



## Research paper

# Photofoams and flotation mechanism of an azobenzene-based surfactant on quartz



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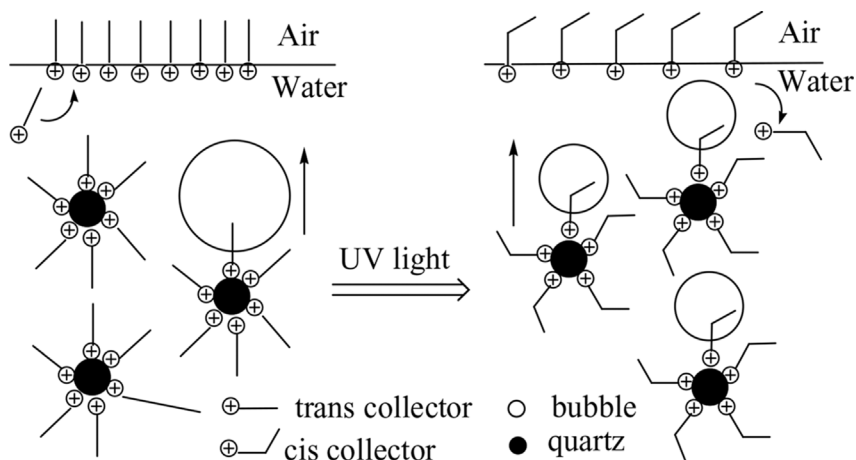
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## GRAPHICAL ABSTRACT

In the present study, the effect of UV light irradiation on the foam stability of the azobenzene-based surfactant solution was studied. The flotation performances of the surfactant in floating quartz were investigated by micro-flotation. The flotation mechanism was studied by zeta potential measurements and adsorption analysis. This study aims to demonstrate the role of photofoams in the mineral flotation.



## ARTICLE INFO

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## ABSTRACT

In this study, the flotation behavior and mechanism of an azobenzene-based surfactant on quartz were studied by micro-flotation tests, zeta potential measurements and adsorption analysis. The stability of foams produced by the surfactant can be controlled by ultraviolet (UV) light irradiation. Photocontrolled foams improve the floatability of quartz due to the significant changes in the foam properties. UV light irradiation decreases the zeta potential values of quartz and the adsorption of the surfactants on quartz. The azobenzene-based surfactant predominantly adsorbed to quartz compared to apatite.

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## 1. Introduction

Foam stabilization is of great importance in froth flotation. In a flotation process, stable foams are initially produced but foams should be easily reduced in the final step [1]. Adjusting the foam stability has great effect on the complex interplay between particles and bubbles. Accordingly, to attain the preferential foam stability, one must manage the flotation process with a huge complexity [2]. In practice, anti-foaming agents are usually used to accelerate foam rupture. But they unavoidably change the chemical composition of the flotation pulp and influence the separation of mineral ores. In addition, they increase the consumption of flotation reagents.

Phosphate rock is neither substitutable nor recyclable. It is mainly used as the key raw material to produce phosphate fertilizers. Quartz is the main gangue mineral in phosphate rock. Cationic surfactants are currently used to separate quartz from phosphate ores [3–6]. Although many strong efforts have been devoted to the flotation, cationic surfactants are seldom used in the industrial flotation of phosphate ores because they usually produce much undesirable foams, which cannot easily be reduced in a controlled way [7]. The problem becomes more pronounced because available phosphate ores are mostly of low grade [8].

## 2. Experimental section

### 2.1. Minerals and reagents

Pure minerals (quartz and apatite) were provided by SKLE. These minerals were over 90% in purity based on mineralogical analysis and X-ray diffraction data. The surfactant, 4-butyl-(4'-(3-trimethylammoniumpropyloxy)-phenyl) azobenzene, was used as a collector. The azobenzene-based surfactant was synthesized according to the procedure described in reference [9]. Its structure was shown in Fig. 1. The purity of the surfactant was checked by  $^1\text{H}$  NMR, using a Varianinova-400 MHz NMR spectrometer.

$^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 400 MHz, TMS),  $\delta$ (ppm): 0.56(t, 3H,  $\text{CH}_3$ ), 0.92(t, 2H,  $\text{CH}_2$ ), 1.10(t, 2H,  $\text{CH}_2$ ), 1.73(d, 2H,  $\text{CH}_2$ ), 2.05(t, 2H,  $\text{CH}_2$ ), 2.86(s, 9H,  $\text{CH}_3$ ), 3.14(t, 2H,  $\text{CH}_2$ ), 3.53(t, 2H,  $\text{CH}_2$ ), 6.64(d, 4H, Ar-H), 7.32(d, 4H, Ar-H).

UV light irradiation was done by a Prizmatix device equipped with photodiodes (YL-512, Landun Photoelectricity, Guangdong, 365 nm). Its maximal power was 10W (UV light) and the intensity of the light was 700 mW/cm<sup>2</sup>. The surfactant solution was exposed for 30 min under UV light before use.

### 2.2. Foam stability

A cylindrical glass container (25 mm internal diameter, 300 mm height) was filled with the test solution (10 ml) and was put into a water bath to keep the temperature at  $25 \pm 0.1^\circ\text{C}$ . Then the surfactant solution was bubbled by air at a flow rate of 50 cm<sup>3</sup>/min using a syringe. The time involving in the rupture of the foam to half an initial height (20 mm),  $t_{0.5}$ , was a measure for foam stability [10]. The results presented in the study are the average of three repeated measurements with a typical variation of  $\pm 0.5\text{s}$ .

### 2.3. Micro-flotation tests

The flotation test was performed in a XFG flotation machine with a volume of 40 dm<sup>3</sup> and an impeller speed of 1650 r/min. Exactly 3 g sample ( $-74 + 38 \mu\text{m}$  fractions) and 30 ml distilled water were added

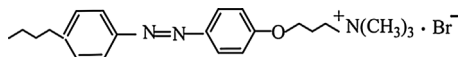


Fig. 1. Azobenzene-based surfactant investigated.

in the cell and conditioned for 2 min. Aqueous solution of sodium hydroxide or hydrochloric acid was added with a conditioning time of 3 min to adjust the pulp pH values. The surfactant in a desired dosage was then added and conditioned for 3 min. The total flotation time was 5 min. The tailing and the concentrate were filtered, dried, and weighed. The flotation recovery was calculated. The results are the average values of three independent experiments under the same conditions. The mean absolute difference of the tests was within  $\pm 0.5\%$ .

### 2.4. Zeta potential

The Zeta potential measurements were performed with a Zetapotential analyzer (Brookhaven Zeta Plus). A 10 mg sample ( $-5 \mu\text{m}$ ) was placed in a 100 ml beaker and 30 ml solution of  $1 \times 10^{-3}$  mol/L  $\text{KNO}_3$  was used as the background electrolyte. The conditioning procedure of the surfactant was the same as the treatment in the micro-flotation test listed in 2.3. The environmental temperature was maintained at  $25.0 \pm 0.5^\circ\text{C}$ . The results presented in the study were the average of five repeated measurements with a typical variation of  $\pm 2$  mV.

### 2.5. Adsorption isotherms

A mineral sample (1 g,  $-74 + 38 \mu\text{m}$  fractions) in 50 ml surfactant solution was added into a conical flask and shaken until the equilibrium was reached (24 h). Then the sample was centrifuged for 20 min at 12000r/min. The surfactant concentration was immediately analyzed by total organic carbon analyzer (TOC-LCPH, Shimadzu Corporation). The results are the average of three independent measurements (measurement error < 1%). The equation of surface adsorption is expressed as follows:

$$\Gamma = (C_0 - C) V / 10^3 m$$

Where  $\Gamma$  is the surface adsorption, mol/g;  $C_0$  and  $C$  are the initial and residual concentration of surfactant in suspension, mol/l;  $V$  is the volume of the solution, ml;  $m$  is the amount of the mineral sample, g.

## 3. Results

### 3.1. Foam properties

Fig. 2 shows the photographs of the foams produced by the surfactant solution. As a whole the surfactant solutions with exposure to UV light produced smaller bubbles than those without exposure. The number of the bubbles in foams was also increased by UV light irradiation.

Fig. 3 shows the  $t_{0.5}$  as a function of the surfactant concentration. The values of  $t_{0.5}$  were apparently decreased by UV light irradiation. In other words, UV light irradiation accelerated foam breaking.

### 3.2. Micro-flotation tests

Results from the micro-flotation experiments are shown in Fig. 4. The recoveries of quartz and apatite increased with an increase in the surfactant concentration. When the surfactant concentration increased to  $1.4 \times 10^{-3}$  mol/L, the recoveries began to decrease because more and more big bubbles were produced and the flotation performance of the surfactant decreased.

Without UV light irradiation, quartz attained a high recovery (90%) and apatite yielded a low recovery (29%). So the surfactant was very useful for quartz flotation. In the presence of UV light irradiation, the recovery of quartz appeared to be significantly increased by 4%; the recovery of apatite was slightly increased by about 1%. The UV light irradiation obviously promoted the flotation of quartz.

The effect of pH on quartz and apatite flotation is showed in Fig. 5.

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