Synergistic Adsorption Mechanism of Anionic and Cationic Surfactant Mixtures on Low-Rank Coal Flotation

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ABSTRACT: Mixed surfactants have a prominent synergistic effect and show advantages in many aspects. In this work, the effects of a mixture of dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS) on the flotation of low-rank coal were studied from the wetting rate, contact angle, surface tension, and zeta potential. Furthermore, the adsorption configuration of the mixed surfactant on the surface of oxygen-containing graphite was simulated at the molecular level by molecular dynamics simulation. The experimental results show that the combustible matter recovery of low-rank coal flotation is improved using the mixed surfactant, and the contact angle test and wetting rate test confirmed the synergistic effect of the mixed surfactant. In the mixed surfactant system, the addition of SDS with an opposite charge to DTAB can reduce the mutual repulsion between DTAB molecules and enhance the degree of DTAB alignment in solution, which was analyzed by surface tension and zeta potential tests. Meanwhile, the simulation results reveal the adsorption behavior of anionic and cationic surfactants on the surface of oxygen-containing graphite from the molecular level and also verify the experimental results. This investigation provides a good understanding of the interaction mechanism of mixed surfactants in low-rank coal flotation.

1. INTRODUCTION

Coal is an important global energy supply and chemical raw material, playing an important role in industrial production. In recent years, with the continuous exploitation of coal resources, resource conservation and secondary utilization have attracted a lot of attention worldwide. As a valuable coal resource, low-rank coal is rich in reserves, but the high ash, high water, and poor surface hydrophobicity of low-rank coal seriously impede its resource utilization. At present, flotation is an effective method to separate the combustible materials and minerals in low-rank coal. However, the low-rank coal has a rough surface and contains a large amount of oxygen-containing functional groups, the rough surface reduces the adhesion probability of particles to bubbles, and the oxygen-containing functional groups increase the hydrophilicity of the surface of the particles, which makes the dosage of traditional hydrocarbon oil collectors (such as diesel oil) increase rapidly in the flotation process. Therefore, how to realize the efficient recovery of combustibles in low-rank coal has become one of the hot spots in this research field.

Surfactants can effectively regulate the properties of a two-phase interface due to their unique parental molecular structure, and they are widely used in various chemical production neighborhoods. In coal flotation, surfactants also play an important role in regulating the surface properties of minerals. Xia et al. studied the effect of cationic surfactant DTAB (dodecyltrimethylammonium bromide) on the flotation of low-rank coal. Through molecular dynamics simulation, it was found that the DTAB pre-adsorbed on the coal surface can improve the adsorption of the collector dodecanal, and the simulation results can well support the experimental data. Singh studied the adsorption of cationic surfactant DAB (dodecyl ammonium bromide) and anionic surfactant SDS on an Indian coal surface and their effects on the moisture of dehydrated filter cake. The results showed that the adsorption capacity of DTAB on the coal surface was higher than that of SDS. The cationic surfactants and anionic surfactants could reduce the moisture of dehydrated filter cake. However, the regulation of single surfactants on the difference of mineral surface wettability is still unsatisfactory, so it is a promising way to combine the different types of surfactants together in the regulation of a mineral flotation interface to...
achieve the synergistic effect, enhancing the regulation effect of the surfactants.

So far, some eye-catching research works have been reported about the application of the mixed surfactant in minerals. Zhang et al. reported the effect of the anionic–non-ionic surfactant mixture on a bentonite structure and the impact of surfactants on pentachlorophenol (PCP) distribution in a liquid system. They found that the anionic surfactant not only reduced adsorption of the non-ionic surfactant but also significantly enhanced PCP desorption from bentonite. The co-adsorption of the anionic and non-ionic surfactants increased ordering conformation of the surfactants on the bentonite surface and improved the thermal stability of the organobentonite system. Huang et al. found that the non-ionic surfactant nonylphenol ethoxylate (NP-10) cannot be adsorbed on the surface of alkaline phosphatase alumina (AKP-50), but after the addition of the cationic surfactant DTAB, NP-10 was adsorbed on the surface of AKP-50 due to the synergistic effect of the two surfactants. The combination of anionic/cationic and non-ionic surfactants plays an important role in the regulation and control of a mineral interface. For the compound of the anionic–cationic mixed surfactant, some researchers believe that the anionic surfactant and the cationic surfactant tend to accumulate in the solution and lose activity due to the opposite charge. On the contrary, other researchers believe that if the molecular weight of anionic surfactants is small, the anionic–cationic mixed surfactant can dissolve in water. Wang et al. studied the adsorption mechanism of different hydrophilic head groups and different proportions of cationic and anionic surfactants on the surface of mineral silicon oxide by using cationic surfactant DTAB and anionic surfactants sodium dodecylbenzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS). The experimental results show that when the head group of anionic surfactants is small, the anionic–cationic surfactants are arranged alternately on the surface of the quartz, and when the concentration of compound surfactants is excessive, double layer adsorption will be formed on the surface of the quartz. Alexandrova et al. tested the back-contact angle and surface tension of tetraalkyltrimethylammonium bromide (C14TAB) and anionic surfactants on silica surface wetting films. It is found that the composite surfactants reduced the contact angle, lower water film fracture rate, and lengthen membrane lifetime. The surface tension data also indicated that the chain length compatibility between anionic and cationic surfactants controls the strength of the interface complex and induces the synergistic reduction of surface tension. Therefore, the cationic–anionic mixed surfactants do not lose activity due to the formation of precipitation, and on the contrary, it shows more excellent activity.

In this study, the effect of cationic surfactants (DTAB) and anionic surfactants (SDS) on the interface regulation of low-rank coal flotation was studied by experiment and molecular dynamics simulation. In the part of simulation calculation, the adsorption configuration of anionic surfactants and cationic surfactants on the surface of oxygen-containing graphite was constructed by referring to the adsorption model constructed by Xia et al., which guided the understanding of the adsorption behavior of complex surfactants on the surface of low-rank coal. In addition, the experimental results show that the synergistic effect between anions and cations in the mixed surfactants reduces the surface tension of the solution, changes the zeta potential on the surface of low-rank coal particles, and improves the adsorption and spreading rate of the collector on the surface of the particles. The hydrophobicity of low-rank coal is effectively improved under the condition of low dosage, which provides a theoretical basis for the regulation and control of the flotation interface of low-rank coal, realizes the purpose of high-efficiency separation and clean utilization of low-rank coal, and also provides help for environmental protection and resource utilization.

2. RESULTS AND DISCUSSION

2.1. Surface Chemical Group Analysis. The surface chemical groups of the low-rank coal were determined from the XPS, as shown in Figure 1. The results from the deconvolution of the C peak for coal samples are shown in Table 1.

According to the results of XPS analysis, the surface of low-rank coal contains many oxygen-containing functional groups,
and the contents of oxygen groups C−O, C≡O, and O═C−O are 30.91%, 8.98%, and 2.84%, respectively. The abundance of oxygen-containing functional groups on the surface of low-rank coal weakens the hydrophobicity of low-rank coal and make its resource utilization difficult.

2.2. Flotation Measurement Analysis. The effect of single surfactant DTAB or SDS and mixed surfactants on low-rank coal flotation is shown in Figure 2. It can be seen from Figure 2 that the combustible matter recoveries of low-rank coal are 78.37 and 75.82% at 0.1 and 0.25 mM mixed surfactants, respectively. However, the combustible matter recoveries of low-rank coal are 34.86 and 43.27% at 0.1 and 0.25 mM single DTAB. In addition, the ash content of concentrate is basically kept constant. The effect of cationic−anionic mixed surfactants on the flotation of low-rank coal is significantly better than that of single SDS and single DTAB. The calculated wetting rates of the coal treated with the mixed surfactant, single DTAB, and single SDS in diesel oil are $8.4 \times 10^{-4}$, $6.4 \times 10^{-4}$, and $5.4 \times 10^{-4}$ g²/s. It is well known that the adsorption rate of coal to diesel is related to the surface properties of coal. The more hydrophobic the surface of coal, the faster the adsorption rate of diesel, and vice versa. In the mixed system, due to the synergistic effect of DTAB and SDS, the surface hydrophobicity of coal samples is distinctly improved. Meanwhile, the water contact angle can directly characterize coal−water interaction. Figure 3b shows the variation of contact angle between coal and water treated with different surfactants and diesel oil with action time. The dosage of surfactants is 0.25 mM, and the amount of diesel oil is 4 kg/t. It can be seen from Figure 3b that the contact angle between raw coal and water is small. After the initial action for 6 s, the water droplets basically spread on the surface of coal, and the hydrophobicity of raw coal is reflected on the side. Among the different
surfactants, the mixed system has the most obvious effect on the hydrophobicity enhancement of low-rank coal surface followed by single SDS and single DTAB. When the cationic surfactant is added to the anionic surfactant SDS, the mutual repulsion between the DTAB molecules is reduced so that the DTAB is favorable for the compact arrangement of the coal surface and the low-rank coal hydrophobicity is improved.

2.4. Synergistic Adsorption Analysis of Anionic and Cationic Surfactant Mixtures. In this section, the synergistic adsorption mechanism of mixed surfactants was analyzed by surface tension and zeta potential tests of surfactant solution. Since surfactants have both hydrophilic and hydrophobic structures, surfactants can be arranged directionally in solution. A small amount of surfactants can reduce the surface tension of the solution. Figure 4a shows the surface tension of the solutions with single surfactant and mixed surfactant systems. It can be seen that the surface tension of the mixed surfactant system is smaller than that of the single system of DTAB and SDS. In a mixed surfactant system, the addition of SDS with an opposite charge to DTAB can reduce the mutual repulsion between DTAB molecules and enhance the degree of DTAB alignment in solution. Therefore, the surface tension of the solution more obviously decreases in the mixed system. The decrease in surface tension of the solution system can be attributed to the diffusion of the collector molecules, which promotes the spread of the collector molecules on the surface of the low-rank coal and improves the hydrophobicity of the surface of the low-rank coal. The variation of zeta potential after adsorption of surfactants in low-rank coal can reveal the adsorption of surfactants, and the results are shown in Figure 4b. The existence of oxygenated functional groups leads to the generation of electric potential of coal particles. The positive hydrophilic head group of DTAB is adsorbed on the surface of low-rank coal by electrostatic force, which increases the zeta potential of low-rank coal. In addition, the low-rank coal surface has a hydrophobic site in addition to the negatively charged oxygen-containing functional group sites. Under the action of hydrophobic force, SDS adsorbs on the surface of low-rank coal, which reduces the low-rank coal zeta potential. In the mixed surfactant system, when the DTAB content exceeds the SDS content, the DTAB can combine with the oxygen-containing sites on the low-rank coal surface or adsorb the free SDS in the solution. Compared with the single DTAB system, the electrical properties of DTAB+ and SDS− in the mixed surfactant system are opposite. Therefore, the effect of mixed surfactants on the zeta potential of the low-rank coal surface is not as obvious as that of single DTAB.

Due to the opposite charges of the SDS and the DTAB hydrophilic head, the electrostatic attraction between SDS and DTAB enhances the unit area adsorption efficiency of DTAB on low-rank coal surfaces, which also promotes the diffusion of diesel oil on the low-rank coal surface. When the SDS is used alone, the electrostatic repulsion between the SDS and the electronegative oxygen-containing functional groups of the low-rank coal is enhanced with the increase in SDS, which hinders the adsorption of SDS on the low-rank coal surface. When the DTAB is used alone, some DTAB molecules can be adsorbed on the surface of low-rank coal under the electrostatic attraction between DTAB and the electronegative oxygen-containing functional groups of the low-rank coal. However, the DTAB molecules are not totally adsorbed on the low-rank coal surface due to the existence of the repulsive force between the same surfactant molecules. Therefore, the

Figure 4. (a) Surface tension curves of a single surfactant and mixed surfactant. (b) Zeta potential of a single surfactant and mixed surfactant.

Figure 5. (a) DTAB+ single surfactant adsorption. (b) SDS− single surfactant adsorption. (c) Mixed DTAB−SDS synergistic adsorption. (d) DTAB+, SDS−, and mixed surfactant structures.
mixed surfactant is more effective than the single surfactant for the flotation effect of low-rank coal.

2.5. Molecular Dynamics (MD) Simulations. The simulation results reveal the adsorption behavior of anionic and cationic surfactants on the surface of oxygen-containing graphite from the molecular level and verify the experimental results too.

The adsorption equilibrium configuration of anionic and cationic surfactants on the surface of oxygen-containing graphite is shown in Figure 6. In Figure 6a, the single DTAB molecule can be adsorbed at the oxygen site, but the adsorption efficiency is low, the single SDS molecule cannot be adsorbed at the oxygen site, and part of the SDS cannot be adsorbed on the graphite surface effectively (Figure 6b). When DTAB and SDS are mixed, the DTAB molecule head group is adsorbed on the oxygen site on the graphite surface, and then the SDS molecule also is adsorbed with the DTAB molecule head group under the electrostatic interaction (Figure 6c). The MDS results reveal the adsorption structure of anionic and cationic surfactants on the oxygen-containing graphite surface. In the mixed use of DTAB and SDS, the head group of DTAB molecules provides an indirect adsorption site for SDS molecules, thus improving the adsorption efficiency of anionic surfactants on the surface of oxygen-containing graphite. The oxygen site is covered by anionic and cationic surfactants in a large extent, and the hydrophobic tail improves the hydrophobicity of the mineral surface, which is beneficial to reducing the amount of flotation collector and improve the flotation efficiency.

3. CONCLUSIONS

Compared with the single surfactant, the mixed surfactant has a significant effect on the low-rank coal flotation, and the combustible matter recovery of low-rank coal can be close to 80% under the condition of low concentration of surfactants (0.1 mM or 0.25 mM). In the mixed surfactant system, the hydrophobicity of the low-rank coal can be largely improved due to the synergistic effect of cationic surfactant DTAB and the anionic surfactant SDS. After adding a small amount of SDS to DTAB, the electronegative SDS can reduce the mutual repulsion between DTAB molecules, at the same time tighten the orientation of DTAB on the surface of low-rank coal, and improve the adsorption efficiency of surfactant molecules on the low-rank coal surface. The molecular simulation results reveal the adsorption behavior of anionic and cationic surfactants on the surface of oxygen-containing graphite from the molecular level and verify the experimental results too.

4. EXPERIMENTAL SECTION

4.1. Coal Samples and Chemicals. The coal sample was collected from Shendong Mining area in China. The raw coal was crushed and ground to less than 0.5 mm and then used in the flotation experiment. Table 2 lists the results of the proximate analysis, namely, moisture content (M), ash content (A), volatile matter content (V), and fixed carbon content (FC) as well as ultimate analysis. The fine coal samples were further ground to less than 0.074 mm for this work test. The cationic surfactant DTAB (purity of >99%) and the SDS (purity of >99%) were purchased from China Chemical Company, while the frother, 2-octanol, was obtained from Tianjin Maoda Chemical Reagent Co., Ltd. (purity of >99%). A traditional collector, diesel oil, was obtained from gas stations. Deionized water was used in all experiments.

4.2. XPS Measurement. XPS measurement was carried out using a surface analysis system (ESCALAB 250Xi, USA). Specifically, Al Kα radiation (hν = 1486.6 eV) from a monochromatic X-ray source and a 900 μm light spot size were used. Spectra were recorded at a pass energy of 20 eV with a step of 0.05 eV. The C 1s peak at 284.6 eV was used to correct the binding energy.

4.3. Flotation Measurement. The test used an XFD-type flotation machine with a volume of 1 L, and the slurry concentration was maintained at 80 g/L. Before the test, the weighed DTAB, SDS, and surfactant mixtures (the mixing ratio is DTAB/SDS = 2:1) were dissolved in a flotation cell, and the concentrations of the surfactant were 0.1, 0.25, and 0.5 mM, respectively. After pulp conditioning (stirring at an impeller speed of 1800 r/min for 30 s), the collector (diesel oil) and frother (2-octanol) were added for contact times of 120 and 30 s, respectively. The dosage of diesel oil was kept at 4 kg/t (kg per ton of dry coal), and the dosage of 2-octanol was kept at 500 g/t. The airflow rate was 1 L/min, and the flotation concentrate of the product was collected over 300 s flotation duration. The concentrates and tailings were filtered and dried.

Table 2. Proximate and Ultimate Analyses of the Coal

|        | proximate analysis (wt %, ad %) | ultimate analysis (wt %, daf %) |
|--------|-------------------------------|---------------------------------|
|        | M                | A                  | V                | FC               | C | H | N | S | O' |
|        | 4.80             | 12.24              | 29.35            | 53.61            | 79.64 | 4.92 | 0.89 | 0.71 | 13.84 |

a, ad, air dry basis. b, daf, ash free basis. c, by difference.
Equation 1 describes the combustible matter recovery, which was used to evaluate the flotation performance. 34,35

\[
\text{combustible matter recovery (\%)} = \frac{M_C (A_e - A_C)}{M_e A_p (100 - A_e)} \times 100
\]

where \(M_C\) is the weight of the concentrate (\%), \(M_e\) is the weight of the feed (\%), \(A_C\) is the ash content of the concentrate (\%), and \(A_e\) is the ash content of the feed (\%).

### 4.4. Wetting Rate Measurement

To analyze the wetting rate of the sample, a series of adsorption experiments were carried out. The sample preparation method was similar to the flotation experiment, but the sample size was \(74 \, \mu\text{m}\). When the surfactant is added, the mixture without collector and frother is stirred for 2 min, and the obtained solid residues were dried in the oven. Then, the wetting rates of the coal samples to diesel oil were measured using a K100 surface tension analyzer (Krüss GmbH, Germany). The coal sample was accurately weighed to 2 g and added to the test tube. The head of the test tube was tightened with a nut, while the tail was sealed with filter paper. A sample tube with a coal sample was attached to the hook of the balance and moved 2 mm above the glass container, which was filled with diesel oil. By adjusting the experimental parameters, the depth of the test tube immersed in the diesel was 2 mm, and one data point was generated every 4 s. When the quality of the tube no longer changed, the test stopped.

### 4.5. Contact Angle Measurement

The contact angle test used a DSA100 contact angle tester from Bruker, Germany. The measuring range was 0–180°, and the measuring error was \(\pm 0.1°\). Before the test, the coal samples treated with different surfactants were pressed on a tabletting machine to form coal pieces with a thickness of about 2 mm, the pressure of the tablet press was set to 50 MPa, and the pressure hold time was 2 min. The measurement of the contact angle at different times was used as a comparison.

### 4.6. Surface Tension Measurement

The surface tension of the surfactant system at different concentrations was measured using the K100 surface tension instrument (Krüss GmbH, Germany). After the instrument was preheated, the sample cell was cleaned and dried. The platinum plate was heated to red and cooled for 2 min. It was installed on the top microbalance of the K100. The distance was manually adjusted between the liquid surface and the sheet by about 1 cm, and then the start button was clicked to measure. The surface tension test was carried out at 23 ± 0.5 °C. The repeatability of the test was verified three times for each test, and the average value of the test results was taken as the final test value.

### 4.7. Zeta Potential Measurement

The raw coal was further ground to less than 74 \(\mu\text{m}\), and 1 g of sample was placed in a 100 mL beaker. Then, the surfactant solution was sequentially added following the concentration of the flotation solution, and the solution was stirred for 30 min to make the raw coal diffuse sufficiently. Finally, the sample to be tested was placed for 12 h. During the test, a certain amount of the suspension was sucked into the electrophoresis tank using a syringe and the gray motor potential at the natural pH (pH = 7) was measured. Each sample was measured three times, and the average value was taken.

### 4.8. Molecular Dynamics Simulation

It is well known that the surface of coal is composed of aromatic polycyclic structures, and XPS results show that there are still many oxygen-containing functional groups on the surface of low-rank coal. Therefore, in the simulation calculation, a graphite layer of 100 \(\times\) 100 \(\AA\) was constructed and nine \(–\text{CH}_2\text{OH}\) groups were grafted at nine different positions, which can simply represent the surface of low-rank coal in the flotation process. Furthermore, in order to simulate the actual coal surface, which is generally negatively charged in a liquid environment, the hydrogen atoms of \(–\text{CH}_3\text{OH}\) near the top of the surface model were removed and nine sodium ions were added to equalize the charge of the system (Figure 7c) The atoms in the oxygen-containing graphite model were constrained to save computation, and then forcite geometry optimization was applied to achieve structural relaxation of the surface model in a constant volume and temperature (NVT) ensemble. 37

The geometric optimization of the simulated structure was carried out by using the Material Studio 8.0 software developed by Accelrys Company. Then, 12 DTAB molecules, 12 SDS molecules, and a mixture with 12 DTAB molecules and 6 SDS molecules were placed vertically on the surface of oxygen-containing graphite, and a vacuum layer of 50 Å was established at the top of each structure to eliminate the influence of periodic boundary conditions (Figure 7d). The condensed-phase optimized molecular potentials were used for
COMPASS (atomistic simulation studies) field and MD computation. The functional form of the COMPASS force field consists of a bonding term and nonbonding term. The bonding term includes bond stretching, bond bending, bond torsion, bond angle bending, and their mutual coupling energy. Nonbonding terms include van der Waals and Coulomb energy. In this study, the form of surface adsorption plays a major role, and the influence of environmental pressure on the whole process was very weak, thus the constant particle number, volume, and temperature (NVT) ensemble with Nosé thermostat and a temperature of 298 K were selected, where the number of particles (N), the simulation box volume (V), and the temperature (T) were kept constant. In the process of simulation and calculation, a time step of 1.0 fs was adopted to integrate the equations of motion. The total simulation time was 500 ps at this time, and the energy and adsorption structure of the system did not change in the advance heuristic simulations, which was sufficient for energy equilibrium. In addition, Ewald summation and atom-based methods were used to calculate long-range electrostatic interactions and van der Waals interactions.

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**Notes**

The authors declare no competing financial interest.

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