Enhanced Flotation Separation of Low-Rank Coal with a Mixed Collector: Experimental and Molecular Dynamics Simulation Study
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ABSTRACT: The efficient flotation separation of low-rank coal is still a difficult problem. The development of a collector is the key to solve the problem. In this study, a kind of mixed collector scheme with a practical value is proposed. The effects of the single collector dodecane (D) and methyl oleate (MO) and mixed collector D−didodecyl dimethyl ammonium bromide (DDAB) and MO−DDAB on flotation separation of low-rank coal were investigated. The flotation test results show that when the molar ratios of the mixed collector D−DDAB and MO−DDAB are 9:1 and the flotation time is 4 min, the cumulative combustible recovery of low-rank coal flotation is 71.49 and 76.73%, respectively, and the cleaned coal ash is 15.26 and 13.03%, respectively. The mixed collector significantly improves the flotation effect of low-rank coal compared with the single collector. According to the analysis results of the contact angle, wetting heat, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy, the hydrophobicity of the low-rank coal surface is enhanced under the action of the mixed collector, and the adsorption between the mixed collector and coal surface is stronger. In addition, molecular dynamics (MD) simulation results show that compared with D or MO, DDAB tends to adsorb on the surface of low-rank coal, and the diffusion coefficients of water molecules on the surface of coal increase. The mixed collector first repels water molecules through its double hydrophobic carbon chain to weaken the binding of the coal surface to water molecules and then uses D or MO to further repel water molecules, thus effectively enhancing the surface hydrophobicity of low-rank coal.

1. INTRODUCTION
Coal is an important part of China’s basic energy and plays an indispensable role in China’s industrial development. A comprehensive analysis of China’s coal storage, coal quality characteristics, consumption status, and other factors shows that low-rank coal will become the focus of China’s coal development and utilization in the future. For the treatment of low-rank coal, foam flotation is the most widely used separation method. As is known to all, the hydrophobicity difference between target minerals and gangue minerals decreases due to a low metamorphism degree and the presence of many oxygen-containing functional groups on the surface of low-rank coal, and the efficient separation and clean utilization cannot be achieved by using conventional flotation collectors. Therefore, the development of efficient collectors is one of the important ways to realize the flotation quality improvement of low-rank coal.

Scholars’ research on efficient collectors for low-rank coal mainly focuses on new collectors, mixed collectors, collectors emulsification, and so on. At present, the development of new collectors and emulsification of collectors have achieved satisfactory results. However, the above-mentioned two methods have some limitations in practical application due to the high cost of agents and cumbersome practical operation.

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methods. To solve the above-mentioned problems, the development of mixed collectors has been extensively studied. On the one hand, the mixed collector is mostly a conventional collector, which has the advantage of sufficient supply and low price. On the other hand, the mixed collector does not need to change the existing process and equipment in practical production, which greatly improves the feasibility of practical application.

At present, the research on the mixed collector of low-rank coal slime has been reported. Xia et al. used coal tar and diesel as a mixed collector to carry out low-rank coal flotation, and the cleaned coal yield increased from 38.6 to 87.4%, effectively improving the flotation effect. Liao et al. investigated the flotation performance of dodecane, ethyl ester, and dodecane–ethyl ester on low-rank coal, and the results showed that the flotation performance of the mixed collector was significantly better than that of a single collector. The mixed collectors reported in the existing literature can improve the flotation effect of low-rank coal to a certain extent. In addition, the amount of the mixed collector must be considered in practical production. Liu et al. conducted flotation tests with dodecane and valeraldehyde as mixed collectors and found that the cost of mixed collectors was about 20% lower than that of conventional collectors. Bao et al. used oleic acid/methyl oleate (MO)/diesel as a mixed collector to carry out the flotation test of low-rank coal, and the test showed that the optimal dosage of the mixed collector was 2000 g/t. Compared with those of diesel, cleaned coal yield increased by 41.40%, and the ash content decreased by 0.91%. Existing studies show that the flotation effect of low-rank coal can be effectively improved by using an appropriate mixed collector. If you want to develop the mixed collector with different characteristics of low-rank coal more specifically, it is essential to explore its mechanism of action.

After selective adsorption of the collector on different mineral surfaces, the hydrophobicity difference of mineral surfaces increases, and then, the target minerals are captured through bubbles, thus achieving effective separation. The mechanism of action of a collector on the coal surface can usually be studied from the adsorption process of the collector and wettability of the coal surface. Understanding the adsorption intensity and form of the collector on the coal surface is helpful to understand the interaction between the collector and coal and the influence of the collector on the wettability of the coal surface. In addition, the contact angle can directly represent the wettability of the coal surface, which is an intuitive research method. The combination of the above-mentioned two methods can explain the mechanism of improving coal surface hydrophobicity with a collector. However, for mixed collectors, the above-mentioned methods cannot be used to deeply understand the synergy between different agents. Molecular dynamics (MD) simulation has been widely used to study the microscopic interaction mechanism between agents and mineral surfaces and the synergistic strengthening mechanism between different agents. Chen et al. found out through MD simulation that dodecane would absorb part of dodecylamine and then promote the adsorption of dodecylamine on the surface of low-rank coal through its good dispersity. The synergistic effect of the two significantly improved the flotation effect of low-rank coal. Zhang et al. obtained the co-adsorption behavior of dodecane and tetraethylene glycol monododecyl ether on the surface of low-rank coal by MD simulation, which increased the distance between the water molecules and coal surface and enhanced the hydrophobicity of the coal surface. In conclusion, it is feasible to study the mechanism of enhanced low-rank coal flotation with a mixed collector by MD simulation.

In this study, the flotation performance of a single collector and mixed collector on low-rank coal was investigated through a laboratory flotation test, and the optimal ratio of the mixed collector was determined. The mechanism of the mixed collector was investigated by analysis of the contact angle, wetting heat, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). In addition, MD simulation was used to reveal the synergistic mechanism of the mixing collector to improve the flotation effect of low-rank coal at the molecular level. The aim is to provide theoretical basis and guidance for the development of high-efficiency mixed collectors of low-rank coal.

### 2. Materials and Methods

#### 2.1. Materials

The coal samples were taken from coal preparation plants in China’s Inner Mongolia region. About 50 and 80% of the coal particles had particle sizes of −48.74 and −95.89 μm after crushing and grinding, respectively. Results of proximate and ultimate analysis of coal are shown in Table 1. Table 1 shows that the water content, ash content, volatile content, and fixed carbon content of coal are 3.62, 29.82, 45.39, and 52.05%, respectively. The content of carbon and oxygen in coal samples is 76.53 and 14.72%, respectively. The above-mentioned analysis results show that the coal samples used in the test belong to typical low-rank coal.

Dodecane (D), MO, didodecyl dimethyl ammonium bromide (DDAB), and sec-octanol alcohol were all purchased from Sinopagic Chemical Reagents Co., Ltd. The mixed collector was prepared according to D or MO of different mole ratios and DDAB.

#### 2.2. Methods

##### 2.2.1. Flotation Tests

The flotation test of low-rank coal was carried out using a 1.0 L XFD flotation machine. At room temperature, the impeller speed of the flotation machine was 1800 rpm, the airflow speed was 1.33 L/min, and the pulp concentration was 50 g/L. After 3 min of slurry mixing, different amounts of D, MO, D–DDAB, or MO–DDAB were added. After stirring for 2 min, sec-octanol (dosage is 200 g/t) was added. After aerating for 20 s, we began to scrape the bubbles. The effects of different molar ratios of D/MO and DDAB and different dosage of reagents on the flotation effect were investigated. After the flotation test, the foam products were filtered, dried, and weighed, and

| Proximate Analysis/% | Ultimate Analysis/% |
|----------------------|---------------------|
| ad | daf | ad | daf | ad | daf | ad | daf | ad | daf |
| 3.62 | 29.82 | 45.39 | 52.05 | 76.53 | 5.12 | 14.72 | 1.15 | 1.46 |

Table 1. Proximate and Ultimate Analysis of the Coal Sample

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ad: air dry basis; daf: dry ash-free basis; a: by difference.
cleaned coal ash and combustible recovery were calculated (eq 1).

\[ \varepsilon_r(\%) = \frac{M_C(100 - A_C)}{M_F(100 - A_F)} \times 100 \]

where \( M_C \) is the concentrate mass (%), \( M_F \) is the feed mass (%), \( A_C \) is the concentrate ash (%), and \( A_F \) is the ash content of the feed (%).

Cumulative combustible recovery can be calculated from eq 2

\[ \varepsilon_r(\%) = \varepsilon_\infty [1 - \exp(-kt)] \]

where \( \varepsilon_r \) is the recovery of coal at time \( t \), \( \varepsilon_\infty \) is the ultimate recovery, and \( k \) is the flotation rate constant.

2.2.2. Contact Angle Measurements. The coal sample was dried in a DHG-9070A electric heating constant temperature drying oven. A 30 mm-diameter and 2 mm-thickness compression plate was prepared using the FY-30 compression plate mechanism. After the preparation, XG-CAMA+ enhanced static contact angle analyzer (Xuanyi, Inc., China) was used to measure the contact angle of the coal sample, and the contact process between water droplets and the tablet surface was recorded. Then, the images of the contact moment between the two were selected for analysis. Each sample was measured three times under the same conditions, and the average value was taken.

2.2.3. Wetting Heat Measurements. First, 10 mg of the dried coal sample (−74 μm) was placed in the product tank of a Setaram C80 microcalorimeter (Caluire, France), and 2 mL of the collector was added to the mixing tank. The film between the collector and the coal sample was punctured at 30 °C to make them fully mixed. Experiments were carried out in reference tanks and sample tanks. Date acquisition software was used to record the moisture and heat flow and obtain the heat flow curve. After integrating the curve, the wettability heat after the interaction between the coal sample and the agent was calculated. Under the same conditions, the results were measured three times and averaged.

2.2.4. FTIR Measurements. FTIR spectra (MB104, ABB Bomem, Canada) were used to measure the infrared spectrum of coal samples before and after the collector. The coal sample and KBr powder were dried before the measurement. The coal samples were analyzed using an infrared spectrum using the KBr tablet pressing method, that is, the coal samples and KBr powder were ground in an agate mortar until the mixture was uniform and then taken out and put into a tablet press for tablet pressing. Then, the spectral resolution was set as 4 cm⁻¹, and the infrared spectra within the range of 400−4000 cm⁻¹ were selected as the measurement results for analysis.

2.2.5. XPS Measurements. XPS analysis of surface chemical properties of coal samples was carried out using an X-ray diffractometer (ESCALAB 250 Xi, Waltham, MA, America) to characterize the change of the surface element content of coal samples before and after adsorption of the collector. Each time, 0.5 g of the coal sample and a certain amount of the collector were scanned and measured in a 5 × 10⁻⁸ Pa vacuum sample chamber. XPSPeak 4.1 software was used for spectral quantification and peak fitting, in which the C 1s hydrocarbon peak at 284.8 eV was regarded as the standard binding energy.

2.2.6. Molecular Dynamics Simulations. Materials Studio 2017 software was used for simulation calculation in this paper. The structural models of different molecules in the simulation system are shown in Figure 1. Figure 1a,b is the flotation three-phase system models with D and MO added separately. Figure 1c,d is the flotation three-phase system models of D−DDAB and MO−DDAB, respectively. The low-rank coal molecular model (Figure 1d) reported by Wender et al. was used. The coal molecular model is based on the analysis of various detection and characterization results and is suitable for low-rank coal such as non-stick coal and long-flame coal.¹³ The AC module was used to establish the coal molecular layer, the collector molecular layer, and the water molecular layer, and the three layers were combined using the Build Layer tool to make the chemical molecule located at the solid−liquid interface (Figure 2). To avoid periodic effects, a vacuum layer of 50 Å is set above the water molecule layer (1500 water molecules). The size of the simulated system is 30 Å × 30 Å × 120 Å.

MD simulation was performed through the Forcite. First, the initial model was geometrically optimized, and the COMPASS II field was used to distribute the whole atomic field. The substance composition and properties of coal molecules and collector solutions in this study can be distributed by whole atoms using this force field, which is consistent with what has been reported in other literature reports. The shape optimization method was the Smart algorithm. After 5000 steps of iterative calculation, the geometrically optimized energy minimization model was obtained. Then, the regular system (NVT), Ewald summation method, and atom-based summation method were used to calculate the electrostatic interaction. The temperature of the system was controlled to 298 K by the Nose temperature control method. The simulation step size was 1 fs, and the total simulation time was 1 ns. Finally, the last 500 ps trajectory file was selected to analyze the dynamics calculation results.
3. RESULTS AND DISCUSSION

3.1. Flotation Results. Flotation results of different molar ratios D and DDAB are shown in Figure 3. Figure 3a shows that cumulative combustible recovery of coal sample flotation is positively correlated with flotation time. When flotation time is more than 4 min, the growth trend of cumulative combustible recovery is not obvious. When D was used as the collector alone, the cumulative combustible recovery after 4 min was only 28.27%. In contrast, the cumulative combustible recovery of the D−DDAB mixed collector was significantly improved. With the increase in DDAB dosage, the cumulative combustible recovery first increased and then decreased. When the molar ratio of D and DDAB is 9:1, the cumulative combustible recovery of flotation is the best, and the cumulative combustible recovery increases to 71.49% after 4 min of flotation. Figure 3b shows the change of cleaned coal ash when D and DDAB with different mole ratios are used as collectors. With the increase in DDAB dosage, cleaned coal ash first decreased and then increased. After flotation for 4 min, the cleaned coal ash content of D is 18.82%. However, when the molar ratio of D and DDAB is 9:1, the cleaned coal ash content of flotation is reduced to 15.26%.

Figure 3. Flotation results of coal samples with different molar ratios of D to DDAB. (a) Cumulative combustible recovery and (b) concentrate ash.

Figure 4. Flotation results of coal samples with different molar ratios of MO to DDAB. (a) Cumulative combustible recovery and (b) concentrate ash.

Figure 5. Effect of collector dosage on flotation results. (a) Cumulative combustible recovery and (b) concentrate ash. The molar ratios of D to DDAB and MO to DDAB are 9:1; flotation time is 4 min.
recovery is consistent with that of the D–DDAB mixed collector. When MO is used alone, the cumulative combustible recovery is 33.25% after flotation for 4 min, which is significantly lower than that of the combined collector of MO and DDAB. With the increase in DDAB dosage, the cumulative combustible recovery first increased and then decreased. When the molar ratio of MO and DDAB is 9:1, the cumulative combustible recovery is the best, and the flotation can reach 76.73% after 4 min. The ash content of flotation-cleaned coal with the MO–DDAB mixed collector is shown in Figure 4b. The change trend of cleaned coal ash is the same as that of D–DDAB with the increase in DDAB dosage. When the molar ratio of the two is 9:1, the ash content of flotation-cleaned coal decreases from 17.13 to 13.03% compared with that of MO alone, that is, the MO–DDAB mixed collector can effectively improve the flotation effect.

Figure 5 shows the flotation results of the single collector and mixed collector with different dosages. Figure 5a shows that within the dosage range of the used collector, the cumulative combustible recovery of both the single collector and mixed collector increases with the increase in dosage. When the amount of the collector is more than 3000 g/t, the increase in cumulative combustible recovery decreases obviously. At the same time, it can be seen from Figure 5b that for D or MO, the ash content of cleaned coal decreases with the increase in the dosage. However, the ash content of cleaned coal decreases first and then increases with the increase in dosage. Compared with the single collector, the mixed collector can effectively reduce cleaned coal ash. The ash content of cleaned coal is the lowest when the amount of the mixed collector is 3000 g/t.

In summary, for low-rank coal, it is impossible to obtain satisfactory results when using D or MO as the collector for flotation. After adding a small amount of DDAB into D or MO, the flotation effect is improved obviously. The flotation effect of MO is better than that of D under the same experimental conditions. The optimal mole ratios of D–DDAB and MO–DDAB are both 9:1. When the dosage of DDAB continues to increase, the cumulative combustible recovery begins to decline, which may be due to the fact that DDAB solution is characterized by high viscosity, and when its concentration is too high, the dispersion of reagents will be weakened, thus reducing the adsorption effect of reagents on mineral surfaces and resulting in a poor flotation effect. When the amount of the mixed collector is more than 3000 g/t, the increase in cumulative combustible recovery is not obvious, but the cleaned coal ash increases slightly. Therefore, the optimal dosage of the mixed collector for low-rank coal flotation in this study is 3000 g/t.

3.2. Contact Angle Analysis. The influence of the mixed collector on the surface wettability of coal samples was investigated, and the contact angle of coal samples under the action of the collector was measured. The results are shown in Figure 6. As can be seen from Figure 6, when D and MO are used alone, the contact angles of coal samples are 40.5° and 44.7°, respectively. Taking the contact angle of raw coal (36.2°) as the control, the contact angle only increased by 4.3° and 8.5° with the single collector. The contact angle of coal samples increases obviously after the action of the mixed collector, and the influence of the proportion of the mixed collector is consistent with the flotation performance. When the mole ratios of D–DDAB and Mo–DDAB are 9:1, the contact angles of coal samples increase to 67.5° and 71.1°, respectively, indicating that the hydrophobicity of coal samples under the action of the mixed collector is significantly improved. The floatability of low-rank coal is poor, mainly because there are many hydrophilic oxygen-containing groups on its surface. The N atoms in DDAB polar groups interact with the hydrophilic oxygen-containing groups of low-rank coal to reduce the exposed oxygen-containing groups and improve hydrophobicity.

3.3. Wetting Heat Analysis. In the process of mineral flotation, the polar groups of the collector are adsorbed with the active sites on the mineral surface, and water molecules are kept away from the mineral surface through the hydrophobic long chain of the collector, thus improving the hydrophobicity of the mineral surface. The calculation results of wettability heat after interaction between the coal sample and collector are shown in Figure 7. Figure 7 shows that the wetting heat of the adsorption between the collector and the coal sample is negative, indicating that the adsorption process is spontaneous. The wetting heat of D and MO alone is 32.52 and 45.76 J/g, respectively, indicating that MO is more likely to adsorb on the coal surface than D. The wetting heat of the mixed collector is significantly higher than that of the single collector, and the adsorption heat reached the maximum value when the molar ratio of the mixed collector is 9:1, which is 164.43 and 168.51 J/g, respectively. Therefore, the adsorption effect of the mixed collector on the coal surface was significantly stronger than that
of the single collector. Therefore, the hydrophobicity of the coal surface under the action of the mixed collector is significantly improved, which is consistent with the law of contact angle measurement results (Figure 6).

### 3.4. FTIR Analysis

FTIR spectrums of low-rank coal after adsorption of different collectors are shown in Figure 8.

![FTIR spectrums of low-rank coal after adsorption with different collectors.](image)

Figure 8. FTIR spectrums of low-rank coal after adsorption with different collectors.

Comparative analysis of the curves in Figure 8 shows that no new characteristic absorption peaks appear after adsorption of single and mixed coal collectors, indicating that the above-mentioned four collectors only carry out physical adsorption with coal. After coal adsorbed the collector, the intensity of the vibration peak of the OH self-association hydrogen bond at 3610–3624 cm\(^{-1}\) decreased, and the order was No > D > MO > D-DDAB > MO-DDAB. At the same time, \(\text{CH}_3\) shear vibration exists at 1435–1460 cm\(^{-1}\), and the amplitude of the mixed collector is stronger than that of the single collector. However, C═O vibration at 1010–1270 cm\(^{-1}\) and C═O–C vibration at 1540–1640 cm\(^{-1}\) are the weakest increase in the coal surface with the adsorptive mixed collector. The above-mentioned results indicate that the coal surface is effectively covered with oxygen-containing functional groups, and the hydrophobic groups on the coal surface are increased after the coal is adsorbed and mixed with the collector, which effectively improves the hydrophobicity of the coal surface.

### 3.5. XPS Analysis

The peak changes on the surface of the coal sample can reflect the effect of the collector. The C 1s peak fitting results of XPS on the surface of coal samples under the action of different collectors are shown in Figure 9. As can be seen from Figure 9, compared with that of raw coal, the C 1s peak on the coal surface is slightly enhanced under the action of D or MO, indicating that a small part of oxygen-containing groups is covered after D or MO is adsorbed on the coal surface. Under the action of the mixed collector, the C 1s peak of the coal surface is significantly enhanced, indicating that the adsorption effect of the mixed collector is better than that of the single collector. Figure 9f shows the content of carbon and oxygen on the surface of coal samples under the action of different collectors. The content of carbon and oxygen on the surface of raw coal is 79.15% and 20.85%, respectively. Under the action of the collector, the coal surface carbon content increases, and the oxygen content decreases, and especially, under the action of the mixed collector, the change range is the most obvious; specifically, the carbon and oxygen content of D–DDAB is 81.79% and 18.21%, respectively, and the carbon and oxygen content of MO–DDAB is 82.02% and 17.89%, respectively. Therefore, it can reflect that the mixed collector of D–DDAB and MO–DDAB can effectively enhance the hydrophobicity of the coal surface.

The peak fitting results of C 1s spectra on the surface of coal samples under the action of different collectors are shown in Figure 10. According to the morphological division of the C element, the content of C═C/C═H in raw coal was 44.92%,

![XPS wide-energy spectrum of the coal surface before and after the action of the collector.](image)

Figure 9. XPS wide-energy spectrum of the coal surface before and after the action of the collector. (a) Raw coal; (b) D; (c) MO; (d) D-DDAB. The molar ratio is 9:1; (e) MO-DDAB. The molar ratio is 9:1; and (f) carbon and oxygen content on the surface of the coal sample.

| Samples     | Cl\(_1s\) (%) | O\(_1s\) (%) |
|-------------|---------------|--------------|
| Raw coal    | 79.15         | 20.85        |
| D           | 79.73         | 20.27        |
| MO          | 79.87         | 20.13        |
| D-DDAB      | 81.79         | 18.21        |
| MO-DDAB     | 82.02         | 17.98        |
and the content of C=H/C=C−H after the action of the single or mixed collector increased to a certain extent compared with that of raw coal, which were 52.13, 54.59, 67.41, and 70.55%, respectively. At the same time, it could be seen that the increase rate under the action of the mixed collector was significantly greater than that under the action of the single collector. The results also showed that the contents of C−O, C=C−O, and O=C−O on the coal surface decreased after the action of the collector, and the most significant decreasing trend was under the action of the mixed collector. Since C=C−H are hydrophobic groups and C−O, C=C−O, and O=C−O are hydrophilic groups, it can be concluded that the polar groups of the collector can effectively reduce the exposed oxygen functional groups after adsorption with the oxygen-containing functional groups on the surface of the coal sample, thus enhancing the hydrophobicity of the coal sample. In conclusion, the hydrophobic performance of D−DDAB and MO−DDAB mixed collectors for coal samples is obviously
superior to that of the D or MO single collector under the same dosage, and the MO–DDAB mixed collector is the best.

### 3.6. Molecular Dynamics Simulation Results.

#### 3.6.1. Spatial Distribution of Different Molecules.

The adsorption of the collector and water molecules on the coal surface is described at the microscopic level. The distribution of the collector and water molecules on the coal surface was analyzed, and the results are shown in Figure 11. Figure 11 shows that water molecules on the coal surface reach the maximum concentration at 51.28 Å when no collector is added, and water molecules tend to be distributed on the coal surface. When D or MO is added, the maximum concentration of water molecules on the coal surface corresponds to 54.10 or 55.63 Å, respectively, and the initial position of water molecules shifts to the right, indicating that the distance between water molecules and the coal surface increases after D or MO is adsorbed on the coal surface, that is, the hydrophobicity of the coal surface increases. Similarly, with the addition of the mixed collector, the maximum concentration of water molecules on the coal surface corresponds to 57.01 and 57.32 Å. The initial position of water molecules further shifted to the right, and the overlap area between water molecules and coal decreased significantly. According to the literature, after the adsorption of the collector on the coal surface, part of the water molecules will be discharged, which will take the water molecules away from the coal surface and enhance the hydrophobicity of the coal surface. Therefore, in this study, compared with the single collector, the mixed collector has a more significant effect on coal surface hydrophobic modification. As can be seen from the distribution of mixed collectors, under the action of D–DDAB and MO–DDAB, DDAB is concentrated at 35.15 Å, while D and MO reach maximum concentrations at 43.54 and 43.54 Å, respectively, indicating that the adsorption position of DDAB is closer to the coal surface than that of D and MO. It indicates that the polar groups of DABD are more inclined to replace water molecules and interact with water-loving points on the coal surface. Based on this, the adsorption effect of DDAB is stronger than that of D and MO.

#### 3.6.2. Interaction Energy.

In order to describe the adsorption effect of different collectors on the coal surface from the perspective of energy, the energy tool in the Forcite module is used to calculate the interaction energy between the collectors and coal surface ($E_{\text{total}}$), and the calculation formula is as follows:

$$E_{\text{inter}} = E_{\text{total}} - (E_{\text{coal}} + E_{\text{collector}})$$

(3)

where $E_{\text{total}}$ is the total interaction energy between the coal surface and the collector system, $E_{\text{coal}}$ is the energy of the coal model, and $E_{\text{collector}}$ is the energy of the collector model. Van der Waals interaction ($E_{\text{vdw}}$) and electrostatic interaction ($E_{\text{elec}}$) are calculated using the same method. A negative value of the interaction energy indicates an attractive force between different components, whereas a repulsive force indicates a repulsive force.

The calculated results of interaction energy between different collectors and low-rank coal are shown in Table 2. Table 2 shows that the $E_{\text{inter}}$ of D, MO, D–DDAB, and MO–DDAB with coal samples is $-332.51$, $-348.15$, $-376.39$, and $-383.67$ kcal/mol, respectively. By comparison, the absolute value of the interaction energy between the mixed collector and the coal sample is much greater than that of the single collector, indicating that the adsorption of the mixed collector and the coal surface is stronger than that of the single collector, and the adsorption energy of MO–DDAB is the largest. In addition, $E_{\text{vdw}}$ and $E_{\text{elec}}$ between the mixed collector and coal sample are stronger than those of the single collector. Therefore, the increased interaction energy between the mixed collector and the coal sample compared with that of the single collector is partly contributed by $E_{\text{vdw}}$ and $E_{\text{elec}}$. The interaction energy between the collector and mineral surface can reflect its adsorption effect, and usually, the adsorption strength of the collector determines its hydrophobic performance. From the perspective of interaction energy, the above-mentioned analysis shows that the mixed collector D–DDAB and MO–DDAB can enhance the hydrophobicity of the coal surface more than D or MO. The simulation results of the mixed collector and single collector show the same variation law as shown by the flotation experiment results.

#### 3.6.3. Diffusion Properties of Water Molecules.

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} r_i(t)^2 = K_{\text{MSD}}$$

(4)

where $N$ is the total number of diffused molecules, $r_i(t)$ and $r_i(0)$ are the position vectors of the particle at time $t$ and time 0, respectively, subscript $i$ is the $i$th diffusive molecule, and $K_{\text{MSD}}$ is the slope of Mean Squared Displacement (MSD).

Figure 12 is the MSD of water molecules on the coal surface in different collector systems, and the diffusion coefficient ($D$) of water molecules is calculated according to eq 4. It can be seen that the diffusion coefficient of water molecules on the coal surface in single collector and mixed collector systems increases compared with that of without the addition of the collector, and the specific order is MO–DDAB > D–DDAB > MO > D. Due to the existence of a large number of oxygen-containing functional groups on the surface of coal, it is easy to

| collector | $E_{\text{inter}}$ (kcal/mol) | $E_{\text{vdw}}$ (kcal/mol) | $E_{\text{elec}}$ (kcal/mol) |
|-----------|-------------------------------|-----------------------------|-----------------------------|
| D         | $-332.51$                     | $-310.68$                   | $-21.83$                    |
| MO        | $-348.15$                     | $-314.02$                   | $-34.13$                    |
| D–DDAB    | $-376.39$                     | $-326.50$                   | $-49.89$                    |
| MO–DDAB   | $-383.67$                     | $-329.62$                   | $-54.05$                    |

Table 2. Interaction Energy between the Collector and Coal Samples
adsorb water molecules, making water molecules more inclined to adsorb on the coal surface. When the collector is adsorbed on the coal surface, it will cover part of oxygen-containing functional groups, thus weakening the binding effect of the coal surface on water molecules. At the same time, the long hydrophobic chain of the collector can take water molecules away from the coal surface. Therefore, it can be judged from the diffusion coefficient of water molecules that the improvement effect of the mixed collector on coal surface hydrophobicity is obviously better than that of the single collector (Table 3).

Table 3. Diffusion Coefficient of Water Molecules in Different Systems

| collector | No | D | MO | D−DDAB | MO−DDAB |
|-----------|----|---|----|--------|---------|
| diffusion coefficient \((10^{-5} \text{ cm}^2/\text{s})\) | 0.168 | 0.186 | 0.192 | 0.224 | 0.233 |

According to the comprehensive contact angle, wetting heat, FTIR, XPS, and MD analysis, the single collector (D and MO) and mixed collector (D−DDAB and MO−DDAB) selected in this study can effectively improve the hydrophobicity of the low-rank coal surface, and the improvement effect of the mixed collector is significantly better than that of the single collector. Based on the above-mentioned analysis results, a schematic diagram of the mechanism of enhancing coal surface hydrophobicity with mixed collectors is obtained (Figure 13). The strengthening mechanism mainly includes two aspects: First, the mixed collector has stronger adsorption energy on the coal surface, which can effectively increase the coverage of oxygen-containing functional groups on the coal surface. Second, the double-carbon chain structure of DDAB preferentially plays a strong hydrophobic role and then performs hydrophobicity again through D or MO. Under the synergistic effect of mixed agents, the binding effect of the coal surface on water molecules is significantly weakened, which enhances the hydrophobicity of the coal surface.

4. CONCLUSIONS

The flotation of low-rank coal using D or MO as the collector could not achieve satisfactory results. However, mixing D or MO with a small amount of DDAB as the collector could significantly improve the flotation separation effect of low-rank coal. Compared with D or MO, the mixed collector has stronger adsorption on the surface of the coal sample, effectively reducing the exposed oxygen-containing functional groups, thus enhancing the hydrophobicity of the coal sample. MD simulation results revealed the synergy mechanism of mixing collectors to improve low-rank coal flotation from the microscopic level. First, compared with D or MO, DDAB tends to adsorb on the surface of low-rank coal, and the mixed collector has stronger adsorption energy on the surface of coal, weakening the binding effect of the coal surface on water molecules. Second, the double-carbon chain structure of DDAB has a strong hydrophobic effect first and then exerts the hydrophobic effect again through D or MO. The synergistic effect of the two significantly improves the hydrophobicity of low-rank coal.

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Author Contributions

CRediT authorship contribution statement: Hua Kang: Conceptualization, Methodology, Validation, Investigation, Supervision, Writing—original draft, and Writing—review and editing. He Zhang: Writing—review and editing, Conceptualization, Software, Methodology, and Investigation.

Notes

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Figure 13. Mechanism diagram of enhancing coal surface hydrophobicity with the mixed collector.
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