Application and Mechanism of Mixed Anionic/Cationic Collectors on Reverse Flotation of Hematite

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Abstract: In order to enhance the reverse flotation effect of hematite, dodecyl trimethyl ammonium chloride (DTAC) and a mixed anionic/cationic collector of DTAC and tall oil were selected for flotation studies on quartz and hematite. Surface tension tests, FT-IR, XPS analysis, and molecular dynamics (MD) simulations were also conducted in order to investigate the interaction mechanism of the mixed collector on the quartz surface. The results revealed that, at a natural pH (approximately 7.0) and 298 K, and with a dosage of 20 mg/L for the mixed collector (m_DTAC:m_tall oil = 3:1) and 4 mg/L for causticized starch, the recovery rates of quartz and hematite were 94.67% and 8.69%, respectively. Compared to the use of a single DTAC, the mixed DTAC/tail oil collector enhanced the flotation effect under constant variables. Additionally, a comparison of temperature and surface tension for monomineral flotation and artificially mixed ore flotation tests showed that the mixed collector was less influenced by temperature, compared to the single DTAC, and exhibited good resistance and more effective separation of quartz and hematite at lower temperatures. The analysis of FT-IR, XPS, and MD simulations revealed that the single DTAC collector primarily adsorbed onto quartz through physical adsorption and hydrogen bonding, while the combination of tall oil and DTAC enhanced the adsorption of the collector on the quartz surface.

Keywords: quartz; hematite; mixed collector; reverse flotation; molecular dynamics simulation

1. Introduction

Steel is widely used in the daily lives of human beings, as transportation, housing construction, and home appliance manufacturing, among other industries, all rely heavily on the supply of the steel industry. The rapid expansion of the steel industry is inevitably leading to a surge in the consumption of iron ore resources, with nearly 98% of the world’s iron ore being utilized for steel production [1]. Currently, the depletion of easily accessible high-grade iron ore reserves has prompted the exploration for alternatives in deeper, lower-to intermediate-grade ores, which are complex and challenging to process in order to satisfy increasing demands [2–4]. Research on the technology of “iron extraction and silicon reduction” has pointed out the development direction for improving the separation index of iron ore in China and reducing production costs. In recent years, through the concerted efforts of mineral processing professionals, significant progress has been made in the beneficiation technology of low-grade hematite. The key technologies of “iron extraction and silicon reduction” include the applications of reverse flotation technology, new magnetic separation equipment, and fine sieve technology, as well as the employment of flotation columns. Among these technologies, the application of reverse flotation technology is the research focus in the field of iron ore flotation.

Reverse flotation technologies include anionic reverse flotation and cationic reverse flotation [5,6]. Anionic reverse flotation was initially developed in China, where anionic collectors selectively adsorb onto the surface of iron ore through specific chemical reactions, enabling the separation of ore from gangue [7]. Oleic acid, among other fatty acid anionic
surfactants, is often used. Studies have shown that, when Ca$^{2+}$ is used as an activator, NaOL shows good harvesting and selectivity to quartz under pH conditions of about 11.5. However, the chemical system of anionic reverse flotation technology is more complex; the slurry needs to be heated to more than 308 K under industrial conditions, the production cost is high, and a higher pH corrodes the equipment [8,9]. Advancements in research reveal that cationic collectors excel in treating certain iron ores, leading reverse flotation technology to focus on optimizing processes and procedures, enhancing concentrated iron quality, increasing recovery rates, and reducing harmful impurities, such as phosphorus and sulfur, thus surpassing other beneficiation methods [10]. In iron ore cationic reverse flotation, the commonly used cationic reverse flotation collector is mostly dodecyl amine, which is different from that used in anionic reverse flotation technology; when using cationic reverse flotation technology to separate quartz and iron minerals, no additional activator is needed to show good recovery of quartz under weak alkaline conditions, but selectivity is poor and the cost is high. In addition, due to the strong frothing ability of dodecyl amine, the problem of defrothing also needs to be solved urgently [11–13]. With the continuous improvement in energy conservation and environmental protection requirements, the problems of both high preparation temperatures and high-use temperatures for iron ore flotation reagents have become increasingly prominent, seriously restricting the development of domestic iron mines. In recent years, through a large number of studies on iron ore reverse flotation technology, it has been found that research on flotation reagents, especially high-efficiency collectors, is still key to improving flotation efficiency. Some novel collecting agents exhibit excellent selectivity, but are challenging and costly to synthesize, while the use of a mixed collector not only minimizes reagent consumption and production costs but also addresses the shortcomings associated with using a single reagent, thereby further boosting flotation efficiency [14–16]. For example, Yang et al. [17] found that the mixed collector of sodium oleate–benzohydroxamic acid (NaOL–BHA), at a molar ratio of 4:1, exhibited excellent performance in the flotation separation of ilmenite from titanaugite. Tian et al. [18] demonstrated that, in the processing of lithium pegmatite ore, utilizing a combination of mixed anionic/cationic collectors, SX (laurylamine and oxidized paraffin wax soap) and MOD (laurylamine and naphthenic acid soap), led to the enhanced grade and recovery of Li$_2$O in spodumene concentrates, achieving levels of 6.02% and 87.34%, respectively.

In this study, reverse flotation tests were carried out on hematite and quartz with dodecyl trimethyl ammonium chloride (DTAC) and an anionic and cationic mixed collector mainly based on DTAC; the flotation behaviors of quartz and hematite under different pH, dosages, depressors, and temperatures, were compared and investigated, and then a surface tension test, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and molecular dynamics simulations were conducted in order to compare and analyze the mixed collector’s mechanism of action, which provided a theoretical basis for the reverse flotation separation of quartz and hematite at room, or low temperature.

2. Materials and Methods
2.1. Mineral Samples and Reagents

The samples of hematite and quartz used in the experiments were high-purity lump ores, purchased from the market, crushed, hand-separated, and ground with an iron hammer. Subsequently, they were screened and graded using 75 µm and 38 µm Taylor standard sieves. The ore samples with particle sizes of $-75 + 38$ µm were utilized for flotation tests, while ore samples with a particle size of $-38$ µm were employed for analysis and detection. The material compositions and surface properties of the hematite and quartz monomineral samples of the two particles’ sizes were identical. The X-ray fluorescence (XRF) analysis and X-ray diffraction (XRD) analysis results of quartz and hematite are shown in Table 1, Figure 1, and Figure 2. The results indicated that the purity of the test ore samples exceeded 95%, thus meeting the requirements of the monomineral test.
Table 1. Chemical compositions of quartz and hematite (%).

<table>
<thead>
<tr>
<th>Minerals</th>
<th>TFe</th>
<th>FeO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>68.43</td>
<td>0.75</td>
<td>0.59</td>
<td>3.54</td>
<td>0.05</td>
<td>-</td>
<td>97.84</td>
<td>0.03</td>
<td>0.13</td>
</tr>
<tr>
<td>quartz</td>
<td>-</td>
<td>-</td>
<td>1.21</td>
<td>98.36</td>
<td>0.18</td>
<td>0.036</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

TFe is the total amount of iron, determined through the chemical analysis of ore samples.

Figure 1. XRD patterns of quartz.

Figure 2. XRD patterns of hematite.

The DTAC and pH adjusters (NaOH and HCl) used in the test were all analytically pure, the causticized corn starch (corn starch and sodium hydroxide, mixed with sodium hydroxide according to a certain mass ratio, and causticized in a water bath at about 363 K for 30 min) was made with industrial-grade products, and the mixed collector of tall oil and DTAC (hereinafter referred to as “the mixed collector”) was laboratory-prepared at a mass ratio of 1:3 and subsequently utilized. Deionized water (18.2 MΩ·cm) was used for both the flotation tests and the investigation of the agent’s mechanism of action.

2.2. Micro-Flotation Tests

The flotation experiment was carried out using an XFG hanging tank flotation machine (Figure 3) from the Jilin Exploration Machinery Plant in Changchun, China, with a spindle speed of 1992 r/min. Each time, 3.0 g of the monomineral quartz or hematite was weighed and placed in a 50 mL flotation tank, and an appropriate amount of DI water was added and mixed for 2 min. Thereafter, the pH was adjusted with HCl or NaOH for 2 min. The
depressor was added and allowed to act for 3 min (this step was only required for depressor tests, not for other condition tests). Collectors were then added and allowed to act for 2 min. Subsequently, the froth was scraped for 5 min. After the flotation process was complete, the froth product and the product in the tank were filtered, dried, and weighed, and the recovery value was calculated. The flotation test process is shown in Figure 4.

![Diagram of the XFG flotation machine and flotation cell](image)

**Figure 3.** (a) Diagram of the XFG flotation machine; (b) flotation cell.

**Figure 4.** Flotation flowsheet of micro-flotation tests and artificially mixed mineral flotation tests.

### 2.3. Flotation Experiments of Artificially Mixed Minerals

In artificially mixed mineral flotation experiments, the weight ratio of hematite to quartz in the raw ore was 2.66: 0.34. The total iron (TFe) grade of the artificially mixed mineral was approximately 60.67%. The slurry mixing process mirrored that of the monomineral flotation, as depicted in Figure 4. The concentrate and tailings were filtered and dried. Post-flotation, the TFe grade was analyzed, and the recovery value was calculated using Equations (1) and (2):

\[
\gamma = \frac{M_1}{M_1 + M_2} \times 100\% \tag{1}
\]

where, “\(\gamma\)” is the flotation productivity, /%; “\(M_1\)” is the concentrate mass /g; “\(M_2\)” is the tailing mass /g. Equation (2) is as follows:

\[
\epsilon = \frac{\beta_1}{\beta_0} \times 100\% \tag{2}
\]

where, “\(\epsilon\)” is the flotation recovery, /%; “\(\beta_1\)” is the concentrate grade, /%; “\(\beta_2\)” is the artificially mixed mineral grade, /%.
2.4. Surface Tension Test

The surface tension of the solution was determined using the BZY-2 surface tension meter, employing the platinum plate method. When the platinum plate was immersed in the liquid to be measured, it was affected by the pull-down effect of the surface tension of the solution. Once equilibrium was achieved, the instrument provided the surface tension value corresponding to the immersion depth of the platinum plate. Each measurement was replicated five times, and the average was calculated.

2.5. Fourier Transform Infrared Spectroscopy Measurements

FT-IR of the samples was measured with a Nicolet 380 FT-IR analyzer (Thermo Fisher, Waltham, MA, USA) using the pellet method. The mineral sample, with a particle size of −38 µm, was placed in a flotation cell and prepared according to the flotation process shown in Figure 3. Following three washes with deionized water and filtration, the sample was dried in a vacuum drying oven before being submitted for FT-IR analysis. The spectral wavenumber range was set from 4000 to 400 cm$^{-1}$, and the solids spectrum was measured using the disk method, with KBr as the matrix [19,20].

2.6. X-ray Photoelectron Spectroscopy (XPS) Measurements

X-ray photoelectron spectroscopy (XPS) analysis samples were prepared following the same procedure as for FT-IR analyses. Detection was performed utilizing a Thermo Scientific K-Alpha X-ray photoelectron spectrometer, fitted with Advantage software, and calibrated based on a 284.80 eV C1s spectrum.

2.7. Molecular Dynamics Simulation

Molecular simulations were primarily conducted using Material Studio 2019 software, with a focus on the Dmol3 module. The collector molecule was chosen to adsorb on the (101) surface of quartz, referencing the existing literature [21–26]. In the Forcite module, an extended optimized surface unit cell of 2 × 3 × 1 was established, based on the COMPASS force field, with a vacuum layer thickness of 30 Å. The optimized crystal structure of quartz and the molecular structure of collectors are shown in Figures 5–7.

The optimized agent molecules were placed on the surface of the quartz mineral, and geometric optimization was carried out again in order to determine the adsorption model of the collector. The adsorption energy and geometric configuration were used to predict and analyze the interaction mechanism between the collector and the quartz mineral surface. The interaction energy is calculated as follows:

$$E_{ads} = E_{surf/dep} - E_{surf} - E_{dep}$$

(3)

where $E_{ads}$ is the adsorption energy of the collector and quartz mineral surface; $E_{surf/dep}$ is the energy of the optimized system; $E_{surf}$ is the total energy of quartz before and after adsorption by the collector; $E_{dep}$ is the total energy of free collector molecules. A negative value of the interaction energy indicates the force of attraction between the mineral and the reagent, while a positive value indicates repulsion between the mineral and the reagent. The lower the $E_{ads}$ value, the stronger the adsorption effect of the agent molecules on the surface of quartz minerals, while a positive $E_{ads}$ value indicates that adsorption between the agent molecules and the surface of quartz minerals does not occur [27].
The relationships between the recovery rates of quartz and hematite and the pH of the slurry are shown in Figure 8, where it can be seen that the recovery rates of quartz and hematite initially increased, and then decreased with a rise in pH under the same collector dosage conditions. The pH significantly influenced the recovery of quartz, with both collectors demonstrating good capture performance for quartz at pH levels between 3 and 10. The mixed collector exhibited relatively better recovery performance, achieving a quartz recovery value of up to 97.84%. In the pH range tested, both collectors displayed poor recovery performance for hematite. When compared to using a single DTAC, the mixed collector resulted in lower hematite recovery values, approximately 15%. Notably,
in neutral and weakly alkaline slurry environments, both DTAC and the mixed collector effectively separated both hematite and quartz. In the comparative analysis, it was found that, under the same dosage conditions, the mixed collector exhibited higher selectivity, had a broader pH adaptability range, and was more conducive to the separation of quartz and hematite. Subsequent experiments were carried out without adding a pH adjuster, maintaining a natural pH (approximately 7.0) environment.

Figure 8. Effect of pH on flotation recovery rates of quartz and hematite using different collectors.

The relationship between the dosages of DTAC and the mixed collector on the recovery rate of quartz under the natural pH (approximately 7.0) condition of the slurry is shown in Figure 9. It was observed that the recovery rates of quartz and hematite increased as the dosage was raised within the measured range, and when the dosage of the agent was ≥20 mg/L, the recovery value of quartz in both collector systems exceeded 90%, with the recovery value using the mixed collector significantly surpassing that with the single DTAC. Compared with the mixed collector, DTAC had a greater impact on the recovery value of hematite with an increase in the collector dosage. The selectivity of the mixed collector was noted to be stronger than that of DTAC, with relatively good selectivity at 20 mg/L.

Figure 9. Effect of collector dosage on flotation recovery value of quartz and hematite under natural pH condition.
Figure 10 shows the effect of the causticized corn starch dosage on the recovery rates of quartz and hematite under the conditions of natural pH (approximately 7.0), fixed DTAC, and a mixed collector dosage of 20 mg/L, and it was observed that, as the dosage of causticized corn starch increased, the recovery rates of both quartz and hematite exhibited decreasing trends. The influence of the causticized corn starch dosage on the floatability of minerals remained consistent for both agents. The impact of causticized corn starch on the recovery of quartz was not pronounced. At a causticized corn starch dosage of 4 mg/L, the recovery rate of hematite was approximately 10%, and the recovery value showed minimal variation with further increases in starch dosage. As the causticized corn starch dosage increased, from 0 to 4 mg/L, the recovery value of hematite decreased, by approximately eight percentage points, to 8.69%. Subsequent increases in the amount of causticized corn starch did not significantly alter the recovery value of hematite. In the comparative analysis, it was found that, under other identical conditions, the addition of depressors had a greater impact on the flotation recovery of hematite. Furthermore, this study revealed that the addition of depressors was more beneficial for enhancing the selectivity of the mixed collector.

![Graph showing the effect of corn starch dosage on flotation recovery values of quartz and hematite under natural pH condition.](image-url)

**Figure 10.** Effect of corn starch dosage on flotation recovery values of quartz and hematite under natural pH condition.

Figure 11 shows the effects of temperature on the recovery values of quartz and hematite under the natural pH condition (approximately 7.0) of the slurry, fixed DTAC, and a mixed collector dosage of 20 mg/L. As shown in Figure 11a, as the temperature decreased, the impact of the mixed collector on the recovery value of quartz was minimal, remaining around 90%. In contrast, the single DTAC collector exhibited a more pronounced effect on the recovery value of quartz with temperature variations, dropping below 80% when the temperature was below 283 K. In Figure 11b, the recovery value of hematite showed insignificant changes with temperature variations under the mixed collector system and slight decreases with decreasing temperature under the single DTAC collector system. Combined with Figure 11a,b, it can be inferred that the single DTAC was more sensitive to slurry temperature, and the mixed collector was less influenced by temperature, demonstrating good adaptability to low-temperature conditions.
3.2. Flotation Test of Artificially Mixed Minerals

The monomineral flotation test indicated that, in comparison to the single DTAC, the mixed collector showed better low-temperature flotation performance. To further validate this conclusion, an artificially mixed mineral flotation test was conducted at various temperatures. The test results are shown in Table 2.

Table 2. Flotation index of artificially mixed ore (the mixed collector: 20 mg/L; DTAC: 20 mg/L; corn starch: 4 mg/L).

<table>
<thead>
<tr>
<th>Collector</th>
<th>Temperature, K</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Grade, TFe (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The mixed collector</td>
<td>298</td>
<td>Concentrate</td>
<td>88.72</td>
<td>66.49</td>
<td>97.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tailing</td>
<td>11.28</td>
<td>14.90</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>60.67</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>Concentrate</td>
<td>88.98</td>
<td>66.27</td>
<td>97.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tailing</td>
<td>11.02</td>
<td>15.47</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>60.67</td>
<td>100.00</td>
</tr>
<tr>
<td>DTAC</td>
<td>298</td>
<td>Concentrate</td>
<td>90.00</td>
<td>65.21</td>
<td>96.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tailing</td>
<td>10.00</td>
<td>19.84</td>
<td>3.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>60.67</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>Concentrate</td>
<td>91.12</td>
<td>63.04</td>
<td>94.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tailing</td>
<td>8.88</td>
<td>36.35</td>
<td>5.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>60.67</td>
<td>100.00</td>
</tr>
</tbody>
</table>

As shown in Table 2, the selectivity and harvesting performance of the mixed collector were found to be stronger than those of the single DTAC when a depressor was added and other conditions remained unchanged, which corresponds to the monomineral flotation test. When the mixed collector was chosen for the reverse flotation of the artificial mixture, the flotation index of the concentrate showed minimal variation at 288 K and 298 K, with a flotation recovery value of approximately 97.20%. In contrast, when the single DTAC was used as the collector, the agent selection and capture performance decreased at 288 K, leading to a decrease in the TFe grade, by around two percentage points. These results confirmed that the mixed collector performed better than DTAC for flotation at lower temperatures.

3.3. The Effect of Temperature on the Surface Tension of the Collector

The surface tension values of the DTAC solution and the mixed collector at 298 K are shown in Figure 11. In comparison with the single DTAC system (12.94 mN/m,
1.00 g/L), the minimum surface tension and CMC value of the mixed collector system (13.64 mN/m, 0.015 g/L) were slightly lower, indicating higher surface activity and better foaming properties, but with a larger CMC value and weaker flotation capture capacity. The former exhibited lower surface tension and CMC values, and better hydrophobic performance of the agent, suggesting that the combined system had a better capture capacity, compared to a single agent, which is consistent with the flotation results. Therefore, concentrations of 0.015 g/L for the mixed collector solution and 1.00 g/L for the DTAC solution were determined as the optimal concentrations for further experimentation [7]. As shown in Figure 13, the surface tension decreased from 21.24 mN/m to 16.64 mN/m (13.64 mN/m, 0.015 g/L) were slightly lower, indicating higher surface activity and better hydrophobic capacity, compared to a single agent, which is consistent with the flotation results. Therefore, concentrations of 0.015 g/L for the mixed collector solution and 1.00 g/L for the DTAC solution were determined as the optimal concentrations for further experimentation [7].

To further investigate the adsorption mode of the mixed collector on the quartz surface, the infrared spectra of quartz, DTAC, and the agent before and after interaction were analyzed. The results are shown in Figure 14. From the figure, it can be observed that the characteristic wavenumbers of quartz were 1880.26, 1081.48, 796.32, 692.22, and 459.69 cm⁻¹. Among them, 1880.26 cm⁻¹ corresponded to the tensile peak of the silicon/oxygen tetrahedron, 1081.48 cm⁻¹ corresponded to the asymmetrical stretching vibration absorption peak...
of Si-O, and 796.32 and 692.22 cm\(^{-1}\) corresponded to the symmetrical stretching vibration absorption peak of Si-O-Si.

![Figure 14. FT-IR spectra of quartz before and after treatment with reagents.](image)

After the action of DTAC, characteristic peaks of DTAC were observed at 3018.76, 2919.38, 2848.98, and 1631.86 cm\(^{-1}\). Specifically, the peak at 3018.76 cm\(^{-1}\) corresponded to the symmetrical stretching vibration absorption peaks of unsaturated -CH, while the peaks at 2919.38 cm\(^{-1}\) and 2848.98 cm\(^{-1}\) were attributed to the asymmetric and symmetrical stretching vibration absorption peaks of -CH\(_2\) and -CH\(_3\) from DTAC, respectively, indicating the occurrence of DTAC adsorption on the quartz surface. Additionally, the bending vibration absorption peak of -OH in \(\equiv\text{SiOH}\) on the quartz surface at 1631.86 cm\(^{-1}\) became more prominent, possibly due to the formation of strong hydrogen bonds between the -NH groups in the reagent structure and the O atoms or -OH groups in the \(\equiv\text{SiOH}\) groups on the quartz surface. When quartz was treated with the mixed collector, the same absorption peak appeared as that observed after DTAC action, indicating that physical adsorption and hydrogen bonding action also took place on the surface of the quartz with the mixed collector. However, the intensity of the peaks was more pronounced, and the peak shape around 1081 cm\(^{-1}\) was wider compared to that of quartz after DTAC action, suggesting stronger adsorption of the mixed collector on the surface of the quartz mineral.

3.5. XPS Analysis

XPS tests are utilized to accurately determine the chemical environment in which an element is exposed and its content. To further investigate the adsorption mechanism of the mixed collector on the quartz surface, XPS tests were conducted on the quartz samples both before and after adsorption. The displacement of the binding energy of the elements present in the mixed collector and the alterations in the relative concentration of each atom were analyzed in detail.

Table 3 reveals a decrease in Si content, an increase in C and O content, and the presence of N in both quartz and the collector, indicating the occurrence of agent adsorption on the mineral surface. Among them, the N elements on the quartz surface following the action of the mixed collector and DTAC were 0.66 and 0.26, respectively (exceeding the instrument error). The N concentration on the quartz surface treated with the mixed collector was significantly higher than that on the quartz surface treated with DTAC, demonstrating the superior adsorption capacity of the mixed collector on the quartz surface compared to that of DTAC. This finding supported the enhanced capture performance of the mixed collector, aligning with the flotation outcomes of the monomineral test.
To further investigate the adsorption mechanism of the mixed collector on the quartz surface, a narrow spectrum of N1 elements was depicted, as illustrated in Figure 15. In Figure 15a, no N1 peaks were observed in the narrow spectrum of pure quartz minerals. Upon the introduction of a single DTAC collector, new peaks emerged. One peak appeared around 398.07 eV, with a relative content of 0.18%, associated with the neutral dodecyl molecule (R) interacting with the quartz mineral surface, primarily through hydrogen bonding; another peak, at approximately 400.03 eV, with a relative content of 0.08%, was linked to the protonated dodecyl group (RNH$_3^+$) interacting with the quartz mineral surface, mainly through physical adsorption [28]. A comparison of Figure 15b,c revealed that, upon the simultaneous addition of tall oil, no new peaks surfaced. The binding energies of the two peaks were 398.05 eV and 401.05 eV, with relative contents of 0.46% and 0.20%, respectively, remaining largely unchanged compared to the addition of a single DTAC collector (within the instrument error range). This suggests that the addition of tall oil did not involve chemical adsorption with the quartz surface. Nonetheless, the total relative N content in quartz treated with the mixed collector, as shown in Table 3, increased to 0.66%, nearly three times that of N after treatment with a single DTAC, indicating a greater adsorption capacity of the mixed collector on the quartz mineral surface. This finding aligned with the results from infrared spectroscopy.

![Figure 15](image.png)

**Figure 15.** N1 spectra on the surface of a quartz sample treated under (a) deionized water, (b) DTAC, and (c) the mixed collector.

### 3.6. DFT Analyses

The adsorption behaviors of DTAC and the mixed collector on the quartz surface were compared and analyzed using MS. Four reagent molecules were introduced to the quartz (101) surface and optimized geometrically with the Forcite module. The van der Waals force and electrostatic energy were calculated utilizing the atomic and the Ewald summation methods. The most stable configurations, as shown in Figure 16a,b, were selected based on the minimum adsorption energy. It is important to note that, since this reverse flotation process is primarily conducted in a natural solution (approximately 7.0), the agent model chosen for the MD simulation consisted of dissociated anionic surfactant ions and undissociated DTAC molecules.
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From Figure 17a,b, it can be seen that the hydrophilic head group of DTAC exhibited uniform and stable adsorption on the quartz surface, with the hydrophobic carbon chains clustering accordingly. The aggregation phenomenon in Figure 17b was more pronounced. When combined with the results from Table 4, it became apparent that both collectors adsorbed onto the quartz mineral surface. Specifically, the adsorption energy of the mixed collector on the quartz surface was $-52.16 \text{ kcal/mol}$ higher than that of DTAC ($-35.10 \text{ kcal/mol}$) on the mineral surface, indicating stronger adsorption of the mixed collector on quartz. This observation suggested that the total adsorption energy of the collector could be significantly enhanced through co-adsorption, a finding consistent with the results of the FT-IR and XPS analyses.

<table>
<thead>
<tr>
<th>Collector</th>
<th>$E_{\text{ads}}$ (kJ/mol)</th>
<th>$E_{\text{surf/dep}}$ (kJ/mol)</th>
<th>$E_{\text{surf}}$ (kJ/mol)</th>
<th>$E_{\text{dep}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The mixed collector</td>
<td>$-52.16$</td>
<td>$-7093.30$</td>
<td>$-6787.48$</td>
<td>$-253.66$</td>
</tr>
<tr>
<td>DTAC</td>
<td>$-35.10$</td>
<td>$-7110.72$</td>
<td>$-6787.66$</td>
<td>$-287.96$</td>
</tr>
</tbody>
</table>

4. Conclusions

In this study, the monomineral flotation tests of hematite, quartz, and their artificially mixed minerals proved that the mixed DTAC/tall oil collector could improve the flotation
separation of quartz from hematite. This application not only increased the efficiency of hematite reverse flotation but also strengthened the temperature adaptability of the collecting agents. The underlying mechanism was analyzed using surface tension tests, FT-IR, XPS, and MD simulations. The main conclusions are as follows:

1. The results of the monomineral flotation test revealed that, under the same conditions, the mixed collector surpassed the single DTAC. Quartz achieved a recovery rate of 94.67%, while hematite reached 8.69%, at a natural pH of around 7.0 and 298 K, indicating potential for the successful reverse flotation of hematite. In the comparative test, with artificially mixed minerals, the mixed collector exhibited strong selectivity compared to the single DTAC and displayed good temperature adaptability.

2. The surface tension tests confirmed the mixed collector’s superior harvesting performance and low-temperature resistance, as well as the physical adsorption and hydrogen bonding of both single DTAC and mixed collector on quartz. It was observed that the adsorption of the mixed collector on the mineral surface was stronger when compared to that of the single DTAC.

3. MD simulations demonstrated that the mixed collector demonstrated more negative adsorption energy on the quartz surface than the single DTAC, leading to a firmer adsorption configuration conducive to flotation.

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