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Synergetic Effect of the Mixed Anionic/Non-Ionic Collectors in Low Temperature Flotation of Scheelite

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Abstract: The synergetic effect of four octaphenyl polyoxyethyienes (TX) on low temperature flotation of scheelite at 9–11 °C was investigated through flotation experiments, and the adsorption mechanism was studied by way of surface tension, zeta potential, and adsorption measurement. The results show that the presence of the four octaphenyl polyoxyethyienes can improve scheelite flotation in a low concentration range, and their synergetic effects increase with the increase of the oxyethyl group (EO) number in their molecular structure, the mixed sodium oleate/TX-15 collector exhibits the best collecting performance for scheelite. Compared with sodium oleate alone, a larger reduced value of zeta potential is seen in the presence of the mixed collectors, and the adsorption of sodium oleate on the scheelite surface is enhanced for a constant sodium oleate concentration. Moreover, the synergetic effect of TX-15 can be well demonstrated through surface tension measurement, a lower critical micelle concentration (CMC) value of the mixed sodium oleate/TX-15 surfactant is obtained, indicating a higher surface property. Therefore, the mixed sodium oleate/TX-15 collector is suitable for low temperature flotation of scheelite.

Keywords: scheelite; low temperature flotation; synergetic effect; nonionic surfactant

1. Introduction

Fatty acid is the most extensively used collector in the flotation practice of scheelite due to the advantages of wide availability of sources and low price. Among various fatty acids, oleate (or sodium oleate) is the most frequently used. It has good foamability, but its use suffers from a higher temperature requirement, sensitivity to slimes and ions, lower selectivity to objective minerals, and relatively high consumption [1,2]. For fine raw ore or tailings with poor grade and complex dissemination, the disadvantages of poor selectivity and no resistance to low temperature (<15 °C) are particularly significant [1].

With the development of reagent synthesis technology, a series of new modified fatty acids have been successfully developed, largely extending the application range of fatty acids and increasing the selectivity [3–5]. However, they are hard to spread in industrial production owing to the complex synthesis process and high cost. Moreover, the collector mixtures—that is the mixed use of fatty acids and other surfactants of the same type or different types—are usually used to enhance the collecting performance and selectivity of fatty acids in scheelite flotation. Several researchers studied the effect of mixing reagent types, such as anionic–anionic, anionic–nonionic, or anionic–cationic. The results show that the synergistic effects of the mixed collectors demonstrate the following aspects: enhancing mineral recovery, decreasing collector dosage, improving the main collector adsorption on mineral surface, and enhancing adsorption selectivity [6–10]. Research by Gao et al. showed that the selective separation of scheelite from calcite can be achieved using a lower dosage of sodium silicate and a mixed collector of HXMA-8 and NaOL [11]. Wang et al., studied the flotation separation of muscovite from quartz using a mixed anionic/cationic collector of sodium oleate and dodecylamine, the results showed that the flotation behavior of muscovite was improved, and the adsorption of dodecylamine was enhanced by the co-adsorption of sodium oleate in the mixed collector system [12]. Filippov et al. reported the synergetic effects of an alcoholic reagent (Exol) for Ca-bearing mineral flotation with sodium oleate, and the results showed that sodium oleate mixed with a nonionic reagent adsorbs onto scheelite surfaces, and the adsorption on the scheelite surface was increased for a constant oleate concentration [13,14].

Compared with synthesis of new reagents, the use of collector mixtures has better flexibility since fatty acids can mix with different reagents according to actual requirements. Meanwhile, the mixed use of reagents can enlarge the use range of reagents, and avoid the complex synthesis process of new reagents, so it is the development trend and important research direction of beneficiation reagents in future. A number of studies show that the addition of non-ionic surfactants (such as Tween-80, NP-4, and so on) can improve the collecting performance of fatty acids at low temperatures, and increases flotation recovery of minerals (scheelite, apatite, diaspore) [15–18] Therefore, it is necessary to systematically study the adsorption mechanism of the mixed collector at a low temperature, which can provide an important theoretical guiding role in flotation practice.

Research by Song et al., showed that the mixtures of octaphenyl polyoxyethyiene and kerosene presented an obvious synergetic effect in coal flotation because it can increase the dispersion of kerosene in water and enhance the hydrophobicity of coal [19]. However, there is little reported on the synergetic effect of octaphenyl polyoxyethyiene in low temperature flotation. Therefore, a series of octaphenyl polyoxyethyiene (TX) with different EO numbers were used as synergists in this paper, attempts were made to enhance scheelite flotation at a low temperature of 10 °C. The flotation behavior of scheelite using single and binary mixtures of sodium oleate and a polyoxyethylene ether as the collector were investigated, and the adsorption mechanism of the mixed anionic/non-ionic collector on scheelite surface was analyzed by zeta-potential and adsorption density measurements.

2. Experimental

2.1. Samples

The pure scheelite samples were taken from Qinghai province, China. After being ground in a pottery ball mill and screening, the fractions of −74 mm + 38 μm size were collected for the single mineral flotation experiments. The chemical analysis results show that the grade of WO_3 is about 77%, and the purity of scheelite was about 94%.

Reagents used in the experiments are shown in Table 1.

Table 1. Reagents used in the experiments.

Reagents	Molecular Formula	Role in Scheelite Flotation
Sodium oleate	$C_{17}H_{33}COOH$	Collector
Octylphenol polyoxyethyiene	$C_8H_{17}C_6H_4O(CH_2CH_2O)_nH$	Synergists
	n = 4, TX-4	
	n = 7, TX-7	
	n = 9, TX-9	
	n = 15, TX-15	
Hydrochloric acid	HCl	pH regulator
Sodium hydroxide	NaOH	pH regulator

2.2. Flotation Experiments

Micro-flotation tests were conducted employing a flotation machine (Jilin Exploring Machinery Plant, Jilin, China) of 40 mL volume, and the impeller speed was fixed at 1650 rpm. For each test, 2 g samples and 30 mL distilled water were placed into the flotation cell and stirred 1 min. The pH value of the mineral suspension was adjusted to a desired value and stirred 2 min. Then the collector was added with the conditioning time of 3 min, and the flotation was performed for 4 min. The floated and unfloated fraction were separately dried and weighed for calculating the recovery. The error of flotation recovery is ±2%.

2.3. Zeta Potential Measurement

The zeta potential of scheelite less than 2 μm were measured by a zeta potential analyzer (Malvern Zetasizer Nano ZEN36900, Malvern, UK). In each experiment, a 0.03 g sample was placed in a 50 mL beaker with 30 mL distilled water, and the mineral suspensions were conditioned with collectors at different pH values. An average zeta potential value of three individual measurements was recorded. The repeated tests showed a measurement error of ±1 mV.

2.4. Adsorption Determination

After preparing the testing samples according to flotation conditions, the mineral suspensions were centrifuged at 9000 r/min for 15 min and the supernatant was piped out for the determination of sodium oleate concentration using copper acetate colorimetric method in a UV spectrophotometer (UV-2600, SHIMADZU Co., Ltd., Kyoto, Japan) at 715 nm. The amount of sodium oleate absorbed on scheelite surface was calculated from the initial and residual concentrations of sodium oleate.

3. Results and Discussion

3.1. Flotation Performance of Scheelite

The ratio of octaphenyl polyoxyethyiene (TX) is defined as the mass fraction of sodium oleate concentration, and the pulp temperature is controlled in the range of 9–11 °C.

3.1.1. Effect of TX Ratio

Figure 1 presents the effect of TX ratio on flotation behavior of scheelite at a constant sodium oleate concentration of 60 mg/L and pH 10. It is clearly shown that the scheelite recovery is improved in the presence of TX. The recovery of scheelite gradually increases when TX ratio increases to 15–20%. After that, the recovery of scheelite appears a decreasing trend as the ratio rises. In addition, the EO number in TX molecule has a significant influence on the synergistic effect of TX, with the increase of EO number, the required TX ratio and the maximum recovery of scheelite increase, and the highest recovery of 80% is obtained in the presence of 20% TX-15.

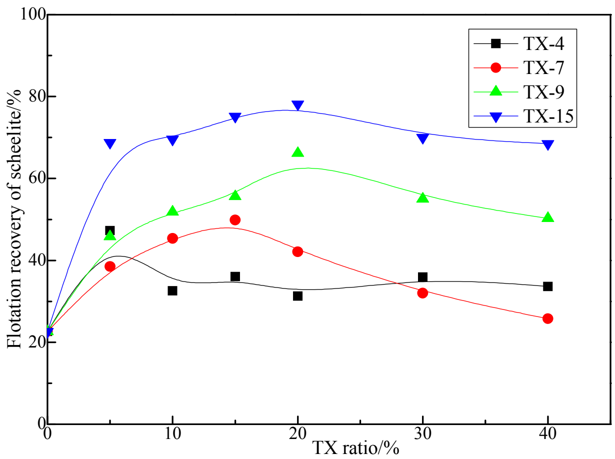

Figure 1. Effect of TX ratio on flotation behavior of scheelite with sodium oleate.

3.1.2. Effect of pH

Flotation performance of scheelite as a function of pH using sodium oleate as the collector in the absence and presence of TX is shown in Figure 2. When sodium oleate is used as the collector, scheelite shows poor floatability, although the flotation recovery increases gradually with the increase of pH value, the recovery of scheelite is only 22% at pH 10. In the mixed collector system, the recovery of scheelite shows an increase in a wide pH range of 4–11, and then decreases. Compared with sodium oleate alone, the recovery of scheelite is significantly improved in the presence of TX. As the EO number rises, the pH range for scheelite flotation is getting to broaden, and the scheelite recovery greatly increases. Similarly, the recovery of scheelite increases in the order of TX-4 < TX-7 < TX-9 < TX-15.

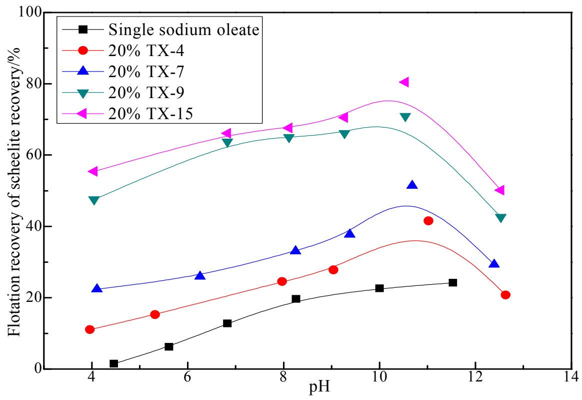

Figure 2. Effect of pH on flotation behavior of scheelite in the single or mixed collector system.

3.1.3. Effect of Collector Concentration

Figure 3 shows the effect of collector concentration on floatability of scheelite at pH 10, and the TX ratio is 20%. It is observed that the recovery of scheelite presents different trends in the single and mixed collector systems. In present of sodium oleate, scheelite recovery increases gradually with the increase of concentration, and a recovery of 80% is obtained at a concentration of 120 mg/L. For the mixed collectors, when sodium oleate concentration is lower than 60 mg/L, the flotation recovery of scheelite gradually increases, but further increases cause a decrease of scheelite recovery. Compared with sodium oleate alone, the mixed sodium oleate/TX-15 collector can attain considerable scheelite recovery (76%) with a much lower concentration of 60 mg/L. However, although the addition of TX-4, TX-7, and TX-9 can enhance scheelite flotation in low concentration range, the highest recovery of scheelite is far beyond the reach of sodium oleate system.

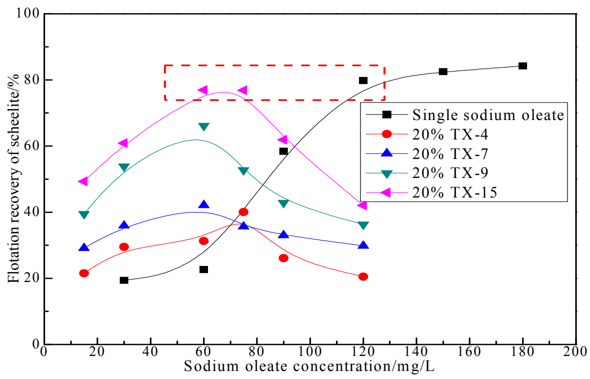

Figure 3. Effect of collector concentration on flotation behavior of scheelite in the single or mixed collector system.

In conclusion, scheelite exhibits a poor floatability using sodium oleate as the collector at a low temperature of 10 °C, and the presence of a non-ionic surfactant TX can improve the recovery of scheelite. The synergistic effect of TX is closely related to the structure (EO number). With the increase of the EO number, the pH range for scheelite flotation becomes wider, and the recovery of scheelite increases. The addition of TX-15 can decrease the concentration of sodium oleate to obtain a considerable scheelite recovery of 80%, truly realizing the improvement of scheelite flotation at a low temperature.

3.2. Relationship between TX Structure and Its Synergistic Effect

From the above results, it can be seen that the synergistic effect of every TX surfactant on scheelite flotation follows the same change principle with the increase of TX ratio, pH value, and sodium oleate concentration. As the EO number in TX molecule increases, the synergistic effect increases, and the flotation recovery of scheelite increases in the order of TX-4 < TX-7 < TX-9 < TX-15. Therefore, the synergistic effect of TX surfactant is closely related to its structure.

For molecular structure, the four surfactants have the same lipophilic group ($C_8H_{17}C_6H_4$–) and different hydrophilic groups (–$O(C_2H_4O)_nH$), so the hydrophile-lipophile balance number (*HLB* value) can be used to characterize the relative strengths of the four surfactants. The *HLB* values of polyethylene glycol and other molecular type surfactants can be calculated according to the following formula [20]

$$HLB = 20\left(\frac{H}{H+L}\right)$$

where H is the total relative atomic mass of hydrophilic group, L is the total relative atomic mass of lipophilic group. The HLB values of TX-4, TX-7, TX-9, and TX-15 are 10.10, 12.65, 13.72, and 15.64, respectively, which increases with the increase of EO number. Therefore, it can be indicated that the hydrophilicity and solubilization are in descending order of TX-4 < TX-7 < TX-9 < TX-15, and the dissolution and dispersion ability of sodium oleate at low temperatures can be greatly improved in the presence of TX-15, thus enhancing scheelite flotation.

3.3. Zeta Potential of Scheelite

Figure 4 presents the effect of pH on zeta potential of scheelite using 60 mg/L NaOL as the collector in the absence and presence of TX at different pH values. The results show that the scheelite surface is negatively charged in the whole experimental pH range, and the zeta potential of scheelite decreases as the pH value rises, which agrees well with previous research [21]. After reacting with sodium oleate, the zeta potential of scheelite shifts to more negative value, and this is because the chemical adsorption of oleate ions on the scheelite surface and bulk precipitation of calcium oleate occur on scheelite surface [22,23]. Compared with sodium oleate alone, a larger reduced value of zeta potential is seen in the presence of the mixed collectors. Since the four nonionic surfactants (TX-4, TX-7, TX-9, TX-15) are in the state of molecules or micelles in aqueous solution, it is suggested that more sodium oleate adsorbs on scheelite surface using the mixed collector, thereby the floatability of scheelite increases. Moreover, the zeta potential of scheelite increases in the order of TX-4 < TX-7 < TX-9 < TX-15, indicating increased adsorption of sodium oleate on scheelite surface increases in the same order.

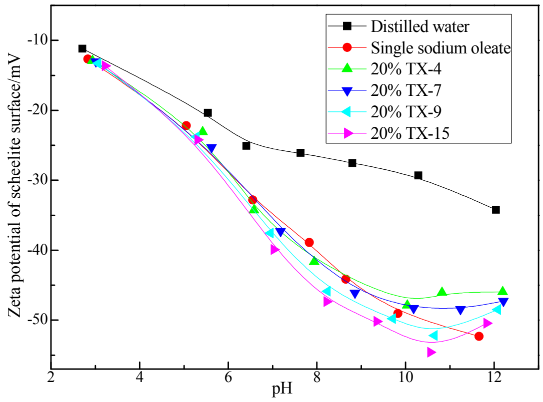

Figure 4. Effect of pH on zeta potential of scheelite surface.

3.4. Adsorption of Sodium Oleate

The different flotation behaviors at different pH values can be explained by the variation of collector adsorption on mineral surface. Figure 5 shows the effect of pH on the adsorption of sodium oleate in the single or mixed collector system at a constant NaOL concentration of 60 mg/L. It is seen that the adsorption of sodium oleate gradually increases with the increase of pH value. Compared with sodium oleate alone, in the presence of the mixed collector, the adsorption of sodium oleate on the scheelite surface is enhanced for a constant sodium oleate concentration. In addition, the adsorption of sodium oleate on scheelite surface increases in the order of single sodium oleate < TX-4 < TX-7 < TX-9 < TX-15, which is consistent with flotation and zeta potential results.

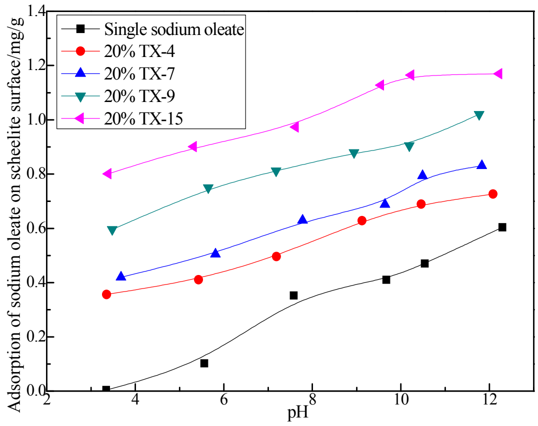

Figure 5. Effect of pH on adsorption of sodium oleate in the absence and presence of TX surfactants.

Based on the species distribution diagram of sodium oleate at a concentration of 60 mg/L and normal temperature, the anionic species $RCOO^-$ and $(RCOO)_2^{2-}$ dominate in aqueous solution at pH 10, meanwhile, a small number of anionic species of $RCOOH \cdot RCOO^-$ and neutral species of $RCOOH_{(aq)}$ are also present [24]. From zeta potential results, the scheelite surface is negatively charged at pH 10, so the adsorption of sodium oleate on scheelite could occur mainly by chemical adsorption between Ca^{2+} and anionic ions of oleate. At low temperatures, the dissolution and dispersion ability of fatty acids decreases, resulting in the reduction of effective concentration of oleate ions in the pulp, so the flotation recovery of scheelite decreases at low temperatures. However, in the mixed sodium oleate/TX-15 solutions, the interaction between sodium oleate and TX-15 can improve the surface activity of sodium oleate, which is effectively demonstrated through surface tension measurement shown in Figure 6. It is suggested that the critical micelle concentration (CMC) of the single and mixed surfactant solution is about 60 and 48 mg/L, respectively, that is, a lower CMC value is obtained in the presence of TX-15, indicating a synergistic effect for the mixed micelle formation [25]. Therefore, the effective concentration of oleate ions in the pulp is increased in the mixed collector system for a constant sodium oleate concentration. In addition, the electrostatic repulsions between the ionic headgroups of sodium oleate can be screened by the co-adsorption of TX on scheelite surface, which is helpful for the tighter adsorption of sodium oleate on scheelite surface, thus enhancing the hydrophobicity and floatability of scheelite.

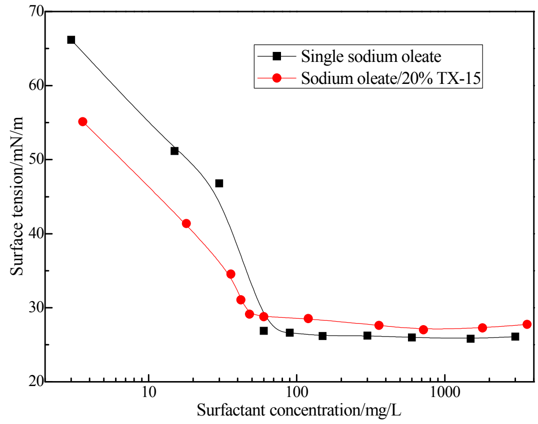

Figure 6. Surface tension of the single and mixed surfactants.

4. Conclusions

In this study, a kind of nonionic surfactant—octaphenyl polyoxyethyiene (TX)—was used as a synergist to improve the low temperature flotation of scheelite using sodium oleate as the collector at a low temperature of 10 °C. Flotation results show that the presence of TX surfactants can enhance scheelite flotation in the low concentration range of sodium oleate, and the synergistic effect increases with the increase of the EO number in the molecular structure. Compared with sodium oleate alone, the mixed sodium oleate/TX-15 collector can obtain considerable scheelite recovery at a much lower concentration of 60 mg/L, making it a superior collector for scheelite flotation. Zeta potential and adsorption measurement show that the addition of the mixed collector causes a larger reduced value of zeta potential, and increases the adsorption of sodium oleate on the scheelite surface. In addition, the CMC value of the mixed sodium oleate/TX-15 surfactant is lower than that of single sodium oleate, indicating a higher surface property and further confirming its synergistic effect on scheelite flotation.

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Author Contributions: Yuehua Hu, Wei Sun, and Wenqing Qin provided the research ideas and guidance, as well as all the required materials used in this study, Chen Chen and Hailing Zhu conducted the experiments and wrote this paper, Runqing Liu was responsible for coordinating the experiments and revised the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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