

## Article

# Effect of Calcium Ion on the Flotation of Fluorite and Calcite Using Sodium Oleate as Collector and Tannic Acid as Depressant

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**Abstract:** In the flotation of semi-soluble minerals such as calcite and fluorite,  $\text{Ca}^{2+}$  is one of the common dissolved components influencing the collector adsorption behaviors on the mineral surfaces. However, there is very limited research focusing on how the dissolved  $\text{Ca}^{2+}$  affects the separation of fluorite and calcite. In the study, with sodium oleate (NaOL) as a collector and tannic acid (TA) as a depressant, a flotation test, zeta potential measurement, and adsorption experiment in the presence of  $\text{Ca}^{2+}$  were conducted. Flotation tests indicated that in the presence of  $\text{Ca}^{2+}$ , fluorite and calcite were both significantly depressed by TA, leading to difficulty in the separation of the two minerals. It was also found that the depression effect on fluorite flotation was minimized with a high concentration of NaOL. Zeta potential measurement and the adsorption experiment results are consistent with the flotation results, revealing that it is only in the low concentration of NaOL that the flotation of fluorite was depressed by TA in the presence of  $\text{Ca}^{2+}$ . Specifically, in the low concentration of NaOL, TA adsorbed on the fluorite surface and depressed the flotation of fluorite due to the preferential interaction between NaOL and  $\text{Ca}^{2+}$  in the solution leading to a shortage in the effective NaOL in the solution. In the high concentration of NaOL, the adsorbed TA on the fluorite surface was displaced by the excessive NaOL in the solution; hence, the flotation of fluorite was recovered. In contrast, TA always hinders the interaction of NaOL with calcite regardless of the presence and absence of  $\text{Ca}^{2+}$  and NaOL, hence, depressing the flotation of calcite. The study presented that a high concentration of NaOL may mitigate the negative effect of  $\text{Ca}^{2+}$  on the fluorite surface and improve the separation of fluorite from calcite.

**Keywords:** calcium ion; fluorite; adsorption mechanism; tannic acid

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## 1. Introduction

Fluorite ( $\text{CaF}_2$ ) is an important strategic mineral that is used primarily for the production of hydrofluoric acid and as a flux agent in steel making [1]. In practice, calcite is one of the common gangue minerals in fluorite ore [2]. Froth flotation has been considered one of the most effective ways to separate fluorite from calcite. Fatty acids and their salts, such as sodium oleate (NaOL), were usually realized as collectors for fluorite and calcite flotation [3–5]. A comprehensive review of the interaction of NaOL onto the fluorite and calcite was reported as chemisorption, followed by the formation of hydrophobic aggregates and surface precipitation of calcium carboxylate from bulk solution [6–8]. In addition, the interaction of NaOL on fluorite and calcite surface is recognized mainly through chemisorption and physical adsorption, respectively [9]. Due to the similar surface properties and chemical reactivity with reagents [10], the separation of fluorite and calcite is relatively difficult, and a selectively depressant is considered the key to their separation.

Many calcite depressants were identified by researchers for the separation of fluorite and calcite, including inorganic and organic [11]. Due to the limit, pH application range, and the dewatering problem of the inorganic depressants, the organic depressants, such as tannic acid [1], psyllium seed gum [12], and sulfonated lignite [13], can selectively adsorb with  $\text{Ca}^{2+}$  on the calcite surface, have become an important direction in studying the separation of fluorite and calcite. Tannic Acid (TA) is one of the most widely used organic reagents for the depression of calcareous and siliceous ores in industry. In the case of calcite flotation, Castro et al. [11] demonstrated that the effect of quebracho, a tannic acid extract is more effective on calcite than on celestite. Yuehua Hu et al. [1] identified the selective adsorption of TA on calcite via  $\text{Ca}^{2+}$  and  $\text{Ca}(\text{OH})^+$  components on the mineral surface and depressed calcite in the fluorite flotation using NaOL as a collector. However, the results of a bench-scale flotation test for a fluorite ore flotation from Hunan, Chenzhou, were not good enough without hydrochloric acid adjustment using NaOL as collector and TA as depressant [14]. Considering the species, especially calcium ion dissolved from calcium-bearing minerals, is inevitable during a long flotation processing, the floatability of fluorite and calcite may be different in a high  $\text{Ca}^{2+}$  content flotation slurry [15–17].

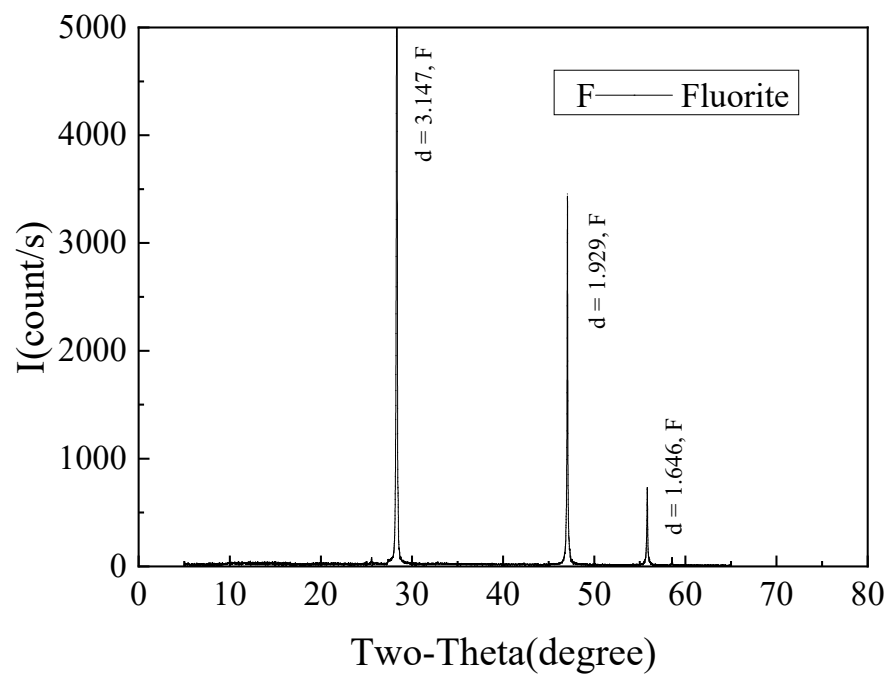
It is documented that the interaction between the collector and  $\text{Ca}^{2+}$  in bulk solution dominated the collector adsorption mechanism at these mineral surfaces [18]. For example, Yijun Cao et al. [15] noted that both scheelite and fluorite were depressed strongly by sodium silicate in the presence of calcium. Many researchers also indicated that the  $\text{Ca}^{2+}$  adsorbed on mineral surface or suspended in solution would also consume the flotation reagent by precipitating into calcium salts, which would significantly reduce the flotation recovery of scheelite [8,19,20]. These investigations provided valuable information for the current study. However, in the fluorite and calcite flotation system, the adsorption mechanisms of NaOL and TA on the mineral surface in the presence of  $\text{Ca}^{2+}$  have not been reported. It was still hard to realize the separation of fluorite from calcite in the presence of  $\text{Ca}^{2+}$  when using TA as a depressant. Therefore, flotation tests, zeta potential measurements, and adsorption experiments were employed to elucidate the effect of calcium ions on the fluorite and calcite flotation and the adsorption mechanism of NaOL and TA in this study.

## 2. Materials and Methods

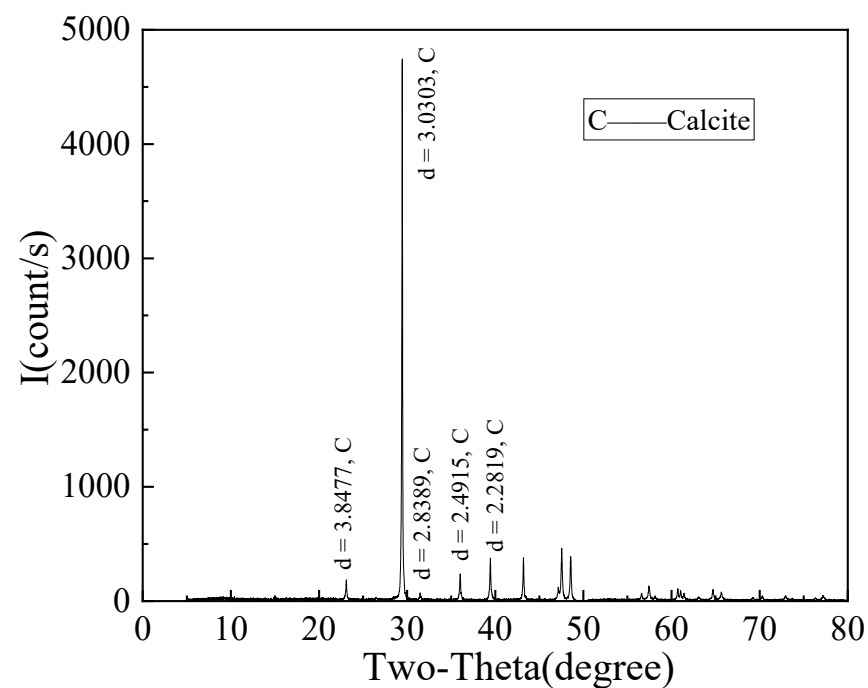
### 2.1. Materials and Reagents

Pure fluorite and calcite samples (each 5 kg) were obtained through hand picking from the faces of a fluorite mine in Guangxi, China. X-ray diffraction analyses were carried out on D8 Advance Bruker (Bruker Co., Berlin, German) with  $\text{Cu K}\alpha$  radiation. The XRD results revealed that the purity of fluorite and calcite is greater than 95%, as shown in Figures 1 and 2. The samples were crushed with a hammer, ground in a laboratory porcelain mill, and then screened to collect  $-74 + 44 \mu\text{m}$  particle size fractions for flotation tests and adsorption experiments. Samples further ground to  $-5 \mu\text{m}$  in an agate mortar were used for zeta potential measurements.

Chemically pure reagents were obtained from the following sources: Sodium oleate (NaOL) and tannic acid (TA) collected from Aladdin Biological Technology Ltd. (Shanghai, China) were used as a collector and a depressant, respectively.  $\text{CaCl}_2$  collected from Baisaiqin Chemical Technology Co., Ltd. (Shanghai, China) was used to adjust the ions concentration in the solution. The pH was adjusted with NaOH or HCl stock solutions. Deionized water was used for all experiments.



**Figure 1.** XRD spectra of fluorite samples used for flotation tests.



**Figure 2.** XRD spectra of calcite samples used for flotation tests.

## 2.2. Flotation Tests

Flotation was performed in a 150 mL mechanical flotation cell at 1400 rpm with an airflow rate of 0.125 L/min. Fluorite or calcite single mineral (5 g) was combined with 120 mL DI water and mixed for 1 min. NaOH solution was then added to adjust pH 9.0, at which fluorite and calcite may be floated with sodium oleate. This pH was maintained throughout the flotation process. The depressant (TA) was added and conditioned over 2 min after the pH adjustment. Then the collector (NaOL) was added, and the suspension was agitated for further 2 min; the froth collection was performed for 8 min finally. When  $\text{CaCl}_2$  was used, it was added prior to the pH adjustment and conditioned for 2 min.

For individual mineral flotation, both the floated and unfloated particles were collected, dried, and weighed to calculate the flotation recovery. Repeat tests were carried out for each flotation 3 times, and the average results are reported as the final values.

### 2.3. Zeta Potential Measurements

The zeta potential of fluorite and calcite were measured at 25 °C using ZetaPlus Zeta Potential Analyzer (Brookhaven Instruments, Austin, TX, USA). All mineral samples were ground to  $-5\ \mu\text{m}$  by an agate mortar. A total of 20 mg ground sample combined with 50 mL DI water was stirred for 2 min. Then the given pH and reagents concentration was added to the solution in the same order in the flotation test. After allowing the suspension to stir and settle, the zeta potential measurement was performed after transferring the supernatant liquor into a Tiselius cell in a ZetaPlus Unit. For each zeta potential measurement, three tests were repeated, and the average zeta potential was reported.

### 2.4. Adsorption Experiments

In this study, total organic carbon (TOC) measurement was introduced to evaluate the NaOL concentration before and after the adsorption in the solution. The adsorption experiment of minerals without TA treatment was conducted as follows: Fluorite or calcite sample (1 g) was added to 50 mL DI water at pH 9.0 in a beaker and agitated for 5 min by a magnetic stirrer. Then NaOL solution of a known concentration was added and conditioned for further 15 min. The solid particles were separated by centrifugation for 30 min at 3000 r/min. The concentration of reagents in the supernatant was measured using Elementar liquid TOCII (Elementar Co., Hesse, Germany).

The adsorption experiment of minerals treated with TA was conducted as follows: Fluorite or calcite (1 g) was placed in a beaker and dispersed in 50 mg/L TA solution at pH 9.0 for 30 min. Then, the TA-treated fluorite and calcite samples were obtained after filtering and drying at room temperature. Next, those samples with various amounts of NaOL were added to the DI water or 15 mg/L  $\text{CaCl}_2$  solution, and the suspension was agitated for further 15 min. All other conditions were the same as those in the adsorption experiment above. The adsorbed amount of collector was then calculated from the difference between the initial (known) concentration and the equilibrium (measured) concentration.

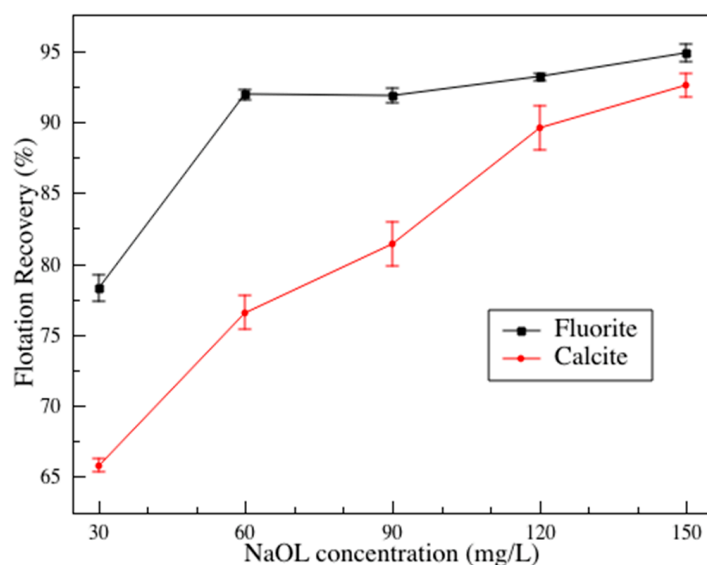
1 g fluorite or calcite in 50 mL DI water at pH 9.0 was used as a blank sample. NaOL dissolved in DI water at pH 9.0 was used to establish the calibration curve. Each adsorption test was repeated three times, and the average was reported in this study.

## 3. Results and Discussion

### 3.1. Microflotation Tests

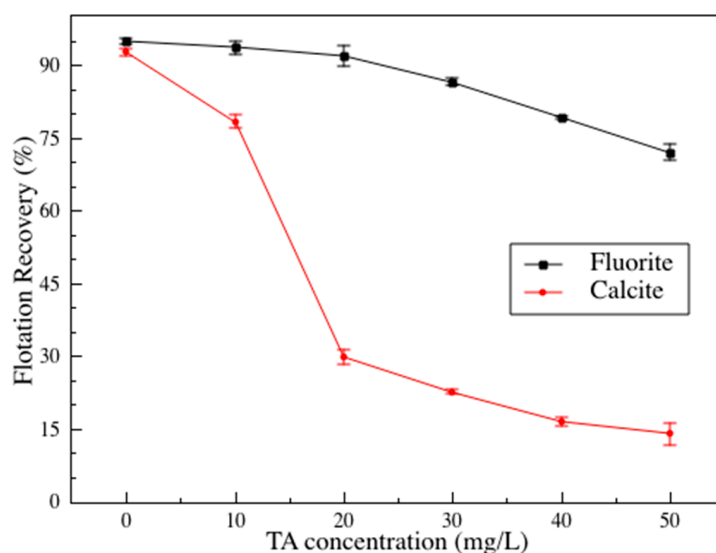
#### 3.1.1. Effect of the NaOL and TA Concentration on the Fluorite and Calcite Flotation

The flotation behavior of fluorite and calcite with various NaOL concentrations at pH 9 is given in Figure 3. The flotation recovery of the two minerals increased gradually with increasing the concentration of NaOL. In the absence of TA, fluorite and calcite exhibited good flotation behavior with 94.8% and 92.6% recovery, respectively, at 150 mg/L NaOL. In addition, the flotation recovery of fluorite was much higher than calcite when the NaOL concentration was below 90 mg/L, and the gap between these two minerals decreases as the NaOL concentration increases. There is no significant difference in flotation recovery between fluorite and calcite at high NaOL concentrations. The results reveal that NaOL has a good adsorption effect on both minerals in alkaline solution [10]. Further, the flotation of fluorite can be achieved at low NaOL concentration due to the stronger chemisorption and the monolayer coverage between  $\text{RCOO}^-$  and  $\text{Ca}^{2+}$  on the fluorite surface [5,21]. At a higher concentration of NaOL, the physical adsorption of calcium oleate colloids may play a significant role in calcite flotation [22].



**Figure 3.** Effect of NaOL concentration on the flotation recovery of fluorite and calcite.

Figure 4 shows the flotation recovery of fluorite and calcite with 150 mg/L NaOL as a function of TA concentrations at pH 9. In the presence of TA, calcite recovery decreased dramatically from 92.6% to 13.8%, and fluorite recovery decreased slightly from 94.8% to 72% as the TA concentration increased in the range from 0–50 mg/L, which is necessary for their separation. From the literature, TA has little effect on the chemisorption of NaOL at the fluorite surface while selectively depressing calcite via weakened the adsorption of NaOL on the calcite surface [1]. However, the separation of fluorite and calcite could be changed by the components dissolved from semi-soluble Ca-bearing minerals. Therefore, the effect of calcium ions on the flotation of two minerals was further examined in this work.

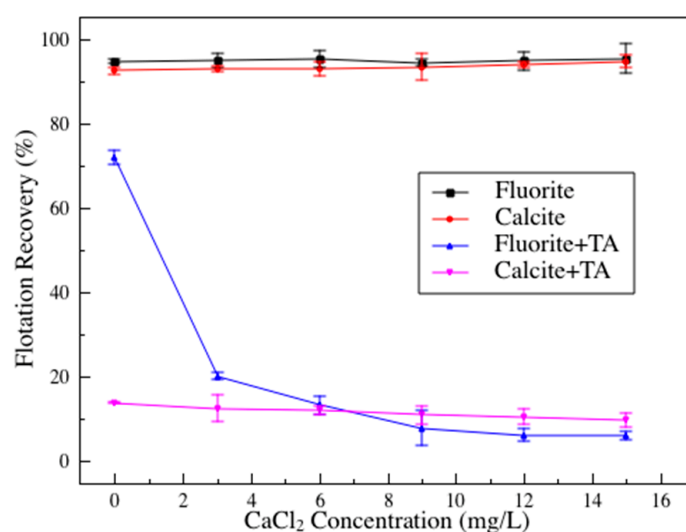


**Figure 4.** Effect of TA concentration on the flotation recovery of fluorite and calcite.

### 3.1.2. Effect of Calcium Ion on Fluorite and Calcite Flotation

Fluorite and calcite flotation were conducted in the presence and absence of 40 mg/L TA as a function of  $\text{CaCl}_2$  concentration, and the results are shown in Figure 5. The flotation recovery of the two minerals remains constant at approximately 93% without TA in the  $\text{CaCl}_2$  concentration range of 0–15 mg/L with 150 mg/L NaOL at pH 9. In the presence of TA, the flotation recovery of fluorite reduced from 72% to 16.2% when  $\text{CaCl}_2$  concentration increased from 0 to 6.0 mg/L. with a further increase in  $\text{CaCl}_2$  concentration, this decrease

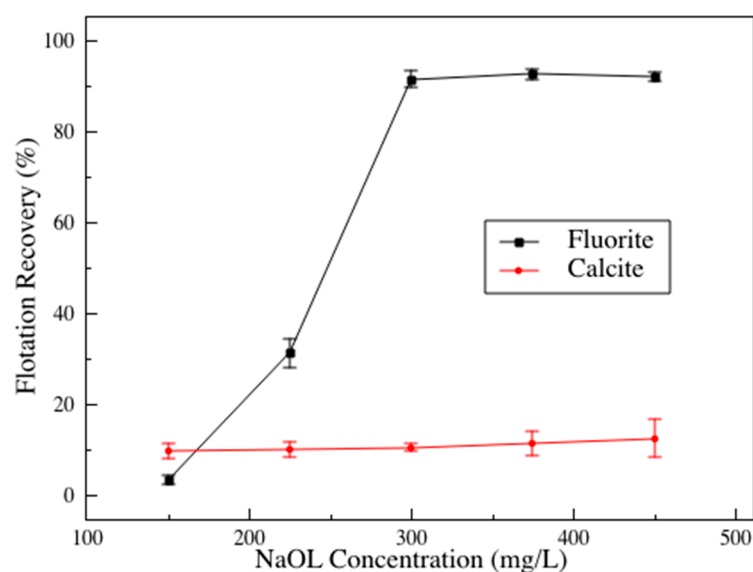
slowed down with a 3% recovery at 15 mg/L  $\text{CaCl}_2$  concentration. Meanwhile, the calcite recovery was low, and the floatability of calcite was hardly affected by adding  $\text{CaCl}_2$  in the presence of TA. Consequently, this phenomenon reveals that it is impossible to separate fluorite from calcite using NaOL as a collector and TA as a depressant in the presence of calcium ions. From this result, it is apparent that the adsorption of NaOL and TA on the fluorite surface may be different in the presence of calcium ions. In DI water, the preferential adsorption of NaOL takes place on the fluorite surface rather than TA, which may explain the limited inhibition of fluorite flotation by TA [1]. With the addition of  $\text{CaCl}_2$ , NaOL was consumed to generate calcium oleate colloids with  $\text{Ca}^{2+}$  in the solution instead of chemisorption on the fluorite surface [19,23]. The physical adsorption between calcium oleate colloids and fluorite surface maintains the floatability of fluorite without TA. However, the TA may have stronger competitive adsorption with fluorite surface than the calcium oleate colloids, and the fluorite could be depressed by TA. This is supported by the flotation test above.



**Figure 5.** Effect of  $\text{Ca}^{2+}$  concentration on the flotation of fluorite and calcite in the presence and absence of TA.

### 3.1.3. Eliminating the Negative Effect of $\text{Ca}^{2+}$ by Increasing the Dosage of NaOL

The float abilities of fluorite and calcite with massive NaOL concentration in the presence of 15 mg/L  $\text{CaCl}_2$  and 50 mg/L TA are shown in Figure 6. It is clear that the fluorite recovery was remarkably improved from approximately 3% to 91.4%, with increasing NaOL concentration from 150 mg/L to 300 mg/L. Thereafter, the recovery increased slightly. This result indicates that TA adsorbed on the fluorite surface could be replaced by the excessive NaOL after precipitating  $\text{Ca}^{2+}$  in solution due to the stronger attractive interaction of NaOL on the fluorite than that of TA [11]. In the case of calcite flotation, calcite recovery remains low with the increased NaOL concentration. This may attribute to the high-concentration  $\text{Ca}^{2+}$  produced by the addition of  $\text{CaCl}_2$  and calcite dissolution, thereby causing the formation of calcium oleate from NaOL in solution [5,24]. Thus, TA prevents the adsorption of calcium oleate on the calcite surface and inhibits calcite flotation. Based on the flotation test, it suggests that the negative effect of  $\text{Ca}^{2+}$  on fluorite flotation could be eliminated by increasing the dosage of NaOL. These findings have been applied in the fifth cleaning flotation flowsheet of a fluorite mine in Guangxi, China. The total consumption of NaOL increased by 7%, approximately, and the flotation recovery of fluorite has improved by nearly 5%, which shows good economic benefits and industrial application value. The interaction of TA and NaOL on the mineral surfaces in the presence and absence of  $\text{Ca}^{2+}$  was investigated in the following section.



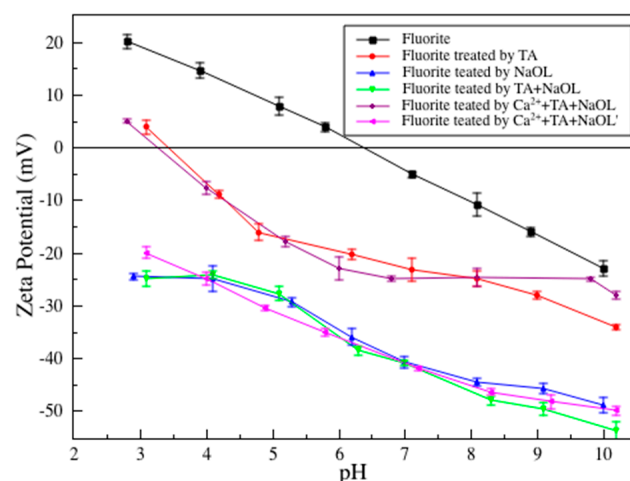
**Figure 6.** Effect of NaOL concentration on the flotation of fluorite and calcite in the presence of  $\text{Ca}^{2+}$  and TA.

### 3.2. Zeta Potential Measurements

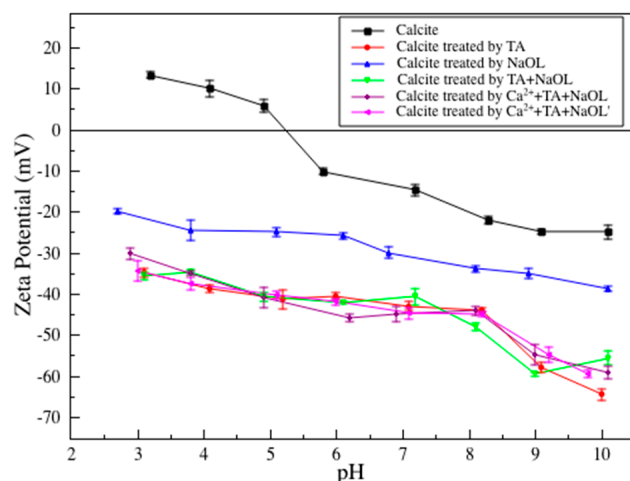
In order to understand the adsorption mechanism of NaOL and TA on the mineral surfaces in the presence of  $\text{Ca}^{2+}$ , the zeta potential was measured, and the results are shown in Figures 7 and 8. Figure 7 shows the zeta potential of fluorite treated and not treated with TA and NaOL as a function of pH in the absence and presence of  $\text{Ca}^{2+}$ . As can be seen, the isoelectric point of fluorite without any reagents is around pH 6.5, which is close to the reported values in previous studies [25]. The zeta potential of fluorite towards the negative values in the presence of NaOL or TA. The reduced values of NaOL are much larger than that of TA, demonstrating that strong adsorption of NaOL occurs on the fluorite surface. Moreover, a similar zeta potential decrease was observed for fluorite treated with TA followed by NaOL or just NaOL, so it is indicated that the adsorption of NaOL on fluorite surfaces cannot be prevented by TA. This is consistent with the flotation test of fluorite above. When calcium ion was added, the zeta potential of fluorite was close to that with TA alone, suggesting that TA played a dominant role on the fluorite surface under the condition of 15 mg/L  $\text{CaCl}_2$  and 150 mg/L NaOL. After increasing the concentration of NaOL to 300 mg/L, the decrease in Zeta potential of fluorite occurred, and the values trended the same with the NaOL alone in the range of pH from 3–10, illustrating that TA is possible desorbed and replaced by excess NaOL from the fluorite surface due to strong chemical adsorption between  $\text{RCOO}^-$  and  $\text{Ca}^{2+}$  on the fluorite surface [16]. The results are correlated well with the fluorite flotation, suggesting that the effect of  $\text{Ca}^{2+}$  on fluorite flotation can be mitigated using a massive NaOL collector.

Figure 8 shows the modification of zeta potential on calcite treated with different reagents as the function of pH. Obviously, calcite becomes highly negatively charged in the presence of reagents. Moreover, a larger negative shift of the zeta potential values of calcite was observed with TA than with just NaOL, indicating that the selective adsorption of TA was generated on the calcite surface. When TA was added prior to NaOL, the zeta potential of calcite was close to that of TA alone, which means the depressant TA can also adsorb on the calcite surface in the presence of NaOL. This result is in accordance with Yuehua Hu [1]. With the addition of  $\text{Ca}^{2+}$ , the zeta potential of calcite remains at the negative values, which is similar to the TA alone. In addition, no evident change was observed in the zeta potential of calcite with 150 mg/L NaOL or 300 mg/L NaOL. This result demonstrates that some preferential adsorption sites for TA always exist on the calcite surface.





**Figure 7.** Effect of the addition of different reagents on the zeta potentials of fluorite (TA = 50 mg/L, NaOL = 150 mg/L, NaOL' = 300 mg/L, CaCl<sub>2</sub> = 16 mg/L).



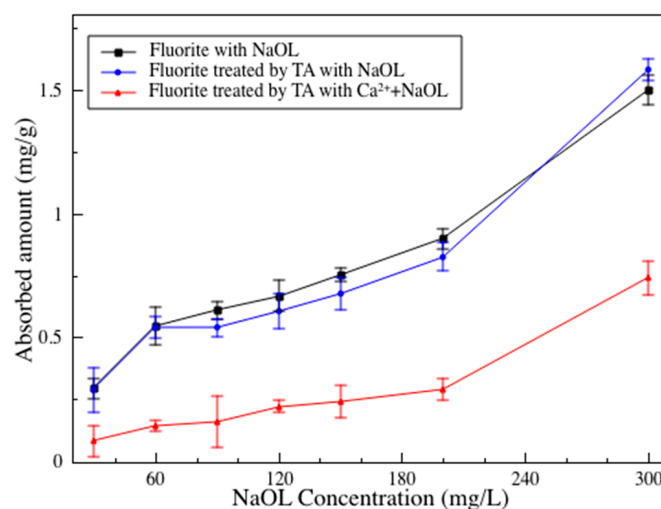
**Figure 8.** Effect of the addition of different reagents on the zeta potentials of Calcite (TA = 50 mg/L, NaOL = 150 mg/L, NaOL' = 300 mg/L, CaCl<sub>2</sub> = 16 mg/L).

### 3.3. Adsorption Mechanism Study

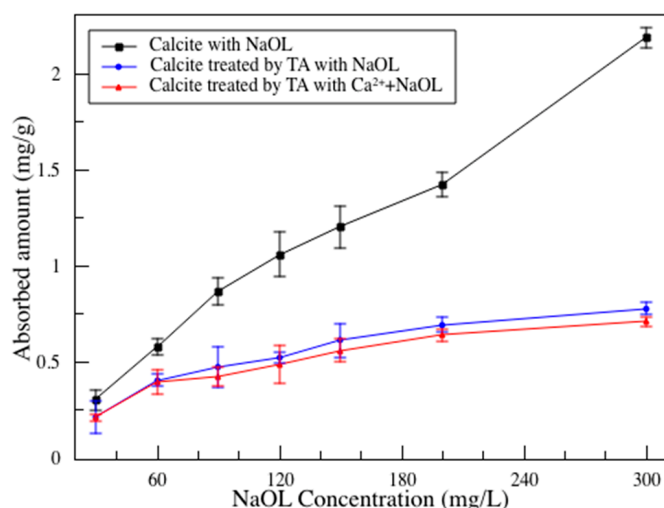
The adsorption of NaOL on the fluorite and calcite under different conditions is shown in Figures 9 and 10. Figure 9 shows the adsorption isotherms of NaOL on fluorite treated or not treated with TA in the absence and presence of Ca<sup>2+</sup>. As can be seen, the adsorbed amount of NaOL on the fluorite surface increased gradually with its initial concentrations increased. In the absence of Ca<sup>2+</sup>, the fluorite surface could be effectively coated with NaOL species. In addition, only a small decrease in NaOL adsorption was found on the fluorite surface with TA treatment, which demonstrates that the stronger chemisorption of NaOL was bonded with the calcium site at the fluorite surface rather than TA. In the presence of Ca<sup>2+</sup>, a reduction in NaOL adsorption amount on the TA-treated fluorite surface was observed with the NaOL concentration below 150 mg/L, while the gradually increasing trend occurred in the range of NaOL concentration from 200 mg/L to 300 mg/L. It is documented that the calcium ion dominates the surfactant adsorption mechanism at the Ca-bearing mineral surface [16]. In this study, the addition of Ca<sup>2+</sup> interacts with the NaOL by forming calcium oleate through carboxylate reactions in the bulk solution, which change the NaOL adsorption mechanism from the chemisorption to the precipitation of calcium oleate collides on the fluorite surface [20]. TA can prevent this physical adsorption of calcium oleate and depress the fluorite with the NaOL concentration below 150 mg/L. With the increase in NaOL concentration, the excess NaOL reabsorb on the fluorite surface after



consuming the  $\text{Ca}^{2+}$  in the solution and then improves the fluorite flotation. This result is consistent with the flotation test shown in Figure 6.



**Figure 9.** Adsorption isotherms of NaOL on fluorite treated or not treated with TA in the absence and presence of  $\text{Ca}^{2+}$ .



**Figure 10.** Adsorption isotherms of NaOL on calcite treated or not treated with TA in the absence and presence of  $\text{Ca}^{2+}$ .

The adsorption isotherms of NaOL on calcite treated or not treated with TA in the absence and presence of  $\text{Ca}^{2+}$  are given in Figure 10. The trend observed for the adsorption of NaOL on calcite was similar to this for fluorite without TA and  $\text{Ca}^{2+}$ , as the amount of NaOL adsorbed on calcite was enhanced by increasing their initial concentration. The relatively high NaOL adsorption on the calcite surface may be related to the high concentration of  $\text{Ca}^{2+}$  dissolved from calcite, thereby causing the physical adsorption of calcium oleate colloids and achieving calcite flotation [24]. Nevertheless, the amount of NaOL adsorbed on the calcite surface after TA treatment was much less in the presence or absence of  $\text{Ca}^{2+}$  even at the high NaOL concentration, suggesting TA cannot be desorbed from the calcite surface. Therefore, the separation of fluorite from calcite could be achieved under the condition of high NaOL concentration using TA as a depressant.

#### 4. Conclusions

In this study, calcium ion has been shown to exhibit a significant impact on fluorite recovery. Flotation experiments illustrate that fluorite and calcite exhibit good floatability

with NaOL. TA is an effective depressant for calcite but exerts little influence on fluorite flotation in deionized water. With the addition of  $\text{Ca}^{2+}$ , fluorite flotation recovery decreased dramatically in the presence of TA. Then, the fluorite flotation can also be recovered by increasing the NaOL concentration. Adsorption tests and zeta potential results consistently showed that TA has little effect on the chemisorption of NaOL on the fluorite surface. However, the adsorption of NaOL on the fluorite surface was strongly weakened in the presence of  $\text{Ca}^{2+}$  and TA at the same time, which caused the problem of the separation of fluorite from calcite. This negative effect of  $\text{Ca}^{2+}$  can be removed by raising the NaOL concentration, suggesting that excessive NaOL can reabsorb on the fluorite surface and then improve its flotation. On the other side, TA always occupies the site of the calcite surface and depresses the calcite flotation in this study, which provides a possibility of separating fluorite from calcite in a calcium species contained solution using high NaOL concentration as a collector and TA as a depressant. These findings also emphasize that it is necessary to consider the inhibition effects and selective adsorption mechanisms of dissolved components from semi-soluble minerals on the mineral surfaces.

**Author Contributions:** Formal analysis, Y.Q.; investigation, X.Q. and B.C.; methodology, Y.H.; resources, T.S. and Z.W.; writing-original draft, Y.Q.; writing-review and editing, Y.H. and Y.Q.; project administration, Y.Q. and T.S. All authors have read and agreed to the published version of the manuscript.

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