International Journal of Minerals, Metallurgy and Materials Volume 22, Number 5, May 2015, Page 447 DOI: 10.1007/s12613-015-1092-0

# Synergistic mechanism between SDBS and oleic acid in anionic flotation of rhodochrosite

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**Abstract:** Pure mineral flotation experiments, zeta potential testing, and infrared spectroscopy were employed to investigate the interfacial reactions of oleic acid (collector), sodium dodecyl benzene sulfonate (SDBS, synergist), and rhodochrosite in an anionic system. The pure mineral test shows that oleic acid has a strong ability to collect products on rhodochrosite. Under neutral to moderately alkaline conditions, low temperature (e.g., 10°C) adversely affects the flotation performance of oleic acid; the addition of SDBS significantly improves the dispersion and solubility of oleic acid, enhancing its collecting ability and flotation recovery. The zeta potential test shows that rhodochrosite interacts with oleic acid and SDBS, resulting in a more negative zeta potential and the co-adsorption of the collector, oleates along with –COO<sup>-</sup> and –COOH functional groups are formed on the mineral surface, indicating chemical adsorption on rhodochrosite. The results demonstrate that oleic acid and SDBS co-adsorb chemically on the surface of rhodochrosite, thereby improving the flotation performance of the collector.

Keywords: rhodochrosite; flotation; sodium dodecyl benzene sulfonate; oleic acid; synergistic effects; temperature

### 1. Introduction

Manganese is an important raw material for industrial applications. Manganese metal and its mineral compounds are widely used in nearly all aspects of life. For example, pure manganese is commonly used to produce special steel in the metallurgical industry, whereas manganese ferroalloys are used as desulphurization reagents and oxygen scavengers in steel manufacturing. Due to its great importance, manganese is considered to be one of the national strategic resources for industry in China [1–2].

As collectors, fatty acids are known to have a number of weaknesses such as poor water solubility, low selectivity, cold intolerance, weak resistance to hard water, and large dosage [3]. In order to overcome the above issues, scholars have mainly focused on two aspects of fatty acid collectors, pharmaceutical modification and reagent combination.

In pharmaceutical modification, the capacity and selectivity of the collector are improved by introducing new functional groups into the reagent. In reagent combination, reagents of a similar nature are used in combination [4]. When combined, two or more reagents undergo reinforced interactions, which are known as synergistic effects. If the addition of a small amount of reagent can significantly improve the flotation performance of the other one, the second reagent is called a synergist [5–7]. At present, the known synergists of fatty acids are divided into two categories: anionic surfactants and nonionic surfactants [8].

In recent years, the following viewpoints have been formed based on a series of studies [9]. Synergists enhance the solubility or dispersion of the collector in aqueous solution, resulting in the solubilization and emulsification. The solubilizer and collector chemically and physically adsorb on mineral surfaces, respectively. The solubilizer causes complementary adsorption, strengthening the combination ability of the collector on mineral surfaces. Additionally, the synergist interacts and forms new compounds with the collector. Due to their significant improvement of the flotation effect, fatty acid synergists are used in a variety of low-grade oxide ores.

Regarding the mechanism underlying various synergistic actions, Lotter and Bradshaw [10] found that the structure

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and performance of the synergist determines its synergistic effect. Sodium dodecyl benzene sulfonate (SDBS) is a synergist that can enhance the dispersion of oleic acid and its resistance to calcium interference. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy (FTIR) showed that most oleic acid molecules are physically adsorbed on the apatite surface, whereas SDBS is chemically adsorbed on the mineral surface via complex molecular associations [11–12].

In the flotation of carbonate manganese ore, the addition of a certain amount of fatty acid collector synergist can moderately improve the flotation pulp conditions and enhance the flotation effect [13]. According to Ref. [14], to obtain the highest pharmaceutical adsorption density or adsorption strength, the proportions of  $-\text{RCOO}^-$  and  $-\text{RSO}^{3-}$ must be maintained at appropriate levels during the oxidation of paraffin wax soap and the co-adsorption of petroleum sulfonate on the mineral surface. In summary, there is strong evidence that synergists can increase the concentrate grade and recovery rate of minerals, reduce the amount of flotation froth, decrease the cost of reagent production, mitigate the impact of calcium, magnesium, and other metal ions, and enable low temperature flotation [15–17]. In the flotation of oxide ores, the addition of synergistic reagents is an effective way to improve the performance and selectivity of the collector. However, the mechanism of synergism between the collector and synergist on the mineral surface is not well understood [8].

In the present study, we have investigated the mechanism of synergism between SDBS and oleic acid in the flotation of rhodochrosite using pure mineral flotation experiments, zeta potential testing, and infrared spectroscopy.

### 2. Experimental

### 2.1. Materials and characterization

Rhodochrosite was bought in a gem market in Hunan province and used in the pure mineral flotation experiment. After manual selection of impurities, the mineral was crushed to -3 mm particles with a steel hammer and further milled to -0.074 mm particles (100%) in a ceramic ball. The mineral particles were washed several times with deionized water before experimental use. The purity of the mineral was examined by X-ray diffraction (XRD) and chemical composition analysis. The results show that the purity (100%) meets the requirements (Fig. 1).



Fig. 1. X-ray diffraction pattern of rhodochrosite used in the pure mineral flotation experiment.

Oleic acid was obtained from Zhuzhou Reagent Limited Company, and SDBS was obtained from Hangzhou Chemical Reagent Company. Other chemicals utilized in testing were also analytically pure. The experiments used distilled water.

### 2.2. Flotation

The pure mineral flotation experiment was performed using a laboratory XFD series flotation machine (Changchun, China) at a speed of 1650 r/min. A 2.0 g sample of pure mineral was loaded into a 40 mL flotation tank, and 35 mL of deionized water was then added. After the pH value was adjusted to a certain pH value with NaOH or HCl for 1 min, the inhibitors or metal ions were added. The collector was added 3 min later. The mixture was allowed to sit for 3 min and then floated for 3 min. Foam products and tank minerals were obtained by filtration, dried, and weighed to calculate the recovery rate of rhodochrosite.

### 2.3. Zeta potential test

Zeta potential was measured with a Coulter Delsa 440SX precision potentiometer analyzer (Beckman Coulter Inc,

USA). The pure mineral was finely ground to  $-2 \mu m$  powder in an agate mortar. The powdered mineral was weighed into beakers (20 mg each) and added to 35 mL of deionized water. The pH value of the slurry was adjusted with NaOH or HCl for 1 min. The reagent was then added, followed by 3 min of stirring with a magnetic stirrer. A small amount of pulp was injected through a syringe into the test electrophoresis tube for the zeta potential test.

#### 2.4. FTIR spectroscopy

FTIR spectra were collected using a Nexus 670 FTIR spectroscope (Nicolet, USA). The mineral (1.0 g) was finely ground to  $-2 \mu m$  in an agate mortar. Half of the ore sample was added to 35 mL of deionized water with reagents in a beaker. The reminder of the ore sample was homogenized for 5 min, filtered, vacuum dried, and then loaded into the FTIR spectroscope for analysis.

### 3. Results and discussion

Despite their importance in the collection of salt minerals and oxide ores, fatty acid collectors have the drawbacks of poor dispersion, low solubility, and weak resistance to the influence of calcium and magnesium ions. Therefore, the collecting ability of fatty acids is poor at low temperatures. In order to strengthen the collecting ability of fatty acids and reduce their production cost, extensive studies have been conducted in recent years on synergists of fatty acid collectors [18]. According to the literature and preliminary experimental results, we employed the anionic surfactant SDBS as a synergist of oleic acid and examined its influence on the flotation behavior of rhodochrosite.

# **3.1.** Collecting ability of oleic acid at different temperatures

During rhodochrosite flotation, the collecting ability of oleic acid on the mineral varies substantially at different temperatures (Fig. 2). At low temperature (10°C), the rhodochrosite recovery rate is significantly low. With rising temperature, the rhodochrosite recovery rate gradually increases. At the same temperature, the recovery rate gradually increases with increasing pH value. The effect of temperature on rhodochrosite flotation is especially apparent in weakly alkaline conditions. At pH 7.5, the rhodochrosite recovery rate increases by 40%. Strengthening the alkaline condition weakens the effect of temperature on rhodochrosite flotation with oleic acid as a collector. At pH >10.5, the recovery rate of rhodochrosite increases to 96% at all tested temperatures

except 10°C. When the pH value is 12 and the temperature is 10°C, the recovery rate reaches the maximum of 95%.

The above phenomena can be explained by the following reasons. Under neutral and alkaline conditions, the main component of oleic acid solution is oleic acid ion, which exhibit mutual cohesion, low solubility, and poor dispersion, especially at low temperature. The concentration of oleic acid ions in the aqueous solution is reduced, leading to a reduction in the reactivity between oleic acid and the mineral surface and thus a decrease in flotation recovery. Elevated temperature promotes the dissociation and dispersion of oleic acid in water; it also improves the activation energy of metal ions on the mineral surface, thereby strengthening the collecting ability of oleic acid. Under alkaline conditions, due to the saponification reaction between oleic acid and NaOH, the aqueous solubility of the resultant oleic acid sodium salt (sodium oleate) is high. Thus, the effect of temperature on its collecting ability is not as significant as it is for oleic acid.



Fig. 2. Effect of temperature on rhodochrosite flotation recovery using oleic acid as a collector.

### **3.2.** Collecting ability of oleic acid with synergistic SDBS at different temperatures

At low temperature, adding a small amount of surfactant (known as a synergist) can improve the dispersion and solubility of oleic acid in water. In this study, we used SDBS as a synergist of oleic acid at a mixture ratio of 9:1 (oleic acid to SDBS). The effect of temperature on rhodochrosite flotation recovery is illustrated in Fig. 3, which compares the oleic acid collector to the mixed collector.

After mixing with SDBS, the collecting ability of oleic acid is significantly improved. At different temperatures, the recovery rate of rhodochrosite is consistently higher with oleic acid + SDBS as a mixed collector compared to oleic acid only as the collector. The difference is especially obvious at 10 and 20°C and pH 7–10. At 10°C and pH 7.5, the

rhodochrosite recovery with oleic acid + SDBS as the collector is 76.58%, representing an increase of nearly 30% with respect to the recovery using oleic acid alone as the collector. When the temperature is 20°C and the pH value is 8, the rhodochrosite recovery with oleic acid + SDBS as collector is 83.74%, which is an increase of 13% compared to the recovery using oleic acid alone as the collector.



Fig. 3. Effect of temperature on rhodochrosite flotation recovery using oleic acid with or without SDBS (synergist) as the collector.

The improvement in oleic acid collecting ability generated by SDBS can be explained as follows. On one hand, the solubility and dispersity of oleic acid increase when the surface tension of water decreases. On the other hand, SDBS may be associated with oleic acid and co-adsorb on the mineral surface, thereby improving the flotation performance of the collector. The synergism of SDBS with oleic acid makes the oleic acid flotation of Mn carbonates possible at low temperature. This result provides a reference for the low temperature fatty acid flotation of other salt minerals and oxidized ores.

## **3.3.** Collecting ability of oleic acid in the presence of metal ions and synergism with SDBS

In pulp,  $Ca^{2+}$  and  $Mg^{2+}$  react with oleic acid to form oleates, decreasing the collecting ability of oleic acid. When a small amount of SDBS is added, the ability of oleic acid to resist the interference of  $Ca^{2+}$  and  $Mg^{2+}$  is significantly improved. Fig. 4 shows the effects of  $Ca^{2+}$  and  $Mg^{2+}$  on the flotation recovery rate of rhodochrosite before and after the use of SDBS.

When using only oleic acid as a collector, the flotation recovery rate of rhodochrosite declines with increasing concentrations of  $Ca^{2+}$  and  $Mg^{2+}$ . When the dosages of  $Ca^{2+}$  and  $Mg^{2+}$  are 100 mg/L, the rhodochrosite recovery rate is re-

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duced to 30% and 38%, respectively. When the mixture of oleic acid and SDBS (9:1) is used as the collector, there is a slight decrease in the rhodochrosite recovery rate with increasing dosages of  $Ca^{2+}$  and  $Mg^{2+}$ . When the amounts of  $Ca^{2+}$  and  $Mg^{2+}$  reach 40 mg/L, the recovery rate remains at approximately 80%. Under the same conditions, the ability of oleic acid to resist interference from  $Ca^{2+}$  and  $Mg^{2+}$  is significantly enhanced by SDBS synergism, thereby greatly improving the flotation recovery rate.



Fig. 4. Comparison of the effects of  $Ca^{2+}$  and  $Mg^{2+}$  concentrations on rhodochrosite flotation recovery with and without the addition of SDBS as an oleic acid synergist (mixture).

The presence of SDBS can eliminate the effect of oleic acid micelles and enhance the pharmaceutical micelle concentration of the mixed reagent; it can also improve the dispersion and solubility of oleic acid in aqueous solution. On the rhodochrosite surface, the adsorption modes of oleic acid carboxyl groups and SDBS sulfonic acid groups are chemical and physical adsorption, respectively. These reactions form a synergistic effect that strengthens the collecting ability of the collector in the chemical mixture. Therefore, the addition of an oleic acid synergist can improve its collecting ability at normal temperature and significantly improve the separation effect at low temperatures. It also enhances the ability of the collector to resist jamming by metal ions such as calcium and magnesium.

## 3.4. Zeta potential of rhodochrosite interacting with reagent

The zeta potential ( $\zeta$ ) of rhodochrosite interacting with the collector and its relationship with pH values are shown in Fig. 5. The point of zero charge (PZC) of rhodochrosite is approximately pH 9.62 in pure water. The zeta potential of rhodochrosite interacting with oleic acid shifts negatively, and the isoelectric point (IEP) drops to approximately pH 7.5. This indicates that the zeta potential becomes more negative as oleic acid adsorbs on the rhodochrosite mineral surface. When rhodochrosite interacts with oleic acid in the presence of SDBS synergist, the zeta potential of rhodochrosite further shifts in the negative direction in the tested pH range. On one hand, SDBS improves the dispersion and solubility of oleic acid in aqueous solution, which promotes more adsorption of oleic acid on the mineral surface and thus results in a more negative zeta potential. On the other hand, SDBS may associate with oleic acid to co-adsorb on the mineral surface, making the zeta potential more negative. Thus, adding a small amount of SDBS promotes the adsorption of the collector on the mineral surface and improves the flotation efficiency.



Fig. 5. Effect of collectors on the zeta potential of rhodochrosite.

## 3.5. FTIR spectra of rhodochrosite interacting with reagents

To further explore the mechanism through which reagents react with rhodochrosite, the FTIR spectra of rhodochrosite interacting with reagents (oleic acid with or without SDBS) were obtained (Fig. 6). The results show that the FTIR spectrum of rhodochrosite is significantly change by interaction with different reagents. A comparison of curves 1 and 2 shows that the absorption peaks at 2850 and 2924 cm<sup>-1</sup> in curve 2 represent the symmetric-stretching vibration peaks of  $-CH_3$  and  $-CH_2$  carbon–hydrogen bonds from the collector. This result demonstrates that oleic acid adsorbs on the surface of rhodochrosite.

A comparison of curves 1 and 3 shows that the absorption peaks at 2850 and 2924 cm<sup>-1</sup> in curve 3 are the symmetric-stretching vibration peaks of  $-CH_3$  and  $-CH_2$  carbon-hydrogen bonds from the collector. This observation indicates that SDBS adsorbs onto the surface of rhodo-chrosite. The absorption peak at 1710 cm<sup>-1</sup> is attributed to the symmetric stretching vibration of -COOH from oleic acid, which overlaps with the asymmetric stretching vibra-

tion peak of  $CO_3^{2-}$  from rhodochrosite (not shown in the diagram). Thus, the different FTIR spectra obtained in this study reveal the adsorption state of oleic acid on the surface of rhodochrosite.



Fig. 6. FTIR spectra of rhodochrosite interacting with different reagents (curves: 1 — rhodochrosite; 2 — rhodochrosite + oleic acid; 3 — rhodochrosite + SDBS; 4 — rhodochrosite + oleic acid + SDBS; 5 — rhodochrosite + oleic acid + SDBS-rhodochrosite).

Curve 5 shows a different spectrum of rhodochrosite + oleic acid + SDBS-rhodochrosite. Absorption peaks at 1594 and 1710 cm<sup>-1</sup> are the symmetric vibration peaks of  $-COO^-$  and -COOH, respectively; this represents a 32 cm<sup>-1</sup> shift compared to the oleic acid symmetric vibration peak of  $-COO^-$  (1563 cm<sup>-1</sup>), indicating that oleates are formed on the rhodochrosite surface through chemical adsorption. Based on a comprehensive comparison of the FTIR spectra of the samples, we conclude that oleic acid and SDBS co-adsorb on the surface of rhodochrosite, resulting in the superior collecting ability of the mixed collector compared to that of the single collector.

### 4. Conclusions

(1) The strong collecting ability of oleic acid on rhodochrosite is adversely affected by low temperature. SDBS improves the collecting ability of oleic acid on the mineral surface and enhances its anti-jamming capability against metal ions such as calcium and magnesium.

(2) SDBS decreases the surface tension of water and increases oleic acid solubility and dispersion. It may associate with oleic acid to co-adsorb on the mineral surface, thereby improving the flotation performance of the collector.

(3) When rhodochrosite interacts with oleic acid, the zeta potential of the mineral becomes negative. When rhodo-

### chrosite interacts with oleic acid with synergistic SDBS, its zeta potential becomes more negative. It is concluded that both of the reagents adsorb on the mineral surface, and SDBS may associate with oleic acid to co-adsorb on the mineral surface. A great number of functional groups such as -COO<sup>-</sup> and -COOH are present on the mineral surface, which is indicative of oleate formation and chemical ad-

(4) In conclusion, oleic acid and SDBS co-adsorb chemically on the surface of rhodochrosite, thereby improving the flotation performance of the collector.

### Acknowledgements

sorption on the mineral surface.

Financial support for this work was provided by the National Natural Science Foundation of China (No. 51104179), the Independent Exploration Innovation Fund of Central South University (No. 2014zzts058), Collaborative Innovation Center for Clean and Efficient Utilization of Strategic Metal Mineral Resources and the Important Science & Technology Special Projects of Hunan Province, China.

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