Effect of Dodecyl Trimethyl Ammonium Bromide on the Migration of Water Molecules in the Pores of Lignite: An Experimental and Molecular Simulation Study

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ABSTRACT: Molecular dynamics simulations and experiments were used to study the influence of dodecyl trimethyl ammonium bromide (DTAB) on the migration of water molecules in the pores of lignite. To simulate the accuracy, $^{13}$C NMR was used to confirm the structure of Shengli lignite. It was found through adsorption experiments that DTAB reduces the specific surface area and pore volume of lignite. Molecular simulations indicate that the lignite and water molecules are primarily connected by hydrogen bonding. DTAB impedes the movement of water molecules in the pores of lignite and the storage space of compressed water molecules. Water molecules are mainly present in the pores of lignite in a posture parallel to the XOY plane, which facilitates the formation of hydrogen-bonding networks. However, this also leads to a decrease in the mobility of water molecules. Experimental and simulation results show that DTAB can enter lignite pores, reducing the water absorption in lignite. This is highly significant for the processing and utilization of lignite.

1. INTRODUCTION

Lignite is a porous material similar to colloids. It consists of a large number of pores and cracks. The pore characteristics of lignite have an essential influence on its surface properties and applications. In recent years, the pore characteristics of lignite have attracted a lot of attention in the research community. The results show that the pore characteristics of lignite, such as the pore volume, shape, and specific surface area, have a significant impact on the properties of lignite.

Researchers believe that there are two main reasons for the difficulty in removing moisture from lignite during lignite drying and upgrading: rich surface oxygen functional groups and developed internal pores. Lester and Kingman used a microwave to dry lignite. The results demonstrate that the rate of microwave dehydration time is fast and occurs in a short time while microwave drying increases the damage to lignite structure. Bergins et al. found that the physical properties of lignite change during the hot-pressing dehydration process. The pore volume of the central pores increased with the increase of temperature, while the pore volume of macropores decreased. Tahmasebi et al. studied the effects of microwave drying on the oxygen functional group content present on the surface of coal samples. It was found that the content of carboxyl and phenolic hydroxyl groups on the surface of lignite decreased and the surface hydrophilicity decreased. Allardice et al. treated low-rank coal by hydrothermal treatment. It was found that hydrothermal treatment changed the molecular structure of low-rank coal.

The abundant oxygen-containing functional groups and complex pore distribution on the surface of lignite also have an important influence on lignite flotation. This is because the oxygen-containing functional groups are polar and can efficiently adsorb polar molecules such as water to form a tight hydration film on the surface of lignite. Similarly, the absorption of water on the pores of the lignite surface increases the degree of hydration on the lignite surface, resulting in poor lignite floatability. Research on flotation agents to improve the floatability of lignite has been conducted. Lyu et al. used molecular dynamics simulation to study the adsorption behavior of NPEO-12 on the surface of a sub-bituminous coal model. The results show that the adsorption of NPEO-12 on the surface of low-rank coal is primarily controlled by the polar interactions between the ethoxy group of NPEO-12 and the hydrophilic group on the coal surface. Jia et al. conducted flotation experiments and reported that the flotation effect of the THF collector is stronger than that of dodecane.

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Polar head groups easily form hydrogen bonds with the oxygen-containing functional groups on the coal surface, and the non-polar ends combine with the coal surface, thereby improving the floatability of the coal. Chang et al. studied the influence of different types of Gemini cationic surfactants on the wettability of coal tar pitch. The results show that the Gemini surfactant changes the surface charge and polarity of coal tar pitch through electrostatic adsorption and van der Waals interactions, thereby affecting the wettability of coal. Though there are numerous reports on the interaction between the surfactant and coal surface, the effect of the surfactant on coal pore water absorption has rarely been studied.

In most cases, the surface of the lignite remains covered with water and water molecules penetrate the lignite. The microscopic interactions at the molecular level are not yet clear, and conclusions on the effect of surfactants on lignite pores are derived from experiments. With the continuous development of molecular simulation technology, it has become important to use molecular simulation to analyze microscopic interactions between molecules. The present work combines molecular simulation and experiments to study the effect of surfactant (DTAB) on the migration of water molecules in the pores of lignite.

2. RESULTS AND DISCUSSION

2.1. 13C NMR Analysis. NMR technology, an advanced experimental method, is currently used widely in the research of coal structure. 13C NMR spectroscopy uses peak fit software to unfold the spectra. Figure 1 shows the original curve and fitting curve of lignite. The peak area of the fitted curve is normalized to estimate the carbon content in different components.

![Figure 1. 13C NMR spectra of lignite.](image)

It can be seen from Figure 1 that the chemical shift range of the 13C NMR nuclear magnetic spectrum is 0–220 ppm. The 13C NMR spectrum mainly shows the absorption peaks of aliphatic carbon (at 0–60 ppm), aromatic carbon (at 100–165 ppm), and the carbonyl and carboxyl carbon (at 175–220 ppm). Twelve main structural parameters and the relative contents of various functional groups of lignite were calculated according to the peak positions (Table 1).

The aromatic carbon in lignite accounts for 56.44%, and the aliphatic portion accounts for 43.56% of the structure (Table 1). The results show that aromatic carbon is still the main component of the lignite macromolecular structure and aliphatic carbon is an important component of the connection of aromatic structural units. In addition, \( f^A \) is 14.29%, showing that the sp2-hybridized carbon in the aromatic ring still has a large number of C==O functional groups around the aromatic ring. The \( f^P \) and \( f^O \) are 9.23% and 1.43%, respectively, indicating the presence of a small number of hydroxyl groups and ether bonds around the aromatic core in the coal-like molecular structure. The oxygen atoms are primarily present in the aliphatic structure. This is consistent with the structural characteristics of the generally accepted low-rank lignite.

According to Table 1, the molecular structure of lignite can be further analyzed. The \( f_0 \) in the lignite molecule consists of \( f^H \) and \( f^K \). The \( f^K \) includes \( f^O \) and \( f^B \). The ratio of aromatic-hydrocarbon carbons to bridge carbons is an important parameter that reflects the degree of polycondensation in aromatic compounds. According to eq 1, the \( X_{BP} \) value of lignite is 0.14. The \( X_{BP} \) values of the benzene and naphthalene rings are 0 and 0.25, respectively. Through mathematical combination analysis, it was found that the aromatic framework of lignite is mainly composed of four naphthalene rings, two benzene rings, one pyridine, and one pyrrole. Therefore, according to the oxygen–carbon ratio and the hydrogen–carbon ratio, the molecular formula of lignite can be obtained as \( C_{64}H_{109}O_{21}N_2 \). The ratio of oxygen-containing functional groups in the lignite molecule is determined according to the structural parameters related to oxygen and its relative content. The ratio between ether bonds, carbonyl groups, carboxyl groups, and hydroxyl groups is approximately 6:4:4:3. The molecular model of lignite is shown in Figure 2. To verify the rationality of the molecular

![Figure 2. Molecular model of lignite.](image)

Table 1. Coal Structure Parameters

|      | \( f^P \) | \( f^O \) | \( f^N \) | \( f^H \) | \( f^K \) | \( f^A \) | \( f^O \) | \( f^B \) | \( f_{CH} \) | \( f_{CH_2} \) | \( f_{CH_3} \) | \( f_{CH_4} \) |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| coal | 56.44% | 14.29% | 42.15% | 13.66% | 28.49% | 9.23% | 13.94% | 5.32% | 43.56% | 18.63% | 23.50% | 1.43% |

Note: \( f^P \) - total sp2-hybridized C; \( f^K \) - carbonyl C and carboxyl C; \( f^O \) - aromatic C; \( f^N \) - non-protonated aromatic C; \( f^H \) - protonated aromatic C; \( f^A \) - aromatic C-bonded hydroxyl or ether oxygen; \( f^K \) - alkylated aromatic C; \( f^B \) - aromatic bridgehead C; \( f_{CH} \) - total sp2-hybridized C; \( f_{CH_2} \) - CH or CH2; and \( f_{CH_3} \) - aliphatic C-bonded oxygen.
structure of lignite, the simulated nuclear magnetic spectrum was compared with the experimental nuclear magnetic spectrum (Figure 3). Both were in good agreement with each other. Thus, a reasonable lignite structure was proposed.

\[ X_{BP} = \frac{I^{BP}}{I_a^{BP} + I_s^{BP} + I_p^{BP}} \]  

(1)

2.2. Pore Distribution Analysis. The low-temperature liquid nitrogen adsorption method is often used to study the pore structure of coal. The Brunauer–Emmett–Teller (BET) algorithm and the Barrett–Joyner–Halenda (BJH) model were used to calculate the specific surface area and pore size distribution of the channels. The adsorption isotherms of low-temperature liquid nitrogen and the pore size distribution of lignite are shown in Figure 4. Morphological characteristics of lignite pores can be analyzed by adsorption isotherms.\(^{30}\)

The low-temperature liquid nitrogen adsorption isotherm of lignite belongs to the second type of adsorption curve (Figure 4a).\(^{31}\) The first half of the adsorption isotherm curve slowly rises, indicating an increase in pressure. At this time, the adsorption of liquid nitrogen gradually changes from a single layer to a multilayer adsorption. The second half of the adsorption curve shows a sharp increase, reaching a maximum adsorption amount of 29.78 cm\(^3\)/g, proving the occurrence of capillary condensation. Based on the adsorption isotherms, the pore size of lignite can be divided into four categories, namely, cylindrical, slit, wedge, and ink bottle. According to the adsorption loop, the pores in the lignite are mainly cylindrical closed at one end.

Figure 4b shows the pore size distribution of lignite. The higher the peak intensity in the pore size distribution diagram, the greater the number of pores of this size. The pore size distribution of lignite in Figure 4b presents a multi-peak distribution with a pore size ranging from 3 to 160 nm and the main peak between 3 and 4 nm. From Figure 4b, it can be seen that the pore content of lignite at 3.4 nm (34 Å) is the largest. Therefore, a cylindrical lignite pore model of 3.4 nm was established by molecular dynamics simulation. The changes in the pore specific surface area and pore volume after lignite adsorbs DTAB are shown in Table 2. The specific surface area and pore volume of lignite pores decrease after DTAB adsorption, indicating that DTAB not only adsorbs on the outer surface of lignite but also forms aggregates in the pores of lignite.

2.3. Weak Interaction Analysis between Molecules. To reveal the effect of DTAB on the migration of water molecules in the pores of lignite, it is necessary to have a better understanding of the interaction between water molecules and lignite molecules. The polar functional groups in lignite have a great influence on the movement of water molecules. Therefore, it is necessary to study microscopic interactions. The independent gradient model (IGM) is an effective method proposed by Lefebvre et al. for studying weak interactions.\(^{32}\) The IGM can distinguish weak interactions between molecules and within molecules. The formula for calculating the density gradient of IGM is as follows:

| sample          | specific surface area (m\(^2\)/g) | pore volume \((10^{-3} \text{ cm}^3)/\text{g}\) |
|----------------|----------------------------------|---------------------------------------------|
| lignite         | 2.13                             | 12.07                                       |
| DTAB (50 mg/L)  | 1.74                             | 10.84                                       |
| DTAB (400 mg/L) | 1.01                             | 8.54                                        |

Table 2. Structural Parameters of Lignite Pores Before and After Adsorption

Figure 4. Pore data of lignite. (a) Liquid nitrogen adsorption isotherm. (b) Distribution of pore size in lignite.
Here, $i$ is the atomic number, $\nabla \rho$ is the gradient vector, and $\text{abs}(\nabla \rho)$ represents the absolute value of each component of the $\nabla \rho$ vector inside.

To further analyze the weak interaction between different components in lignite and water molecules, polar functional groups such as carboxyl, phenolic hydroxyl, carbonyl, ether, pyridine, and pyrrole were selected. Subsequently, the IGM analysis was performed.\textsuperscript{33} The IGM isosurface and scatter plots are shown in Figure 5 where weak interactions between molecules can be deduced. Different types of weak interactions are denoted by blue/green/red colors. Blue indicates hydrogen-bond interactions, green indicates the effect of dispersive forces, and red indicates the presence of a steric effect.

The IGM isosurface is mainly dominated by dark-blue regions with scattered green areas, indicating that the interaction between water molecules and each functional group is due to hydrogen bonding and dispersing forces. The two dark-blue regions in Figure 5a indicates the formation of two hydrogen bonds. The scatter plot shows that peaks with different peak intensities appear at $-0.04$ on the abscissa. The electron density at this position is not substantial or close to 0. The peak is of high intensity, which reflects the strong hydrogen bond in the weak interaction.

The hydrogen-bond strength between water molecules and different components reflects the hydrophilicity of the corresponding components. The total hydrogen bond energy, hydrogen bond length, and bond angle for each adsorption configuration were calculated according to the International Union of Pure and Applied Chemistry (IUPAC) convention. The statistical results are shown in Table 3. The hydrogen bonds in each adsorption model can be divided into three categories, namely, O–H···O, N–H···O, and O–H···N (Figure 5). The bond lengths are 1.70, 1.91, and 1.94 Å, while the hydrogen bond angles are 142.01°, 178.20°, 179.75°, and 178.37°, respectively. The sum of the van der Waals radii of hydrogen and oxygen atoms and nitrogen atoms are 2.72 and 2.75 Å, respectively. By comparing the length of the hydrogen bond with the van der Waals radius, it can be found that the two atoms forming the hydrogen bond penetrate each other. It is generally believed that, in a hydrogen bond, the smaller the bond length, the greater the bond angle and the higher the bond strength. Energy analysis reveals that the total bond energy of hydrogen bonds formed by carboxyl groups is the

| types | hydrogen-bond length (Å) | hydrogen bond angle (°) | total hydrogen bond energy (kJ/mol) |
|-------|--------------------------|-------------------------|------------------------------------|
| a     | 1.88                     | 142.01                  | -61.89                             |
|       | 1.70                     | 159.68                  |                                    |
| b     | 1.87                     | 176.60                  | -47.86                             |
| c     | 1.94                     | 178.37                  | -41.38                             |
| d     | 1.91                     | 178.20                  | -41.61                             |
| e     | 1.87                     | 172.87                  | -40.96                             |
| f     | 1.97                     | 179.75                  | -30.57                             |

Figure 5. Weak interactions between different components of lignite and water molecules. (a) carboxyl, (b) phenolic hydroxyl, (c) pyridine, (d) carbonyl, (e) ether, and (f) pyrrole.

Table 3. Analysis of Hydrogen-Bond Properties
largest but the bond angle is the smallest. This is caused by the geometric interaction between the two hydrogen bonds formed by the carboxyl group. The statistical results show that the hydrophilic order of the different components in the lignite molecule is carboxyl > phenolic hydroxyl > carbonyl > pyridine > ether > pyrrole (Table 3).

2.4. Structural Properties of Water Molecules and DTAB. 2.4.1. Relative Concentration Distribution. DTAB affects the movement of water molecules in the pores of lignite. Figure 6 shows the variation of the number of water molecules in the pores of lignite with simulation time. A number of water molecules in the pores of lignite, rich in polar functional groups, take considerable time to reach saturation. In DTAB-containing systems, the lag time is significant. Moreover, the number of water molecules in the pores of lignite after equilibrium is less.

The equilibrium configuration of water molecules and DTAB in the pores of lignite is shown in Figure 7. It can be seen that, as part of the DTAB molecules enter the pores of the lignite, they are attracted by the polar functional groups on the surface of the lignite and form agglomerations inside the pores of the lignite. This increases the relative concentration of DTAB. As DTAB enters the pores of the lignite, the arrangement of water molecules in the pores of the lignite gets affected first. Due to the space limitation of DTAB, only a few water molecules can enter the bottom of lignite pores. Therefore, between 0 and 27 Å, the relative concentration of water molecules in a system containing DTAB is lower. In DTAB systems, between 27 and 50 Å, the higher relative concentration of water molecules is mainly due to the attraction of lignite molecules and the reduction of the occurrence space, which leads to a tighter distribution of water molecules. The lignite surface near 50 Å is not smooth, and ravines can be seen (Figure 15). Due to the competitive adsorption relationship between DTAB and water molecules on the surface of lignite, smaller water molecules can easily enter the gully, which reduces the relative concentration of DTAB. Between 50 and 110 Å, the increase in the relative concentration of water molecules is mainly due to the rise in the number of water molecules outside the pores of the lignite.

2.4.2. Radial Distribution Function (RDF). The radial distribution function (RDF) is often used to study the aggregation characteristics of liquid molecules or gas molecules in a fluid. The oxygen and nitrogen atoms in lignite are denoted as OC and NC, respectively. Similarly, oxygen and hydrogen atoms in water molecules are labeled as OW and HW, respectively. The nitrogen atoms in the DTAB head group are labeled as NDTAB. Figure 9 shows the radial distribution functions of OC−HW, NC−HW, OW−OW, O−O, NDTAB−OW, and NDTAB−HW.

The peak position and intensity of the RDF indicate the spatial adsorption distance and the order degree, respectively. The Ow−Ow radial distribution function can be used to describe the relative position and order of water molecules. The peak position appears near 2.73 Å, which is in agreement with previous reports (2.7 Å)34,35 (Figure 9c). The position of this peak corresponds to the distance of the first coordination ring between water molecules. It is similar to the distance in the pores of lignite.

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between two oxygen atoms in pure water. When \( r > 4 \) Å, the distribution of water molecules begins to become uniform and the curve starts to approach 1. As the distance increases, the influence of lignite and DTAB on water molecules becomes smaller, so the peak intensity decreases. The DTAB head group is hydrophilic. Due to the strong attraction of lignite molecules, the head group is nearer the polar functional groups of lignite molecules (Figure 9e,f). Moreover, the arrangement of water molecules near the DTAB head group shows a strong order. This phenomenon is mainly caused by the double attraction of the polar tube energy group and the hydrophilic head group of DTAB by the water molecules near the inner wall of lignite pores (Figure 9a,b). The water molecules in the middle of the pores of the lignite also show an orderly arrangement due to the small space and the rejection of the hydrophobic DTAB tail chain. Therefore, in DTAB-containing systems, the first RDF peak increases (Figure 9c).

The first peak of the radial distribution function of \( \text{O}_\text{C}^{-}\text{H}_\text{W} \), \( \text{N}_\text{C}^{-}\text{H}_\text{W} \), \( \text{O}_\text{W}^{-}\text{O}_\text{W} \), \( \text{O}_\text{W}^{-}\text{H}_\text{W} \), \( \text{N}_\text{DTAB}^{-}\text{O}_\text{W} \), and \( \text{N}_\text{DTAB}^{-}\text{H}_\text{W} \) represents the average length of hydrogen bonds. The first peak of the radial distribution curves of \( \text{O}_\text{W}^{-}\text{H}_\text{W} \) shows that the average length of the hydrogen bonds between water molecules is approximately 1.79 Å. The average hydrogen-bond length formed by oxygen atoms/nitrogen atoms and hydrogen atoms on the surface of lignite is 1.85 and 1.87 Å, respectively. After the addition of DTAB, the peak position of the RDF does not change, indicating that DTAB does not affect the adsorption distance between particles (Figure 9). However, the peak intensity of the RDF increases, which suggests that the degree of order is enhanced. Thus, the probability of target particles appearing around the center particle is higher.

2.4.3. Orientation Distribution. The angles \( \psi \) and \( \varphi \) between the H–H/water dipole and the Z-axis normal vector can be used to determine the orientation characteristics of...
water molecules in the pores of lignite. The angles $\psi$ and $\varphi$ are
determined from the $\cos(\psi)/\cos(\varphi)$ value and then calculated
by the inverse trigonometric function. The angular probability
distribution statistics can better estimate the distribution of
water molecules in the pores of lignite. It is worth mentioning
that $\psi$ is an acute angle.

The orientation distribution indicates that the angle
distribution between the dipole of H–H/water molecules
and the Z axis in the pores of lignite is mainly concentrated at
90° (Figure 10). The results show that the water molecules in
the pores of lignite are primarily distributed parallel to the XOY
plane, which facilitates the formation of hydrogen bonds.36,37
In the absence of DTAB, the angle between the dipole of the
water molecule and the Z axis changes significantly in the range
of 65°–115°. Similarly, the angle between the H–H and Z axis
also shows significant fluctuations. The combination of the two
orientations shows that, in the system without DTAB, the
movement of water molecules intensifies and the range of the
orientation distribution is larger.

2.5. Dynamic Properties of Water Molecules and
DTAB. 2.5.1. Mean Square Displacement (MSD). MSD is a
time-dependent statistical value used to describe the degree of
deviation of the target particle’s spatial position relative to the
initial position at a specific moment in the system. The MSD
can be expressed as

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}(t) - \mathbf{r}(0))^2$$  \hspace{1cm} (5)

Here, $N$ is the number of diffusing molecules and $\mathbf{r}(t)$ and $\mathbf{r}(0)$
represent the position vectors of the molecules at time $t$ and $t =
0$, respectively. The diffusion coefficient of the molecule can be
obtained by the following Einstein formula:

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} (\mathbf{r}(t) - \mathbf{r}(0))^2$$  \hspace{1cm} (6)

The diffusion coefficient of water molecules can be obtained
by combining eqs 5 and 6. The MSD of the confined water
molecules is smaller than that of the bulk phase (Figure 11).
This indicates that the pores have a specific limit to the
diffusion of water molecules. Based on the slope of the MSD,
the diffusion coefficients of the water molecules in the bulk
phase can be calculated as $2.62 \times 10^{-9} \text{m}^2/\text{s}$ and $2.60 \times 10^{-9}
\text{m}^2/\text{s}$, which is in good agreement with the SPC water model
diffusion coefficient ($2.67 \times 10^{-9} \text{m}^2/\text{s}$).38 However, due to

space constraints within the pores of lignite, the diffusion
coefficient of water molecules is less than that of bulk water.
The decrease in the diffusion coefficient inside the pores is
because DTAB enters the interior of the lignite pores, causing
compression in the space where the water molecules reside.
There are electrostatic interactions between water molecules
and polar groups on the surface of lignite molecules/DTAB
polar head groups, which hinder the migration of water
molecules.

2.5.2. Hydrogen Bond Statistics. Hydrogen bonding is an
essential factor affecting the movement of water molecules.
According to the Material Studio definition of hydrogen
bonding, the maximum hydrogen acceptor distance is 2.5 Å
and the minimum donor–hydrogen acceptor angle is 90°.
Figure 12 is a schematic diagram of hydrogen bonding. Figure
13 gives a statistical result of the number of hydrogen bonds
formed by water molecules. Figure 14 shows the hydrogen-
metal length distribution formed by water molecules.

With the passage of simulation time, the number of
hydrogen bonds usually decreases first and then increases.
Finally, it tends to become constant. This is because, at
the beginning of the simulation, polar molecules such as water are
easily attracted to lignite and move toward the lignite pores.
The hydrogen-bond network between water molecules is
destroyed. As the number of water molecules in the pores
gradually increases, a large number of hydrogen bonds are
formed between the water molecules and the polar functional
groups. Finally, when the number of water molecules in the
pores of lignite becomes stable, the number of hydrogen bonds
also stabilizes. The average hydrogen-bond number of the two
systems was calculated and compared. It was found that DTAB
promotes the formation of hydrogen bonds, explaining the
change in the diffusion coefficient of water molecules, which is

![Figure 11. MSD of water molecule. (a) Restricted water molecules in lignite channels. (b) Water molecules in bulk.](https://dx.doi.org/10.1021/acsomega.0c04012)

![Figure 12. Schematic diagram of the hydrogen bond.](https://dx.doi.org/10.1021/acsomega.0c04012)
also consistent with the result of the orientation analysis of water molecules.

Similarly, the distribution of the hydrogen-bond length is also different. This is different from the hydrogen-bond length indicated by the RDF. The hydrogen-bond length calculated by the RDF gives the average value. In systems containing DTAB, the hydrogen-bond length distribution is primarily concentrated between 1.7 and 1.8 Å (Figure 14). In contrast, in the absence of DTAB, the hydrogen-bond length distribution is mainly focused between 1.8 and 1.9 Å. This shows that the addition of DTAB brings water molecules closer to the water molecules/lignite molecules. The result is consistent with the results of the radial distribution function.

3. CONCLUSIONS
Through experiments and molecular simulations, the weak interaction between water molecules and lignite molecules was investigated and the effect of the surfactant (DTAB) on the migration of water molecules in the pores of lignite was analyzed.

(1) The aromatic hydrocarbon content in Shengli lignite was 56.44%, and the aliphatic carbon content was 43.56%, indicating a low carbonization degree of long lignite. The skeleton structure of lignite is mainly composed of benzene and naphthalene rings and contains a large number of oxygen-containing functional groups.

(2) The pore channels of Shengli lignite are mainly mesopores. Adsorption experiments show that, with the increase of the surfactant concentration, DTAB gives rise to adsorption and aggregation in the pores of lignite.

(3) Through independent gradient analysis, it was found that water molecules and various polar functional groups are mainly connected by hydrogen bonds, accompanied by dispersion interactions. The order of hydrophilicity between polar functional groups is carboxyl > phenolic hydroxyl > carbonyl > pyridine > ether > pyrrole.

(4) Molecular dynamics simulations were used to study the effect of DTAB on the migration of water molecules in lignite channels. The simulation results show that DTAB can hinder the movement of water molecules in the lignite tunnel. Due to the influence of DTAB, the existing space of water molecules in the channel is compressed. The water molecules in the pores mainly exist in the lignite pores in a posture parallel to the XOY plane. The number of hydrogen bonds formed between water molecules and water molecules/lignite molecules is high, which results in the restriction of the movement of water molecules.

Therefore, DTAB reduces the hydrophilicity of lignite not only by covering the oxygen-containing functional groups on the surface of lignite but also by affecting the migration of water molecules in the internal pores of lignite.

4. EXPERIMENTAL AND SIMULATION STUDIES

4.1. Materials. The lignite sample was obtained from a coal preparation plant (Inner Mongolia Autonomous Region, China). The industrial analysis of the coal sample is presented in Table 4 where \( M_{\text{ad}} \) represents the moisture content, \( A_{\text{ad}} \) is the ash content, \( V_{\text{daf}} \) is the volatile content. The industrial analysis shows that the ash content of the coal sample is 4.66%. Also, the elemental analysis showed that the oxygen content is 21.94%. This indicates that the addition of surfactants gives better separation and purification in the lignite flotation process. The cationic surfactant, dodecyl trimethyl ammonium bromide (DTAB, analytical grade, purity \( \geq 99\% \)), was obtained from Sinopharm Chemical Reagent Co., Ltd., China.

4.2. \(^{13}\)C NMR Measurement. \(^{13}\)C NMR tests were performed on an AVANCE III 600 spectrometer (Bruker, Germany) at a resonance frequency of 75.425 MHz. A contact time of 0.05 s, a recycle delay of 4 s, and a scan number of 7000 were used for the measurement. A solid-state cross-polarization/magic-angle spin (CP/MAS) broadband dual resonance probe was used to obtain the nuclear magnetic resonance carbon spectrum of long-flame coal under high sensitivity.

4.3. Adsorption Experiment and Pore Size Measurement. Surfactant solutions (50 and 400 mg/L) were initially
prepared. The 60-mesh lignite obtained by crushing and sieving was used for pore size measurements. The prepared medicament and the coal sample were mixed in a solid–liquid ratio of 1:1. They were placed in a constant temperature water bath, stirred at a constant speed for 2 h at room temperature, and subsequently dried. After 12 h of vacuum degassing, the liquid nitrogen adsorption experiment was carried out at a temperature of 77.35 K and a standard atmospheric pressure. A specific surface area/pore analyzer (ASAP 2020, U.S.A.) was used to determine the pore structure and diameter.

4.4. Molecular Simulation. Researchers have proposed the Wiser model and the Hatcher model of coal structure. In order to simulate the accuracy, the molecular model of lignite was established by analyzing the 13C NMR of lignite.

The geometric optimization task in the Dmol3 module was used to calculate the adsorption configuration between a water molecule and the different components of a lignite molecule. The exchange-correlation function used in the geometric optimization task is the generalized gradient approximation function (GGA-PBE) proposed by Perdew, Burke, and Ernzerhof. It uses the density functional theory (DFT-D) to correct the dispersion force. The convergence accuracy of the self-consistent field (SCF) in the geometric optimization task was set to $1.0 \times 10^{-5}$. Multiwfn and Visual Molecular Dynamics (VMD) software were used to analyze the weak interactions between water molecules and different components of lignite molecules in stable adsorption configurations.

Lignite has a complex structure, and hence the lignite macromolecular model is not directly used in molecular dynamics calculations. According to the adsorption experiment, a carbon nanotube with a diameter of 3.4 nm was created at the center of a $60 \times 60 \times 50 \times (X \times Y \times Z)$ 3D box. The lignite molecules were then randomly added to the periphery of the carbon nanotube. To further reduce the unreasonable contact of lignite molecules, a Nosé thermostat was used for annealing (5 times) from 300 to 500 K after the geometric optimization, and the lowest energy configuration was selected for subsequent calculations. It is worth pointing out that the carbon nanotubes were fixed to ensure a constant pore diameter during the annealing process. Finally, the carbon nanotubes are deleted in the lowest energy configuration obtained (Figure 15). Subsequently, 6000 water molecules and 8 DTAB molecules were added along the Z axis direction. The composition of the entire system is shown in Table 5. A vacuum with a thickness of 50 Å was applied on top of the water molecules to avoid any interaction between the top and bottom surfaces of the model due to periodic boundary conditions. The total length of the box in the Z-axis direction is 180 Å (Figure 16). It should be noted that a simple point charge (SPC) water model was used.

| Material | Number |
|----------|--------|
| water    | 6000   |
| lignite  | 60     |
| DTAB (8 C12H25N(CH3)3+ and 8 Br−) | 8 |

Molecular dynamics simulation (MD) was performed on the Forcite Plus module in Materials Studio 7.0 software. Following geometry optimization, MD simulation was performed at 298 K using the NVT ensemble with a simulation time of 1 ns and a time step of 1 fs. Electrostatic interactions were computed using the Ewald summation method with an Ewald accuracy of $10^{-4}$ kcal/mol. Van der Waals interactions were calculated using the atom-based summation method with a cutoff distance of 15.5 Å. In the whole simulation process, the Nosé–Hoover function was used to control the temperature with a default constant of 0.01. The simulation data of the last 300 ps were used for analysis. The COMPASS force field was employed in the molecular dynamics simulation. In addition, the movement of water molecules in the pores of lignite was also simulated in the absence of DTAB.

**Table 5. Material Composition in Simulation**

**Figure 15. Surface model of lignite: (a) front view and (b) top view.**

**Figure 16. Molecular dynamics calculation model.**

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REFERENCES
(1) Wijaya, N.; Choo, T. K.; Zhang, L. Generation of ultra-clean coal from Victorian brown coal — Sequential and single leaching at room temperature to elucidate the elution of individual inorganic elements. *Fuel Process. Technol.* 2011, 92, 2127−2137.
(2) Fei, Y.; Giroux, L.; Marshall, M.; et al. A comparison of primary lignite structure as determined by pyrolysis techniques with chemical characteristics determined by other methods. *Fuel* 2006, 85, 998−1003.
(3) Fei, Y.; Zhang, C.; Marshall, M.; et al. The effect of cation content of some raw and ion-exchanged Victorian lignites on their equilibrium moisture content and surface area. *Fuel* 2007, 86, 2890−2897.
(4) Fei, Y.; Artanto, Y.; Giroux, L.; Marshall, M.; Jackson, W. R.; MacPhee, J. A.; Charland, J.-P.; Chaffee, A. L.; Allardice, D. J. Comparison of some physico-chemical properties of Victorian lignite dewatered under non-evaporative conditions. *Fuel* 2006, 85, 1987−1991.
(5) Yu, Y.; Liu, J.; Wang, R.; et al. Effect of hydrothermal dewatering on the slurryability of brown coals. *Energy Convers. Manage.* 2012, 57, 8−12.
(6) Charrière, D.; Behra, P. Water sorption on coals. *J. Colloid Interface Sci.* 2010, 344, 460−467.
(7) Švábová, M.; Weishauptová, Z.; Pribyl, O. Water vapour adsorption on coal. *Fuel* 2011, 90, 1892−1899.
(8) Miura, K.; Mae, K.; Li, W.; et al. Estimation of Hydrogen Bond Distribution in Coal through the Analysis of OH Stretching Bands in Diffuse Reflectance Infrared Spectrum Measured by in-Situ Technique. *Energy Fuels* 2001, 15, 599−610.
(9) Lester, E.; Kingman, S. Effect of Microwave Heating on the Physical and Petrographic Characteristics of A.U.K. Coal. *Energy Fuels* 2004, 18, 140−147.
(10) Bergins, C.; Hulston, J.; Strauss, K.; Chaffee, A. L. Mechanical/ thermal dewatering of lignite. Part 3: Physical properties and pore structure of MTE product coals. *Fuel* 2007, 86, 3−16.
(11) Tahmasebi, A.; Yu, J.; Li, X.; et al. Experimental study on microwave drying of Chinese and Indonesian low-rank coals. *Fuel Process. Technol.* 2011, 92, 1821−1829.
(12) Tahmasebi, A.; Yu, J.; Han, Y.; et al. Study of Chemical Structure Changes of Chinese Lignite upon Drying in Superheated Steam, Microwave, and Hot Air. *Energy Fuels* 2012, 26, 3651−3660.
(13) Allardice, D. J.; Clemow, L. M.; Favas, G.; et al. The characterisation of different forms of water in low rank coals and some hydrothermally dried products. *Fuel* 2003, 82, 661−667.
(14) Xia, Y.; Yang, Z.; Zhang, R.; et al. Performance of used lubricating oil as flotation collector for the recovery of clean low-rank coal. *Fuel* 2019, 239, 717−725.
(15) Xia, Y.; Wang, L.; Zhang, R.; et al. Enhancement of flotation response of fine low-rank coal using positively charged microbubbles. *Fuel* 2019, 245, 505−513.
(16) Chen, S.; Wang, S.; Li, L.; et al. Exploration on the mechanism of enhancing low-rank coal flotation with cationic surfactant in the presence of oily collector. *Fuel* 2018, 227, 190−198.
(17) Shen, M.; Liu, et al. Improving Coal Flotation by Gaseous Collector Pretreatment Method and its Potential Application in Preparing Coal Water Slurry. *Processes* 2019, 7, 500.
(18) Chen, Z.; Qiu, H.; Hong, Z.; et al. Molecular dynamics simulation of a lignite structure simplified model absorbing water. *Mol. Simul.* 2020, 71.
(19) Temel, H. A.; Bozkurt, V.; Ayhan, F. D. Desulfurization and Deashing of Adriyaman-Goelbasi Lignite by Flootation. *Energy Sources* 2010, 32, 727−743.
(20) Kelebek, S.; Demir, U.; Sahbaz, O.; et al. The effects of dodecylamine, kerosene and p H on batch flotation of Turkey’s Tuncbilek coal. *Int. J. Miner. Process.* 2008, 88, 65−71.
(21) Vamvakia, D.; Agridiotis, V. The effect of chemical reagents on lignite flotation. *Int. J. Miner. Process.* 2001, 61, 209−224.
(22) Lyu, X.; You, X.; He, M.; et al. Adsorption and molecular dynamics simulations of nonionic surfactant on the low rank coal surface. *Fuel* 2018, 211, 529−534.
(23) Jia, R.; Harris, G. H.; Fuerstenau, D. W. An improved class of universal collectors for the flotation of oxidized and/or low-rank coal. *Int. J. Miner. Process.* 2000, 58, 99−118.
(24) Chang, H.; Zhang, H.; Jia, Z.; Li, X.; Gao, W.; Wei, W. Wettability of coal pitch surface by aqueous solutions of cationic Gemini surfactants. *Colloids Surf., A* 2016, 494, 59−64.
(25) Argyris, D.; Ho, T.; Cole, D. R.; et al. Molecular Dynamics Studies of Interfacial Water at the Alumina Surface. *J. Phys. Chem. C* 2011, 115, 2038−2046.
(26) Argyris, D.; Tummala, N. R.; Striolo, A.; et al. Molecular Structure and Dynamics in Thin Water Films at the Silica and Graphite Surfaces. *J. Phys. Chem. C* 2008, 112, 13587.
(27) Argyris, D.; Cole, D. R.; Striolo, A. Dynamic Behavior of Interfacial Water at the Silica Surface. *J. Phys. Chem. C* 2009, 113, 19591−19600.
(28) Wang, S.; Hu, Y.; Yang, X.; et al. Examination of adsorption behaviors of carbon dioxide and methane in oxidized coal seams. *Fuel* 2020, 273, 117599.
(29) Okolo, G. N.; Neomagus, H. W. J. P.; Everson, R. C.; et al. Chemical-structural properties of South African bituminous coals: Insights from wide angle XRD-carbon fraction analysis, ATR-FTIR, solid state C-13 NMR, and HRTEM techniques. *Fuel* 2015, 158, 779−792.
(30) Cai, Y.; Liu, D.; Pan, Z.; et al. Pore structure and its impact on CH4 adsorption capacity and flow capability of bituminous and subbituminous coals from Northeast China. *Fuel* 2013, 103, 258−268.
(31) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physiosorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2016, 87, 1051−1069.
(32) Lefebvre, C.; Rubez, G.; Khartabil, H.; et al. Accurately extracting the signature of intermolecular interactions present in the NCI plot of the reduced density gradient versus electron density. *Phys. Chem. Chem. Phys.* 2017, 19, 17928.
(33) Lu, T. molclus program; Version 1.9.5, http://www.keinsci.com/research/molclus.html.
(34) Xiong, W.; Liu, J. Z.; Ma, M.; et al. Strain Engineering Water Transport in Graphene Nano-channels. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* 2011, 84, No. 056329.
(35) Mosaddeghi, H.; Alavi, S.; Kowsari, M. H.; et al. Simulations of structural and dynamic anisotropy in nano-confined water between parallel graphite plates. *J. Chem. Phys.* 2012, 184703.
(36) Hirunsit, P.; Balbuena, P. B. Effects of Confinement on Water Structure and Dynamics: A Molecular Simulation Study. *J. Phys. Chem. C* 2007, 111, 1709−1715.
(37) Pertsin, A.; Grunze, M. WaterGraphite Interaction and Behavior of Water Near the Graphite Surface. *J. Phys. Chem. B* 2004, 108, 1357−1364.
(38) Mashl, R. J.; Joseph, S.; Aluru, N. R.; et al. Anomally immobilized water: A new water phase induced by confinement in nanotubes. *Nano Lett.* 2015, 3, 589−592.
(39) Jurkiewicz, A. Second moment of n.m.r. line for the Wiser model of coal. *Fuel* 1986, 65, 1022−1024.
(40) Hatcher, P. G. Chemical structural models for coalified wood (vitrinite) in low rank coal. Org. Geochem. 1990, 16, 959–968.
(41) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(42) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 2006, 27, 1787–1799.
(43) Kavimani, M.; Balachandran, V.; Narayana, B.; et al. Topological analysis (BCP) of vibrational spectroscopic studies, docking, RDG, DSSC, Fukui functions and chemical reactivity of 2-methylphenylacetic acid. Spectrochim. Acta, Part A 2017, 190, 47–60.
(44) Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, S80.
(45) Lim, J. Y. C.; Marques, I.; Ferreira, L.; et al. Enhancing the enantioselective recognition and sensing of chiral anions by halogen bonding. Chem. Commun. 2016, 52, 5527–5529.
(46) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. J. Mol. Graph. 1996, 14, 33–38.