Experimental investigation on the effect of ethanol on micropore structure and fluid distribution of coalbed methane reservoir

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Abstract
The development of coalbed methane not only ensures the supply of natural gas but also reduces the risks of coal mine accidents. The micropore structure of coalbed methane reservoir affects the seepage of coalbed methane; improvement of pore structure is one of the effective methods to enhance the efficiency of coalbed methane exploitation. In this study, low-pressure nitrogen gas adsorption, specific surface area analysis, nuclear magnetic resonance spectroscopy, and centrifugation experiment were used to evaluate the effect of ethanol on coal microscopic pore structure and fluid distribution during hydraulic fracturing. Seven coal samples were collected from the No. 3 coal seam in Zhaozhuang Mine, Qinshui Basin. The samples are mainly composed of micropores, transition pores, and mesopores. The experimental results show that ethanol can significantly change the pore structure by increasing the pore diameter. The average specific surface area, pore volume, and pore diameter of rock samples before ethanol immersion are 1.1270 m²/g, 0.0104 cm³/g, and 14.20 nm, respectively. The three parameters of rock samples after ethanol immersion are 0.5865 m²/g, 0.0025 cm³/g, and 29.37 nm. Ethanol improves the connectivity between micropores and mesopores. The average irreducible fluid saturation of samples saturated with formation water after centrifugation is 86%, and the average irreducible fluid saturation of samples soaked in three concentrations of ethanol solution decreases. It is

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considered that an ethanol solution of 0.4% concentration has the best effect on improving the pore structure and fluid distribution.

Keywords
Ethanol, coalbed methane, pore structure, fluid distribution, experiments

Introduction
Coalbed methane (CBM) is an important unconventional natural gas resource (Lau et al., 2017). In recent years, CBM development has gained great attention because of the increasing demand for fossil fuels. Unlike conventional reservoirs, CBM reservoir is characterized by complex pore-fracture networks, high heterogeneity, low porosity, and low permeability. Pore structure and fluid distribution play a vital role in CBM exploitation, especially in the stage of hydraulic fracturing.

The pore structure of coal has been extensively studied by different experimental methods including low-pressure nitrogen gas adsorption (LP-N₂GA) (Hazra et al., 2018; Zheng et al., 2013), high-pressure mercury injection (HPMI) (Zheng et al., 2013), nuclear magnetic resonance (NMR) spectroscopy (Yao et al., 2010; Zhu et al., 2016), atomic force microscope (Bruening and Cohen, 2005), and small-angle X-ray scattering (Pan et al., 2016). However, most of these experimental methods mainly provide qualitative description of pore structures. Alternatively, fractal theory provides an important means to quantitatively evaluate the pore structure parameters of coal reservoirs. Mahamud and Novo (2008) studied four types of bituminous coal and oxidized bituminous coal samples and analyzed the data obtained by mercury porosimetry from the fractal perspective. They further evaluated the sensitivity of fractal dimension and fractal distribution to oxidation treatment. Zhou et al. (2018) analyzed the fractal dimensions of particle size distribution to evaluate the wettability and surface characteristics of coal. Their results show that pore volume significantly increases with fractal dimension, indicating that pore structure is highly developed.

Some achievements have been made on the improvement of coal pore structure. Mae et al. (1997) extracted coal sample pretreated with oxidant in a binary solvent containing alcohol. Their results indicate that alcohol destroys hydrogen bonding in coal structure and that alcohol reacts with oxygen-containing functional groups. Burke et al. (1992) used trifluoroperacetic acid solution to oxidize a coal sample. They reported that a part of the coal sample dissolves in the solution, and the quality of dissolved part increases with the decreasing deterioration degree of coal. Crawford and Mainwaring (2001) used sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), and other surfactants to change the surface structure of three different types of Australian coal, and suggest that the surfactant can increase the adsorption capacity and hydrophobicity of coal surface to a certain extent. Yan et al. (2014) found that the coal structure becomes more associated and compact after solvent treatment, and the pyrolysis reactivity of treated sample is slightly lower than that of raw coal. Li et al. (2018) found that the enlargement of pore structure after solvent treatment reduces the collision between methane molecules and pore walls, thus improving the efficient of methane diffusion.
This study aims to (1) evaluate the pore structure of No. 3 coal seam in the Qinshui Basin and (2) investigate the effect of ethanol on pore structure for No. 3 coal seam. LP-N₂GA, specific surface area (SSA) analysis, NMR spectroscopy, and centrifugation experiment were conducted on seven core samples from the No. 3 coal seam in the Zhaozhuang mine, Qinshui Basin. This study is divided into three sections: Experiments section describes the experimental process. Analysis of pore structure change section provides a comparative analysis of changes in pore structure before and after ethanol immersion. Comparative analysis of fluid distribution section evaluates how changes in fluid distribution are related to pore structure.

Experiments

Seven samples were selected from the No. 3 coal seam of Zhaozhuang mine, which is located in the southeastern Qinshui Basin, China. Table 1 shows the length, diameter, and dry weight of the samples. Small pieces of coal were crushed and ground into 40-mesh powder. Approximately 1.5 g of pulverized coal was obtained from each sample for the LP-N₂GA experiment.

LP-N₂GA

This study employed the 3H-2000PS1 SSA and porosity analyzer (Figure 1) provided by Beesd Instrument Technology (Beijing) Co., Ltd. to measure the pore size distribution through the adsorption and desorption method. The pore size distribution ranges from 0.35 nm to 500 nm, and SSA is greater than 0.01 m²/g. Nitrogen with a purity of 99.999% was used for the adsorption experiments, and the temperature was controlled using liquid nitrogen. The adsorption experiment was started with a preset pressure to determine the nitrogen adsorption under different pressures. SSA of each pore was calculated using the Brunauer–Emmett–Teller (BET) theory, and the pore distribution was calculated using the Barrett–Joyner–Halenda (BJH) equation.

To evaluate the effect of ethanol on the micropore structure and fluid distribution, the sample was immersed in a certain concentration of ethanol solution for 5.5 h. The sample was dried before preforming the LP-N₂GA experiment.

Table 1. Basic parameters of coal samples.

| Core number | Length, cm | Diameter, cm | Volume, cm³ | Dry weight, g |
|-------------|------------|--------------|-------------|--------------|
| A           | 5.280      | 2.500        | 25.925      | 34.641       |
| B           | 5.398      | 2.500        | 26.504      | 39.675       |
| C           | 5.424      | 2.500        | 26.632      | 39.764       |
| D           | 5.020      | 2.500        | 24.648      | 37.372       |
| E           | 5.560      | 2.500        | 27.299      | 37.158       |
| F           | 5.313      | 2.500        | 26.087      | 32.969       |
| G           | 5.694      | 2.500        | 27.958      | 35.294       |
A SPEC-RC1 porous medium seepage experimental analyzer (Figure 2) produced by the Beijing Spike Company was used for the NMR experiments. The magnetic field strength is 0.28 T, and the hydrogen proton resonance frequency is 12 MHz. Samples were placed into the drying oven at 105°C for about 12 h and then cooled to room temperature. Each sample was cut into four pieces on average to determine the saturation of different solutions. The four solutions are formation water, 0.2% ethanol, 0.4% ethanol, and 0.6% ethanol. The salinity of formation water is 870 mg/L. After the sample was saturated, it was placed in the NMR instrument for testing.
Analysis of pore structure change

Pore types

Organic solvents have an erosive effect on the pore walls in coal samples, increasing the pore size. Because micropores are extremely small, liquid cannot enter all of them. The variation range of small pores is relatively smaller than that of large pores (Ji et al., 2015). According to adsorption and condensation theory, when the adsorption test is carried out on a solid with capillary pores, capillary condensation occurs at the corresponding Kevin radius with increasing relative pressure (Gan et al., 1972). If the relative pressures during condensation and evaporation are same, the adsorption and desorption branches of the adsorption isotherm overlap. If the two relative pressures are different, the two branches of adsorption isotherm will separate, forming an adsorption loop.

According to the IUPAC manual, the first step is to identify the isotherm type and thus the nature of adsorption. As shown in Figure 3, the modern version of IUPAC classification scheme has six types of isotherms for gas–solid equilibria. It is based on an earlier classification by Brunauer, which had five types of isotherms.

Figure 4 shows the LP-N₂GA isotherms of four coal samples (Core C–F). According to the classification schemes reported by Willi et al. (2014), the isotherms of samples B, C, E, and G are classified as Type V. The adsorption line shows a stable rise, and the latter part of adsorption range increases, from single molecular layer to multilayer adsorption. The desorption line is located in the lower relative pressure section, and the adsorption–desorption coincides. The results show a hysteresis loop that adsorption curve of isotherm is not consistent with the desorption curve. When the adsorption capacity of single molecular layer is about 0.10 $P/P_0$, multimolecular layer adsorption occurs ($P/P_0$ is about 0.10–0.80), in this stage, with the increase of pressure, the adsorption capacity of this section increases slowly. When $P/P_0$ is 0.80–1.00, the adsorption curve of this stage rises rapidly, and the adsorption
saturation is still not shown near the saturated vapor pressure, mainly due to the existence of large pores in the shale, and the large pore filling due to the capillary condensation, indicating that there are many pore types in the coal sample. A platform can be observed in the region with high P/P₀ value, and the final transition of isotherm ends up. When the desorption curve is 0.42–0.52 in P/P₀, the phenomenon of “forced closure” appears in this stage, which is called “tensile strength effect,” mainly because the hemispherical and crescent pores with pore diameter less than 4 nm in shale collapse due to capillary evaporation. With the change in relative pressure, a hysteresis loop appears, but no sharp decline section is observed. The pores are open flat micropores, and wedge-shaped or parallel plate micropores closed at one end with a smaller pore diameter are present. When the condensation effect occurs, the gas level is flat, and when the evaporation effect occurs, the gas level is cylindrical. Therefore, the relative pressure is not the same when the two phenomena occur, resulting in an adsorption loop. Because of the presence of micropores with various pore sizes and shapes, the evaporation effect first occurs in the larger micropores, the adsorption capacity decreases, and the desorption line significantly decreases. When the nitrogen condensate present in the open pores with a radius of 1.38 nm or more completely evaporates, a

Figure 4. Isothermal adsorption–desorption curves of samples. (a) Core-C, (b) Core-D, (c) Core-E, and Core-F before and after ethanol immersion.
turning point (0.5 relative pressure) is observed, and the desorption line sharply drops. The condensate present in the closed micropores at the last end begins to evaporate, and this process does not produce a hysteresis loop.

The isotherms are classified as Type C1 for samples A, D, and F. The adsorption line shows a segmented change. At this time, the force between the solid surface and the adsorbed molecules is relatively weak, while the force between the adsorbed molecules is relatively strong. Due to the strong force between the adsorbed molecules, the adsorption of the single molecular layer is often not completed, and the adsorption of the multimolecular layer should start. The relative pressure ranges from 0 to 0.9 with almost no rise, and monolayer adsorption occurs on the larger pore wall. After the monolayer is full, the adsorption layer thickens; the relative pressure is 0.9–1.0 and sharply rises. The adsorption layer increases and capillary condensation occurs in the corresponding larger pore. The desorption line coincides with the adsorption line, and no hysteresis loop is observed.

The pore structure mostly consists of small holes, and the micropores of wedge-shaped hole and cylinder hole are closed at one end. When condensation and evaporation occur in this type of pore, the gas–liquid interface has the same hemispherical meniscus. Therefore, the condensation and evaporation effects act on the same relative pressure, resulting in no hysteresis loop.

Analysis of aperture and specific surface

Table 2 lists the pore structure parameters of coal samples. The SSA of samples was calculated using the BET multipoint method (Liu et al., 2018), and the pore size distribution characteristics were calculated using the BJH method according to the desorption branch of LP-N2GA test (Okolo et al., 2015). According to the previous decimal pore classification standard (Zhang et al., 2017), the pore structure can be divided as follows: macropores (>1000 nm), mesopores (100–1000 nm), transition pores (10–100 nm), and micropores (<10 nm).

The BET SSA of coal samples before ethanol treatment ranges from 0.3393 m²/g to 3.851 m²/g, with an average of 1.1270 m²/g. The pore volume ranges from 0.002 cm³/g to
0.0337 cm³/g, with an average of 0.0104 cm³/g. The small SSA of coal sample indicates poor gas adsorption. The total pore volume is small, indicating that the coal pores are small, and the physical properties of reservoir are poor. The average pore diameter of coal sample ranges from 6.35 nm to 27.93 nm, with an average of 14.20 nm. The pores in the coal sample primarily fall into the transitional size.

After ethanol immersion, the SSA, pore volume, and average pore diameter of coal samples are changed. The SSA of coal sample ranges from 0.2013 m²/g to 1.4115 m²/g, with an average of 0.7436 m²/g. Pore volume ranges from 0.0004 cm³/g to 0.0098 cm³/g, with an average of 0.0053 cm³/g. The average pore diameter of coal sample ranges from 12.43 nm to 44.48 nm. Pores in the ethanol-treated coal sample primarily have the transitional size, and the pore radius is small. The average pore diameter of coal sample significantly increases after ethanol immersion, increasing the pore diameter.

Table 3 compares the pore volume before and after ethanol immersion. Table 4 compares the contribution rate of different pores to pore volume before and after ethanol immersion.

According to the pore diameter distribution measured using the BJH method in Zhaozhuang block, the pore size has two peak values at 15 nm and 30 nm, which are the dominant pore sizes. Therefore, the primary coal sample size aperture lies in the transition range, indicating that the coal samples in this block primarily contain micropores and transition pores, with a small amount of mesopores and without macropores. Table 3 shows that

| Samples | Micropore | Transition pore | Mesopore | Total pore volume | Micropore | Transition pore | Mesopore | Total pore volume |
|---------|-----------|----------------|----------|------------------|-----------|----------------|----------|------------------|
| A       | 0.0070    | 0.0097         | 0        | 0.0167           | 0.0002    | 0.0067         | 0        | 0.0069           |
| B       | 0.0092    | 0.0105         | 0.0037   | 0.0234           | 0.0022    | 0.0010         | 0.0061   | 0.0093           |
| C       | 0.0124    | 0.0290         | 0.0147   | 0.0561           | 0.0026    | 0.0034         | 0.0039   | 0.0099           |
| D       | 0.0053    | 0.0117         | 0.0075   | 0.0245           | 0.0020    | 0.0032         | 0.0023   | 0.0075           |
| E       | 0.0059    | 0.0071         | 0.0028   | 0.0158           | 0.0012    | 0.0009         | 0.0006   | 0.0027           |
| G       | 0.0071    | 0.0103         | 0        | 0.0174           | 0.0001    | 0              | 0.0003   | 0.0004           |

It should be noted that the pore volume in Table 2 is determined by the Barrett–Joyner–Halenda (BJH) method, and the total pore volume in Table 3 is the sum of the volumes of micropore, transition pore, and mesopore.

Table 4. Comparison of contribution rate of pore volume before and after ethanol immersion.

| Samples | Micropore | Transition pore | Mesopore | Micropore | Transition pore | Mesopore |
|---------|-----------|----------------|----------|-----------|----------------|----------|
| A       | 41.92     | 58.08          | 0        | 2.89      | 97.11          | 0        |
| B       | 39.32     | 44.87          | 15.81    | 23.65     | 10.75          | 65.60    |
| C       | 22.10     | 51.70          | 26.20    | 26.26     | 34.34          | 39.40    |
| D       | 21.63     | 47.76          | 30.61    | 26.66     | 42.66          | 30.68    |
| E       | 37.34     | 44.94          | 17.72    | 44.44     | 33.33          | 22.23    |
| G       | 40.80     | 59.20          | 0        | 25.00     | 0              | 75.00    |
the micropores are relatively abundant in the tested coal samples. Specifically, the pore volume of micropores ranges from 0.0059 cm$^3$/g to 0.0124 cm$^3$/g and accounts for 21.63–41.92% of the total pore volume. After ethanol immersion, the pore volume of micropores ranges from 0.0001 m$^2$/g to 0.0026 m$^2$/g and accounts for 44.94–53.54% of the total pore volume. The pore volume of transition pores ranges from 0.0071 m$^2$/g to 0.0290 m$^2$/g and accounts for 47.76–59.20% of the total pore volume. After ethanol immersion, the transition pore volume ranges from 0 to 0.0067 m$^2$/g and accounts for 0–97.11% of the total pore volume. The mesopore volume ranges from 0 to 0.0147 cm$^3$/g and accounts for 0–30.61% of the total pore volume. After ethanol immersion, the pore volume of mesopores ranges from 0 to 0.0039 m$^2$/g and accounts for 0–75.00% of the total pore volume. The pore volume of coal samples with micropores, transition pores, and mesopores is significantly smaller, and the pore volume ratio is larger after ethanol immersion.

The proportion of micropores in coal seam is relatively high, while the proportion of mesopores is relatively small. The pore volume is primarily composed of micropores and transition pores, and the pore volume ratio exceeding 50% in all seven coal samples is 0 (Figure 5). The SSA is dominated by micropores, and its SSA ratio exceeds 50% in all seven samples, with a maximum of 61.78%. Within the small pore range, the SSA is inversely proportional to pore diameter, and small pores contribute less to the SSA of coal. During the transition from small pores to micropores, the curve significantly changes, and the distribution of different pore sizes is uneven.

The relationship curves of cumulative pore volume versus pore radius (Figure 6) and differential pore volume versus pore radius (Figure 7) were further analyzed to investigate the pore structure characteristics of core samples.

Pore volume, SSA, and differential pore volume of coal samples are closely related to the most probable pore size. Taking sample G as an example, before ethanol immersion, micropores and pinholes are developed in the experimental coal samples, which are mainly composed of micropores. The cumulative pore volume abruptly decreases in terms of micropores.

![Figure 5. Histogram of micropore/transitional/mesopore ratio after saturating samples by (a) mineralized water and (b) ethanol.](image_url)
with pore diameter less than 10 nm after ethanol immersion, while the cumulative pore volume rapidly increases with increasing pore diameter in terms of micropores with a pore diameter ranging from 10 nm to 100 nm after ethanol immersion. For pore diameters greater than 100 nm, the pore volume significantly increases, and the increased speed is stable. The peak of differential pore volume distribution curve is strong at 10–20 Å, and there is an obvious distribution peak. In the cumulative pore volume distribution curve, the differential pore volume of coal samples increases first and then decreases, and the volume of adsorbed gas increases with increasing pore size.

The micropore volume is significantly reduced after ethanol immersion. Overall, the micropore volume and transitional pore volume increase faster than the micropore volume. Because of the erosion of pore wall by ethanol, the size of small pores increases. Therefore, the pore volume occupied by smaller pores sharply decreases, whereas the pore volume occupied by larger pores increases. However, ethanol cannot enter extremely small pores; therefore, the variation range is not as large as large pores.

Figure 6. Cumulative pore volume versus radium for core samples A–G.

Figure 7. Differential pore volume versus radium.
Comparative analysis of fluid distribution

Fluid distribution

After the coal samples being dried, they were saturated with mineral water and ethanol solutions of different concentrations, and then centrifuged prior to the NMR experiments. The $T_2$ spectra of the seven coal samples were obtained, and representative $T_2$ spectra for samples B–F were collected (Figure 8).

The NMR $T_2$ spectral distribution of the seven coal samples shows that the right boundary of $T_2$ relaxation peak of mineralized water is 4 ms, 4 ms, 6 ms, 11 ms, 4 ms, 5 ms, and 5 ms, with an average of 5 ms. The right boundary of $T_2$ relaxation peak of ethanol of the seven coal samples is 30 ms, 24 ms, 22 ms, 27 ms, 22 ms, 19 ms, and 21 ms, with an average of 23.5 ms.

The $T_2$ relaxation peak of coal samples saturated with ethanol is generally on the right side of $T_2$ relaxation for samples saturated with mineralized water. As the $T_2$ relaxation time decreases, the pore size decreases (i.e., the curve is closer to the left and the pore size is smaller), indicating that the water primarily stays in the micropores for the mineralized water samples, and the water in the immersion samples primarily stays in the micropores (Xu et al., 2017).

Comparative analysis shows that the area enclosed by saturated $T_2$ spectrum curve and abscissa for mineralized water is larger than that for organic solvent in all samples except sample F. One may expect that ethanol can thus effectively displace water in cores.

The irreducible water saturation of most cores is significantly smaller after ethanol immersion (Table 5). This indicates that ethanol can effectively improve the reservoir pore structure. As shown in Figure 9, the reduction in irreducible water saturation is different among samples A–G. The results show negligible change in the irreducible water saturation in samples A, F, and G, while that in other samples are relatively more pronounced. The possible reason for the negligible change in irreducible water saturation in samples A, F, and G is that the pore extracted by ethanol in these samples is mainly micropore, which does not affect the irreducible water saturation.

According to the isothermal adsorption curve, 0.4% ethanol has the best effect on improving pore structure. Taking sample F as an example, Figure 10 shows an upward trend in all curves, and the adsorption amount increases with the increase of $P/P_0$. After immersion in mineralized water, the curve is relatively stable and has no obvious change. When $P/P_0$ is at 0–0.45, the adsorption amount of 0.2% ethanol is higher than 0.6%, and when $P/P_0$ is higher than 0.45, the result is opposite. The adsorption capacity of 0.4% ethanol is significantly higher than other concentrations of solvent ethanol in the whole process, and the slope of the curve increases rapidly. One may thus expect that 0.4% ethanol effectively enlarges the pore diameter, improves the pore structure, and increases the contact area between fluid and pore.

Fluid saturation correlation

Yao et al. (2010) divided the $T_2$ spectrum of saturated water into micropores, mesopores, and fissures from small to large sizes as follows: (1) Micropore peaks are primarily distributed between 0.5 and 2.5 ms at $T_2$, characterized by almost no difference between the two $T_2$ spectra before and after centrifugation; (2) mesopore peaks are primarily distributed
Figure 8. Comparison of $T_2$ spectra of coal samples A–G before and after ethanol immersion.
Table 5. Statistical results of irreducible water saturation in core samples for scenarios with different concentrations of ethanol.

| Samples | Mineralized water | 0.2% ethanol | 0.4% ethanol | 0.6% ethanol |
|---------|-------------------|---------------|---------------|---------------|
| A       | 0.7568            | 0.7545        | 0.7501        | 0.7428        |
| B       | 0.8593            | 0.8418        | 0.8210        | 0.7909        |
| C       | 0.7589            | 0.7466        | 0.7326        | 0.7014        |
| D       | 0.8521            | 0.8319        | 0.8121        | 0.8004        |
| E       | 0.9539            | 0.9455        | 0.9304        | 0.8995        |
| F       | 0.9137            | 0.9003        | 0.9000        | 0.8996        |
| G       | 0.9255            | 0.9210        | 0.9202        | 0.9188        |

Figure 9. Comparison of irreducible water saturation of core samples treated with different concentrations of solvent.

Figure 10. Isothermal adsorption curves of samples with different concentrations of solvent ethanol immersion.
between 20 and 50 ms at $T_2$, generally smaller than that of micropores with some spectral peaks disappearing after centrifugation; (3) fracture peaks are primarily distributed in the section, which are greater than 1000 ms. Fracture peaks disappear after centrifugation.

The $T_2$ spectra of the seven coal samples can be described as follows: (1) the saturated $T_2$ spectrum has an approximate bimodal structure. The micropore peak is the most developed, followed by the large pore peak; no fissure peak is present in the samples; (2) according to the $T_2$ spectrum cutoff value, movable fluid is present in the micropore, which is thrown out by centrifugation, causing the micropore peak to move left. However, the negligible change in spectral morphology of micropore peaks before and after centrifugation implies relatively poor connectivity of micropores, resulting in most of the fluid confined in the micropores unable to be discharged during centrifugation (Sun et al., 2018). The peak value of large pore peak is small, and the peak disappears after centrifugation. This indicates that the large pores in the coal sample are moderately developed and have relatively good connectivity (Chen et al., 2018), allowing free fluid to be discharged through centrifugation; (3) discontinuity between the two peaks of micropores and mesopores in the $T_2$ spectra of samples A, D, F, and G indicates poor connectivity between these two types of pores. The micropore and mesopore $T_2$ spectra peaks of coal samples B, C, and E are continuous. This indicates that the connectivity between the two types of pores is relatively good, and the micropore peak value increases after centrifugation.

According to the $T_2$ spectrum curve of saturated NMR before and after ethanol immersion, the curve moves to the right after immersion. This indicates that ethanol improves the micropore structure, increases the connectivity between micropores and mesopores, makes the saturated fluid enter the larger pores, and increases the movable fluid saturation. The changes in pore structure relative to different concentrations of ethanol are quite different. Although the 0.2% and 0.6% ethanol curves shift the spectrum to the right, the 0.4% ethanol curve shifts to the right to a greater extent. In addition, 0.4% ethanol significantly increases the signal volume of fluid and the movable fluid content, while the signal volume of 0.2% and 0.6% ethanol does not change much. Thus, 0.4% ethanol has the largest improvement.

Most previous experimental studies focus on the effect of surfactants on the pore structure of coal, such as tetrahydronaphthalene, SDS, CTAB, and Teric G12A8. The main research methods used are Fourier transform infrared spectroscopy (FTIR), $^{13}$C NMR, and thermo-gravimetric analyzer coupled with mass spectroscopy (TG-MS). In contrast, this study focuses on the effect of organic solvent on the pore structure of coal. The primary tools used are the LP-N$_2$GA experiment and the NMR test, which provide relatively more convenient and intuitive observation of pore size changes and fluid distribution.

Compared with other methods, organic solvent is more economical and environmental friendly, clean, and pollution-free, raw materials are easier to obtain, and the experimental process is safer. In the actual production and development, compared with the use of surfactants or other methods, the use of organic solvents to improve the pore structure of the reservoir has lower requirements for field equipment, it can not only reduce costs but also water lock damage. Therefore, it is of great significance in the field production and development of coal.

Conclusions

1. The pore structure characteristics and water distribution were studied on seven core samples from the No. 3 coal seam in Qinshui Basin using LP-N$_2$GA, SSA analysis,
and NMR spectroscopy. Samples are primarily composed of micropores and transition pores; micropores are the most abundant, with a small amount of mesopores. However, experimental results show no macropore in core samples. The identification of macropores might be constrained by sample properties, instrument precision, and experimental operation.

2. Ethanol can significantly change the pore structure of coal samples by increasing the pore diameter. The average SSA, pore volume, and pore diameter of rock samples before ethanol immersion are 1.1270 m²/g, 0.0104 cm³/g, and 14.20 nm, respectively; these three parameters of rock samples after ethanol immersion are 0.5865 m²/g, 0.0025 cm³/g, and 29.37 nm, respectively.

3. The T₂ spectrum curve moves to the right after ethanol immersion, indicating that ethanol increases the connectivity between micropores and mesopores and enables saturated fluid to enter larger pores. At the same time, ethanol can effectively displace water and increases the movable fluid saturation. The ethanol solution of 0.4% concentration is expected to be more effective for improving the pore structure and fluid distribution.

4. Compared with other methods, organic solvent is more economical and environmentally friendly, clean, and pollution-free; raw materials are easier to obtain; and the experimental process is safer. Employing organic solvents to improve the pore structure of the coal reservoir has lower requirements for field equipment; it can not only reduce costs but also water-block damage.

Declaration of conflicting interests

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