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Evaluation of Sulfonate-Based Collectors with Different Hydrophobic Tails for Flotation of Fluorite

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Abstract: This investigation aims to demonstrate the effects of hydrophobic tails on the affinity and relevant flotation response of sulfonate-based collectors for fluorite. For this purpose, a series of alkyl sulfonates with different hydrophobic tails, namely sodium decanesulfonate (C10), sodium dodecylsulfate (C12), sodium hexadecanesulfonate (C16), and sodium dodecylbenzenesulfonate (C12B) were applied. The flotation tests showed that C12 and C12B had a better collecting performance than C10 and C16 at pH < 10, and the flotation recovery of fluorite was higher when adopting C12B as a collector compared with C12 with a strong base. The adsorption behaviors of collectors on the fluorite surface were studied through zeta potential, Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses. It was found that the affinity of alkyl sulfonates for fluorite was enhanced with the increase of the alkyl chain length from C10 to C16. The existence of phenyl in the hydrophobic tail of sulfonates could improve its activity for fluorite by reducing its surface tension. The abnormal phenomenon C16 with a high affinity for fluorite had a low collecting performance for fluorite mainly due to its overlong alkyl chain, resulting in low solubility in pulp, which restrained its interaction with fluorite. We concluded that C12B was the most applicable collector for fluorite among these reagents due to its high activity, high solubility, and low cost, which was further substantiated by calculating their molecular frontier orbital energy.

Keywords: fluorite; sulfonate-based collectors; adsorption behavior; molecular frontier orbital energy

1. Introduction

Fluorite (CaF₂), an important nonrenewable mineral that is primarily used for the manufacture of hydrofluoric acid, glass, cement, fillers, and as a flux reagent in steel making, has in recent years been considered an important strategic mineral [1–4]. In natural ore deposits, fluorite is mostly associated with other calcium-bearing minerals, such as calcite and scheelite. By now, flotation has been regarded as one of the most commonly used techniques for separating fluorite from gangue minerals, employing fatty-acid collectors and sometimes associated with highly selective depressants [5,6]. However, it should be noted that the flotation separation of fluorite from calcium-bearing minerals is a very challenging task due to the fact that their surface reactivity is similar to that of traditional fatty-acid collectors [7,8].

As fatty-acid collectors possess poor selectivity and low water-solubility at a low temperature, the separation is not always satisfactory on an industrial level without adding highly selective depressants. Therefore, the previous study suggested the use of alkyl sulfonates as collectors, since they are more selective than fatty-acid salts [9]. Alkyl sulfonates are a kind of well-known organic surfactant that have received considerable attention in many fields. The main active substance of the alkyl sulfonates collector is sulfonate, which has a highly hydrophilic sulfogroup connected with alkyl, giving rise

to a structural formula of RSO_3Na , where R is an alkyl group [10,11]. Sulfonate is also the main active component of sodium petroleum sulfonate (SPS), which is the byproduct of petroleum under refining; the source of alkyl sulfonates is therefore abundant. In the literature, there are many studies focusing on the utilization of alkyl sulfonates in froth flotation in mineral processing. For instance, Martínez-L et al. [12] reported that celestite could be selectively separated using sodium dodecyl sulfonate (C12) as a collector and that the celestite concentrates contained about 98% of SrSO_4 grade with up to 96% of SrSO_4 recovery under optimum conditions. The synergistic effects between C12 and a mixed fatty-acids collector for apatite flotation were investigated by Cao et al. [13]; it was found that the addition of C12 could benefit the apatite flotation at pH 9.5 by improving the surfactant adsorption at the apatite surface. González-Martín et al. [9] studied the interaction mechanism of C12 with fluorite by infrared attenuated total reflection (ATR), proposing a two-step mechanisms: sulfonate ions first chemisorbed on the fluorite surface, followed by a physisorption process. It is worth pointing out that the alkyl sulfonates applied in these earlier studies were usually the sulfonate with a dodecyl hydrophobic tail.

For an amphiphilic surfactant, apart from the polar functional group, the hydrophobic aliphatic chain also plays an important role in determining its properties in an aqueous solution, e.g., a steric effect. Chen et al. [11] utilized SPS with different molecular weights as collectors for the flotation of kyanite ore and demonstrated that the higher molecular weight of the collector was, the higher the kyanite recovery obtained was. Due to the similar hydrophilic polar head of SPS, different molecular weights indicated that there were different kinds of hydrophobic tails connecting to the polar head groups, possessing discrepant reactivity of SPS for kyanite. Taguta et al. [14] recently studied the effect of alkyl chain length thiol collectors on the heat of adsorption and floatability of sulphide, finding that both the heat of adsorption and flotation recoveries increased with an increase in the collector chain length for xanthate homologues. The effects of hydrophobic tails on the properties of xanthates, amines, and fatty-acids collectors have also been studied by Ackerman and Fuerstenau [15,16], respectively. Meanwhile, to the best of our knowledge, systematic studies of the characteristics of sulfonate-based collectors with different hydrophobic tails have seldom been reported [11].

In the present work, several common alkyl sulfonates, which connected with a decane (C10), dodecyl (C12), hexadecane (C16), and dodecylbenzene (C12B) hydrophobic tail, respectively, were utilized as collectors to investigate their collecting performance for fluorite. In addition, surface tension analyses, zeta potential measurements, FTIR, and XPS were employed to elucidate the adsorption behaviors of collectors on the fluorite surface. The chemical reactivity and water-solubility were further analyzed by calculating their molecular frontier orbital energy and via hydrophile–lipophile balance (HLB).

2. Materials and Methods

2.1. Materials and Reagents

The natural colorless fluorite (CF) sample was obtained from the Inner Mongolia fluorite deposit in China. The hand-picked high-grade fluorite sample was first crushed with a hammer, then ground in laboratory porcelain, before being screened to obtain a 45–74 μm size fraction for micro-flotation tests. A portion of the 45 μm size fraction particles was further ground to 5 μm for zeta potential measurements, FTIR studies and XPS analyses. The XRD pattern of the powdered fluorite is given in Figure 1, showing that the fluorite sample utilized in the tests was of high purity.

The sulfonate-based collectors (C10, C12, C16, and C12B) with chemical pure grade ($\geq 98\%$) were purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China), and their chemical structures are shown in Figure 2. All pH adjustments were done using hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. For the zeta potential measurements, potassium chloride (KCl) was used as the background electrolyte. The water used throughout the experiments was deionized water, whose resistivity was 18.25 $\text{M}\Omega\cdot\text{cm}$.

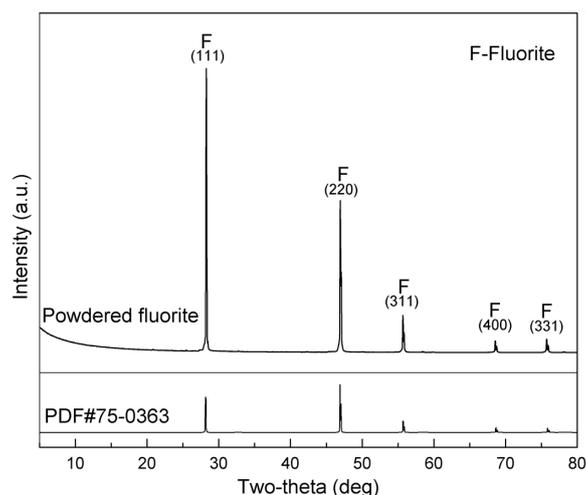


Figure 1. XRD pattern of powdered fluorite.

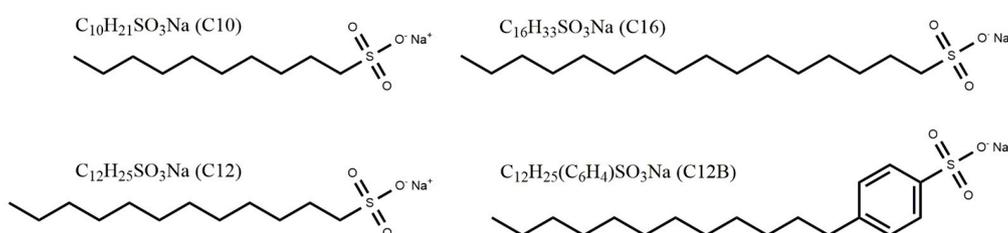


Figure 2. Chemical structures of sulfonate-based collectors.

2.2. Methods

2.2.1. Micro-Flotation Tests

The micro-flotation tests were carried out in a laboratory XFG-35 flotation apparatus (Rock Crush & Grand Equipment Co., Ltd., Wuhan, China) with an effective volume of 120 mL at room temperature. For each test, prepared mineral particles (10.0 g) were placed into a plexiglass cell and then filled with 100 mL of deionized water. 1 mol/L of HCl or NaOH solution was added to adjust the pulp pH. After adding the desired amount of collector reagents, the suspension was continuously agitated at 1600 rpm for 2 min. The flotation test duration was 5 min. The obtained concentrate products and tailings were filtered, dried, and weighed to calculate the flotation recovery of the fluorite sample under various flotation conditions.

2.2.2. Zeta Potential Measurements

Zeta potential measurements were carried out by a Zeta Nano ZS90 zeta potential analyzer (Malvern Instruments Ltd., Worcestershire, UK). A suspension containing 0.1 wt % mineral particles ($-5 \mu\text{m}$ size fraction) was prepared in a 1 mM KCl solution and conditioned by magnetic stirring for 5 min with or without collectors. After allowing the solution to settle for 10 min, the supernatant of the diluted fine particle suspension was removed for zeta potential characterization. Each sample was measured three times and the average values were reported.

2.2.3. Surface Tension Measurements

The surface tension of the collector solution was performed via the Wilhelmy plate method using the K100MK2 tensiometer (Krüss GmbH, Hamburg, Germany). The desired amount of collector solution with a given pH value was added into the sample pool, and the measurement was performed automatically as the plate came into contact with the solution surface. The value of the surface tension

of each solution can be read on the screen after measurement completion. Each solution was measured several times as the standard deviation was below the default and the average value was adopted.

2.2.4. FTIR Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) at room temperature (25 °C) in the range of 4000–400 cm^{-1} . Prior to the test, the samples conditioned with collectors were washed three times with distilled water and then vacuum dried at 40 °C. The spectra of the solids were taken with KBr pellets.

2.2.5. XPS Analyses

XPS spectra of the mineral samples with or without treatment of collectors were recorded by an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The Al $K\alpha$ X-rays meter with an energy of 20 eV for narrow scans was employed for observations, and the pressure in the analysis chamber was more than 5×10^{-10} mbar. The pretreatment of samples to be tested was the same as for the FTIR measurements described above.

2.2.6. Calculation of Frontier Orbital Energy

The frontier orbital energy of the collector molecule was calculated using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional based on the density functional theory, with the help of the DMol3 module in the Materials Studio 8.0 package (Accelrys, Inc., San Diego, CA, USA) [17]. The all-electron Kohn–Sham wave functions and double numerical plus polarization (DNP) with a basis file of 3.5 were selected. Other parameters were default settings, as applied in previous studies [18,19].

3. Results and Discussion

3.1. Micro-Flotation Test Results

Using alkyl sulfonates with different hydrophobic tails as collectors, the flotation performance of fluorite was evaluated via single mineral flotation tests and the results are given in Figure 3. Figure 3a reveals the flotation recovery of fluorite as a function of the agent dosage of the four collectors. The general trend in flotation recovery of fluorite was similar for different collectors when increasing their dosage. Using C12B or C12 as collectors, the recovery of fluorite increased rapidly and achieved a high value even at low concentrations, while the fluorite recoveries were low for C10 and C16. The flotation experiments showed that C12B and C12 had a much better collecting performance for fluorite than did C10 and C16.

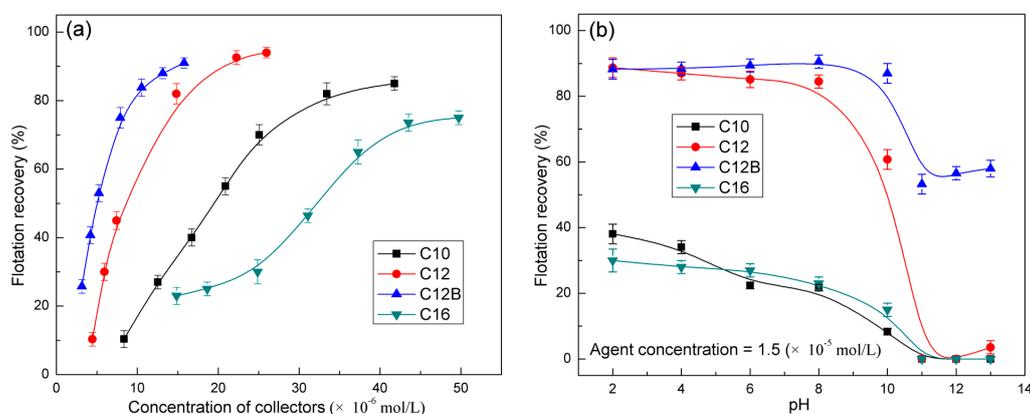


Figure 3. Using different sulfonate-based collectors, the effects of (a) the collectors' concentration and (b) of their pH on the flotation performance of fluorite.

Furthermore, Figure 3b shows that the sulfonate-based collectors with different hydrophobic tails possessed totally different collecting performances for fluorite, even though their polar functional groups are the same ($-\text{SO}_3^-$). The flotation recoveries of fluorite using C12 and C12B were higher than those of C10 and C16, and they remained about 92% at a pH of 2–8. The C10 and C16 yielded an unsatisfactory recovery below 40% in the total pH range, and they decreased as the pulp pH increased. As the pulp pH exceeded 10, the fluorite recoveries dropped rapidly when adopting C12 and C12B as collectors. The main reason might be the decrease of the adsorption capacity of collectors on the fluorite surface due to the electrostatic repulsion between collectors and the fluorite surface, because fluorite charged a negative potential under the strong alkaline environment. C12B showed a stronger affinity for fluorite than did C12 in a strong base given its higher recovery. The results of the flotation tests indicated that hydrophobic tails could influence the properties of surfactants, performing a different affinity for fluorite.

3.2. Zeta Potential Measurement Results

The zeta potentials of fluorites in the absence and presence of sulfonate-based collectors holding the same concentration are illustrated as a function of the pH in Figure 4. For bare fluorite, the zeta potential remained at a high positive level (60 mV) at $\text{pH} < 8$ and decreased markedly when the solution became alkaline. In the presence of C10 and C12, the potential of fluorite witnessed different decreases (with C10 from 60 mV to 40 mV, and C12 from 60 mV to 15 mV), but still appeared to be a positive potential. It was interesting that with treatment of C16 and C12B, the potential of fluorites changed from positive to negative over the entire pH range. The significant drops in zeta potential were attributed to the adsorption of anionic molecules (RSO_3^-) on the fluorite surface through electrostatic forces, changing its surface properties in the solutions [2].

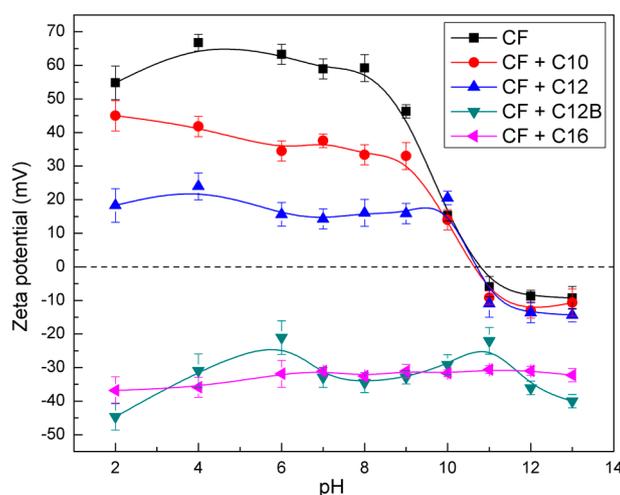


Figure 4. Zeta potentials of fluorites with and without pretreatment of sulfonate-based collectors.

The zeta potential of fluorite decreased more after addition of C12 than C10, and even became negative after addition of C12B or C16, indicating a different adsorption capacity of the collectors on the fluorite surface; we deduced from this that the hydrophobic tails of alkyl sulfonates would influence their affinity for fluorite. Concretely, the increase in the alkyl chain length of alkane sulfonates could favor their affinity for fluorite, and the addition of a phenyl in the hydrophobic tail of the collector was also advantageous when comparing C12B with C12.

3.3. Surface Tension Measurement Results

The hydrophilic and hydrophobic properties of the solid surface are important factors affecting the wetting film stability during the flotation process. The property of a liquid, such as surface tension,

is of equal importance because flotation is a complex process involving all three phases: liquid, gas, and solid. Surfactants can reduce the surface tension of the aqueous solution and facilitate the formation of bubbles, which are necessary for separation by flotation. In addition, the surface tension of a surfactant solution reflects its surface activity [20]; the surface tension of alkyl sulfonate solutions with the same concentration was therefore measured as a function of the pH. As shown in Figure 5, the surface tension of the water solution was about 72.57 mN/m at pH = 7, nearing its theoretical value (72.37 mN/m) [21] before decreasing remarkably in the strong alkaline solution. With the addition of C10 and C12, the surface tension of the solution declined slightly compared to water. Meanwhile, the situation was quite different when C16 and C12B were added to the solution. The surface tension decreased from about 72 mN/m to 58 mN/m and to 50 mN/m with the presence of C16 and of C12B, respectively. The lower the surface tension of the solution is, the higher its surface activity is. The surface tension results of alkyl sulfonate solutions indicated that the surfactants C12B and C16 owned a higher surface activity than did C10 and C12, which was in accordance with the experimental results obtained above.

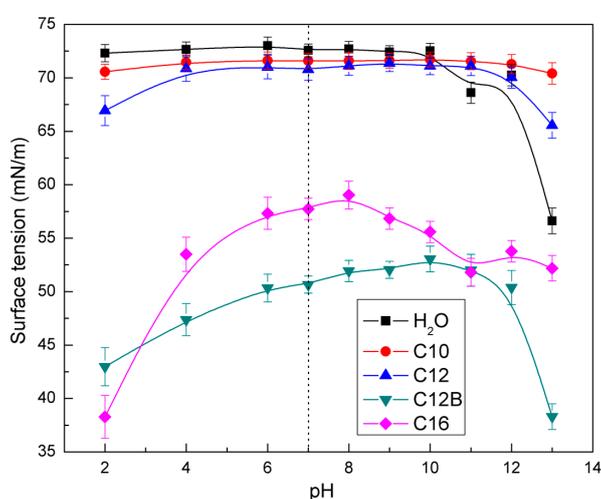


Figure 5. Surface tension of the collector solutions compared with water, as a function of the pH.

3.4. IR Spectroscopic Analysis Results

In order to investigate the adsorption behaviors of sulfonate-based collectors on the fluorite surface, the infrared spectra of collectors and fluorites treated with C10, C12, C16, and C12B at pH = 7 were measured. The results are shown in Figure 6. For all collectors, the adsorption band around 2957 cm^{-1} was related to the asymmetric stretching vibration of $-\text{CH}_3$ in alkyl chains, and the peaks around 2920 cm^{-1} and 2850 cm^{-1} were attributed to $-\text{CH}_2$ asymmetric and symmetric stretching frequencies [3,22]. A strong band at about 1468 cm^{-1} existing in C10, C12, and C16 was attributed to the deformation vibration of $-\text{CH}_2$, associated with wagging of $-(\text{CH}_2)_n$ at 720 cm^{-1} [9]. The significant bands of sulfonate were $-\text{S}=\text{O}$ vibrations, which were found around 1170 cm^{-1} (antisymmetric stretching) and 1065 cm^{-1} (symmetric stretching) [9].

With the treatment of the collectors, the stretching bands of the $-\text{CH}_3$ and $-\text{CH}_2$ groups emerged around 2920 cm^{-1} and 2850 cm^{-1} , indicating that the collectors have been adsorbed on to the surface of the fluorites. For C10, the $-\text{S}=\text{O}$ vibration was not detected on the treated fluorite mainly due to its low adsorption capacity on the fluorite surface, limiting the possibility of detection during the IR analysis. For C12, the shifts of the $-\text{S}=\text{O}$ stretching bands from 1171.2 cm^{-1} to 1182.3 cm^{-1} and from 1066.8 cm^{-1} to 1076.6 cm^{-1} suggested that the adsorption was in essence chemical [9,23,24]. The $-\text{S}=\text{O}$ stretching bands were also detected on the fluorite surface with the C16 treatment. For C12B, due to the existence of phenyl in the hydrophobic tail, the $-\text{S}=\text{O}$ stretching information was hidden

while the characteristic absorption bands of phenyl were observed around 1433 cm^{-1} . The IR spectra analyses agreed well with the zeta potential measurements discussed above.

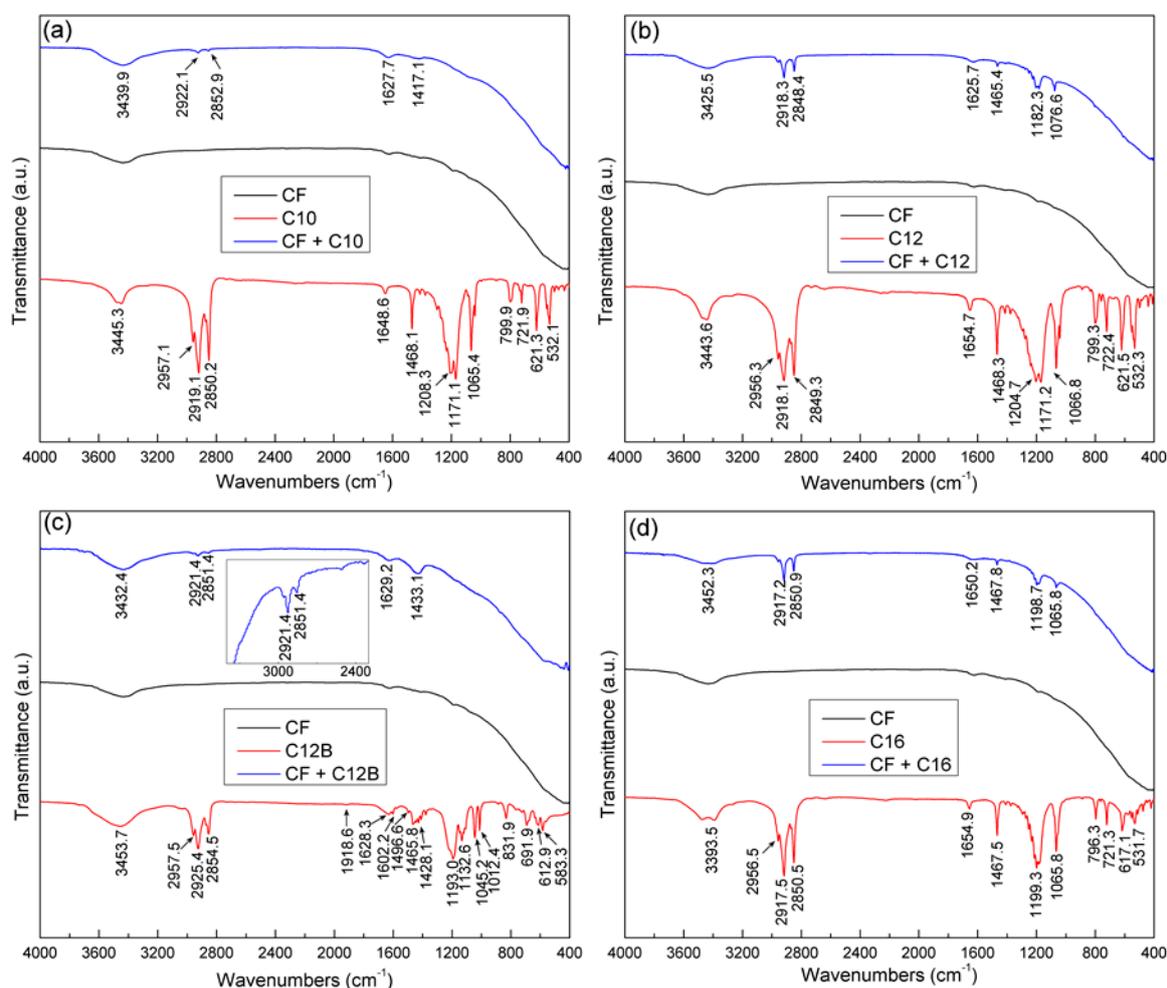


Figure 6. FTIR spectra of fluorites before and after adsorption of sulfonate-based collectors. (a) C10; (b) C12; (c) C12B; and (d) C16.

3.5. XPS Analyses

To further examine the interactions between sulfonate-based collectors and the fluorite surface, the XPS spectra of fluorite samples were obtained before and after reacting with collectors, and the results are given in Figure 7. As expected, C, O, Ca, and F were the major constituents and no evidence of contamination by other elements or impurities was found in bare fluorite. The existence of C and O elements were mainly due to adventitious contamination that occurred during the pretreatment or measurement of the samples. After the adsorption of the collectors on the fluorite, apart from the presence of the characteristic peaks of C(1s), O(1s), Ca(2p), and F(1s); the peaks of S(2p) and S(2s); and the positioned element of the sulfonates, were detected with a binding energy at approximately 168.8 eV and 229.5 eV on the fluorite samples treated with C12, C16, and C12B.

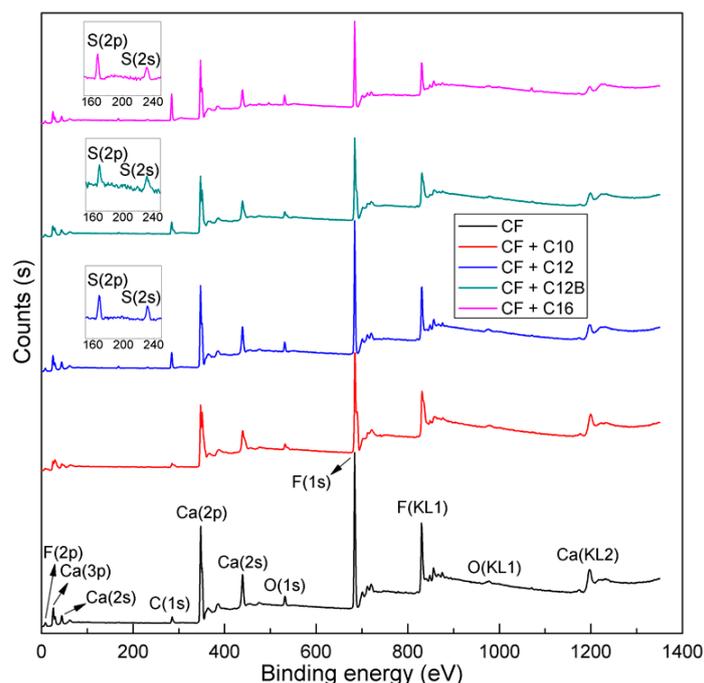


Figure 7. Full-scan XPS spectra of fluorites with and without pretreatment of sulfonate-based collectors.

Table 1 reveals the relative atomic concentration of the fluorite surface elements after the treatment with the collectors. The atomic concentration of C and O increased after the adsorption of the collectors, as did the detection of the sulfur element. The increase in the XPS S concentration that was due to the different adsorption capacities of the collectors on the fluorite surface. By further analyzing the accurately narrow S(2p) spectra of samples, it was found that the S(2p) peak could be detected on all samples, indicating that all the collectors have been adsorbed on to the surface of the fluorites (Figure 8). Furthermore, we found that the signal-to-noise ratio (SNR) of S(2p) spectra was in a totally different level: the SNR of S(2p) from CF + C10 (Figure 8a) was stronger than the others, also demonstrating a lower adsorption capacity of C10 on the fluorite, which was consistent with the results in Table 1.

Table 1. Relative atomic concentration of the fluorite surface elements in the absence and presence of the collectors.

Sample	Relative Atomic Concentration (%)				
	Ca(2p)	F(1s)	C(1s)	O(1s)	S(2p)
CF	29.72	59.24	6.71	4.33	-
CF + C10	28.71	58.91	7.48	4.67	0.23
CF + C12	26.47	51.16	15.96	5.45	0.96
CF + C12B	26.09	49.26	17.95	5.57	1.13
CF + C16	23.42	46.12	22.58	6.49	1.39

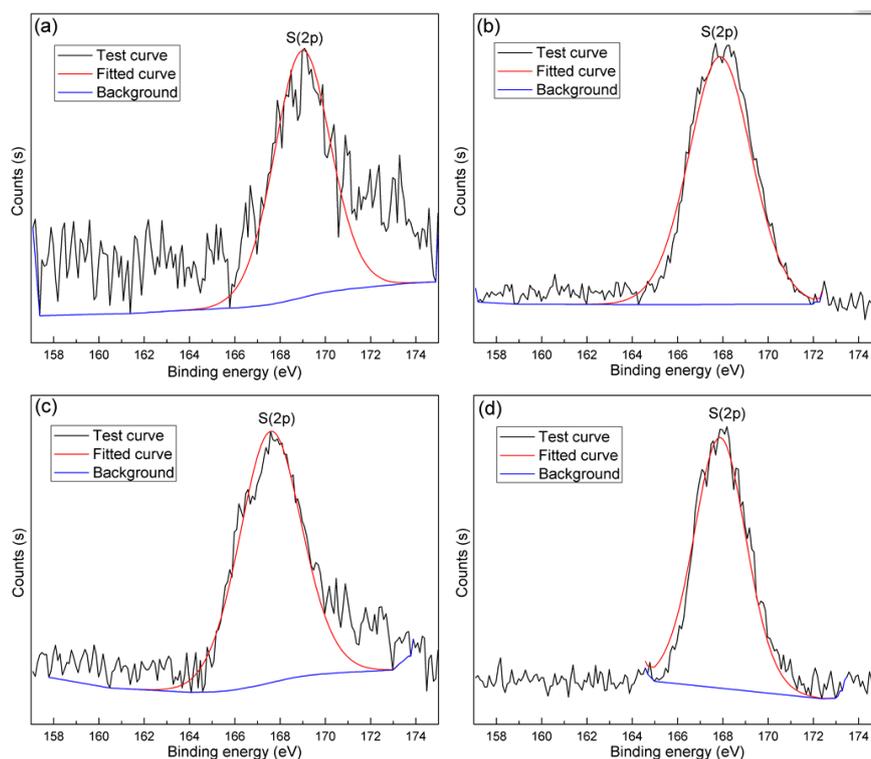


Figure 8. The S(2p) XPS spectra of fluorites treated with sulfonate-based collectors. (a) C10; (b) C12; (c) C12B; and (d) C16.

3.6. Molecular Frontier Orbital Energy and HLB Calculation

The molecular orbital theory has been very successful in predicting chemical behaviors for an enormous number of molecules; it was first proposed by Fukui in 1952 [25]. The central idea of the theory was that the highest occupation molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) played a prominent role in governing the chemical reactions of organics [24]. The energy gap between HOMO and LUMO is an important stability index, e.g., a large HOMO–LUMO gap implies a high stability for the molecule in chemical reactions [26,27]. Therefore, the molecular frontier orbital energies of sulfonate-based collectors were calculated to predict their chemical characteristics, and the results are given in Figure 9 and Table 2.

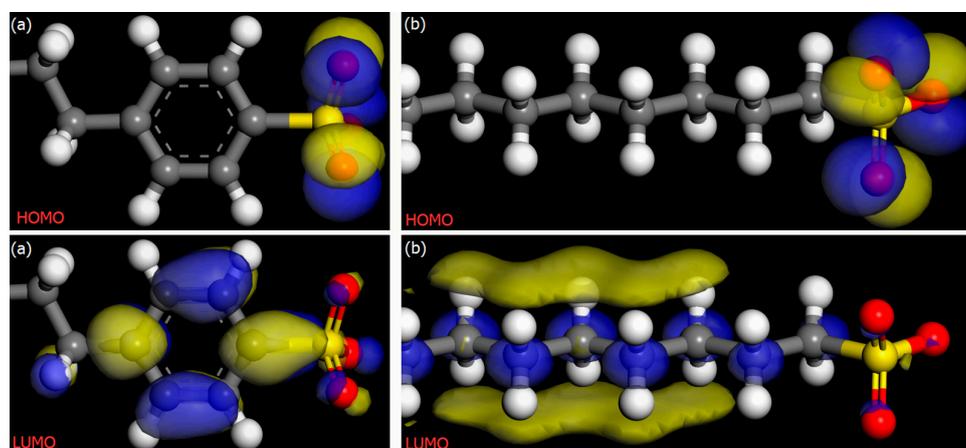


Figure 9. Isosurfaces of the frontier orbitals of (a) C12B and (b) C12 (Color codes: Red—O, Yellow—S, Gray—C, and White—H).

Table 2. Frontier orbital energies of sulfonate-based collectors

Sulfonate Type	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
C10	−5.559	1.362	6.921
C12	−5.561	1.352	6.913
C16	−5.561	1.340	6.901
C12B	−5.709	−1.448	4.261

As shown in Figure 9, the HOMO isosurfaces of C12B and C12 were all located on the sulfonate group with the energy of −5.709 eV and −5.561 eV. On the other hand, the distributions of their LUMO isosurfaces were absolutely different: the LUMO isosurface of C12 mainly distributed over the alkyl chain; for C12B, the LUMO isosurface was located on the six-membered aromatic phenyl group with an energy of −1.448 eV. The isosurfaces of the frontier orbitals of C10 and C16 were similar to C12, and were not shown on paper. Additionally, their frontier orbital energies and associated HOMO–LUMO gap were calculated in Table 2. It was obvious that the HOMO–LUMO gap of C12B was the lowest among the collectors, reflecting that C12B has the highest chemical reactivity based on the frontier molecular orbital theory. These results can explain why C12B possessed a high collecting performance for the fluorite mineral, which was also in accordance with the above analyses.

It should be noted that theoretically C16 also possessed a high affinity for fluorite based on its property analysis above, while the practical fluorite recovery was at a low level when adopting C16 as a collector, which seemed to be abnormal. As is commonly known of collectors, apart from reactivity, their water solubility plays a significant role in determining the collecting performance for a mineral because the flotation of the mineral is conducted in a solution system. In other words, the behavior of long-chain collectors in a solution is determined by the properties of the polar heads and hydrophobic tails and their resultant solvent power [20]. The intensity of the polar portion to non-polar portion in a molecule of the collector can be quantitatively evaluated by the values of the hydrophile–lipophile balance (HLB), which can be calculated via the Davies equation [28]

$$\text{HLB} = \Sigma(\text{hydrophilic group numbers}) - \Sigma(\text{hydrophobic group numbers}) + 7 \quad (1)$$

The values of the hydrophilic and hydrophobic group numbers of the different surfactants can be obtained via a table lookup. By these means, we were able to calculate that the HLB value would gradually decrease with the increase of the alkyl chain length of the surfactant from C10 to C16. The results showed that C16 possessed a much lower solubility than did C10 and C12 in the water solutions [28,29], further retraining its collecting performance for minerals during flotation, which would offer a good explanation as to why C16 contained an unexpectedly weak collecting performance for the fluorite.

4. Conclusions

We investigated the flotation performance of fluorite that adopted sulfonate-based collectors with different hydrophobic tails. We found that hydrophobic tails played a significant role in determining the properties of surfactants (collectors), further affecting their collecting performance for fluorite during flotation experiments. C12 and C12B possessed a better collecting performance for fluorite than did C10 and C16. The surface tension of the collectors decreased with an increase of the alkyl chain length from C10 to C16, as well as with the existence of phenyl in the hydrophobic tail. However, the overlong alkyl chain length made C16 have low solubility in water due to its lower HLB, thus having a dissatisfactory collecting performance for fluorite. The zeta potential results showed that the fluorite potential decreased because of the adsorption of anionic molecules (RSO_3^-) on the fluorite surface through electrostatic forces. It was further found that the reducing of fluorite potential was in a different degree mainly due to a different adsorption capacity of the collectors on the fluorite surface. The FTIR measurements demonstrated that all the collectors were chemisorbed on the fluorite surface,

which was confirmed by the XPS analyses. What was more, the XPS analyses also demonstrated the different adsorption capacity of sulfonate-based collectors on fluorite: C16 and C12B possessed a higher affinity for fluorite than C10 and C12 due to their higher relative atomic concentration of S(2p). In conclusion, C12B, having the highest chemical reactivity, was regarded as the most applicable collector for fluorite among the four surfactants, which was testified by calculating their molecular frontier orbital energy. The findings in this study suggested that the effects of hydrophobic tails of sulfonate-based collectors should not be neglected during the design, development, and selection of reagents for flotation.

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

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