Chemical Modification Effect of Compound Solutions of Surfactants with Acetic Acid on Coal Pores

Jun Xie, Haigang Du,* Shanle Chen, Xiangke Sun,* and Lin Xin

ABSTRACT: Coal seam pores are the major places for coalbed methane storage, diffusion, and seepage, and changes in the pore structure cause changes in the porosity. The porosity of coal seams can be effectively improved by applying strongly corrosive and oxidative chemical reagents to coal seam pores, but these reagents may pose threats to coal workers, corrode mining equipment, and pollute the environment. In this study, coal samples were treated with solutions compounded by acetic acid and anionic, cationic, and non-ionic surfactants. The variations of pores in coal samples after the compound modification of surfactants and acetic acid were investigated. Experimental methods of SEM, MIP, LTNA, PAC, and FTIR and fractal theory are applied in this work. The results reveal that the compound modification of surfactants and acetic acid conduces to the transformation of pore shape and affects a wider pore size range. The anionic and cationic surfactants can increase the hydrophilicity and can promote the connection of larger pores. The non-ionic surfactant reduces the hydrophilicity and capillary effect yet increases the porosity. Thus, it promotes the connection of pores and makes the pore surface smooth and the pore structure simple. Comparing the three kinds of surfactants, non-ionic surfactants are more conducive to coal seam pore reconstruction.

1. INTRODUCTION

Coal is a pore-fracture reservoir with dual pore systems. The main types of pores include primary pores, epigenetic pores, exogenous pores, and mineral pores and the main shapes include cylinder, parallel plate, slit, thin-neck bottle, and wedge. According to the occurrence state and pore size of coalbed methane (CBM), pores can be classified into two categories: seepage pores [including ultra-large pores (>10^4 nm), macro-pores (10^4 to 10^3 nm), and meso-pores (10^3 to 10^2 nm)] and adsorption pores [including transition pores (10^2 to 10 nm) and micro-pores (10–0 nm)].

The porosity of coal seams influences the desorption, diffusion, and seepage of CBM. For the purpose of improving the porosity of coal seams, promoting pore connectivity, and enhancing the permeability of coal seams, scholars have carried out in-depth research studies on the chemical modification of low-rank coal. The key to chemical modification lies in the dissolution of minerals on the surface and in pores of coal reservoirs with chemical reagents, which transforms the pore structure and improves the porosity of coal. At present, chemical modification is mainly realized by three methods: (1) acidification using strong acid or high-concentration weak acid, (2) modification by ionic liquids and surfactants, and (3) oxidation by strong oxidants. In terms of (1) acidification, the compound acid systems prepared using single or multiple strongly corrosive acids (including hydrofluoric acid, hydrochloric acid, nitric acid, sulfuric acid, etc.) can well corrode the minerals in coal, destroy the coal matrix, make the coal sample surface rough, and change the pore type, hence increasing the porosity of coal. In addition, high-concentration organic acids (including acetic acid, formic acid, and oxalic acid) can also corrode minerals in coal and destroy the crystal structure of coal, which improves the porosity of coal. The coal acidification process contains three stages: the initial contact stage, crystal failure stage, and reaction deceleration stage. After the minerals in coal are acidified and corroded, new precipitates are generated, which changes the compressive strength of coal. In terms of (2) modification of ionic liquids and surfactants, ionic liquids (including imidazole, sodium salicylate-imidazole, and ammonium carbamate) can dissolve the reducing groups in coal, generate many ether, carboxyl, and aromatic benzene ring structures, improve the cohesive energy of coal molecules, and change the functional groups and pore structure of coal. Surfactant solutions (such as cetyltrimethyl ammonium chloride and sodium dodecyl sulfate), which have good dispersion, can dissolve montmorillonite, increase the...
number of oxygen-containing functional groups in coal, ease the blockage of minerals in pores, and reduce the occupation of pore channels by clear water, thereby improving the porosity. In terms of (3) the oxidation of strong oxidants, strong oxidants (such as hydrogen peroxide and acetone) can break the aromatic side chains and bridge bonds, reduce the number of functional groups (such as hydroxyl, methylene, oxygen-containing functional groups, and aromatics), weaken the hydrophilicity of coal, and transform some micro-pores into mesopores and macropores, leading to an increase in porosity. After a surfactant and an ionic liquid are added to strong acid, the ion exchange capacity of the solution is strengthened and the substitution reaction of benzene ring structure of coal molecules improves. Accordingly, the porosity of coal multiplies exponentially.

The main method for CBM mining in China is underground extraction, which is an important technical means for CBM and coal mine safety. The porosity of coal seams is improved through chemical modification, which requires pressurized injection of chemical modification reagents through underground drilling and hydraulic measures. However, most of the chemical reagents reported in previous research studies show strong corrosion, strong oxidation, explosiveness, and toxicity, for example, hydrochloric acid, hydrofluoric acid, sulfuric acid, nitric acid, hydrogen peroxide, and acetone. For acetic acid, its mass fraction is also greater than 20%. If they are adopted for chemical modification through underground construction, they may not only pose potential threats to personnel safety and coal quality but also cause water pollution. Therefore, on the basis of previous studies, we select easily degradable anionic, cationic, non-ionic surfactants and low-concentration acetic acid to prepare a composite solution of different components for analyzing. By observing the pores of coal samples with composite solution, comparing changes in structural parameters (such as pore volume, pore specific surface area, average pore size, pore surface roughness, pore structure complexity, and porosity), and analyzing the impact of solution reformation on coal quality, we revealed the pore characteristics of coal after reformation.

2. SAMPLE COLLECTION AND EXPERIMENT

2.1. Sample Collection. The coal samples were collected from Wulunshan coal mine, Guizhou Province, China. They belong to anthracite whose vitrinite reflectance is 2.942%. In order to minimize the experimental error caused by the different coal samples, all the samples were from the same coal block (Figure 1).

2.2. Sample Processing.

(1) The collected fresh large coal block was prepared into coal samples of three specifications: cubic coal (length × width × height of 10 × 10 × 10 mm), granular coal (10–20 meshes), and coal powder (200–300 meshes). The mass difference between cubic samples was within 0.01 g.

(2) SDBS, HATB, and polyacrylamide (NPAM) served as the representative reagents of anionic, cationic, and non-ionic surfactants, respectively. The mass fraction of SDBS, CATB, and NPAM were all 0.5%.

(3) Five experimental solutions of different components were prepared: distilled water, acetic acid, acetic acid and SDBS, acetic acid and HATB, and acetic acid and NPAM. The mass fraction of acetic acid was 10%.

(4) Samples of the three specifications were soaked in the five experimental solutions in a constant-temperature (25 °C) water bath for 48 h.

(5) The soaked samples were washed with distilled water until the pH value became neutral. The samples, except for those reserved for proximate analysis, were put in a drying oven to dry at 80 °C for 24 h.

(6) The untreated raw coal sample was named 0# (raw coal sample), and the samples treated with the above five experimental solutions were named 1# (treated with distilled water), 2# (treated with acetic acid), 3# (treated with acetic acid and SDBS), 4# (treated with acetic acid and HTAB), and 5# (treated with acetic acid and NPAM), respectively.

(7) The treated test samples underwent scanning electron microscopy observation (SEM), mercury injection test (MIP), low-temperature nitrogen adsorption test (LNTA), proximate analysis of coal (PAC), and Fourier transform infrared spectroscopy (FTIR) (Figure 1).

Figure 1. Schematic diagram of experimental procedure (photograph courtesy Haigang Du. Copyright 2021).
2.3. Experiment and Analysis Method. 2.3.1. SEM Observation and Fractal Calculation. SEM can directly show the morphological characteristics, such as development scales and morphology, of pores on the surfaces of coal samples. A Quanta-250 scanning electron microscope was used to observe the microscopic morphology of the coal sample. There are three coal samples under the same treatment conditions, and the images are magnified at 1000× and 5000×. The SEM images (1000× and 5000×) were binarized through Image J software, and then, the porosities and pore fractal dimensions of coal samples were calculated. According to the binarized image, the box-counting model is used to calculate the slope of \( \log(N/\epsilon) \) and \( \log(1/L) \) to obtain the fractal dimension value \( D \) of pores. The calculation formula is

\[
D = \lim_{L \to \infty} \frac{\log(N/\epsilon)}{\log(1/L)}
\]

where \( \epsilon \) is the length of the box, \( N/\epsilon \) is the number of boxes covered, and \( D \) is the fractal dimension.

2.3.2. Mercury Intrusion Test and Fractal Calculation. Mercury intrusion assumes that the pores in coal all are cylindrical pores with different diameters and two open ends, and they are connected with the outer surface of coal particles. The pore structure parameters were calculated according to the volume of injected mercury and the pressure of injection. An AutoPore IV 9500 mercury porosimeter was used to test the pore structure of coal. The BJH method is used to calculate the adsorption curve and to get the pore distribution. Based on the MIP results, the slopes of \( \ln V_P \) and \( \ln(P - P_t) \) were calculated with the aid of the Sierpinski gasket model to obtain the pore fractal dimension \( D_S \) value. The pore fractal dimension \( D_S \) can be divided into \( D_{S1} \) (seepage pore fractal dimension) and \( D_{S2} \) (adsorption pore fractal dimension). The complexity of the pore structure is characterized using the calculation value of fractal dimension. A larger fractal dimension value means a more complex pore structure and worse connectivity between pores. The calculation formula is

\[
V_P = A(P - P_t)^{(3-D)}
\]

Take the logarithm of both sides of (2) to get

\[
\ln V_P = (3-D)\ln(P - P_t) + \ln A
\]

where \( V_P \) is the amount of mercury injected, \( \text{cm}^3/\text{g} \), \( P \) is experimental pressure, MPa, \( P_t \) is threshold pressure, MPa, \( D \) is the fractal dimension, and \( A \) is the fitting constant.

2.3.3. LNTA Test and Fractal Calculation. When the pore structure of coal is tested with mercury injection, coal suffers compression failure at the high-pressure stage, which affects the accuracy of small-pore test results. Therefore, according to the Chinese national standard GB/T19587-2004, an ASAP 2460 3.00 automatic surface area tester is used to conduct supplementary testing of the full-pore (0–300 nm) structure of the coal sample. The fractal dimensions \( D_1 \) and \( D_2 \) of pores were calculated based on the LNTA test results through the FHH model, with \( P/P_0 = 0.5 \) being the cutoff point. \( D_1 \) and \( D_2 \) characterize the pore surface roughness and the complexity of pore structure, respectively. The calculation formula is

\[
\ln V = C + K \ln \left( \frac{P_0}{P} \right)
\]

\[
D = 3 + K
\]

where \( P \) is the equilibrium pressure, MPa, \( P_0 \) is the saturation pressure of nitrogen, MPa, \( V \) is the volume of adsorbed nitrogen, \( \text{cm}^3/\text{g} \), \( C \) is a constant, and \( K \) is the slope of FHH.

2.3.4. Approximate Analysis. According to the Chinese standard GB/T212-2008, a SE-MF6100 industrial analyzer was used to determine the moisture, ash, volatile, and fixed carbon.
content of coal samples and to study the characteristics of coal samples under the six conditions.

2.3.5. FTIR. The coal samples and dry potassium bromide (Kbr) under the six treatment conditions were weighed. Then, they were ground in an agate mortar. After that, they were thoroughly ground and mixed, and the sample was put in a tablet press instrument. An IRTracer-100 infrared spectrometer was used to test the coal samples. Finally, the peak fitting processing was performed on the infrared spectrum.

3. RESULTS AND DISCUSSION

3.1. Analysis of Results of Coal Pore Structure Parameters. 3.1.1. Analysis of SEM Observation Results. Figures 2–4 shows the SEM image (1000× and 5000×) and energy-dispersive spectrometry (EDS) analysis of the typical raw coal sample (0#), the sample treated with acetic acid (2#), and the sample treated with the other four solutions, respectively.

The following phenomena can be observed from Figure 2–4:

The raw coal sample (0#): minerals disperse in the forms of thin layers and micro-particles, and the coal surface is rough. The pores are filled with minerals such as kaolinite and albite. The exposed pores are mainly wedge-shaped pores larger than 220 nm in diameter.

Coal treated with distilled water (1#): minerals are embedded in the coal matrix, and the coal surface is smooth. It has a small number of exposed pores whose diameters are beyond 80 nm, and there are circular dense pore groups.

Coal treated with acetic acid (2#): minerals are loosely accumulated and dispersed in the form of micro-particles. The coal surface is rough. Minerals, such as kaolinite and albite, are embedded in the ultra-large pores (slit-shaped), and other types of pores have smooth surfaces. There is an increase in the number and types of exposed pores whose diameters are over 76 nm.

Coal treated with acetic acid and sodium dodecyl benzene sulfonate (SDBS) (3#): minerals on the coal surface are adhered in the shape of burrs and dispersed in the form of micro-
particles. The coal surface is smooth on the whole and rough locally. The exposed pores are round and wedge with smooth surfaces and diameters exceeding 70 nm.

Coal treated with acetic acid and HTAB (4#): minerals on the coal surface are embedded in thin layers and dispersed as micro-particles, and the coal surface is smooth on the whole and rough locally. The surfaces of ultra-large pores are rough, while those of other types are smooth. Pores are densely distributed locally, and the pore diameters are greater than 60 nm.

Coal treated with acetic acid and NPAM (5#): minerals on the coal surface disperse in forms of micro-particles and pods, and the coal surface is rough. Ultra-macropores have rough surfaces while other types of pores have smooth surfaces. The pore diameters are beyond 74 nm, the pore shapes are slit and wedge, and the surface morphology of the coal sample is similar to that of the one treated with acetic acid.

3.1.2. Analysis of Mercury Intrusion Test Results. Figure 5 shows the mercury injection and ejection curves of coal samples. Figure 6 exhibits the distribution of pores with different sizes, and Table 1 lists the pore structure parameters.

![Figure 5](https://doi.org/10.1021/acsomega.1c04430)  
**Figure 5.** Sample mercury intrusion and extrusion curves.

![Figure 6](https://doi.org/10.1021/acsomega.1c04430)  
**Figure 6.** Sample pore distribution of MIP.

It can be observed from Figures 5 and 6 that the mercury intrusion and extrusion curves of coal samples are approximately parallel; no abrupt turning point exists in the mercury extrusion curves, and the hysteresis loops are not notable. At the high-pressure stage, the mercury intrusion and extrusion curves gradually coincide with a small pressure difference. After the surfactants are added to acetic acid, the mercury intrusion and extrusion curves gradually coincide and the hysteresis loops become smaller. Micro-pores, transition pores, and ultra-large pores are the main developed pores.

It can be observed from Table 1 that the porosities, pore volumes, and average pore sizes of coal samples increase after the treatment with the five experimental solutions. Micro-pores and transition pores are the primary contributors to the pore specific surface areas. The volume of small pores decreases while that of ultra-large pores increases. The coal sample treated with acetic acid and NPAM experiences the most notable variations of the pore structure parameters. Specifically, its porosity increases by 33.70%, the pore volume jumps by 36.83%, and the average pore size experiences an over twofold increase. In addition, its capillary pressure varies obviously, falling by 33.95, 35.45, and 19.53% for the pore sizes of 100, 1000, and 10,000 nm, respectively. In contrast, for coal samples treated with other experimental solutions, the capillary pressures vary little.

3.1.3. Analysis of Low-Temperature Adsorption Test Results. Figure 7 shows the adsorption/desorption curves of coal samples. Figure 8 shows the curves of pore distributions in coal samples. Table 2 gives the pore structure parameters.

It can be seen from Figure 7 that according to the differences in pore structures and N₂ adsorption mechanism, the adsorption/desorption curves can be divided into three regions: region A, region B, and region C. Region A belongs to single-layer adsorption filling of adsorption pores, with a relative pressure below 0.2; region B belongs to the capillary effect, initial multi-layer adsorption, and multi-layer adsorption, with a relative pressure of 0.2–0.5; and region C also belongs to the capillary effect, initial multi-layer adsorption, and multi-layer adsorption, with a relative pressure of 0.5–1. The adsorption curves of the six coal samples are all type IV, and the adsorption/desorption curves form H3 hysteresis loops of different areas. The treatment with distilled water (1#) increases the area of the hysteresis loop, while the treatment with the other four solutions narrows the area. In particular, for the coal samples treated with acetic acid and surfactants, the areas of the hysteresis loops plunge. For the raw coal sample (0#), the one treated with distilled water (1#) and the one treated with acetic acid (2#), the desorption curves display an obvious turning point near a relative pressure of 0.5. For those treated with acetic acid and surfactants, the adsorption curves have no abrupt turning point and the desorption curves are closer to the adsorption curves. In particular, samples #1 and #3 showed a decreasing trend in the range of relative pressure (P/P₀) from 0.2 to 0.7, and the adsorption curves of samples were approximately reversed “S” type. The possible reason is that the sample goes from monolayer adsorption to multilayer adsorption. During this process, the pore structure deforms and collapses in liquid nitrogen.

According to Figure 8, the micro-pores, transition pores, and mesopores of the raw coal sample (0#) are developed to different extents. After coal samples are treated with the five solutions, they correspond to different pore developments and distributions. For the one treated with distilled water (1#), the micro-pores are not developed. After the coal samples are treated with acetic acid (2#) and acetic and SDBS (3#), they have similar pore distributions and the pores with smaller sizes in the micro-pore size range are not developed. After the coal samples are treated with acetic acid and HTAB (4#) and acetic acid and NPAM (5#), their ranges of pore distributions expand. Table 2 suggests that after the coal samples are treated with the five experimental solutions, their total adsorption capacities and pore volumes decrease. Among the five, the one treated with acetic acid and HTAB (4#) experiences the greatest decreases by 47.73 and 45.95%. After the coal sample is treated with
distilled water (1#), the specific surface area increases by 17.94%. In contrast, the treatment with acetic acid and surfactants leads to a decrease in the specific surface area. Among them, the one treated with acetic acid and SDBS experiences the most significant decline by 68.09%. In terms of the average pore size, the coal samples treated with distilled water (1#) and acetic acid (2#) undergo decreases by 21.32 and 5.64%, respectively, while those treated with acetic acid and surfactants experience increases by 10.31, 1.19, and 13.87%, respectively.

3.2. Fractal Characteristics of the Coal Pore Structure. 3.2.1. Analysis of Fractal Calculation Results of SEM. Figure 9 shows the average values of porosity and fractal dimension of three coal samples under six kinds of treatment conditions.

According to Figure 9, after the surfaces of the coal samples are magnified 1000 times, the porosity and fractal dimension of the sample treated with acetic acid and NPAM (5#) are the largest while the smallest for the sample treated with distilled water (1#). The porosities of coal samples treated with acetic acid (2#), acetic acid and SDBS (3#), and acetic acid and HTAB (4#) are larger than those of the raw coal sample. After the local areas randomly selected on the surfaces of coal samples are magnified 5000 times, the following phenomena can be observed. The porosity and fractal dimension of the coal sample treated with acetic acid and NPAM (5#) are the largest while the smallest for the sample treated with distilled water (1#). However, with acetic acid (2#) treatment, the porosity of the coal sample is slightly equal to that of the original coal sample. Using acetic acid and SDBS (3#) and acetic acid and HTAB treatment (4#), the porosity of the coal sample is less than that of the original coal sample. The porosities and fractal dimensions increase linearly after the treatment with the five experimental solutions.

3.2.2. Analysis of Fractal Calculation Results of MIP. Figure 10 shows the fitting calculation results of fractal dimensions. According to Figure 10, for seepage pores in coal samples, the fractal dimension \(D_{v1}\) value lies in the range of 2.800–2.941, with an average of 2.902, and the correlation coefficient \(R^2\) value lies in the range of 0.512–0.987, with an average of 0.619. For adsorption pores, the fractal dimension \(D_{v2}\) value lies in the range of 2.703–2.890, with an average of 2.829, and the correlation coefficient \(R^2\) value lies in the range of 0.902–0.953, with an average of 0.923. After the coal samples are treated with the five experimental solutions, their fractal dimensions of seepage pores fall, yet their fractal dimensions of adsorption pores rise. For the coal sample treated with acetic acid and SDBS, the fractal dimension of seepage pores plunges the most. For the one treated with acetic acid and NPAM, the fractal dimension of adsorption pores jumps the most.

3.2.3. Analysis of Fractal Calculation Results of LTNA. Figure 11 illustrates the fitting calculation results of fractal dimensions. The following findings can be obtained: the \(D_1\) value is in the range of 2.040–2.841, with an average of 2.504; the correlation coefficient \(R^2\) value is in the range of 0.234–0.942, with an average of 0.787; the \(D_2\) value is in the range of 2.235–2.572, with an average of 2.483, and the correlation coefficient \(R^2\) value lies in the range of 0.950–0.992, with an average of 0.971. The fractal dimensions \(D_1\) and \(D_2\) of coal samples vary differently after the samples are treated with the five experimental solutions. After the coal samples are treated with distilled water (1#) and acetic acid and SDBS (3#), the pore surfaces become rough and the pore structures get simple. For the one treated with acetic acid (2#), the pore surface becomes smooth and the pore structure becomes complex. For the one treated with acetic acid and HTAB (4#), the pore surface becomes smooth and the pore structure becomes slightly complex. For the one treated with acetic acid and NPAM (5#), the pore surface becomes smooth and the pore structure becomes simple.

3.3. Coal Characteristics Analysis. For the purpose of further identifying the changes in the pore structure of coal samples after action of composite solution, industrial analysis and FTIR spectroscopy were performed on six coal samples. The results are as follows:

Table 3 shows the approximate analysis results of coal samples. The water content of the six coal samples was 1.63, 3.16, 2.98, 4.79, 4.08, and 2.56%. After treatment with five kinds of experimental solutions, the free water content of coal samples increased by 93.86, 82.82, 193.86, 150.31, and 57.06%, respectively. Ash and volatile matter are reduced. The fixed carbon content of the coal sample treated with NPAM increased, and the change in other coal samples was not significant.

Figure 12 shows the infrared spectrum curve of a coal sample. According to the overall trend of the infrared spectra of the six coal samples, it can be found that there is almost no change in the spectra of the raw coal sample (0#) and water treatment (1#). Coal samples treated with acetic acid (2#), acetic acid and SDBS (3#), acetic acid and HTAB (4#), acetic acid and NPAM (5#) changed significantly in the 3700–3000 cm\(^{-1}\) zone, 2340–2250 cm\(^{-1}\) zone, 1750–1500 cm\(^{-1}\) zone, and 1100–910 cm\(^{-1}\) zone, respectively.54 With the combined treatment of acetic acid and surfactants, the hydroxyl content in the coal sample increased significantly, among which NPAM was the most...
obvious; for the triple-bond and cumulative double-bond region (2340–2250 cm\(^{-1}\)), the characteristic peaks of coal samples from 2\# to 4\# changed obviously and the coal samples treated with acetic acid and NPAM (5\#) showed reverse changes; for the double-bond zone (1750–1500 cm\(^{-1}\)), the stretching vibration peaks of the coal samples 3\#–4\# increased in turn; for the single-bond zone (1100–910 cm\(^{-1}\)), the stretching vibration peaks gradually decreased and the most obvious after treatment with acetic acid and NPAM.

4. DISCUSSION

The surface of the raw coal sample is rough, with most semi-closed pores and a few open pores. The pore distribution range is wide, and the most common pore shape of raw coal samples with pore diameter less than 300 nm is like the shape of a flask. The pores are filled with minerals, the overall connectivity is poor, and the pore morphology and distribution are complicated. Distilled water treatment can reduce the minerals scattered on the surface of coal samples and makes the surface smooth. Due to the water absorption and expansion of minerals, the pore channel is reduced or blocked, some pores are transformed into closed pores, the number of effective pores is reduced, the porosity is reduced, and thus, the pore morphology and distribution become simple.

The acidification process of coal can be divided into three stages: initial contact, crystal destruction, and attenuation. \(^{18}\) After acetic acid treatment, some minerals and the fatty side chains and bridge bonds of organics will be corroded and

![Adorption/desorption curves of coal samples.](https://doi.org/10.1021/acsomega.1c04430)
destroyed respectively, resulting in a rough coal sample surface, increased exposed pore type and quantity, and increased porosity. The pore channels of pores with different shapes in coal samples increase, the pore surface becomes smooth, and the pore structure becomes complex. When some minerals in the coal sample corrode, dissolve, agglomerate, fall off, and migrate, the coal matrix will be destroyed. At the same time, the water absorption and expansion of new sediments and pore minerals cause the deformation of the coal matrix skeleton around the pores, which will make the isolated or poorly connected pores communicate or be closed, and finally transform the pore structure into “communication closure”, resulting in the change of porosity.

Table 2. LNTA Pore Structure Parameters

| sample. no | \(V_{P/P_0}\) | \(V\) | \(S_{BET}\) | \(D_{med}\) |
|------------|---------------|------|-------------|----------|
| 0#         | 0.9798        | 0.001456 | 0.4225 | 14.35    |
| 1#         | 0.9007        | 0.001546 | 0.4983 | 11.29    |
| 2#         | 0.6898        | 0.00914 | 0.1902 | 13.54    |
| 3#         | 0.6299        | 0.000812 | 0.1348 | 15.83    |
| 4#         | 0.5121        | 0.000787 | 0.1812 | 14.52    |
| 5#         | 0.6168        | 0.000941 | 0.1926 | 16.34    |

*Note: \(D_{med}\) is the average pore size, nm; \(V_{P/P_0}\) is the total adsorption capacity of the sample under relative specific pressure, \(cm^3/g\); \(V\) is the total pore volume, \(cm^3/g\); and \(S_{BET}\) is the total specific surface area, \(m^2/g\).*

**Figure 8.** Sample pore distribution (LTNA).
Figure 9. Fractal dimension and porosity of the coal sample surface.

Figure 10. Scatter plots of $\ln V_P$ and $\ln(P - P_t)$ with different apertures.
reactions with the coal surface. However, they will destroy and transform the functional group structure of coal samples.

Because the acidification reaction of acetic acid is an exothermic reaction, they will reduce the molecular force of the solutions, generate moist heat, and promote the oxidation of the solutions, thereby promoting the acidification of acetic acid to various degrees. The anionic surfactant (SDBS) can reduce the molecular force of solution, significantly increase the hydrophilicity of coal samples, increase the water absorption and expansion capacity of minerals in pores, weaken the dissolution and migration capacity of minerals in pores, and finally slightly reduce the porosity. Compared with SDBS, the cationic surfactant (HTAB) has a weaker promoting effect on the hydrophilicity of coal samples, but its solution has stronger permeability and enters small pores more easily, which will

![Figure 11. Scatter plots of ln V and ln(P/P0) with different apertures.](https://doi.org/10.1021/acsomega.1c04430)

**Table 3. Proximate Analysis Value of Coal Samples**

| sample. no | proximate analysis (%) |
|------------|------------------------|
|            | M_ad | A_ad | V_ad | FC_ad |
| 0#         | 1.63 | 18.40 | 10.60 | 69.47 |
| 1#         | 3.16 | 17.77 | 10.18 | 68.89 |
| 2#         | 2.98 | 17.12 | 10.09 | 69.81 |
| 3#         | 4.79 | 16.38 | 9.77  | 69.06 |
| 4#         | 4.08 | 17.07 | 9.68  | 69.17 |
| 5#         | 2.56 | 16.24 | 9.55  | 71.65 |

**Note:** M_ad—moisture content (wt %, air dry basis), A_ad—ash yield (wt %, air dry basis), V_ad—volatile matter (wt %, air dry basis), and FC_ad—fixed carbon (wt %, air dry basis).
increase the pore size and pore transformation range and finally decrease the porosity. For the non-ionic surfactant (NPAM), the surfactant promotes the acidification of acetic acid and reduces the molecular force of the solution. Due to the strong water retention of NPAM attached to the surface of coal samples, the increase in hydroxyl content in coal samples is the largest. Besides, the strong hydrophilicity of NPAM lowers the hydrophobicity of the coal sample and weakens the capillary effect. Therefore, the water absorption and expansion ability of minerals in pores is weakened, while the corrosion, dissolution, and migration ability of minerals in pores is enhanced. Then, the pore surface becomes smooth, the pore structure becomes simple, and the porosity of the coal sample increases.

Overall, the compound modification of surfactants and acetic acid conduces to the transformation of pore shapes and affects a wider pore size range. When the anisotropy of the seepage pores of coal samples is weakened, the pore connectivity increases and the pore structure becomes simpler; when the anisotropy of coal samples’ adsorption pores increases, the pore connectivity decreases and the pore structure becomes more complex. For large pores, anionic and cationic surfactants can promote pore connection rather than inhibiting it. For small pores, their inhibiting effect on pore connection is stronger than the promoting effect. The non-ionic surfactant can promote the connection of full-size pores. Comparing three typical surfactants, adding non-ionic surfactants to acetic acid is the most suitable method for pressure injection transformation of coal seams underground, which can largely avoid water lock injury.51,52

5. CONCLUSIONS

(1) The raw coal sample has a rough surface, and its pores are filled with minerals such as kaolinite and albite. In addition, its pore morphology and distribution are complex. The pores mainly belong to poorly connected wedge-shaped and thin-neck bottle-shaped pores. After the coal samples are treated with the experimental solutions of different components, the pore shapes are transformed into cylinders and parallel plates and small pores are transformed into large pores.

(2) Overall, after coal samples are treated with the experimental solutions, anisotropy of seepage pores of coal samples weakens, the pore connectivity increases slightly, and the pore structure simplifies. In contrast, anisotropy of adsorption pores is strengthened, the pore connectivity declines, and the pore structure becomes complicated.

(3) After the compound modification of surfactants and acetic acid, the anionic surfactant (SDBS) can make the pore surface rougher and the pore structure simpler. The solution cannot enter smaller pores, so the porosity of the coal sample drops. The cationic surfactant (HTAB) and non-ionic surfactant (NPAM) can facilitate the entry of the solution into small pores, which expands the pore size range affected by the synergistic effect. However, the cationic surfactant (HTAB) reduces the porosity of the coal sample, while the non-ionic surfactant (NPAM) increases the porosity.

Figure 12. FTIR spectral lines of coal samples.

AUTHOR INFORMATION

Corresponding Authors
Haigang Du – State Key Laboratory of Mining Disaster Prevention and Control Co-founded by Shandong Province and the Ministry of Science and Technology, College of Safety and Environmental Engineering, and College of Energy and Mining Engineering, Shandong University of Science and Technology, Qingdao 266590, China; College of Mining and Civil Engineering, Liupanshui Normal University, Liupanshui 553004, China; orcid.org/0000-0001-8784-1248; Email: haigangdu@126.com
Xiangke Sun – State Key Laboratory of Mining Disaster Prevention and Control Co-founded by Shandong Province and the Ministry of Science and Technology and College of Safety and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China; Email: sun15725270190@126.com

Authors
Jun Xie – State Key Laboratory of Mining Disaster Prevention and Control Co-founded by Shandong Province and the Ministry of Science and Technology and College of Safety and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China; orcid.org/0000-0002-0857-5332
Shanle Chen – College of Mining and Civil Engineering, Liupanshui Normal University, Liupanshui 553004, China
Lin Xin – State Key Laboratory of Mining Disaster Prevention and Control Co-founded by Shandong Province and the Ministry of Science and Technology and College of Safety and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04430

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (nos. 51504142 and 51674157), the Guizhou Province Key Laboratory of Coal Mine Gas Prevention and Control Characteristics (no. KY [2019] 054), the Geological Evaluation and Development of Unconventional Natural Gas in Guizhou Province (no. KY [2018] 029), the Guizhou Education Department Special Field Project (no. 55354)
KY [2020] 061), and the Science and Technology Fund Project of Guizhou Province (no. [2018] 1415).

REFERENCES

(1) Warren, J. E.; Root, P. J. The behavior of naturally fractured reservoirs. Soc. Pet. Eng. J. 1963, 3, 245–255.
(2) Wu, J. Study on the characteristics of coal micropores and their relationship with oil and gas migration and storage. Sci. China, Ser. B 1993, 23, 77–84.
(3) Ping, C.; Tang, X. Y. The research on the adsorption of nitrogen in low temperature and micro-pore properties in coal. J. China Coal Soc. 2001, 26, 552–556.
(4) Hui, Z. Genetical type of proes in coal reservoir and its research significance. J. China Coal Soc. 2001, 26, 40–44.
(5) Hodot, B. B. Outburst of Coal and Coalbed Gas; China Industry Press: Beijing, 1966.
(6) Wang, Z.; Cheng, Y.; Qi, Y.; Wang, R.; Wang, L.; Jiang, J. Experimental study of pore structure and fractal characteristics of pulverized intact coal and tectonic coal by low temperature nitrogen adsorption. Powder Technol. 2019, 350, 15–25.
(7) Zhou, H. W.; Zhong, J. C.; Ren, W. G.; Wang, X. Y.; Yi, H. Y. Characterization of pore-fracture networks and their evolution at various measurement scales in coal samples using X-ray CT and a fractal method. Int. J. Coal Geol. 2018, 189, 35–49.
(8) Niu, Q.; Pan, J.; Jin, Y.; Wang, H.; Li, M.; Ji, Z.; Wang, K.; Wang, Z. Fractal study of adsorption-pores in pulverized coals with various metamorphism degrees using N2 adsorption, X-ray scattering and image analysis methods. J. Pet. Sci. Eng. 2019, 176, 584–593.
(9) Yao, Y.; Liu, D.; Tang, D.; Tang, S.; Huang, W.; Liu, Z.; Che, Y. Fractal characterization of seepage-pores of coals from China: An investigation on permeability of coals. Comput. Geosci. 2009, 35, 1159–1166.
(10) Cheng, X. Q.; Tian, J. J.; Wang, H. C.; Zhang, Y. Y.; Hao, H. L.; Zhang, Z. H. Experimental research on the effect of H2S solution on pore structure of low-rank coal. J. China Coal Soc. 2020, 45, 1436–1444.
(11) Li, S.; Luo, M. K.; Fan, C. J.; Bi, H. J.; Ren, Y. P. Quantitative characterization of the effect of acidification in coals by NMR and low-temperature nitrogen adsorption. J. China Coal Soc. 2017, 42, 1748–1756.
(12) Ni, G.; Li, S.; Rahman, S.; Xun, M.; Wang, H.; Xu, Y.; Xie, H. Effect of nitric acid on the pore structure and fractal characteristics of coal based on the low-temperature nitrogen adsorption method. Powder Technol. 2020, 367, 506–516.
(13) Behera, S. K.; Chakraborty, S.; Meikap, B. C. Chemical demineralization of high ash Indian coal by using alkali and acid solutions. Fuel 2017, 196, 102–109.
(14) Balucan, R. D.; Turner, L. G.; Steel, K. M. Acid-induced mineral alteration and its influence on the permeability and compressibility of coal. J. Nat. Gas Sci. Eng. 2016, 33, 973–987.
(15) Li, S.; Ni, G.; Wang, H.; Xun, M.; Xu, Y. Effects of acid solution of different components on the pore structure and mechanical properties of coal. Adv. Powder Technol. 2020, 31, 1736–1747.
(16) Liu, Z.; Liu, D.; Cai, Y.; Qiu, Y. Permeability, mineral and pore characteristics of coals response to acid treatment by NMR and QEMSCAN: Insights into acid sensitivity mechanism. J. Pet. Sci. Eng. 2021, 198, 108205.
(17) Yang, H.; Yu, Y.; Cheng, W.; Rui, J.; Xu, Q. Influence of acid dissolution time on evolution of coal phase and surface morphology. Fuel 2021, 286, 119464.
(18) Yu, Y.; Yang, H. T.; Cheng, W. M.; Gao, C. W.; Zheng, L.; Xin, Q. L. Effect of acetic acid concentration on functional group and microcrystalline structure of bituminous coal. Fuel 2020, 288, 119711.
(19) Li, P.; Zhou, S.; Zhang, X.; Li, J.; Liu, M.; Chen, K.; Zhang, C.; Sun, Z.; Meng, B. Distributions and evolution model of water-soluble organic acids for coals with different thermal maturing. Fuel 2021, 283, 118663.
(41) Rootare, H. M.; Prenzlow, C. F. Surface areas from mercury porosimeter measurements. J. Phys. Chem. A 2002, 71, 2733–2736.
(42) Mendhe, V. A.; Bannerjee, M.; Varma, A. K.; Kamble, A. D.; Mishra, S.; Singh, B. D. Fractal and pore dispositions of coal seams with significance to coalbed methane plays of East Bokaro, Jharkhand, India. J. Nat. Gas Sci. Eng. 2017, 38, 412–433.
(43) Jia, T. F.; Wang, M.; Gao, X. Y.; Zhao, J. G.; Zhu, J. Q. Pore structure characteristics of low-rank coal reservoirs and evaluation of fractal models. Nat. Gas Geosci. 2021, 32, 423–436.
(44) Guo, H.; Yuan, L.; Cheng, Y.; Wang, K.; Xu, C. Experimental investigation on coal pore and fracture characteristics based on fractal theory. Powder Technol. 2019, 346, 341–349.
(45) Zhang, S.; Tang, S.; Tang, D.; Huang, W.; Pan, Z. Determining fractal dimensions of coal pores by FHH model: Problems and effects. J. Nat. Gas Sci. Eng. 2014, 21, 929–939.
(46) Pfeifer, P.; Wu, Y. J.; Cole, M. W.; Krim, J. Multilayer adsorption on a fractally rough surface. Phys. Rev. Lett. 1989, 62, 1997–2000.
(47) Lu, G.; Wang, J.; Wei, C.; Song, Y.; Yan, G.; Zhang, J.; Chen, G. Pore fractal model applicability and fractal characteristics of seepage and adsorption pores in middle rank tectonic deformed coals from the Huaihe coal field. J. Pet. Sci. Eng. 2018, 171, 808–817.
(48) Mendhe, V. A.; Bannerjee, M.; Varma, A. K.; Kamble, A. D.; Mishra, S.; Singh, B. D. Fractal and pore dispositions of coal seams with significance to coalbed methane plays of East Bokaro, Jharkhand, India. J. Nat. Gas Sci. Eng. 2017, 38, 412–433.
(49) Han, W.; Zhou, G.; Gao, D.; Zhang, Z.; Wei, Z.; Wang, H.; Yang, H. Experimental analysis of the pore structure and fractal characteristics of different metamorphic coal based on mercury intrusion-nitrogen adsorption porosimetry. Powder Technol. 2020, 362, 386–398.
(50) Ibarra, J.; Edgar, M.; Rafael, M. FTIR study of the evolution of coal structure during the coalification process. Org. Geochem. 1996, 24, 725–735.
(51) Zhang, K.; Cheng, Y.; Wang, L.; Dong, J.; Hao, C.; Jiang, J. Pore morphology characterization and its effect on methane desorption in water-containing coal: An exploratory study on the mechanism of gas migration in water-injected coal seam. J. Nat. Gas Sci. Eng. 2020, 75, 103152.
(52) Zhiguo, X.; Wang, Z. F. Experimental Study on Inhibitory Effect of Gas Desorption by Injecting Water into Coal-sample. Procedia Eng. 2011, 26, 1287–1298.