



Adsorption behavior of mixed cationic/anionic surfactants and their depression mechanism on the flotation of quartz

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ABSTRACT

Mixed cationic/anionic surfactants are generating increasing attention as effective collectors during the flotation of muscovite, feldspar and spodumene ores. Many papers have been published focusing on the flotation mechanisms of these valuable minerals. However, the depression mechanisms on gangue minerals such as quartz have rarely been reported. In this study, mixed dodecylamine (DDA)/sodium oleate (NaOL) surfactants were used in the flotation separation of muscovite and quartz, and their depression mechanisms on quartz were investigated. Compared to DDA alone, the use of mixed surfactants resulted in a significantly higher adsorption amount of surfactants on the quartz but a lower flotation recovery and contact angle with the quartz. This is attributed to the different molecular self-assembly mechanisms between solely DDA and mixed surfactants at the quartz/water interface, as revealed by molecular dynamics simulations. A hydrophobic monolayer coating forms for solely DDA, with the head groups adsorbing on the quartz via electrostatic interactions. In the case of mixed surfactants, DDA preferentially interacts with NaOL via electrostatic interaction through the oppositely charged head groups and hydrophobic interactions between their carbon chains. As a result, most DDA and NaOL molecules form hydrophilic spherical-like micelles near quartz, whereas only a few DDA molecules adsorb directly on the quartz via hydrogen bonding. These act as a bridge linking the rest of the surfactants, leading to a relatively lower flotation recovery and contact angle for the quartz. This study is beneficial for complementing the flotation theories and mechanisms of mixed cationic/anionic surfactants on minerals.

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1. Introduction

Mixed cationic and anionic surfactants are interesting to many researchers because of their superior physicochemical properties and extensive applications in many areas, such as dispersion/flocculation, flotation, detergents, cosmetics, paints and nanolithography [1]. Due to the strong interactions between two surfactant molecules with oppositely charged head groups, most of the mixed cationic and anionic surfactants possess a synergistic advantage in reducing the surface tension and critical micelle concentration [2,3].

Froth flotation is an effective method of separating mineral particles on the basis of their surface chemistries, specifically their hydrophobicity [4,5]. The hydrophobic particles attach to the bubbles and rise to the top of the reaction vessel to form a froth that flows over the lip of the vessel, whereas the hydrophilic particles remain in the liquid [6,7]. In the process, a surfactant is often used as a collector for surface modifications to adjust the wetting properties of mineral particles. Using mixed cationic/anionic surfactants as collectors is highly desirable because of

their important influence on flotation selectivity and recovery in many mineral processes.

In practice, mixed cationic/anionic surfactants are frequently used as collectors in the flotation of muscovite, feldspar, spodumene and fluorite minerals [8–11]. A new flotation process with no fluoride using mixed cationic/anionic collectors for the separating of feldspar from quartz was investigated by A. Vidyadhar and has been reported to have been applied in industrial practice [12,13]. Although sodium oleate alone does not adsorb on muscovite and biotite, muscovite is floated selectively from biotite at basic pH values using a mixture of sodium oleate and dodecylamine surfactants as collectors [10]. Similarly, muscovite can be successfully separated from quartz at alkaline conditions using these types of mixed surfactants [9]. Among the aforementioned mineral ores, quartz is the main gangue mineral. Many papers have focused on the flotation mechanism and adsorption behavior of valuable minerals. However, only a few of these have investigated the depression mechanism of gangue minerals using mixed cationic/anionic collectors.

Extensive investigations have been performed with the goal of understanding the interactions and adsorption mechanisms of mixed cationic/anionic surfactants at the solid/liquid interface and their effect on flotation performance, including the depression mechanism [14–17]. As

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reported, the flotation performance of mixed cationic/anionic surfactants depends on the surfactant concentration, their chemical structure and the molar ratios of their components [8,18]. A. Vidyadhar et al. investigated the adsorption mechanism of mixed cationic alkyl diamine and anionic sulfonate surfactants on feldspar and quartz [10]. The results confirmed that the ratio of the cationic/anionic surfactants concentration during the wetting of the minerals was perceived to be significant. Both the surfactant tails were directed towards the solution only when the sulfonate surfactant concentration did not exceed the diamine concentration. Otherwise, the alkyl chains were found to be in a chaotic orientation with a number of head groups directing towards the solution, which resulted in the minerals becoming hydrophilic. L. Alexandrova et al. studied the influence of mixed cationic/anionic surfactants at a 1/1 M ratio on the three-phase contact parameters in silica–solution systems. The use of mixed surfactants resulted in lower contact angles, lower rates of the thin aqueous film rupture and longer film lifetimes compared to a pure cationic surfactant [19].

Our previous study introduced the use of mixed sodium oleate/dodecylamine surfactants as collectors in the flotation separation of muscovite from quartz [20]. Compared with using only dodecylamine, mixed surfactants exhibited better selectivity in the system examined. Although the wettability and flotation of quartz have been studied in several papers using cationic/anionic surfactants, little is known about the detailed adsorption model for mixed surfactants in quartz [12,19,21]. Due to limitations at the nanoscale, experimental studies cannot provide detailed structural information on mixed surfactant arrangements and their interactions in the quartz/water interface. Therefore, the adsorption structure of mixed surfactants on quartz can only be hypothesized.

In past decades, molecular dynamics (MD) simulation has proven to be a great tool to provide detailed structural information of surfactant complexes at the microscopic level, which is not easy to derive from experimental results [22]. For instance, Wang et al. carried out MD simulations of an oppositely charged polyelectrolyte and an ionic surfactant at the air/water interface [23]. From their study, a multilayer structure of a polymer–surfactant complex was found to form at the interface, and the electrostatic interaction was found to be the main driving force for the binding of surfactants to the polyelectrolyte.

The purpose of this work is to investigate the adsorption behavior of mixed cationic dodecylamine bromide (DDA)/anionic sodium oleate (NaOL) surfactants on the quartz/water interface. The contact angle and adsorption amount of quartz in the presence of mixed surfactants were first assessed as a function of pH, surfactant concentration and molar ratio of the components. Molecular dynamics (MD) simulations were then carried out to investigate the adsorption structure of pure DDA, pure NaOL and their mixtures at the quartz/water interface.

2. Materials and methods

2.1. Materials and reagents

Hand-picked quartz samples were obtained from Shanxi province in China. The samples were crushed and ground in an agate mortar to yield $-74 + 38 \mu\text{m}$ fractions for micro-flotation and adsorption experiments. The specific surface area of quartz powder was determined by a Quantachrome instrument and was found to be $0.477 \text{ m}^2/\text{g}$.

The cationic surfactant DDA and anionic surfactant NaOL with an analytical purity of 99.9% were purchased from Sinopharm Chemical Reagent Co., Ltd. The dodecyl amine-hydrochloride (DDA) solution was prepared by mixing equimolar mixtures of dodecylamine and hydrochloric acid (HCl). The mixed DDA/NaOL collectors were freshly prepared at the time of use to avoid precipitation. Reagent grade sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) from the Damao Chemical Reagent Co., Ltd. (China) were used as pH modifiers, and deionized water was used in all of the experiments.

2.2. Micro-flotation test

The micro-flotation experiments on pure minerals were carried out as a function of pH, collector concentration and molar ratio of cationic/anionic surfactants in an XFG5-35 flotation machine with a 40-mL effective cell volume. Quartz powder (2 g) was placed in a plexiglass cell and filled with distilled water. After 1 min of mixing time, H_2SO_4 or NaOH was added to adjust the pH. Collectors were added after 2 min, and the flotation was conducted for a period of 3 min after 3 min into the experiment. The floated and unfloat fractions were separately filtered, dried, and weighed to calculate the flotation recovery.

2.3. Contact angle measurement

Experiments on the contact angles of quartz before and after treatment with surfactants were carried out using the sessile drop method with the MiniLab ILMS (GBX, France). In brief, a hand-picked pure quartz crystal was cut and polished carefully to a proper size of $2 \times 2 \times 1 \text{ cm}^3$. After thoroughly cleaned, the quartz sample was immersed in a beaker containing a given surfactant solution at pH 10 for 10 min. Afterwards, the quartz was washed with deionized water for five minutes and dried with nitrogen. Finally, 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 on different parts of the same plate. Each contact angle data point presented in this paper was the average value of at least three measurements.

2.4. Adsorption amount measurement

Adsorbed amounts of surfactants on quartz were determined using solution depletion. The amount of surfactants in the supernatant solution was determined using an automated total organic (TOC) analyzer (TOC-VCPH, Shimadzu, Japan) in this work. Using DDA alone, it was found that DDA concentrate calculated from N using the TOC analyzer is slightly larger than the actual concentrate. However, there are good linear correlations between the N concentrate and the real DDA concentrate (Fig. 1). The DDA concentration of the sample solution was determined by comparing the absorbance to the standard curve. After that, the concentrate of NaOL can be back calculated by the carbon concentration in solution. If the determined concentration exceeds $3 \times 10^{-3} \text{ mol/L}$, the sample solution was diluted and retested.

Surfactant mixture solutions (40 mL) combined with quartz powder (2 g) were placed in 100-mL flasks. The pH was adjusted with the

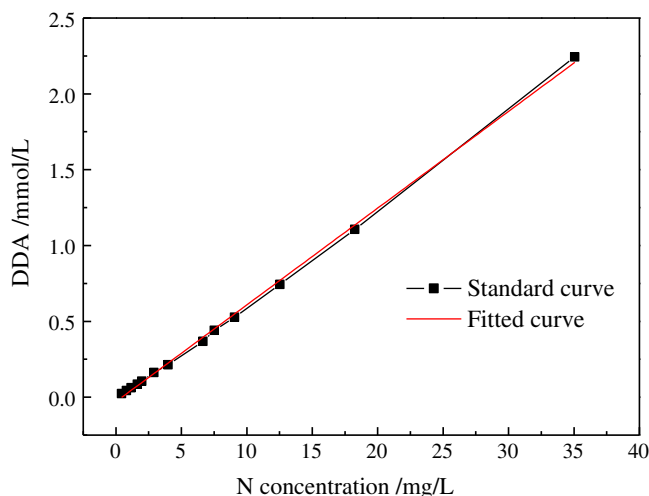


Fig. 1. Standard curve the linear relationship between N and DDA.

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