine concentration, the rapid rise in quartz recovery begins at about pH 3.5 and at higher level, the on-set pH for flotation is decreased to 2.5. The flotation of microcline begins to occur at a very low pH region of 1.5–2.0. At this pH region, the recovery of microcline is about 60% using 5×10^{-5} M diamine, while quartz is not floated. However, there is no difference in the flotation responses of quartz and microcline above pH 4 and both minerals are floated equally well using 5×10^{-5} M diamine. With anionic collectors, neither of the minerals is floated in the pH range studied.

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