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Low-Temperature Flotation Separation of Diaspore from Kaolinite by Using a Mixed Collector

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Abstract: In this paper, the effect of a new mixed collector sodium oleate (NaOl)/tert dodecyl mercaptan (TDM) on the separation of diaspore and kaolinite at 283 K was investigated. The molar ratio of NaOl to TDM is 8:2. The properties of the mixed collector and its adsorption mechanism on diaspore and kaolinite were studied by surface tension measurements, Zeta potential determinations and XPS analysis. The flotation results show that the mixed collector NaOl/TDM has a good collection ability for diaspore and a good selectivity for kaolinite at low temperatures. Therefore, the mixed collector NaOl/TDM can effectively separate diaspore and kaolinite under alkaline conditions at 283 K. The results of surface tension measurements show that the molecular density, hydrophobic association ability and collection ability of the mixed collector NaOl/TDM are better than those of the single collector at 283 K. In addition, the formation of a micelle effect of the mixed collector NaOl/TDM has a synergistic effect, which improves the reagent activity at low temperatures with the flotation effect enhanced. The results of the Zeta potential determinations and XPS analysis show that the total adsorption capacity of the mixed collector NaOl/TDM on the surface of the diaspore at low temperatures is higher than that of NaOl, and the adsorption capacity on the surface of kaolinite is similar to that of NaOl. The mixed collector NaOl/TDM may be adsorbed on the surface of diaspore and kaolinite by a hydrogen bond at 283 K.

Keywords: low-temperature flotation; diaspore; kaolinite; sodium oleate; tert dodecyl mercaptan

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1. Introduction

Diaspore-type bauxite is the main aluminum resource in China [1]. However, the mass ratio of Al_2O_3 to SiO_2 (A/S) for this type of bauxite resource is only between 4–6, which has a difficult time meeting the raw material requirements (A/S > 10) for alumina production by the Bayer process [2]. Flotation can effectively separate diaspore and kaolinite, and improve A/S of this type of bauxite [3,4].

In recent years, many novel surfactants have been used in the direct flotation separation of diaspore and kaolinite [5], such as propyl gallate [6], hydroxamic acids [7], N-(6-(hydroxyamino)-6-oxohexyl) decanamide [8], cetyltrimethylammonium chloride [9] and so on. However, the oleic acid collector is still one of the most widely used collectors in bauxite flotation in China due to its excellent collection performance and low price [10–12]. However, the oleic acid collector also has obvious drawbacks [13]. Its sensitivity to temperature significantly reduces its flotation effect in alpine areas [14]. In order to improve the difficulty of NaOl in dissolving at low temperatures, the research shows that the synergistic effect of two or more mixed collectors can better adapt to the environment

of low-temperature flotation and realize the effective separation of diaspore and kaolinite [15,16]. Tert dodecyl mercaptan (TDM) is a non-ionic surfactant that can reduce the surface tension of the oil–water interface and improve the low-temperature solubility and selectivity of the collector [17,18]. However, as far as we know, the flotation behavior and adsorption mechanism of the NaOl and TDM mixed collector for diaspore and kaolinite at low temperatures has not been studied. Therefore, this paper studies the synergistic effect of the mixture of NaOl and TDM in bauxite low-temperature flotation in order to improve the low-temperature solubility and selectivity of NaOl, reduce consumption, and provide theoretical guidance for the wide application of NaOl in the separation of diaspore and kaolinite.

In this paper, a novel mixed collector, including sodium oleate (NaOl) and tert dodecyl mercaptan (TDM), was prepared and used as a collector of diaspore at low temperatures. Its flotation performance of diaspore and kaolinite at different temperatures was evaluated by flotation tests of pure minerals and artificial mixed minerals. In addition, the adsorption mechanism of the mixed collector NaOl/TDM on the surface of diaspore and kaolinite at 283 K was studied by surface tension measurements, Zeta potential determinations and XPS analysis.

2. Materials and Methods

2.1. Materials

Similar to our previous studies, the pure minerals used in the experiments were diaspore and kaolinite, respectively. The results of the X-ray diffraction (D8 discover, Bruke, Karlsruhe, Germany) and chemical composition of the diaspore and kaolinite are shown in Figure 1 and Table 1, respectively. The results show that the purity of the diaspore and kaolinite was more than 90%. After handpicking massive ores, artificial crushing, sorting and grounding in porcelain ball milling, 38–74 μm minerals were screened out for flotation. The screened minerals were ground to −5 μm by an agate mortar for Zeta potential measurements and XPS analysis.

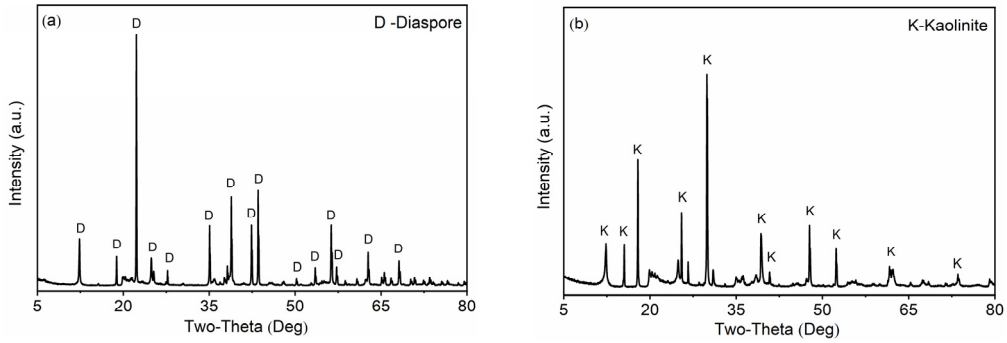

Figure 1. XRD patterns of the purified samples: (**a**) diaspore; (**b**) kaolinite (D = Diaspore, K = Kaolinite).

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

Sample	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Diaspore	80.77	0.89	2.76	0.756	0.01	0.053	0.008	0.025
Kaolinite	33.68	45.44	0.97	0.88	0.24	0.077	0.89	-

2.2. Reagents

Sodium oleate (NaOl) and tert dodecyl mercaptan (TDM) were used as collectors, both of which were analytically pure products. The mixed collector NaOl/TDM was prepared and used on the spot to avoid reagent failure. Hydrochloric acid (HCl) and

sodium hydroxide (NaOH) were used as pH regulators. The water used in all the tests was deionized water (Resistivity = 18.3 MΩ·cm).

2.3. Flotation Tests

The single mineral flotation test was carried out in a FMG hanging cell flotation machine (Shunze, Hunan, China). A 2 g mineral sample was weighed and put into the flotation cell, 35 mL of deionized water was added, the pH value was adjusted by HCl or NaOH, the slurry was adjusted for 3 min, the collector was added and then the flotation was conducted for 3 min. After flotation, the foam product and the product in the tank were filtered, dried and weighed, respectively, and the flotation recovery rate was calculated. The flotation process is shown in Figure 2.

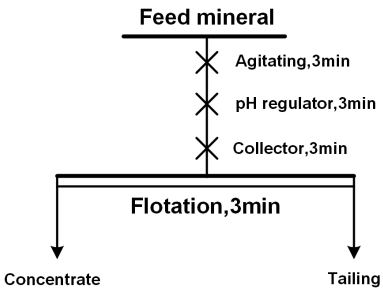

Figure 2. Flowsheet of the flotation tests.

The flotation process of the artificial mixed mineral was the same as that of the single mineral flotation. After the flotation was finished, the foam products and the products in the tank were filtered, dried and weighed. The contents of Al_2O_3 and SiO_2 were analyzed, and the flotation recovery rate was calculated. The mass ratio of diaspore to kaolinite in the artificial mixed minerals was 3:1, and the A/S ratio of mixed minerals was 3.49.

2.4. Surface Tension Measurements

The surface tensions of the different collectors in the solution were measured by the platinum hanging sheet method with a K100 surface tension instrument (Kruss, Hamburg, Germany). The test temperature was 283 K. Before the test, the platinum hanger was cleaned with deionized water and alcohol, respectively, and then put into the flame of the outer ring of the alcohol lamp to remove the residual substances from the last measurement. The number of measurements was set to three, so each result was the average of the measurements.

2.5. Zeta Potential Determinations

The Zeta potentials before and after the interaction between the collectors and minerals at 283 K were measured by an LA-960V2 (Horiba, Kyoto, Japan). A 30 mg ore sample was weighed and then added to 40 mL of a potassium chloride (KCl) solution (concentration = 0.01 M). The slurry was stirred up for 3 min, and its pH was adjusted. After the pH was stabilized, the collector was added, and then the pulp was stirred for 3 min to fully interact with the mineral. After the stirred pulp was kept still for 1 min, the supernatant was extracted with a syringe to measure the Zeta potential, and the result was the average value of three measurements.

2.6. XPS Measurements

A K-Alpha$^+$ (Thermo Fisher Scientific Co., Waltham, MA, USA) X-ray photoelectron spectrometer was used to measure the energy spectrum before and after the interaction between the reagents and the minerals at 283 K. A total of 0.5 g of the sample was added to 35 mL of deionized water. The pulp pH was adjusted, and the collector was added. The pulp was stirred for 40 min and then was allowed to stand for 40 min. After the mineral was completely settled, the supernatant was carefully separated out and then washed

three times with deionized water with the same pH value. The solid sample was dried in a vacuum oven at 283 K for 24 h, pressed into tablets and tested.

3. Results and Discussions

3.1. Micro-Flotation

The preliminary single mineral flotation tests showed that when the temperature was 298 K, the selection effect of the NaOl/TDM collector on the diaspore was better than that of NaOl or TDM alone [19]. Previous studies [19] have shown that the optimal pH conditions for NaOl, TDM and the mixed collector NaOl/TDM are 10, 9 and 9, respectively. The optimum molar ratio of NaOl to TDM in the mixed collector is 8:2 at 298 K. Figure 3 shows the effect of the dosage of NaOl, TDM and NaOl/TDM on the flotation recovery of the diaspore and kaolinite under the optimal pH condition at 298 K in the single mineral flotation tests. As shown in Figure 3, when the collector concentration is less than 0.1 mM, the flotation recovery of the diaspore increases rapidly with the increase in the collector dosage. When the collector concentration is more than 0.1 mM, the increase rate of recovery slows down. Under different collector concentrations, the recovery of diaspore by NaOl/TDM is higher than that by NaOl. When the collector concentration is 0.1 mM, the recoveries of NaOl and NaOl/TDM of the diaspore are 84.62% and 91.35% respectively. For kaolinite flotation, the recovery of kaolinite increases slowly with the increase in collector concentration. Under various concentration conditions, the recovery of kaolinite under the action of NaOl/TDM is much lower than that of NaOl. When the collector concentration is 0.1 mM, the recovery of kaolinite is 16.7%. At this time, the recovery of kaolinite by NaOl/TDM is only 11.5%. In addition, the ability of TDM to collect diaspore and kaolinite is weak, so it is not suitable to be used as a collector alone. Therefore, compared with the single collector NaOl or TDM, NaOl/TDM has a better separation effect on diaspore and kaolinite at 298 K.

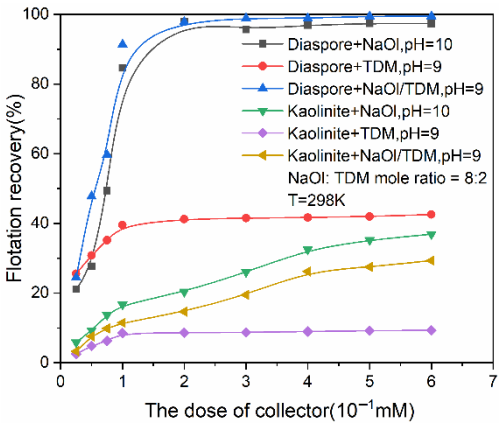

Figure 3. Effect of the collector dosage on the diaspore and kaolinite flotation recovery with NaOl (pH = 10), TDM (pH = 9) or NaOl/TDM (pH = 9, NaOl:TDM mole ratio = 8:2) as collectors at 298 K.

Another remarkable feature of NaOl is that the collector performance decreases sharply at low temperatures. In order to further explore the performance of NaOl/TDM, the relationship between the flotation temperature and collector performance was explored. Figure 4 shows the effect of the flotation temperature on the flotation of diaspore and kaolinite with NaOl or NaOl/TDM. As shown in Figure 4, NaOl is extremely sensitive to temperature. When the pulp temperature increases from 283 K to 308 K, the recovery of diaspore increases rapidly from 30.33% to 95.65%. The recovery rate of kaolinite also increases slowly with the increase in temperature. When the pulp temperature increases from 283 K to 308 K, the recovery rate of kaolinite increases slowly from 6.55% to 30.25%.

Under the action of NaOl/TDM, the recovery of diaspore increases with the increase in temperature. When the pulp temperature increases from 283 K to 308 K, the recovery of diaspore increases rapidly from 55.28% to 97.50%. When the temperature is lower than

293 K, the ability of NaOl/TDM to collect diaspore is significantly higher than that of NaOl alone. The addition of TDM can effectively reduce the sensitivity of NaOl to temperature. The recovery rate of kaolinite also increases slowly with the increase in temperature. When the pulp temperature increases from 283 K to 308 K, the recovery rate of kaolinite increases slowly from 5.56% to 19.26%. When the temperature is lower than 293 K, the collection capacity of NaOl/TDM for kaolinite is slightly lower than that of NaOl. Therefore, the separation effect of NaOl/TDM on diaspore and kaolinite is much better than that of NaOl at low temperatures.

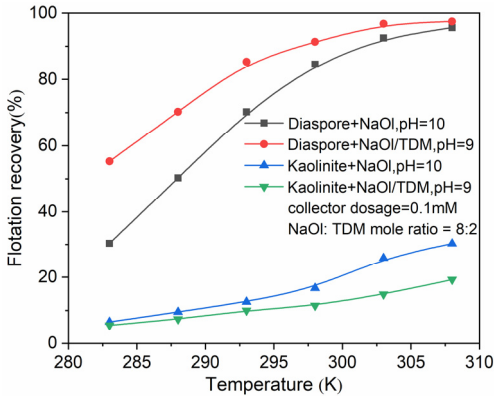

Figure 4. Effect of the flotation temperature on diaspore and kaolinite flotation with NaOl (pH = 10, dosage = 0.1 mM) or NaOl/TDM (pH = 9, dosage = 0.1 mM, NaOl:TDM mole ratio = 8:2).

In order to further explore the flotation effect of NaOl/TDM at low temperatures, the separation effect of NaOl/TDM on mixed minerals of diaspore and kaolinite at specific pH values at 283 K was studied. Figure 5 shows the separation results of mixed minerals as a function of pH at 283 K. As shown in Figure 5, the recovery of Al_2O_3 using NaOl first increases and then decreases with the increase in pH. When the pH is 10, it reaches the maximum of 70.99%. The A/S of the concentrate decreases with the increase in the pH value. When the pulp pH increases from 8 to 11, the A/S decreases from 11.35 to 8.93. When NaOl/TDM is used, the recovery of Al_2O_3 first increases and then decreases with the increase in pH. When the pH is 9, it reaches the maximum value of 73.55%. The A/S of the concentrate decreases with the increase in the pH value. When the pulp pH increases from 8 to 11, the A/S decreases from 13.05 to 10.75. By comparing the recovery and A/S of Al_2O_3 treated by NaOl (pH = 10) and NaOl/TDM (pH = 9), the A/S ratios of the concentrate are 9.75 and 11.85, respectively, and the recovery of Al_2O_3 with NaOl/TDM is 2.56%—higher than that of NaOl. The flotation test of mixed binary minerals further proves that, compared with NaOl, NaOl/TDM can better realize the effective separation of diaspore and kaolinite at low temperatures.

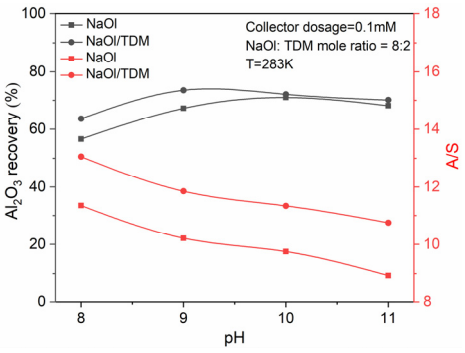

Figure 5. Separation results of mixed minerals under the action of the NaOl (pH = 10, dosage = 0.1 mM) or NaOl/TDM (pH = 9, dosage = 0.1 mM, NaOl:TDM mole ratio = 8:2) collector at 283 K.

3.2. Surface Tension Measurements

The surface tension of the collector is one of the parameters to measure collector performance in flotation. The surface tensions of NaOl, TDM and NaOl/TDM at different concentrations at 283 K were measured, and the concentration-related function is plotted in Figure 6. The following relations—1–3—are used to calculate the different surface and micelle formation parameters of the three collectors at 283 K. All parameters are shown in Table 2.

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{\partial\gamma}{\partial logC}\right)_T \times 10^{-3} \quad (1)$$

$$A_{min} = \frac{10^{18}}{\Gamma_{max}N_A} \quad (2)$$

$$\Delta G_m^0 = RTlnX_{CMC} \quad (3)$$

where the value 2.303 is the approximate value of ln (10), n is 1 for mixed-collector systems and 2 for single-collector systems [20], R is the universal gas constant (8.31 J $mol^{-1}{\cdot}K^{-1}$), T is the absolute temperature (298.15 K), $(\partial\gamma/\partial logC)_T$ is the slope of the linear portion of the curve below the critical micelle concentration (CMC) at 283 K [21], N_A is the Avogadro number (6.02×10^{23} molecules), X_{CMC} is the measured critical micelle concentration (CMC) value [22], Γ_{max} is in (mol/m^2), A_{min} is in nm^2 and $-\Delta G_m^0$ is in kJ/mol.

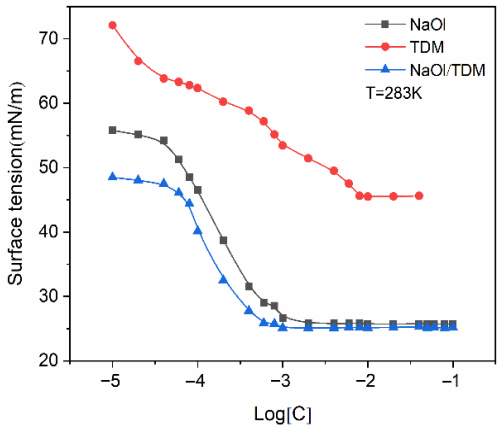

Figure 6. Surface tension for the individual collectors NaOl and TDM and the mixed collector NaOl/TDM at 283 K.

Table 2. Surface and thermodynamic properties of NaOl, TDM and NaOl/TDM at 283 K.

Surfactants	CMC(mol/L)	γ_{CMC}(mN/m)	Γ_{max}(mol/m^2)	A_{min}(nm^2)	$-\Delta G_m^0$(kJ/mol)
NaOl	2×10^{-3}	25.87	8.84×10^{-7}	1.88	14.62
TDM	8×10^{-3}	45.61	2.01×10^{-6}	0.83	11.36
NaOl/TDM	1×10^{-3}	25.13	1.55×10^{-6}	1.07	16.25

As shown in Figure 6, the CMC and γ_{CMC} of TDM are relatively large, indicating that its surface hydrophobicity is weak and that its surface activity is relatively low. This also explains the low flotation recovery when TDM is used as a single collector at low temperatures. By comparing the surface tension curves of the NaOl and NaOl/TDM solutions, the mixed collector NaOl/TDM is found to be more efficient than the single collector NaOl in decreasing the air−water interfacial tension, particularly in low surfactant concentration conditions. This shows that the formation of the micelle effect of the mixed collector NaOl/TDM has a synergistic effect, which improves the reagent activity at low temperatures and improves the flotation effect.

The saturation adsorption value (Γ_{max}) and average minimum area per molecule (A_{min}) are considered to be important indicators in evaluating the molecular bulk density

of collectors at the air–liquid interface [23]. Generally speaking, the larger the Γ_{max} value or the smaller the A_{min} value of the collector, the denser the molecular arrangement of the collector on the air–water interface. In Table 2, the Γ_{max} value and A_{min} value of the mixed collector NaOl/TDM are respectively greater than and less than those of NaOl as a collector alone, which indicates that the density of the reagent molecules in the mixed collector system is higher than that in the NaOl system at 283 K. The order of the standard Gibbs free energy change for micelle formation at CMC ($-\Delta G_m^0$) of the three surfactants is NaOl/TDM > NaOl > TDM at 283 K. The $-\Delta G_m^0$ value of the mixed collector is the lowest, which indicates that the hydrophobic association and collection ability of the mixed collector are better than those of a single collector at 283 K.

3.3. Zeta Potential Determinations

Zeta potential determinations before and after the interaction between minerals and reagents is an effective means to find the changes in the electrical properties on the mineral surface, explain the adsorption phenomenon and analyze the adsorption mechanism. The Zeta potentials of diaspore and kaolinite in the presence of various flotation reagents at 283 K are shown in Figures 7 and 8. In the absence of a collector, the isoelectric points (IEP) of diaspore and kaolinite are found to be pH 6.9 and 3.8, respectively, which agree with the previous investigations [1,24,25].

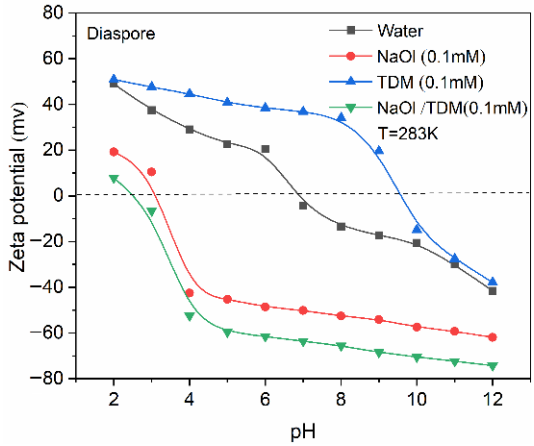

Figure 7. Zeta potentials of diaspore in the presence of various flotation reagents at 283 K.

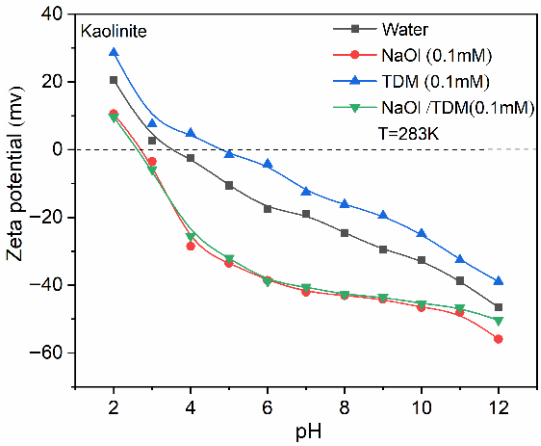

Figure 8. Zeta potentials of kaolinite in the presence of various flotation reagents at 283 K.

As shown in Figures 7 and 8, in the presence of NaOl, the Zeta potentials of diaspore and kaolinite are shifted negatively, which indicates that NaOl is adsorbed on the surface of diaspore and kaolinite. Moreover, the decrease in the Zeta potentials of diaspore is greater

than that of kaolinite, which means that NaOl has a stronger affinity for diaspore than kaolinite. When TDM is added alone, the Zeta potentials of diaspore and kaolinite are shifted positively, indicating that TDM is adsorbed on the surfaces of the two minerals. In the presence of the mixed collector NaOl/TDM, the Zeta potential of diaspore is more negative than that of NaOl alone, indicating that the interaction between the mixed collector NaOl/TDM and the diaspore surface is stronger. After the addition of the mixed collector NaOl/TDM, the Zeta potential on the surface of kaolinite is shifted slightly positive compared to that of NaOl alone, indicating that the interaction of the mixed collector NaOl/TDM on the surface of kaolinite is weaker than that of NaOl alone. This may be because the adsorption of TDM on the kaolinite surface in the NaOl/TDM collector is very weak and affects the adsorption of NaOl on the kaolinite surface.

3.4. XPS Analysis

XPS analysis can determine the chemical states of mineral surface elements, which is of great significance in analyzing the adsorption phenomenon on the mineral surface in the process of flotation. In order to further explore the adsorption mechanism of three reagents on the mineral surface, the atomic compositions of the diaspore and kaolinite interfaces treated or untreated by NaOl or NaOl/TDM are listed in Table 3, and the binding energy of Al 2p in the diaspore and kaolinite samples before and after the adsorption of the collector was measured by XPS analysis, as shown in Figures 9 and 10.

Table 3. Atomic concentration of elements for mineral interfaces, as determined by XPS at 283 K.

Samples	Atomic Concentration of Elements (Atomic %)				
	C	O	Al	Si	S
Diaspore	18.58	57.37	19.71	4.33	-
Diaspore + NaOl	47.51	36.22	12.96	3.31	-
Δ^a	28.93	−21.15	−6.75	−1.02	-
Diaspore	18.58	57.37	19.71	4.33	-
Diaspore + NaOl/TDM	53.42	32.52	11.45	2.45	0.17
Δ^a	34.84	−24.85	−8.26	−1.88	-
Kaolinite	10.14	61.38	13.21	15.27	-
Kaolinite + NaOl	21.26	53.16	12.16	13.42	-
Δ^a	11.12	−8.22	−1.05	−1.85	-
Kaolinite	10.14	61.38	13.21	15.27	-
Kaolinite + NaOl/TDM	21.29	52.83	12.34	13.47	0.08
Δ^a	11.15	−8.55	−0.87	−1.80	-

Δ^a is defined as the value before treatment minus that of the NaOl or NaOl/TDM treatment.

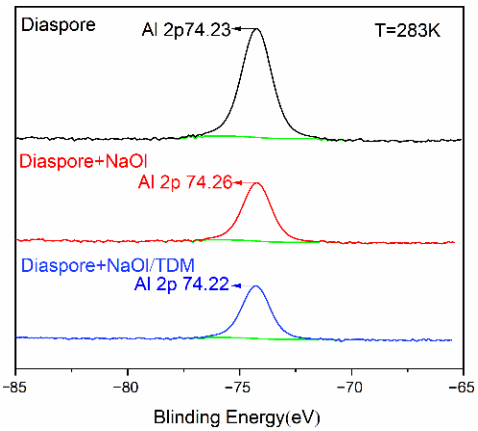

Figure 9. XPS spectra of the Al 2p layer of diaspore with different collectors at 283 K.

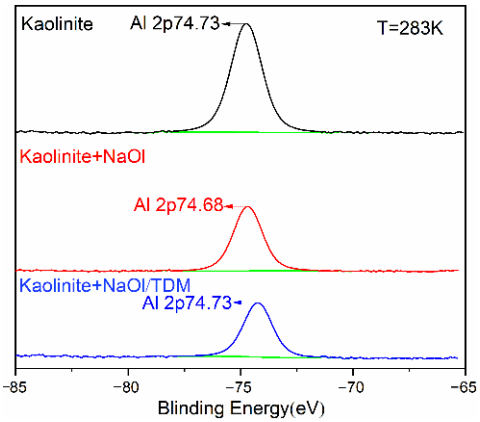

Figure 10. XPS spectra of the Al 2p layer of kaolinite with different collectors at 283 K.

Table 3 shows that, after NaOl treatment, the atomic concentrations of O, Al and Si decrease, and the atomic concentration of C increases at 283 K. Therefore, it is inferred that NaOl can adsorb on the surface of diaspore and kaolinite at 283 K. The change values of the atomic concentrations of C, O and Al on the surface of diaspore are much larger than those on the surface of kaolinite, which indicates that the adsorption capacity of NaOl on the surface of diaspore is higher than that of kaolinite at 283 K. This is consistent with the previous results of the Zeta potential measurements. Compared with diaspore treated by NaOl alone, the atomic concentrations of C, O, Al and Si on the surface of diaspore change more after the NaOl/TDM treatment at 283 K, which shows that the total adsorption capacity of NaOl/TDM is higher than that of NaOl alone at low temperatures. On the contrary, the change value of the atomic concentrations of C, O, Al and Si on the surface of kaolinite after the NaOl/TDM treatment at 283 K is very similar to that of NaOl, which indicates that the collection capacity of the mixed collector NaOl/TDM on kaolinite is not improved compared with that of NaOl. In addition, the atomic concentration of S detected on the surface of diaspore and kaolinite is very low, which indicates that the TDM in the mixed collector NaOl/TDM has adsorption on the mineral surface, but its adsorption capacity is limited.

Figure 9 displays a peak of diaspore at 74.23 eV. When diaspore is treated by NaOl at 283 K, the peak has no obvious shift. This shows that the adsorption of NaOl on the surface of diaspore is not chemical adsorption at 283 K but may be caused by hydrogen bonding, which is consistent with the conclusions of other researchers [21]. When diaspore is treated by NaOl/TDM at 283 K, the peak still has no obvious shift. This shows that the adsorption form of the mixed collector NaOl/TDM on the diaspore surface is not chemical adsorption. It may be that the formation of the mixed collector NaOl/TDM micelle effect has a synergistic effect, which improves the agent activity at low temperatures and enhances the interaction of the hydrogen bond between NaOl/TDM and diaspore.

For kaolinite, as shown in Figure 10, after NaOl treatment, the peak appears at 74.68 eV, which is almost unchanged from the original peak at 74.73 eV. In addition, after NaOl/TDM treatment, the peak appears at 74.73 eV, and there is still no significant change. This shows that the addition of TDM cannot change the adsorption form of NaOl on the surface of kaolinite at 283 K.

4. Conclusions

In this study, the effect of a new mixed collector, NaOl/TDM (the molar ratio 8:2 of NaOl:TDM), on the separation of diaspore and kaolinite at 283 K was investigated. The properties of the mixed collector NaOl/TDM and its adsorption mechanism on diaspore and kaolinite were studied by surface tension tests, Zeta potentials and XPS analysis. According to the experimental results, the following conclusions can be drawn:

The flotation results show that the mixed collector NaOl/TDM has a good collection ability for diaspore and a good selectivity for kaolinite at low temperatures. The NaOl/TDM collector can effectively separate diaspore and kaolinite under alkaline conditions at 283 K.

The results of the surface tension tests show that the molecular density, hydrophobic association ability and collection ability of the mixed collector NaOl/TDM are better than those of the single collector at 283 K. In addition, the formation of the micelle effect of the mixed collector NaOl/TDM has a synergistic effect, which improves the reagent activity at low temperatures and improves the flotation effect.

The results of the Zeta potentials and the XPS analysis show that the total adsorption capacity of the mixed collector NaOl/TDM on the surface of diaspore at low temperatures is higher than that of NaOl, and the adsorption capacity on the surface of kaolinite is similar to that of NaOl. The mixed collector NaOl/TDM may be adsorbed on the surface of diaspore and kaolinite by a hydrogen bond at 283 K.

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