Study of the Micromechanism of the Effect of Fatty Alcohol Poly(oxyethylene) Ether-9 on the Wettability of Jincheng Anthracite

Xiangjun Chen, Peiqi Zuo,* Guixin Zhang, Rui Min, and San Zhao

ABSTRACT: The influence mechanism of the adsorption of fatty alcohol poly(oxyethylene) ether (AEO₉) on the wettability of anthracite coal was studied by means of experiments and simulations. First, the contact angle and surface tension were measured. When the AEO₉ concentration was 0.5 wt %, the contact angle and surface tension were the smallest, which were 10.28° and 25.39 mN m⁻¹, respectively. X-ray photoelectron spectroscopy (XPS) indicated that the content of C−O functional groups on the anthracite surface increased by 20.76% after adsorption of AEO₉. The molecular orbital energy and electrostatic potential of AEO₉ and anthracite were calculated by density functional theory (DFT). There are two modes of electron transfer between the two orbitals: highest occupied molecular orbital (HOMO) transfer of AEO₉ to lowest unoccupied molecular orbital (LUMO) transfer of anthracite and HOMO transfer of anthracite to LUMO transfer of AEO₉. The dynamics simulation results show that the addition of AEO₉ increases the migration rate of water molecules, promotes the movement of a large number of water molecules toward the surface of anthracite, and enhances the thickness of the water molecular layer on the surface of anthracite. The analysis of the relative concentration shows that AEO₉ is distributed at the anthracite/water interface. AEO₉ molecules are intertwined and connected by hydrophobic chains to form a network structure, which covers the anthracite surface horizontally, thus promoting the strength of the anthracite/water interaction.

1. INTRODUCTION

The transport and use of coal generates large amounts of dust, which endangers the occupational health and safety of workers.¹,² By the end of 2021, there were 11,809 cases of occupational pneumoconiosis in China, accounting for 76.65% of new occupational diseases. Therefore, developing effective dust control technology for the safety of miners is critical.

At present, most underground coal mines use water spray dust suppression to reduce the dust concentration at the working face. Improving coal dust wettability by adding surfactants is a research focus. Sun et al.³ analyzed the wetting process of bituminous coal by SDS, SDBS, and SDDS through experiments and simulations and pointed out that the wetting efficiency of three surfactants for bituminous coal is: SDS > SDDS > SDBS. Shi et al.⁴ studied the synergistic effect between noncationic surfactants and pointed out that the addition of noncationic surfactants reduced the electrostatic repulsion between anionic surfactants, thus increasing the adsorption density of coal surfactants. Xu et al.⁵ analyzed the coal dust wettability from three anionic surfactants and found that the wettability was determined by the adsorption density and hydrophilic−lipophilic balance (HLB) value. High adsorption density and low HLB or low adsorption density and high HLB surfactants wetted the coal samples for a relatively long time. Wang et al.⁶ found that with increasing surfactant concentration, the spray dust reduction efficiency first increased and then decreased through wind tunnel experiments, with OP-10 significantly outperforming the other surfactants in terms of wetting performance. However, the selection of dust suppressants is currently relatively undefined, relying mainly on past experience. The dust suppression performance evaluation by experimental means is time-consuming and laborious, and a complete system for evaluating wettability has not yet been developed.⁷,⁸ There are often large differences between the results of different experiments.⁹ Zhao et al.¹⁰ compared the effects of static and dynamic experiments on dust suppression performance and found that the two conclusions were not the same. One of the main reasons is the lack of research into the micromechanisms of wetting.

Received: September 20, 2022
Accepted: November 3, 2022
Published: November 12, 2022
Molecular dynamics simulations can be used to study the interaction of substances at the microscopic level. It is an effective way to study the wetting mechanism of dust suppressants on coal dust.\textsuperscript{11–15} Li et al.\textsuperscript{16} studied the effect of benzene rings on the adsorption of coal/surfactants through molecular dynamics simulation. The benzene ring enhanced the adsorption strength of the surfactant on the high-rank coal surface through $\pi$ bonds; however, on lower-order coals, the impact was less. Niu et al.\textsuperscript{17} described the wetting mechanism of dodecyl glycoside (APG-12) on subbituminous coal at the molecular level. The hydrogen bond adsorption mechanism was analyzed in conjunction with density functional theory, which was mutually verified by contact angle and electron microscopy scanning experiments and simulations. Sun et al.\textsuperscript{18} studied the adsorption configuration of SDS and APG1214 on the surface of bituminous coal by molecular dynamics simulation and determined the best combination ratio of SDS and APG1214 in combination with the wetting coal, and its greater hydrophobicity may cause more harm to the surface of bituminous coal by molecular dynamics simulation. The benzene ring enhanced the adsorption strength of the surfactant on the high-rank coal surface through $\pi$ bonds; however, on lower-order coals, the impact was less. Niu et al.\textsuperscript{17} described the wetting mechanism of dodecyl glycoside (APG-12) on subbituminous coal at the molecular level. The hydrogen bond adsorption mechanism was analyzed in conjunction with density functional theory, which was mutually verified by contact angle and electron microscopy scanning experiments and simulations. Sun et al.\textsuperscript{18} studied the adsorption configuration of SDS and APG1214 on the surface of bituminous coal by molecular dynamics simulation and determined the best combination ratio of SDS and APG1214 in combination with the wetting experiment. However, These surfactant adsorption models are all based on low metamorphic coal. There is little research on high metamorphic coal. Most scholars have shown that hydrophilic oxygen-containing functional groups, mainly hydroxyl and ether bonds, are gradually shed from the coal surface during the coalification process, resulting in an increase in hydrophobicity and a decrease in hydrophilicity of coal.\textsuperscript{20–22} As a result, high-rank coal is more hydrophobic than low-rank coal, and its greater hydrophobicity may cause more harm to coal miners. Therefore, studying the wetting characteristics of high-rank coal for mine dust removal is significant.

Herein, the mechanism of action of nonionic surfactant AEO\textsubscript{9} in improving the anthracite surface wettability was studied by experiments and simulations. First, preliminary analyses of the AEO\textsubscript{9} wetting characteristics were carried out by surface tension and contact angle experiments. Scanning electron microscopy (SEM) and XPS were used to analyze the variation trend of elements and functional groups on the surface of anthracite before and after the adsorption of the surfactant. Combined with Materials Studio, the molecular orbital energy of AEO\textsubscript{9} and anthracite as well as the changes in surface electrostatic potential before and after adsorption were analyzed based on density functional theory (DFT). The anthracite/AEO\textsubscript{9}/H\textsubscript{2}O system was constructed from the perspective of molecular dynamics. Setting the anthracite/H\textsubscript{2}O system as the control group, the interaction energy, relative concentration distribution, and diffusion coefficient of water molecules were analyzed to gain a deeper understanding of the AEO\textsubscript{9} wetting effect on anthracite from a molecular level.

2. EXPERIMENTAL METHODS

2.1. Instruments and Materials. 2.1.1. Instruments. The instruments used in this experiment are shown in Table 1.

| Instrument Name | Model |
|-----------------|-------|
| Electronic Balance | J602 |
| Organic Element Analyzer | FLASH2000 |
| Constant-Temperature Magnetic Stirrer | 85-2 |
| Vacuum Drying Oven | DZF-6020AB |
| Optical Contact Angle Measuring Instrument | Kruss DSA30 |
| High-Resolution Scanning Electron Microscope | Merlin Compact |
| X-ray Photoelectron Spectrometer | Thermo Scientific Escalab 250Xi |

Table 1. Types of Experimental Instruments

2.1.2. Surfactants. Because nonionic surfactants do not ionize when dissolved in water, their high stability makes them less susceptible to strong electrolytes and not easily affected by acids and bases. They are mixed with other surfactants, have excellent compatibility, and are widely used in mining, petroleum, textile, and cosmetic industries. Therefore, the nonionic surfactant AEO\textsubscript{9} was selected as the research object in this study. The chemical structure and stick model of AEO\textsubscript{9} are shown in Figure 1b. AEO\textsubscript{9} is prepared by the addition of long-chain fatty alcohols and oxirane molecules. These surfactants have better stability, excellent biodegradability, water solubility, wettability, and permeability.

2.1.3. Anthracite Structure. The Jincheng anthracite was selected as the experimental coal sample, and the experimental coal sample was prepared according to the GB/474-2008 standard. The results of the industrial and elemental analyses of anthracite are given in Table 2. Anthracite was crushed to obtain coal samples with particle sizes below 200 mesh and dried for subsequent experiments. The anthracite model constructed by Professor Zhang was used. The molecular structure of anthracite is shown in Figure 1a.

2.2. Surface Tension and Contact Angle. The coal sample selected is Jincheng anthracite with a particle size below 0.075 mm, which is dried in a DZF-6020AB vacuum drying oven at 105 °C. Finally, the samples were pressed into smooth round coal cakes with a diameter of 50 mm and a thickness of 2 mm using a tabletop press. We select APG with a purity of 50 wt % as the raw material, add water to dilute it to 0.01, 0.03, 0.05, 0.07, 0.10, 0.3, and 0.5 wt %, respectively, and set clear water as the control group. The contact angle of anthracite was measured by a Kruss DSA30 optical contact angle measuring instrument, and the surface tension of surfactant solutions with different concentrations was measured by this instrument. To reduce the experimental error, the anthracite samples were measured three times at different positions and the average value was calculated.

2.3. Scanning Electron Microscopy. To study the change in surface morphology of anthracite after AEO\textsubscript{9} treatment, scanning electron microscopy was used to collect images in high vacuum mode. Anthracite samples treated with clean water and anthracite samples treated with 0.05 and 0.5 wt % AEO\textsubscript{9} were set as the control group. Scanning electron microscopy was carried out under a 25 kV accelerating voltage and magnification of 400X to visually observe the binding and adsorption effect of the surfactant on the anthracite surface. This helps to analyze the dust suppression characteristics of AEO\textsubscript{9} on the anthracite surface.

2.4. XPS Analysis. A Thermo Scientific Escalab 250Xi X-ray electron spectrometer was selected to analyze the surface element content of anthracite before and after adsorption of AEO\textsubscript{9}. Spectral information was recorded using Al Ka radiation ($h\nu = 1486.6$ eV) from a monochromatic X-ray source and a 400 μm spot at a passage energy of 20 eV and a step size of 0.05 eV. The C 1s of contaminated carbon (284.8 eV) was selected for calibration of the binding energy, and then the data were processed by peak splitting fitting with Avantage software.

2.5. Molecular Dynamics Simulation. Materials Studio software was chosen to carry out the simulation. First, electrostatic potential simulations were performed in the DMol\textsuperscript{3} module to optimize the structure of each molecular
model and to analyze the Mulliken charge changes. The specific settings are as follows: the PW91 functional was based on the generalized gradient approximation (GGA), and the basis set was the double numerical polarization basis set (DNP).

Anthracite/AEO₉/water and anthracite/water systems were constructed using the AC module. Each system contains 8 surfactant molecules, 20 anthracite molecules, and 1000 water molecules. The two systems were geometrically optimized and annealed several times using the Forcite module to obtain the lowest energy and most stable configuration. The molecular dynamics simulation of the two systems was carried out using the Forcite module. Finally, the NVT was selected for the ensemble, the temperature was set to 298 K, and the nose temperature control method was selected. The simulation duration was 1000 ps, ensuring that the system has sufficient time to reach the adsorption equilibrium state. The Ewald algorithm was used for electrostatic interactions with an accuracy of 0.001 kcal/mol. An atom-based algorithm was used for van der Waals interactions with a truncation radius of 1.25 nm. In addition, a vacuum layer of 50 Å was added to each model to eliminate the effect of periodic boundary conditions. To reduce the computational time, two-thirds of the coal structure model was fixed in each system so that one-third of the top was in a free state. According to You et al., the restrictive method has almost no effect on the calculations. After the calculation was completed, combined with the energy and temperature curve, the first 400 ps was used for the system to reach the equilibrium state, and the last 600 ps was used for data analysis and calculation.

Dynamic simulation is carried out in COMPASS force field. This force field has a high precision computing ability for the properties of condensed molecules, suitable for most covalent molecular systems. At present, it has covered common organic substances, inorganic molecules, polymers, some metal ions, metal oxides, and others (Figures 2).

### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of Surface Tension and Contact Angle.

The surface tension of AEO₉ at different concentrations is shown in Figure 4a. When the concentration increased from 0 to 0.1 wt %, the surface tension of the AEO₉ solution decreased rapidly from 72.17 to 31.39 mN m⁻¹. When the concentration of the solution exceeds 0.1 wt %, the surface tension of the solution does not decrease significantly with increasing concentration and tends to be smooth gradually, indicating that 0.1 wt % is close to the CMC of AEO₉. Combined with the contact angle in Figures 4b and 3, the anthracite surface without the adsorbed surfactant has more hydrophobicity. When the initial concentration of 0.1 wt % AEO₉ was used, the contact angle decreased significantly from 70.14 to 37.5° with a reduction rate of 47%. When the solution concentration increased from 0.1 to 0.5 wt %, the contact angle began to decrease slowly, and finally gradually stabilized. There are lot of hydrophobic sites on the anthracite surface. At low concentrations, AEO₉ molecules are adsorbed on the

![Figure 1. (a) Molecular structures of anthracite. (b) Molecular structures of AEO₉.](http://pubs.acs.org/journal/acsodf)

### Table 2. Industrial Analysis of Jincheng Anthracite

| industrial analysis (%) | elemental analysis | density (g/cm³) |
|-------------------------|--------------------|-----------------|
| M₉₀ | A₉₀ | V₉₀ | FC₉₀ | C | H | O | N | S | |
| 0.68 | 25.96 | 6.72 | 69.44 | 89.75 | 4.67 | 2.61 | 2.23 | 0.74 | 1.43 |
Figure 2. (a) Anthracite/AEO$_9$/H$_2$O system. (b) Anthracite/H$_2$O system (for the convenience of observation, AEO$_9$ is shown with purple markings and the lower fixed area of anthracite is shown in orange).

Figure 3. Test chart of the contact angle between AEO$_9$ solution with different concentrations and anthracite.

Figure 4. (a) Surface tension curves of AEO$_9$ solutions with different concentrations. (b) Contact angle curves of AEO$_9$ solution with the anthracite surface at different concentrations.
anthracite surface, and the hydrophilic group of AEO is exposed to the water phase, providing a large number of hydrophilic points for anthracite, which makes the contact angle of anthracite rapidly reduce and the hydrophilicity rapidly increase. When the surfactant concentration exceeds the critical micelle concentration (CMC), the surfactant will exist in the aqueous solution in the micellar state, so that the decrease in contact angle tends to gradually stabilize. The experimental results show that AEO can enhance the wetting ability of anthracite at certain concentrations. After exceeding the concentration range, the wettability does not fluctuate significantly with changes in the concentration.

3.2. SEM and EDS Analysis. Figure 5 shows the surface of the anthracite sample sprayed with clean water. SEM magnification of 400 times that the coal dust particle size is small and the particles are relatively loose, indicating that the coal dust particles diffuse easily, thus causing serious environmental pollution. Figure 5b,c shows the anthracite surface sprayed with 0.05 and 0.5 wt % AEO solution, respectively. After the surfactant is sprayed, fine particles combine with each other, increasing the fine particle size. When fine anthracite particles are wetted, a liquid bridge is formed between the wetted anthracite particles under hydrogen bond action. Under the liquid bridge action, they rapidly combine with each other to form larger aggregates. When the coal dust is dried, the water in the agglomerates gradually evaporates, and the liquid bridge is transformed into a solid bridge so that the coal dust continues to maintain the agglomerated large particles form. The presence of surfactants promotes the formation of liquid bridges, which not only improves the wetting efficiency of anthracite but also plays a role in binding and consolidating coal dust.

3.3. XPS Analysis. To further explore the effect of AEO adsorption on the physical and chemical properties of the anthracite surface, the change in oxygen-containing functional group content on the anthracite surface was analyzed by XPS. Figure 6 shows that there are carbon and oxygen peaks, but the peaks are not obvious due to the low content of N. The XPS full spectrum scanning data are shown in Table 3. The contents of C and O on the anthracite surface changed significantly before and after treatment with AEO solutions of different concentrations. The content of O in untreated anthracite is only 9.31%, which indicates that there are fewer oxygen-containing functional groups in the molecule of anthracite, with poor hydrophilicity and wettability. After AEO treatment, the O content of anthracite increased significantly, while the C content decreased significantly. After adsorption of 0.05 and 0.5 wt % AEO, the O contents of anthracite are 13.15 and 14.59%, respectively. The reason is that the hydrophilic end of the surfactant has replaced the hydrophobic aromatic hydrocarbons on the anthracite surface through adsorption, which is equivalent to increasing the O content at the hydrophobic sites. In the concentration range of 0.05–0.5 wt %, with increasing AEO concentration, the hydrophobicity of the anthracite surface is obviously decreased, and the wettability is increased. After 0.5 wt % AEO adsorption, the O/C on the anthracite surface increases from 10.47 to 17.49% (Table 4).
3.4. Dynamic Simulation Analysis. 3.4.1. Electrostatic Potential Analysis. The magnitude of the electrostatic potential can directly reflect the charge distribution characteristics of molecules (including nuclei and electrons). By analyzing the electrostatic potential diagram, various possible chemical properties of molecules can be predicted, such as the active sites of electrophilic or nucleophilic reactions. Therefore, the electrostatic potential plays an important role in the analysis of intermolecular interactions. The molecular electrostatic potential was analyzed by the DMol3 module. As shown in Figure 6, the red area represents the most negative electrostatic potential value of the molecule, showing electrophilic. At this time, the energy level of the electron is high, the density of the electron cloud is large, and it is easy to lose electrons to form hydrogen bonds. The blue area represents the most positive electrostatic potential value of the molecule, showing nucleophilic. At this time, electrons are relatively scarce, not easy to lose, vulnerable to attack by nucleophilic atoms, and easily obtain electrons to form hydrogen bonds. The white area indicates that the electrostatic potential in this area is zero or relatively low, and the structure is more stable.

Table 3. XPS Full Spectrum Scanning Data of Anthracite Treated with AEO₉ of Different Concentrations

| types     | area (P) | atomic (%) | area (P) | atomic (%) | area (P) | atomic (%) |
|-----------|----------|------------|----------|------------|----------|------------|
| C 1s      | 178,016.29 | 88.93      | 145,233.35 | 84.81      | 134,462.09 | 82.92      |
| O 1s      | 49,288.71  | 9.31       | 59,743.86  | 13.19      | 62,203.30  | 14.50      |
| N 1s      | 5702.37    | 1.76       | 5540.78    | 2.00       | 6764.32    | 2.58       |
| (O/C) ratio (%) | 10.47 | 15.55 | 17.49 |

Table 4. Organic Carbon Content and Weight Ratio of Different Anthracite Samples

| anthracite samples | relative concentration ratio of different forms of organic C (%) | C=O | C=O | C=H, C–C |
|--------------------|---------------------------------------------------------------|-----|-----|----------|
| anthracite         |                                                              | 2.48 | 4.56 | 92.96    |
| 0.05% AEO₉ + anthracite |                                                          | 2.02 | 19.86 | 78.12    |
| 0.5% AEO₉ + anthracite   |                                                          | 2.79 | 25.32 | 71.89    |

3.4. Dynamic Simulation Analysis. 3.4.1. Electrostatic Potential Analysis. The magnitude of the electrostatic potential can directly reflect the charge distribution characteristics of molecules (including nuclei and electrons). By analyzing the electrostatic potential diagram, various possible chemical properties of molecules can be predicted, such as the active sites of electrophilic or nucleophilic reactions. Therefore, the electrostatic potential plays an important role in the analysis of intermolecular interactions. The molecular electrostatic potential was analyzed by the DMol3 module. As shown in Figure 6, the red area represents the most negative electrostatic potential value of the molecule, showing electrophilic. At this time, the energy level of the electron is high, the density of the electron cloud is large, and it is easy to lose electrons to form hydrogen bonds. The blue area represents the most positive electrostatic potential value of the molecule, showing nucleophilic. At this time, electrons are relatively scarce, not easy to lose, vulnerable to attack by nucleophilic atoms, and easily obtain electrons to form hydrogen bonds. The white area indicates that the electrostatic potential in this area is zero or relatively low, and the structure is more stable.

The electrostatic potential diagrams of AEO₉ and anthracite molecules are shown in Figure 7a,b. The vicinity of the hydroxyl substituent group in the AEO₉ molecule is shown in red, indicating that a large number of negative charges are mainly concentrated on the polar hydroxyl group of the AEO₉ molecule. This indicates that the hydroxyl group in the AEO₉ molecule is a potential active site. The nitrogen atoms and hydroxyl groups in anthracite molecules are blue and red, indicating that a large number of positive and negative charges accumulate near the two atoms, which can form hydrogen bonds with hydroxyl and water molecules in surfactants. As shown in Figure 7c, the surfactant is adsorbed on the anthracite surface in the configuration with the hydrophobic end close to the anthracite molecule and the hydrophilic end toward the water molecule. At this time, the negative charge in...
the AEO$_9$ molecule is distributed on the oxygen atom of hydroxyl groups, such as $-0.461e$, $-0.457e$, $-0.467e$, $-0.468e$, $-0.449e$, $-0.441e$, and $-0.413e$. They easily form a large number of hydrogen bonds with water molecules, which can fix water molecules to achieve coal dust wetting.

Figure 8 shows the orbital energy diagram of the highest occupied molecular orbital (HOMO) and the lowest empty orbital (LUMO) of AEO$_9$ and anthracite molecules. Table 5 shows the quantum chemical calculation results of the orbital energy. Figure 8 shows that the HOMO orbitals of AEO$_9$ molecules are distributed on the oxygen atoms of hydrophilic groups, while the LUMO orbitals are distributed on the hydrogen atoms of hydrophilic groups. The energies of $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ were $-5.5968$ and $0.8576$ eV, respectively. According to frontier orbital theory, the difficulty of the interaction between two molecules depends on the energy difference ($\Delta E$) between the HOMO of the electron donor and the LUMO of the electron acceptor. The smaller $\Delta E$ is, the closer the energies are, and the greater the orbital interaction is. When the energy difference between HOMO and LUMO is less than 6 eV, the electron can jump between the two orbitals. According to Table 5, the difference $\Delta E_1$ between the HOMO of AEO$_9$ and the LUMO of anthracite is 2.7042 eV, and the difference $\Delta E_2$ between the HOMO of anthracite and the LUMO of AEO$_9$ is 4.698 eV, which is less than 6 eV; therefore, electrons can jump between two orbits. However, the energy difference $\Delta E_3$ between the HOMO and

Table 5. Computational Results of Orbital Energy at GGA/PW91 (d) Level (eV)

| molecule   | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | $\Delta E_1$ | $\Delta E_2$ | $\Delta E_3$ |
|------------|------------------|------------------|--------------|--------------|--------------|
| AEO$_9$    | $-5.5968$        | $0.8576$         | 2.7042       | 4.698        | 6.4544       |
| anthracite | $-3.8404$        | $-2.8926$        | 0.9479       |              |              |
LUMO of $\text{AEO}_9$ was larger than 6 eV, indicating that $\text{AEO}_9$ was not active and could not jump electrons in the two orbits of $\text{AEO}_9$.

($\Delta E_1$ is the difference between the HOMO of $\text{AEO}_9$ and the LUMO of anthracite, $\Delta E_2$ is the difference between the HOMO of anthracite and the LUMO of $\text{AEO}_9$, and $\Delta E_3$ is the difference between the HOMO and LUMO of $\text{AEO}_9$).

3.4.2. Interaction Energy. The interaction energy ($E_{\text{int}}$) of the $\text{H}_2\text{O}$/anthracite system was calculated to evaluate the wetting effect of $\text{AEO}_9$ on the anthracite surface. The calculation formula is as follows

$$E_{\text{int}} = \frac{E_{\text{t}} - E_{\text{vdw}} - E_e + E_v + E_s}{2}$$

where $E_{\text{int}}$ is the total interaction energy of the system, kcal/mol; $E_t$ represents the total energy of the system; $E_e$ is the energy of anthracite; $E_w$ is the energy of water molecules; $E_v$ is the energy of surfactants; $E_v$ represents van der Waals interaction energy; and $E_s$ stands for electrostatic interaction. The greater the absolute value of $E_{\text{int}}$ the stronger the interaction between the anthracite surface and water molecules, and the better the wettability. The calculation results are shown in Table 6.

In the anthracite/$\text{H}_2\text{O}$ system, the interaction energy between anthracite and water molecules is $-233.001$ kcal/mol, indicating that the surface of anthracite has poor hydrophilicity and is not easily wetted by water. This is consistent with the molecular structure of anthracite. The low content of O in anthracite molecules indicates that there are few polar oxygen-containing functional groups. There are a large number of hydrophobic sites on the surface of anthracite, which are dominated by aromatic hydrocarbons and other functional groups, resulting in a strong hydrophobicity of anthracite as a whole. After adding the surfactant, the interaction energy is $-513.469$ kcal/mol, indicating that the addition of $\text{AEO}_9$ makes the system release more energy, enhances the interaction between anthracite and water, and makes the adsorption configuration more stable.

3.4.3. Relative Concentration Distribution. The relative concentration distributions of anthracite/$\text{H}_2\text{O}$ and anthracite/$\text{AEO}_9$/H$_2$O systems after adsorption equilibrium were analyzed by the Forcite module. As anthracite molecules are limited, Figure 9 shows that the distribution range of anthracite

**Table 6. Interaction Energy between $\text{AEO}_9$ and the Anthracite/$\text{H}_2\text{O}$ Interface**

| system                  | $E_t$(kcal/mol) | $E_{\text{vdw}}$(kcal/mol) | $E_e$(kcal/mol) | $E_{\text{int}}$(kcal/mol) |
|-------------------------|-----------------|-----------------------------|----------------|-----------------------------|
| anthracite/$\text{H}_2\text{O}$ | $-233.001$     | $-130.336$                  | $-102.665$    | $-233.001$                  |
| anthracite/$\text{AEO}_9$/H$_2\text{O}$ | $-513.469$     | $-291.746$                  | $-221.723$    | $-513.469$                  |

![Figure 9](https://example.com/figure9.png)

**Figure 9.** Relative concentration distribution. (a) Anthracite/$\text{H}_2\text{O}$ system. (b) Anthracite/$\text{AEO}_9$/H$_2\text{O}$ system.

![Figure 10](https://example.com/figure10.png)

**Figure 10.** (a) Relative concentration distribution of $\text{AEO}_9$ in different sites. (b) Top view of $\text{AEO}_9$ after adsorption equilibrium.
is unaffected by the surrounding environment. In the anthracite/H2O system, the starting point of water molecules is ~20 Å, and there is a more stable water layer at 34 Å, with a thickness of 24 Å and a peak intensity of ~3.4. However, after adding the surfactant, the starting point of water molecules obviously moves to 30 Å, and the thickness of the water layer becomes 29 Å. It shows that the addition of the surfactant is equivalent to adding a layer of “protective film” or “water resisting layer” on the surface of anthracite. The “protection” effect of this layer increases the difficulty of diffusion of water molecules to the depth of anthracite. At the same time, the increased hydrophilic group has the ability to attract and fix water molecules, which increases the thickness of the water layer. In short, the addition of the surfactant increases the content of oxygen-containing functional groups on the surface of anthracite, enhances the interaction between the interface and water molecules, and thus improves the wettability of anthracite.

To further explore the adsorption morphology distribution of AEO9 on the anthracite surface, the relative concentration distribution of AEO9 at the hydrophilic end and hydrophobic end was determined. Figure 10 shows that AEO9 is mainly distributed on the anthracite surface in the range of 20–40 Å, indicating that the surfactants form a dense network structure and are concentrated at the anthracite/H2O interface. In combination with Figure 10, there is little difference between the peak positions of hydrophilic and hydrophobic sites of AEO9. The hydrophilic group peak appears at 33 Å and the hydrophobic peak appears at 31 Å. This shows that AEO9 is in a lying adsorption configuration on the anthracite surface, covering the hydrophobic part of anthracite. The polar hydrophilic group faces the water molecules, attracting more water molecules to move to the anthracite surface to achieve wetting.

3.4.4. Mean Square Displacement. The MSD and diffusion coefficient D can characterize the speed of molecular movement to some extent. The equation of motion is as follows

\[
\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} [r(t) - r(0)]^2
\]

\[
D = \lim_{t \to \infty} \frac{d}{dt} \left( \frac{\text{MSD}}{6t} \right) = \frac{1}{6K_{\text{MSD}}}
\]

where MSD represents the mean square displacement; N represents the total number of diffusion molecules; \(r(t)\) and \(r(0)\) are the position vectors of \(i\) molecule at time \(t\) and \(t = 0\), respectively; and \(K_{\text{MSD}}\) represents the slope of the MSD curve, that is, the diffusion coefficient is 1/6 of the slope of the MSD curve.

Figure 11 shows the MSD of water molecules in the two systems. The diffusion coefficient of water molecules in the water/anthracite system is \(7.54 \times 10^{-5}\) cm²/s, and after adding the surfactant, the diffusion coefficient of water molecules is \(8.84 \times 10^{-5}\) cm²/s. This shows that the addition of AEO9 changes the migration rate of water molecules. When AEO9 is adsorbed on the anthracite surface, a large number of hydrophilic functional groups at the head are exposed to the water phase, attracting water molecules to move rapidly to the anthracite surface, intensifying the migration rate of water molecules and wetting the anthracite.

4. CONCLUSIONS

Through experiments and molecular simulation, the adsorption principle of the surfactant fatty alcohol poly(oxyethylene) ether (AEO9) on the surface of anthracite and its influence on the wettability of anthracite were studied. The experimental results of surface tension and contact angle show that AEO9 can greatly reduce the surface tension of water and improve the hydrophilicity of anthracite. Combined with SEM and XPS experiments, it is found that after adding AEO9, the content of element C in anthracite decreases, the content of C–H/C–C and other groups decreases, and the thickness of the water layer increases significantly, from 5.46 to 25.32%. The change of these elements causes the change of the surface wettability of anthracite. The change of electrostatic potential before and after adsorption was calculated by DFT. The oxygen atom on AEO9 either group is the electrophilic reaction zone on the surfactant molecule, which is the main driving force for adsorption. Based on the frontier orbital theory, it is found that there are two transfer directions in the process of electron interaction, namely, the transfer from the HOMO orbital of AEO9 to the LUMO orbital of anthracite and the transfer from the HOMO orbital of anthracite to the LUMO orbital of AEO9. The adsorption equilibrium process of AEO9 on the anthracite surface was studied by molecular dynamics simulation. The results show that AEO9 is distributed in a netlike fashion at the anthracite/water interface, and it is mainly adsorbed on the anthracite surface in a flat adsorption configuration. The hydrophilic group plays a role in gathering water molecules toward the water phase.

■ AUTHOR INFORMATION

Corresponding Author
Peiqi Zuo – State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University), Jiaozuo 454003, China; orcid.org/0000-0003-1992-6850; Email: hidari9772@126.com

Authors
Xiangjun Chen – State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University), Jiaozuo 454003, China; orcid.org/0000-0003-1992-6850; Email: hidari9772@126.com

https://doi.org/10.1021/acsomega.2c06084
ACS Omega 2022, 7, 42582−42592
University), Jiaozuo 454003, China; State Collaborative Innovation Center of Coal Work Safety and Clean-efficiency Utilization (Henan Polytechnic University), Jiaozuo 454003, China; College of Safety Science and Engineering (Henan Polytechnic University), Jiaozuo 454003, China; orcid.org/0000-0003-4849-8349

Guixin Zhang – State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University), Jiaozuo 454003, China

Rui Min – State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University), Jiaozuo 454003, China

San Zhao – State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University), Jiaozuo 454003, China; orcid.org/0000-0002-1334-3593

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c06084

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (Nos. 51874122 and 52074105) and the Key R&D and Extension Projects of Henan Province (Nos. 202102310223 and 222102320017).

REFERENCES

(1) Liu, T.; Liu, S. The Impacts of Coal Dust on Miners’ Health: A Review. Environ. Res. 2020, 190, No. 109849.

(2) Zazouli, M. A.; Dehbandi, R.; Mohammadian, M.; Aarabi, M.; Dominguez, A. O.; Kelly, F. J.; Khodabakhshloo, N.; Rahman, M. M.; Naidu, R. Physico-Chemical Properties and Reactive Oxygen Species Generation by Respirable Coal Dust: Implication for Human Health Risk Assessment. J. Hazard. Mater. 2021, 405, No. 124185.

(3) Sun, L.; Ge, S.; Liu, S.; Jing, D.; Chen, X. Experimental and Molecular Dynamics Simulation Study for Preferring Coal Dust Wetting Agents. ACS Omega 2022, 7, 17593–17599.

(4) Shi, G.; Qi, J.; Wang, Y.; Shen, H. Synergistic Influence of Noncationic Surfactants on the Wettability and Functional Groups of Coal. Powder Technol. 2021, 385, 92–105.

(5) Xu, C.; Wang, D.; Wang, H.; Ma, L.; Zhu, X.; Zhu, Y.; Zhang, Y.; Liu, F. Experimental Investigation of Coal Dust Wetting Ability of Anionic Surfactants with Different Structures. Process Saf. Environ. Prot. 2019, 121, 69–76.

(6) Wang, P.; Han, H.; Tian, C.; Liu, R.; Jiang, Y. Experimental Study on Dust Reduction via Spraying Using Surfactant Solution. Atmos. Pollut. Res. 2020, 11, 32–42.

(7) Zhou, Q.; Qin, B. Coal Dust Suppression Based on Water Mediums: A Review of Technologies and Influencing Factors. Fuel 2021, 302, No. 121196.

(8) Xu, G.; Chen, Y.; Eksteen, J.; Xu, J. Surfactant-Aided Coal Dust Suppression: A Review of Evaluation Methods and Influencing Factors. Sci. Total Environ. 2018, 639, 1060–1076.

(9) Chang, P.; Zhao, Z.; Xu, G.; Ghosh, A.; Huang, J.; Yang, T. Evaluation of the Coal Dust Suppression Efficiency of Different Surfactants: A Factorial Experiment. Colloids Surf., A 2020, 595, No. 124686.

(10) Zhao, Z.; Chang, P.; Xu, G.; Ghosh, A.; Li, D.; Huang, J. Comparison of the Coal Dust Suppression Performance of Surfactants Using Static Test and Dynamic Test. J. Cleaner Prod. 2021, 328, No. 129633.

(11) Zhou, G.; Wang, C.; Liu, R.; Li, S.; Zhang, Q.; Liu, Z.; Yang, W. Synthesis and Characterization of Water Injection Fracturing Fluid for Wetting and Softening Coal Seam. Int. J. Rock Mech. Min. Sci. 2022, 150, No. 105024.

(12) Liu, Z.; Zhou, G.; Duan, J.; Liu, D.; Zhang, Q.; Guo, S. Preparation of Composite High-Efficiency Dust Suppressant and Relevant Molecular Dynamics Simulation for Wetting Coal Surface. Fuel 2021, 296, No. 120579.

(13) Hou, J.; Lin, S.; Du, J.; Sui, H. Study of the Adsorption Behavior of Surfactants on Carbonate Surface by Experiment and Molecular Dynamics Simulation. Front. Chem. 2022, 10, No. 847986.

(14) Li, N.; Pan, L.; Wang, L.; Huang, Y.; Yuan, D. Molecular Dynamics Study on the Wettability of the Lithium Droplet and Tungsten Surface. Langmuir 2022, 38, 2502–2514.

(15) Li, C.; Li, Y.; Yuan, R.; Lv, W. Study of the Microcharacter of Ultrastable Aqueous Foam Stabilized by a Kind of Flexible Connecting Bipolar-Headed Surfactant with Existence of Magnesium Ion. Langmuir 2013, 29, 5418–5427.

(16) Li, B.; Guo, J.; Liu, S.; Abijanics, B.; Zhang, L.; Sun, X. Molecular Insight into the Mechanism of Benzene Ring in Nonionic Surfactants on Low-Rank Coal Floatability. J. Mol. Liq. 2020, 302, No. 112563.

(17) Niu, W.; Nie, W.; Yuan, M.; Bao, Q.; Zhou, W.; Yan, J.; Yu, F.; Liu, C.; Sun, N.; Xue, Q. Study of the Microscopic Mechanism of Lauryl Glucoside Wetting Coal Dust: Environmental Pollution Prevention and Control. J. Hazard. Mater. 2021, 412, No. 125223.

(18) Sun, L.; Ge, S.; Jing, D.; Liu, S. Chen, X. Wetting Mechanism and Experimental Study of Synergistic Wetting of Bituminous Coal with SDS and APG1214. ACS Omega 2022, 7, 780–785.

(19) Mathews, J. P.; Chaffee, A. L. The Molecular Representations of Coal — A Review. Fuel 2012, 96, 1–14.

(20) Xu, C.; Wang, D.; Wang, H.; Xin, H.; Ma, L.; Zhu, X.; Zhang, Y.; Wang, Q. Effects of Chemical Properties of Coal Dust on Its Wettability. Powder Technol. 2017, 318, 33–39.

(21) Hu, Y.; Zhang, Q.; Zhou, G.; Wang, H.; Bai, Y.; Liu, Y. Influence Mechanism of Surfactants on Wettability of Coal with Different Metamorphic Degrees Based on Infrared Spectrum Experiments. ACS Omega 2021, 6, 22248–22258.

(22) Wang, H.; Zhang, L.; Wang, D.; He, X. Experimental Investigation on the Wettability of Respirable Coal Dust Based on Infrared Spectroscopy and Contact Angle Analysis. Adv. Powder Technol. 2017, 28, 3130–3139.

(23) Wei, S.; Yan, G.; Zhang, Z.; Liu, S.; Zhang, Y. Molecular structure analysis of Jincheng anthracite coal. J. China Coal Soc. 2018, 43, 555–562.

(24) Yan, G.; Ren, G.; Bai, L.; Feng, J.; Zhang, Z. Molecular Model Construction and Evaluation of Jincheng Anthracite. ACS Omega 2020, 5, 10663–10670.

(25) Nie, W.; Yuan, M.; Bao, Q.; Yan, J.; Zhou, W.; Guo, C.; Guo, L.; Niu, W.; Yu, F.; Hua, Y. Experimental and Molecular Dynamics Simulation Research on Compound Dust Suppressant Based on Locust Bean Gum. Adv. Powder Technol. 2022, 33, No. 103485.

(26) You, X.; He, M.; Wang, Z.; Wei, H.; Lyu, X.; He, Q.; Li, L. Molecular Dynamics Simulations of Nonylphenol Ethoxylate on the Hatcher Model of Subbituminous Coal Surface. Powder Technol. 2018, 332, 323–330.

(27) Sun, H. COMPASS: An Ab Initio Force-Field Optimized for Condensed-Phase ApplicationsOverview with Details on Alkane and Benzene Compounds. J. Phys. Chem. B 1998, 102, 7338–7364.

(28) Zhang, L.; Somasundaran, P.; Mallets, C. Adsorption of N-Dodecyl-β-d-Maltoside on Solids. J. Colloid Interface Sci. 1997, 191, 202–208.

(29) Zhao, B.; Li, S.; Lin, H.; Cheng, Y.; Kong, X.; Ding, Y. Experimental Study on the Influence of Surfactants in Compound Solution on the Wetting-Agglomeration Properties of Bituminous Coal Dust. Powder Technol. 2022, 395, 766–775.

(30) Yao, Q.; Xu, C.; Zhang, Y.; Zhou, G.; Zhang, S.; Wang, D. Micromechanism of Coal Dust Wettability and Its Effect on the Selection and Development of Dust Suppressants. Process Saf. Environ. Prot. 2017, 111, 726–732.

42591 https://doi.org/10.1021/acsomega.2c06084
ACS Omega 2022, 7, 42582–42592
(31) An, X.; Kang, Y.; Li, G. The Interaction between Chitosan and Tannic Acid Calculated Based on the Density Functional Theory. Chem. Phys. 2019, 520, 100–107.
(32) Du, A.; Mao, J.; Wang, D.; Hou, C.; Lin, C.; Yang, X.; Cao, H.; Mao, J. Wettability Alteration at a Water-Wet Quartz Surface by a Novel Trimeric Surfactant: Experimental and Theoretical Study. J. Mol. Liq. 2022, 354, No. 118771.
(33) Guo, L.; Kaya, S.; Obot, I. B.; Zheng, X.; Qiang, Y. Toward Understanding the Anticorrosive Mechanism of Some Thiourea Derivatives for Carbon Steel Corrosion: A Combined DFT and Molecular Dynamics Investigation. J. Colloid Interface Sci. 2017, 506, 478–485.
(34) Chen, X.; Yan, G.; Yang, X.; Feng, Z.; Wei, S.; Geng, N. Molecular dynamics simulation of the effect of SDS/SDBS on the wettability of anthracite. Coal Sci. Technol. 2021, 1–14.
(35) Jin, H.; Zhang, Y.; Dong, H.; Zhang, Y.; Sun, Y.; Shi, J.; Li, R. Molecular Dynamics Simulations and Experimental Study of the Effects of an Ionic Surfactant on the Wettability of Low-Rank Coal. Fuel 2022, 320, No. 123951.
(36) Lu, X.-X.; Xing, Y.; Fu, X.-H.; Jiang, C.-L. High-Efficient Dust Trapping Performance of AES/Polyacrylamide Strengthen Foam Based on the Structure Stability and Dust Wettability. Langmuir 2022, 38, 10442–10453.
(37) Yuan, M.; Nie, W.; Yu, H.; Yan, J.; Bao, Q.; Zhou, W.; Hua, Y.; Guo, L.; Niu, W. Experimental and Molecular Dynamics Simulation Study of the Effect of Different Surfactants on the Wettability of Low-Rank Coal. J. Environ. Chem. Eng. 2021, 9, No. 105986.
(38) Shi, L.; Tummala, N. R.; Striolo, A. C12E6 and SDS Surfactants Simulated at the Vacuum–water Interface. Langmuir 2010, 26, 5462–5474.
(39) Liu, Z.; Zhou, G.; Li, S.; Wang, C.; Liu, R.; Jiang, W. Molecular Dynamics Simulation and Experimental Characterization of Anionic Surfactant: Influence on Wettability of Low-Rank Coal. Fuel 2020, 279, No. 118323.