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Influence of bromine modification on collecting property of lauric acid

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ABSTRACT

Bromine atom with strong electronegativity was introduced to α-carbon position of lauric acid (LA) by solvent-free method (Hell–Volhard–Zelinski reaction) at ambient pressure in laboratory, and the synthesized product α-Bromolauric acid ($CH_3(CH_2)_9CHBrCOOH$, α-BLA) was used as a new type collector for the flotation of quartz mineral. The flotation properties of pure quartz using α-BLA as a collector were investigated by single mineral flotation tests. The adsorption mechanism of α-BLA collector on quartz surface was established by zeta potential measurements, Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), in conjunction with the results of quartz micro-flotation tests. Pure mineral flotation results showed that the collector α-BLA exhibited an excellent performance at alkaline conditions (pH $\geqslant$ 11.50), activator $CaCl_2$ concentration 1.0×10^{-4} mol/L, and collector concentration 1.5×10^{-4} mol/L in a relatively lower temperature 15 °C, where about 99.8% of the quartz could be floated out. Compared with collector LA, the new synthesized collector α-BLA is more tolerant to lower pulp temperature and fluctuations of the reagents dosages. The study revealed that the α-BLA collector had adsorbed on the surface of pure quartz in the forms of chemical interaction, electrostatic adsorption and hydrogen bonding adsorption based on the results of zeta potential measurements, FT-IR spectra, and XPS.

1. Introduction

Anionic reverse flotation has been considered as one of the most widely applied technologies for the economical utilization of iron ore resources (Scott and Smith, 1993; Uwadiale, 1992; Hout, 1983). The main technical feature of this process is to float out the main gangue minerals, while the iron oxides are kept depressed with the help of starches (Iwasaki, 1983; Numela and Iwasaki, 1986).

The most extensively used types of anionic collectors are long-chain fatty acids and their salts (Quast, 2006). Poor solubility – the solubility of the straight chain, saturated fatty acids containing between 6 and 18 carbon atoms in water decrease from 8.3×10^{-2} mol/L to 3.0×10^{-7} mol/L with increasing chain length as would be expected (Kirk, 1993). The requirement of higher pulp temperature to maintain the activity and solubility of fatty acid anionic collectors leads to a great deal of energy consumption which prompts the researches on new collectors in hopes of finding a solution in cutting the energy consumption, thus minimizing the emission of carbon dioxide (CO_2) and other greenhouse gases for the protection of the global environment (Clifford et al., 1998; Sis and Chander, 2003).

Japanese scientist Ogata et al. (1979) found that the modified saturated fatty acid with chlorine (Cl) atom introduced to α-carbon position could improve the solubility of these reagents. And, the enhancement of electronegative of fatty acid by Cl atom resulted in a stronger adsorption among active sites of O atoms of carboxyl group with hydroxyl of quartz surface (Wang and Hu, 1989). Based on these findings, RA series collectors (RA-315, RA-515, RA-715, and RA-915) were synthesized by chloridization and oxidization of tail oil as its essential raw material, and had been proved to be with good properties of low cost and non-toxicity (Lin et al., 1993). LKY and KS-II synthesized later possessed the advantages of wide raw material sources, simple synthesis method, and high yield (Mei et al., 2009; Zhang and Liu, 2003). However, the flotation pulp still should be maintained at a relatively higher temperature when these kinds of collectors were used for the reverse flotation of iron ores in China (Li, 2009; Meng et al., 2010; Zhang et al., 2011).

The attempt of this paper is to synthesize a new type modified collector with twelve carbon atoms in hydrocarbon chain, with strong electronegativity bromine atom introduced into the α-carbon position by solvent-free method at ambient pressure in order to improve the activity and solubility of the reagent.

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Micro-flotation tests using lauric acid and α-BLA as a collector were conducted to confirm whether the new collector could be adopted at a comparatively lower pulp temperature. Adsorption mechanism of the new collector α-BLA on quartz surface was also studied by means of zeta-potential measurements, FT-IR spectroscopy, and XPS. This paper is a study of finding new type collectors which can be used in a relatively lower temperature to reduce the energy consumption.

2. Experimental

2.1. Mineral

The pure quartz samples from Anqian iron mine, Liaoning Province, China, were carefully hand-picked, crushed, ground, and wet-sieved to obtain the size fractions from 0.038 mm to 0.10 mm for the micro-flotation tests. X-ray fluorescence spectrometer (XRF) was used to study elemental composition of quartz samples. As seen in Table 1, it is obvious to be seen that the quartz consists of 99.90 wt.% SiO_2, which meets the desirable requirement of purity for the experiments.

2.2. Reagents

Analytical purity of calcium chloride was used as the activator source of Ca(II) supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China. Potassium bromide of spectroscopic purity was used to conduct the experiments of infrared spectra obtained from Sinopharm Chemical Reagent Co., Ltd., China. Potassium chloride of analytical grade was used as background electrolyte. Solutions of HCl 0.10 mol/L and NaOH 0.10 mol/L were used to adjust the pH value of the system. Ultra-pure water was used in all tests.

2.3. Synthesis of α-Bromolauric acid

The new type collector α-BLA was synthesized by solvent-free method (Hell–Volhard–Zelinski reaction (Carey, 2008)) in our laboratory. This procedure involved treatment of the lauric acid with bromine in the presence of a small amount of phosphorus trichloride (PCl_3) as a catalyst. The reaction is given by Eq. (1).

$$CH_3(CH_2)_{10}COOH + Br_2 \xrightarrow[PCl_3]{80-90\,^\circ C,\ 7\ h} CH_3(CH_2)_9CHBrCOOH + HBr \quad (1)$$

Lauric acid (100.16 g, 0.50 mol) was heated to melt at 65 °C with a magnetic stirrer in a 500 mL three-neck round bottom flask. Catalyst PCl_3 (6.01 g, 6%) was added into the reactor, and then the reaction mixture was agitated for 1 h at a certain temperature of 75 °C. The reaction temperature was raised to 85 °C, and bromine (90.45 g, 0.565 mol) was dripped to the reaction system in 5 h. After addition, the mixture was kept stirring for 7 h to ensure the reaction to be carried out thoroughly as much as possible. The unreacted bromine was treated with sodium sulfite solution until the color of product transformed from reddish brown to grayish white. Continually, the oily layer washed with ultra-pure water for several times. H_2O was then removed from the mixture by atmospheric distillation at 100 °C for 1 h. Finally, the grayish white solid (137.20 g) was obtained as the target product with a purity of 94.5%. This synthesis procedure has the advantages of high yield, easy operation and realization in laboratory.

Table 1
Chemical composition of the single quartz (wt.%).

SiO_2	Al_2O_3	Na_2O	K_2O	P_2O_5	Fe_2O_3	CaO	Loss
99.90	0.02	0.02	0.01	0.005	0.02	0.01	0.015

2.4. Flotation tests

The micro-flotation tests were conducted in a 50 mL flotation cell of a XFG_{II50} laboratory flotation machine (Liu et al., 2010). Quartz samples (2 g) were placed in a plastic cell in which 50 mL ultra-pure water were filled. The pulp was stirred for 2 min at a rotating speed of 1900 rpm before adding the HCl or NaOH solution to adjust the pH of pulp. The reagents were added into the cell every 2 min continually in the order of pH regulator, activator $CaCl_2$ and collector α-BLA, respectively. The suspension was agitated for 3 min after adding all the desired amount of reagents, and the flotation was conducted for 4 min. Finally, the froth products and tailings were weighed respectively after drying, and the recovery was calculated based on the weight of the products.

2.5. Zeta potential measurements

Zeta potentials were measured by Malvern Instruments Nano-ZS90 zeta potential analyzer. The suspension containing of 0.04 wt.% −0.005 mm quartz solid was agitated for 15 min with a magnetic stirrer. Pulp pH was regulated with 0.10 mol/L HCl or 0.10 mol/L NaOH solution, and the zeta potentials of quartz surface were measured in the presence of predetermined concentration of reagents at the constant temperature of 25 °C. The measurement tolerance was within ±2 mV after at least 3 measurements.

2.6. Fourier transform infrared spectroscopy

Characteristic peaks can be used to analyze the adsorption between collector and mineral surface on the basis of organic functional groups and the essential structure of the material (López et al., 2000; Lima et al., 2005). The mineral samples used for this purpose were ground to −0.002 mm in an agate mortar. Then, 2 g of mineral samples were added to 50 mL aqueous solution in absence and presence of 1.0×10^{-4} mol/L $CaCl_2$ and 1.5×10^{-4} mol/L α-BLA at pH 11.50, 15 °C. After being stirred for 0.5 h, the mineral samples were filtered, washed with ultra-pure water for three times, and dried in a vacuum oven at 40 °C for 24 h (Huang et al., 2014). The spectra were recorded in the range of 4000–400 cm^{-1} with 4 cm^{-1} resolution. 256 scans were collected for each specimen. The analyses were carried out by Nicolet 380 FT-IR spectrometer using potassium bromide pellets about 1 mg sample accompanied with 100 mg KBr usually.

2.7. X-ray photoelectron spectroscopy

The XPS spectra of quartz particles untreated and treated by $CaCl_2$/α-BLA at pH 11.50 were collected from a surface of size about 2 mm × 2 mm on an America Thermo VG ESCALAB250 spectrometer using Al Kα X-rays (1486.6 eV) as the sputtering source at a power of 150 W (15 kV × 10 mA). The pressure in the analysis chamber was 5.0×10^{-10} mbar during spectral acquisition. A value of 284.8 eV was adopted as the standard C (1s) binding energy. The quantification and curve fitting of the spectra were determined with the Thermo Scientific Advantage software.

3. Results and discussion

3.1. Characterization of collector α-Bromolauric acid

Physical and representative spectral data of α-BLA collector were demonstrated below.

The freezing point of LA was 44.2 °C (Quast, 2006), while the freezing point of α-BLA decreased to about 14 °C due to the inductive effect of the introduced electron-acceptor bromine atom. The