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Study on the Effect of Fe^{3+} on Zircon Flotation Separation from Cassiterite Using Sodium Oleate as Collector

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Abstract: The effect of ferric ions (Fe^{3+}) on the flotation of zircon and cassiterite using sodium oleate (NaOL) was investigated by single mineral flotation tests, adsorption density tests, zeta potential measurements, solution chemistry analyses, and FTIR analyses. It is difficult for zircon to be separated from cassiterite by using NaOL alone. Nevertheless, the flotation of zircon was activated while that of cassiterite was depressed in the presence of Fe^{3+}. Adsorption density tests indicated that the addition of Fe^{3+} enhanced the adsorption of NaOL on zircon surfaces, whereas it receded on cassiterite surfaces. Zeta potential measurements and solution chemistry analyses found that $H(OL)_2^-$ was the predominant species to determine the flotation behaviors of zircon and cassiterite. Furthermore, the addition of Fe^{3+} at pH < 8 reduced the negative charges on the zircon and cassiterite surfaces. It was confirmed that the positive charges of zircon were caused by the positively charged species of Fe^{3+}, including Fe^{3+}, $Fe(OH)^{2+}$, and $Fe(OH)_2^+$. Meanwhile, these results revealed that the hydroxy complex and the precipitate of $Fe(OH)_3$(s) adsorbed onto the cassiterite surfaces caused the flotation of cassiterite to be inhibited. It can be concluded from FTIR analyses that the peaks of zircon at 894.14 cm^{-1} and 611.65 cm^{-1} were strengthened and the adsorption on zircon surfaces was found to be chemisorption due to the addition of Fe^{3+}, whereas both chemical and physical adsorptions of NaOL on cassiterite surfaces were weakened, resulting in the different flotation behaviors of zircon and cassiterite in the presence of Fe^{3+}.

Keywords: ferric ions; zircon; cassiterite; flotation; sodium oleate

1. Introduction

Zircon ($ZrSiO_4$), which is the most important zirconium-containing mineral on earth, has direct applications in the cast, glass, ceramic, and pigment industries because of its high melting point and steady chemical properties. And it is also used in the production of zirconium dioxide (ZrO_2) which is a highly refractory material. Zircon is known as a heavy mineral and defined as having a specific gravity greater than 3.5 [1], and it usually coexists with some heavy minerals including cassiterite, tantalum, niobium, magnetite, ilmenite, and some other minerals such as quartz, feldspar, and clay [2–5]. The enrichment of Zircon commonly occurs in pegmatite and placer deposits.

Due to the relatively high specific gravity of zircon, the beneficiation of zircon along with other heavy minerals can be achieved by means of gravity separation when the gravity property differences between zircon and other minerals are significant. It is easy for light minerals to be removed in the

first stage, and the product of zircon from the first stage then needs further processing. However, gravity separation methods will perform well only when the particle size meets the requirements [6]. Both too fine and coarse particle sizes will negatively affect the results. Hence, the fine fraction of zircon concentrate from gravity separation still contains large amounts of impurities which cannot be removed effectively. To improve the quality of products, zircon is further separated from other heavy minerals, such as magnetite, ilmenite, and cassiterite, by a series of magnetic and electrostatic separation processes. Usually, the removal of magnetite and ilmenite from zircon is easier to achieve via magnetic separation because these two minerals are magnetic. The electrostatic separation method [7] based on the different electric properties between the gangue and the valuable minerals requires clean mineral surfaces. The mineral surfaces of zircon are usually coated with some electric metal minerals which contain titanium, iron, and other materials such as clay. These contaminants make it very difficult to achieve an effective separation using electrostatic separation. According to the information mentioned above, the light minerals and magnetic minerals can be removed, and cassiterite as the main contaminant in zircon concentrate cannot be removed effectively. As a result, the fine zircon concentrate of poor quality must be purified using other beneficiation methods. Flotation is usually employed to treat this kind of mineral. Using flotation to purify zircon is certainly worth investigation for both technical and economic reasons [8].

Some researchers investigated the flotation of zircon. Zircon flotation could be achieved using fatty acids, alkyl sulfates, or cationic collectors [9]. Sodium oleate (NaOL), as a typical fatty acid surfactant, has been widely used as an effective collector of silicates and metal oxide minerals for years in industry. Meanwhile, the application of NaOL in zircon flotation was studied by Pavez and Peres in a system of monazite–rutile–zircon by using NaOL and hydroxamates [10]. Abeidu also used oleic acid to treat the flotation system of monazite–zircon [11]. Furthermore, phosphate-containing anionic collectors and even xanthates were used for the selective flotation of zircon [12]. Bulatovic and De Silvio [13] employed modified sulfosuccinamate-based mixtures as a collector, H_2SiF_6, HOOC–COOH and Na_2SiO_3 as the depressants in a strong acidic environment for the separation of zircon and tantalite–columbite from cassiterite concentrates, and good results were obtained.

Because of the association of magnetite, hematite, and ilmenite with zircon, ferric ions (Fe^{3+}) usually exist in the lattice of cassiterite [14]. The release of Fe^{3+} from these iron-bearing minerals during the separation process makes the flotation environment more complex. It was reported that the metal ions in silicates had a significant effect on the flotation separation [15,16]. Fe^{3+} effectively activated the flotation of silicates including spodumene, albite, and quartz in a NaOL system [17]. However, the effect of Fe^{3+} on zircon flotation in a NaOL system is rarely reported. Hence, it is necessary to study the effect of dissolved Fe^{3+} on the flotation of zircon and cassiterite.

In this work, the effect of Fe^{3+} on the flotation of zircon and cassiterite at various concentrations and pH levels using an anionic NaOL collector was investigated. This study presents the surface chemistry profiles and flotation behaviors in terms of single mineral flotation tests, adsorption density tests, zeta potential measurements, solution chemistry analyses, and FTIR measurements.

2. Experimental

2.1. Minerals

This study was conducted with pure minerals. To ensure a better performance, the pure minerals were prepared without any addition of chemicals. High-purity, handpicked cassiterite was obtained from Kunming, Yunnan province, China. To obtain the pure zircon, a beach placer from Australia was preliminarily utilized for gravity separation, including the use of a spiral chute and a shaking table to remove the light minerals. The rough concentrate was then further enriched by high-gradient magnetic separation (1 Tesla) and electrostatic separation to remove the magnetic and the electric impurities, respectively. The purified zircon and cassiterite were ground using a porcelain mill and then wet-sieved with distilled water. The fraction with particle size of −0.053 + 0.044 mm was selected

for flotation tests, and the finer fraction (−0.044 mm) was used for FTIR analyses. A portion of this fraction (−0.044 mm) was further ground in an agate mortar and then micro-sieved to obtain particles of size less than 5 μm for zeta potential measurements.

The pure mineral samples were confirmed by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). Figure 1 shows the XRD patterns of the purified zircon (a) and cassiterite (b) samples. The diffraction peaks recorded for zircon and cassiterite matched well with the patterns of standard diffraction peaks [18]. According to the results, there were few impure peaks in Figure 1, indicating that the zircon and cassiterite were of high purity. The chemical compositions of the samples are listed in Table 1. The purity of zircon was about 92%, while that of cassiterite was above 95%, based on XRD and XRF results.
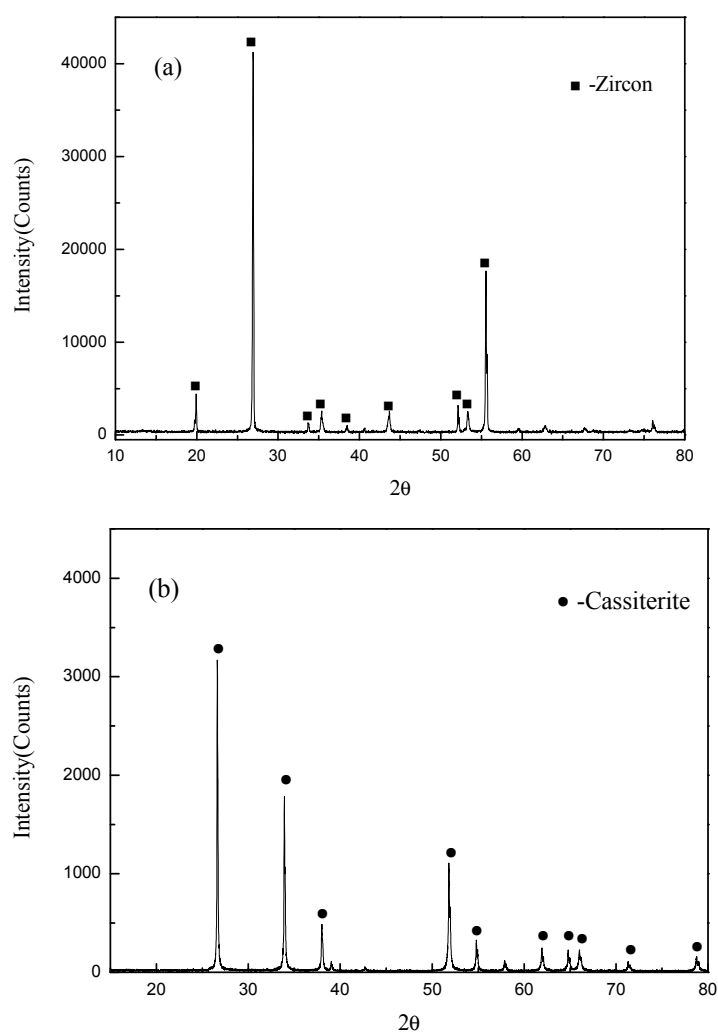

Figure 1. X-Ray diffraction (XRD) patterns of zircon (**a**) and cassiterite (**b**).

Table 1. Chemical compositions of the purified samples (mass fraction, %).

Sample	Na_2O	Al_2O_3	SiO_2	MgO	P_2O_5	Pb	K_2O	CaO
Zircon	0.109	1.206	33.341		0.098		0.153	0.146
Cassiterite		0.72	0.97	0.32		0.03		0.59
Sample	**SnO_2**	**TiO_2**	**Fe_2O_3**	**ZrO_2**	**La_2O_3**	**HfO_2**	**U_3O_8**	**ThO_2**
Zircon		0.171	0.19	61.78	0.852	1.406	0.052	0.065
Cassiterite	95.7		0.44					

2.2. Reagents

Sodium oleate (NaOL) was used as an anionic collector throughout the experiments. Freshly prepared NaOL solutions were used in all the experiments. Dilute solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of the mineral suspension. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was used as the source of Fe^{3+}. All the chemicals used in this investigation were provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and were of analytical grade. The water used throughout the experiments was distilled water.

2.3. Flotation Tests

Single mineral flotation tests were conducted using a XFG flotation machine with a volume of 50 mL, and the stirring speed was kept at 1750 r/min. The experiments were performed based on the procedure shown in Figure 2. A mineral suspension was prepared by successively adding 3.0 g selected pure mineral particles of −0.053 + 0.044 mm and 45 mL distilled water into the 50 mL flotation cell. The suspension was conditioned by stirring for 1 min without adding any chemicals. The regulators used were Fe^{3+}, HCl, and NaOH, while the collector used was NaOL. The pH of the mineral suspension was adjusted to the predetermined value by adding HCl or NaOH solutions. The differences of the pH measured before and after each flotation test were typically less than 0.2 pH units. The prepared $FeCl_3$ and NaOL solutions were added to the suspension in sequence. Each reagent was conditioned for 2 min. Flotation was performed for a total of 3 min. The floating particles and the remaining materials were separately collected, filtered, and dried in an oven at 75 °C for 2 h and then cooled in a desiccator. Finally, flotation recoveries were calculated based on the sample weights.
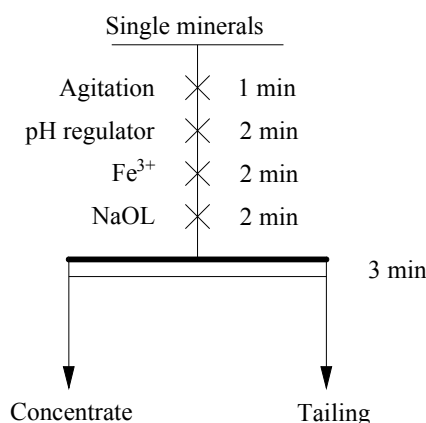

Figure 2. Flowsheet of single mineral flotation tests.

2.4. Adsorption Tests

The adsorption of NaOL on the surfaces of each mineral was evaluated by the solution depletion method, and the procedure of adsorption tests was similar to that used for the flotation tests; the concentrations of NaOL are measured before and after adsorption. The difference was assumed to be due to adsorption of NaOL onto the surface. The adsorption amount of the collector was calculated based on the following equation:

$$\Gamma = \frac{(C_0 - C) \times V}{m} \tag{1}$$

where Γ is the adsorbed amount of NaOL on the mineral surfaces in the absence and presence of Fe^{3+}; C_0 and C are the concentrations of NaOL in the pulp suspension before and after the interaction of NaOL with the mineral surfaces, respectively, for the desired time; V is the volume of the resultant solution; and m is the weight of mineral particles.

Three grams of mineral sample were added to 50 mL of aqueous solution with the desired pH and concentration of Fe^{3+} (8×10^{-5} mol/L) and NaOL (4×10^{-4} mol/L). The suspension was stirred at 25 °C for 10 min. After the adsorption, the suspension was centrifuged at 9000 rpm for 15 min, then the solution was immediately gathered to analyze the concentration of NaOL by a direct method using an UV-Visible spectrophotometer (UV-5500). To detect the characteristic peak, the absorbances of NaOL solutions with the concentration of 2×10^{-4} mol/L at various pH were determined by full spectrum scan (0.5 nm/s), and the spectra shown in Figure 3 indicated that one characteristic peak was observed for each solution sample in the range of 228.5 to 236 nm. It was seen from the spectra that there was a slight difference between the two maximum values of the characteristic peaks at pH 6 and 8; meanwhile, the two peaks were observed in the range of 228.5 to 232.5 nm. As a result, the wavelength at 230 nm was selected as the optimal wavelength for absorbance tests, and the centrifuged solution was adjusted to pH 8 to prevent the negative effects of various forms of NaOL on the absorbance. The concentrations of the standard solution samples used for the standard curve shown in Figure 4 were 0, 0.5, 1, 1.5, 2, and 2.5×10^{-4} mol/L, respectively.
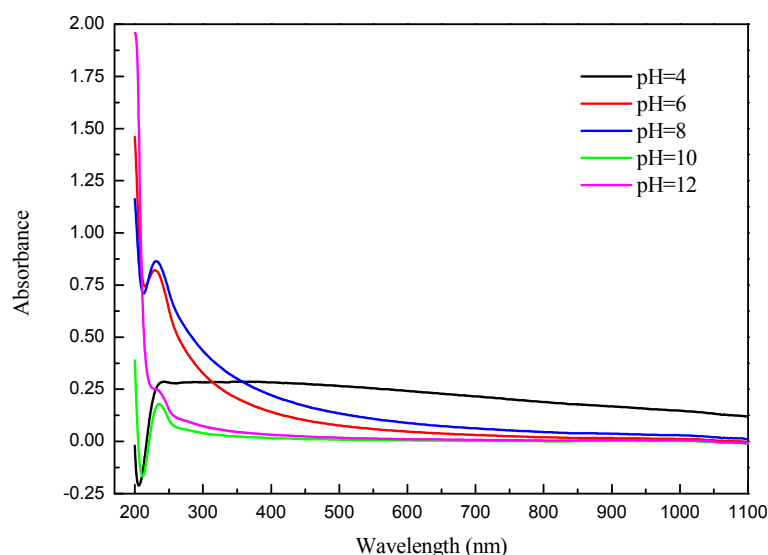

Figure 3. UV spectra of NaOL solution as a function of pH (NaOL: 2×10^{-4} mol/L).
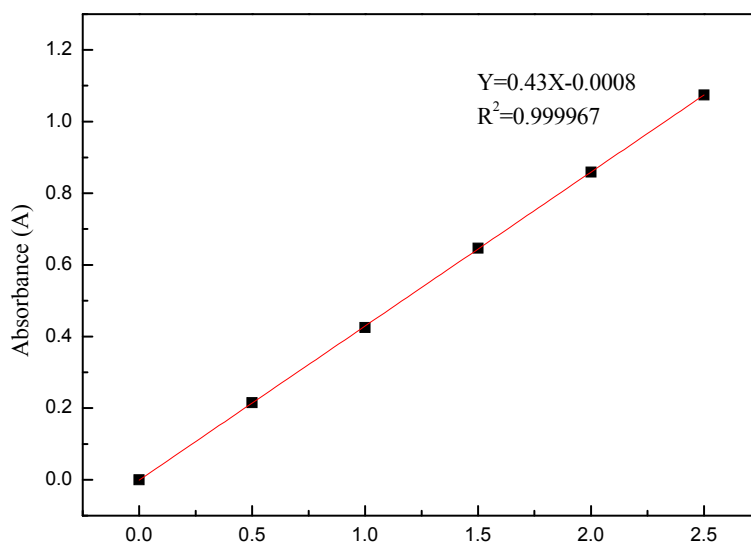

Figure 4. Standard curve of NaOL.

2.5. Zeta Potential Measurements

Zeta potentials were measured using a Malvern Zetasizer Zeta-Nano (Malvern Instruments, Malvern, Worcestershire, UK). All measurements were conducted in a 0.1×10^{-3} mol/L NaCl background electrolyte solution. Purified mineral samples were ground to a particle size less than 5 μm. The fine particles (0.1 g) were placed into a 50 mL beaker containing distilled water (45 mL), and the suspension was stirred magnetically, followed by pH adjustment using HCl and NaOH solutions. Then Fe^{3+} and/or NaOL was added at various pH levels, respectively. Each reagent was stirred for 2 min. Subsequently, the zeta potentials of the resultant suspensions were determined. The measurements were performed at 25 °C.

2.6. FTIR Spectroscopy Measurements

The FTIR spectra were obtained using a Nicolet 6700 spectrophotometer from Thermo Scientific (Waltham, MA, USA) to characterize the nature of the interaction between the collector and the minerals, and revealed the effect of Fe^{3+} on the interaction. Approximately 1% (mass fraction) of the solid sample was mixed with spectroscopic grade potassium bromide (KBr). The wavenumber range of the spectra was 400–4000 cm^{-1}.

To prepare the samples for FTIR analyses, pure particles ground by porcelain mill were wet-sieved, and the fraction (−0.044 mm) was then dried and selected. The conditioning procedure was similar to that used for the flotation tests. After the conditioning, the samples were centrifuged and the supernatant decanted, followed by three repeated rinses to remove residual or physically adsorbed collectors, using distilled water at the same pH adjusted by the prepared HCl or NaOH aqueous solutions. Finally, the wet solid samples were allowed to dry prior to FTIR analyses.

3. Results and Discussion

3.1. Flotation Performance of Single Minerals

The objective of this study was to investigate the underlying mechanism of a NaOL collector in the preferential flotation of zircon from a mixture of zircon and cassiterite minerals. As a result, the flotation behaviors of zircon and cassiterite using NaOL as a collector with and without Fe^{3+} were investigated by single mineral flotation tests. Figure 5 shows the flotation responses of zircon and cassiterite using NaOL at pH 8.
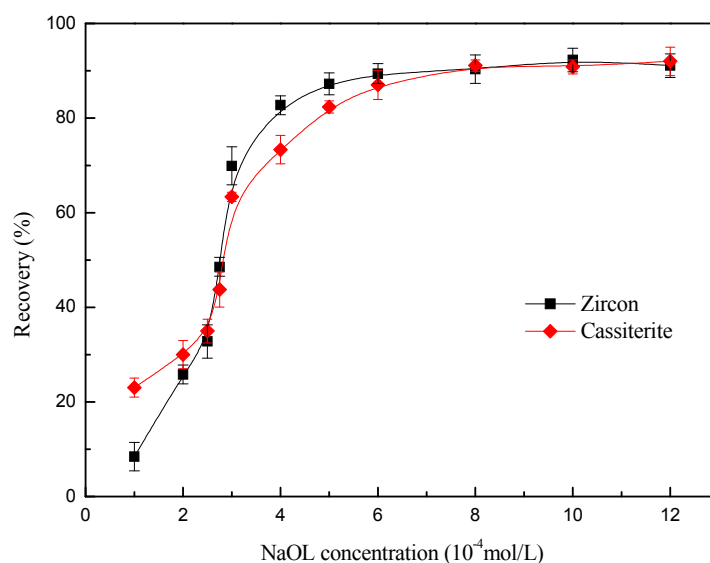

Figure 5. Flotation recoveries of zircon and cassiterite as a function of NaOL concentration (pH = 8).

The results clearly illustrated that the floatability of zircon and cassiterite improved with the increase of NaOL concentration. The maximum recoveries of zircon and cassiterite were approximately 92% and 91%, respectively, in the condition of NaOL concentration at 1×10^{-3} mol/L. The NaOL concentration had a significant effect on the recoveries of zircon and cassiterite. The recovery of zircon increased gradually when the NaOL concentration was lower than 2.5×10^{-4} mol/L, and then increased rapidly in the range of 2.5×10^{-4} to 4×10^{-4} mol/L. After the rapid increase, the recovery of zircon continued to increase until reaching a maximum at the concentration of 1×10^{-3} mol/L. The recovery of cassiterite, in the whole concentration range of NaOL, had a similar trend to that of zircon. However, it was a surprise that the recovery of cassiterite was higher than that of zircon with the NaOL concentration lower than 2.5×10^{-4} mol/L; as the collector concentration increased, the recovery of zircon became higher than that of cassiterite until their recoveries were relatively steady. But, the differences in recovery between zircon and cassiterite were not enough to achieve their effective separation. It can be inferred that the phenomenon might be caused by the weak selectivity of NaOL [19].

The subsequent flotation tests focused on the responses of single mineral flotation in the presence of Fe^{3+} with 4×10^{-4} mol/L NaOL at pH 8. The results are shown in Figure 6. The recovery of zircon increased with increasing Fe^{3+} concentration when the concentration of Fe^{3+} was lower than 8×10^{-5} mol/L; with the continuously increasing concentration, the recovery of zircon decreased rapidly to around 80%. However, the recovery of cassiterite presented a trend of gradual decrease with increasing addition of Fe^{3+} until the Fe^{3+} concentration reached 9×10^{-5} mol/L. Meanwhile, Figure 6 clearly shows that Fe^{3+} caused a slight improvement in the flotation of zircon, but a strong depression to that of cassiterite. As a result, an optimum concentration of Fe^{3+} can help to achieve the flotation separation of zircon from cassiterite.
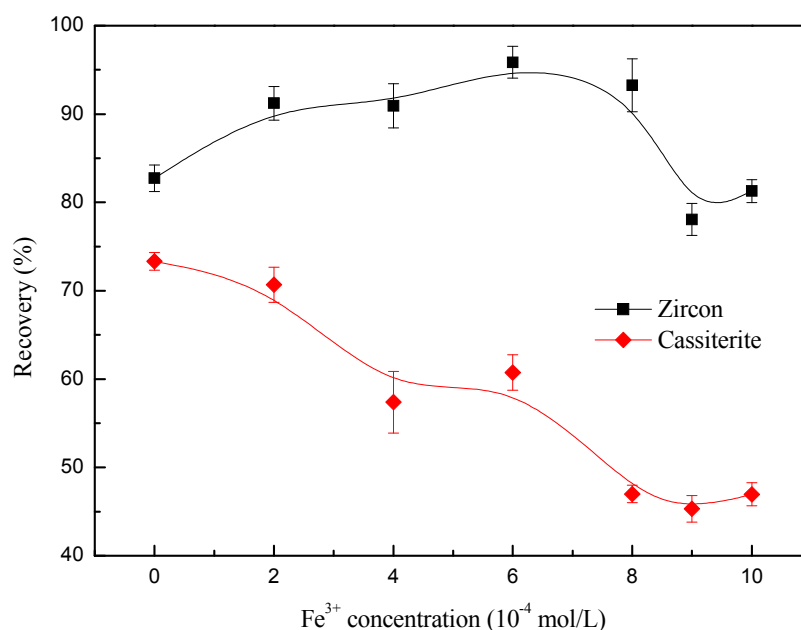

Figure 6. Flotation recoveries of zircon and cassiterite as a function of Fe^{3+} concentration (NaOL: 4.0×10^{-4} mol/L; pH = 8).

The flotation responses of zircon and cassiterite throughout the pH range using 4×10^{-4} mol/L NaOL with and without 8×10^{-5} mol/L of Fe^{3+} are presented in Figures 7 and 8, respectively. Figure 7 shows that the recovery of zircon increased until reaching a relatively high recovery around 80% in the pH range of 7 to 9, and then decreased rapidly to approximately 40% when NaOL was added alone. With the addition of NaOL and Fe^{3+}, the recovery of zircon increased gradually before reaching pH

8 where a maximum recovery of 93% was obtained. Subsequently, the recovery of zircon began to decrease rapidly with the increase of pH. The results indicated that Fe^{3+} slightly aided the flotation of zircon when using NaOL as a collector. The maximum recovery increased from 85.68% without Fe^{3+} at pH 9 to 93.26% with Fe^{3+} at pH 8. Figure 8 shows that the recovery of cassiterite in the NaOL system without Fe^{3+} increased gradually with the increase of pH before reaching pH 8, after which a decreasing recovery of cassiterite was observed. When the flotation of cassiterite was conducted in a NaOL system with Fe^{3+}, the results indicated that the flotation was strongly decreased. In addition, increasing the pH of the suspension caused an even greater decrease in flotation.
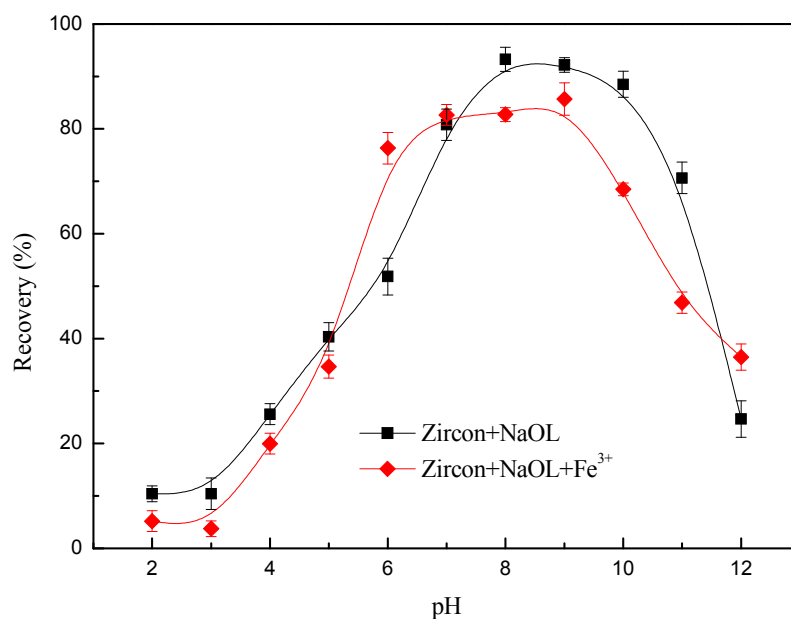
Figure 7. Flotation recovery of zircon as a function of pH with and without Fe^{3+} (Fe^{3+}: 8×10^{-5} mol/L; NaOL: 4×10^{-4} mol/L).
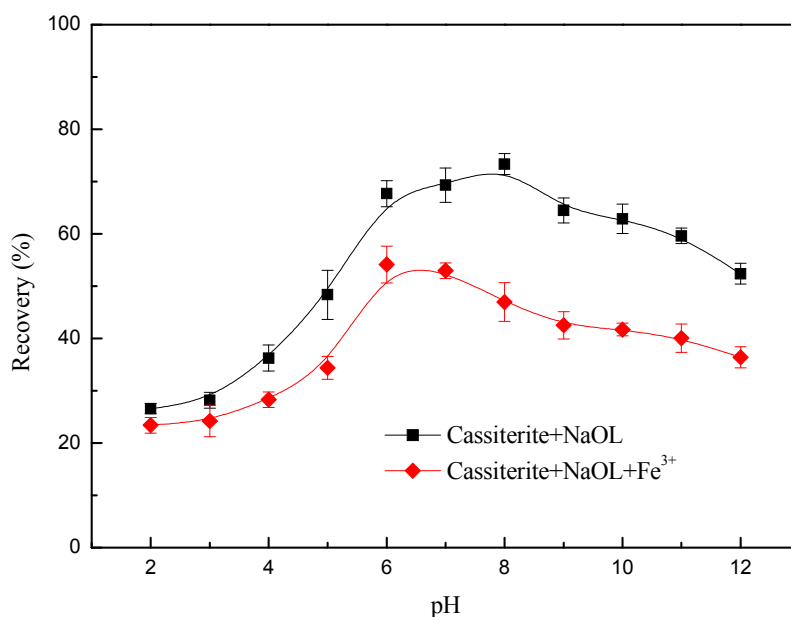

Figure 8. Flotation recovery of cassiterite as a function of pH with and without Fe^{3+} (Fe^{3+}: 8×10^{-5} mol/L; NaOL: 4×10^{-4} mol/L).

3.2. Adsorption Tests

In adsorption tests, the adsorption density results were plotted as a function of pH with and without Fe^{3+} to reveal the effect of Fe^{3+} on the flotation of zircon and cassiterite minerals. The initial concentration of NaOL was kept at 4×10^{-4} mol/L, and that of Fe^{3+} was 8×10^{-4} mol/L if it needed to be used, throughout the adsorption tests. The concentrations of NaOL left in the solution samples were measured by a direct spectrophotometric quantification method at a wavelength of 230 nm.

The adsorption test responses of zircon with and without Fe^{3+} are shown in Figure 9. When NaOL was used as the collector without the addition of Fe^{3+}, the adsorption density of NaOL steadily increased with increasing pH from 4 to 6, and then kept a relatively high adsorption density before reaching pH 10, after which it decreased rapidly. When ferric chloride was added into the flotation system, there was an increase in the adsorption density with increasing pH from 3 to 10, and thereafter decreased rapidly until the adsorption was lower than that in the flotation without Fe^{3+}. It is interesting to note that a higher adsorption density with the addition of Fe^{3+} and NaOL was observed at pH 6–9 and the highest adsorption density around 9×10^{-6} mol/g was obtained at pH 9. The adsorption of NaOL onto zircon surfaces in the presence of Fe^{3+} was higher than that without Fe^{3+} at pH 3–10, where the results were consistent with the flotation tests. However, the adsorption with and without the addition of Fe^{3+} at pH 2, where the adsorption was abnormally high, did not match the flotation tests. Figure 7 shows the recovery of zircon was slightly improved by the addition of Fe^{3+}; meanwhile, Figure 9 shows that Fe^{3+} can enhance the adsorption of the collector onto zircon surfaces. As a result, it can be inferred that the activation of Fe^{3+} in zircon flotation was achieved by enhancing the adsorption of NaOL.
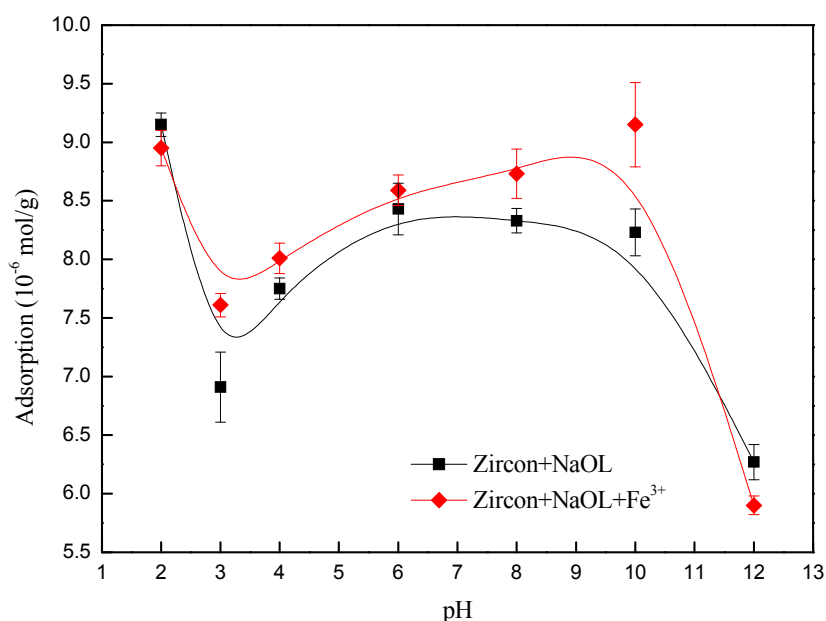

Figure 9. Adsorption of NaOL on zircon as a function of pH with and without Fe^{3+} (Fe^{3+}: 8×10^{-5} mol/L; NaOL: 4×10^{-4} mol/L).

Figure 10 shows that the adsorption of NaOL on cassiterite surfaces in a NaOL system without Fe^{3+} decreased rapidly before reaching pH 4, followed by an increase at pH 4–8, finally, adsorption decreased gradually. The trend of cassiterite in a NaOL system with Fe^{3+} was similar to that without Fe^{3+}, while a maximum adsorption density was obtained at pH 8. At pH 4–12, the adsorption of NaOL on cassiterite surfaces was decreased to a certain extent, and the adsorption density decreased by 1.08×10^{-6} mol/g at pH 8. The trend of the adsorption was consistent with the flotation tests at pH 4–12, but did not match the flotation tests at pH 2–3.
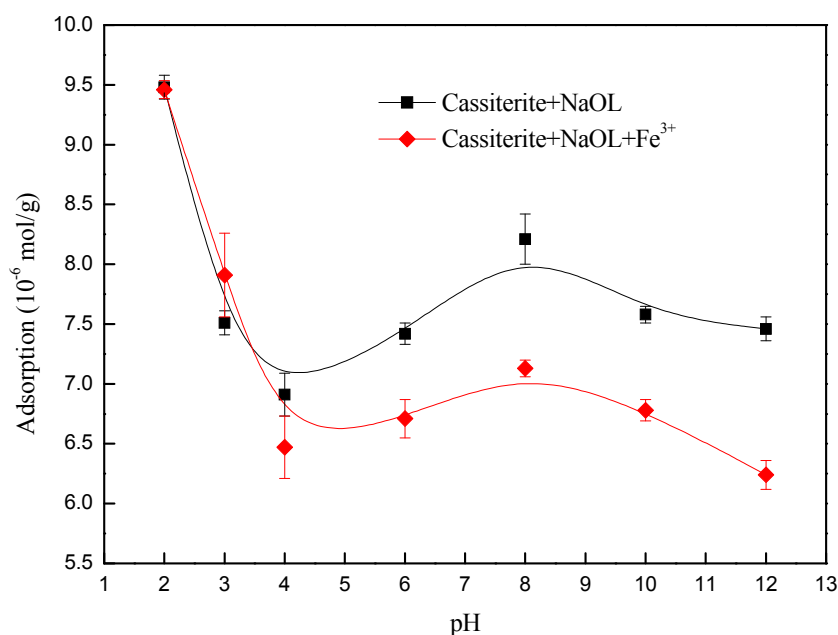
Figure 10. Adsorption of NaOL on cassiterite as a function of pH with and without Fe^{3+} (Fe^{3+}: 8×10^{-5} mol/L; NaOL: 4×10^{-4} mol/L).

Figures 9 and 10 show that the adsorption of NaOL was relatively high in both flotation systems when the pH was low. It is known that NaOL is a salt of strong alkali weak acid [20]. When the pH of the solution was kept at a low level, the anion will be hydrolyzed into the oleic acid. So, it can be inferred that the abnormal adsorption results were attributed to the low pH where the collector mainly existed in the form of oleic acid which was difficult to be dissolved and adsorbed in this form due to its hydrolysis. Once the analysis of the suspension condition was completed, the solution was centrifuged. During the process of centrifugation, the collector, in the form of oleic acid, was removed by adsorption onto the surfaces of cells and tubes because of the insoluble characteristics of oleic acid at a low pH. Therefore, the high adsorption amounts at low pH were not caused by the adsorption of NaOL onto the mineral surfaces but the removal of NaOL as the result of hydrolysis. The flotation was affected positively by the adsorption at relatively high pH due to the weaker hydrolysis.

3.3. Zeta Potential

Figure 11 presents the zeta potentials of zircon and cassiterite as a function of pH. The results indicated that the surface charges of both minerals became more negative when the pH increased. The isoelectric points (IEPs) of the zircon and cassiterite minerals were calculated to be at pH 3.8 and 4.5, respectively. The IEP of zircon is higher than that of cassiterite. Bogdanova et al. reported the IEP of cassiterite was located in the region of 3.8−5.5, depending on the sample origin, type of electrolyte, and the determination procedure [21]. In addition, the measured data of cassiterite and zircon were in excellent agreement with the results reported by Wang et al. [22] and Moreno et al. [23], respectively. When the pH of the suspension was lower than the IEP, the mineral surfaces were charged positively, and the zeta potentials got more negative with the increase of pH from the IEP.
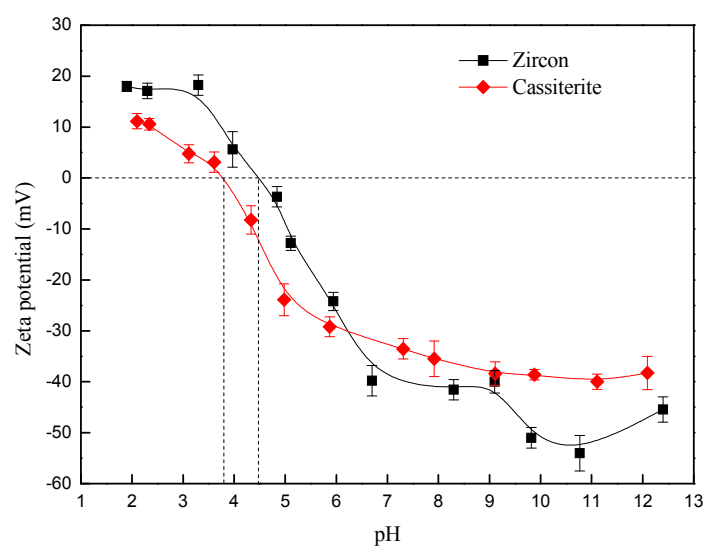
Figure 11. Zeta potentials of zircon and cassiterite as a function of pH.

The zeta potentials of zircon and cassiterite minerals in the presence of Fe^{3+} and/or NaOL as a function of pH are shown in Figures 12 and 13, respectively. Fe^{3+} had a strong influence on the zeta potentials of both minerals. The minerals acquired an increasingly positive charge at approximately pH 4−5, and after reaching that highest value, the zeta potentials of the minerals decreased, with a charge reversal occurring at pH 7−8. The behaviors of zeta potentials can be inferred to be caused by the adsorption/precipitation of Fe^{3+} onto the negatively charged mineral surfaces through electrostatic interactions. The concentration of NaOL had a slight effect on the zeta potentials of the minerals in the whole pH range. The NaOL collector decreased the negative charges of zircon and cassiterite at acidic pH. The zeta potentials of the minerals were more positive in the presence of NaOL and Fe^{3+}, compared to NaOL alone. However, the zeta potentials between the two minerals had differences in the presence of Fe^{3+} alone. The charges of the zircon surfaces were more positive than that of cassiterite below pH 7.
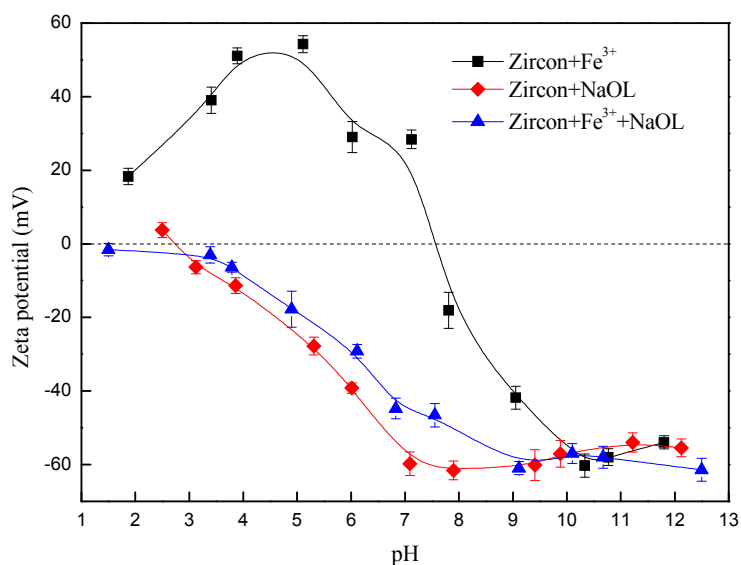

Figure 12. Zeta potential of zircon as a function of pH in the presence of Fe^{3+} and/or NaOL (Fe^{3+}: 8×10^{-5} mol/L; NaOL: 4×10^{-4} mol/L).
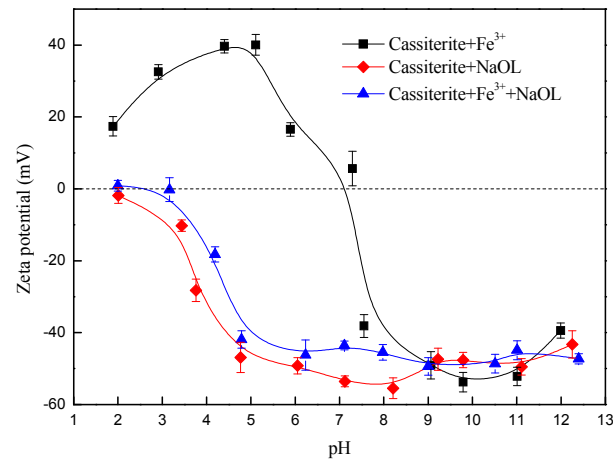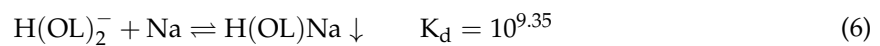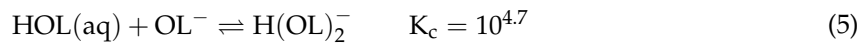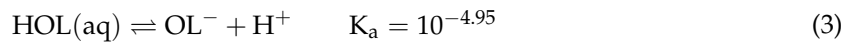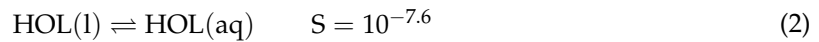
Figure 13. Zeta potential of cassiterite as a function of pH in the presence of Fe^{3+} and/or NaOL (Fe^{3+}: 8×10^{-5} mol/L; NaOL: 4×10^{-4} mol/L).

3.4. Solution Chemistry Analyses

In the flotation tests, the pulp collectors and Fe^{3+} exhibited different forms in different pH environments. The existing forms of NaOL and Fe^{3+} affected the flotation behaviors. The solution chemistries of NaOL and Fe^{3+} can be calculated to generate the concentration logarithmic diagram of each component at different pH values. In addition, the species distribution diagram for Fe^{3+} and oleate ions can help to explain the results obtained from the zeta potential experiments.

Various oleate species are formed in aqueous solution, and the distribution diagram as a function of pH is shown in Figure 14, according to the following equations [24].

$$HOL(l) \rightleftharpoons HOL(aq) \qquad S = 10^{-7.6} \tag{2}$$

$$HOL(aq) \rightleftharpoons OL^- + H^+ \qquad K_a = 10^{-4.95} \tag{3}$$

$$2OL^- \rightleftharpoons (OL)_2^{-2} \qquad K_b = 10^4 \tag{4}$$

$$HOL(aq) + OL^- \rightleftharpoons H(OL)_2^- \qquad K_c = 10^{4.7} \tag{5}$$

$$H(OL)_2^- + Na \rightleftharpoons H(OL)Na \downarrow \qquad K_d = 10^{9.35} \tag{6}$$

$$C_{T1} = [HOL(aq)] + [OL^-] + 2\left[(OL)_2^{-2}\right] + 2\left[H(OL)_2^-\right] \tag{7}$$
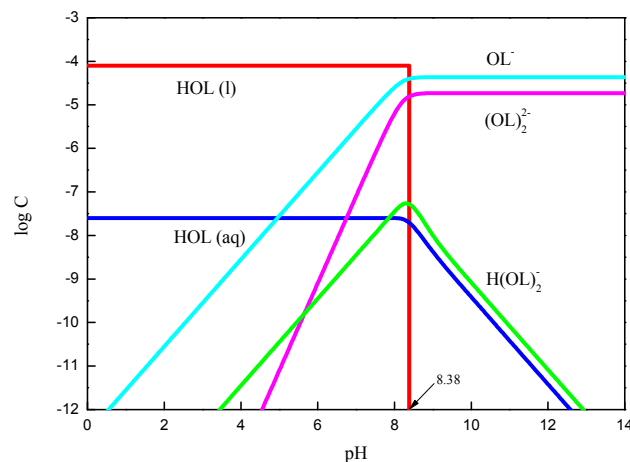

Figure 14. Species distribution diagram of NaOL as a function of pH (NaOL: 4×10^{-4} mol/L).

Similarly, the species distribution of Fe^{3+} was calculated according to the equations listed below [25], and the diagram is shown in Figure 15.
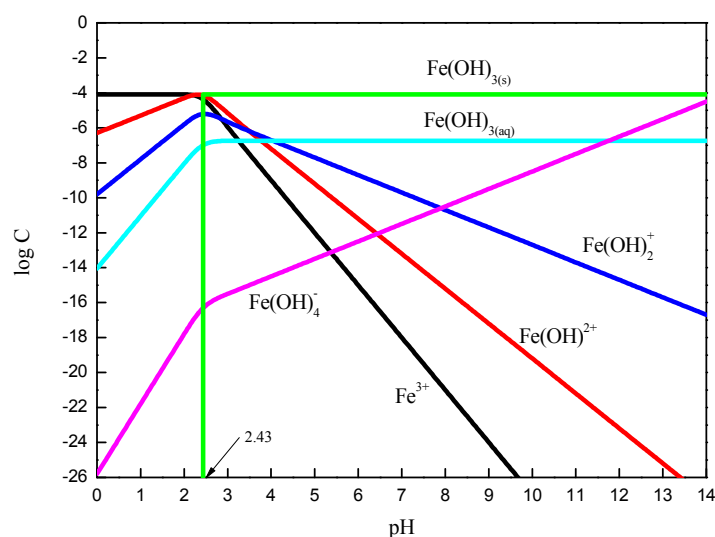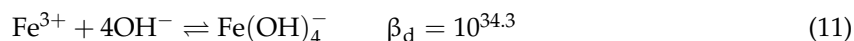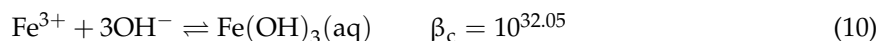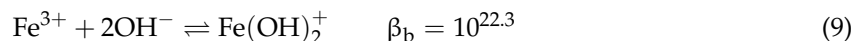
$$Fe^{3+} + OH^- \rightleftharpoons Fe(OH)^{2+} \qquad \beta_a = 10^{11.8} \tag{8}$$

$$Fe^{3+} + 2OH^- \rightleftharpoons Fe(OH)_2^+ \qquad \beta_b = 10^{22.3} \tag{9}$$

$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3(aq) \qquad \beta_c = 10^{32.05} \tag{10}$$

$$Fe^{3+} + 4OH^- \rightleftharpoons Fe(OH)_4^- \qquad \beta_d = 10^{34.3} \tag{11}$$

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^- \qquad K_{SP} = 10^{-38.8} \tag{12}$$
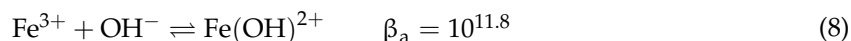

Figure 15. Species distribution diagram of Fe^{3+} as a function of pH (Fe^{3+}: 8×10^{-5} mol/L).

Figure 14 shows that all the species of the NaOL collector had a negative charge at pH > 8.38, thereby promoting the electrostatic interactions between the minerals and collector. The negatively charged oleate ions and dimers existed in the basic pH region and below pH 8.38, where NaOL was in the form of non-dissociated oleic acid. The recoveries of zircon and cassiterite (Figures 7 and 8) had a trend of being the same as that of $H(OL)_2^-$, existing at pH 4–14, increasing at the beginning and then decreasing. As a result, $H(OL)_2^-$ was confirmed as the predominant species which significantly affected the flotation behaviors. NaOL decreased the negative charges of the zircon at acidic pH, indicating that the negatively charged species of NaOL in solution were adsorbed onto the mineral surfaces. Figure 15 shows the positively charged Fe^{3+}, $Fe(OH)^{2+}$, and $Fe(OH)_2^+$ species all existed across the acidic pH region, and above pH 8, the main species were molecular $Fe(OH)_3$ and $Fe(OH)_4^-$. Fe^{3+} was the main species below pH 3, which interacted with OL^-, generating the precipitation of $Fe(OL)_3$ which decreased the concentration of NaOL. Hence, there was an abnormal adsorption of NaOL and the flotation of both minerals was inhibited. The zeta potential tests (Figures 12 and 13) show that the addition of Fe^{3+} changed the surface charges of zircon and cassiterite to positive from negative at acidic pH, which indicated that the species of Fe^{3+} were expected to adsorb on the zircon and cassiterite mineral surfaces in this pH region. According to the theory of electrostatic attraction, a positive surface can attract the negatively charged species. In theory, the flotation of both zircon and cassiterite should be enhanced in the presence of Fe^{3+}. In contrast, the flotation of cassiterite was decreased, which can be inferred to be due to the adsorption of $Fe(OH)_3(s)$ on cassiterite surfaces, while $Fe(OH)_3(s)$ had the similar zeta potentials to that of cassiterite measured with Fe^{3+} alone [26]. This also indicated that the surface of the cassiterite was covered with $Fe(OH)_3(s)$ and that a hydrophilic film formed which prevented the adsorption of NaOL to inhibit the flotation. The reason that the zeta

potentials of zircon were further below pH 7 than that of cassiterite, was that the adsorption of the positively charged species, including Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$, enhanced the adsorption of NaOL, thus promoting flotation.

3.5. FTIR Analyses

Figure 16 shows the FTIR spectra of NaOL, zircon, and cassiterite. In the FTIR spectrum of NaOL, the peaks at 2921.13 cm^{-1} and 2851.03 cm^{-1} were attributed to the C–H stretching vibration of the –CH_2– and –CH_3 groups, respectively. The peaks at 1559.7 cm^{-1}, 1446.06 cm^{-1}, and 1425.26 cm^{-1} were attributed to the –COO– vibration. Among these peaks, the peak at 1559.7 cm^{-1} was attributed to the –COOC– asymmetric stretching vibration. The peaks at 1446.06 cm^{-1} and 1425.26 cm^{-1} were attributed to the –COOC– symmetric stretching vibration. The peak at 721.79 cm^{-1} was attributed to the –$(CH_2)_n$– deformation [27,28]. In the spectrum of zircon, the peaks at 611.79 cm^{-1} and 900.81 cm^{-1} were attributed to the bending and stretching vibration of $SiO_4{}^{2-}$ [29], respectively. The characteristic peaks of cassiterite were around 629.3 cm^{-1} and 530.8 cm^{-1}.

Figure 17 shows the spectra of zircon with NaOL and/or Fe^{3+} at pH 8. Compared to the FTIR spectrum of the purified zircon shown in Figure 16, the spectrum of zircon interacted with NaOL had the new peaks at 2921.6 cm^{-1} and 2851.44 cm^{-1} which were attributed to the C–H stretching vibration of the –CH_2– and –CH_3 groups, respectively. The peak at 1446.06 cm^{-1} was attributed to the –COOC– symmetric stretching vibration; however, the peak frequency did not change. Meanwhile, the new peak at 1781.5 cm^{-1} was due to the chemisorption of NaOL because it cannot be observed in the NaOL or purified zircon [30]. The spectrum of zircon with NaOL in the presence of Fe^{3+} showed the adsorption of the collector occurred on the surfaces because of the peaks at 2920.3 cm^{-1} and 2851.15 cm^{-1}. And the new peak at 1630 cm^{-1} was previously attributed to the –COO– vibration [31]. The peak at 1559.7 cm^{-1} shifted to a higher wavenumber by 70.3 cm^{-1}, compared to the FTIR spectrum of NaOL, indicating that the NaOL reacted with zircon and was chemisorbed onto the zircon surfaces. The characteristic peaks of zircon in the presence of Fe^{3+} with and without NaOL around 894.14 cm^{-1} and 611.65 cm^{-1} were strengthened compared to the FTIR spectrum of zircon, which may be caused by the entrance of Fe^{3+} into the lattice of zircon.
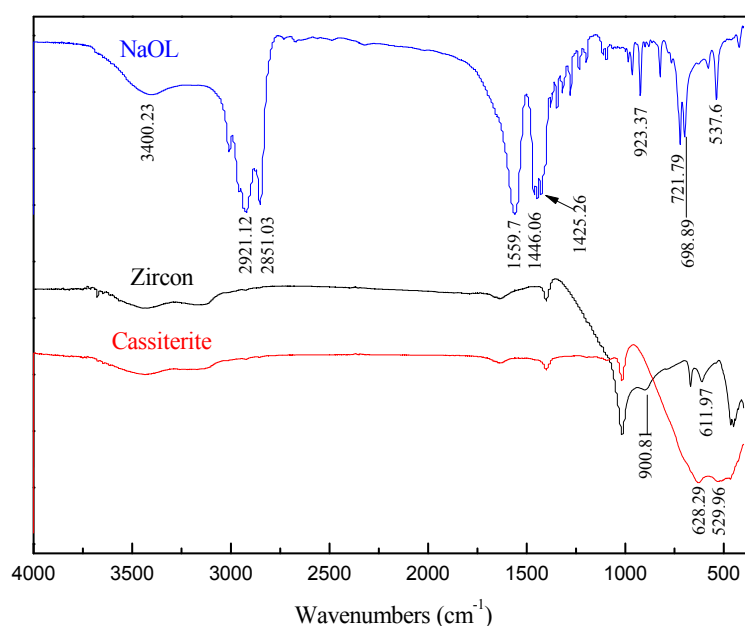

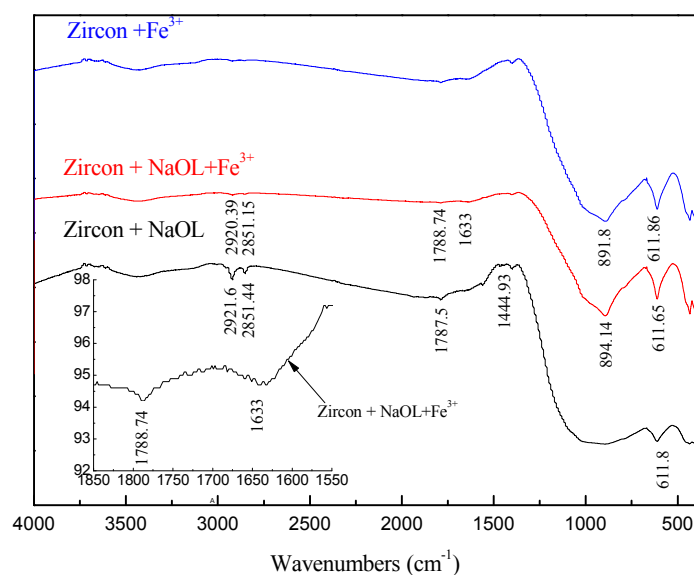**Figure 16.** FTIR spectra of NaOL, cassiterite and zircon.

Figure 17. FTIR spectra of Zircon with NaOL and/or Fe^{3+} at pH 8 (NaOL: 4×10^{-4} mol/L; Fe^{3+}: 8×10^{-5} mol/L).

Figure 18 shows the spectra of cassiterite with NaOL and/or Fe^{3+} at pH 8. The new peaks at 2922.11 cm^{-1} and 2852.85 cm^{-1} were also attributed to the C–H stretching vibration of the –CH_2– and –CH_3 groups, respectively. The frequency did not change. The new peak at 1638.5 cm^{-1} was previously attributed to the –COO– vibration. The peak at 1538.5 cm^{-1} shifted to a lower wavenumber by 21.2 cm^{-1}, compared to the FTIR spectrum of NaOL, and the new peak at 1020.49 cm^{-1} indicated that a chemical reaction occurred [32]. The spectrum of cassiterite with NaOL in the presence of Fe^{3+} shows a weaker peak at 2923.7 cm^{-1}, and the peaks at 1538.5 cm^{-1} and 1020.49 cm^{-1} disappeared. The results illustrated that the addition of Fe^{3+} weakened both the physical and chemical adsorption of NaOL onto the cassiterite surfaces. As a result, the flotation was decreased after adding Fe^{3+}.
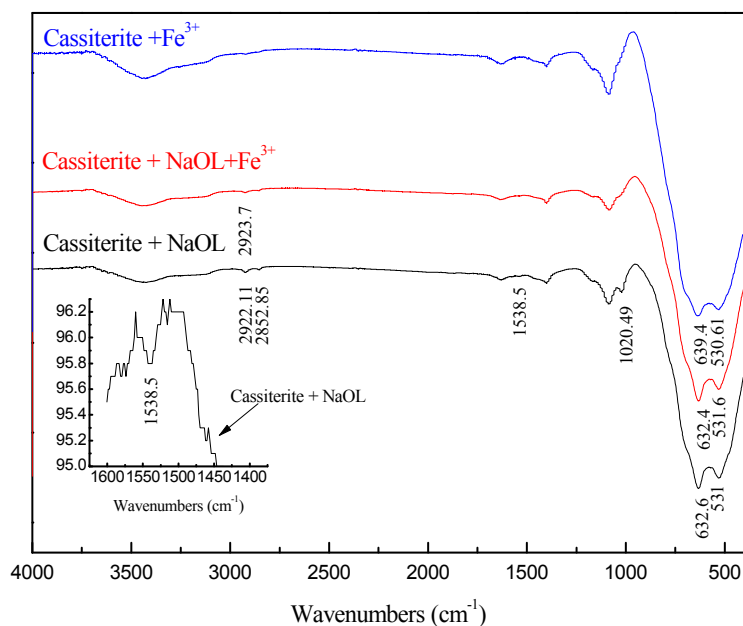

Figure 18. FTIR spectra of cassiterite with NaOL and/or Fe^{3+} at pH 8 (NaOL: 4×10^{-4} mol/L; Fe^{3+}: 8×10^{-5} mol/L).

4. Conclusions

(1) The single mineral flotation of zircon and cassiterite using sodium oleate (NaOL) as an anionic collector with and without Fe^{3+} was conducted. The results indicated that NaOL performed badly in the zircon flotation separation from cassiterite without Fe^{3+}, due to the strong collecting power and weak selectivity of NaOL. The recoveries of both zircon and cassiterite, being restricted by the hydrophobic surfaces of flotation cells made up with organic glass, reached around 90% when the concentration of NaOL was 4×10^{-4} mol/L. The flotation of zircon using 4×10^{-4} mol/L NaOL with 8×10^{-5} mol/L Fe^{3+} at pH $6-9$ was slightly increased and the recovery increased by 5–7%, while that of cassiterite was inhibited across the whole pH range and a 30% change was obtained for the maximum decrease of recovery.

(2) Based on the adsorption tests, zeta potential measurements, and solution chemistry analyses, we confirmed that adsorption of NaOL on both zircon and cassiterite surfaces had occurred in the NaOL system. Adsorption tests indicated that the addition of Fe^{3+} can enhance the adsorption of the collector on zircon surfaces while weakening adsorption on cassiterite surfaces. Furthermore, the abnormal adsorption of NaOL was caused by the excessively low pH where the adsorption cannot be achieved effectively. Zeta potential measurements and solution chemistry analyses confirmed $H(OL)_2^-$ as the predominant species which significantly affected the flotation behaviors. The adsorption of positively charged species of Fe^{3+} caused the negative charges of both minerals to become more positive at acidic pH, while the positive charges of cassiterite were caused by the adsorption of $Fe(OH)_3(s)$, and then the hydrophilic film formed and the flotation was decreased. Meanwhile, the surface of zircon attracted the positively charged species of Fe^{3+}, which enhanced the adsorption of the negatively charged species of NaOL, and so the flotation was slightly increased.

(3) FTIR analyses indicated that the adsorption of the collector onto the surfaces of zircon and cassiterite was chemisorption. After the addition of Fe^{3+} into NaOL flotation system, the peaks of zircon around 894.14 cm^{-1} and 611.65 cm^{-1} were strengthened compared to the FTIR spectrum of zircon, which was caused by the entrance of Fe^{3+} into the lattice of zircon. Meanwhile, a new peak was observed at 1633 cm^{-1} and was previously attributed to the –COO– vibration, and was caused by chemisorption. As a result, Fe^{3+} slightly increased the flotation of zircon. In contrast, the addition of Fe^{3+} caused the peaks of NaOL at 2923.7 cm^{-1} to weaken, and the peaks at 1538.5 cm^{-1} and 1020.49 cm^{-1} disappeared. As a result, the flotation of cassiterite was inhibited. The FTIR results were in good agreement with the flotation tests.

Author Contributions: W.L. and H.P. conceived and designed the experiments; H.P., D.W. and X.B. performed the experiments; W.L. and D.W. analyzed the data; Y.L. contributed reagents/materials/analysis tools; W.L. and H.S. wrote the paper.

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

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