

# Physicochemical Effect on Coal Pores of Hydrocarbon Chain Length and Mixing of Viscoelastic Surfactants in Clean Fracturing Fluids

Mengmeng Yang,\* Junyue Zhang, Liang Zhang, and Shihui Gong



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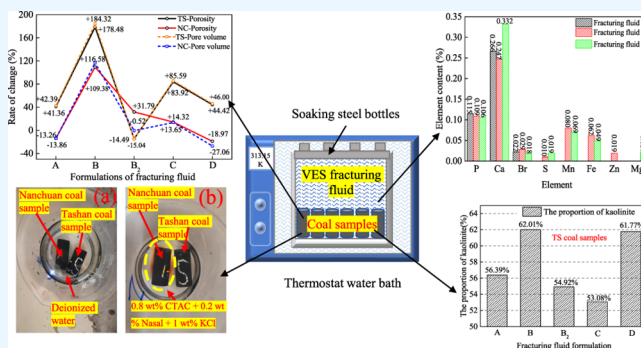
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**ABSTRACT:** Clean fracturing fluids are environmentally friendly and could have broad applications in permeability enhancement of coal seams. The hydrophobic chain length of the viscoelastic surfactant (VES) and the mixing of VESs with different ionic types have marked effects on the performance of clean fracturing fluids. This paper analyzes the effects of the hydrocarbon chain length of VES and mixing of VESs with different ion types on the pores of coal and discusses the mechanisms controlling the pore changes from a physical and chemical perspective. We found that the coal samples treated with clean fracturing fluid B had the largest porosity change. Adding two methylene groups to the hydrocarbon chain of the cationic VES will increase clay swelling in coal treated with fracturing fluids. Adding 0.1 wt % cocoamidopropyl betaine (zwitterionic VES) to cationic VES fracturing fluids can reduce the extent of clay expansion induced by fracturing fluids. VES with a long hydrocarbon chain has a strong ability to remove kaolinite in hard coal, and the addition of zwitterion VES increases the ability of a clean fracturing fluid to remove kaolinite. These results provide theoretical guidance for the synthesis of new VES molecules and the design of new fracturing fluid formulations.



## 1. INTRODUCTION

Coalbed methane (CBM) extraction can effectively alleviate energy shortages, improve mine safety, and reduce greenhouse gas emissions. In recent years, measures such as hydraulic slotting, hydraulic cavitating, chemical stimulation to promote the exploitation of CBM have been applied.<sup>1–3</sup> The strong heterogeneity and low permeability of coal reservoirs make it difficult to effectively exploit CBM by conventional methods.<sup>4–6</sup> Hydraulic fracturing is an effective method to improve the permeability of rock masses<sup>7–10</sup> and, in recent years, has been increasingly used in coal reservoirs.<sup>11–13</sup> Hydraulic fracturing involves the injection of high-pressure fracturing fluids into a rock mass to produce fractures, thus increasing permeability. The fracturing fluid is the core component of the hydraulic fracturing process. The fluid's properties can influence the permeability enhancement of coal seams and thus affect the production of CBM. The formulation and application of fracturing fluids have been extensively studied for conventional oil and gas production; however, coal seams are characterized by low strength, complex pore structure, and strong sensitivity relative to conventional reservoirs,<sup>14</sup> and the special fracturing fluids used in conventional oil and gas reservoirs are not suitable for coal reservoirs because of its complex composition and residual additives. At present, the fracturing fluids used in coal seams include clean water, active water fracturing fluids, cross-linked gel fracturing fluids, foam

fracturing fluids, and clean fracturing fluids. Clean water is commonly used for coal-seam fracturing, but its viscosity is low and its fracturing effect is poor.<sup>15</sup> The viscosity of active hydraulic fracturing fluids is low, and the scale of renovation is limited, making it difficult to control the longitudinal extension of fractures.<sup>16</sup> Cross-linked gel fracturing fluids cause significant damage to coal reservoirs. Coal has a high adsorption capacity for the guar gum and broken chain organic polymer compounds after breaking the gel.<sup>17</sup> The foam fracturing fluids have some problems such as complicated technology, long construction preparation time, and high construction costs.<sup>18,19</sup> Clean fracturing fluids have attracted attention because of their high interfacial activity, high viscoelasticity, and lack of residue after gel breakage.<sup>20</sup> Some studies have shown that clean fracturing fluids can improve the effect of coalbed methane extraction and are environmentally friendly.<sup>21–23</sup> Clean fracturing fluids have broad application prospects in coal-seam permeability enhancement.

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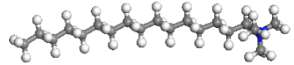
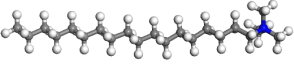
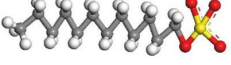
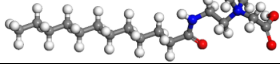
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Table 1. Structures of the VESs Used in This Study

| Name   | Molecular formula   | Molar mass (g mol <sup>-1</sup> ) | Structure  |
|--|---|-----------------------------------|--|
| Hexadecyl trimethyl ammonium chloride (CTAC) | C <sub>19</sub> H <sub>42</sub> ClN                           | 320.0                             |  |
| Stearyl trimethyl ammonium chloride (STAC)   | C <sub>21</sub> H <sub>46</sub> ClN                           | 348.05                            |  |
| Sodium dodecyl sulfate (SDS)                 | C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na            | 288.38                            |  |
| Cocoamidopropyl Betaine (CAB)                | C <sub>19</sub> H <sub>38</sub> N <sub>2</sub> O <sub>3</sub> | 342.52                            |  |

The main agent in a clean fracturing fluid is one or more viscoelastic surfactants (VESs). The VES molecular structure includes nonpolar long chain hydrophobic groups and charged or uncharged polar hydrophilic groups. The hydrophobic group of VES can affect the self-assembled structure of its micelles, thereby affecting the performance of clean fracturing fluids. The self-assembled structure of viscoelastic surfactants enables solutions to exhibit surface and colloidal properties. The surface properties (wettability) of VES can affect the ability of the fracturing fluid to spread on the surface of coal pores, dissolve mineral impurities, and remove clogged pulverized coal.<sup>24</sup> The colloidal properties (viscosity) of the fracturing fluid can affect the filtration property of the fluid and the length and width of the fractures.<sup>25</sup> Adding other types of VESs, especially anticharge ionic VES, to a solution containing one type of VES can markedly change the size and shape of the ordered assembly of molecules. Although a mixed system of cationic VES and anionic VES has high surface activity, for longer chain lengths of VES, the mixed solution is prone to turbidity, phase separation, and even precipitation, thereby reducing the surface activity of the solution. Zwitterion VES has good compatibility with cationic VES and anionic VES. The cationic group of zwitterion VES is usually a nitrogenous group, while the anionic group is usually a carboxylic acid group or sulfonic acid group. Sehgal et al.<sup>26</sup> studied the properties of mixed micelles and mixed monolayers formed by mixing cationic VES and zwitterionic VES and found that there was a weak synergistic effect between the formation of mixed micelles and the attraction between the positive charge of cationic VES and the anionic sulfonic group of zwitterionic VES, thereby stabilizing the mixed micelles. Baruah et al.<sup>27</sup> noted that anionic–zwitterionic–mixed surfactant systems offer synergistic interactions in an aqueous medium. Thus, the hydrophobic chain length of the VES and the mixing of ionic types of VESs have a notable impact on the performance of clean fracturing fluids. Selecting a suitable chain length hydrophobic group VES or mixture of cationic–zwitterionic VES and anionic–zwitterionic VES can greatly improve the effect of fracturing fluids on coal.

CBM adsorption mainly occurs in pores smaller than 10 nm in size, diffusion mainly occurs in pores ranging from 10 to 100 nm, and seepage mainly occurs in pores larger than 100 nm. CBM is mainly adsorbed in the pores of coal bodies, and changes in pore size, distribution, porosity, shape, connectivity, and surface area affect the adsorption, desorption, diffusion, and seepage of CBM. Only 20–30% of the injected fracturing

fluids can flow back after fracturing. Capillary force causes adsorption of residual fracturing fluids into pores, meaning that the fluid comes into contact with the minerals on the pore surfaces, causing physical and chemical reactions. The effect of clean fracturing fluids on coal pores has been extensively studied. Lu et al.<sup>28</sup> determined that the clean fracturing fluid increased coal pore volume by 33.3%, compared to samples treated with water. Wang et al.<sup>29</sup> found that, after treating coal samples with clean fracturing fluids (cationic VES or anionic VES as the main agent), the content of clay minerals in the coal decreased significantly, and originally blocked pores had been cleared. Lu et al.<sup>30</sup> believed that temperature could affect the pore characteristics of coal samples treated by clean fracturing fluid, noting that the most effective temperature for clean fracturing fluid to change the pores. Wang et al.<sup>31</sup> pointed out that the temperature and gas-pressure can influence the effect of clean fracturing fluid on pores. Ge et al.<sup>32</sup> found through experiments that the adsorption pores and mesopores of coal samples decreased by 17.6 and 26.7%, respectively, after clean fracturing fluid treatment. Xue et al.<sup>33</sup> discovered that the residue of the clean fracturing fluid may alter the shape of the ink-bottled pores of coal. Huang et al.<sup>22</sup> suggested that the clean fracturing fluid altered the coal pore structure mainly because the clean fracturing fluid residue entered the coal pore system and adhered to the pore wall or blocked the pore throat. Dong et al.<sup>34</sup> indicated that the pore volume of coal samples treated with clean fracturing fluids containing zwitterionic VES increased. At present, there is a lack of research on the laws and mechanisms of the influence of the VES molecular structure and VES mixing on the pores of coal treated with a clean fracturing fluid. Exploring the physical and chemical effects of clean fracturing fluids on minerals in pores can provide theoretical guidance for studying the mechanism of enhancing permeability through hydraulic fracturing and gas desorption and migration after fracturing in coal seams. Studying how the VES molecular structure and VES mixing influence coal pores can provide a theoretical basis for designing new formulations of clean fracturing fluid.

In this study, the effects of the hydrocarbon chain length of hydrophobic groups and mixing of VESs on the porosity and pore volume of coal with different levels of hardness were investigated. Then, by conducting elemental analysis of clean fracturing fluids after soaking of coal samples and testing the mineral composition and content in coal samples treated with clean fracturing fluids, the effect of the hydrocarbon chain length of hydrophobic groups and mixing of VESs on mineral

dissolution in coal is unveiled. Finally, the removal mechanisms of different types of clean fracturing fluids on different clay minerals were revealed.

## 2. MATERIALS AND METHODS

**2.1. Materials.** The viscoelastic surfactants used in this study and their molecular structures are listed in Table 1. Hexadecyl trimethylammonium chloride ( $C_{19}H_{42}ClN$ , CTAC, a cationic surfactant, analytical grade), stearyl trimethylammonium chloride ( $C_{21}H_{46}ClN$ , STAC, a cationic surfactant, analytical grade), and sodium dodecyl sulfate ( $C_{12}H_{25}SO_4Na$ , SDS, an anionic surfactant, analytical grade) were purchased from Chongqing Huanghui Chemical Dangerous Goods Sales Co., Ltd., China. Cocoamidopropyl betaine ( $C_{19}H_{38}N_2O_3$ , CAB, a zwitterionic surfactant) was synthesized by Shandong Yousuo Chemical Technology Co., Ltd., China, with a solids content of 35 wt %. Sodium salicylate ( $C_7H_5NaO_3$ , NaSal) was used as a micellar promoter of cationic surfactant, and potassium chloride (KCl) acted as a counterion and antiswelling agent. NaSal (analytical grade) and KCl (analytical grade) were purchased from Chongqing Huanghui Chemical Dangerous Goods Sales Co., Ltd., Chongqing, China. Deionized water was prepared using a water purification system (Aquapro, China).

**2.2. Clean Fracturing Fluid Preparation.** Deionized water, which was used as the control, was labeled as group A fracturing fluid. Cationic VES CTAC and STAC with different hydrocarbon chain lengths were selected to prepare clean fracturing fluids B and B<sub>2</sub> with NaSal and KCl according to the ratios listed shown in Table 2. Cationic VES STAC and

**Table 2. Chemical Compositions of the Experimental Clean Fracturing Fluids<sup>36</sup>**

| number         | formulation  | temperature for experiment and test (K) | viscosity (mPa·s) |
|----------------|--|---|-------------------|
| A              | deionized water  | 313.15                                  | 1.01              |
| B              | 0.8 wt % CTAC + 0.2 wt % Nasal + 1 wt % KCl                | 313.15                                  | 24.48             |
| B <sub>2</sub> | 0.8 wt % STAC + 0.2 wt % Nasal + 1 wt % KCl                | 313.15                                  | 20.50             |
| C              | 0.8 wt % STAC + 0.1 wt % CAB + 0.2 wt % Nasal + 1 wt % KCl | 313.15                                  | 24.85             |
| D              | 1.75 wt % CAB + 0.6 wt % SDS + 3 wt % KCl                  | 313.15                                  | 22.95             |

zwitterionic VES CAB were used as the main agents of clean fracturing fluid C. Anionic VES SDS and zwitterionic VES CAB were combined to form the main agent of clean fracturing fluid D. In the preparation process, the beakers were placed in a thermostat water bath at a temperature of 313.15 K, and each agent was stirred until it had dissolved. The viscosity of clean fracturing fluids B–D was measured at 313.15 K using an MCR 302 rotary rheometer (Anton Paar GmbH, Graz, Austria). Before viscosity testing, the prepared clean fracturing fluids were placed in a thermostat water bath and let it stand for 1 h at a temperature of 313.15 K to ensure that there are no bubbles. The viscosity was tested according to the recommendations of Chinese Standard SYT5107-2005 (recommended practices on measuring the properties of water-based fracturing fluid). The fixed test lasted 50 s with 50 measurement points at 313.15 K and a constant shear rate of  $170\text{ s}^{-1}$ .<sup>35,36</sup> The viscosity of these fluids was 20–25 mPa·s.

**2.3. Sample Processing.** Cheng and Pan<sup>37</sup> pointed out that the chemical composition and structure of soft coal are different from that of hard coal, and soft coal has low strength and weak bonding force. The physical and chemical effects of clean fracturing fluids on soft coal and hard coal are different. In this study, two kinds of coal samples with different hardness coefficients were selected for the experiments. Fresh coal blocks were collected from the Tashan (TS) coal mine of the Datong coalfield in Shanxi, China and the Dongsheng coal mine of the Nanchuan (NC) district in Chongqing, China. Detailed information including the moisture, ash, volatile, and fixed carbon contents of the TS and NC coal samples are provided by Lu et al.<sup>30</sup> and Yang et al.<sup>36</sup> The hardness coefficient ( $f$ ) of the TS coal sample is 1.31, indicating a harder coal quality, while the hardness coefficient ( $f$ ) of the NC coal sample is 0.35, indicating a softer coal quality. A coring machine was used to prepare raw coal samples with a core axis length of  $50 \pm 0.5$  mm and a diameter of  $25 \pm 0.1$  mm. Samples that possessed no obvious natural cracks or had not been damaged by coring were selected for the experiment. The average geothermal gradient in coal mines is 2.5 K/hm. At present, the depth of coalbed methane mining is generally less than 2000 m. After fracturing, the pressure must be maintained at least 2 days.<sup>28,30,38</sup> Therefore, the coal samples were put into soaking steel bottles containing fracturing fluids of different formulations and soaked at 313.15 K for 48 h. Zhou et al.<sup>39</sup> believed that the fracturing fluids would be driven by capillary force and osmotic pressure, resulting in water absorption. To ensure that the fracturing fluids could enter the pores of the coal samples during the soaking process, an ISCO pump was used to suck out the gas in the coal samples.

**2.4. Sample Testing.** **2.4.1. Porosity Testing.** The porosity ( $\phi$ ) of a rock is the ratio of the pore volume in the rock ( $V_K$ ) to the total volume of the rock ( $V_b$ ).

$$\phi = \frac{V_K}{V_b} \times 100\% \quad (1)$$

Porosity is a fundamental physical quantity that characterizes the pore and permeability characteristics of rocks. All of the measured porosity in this paper are open porosity. We used the double-chamber method of Boyle's law for porosity testing. The testing equipment was an Ultracore-300 automatic helium porosity measuring instrument from the American Core Lab (Figure 1), with a testing pressure of 200 psi and a testing range of  $0.01\text{--}104\text{ }\mu\text{m}^2$ .

**2.4.2. Measurement of Elemental Contents.** An X-ray fluorescence (XRF) spectrometer (Zetium, PANalytical, Netherlands) was used to measure the elements in the clean fracturing fluid after the coal samples had been soaked. The analytical concentration range of this equipment is parts per million to 100%, and the range of measurable elements is from Na to U.

**2.4.3. Measurements of Mineral Composition.** X-Ray diffractometry (XRD) was used to measure the mineral composition of the coal samples after they were soaked in clean fracturing fluids. The equipment (D8 Advance X-ray diffractometer, Bruker, Germany) uses a closed X-ray tube Cu target with a maximum tube current of 80 mA. The goniometer of this equipment adopts optical encoder technology, the minimum step angle is  $0.0001^\circ$ , and the angle reproducibility is 0.0001. The temperature range is from room temperature to  $1600\text{ }^\circ\text{C}$ .



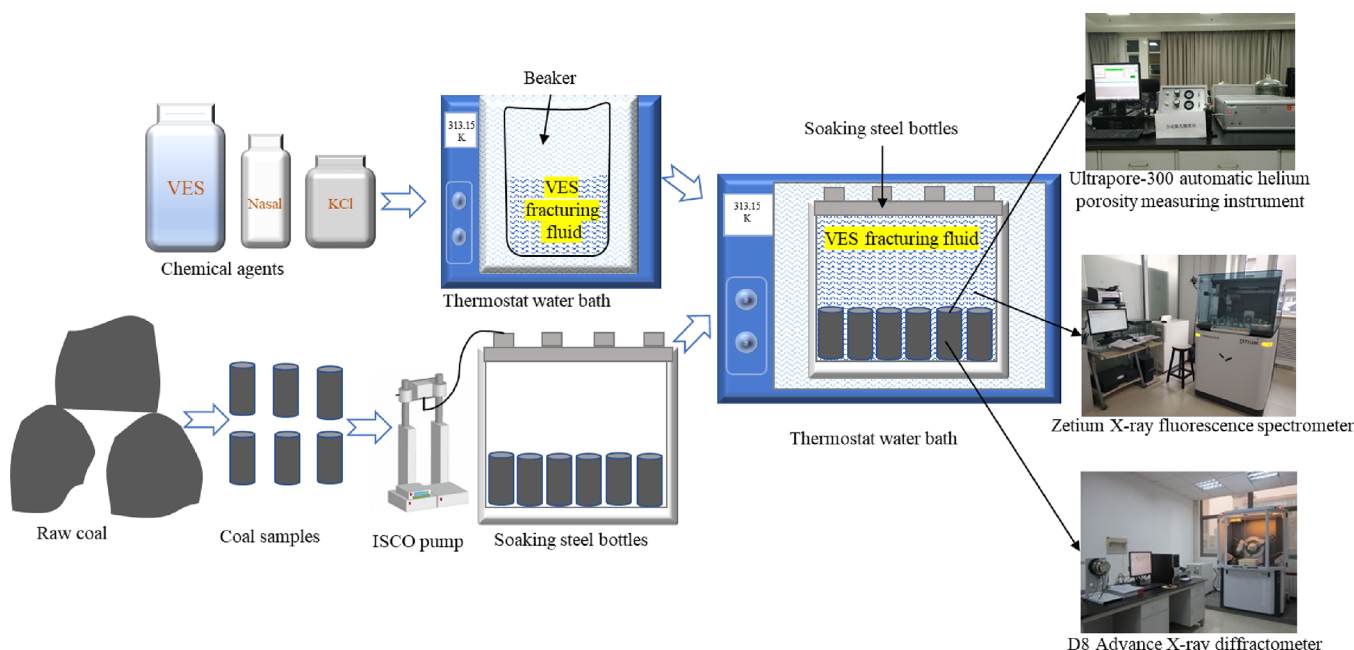


Figure 1. Processing of test coal samples and the testing flow diagram.

### 3. RESULTS AND DISCUSSION

**3.1. Effects of Hydrocarbon Chain Length of Hydrophobic Groups in VES and Mixing of VESs on Coal Pores.** The changes in porosity and pore volume of TS and NC coal samples before and after treatment with different formulations of fracturing fluids are illustrated in Figure 2. The

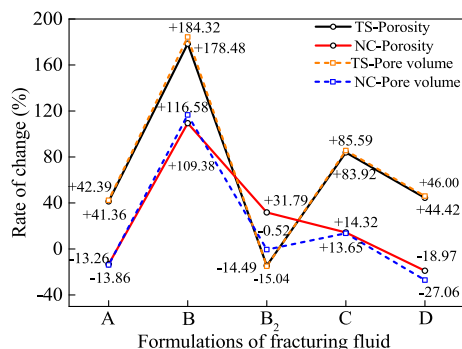


Figure 2. Porosity and pore volume changes of TS and NC coal samples before and after treatment with fracturing fluid.

porosity and pore volume of TS coal samples treated with deionized water and clean fracturing fluids B, C, and D increased, with the samples treated with clean fracturing fluid B exhibiting the greatest changes (porosity increase approximately 178%, pore volume increase approximately 184%). The porosity of NC coal samples treated with clean fracturing fluids B, B<sub>2</sub>, and C increased, with the greatest porosity change (ca. 109%) observed in samples treated with clean fracturing fluid B. The pore volume of TS and NC coal samples decreased after treatment with clean fracturing fluid B<sub>2</sub>.

Immersion of rock in fracturing fluids can lead to the dissolution of soluble salts,<sup>40</sup> and intrusion of fracturing fluids into rock can lead to clay expansion and fine particle migration.<sup>41</sup> Clay swelling is the main reason for the decrease in rock permeability.<sup>42</sup> Thus, dissolution of soluble salts, clay

expansion, and migration of coal surface particles are the main reasons for the changes in porosity and pore volume of coal (Figure 3). Treatment with clean fracturing fluid B resulted in

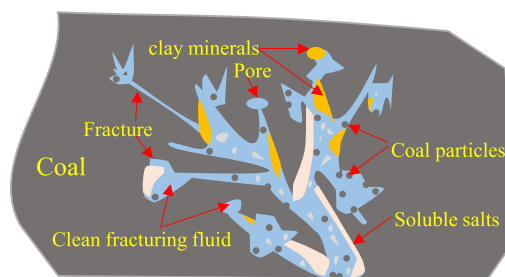
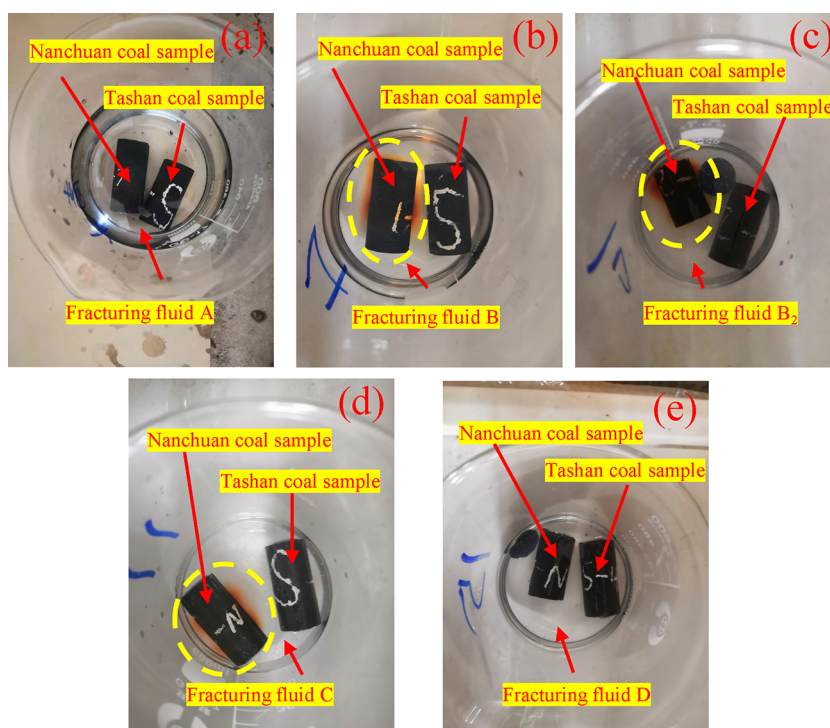


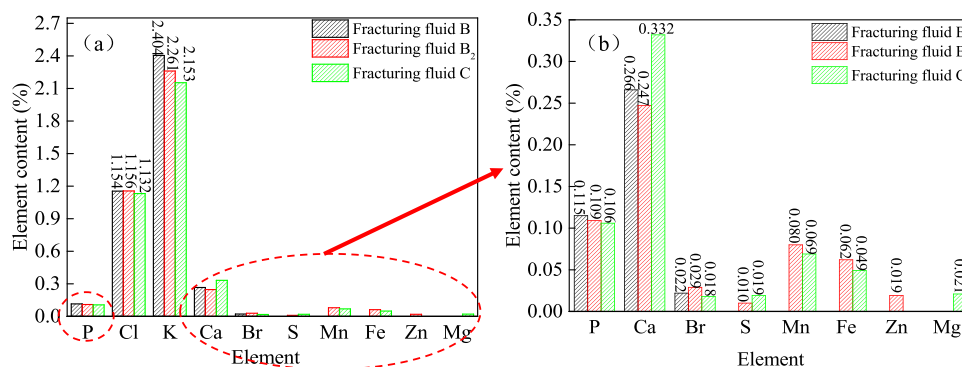
Figure 3. Dissolution of soluble salts, clay expansion, and migration of coal surface particles in the pores and fractures of coal treated with clean fracturing fluid.

the greatest increases in porosity and pore volume for both TS and NC coal samples, indicating that the main effect of fluid B is soluble salt dissolution or coal particle migration.

The hardness coefficient ( $f$ ) of TS coal samples is 1.31, indicating a harder coal quality, and  $f$  of NC coal samples is 0.35, indicating a softer coal quality. The porosity and pore volume of NC coal samples treated with deionized water and clean fracturing fluid D were lower than the values before treatment, implying that, for softer NC coal samples, the expansion of clay minerals had a great impact on the porosity and pore volume. The porosity and pore volume of NC coal samples treated with clean fracturing fluid D decreased more than those of samples treated with deionized water, indicating that mixed anionic and zwitterionic VES was more likely to cause clay swelling in soft coal. The porosity and pore volume of TS coal treated with deionized water and clean fracturing fluid D increased by approximately 40% relative to those of untreated samples, indicating that dissolution of soluble salts or migration of coal particles was important in hard coal. The notable difference in pore volume changes after treatment of



**Figure 4.** Coal samples and fracturing fluids after soaking: (a) soak TS and NC coal samples in fracturing fluid A, (b) soak TS and NC coal samples in fracturing fluid B, (c) soak TS and NC coal samples in fracturing fluid B<sub>2</sub>, (d) soak TS and NC coal samples in fracturing fluid C, and (e) soak TS and NC coal samples in fracturing fluid D.

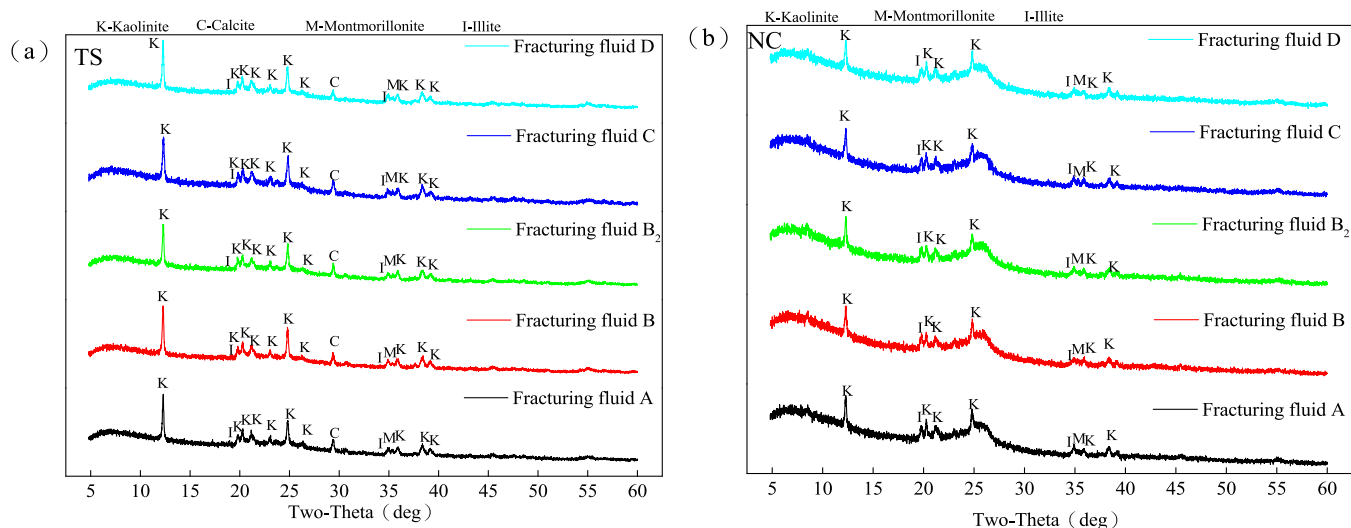


**Figure 5.** Elemental analysis of fluids B, B<sub>2</sub>, and C around the NC coal samples by XRF: (a) elements contained in fluids B, B<sub>2</sub>, and C and (b) elements that are not present in the original fracturing fluid (these elements were derived from the coal samples).

coal samples with clean fracturing fluids B and B<sub>2</sub> indicates that adding two methylene groups to hydrocarbon chain of hydrophobic groups of VES will increase clay swelling, and the influence of clay swelling on pores exceeds that of soluble salt dissolution or coal particle migration. The main adsorption modes of clean fracturing fluids B and B<sub>2</sub>, containing cationic surfactants on the surface of clay minerals, are electrostatic adsorption and aggregation layer adsorption, where the adsorption of the aggregation layer is influenced by the length of the hydrocarbon chain. VESs adsorb on clay mineral surfaces through hydrophobic bonds. Meanwhile, the adsorbed VESs form semimicelle adsorption on the clay mineral surface through the Vander Waals force between hydrocarbon chains.<sup>43,44</sup> When the solution concentration is the same, VESs with more methyl groups adsorb more on the surface of the clay minerals, forming larger aggregates. VESs with longer carbon chains have a greater aggregation driving force. VES can increase the interlayer distance of clay minerals, and the

chain length of VES has a significant impact on the effectiveness of this action.<sup>45</sup> Therefore, lengthening the hydrophobic chain in VES will increase the swelling of clay. The change in pore volume after treatment of coal samples with fluid C suggests that adding 0.1 wt % CAB (Zwitterionic VES) to fluid B can reduce the extent of clay expansion induced by the fracturing fluid.

**3.2. Elemental Analysis of Clean Fracturing Fluids after Soaking of Coal Samples.** After soaking TS and NC coal samples with deionized water and clean fracturing fluids B, B<sub>2</sub>, C, and D for 48 h, the color change of the clean fracturing fluids was assessed. Clean fracturing fluids B, B<sub>2</sub>, and C around the NC coal samples were orange (Figure 4). Clean fracturing fluids B, B<sub>2</sub>, and C reacted more obviously with the NC coal samples with a smaller hardness coefficient (TS:  $f = 1.31$ ; NC:  $f = 0.35$ ). Elemental analysis of fluids B, B<sub>2</sub>, and C around the NC coal samples was carried out using XRF (Figure 5). Fluids B, B<sub>2</sub>, and C contain P, Cl, K, Ca, Br, S, Mn, Fe, Zn, and Mg. P,



**Figure 6.** XRD mineral component analysis of coal samples treated with deionized water and clean fracturing fluids B, B<sub>2</sub>, C, and D: (a) TS coal samples and (b) NC coal samples.

Ca, Br, S, Mn, Fe, Zn, and Mg were not present in the original fracturing fluid: these elements were derived from the coal samples. The main mineral containing Ca in coal is calcite. The main iron-bearing mineral in coal is pyrite. Illite often contains Mg<sup>2+</sup>, Fe<sup>2+</sup>, and other metal cations. Montmorillonite includes Mg<sup>2+</sup>, Al<sup>3+</sup>, and other metal cations. These findings indicate that fluids B, B<sub>2</sub>, and C are conducive to the dissolution of calcite, pyrite, Illite, and montmorillonite. The orange precipitates in the clean fracturing fluids are iron-containing minerals from the coal.

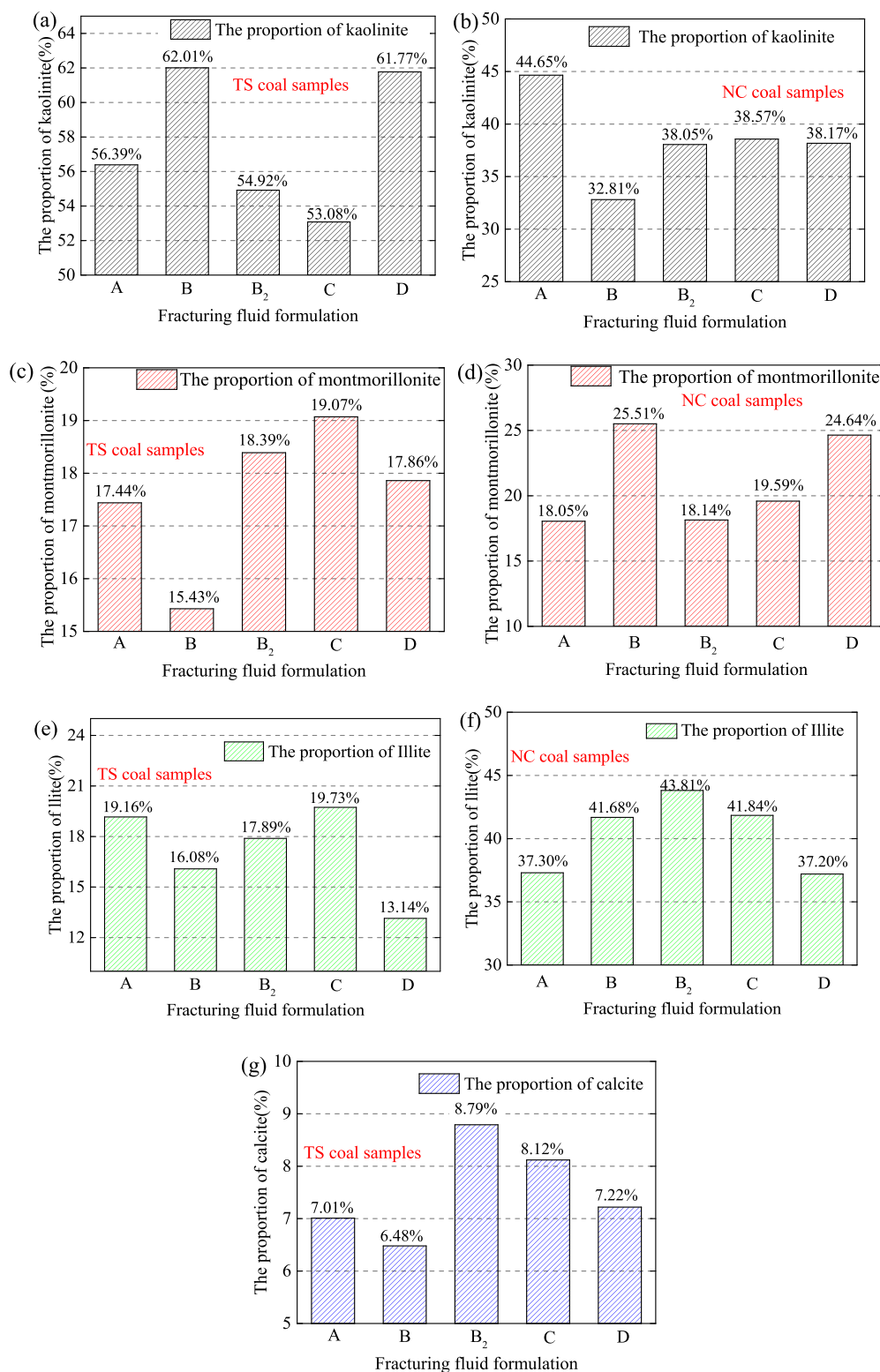
Clean fracturing fluids B, B<sub>2</sub>, and C all contain cationic VES and NaSal (micellar promoter), but fluid D does not. Clean fracturing fluids containing cationic VES and NaSal are more likely to interact with NC coal samples ( $f = 0.35$ ). Nasal contains both carboxyl and hydroxyl groups. The acid hydrolysis activity of the solution is stronger than its alkaline hydrolysis activity. The VES fracturing fluid is, therefore, weakly acidic. The possible chemical reactions are listed by Ge et al.,<sup>23</sup> Lu et al.,<sup>28</sup> and Lu et al.<sup>46</sup> Fluid B readily dissolves minerals containing P, Ca, and Br (Figure 5). Fluid B<sub>2</sub> can dissolve minerals containing P, Ca, Br, S, Mn, Fe, and Zn. This difference indicates that there are more types of dissolved minerals in the fracturing fluid prepared with STAC containing more methylene groups. Clean fracturing fluid C (mixed cationic and zwitterionic VES) can dissolve minerals containing P, Ca, Br, S, Mn, Fe, and Mg and has the greatest ability to dissolve Ca-containing minerals. This result shows that mixing cationic and zwitterionic VES can promote dissolution of Ca-containing minerals.

**3.3. Mineral Composition and Content in Coal Samples Treated with Clean Fracturing Fluids.** Soaking the coal samples in clean fracturing fluids caused the relatively unstable minerals in the coal to undergo dissolution. XRD analysis (Figures 6 and 7) demonstrated that the TS coal samples after treatment with deionized water and clean fracturing fluids mainly contained kaolinite (Al<sub>2</sub>(Si<sub>2</sub>O<sub>5</sub>)(OH)<sub>4</sub>, clay mineral), montmorillonite ((Na,Ca)<sub>0.3</sub>(Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·xH<sub>2</sub>O, clay mineral), Illite (K<sub>0.7</sub>Al<sub>2.1</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>, clay mineral), and calcite (CaCO<sub>3</sub>, carbonate mineral). The NC coal samples treated with deionized water and clean fracturing fluids mainly

contained the clay minerals kaolinite, montmorillonite, and Illite. TS coal samples treated with deionized water and clean fracturing fluids possessed a low calcite content (less than 10%), less than 20% montmorillonite and Illite, and more than 50% kaolinite (Figure 7). The NC coal samples treated with deionized water and clean fracturing fluids contained kaolinite (30–45%), montmorillonite (18–26%), and Illite (37–44%) (Figure 7).

In kaolinite, one side of the crystal layer is composed of oxygen, and the other side is composed of hydroxyl (Figure 8a). The crystal layers are tightly bound by hydrogen bonds, the interlayer gravity is strong, and water does not easily enter the lattice, so kaolinite is relatively stable in the fracturing fluids. The montmorillonite crystal frame is composed of two silicon-oxide wafers and one aluminum-hydroxide wafer (Figure 8b). Montmorillonite is a 2:1-type mineral. Because both sides of its crystal unit are oxygen, the interlayer gravitation is mainly intermolecular and the connection between adjacent crystal layers is weak, so the mineral readily expands when it encounters water.<sup>47</sup> Illite also possesses a 2:1-type cell and includes potassium ions between the two cells. The attraction between crystal layers is mainly electrostatic force, and the bonding strength between crystal layers is weaker than that of kaolinite but higher than that of montmorillonite. Illite is a nonexpansive clay mineral (Figure 8c).

Kaolinite, montmorillonite, and Illite are silicate minerals with permanently negatively charged undersides. Clean fracturing fluids B, B<sub>2</sub>, and C contain high concentrations of quaternary ammonium cationic VES, which can be adsorbed on the surface of negatively charged silicate minerals by electrostatic force, and can also form semimicellar adsorption (hydrophobic adsorption) on the surface of minerals by van der Waals force between hydrocarbon chains.<sup>43,44</sup> Therefore, the hydrocarbon chain length of VES has a great effect on the removal of silicate minerals by clean fracturing fluids. The anionic VES and zwitterion VES in clean fracturing fluid D will combine with the hydroxyl groups on the surface of kaolinite. The electrostatic repulsion force will hinder the adsorption of anionic VES in clean fracturing fluid D on the surface of montmorillonite. However, there are large amounts of cations

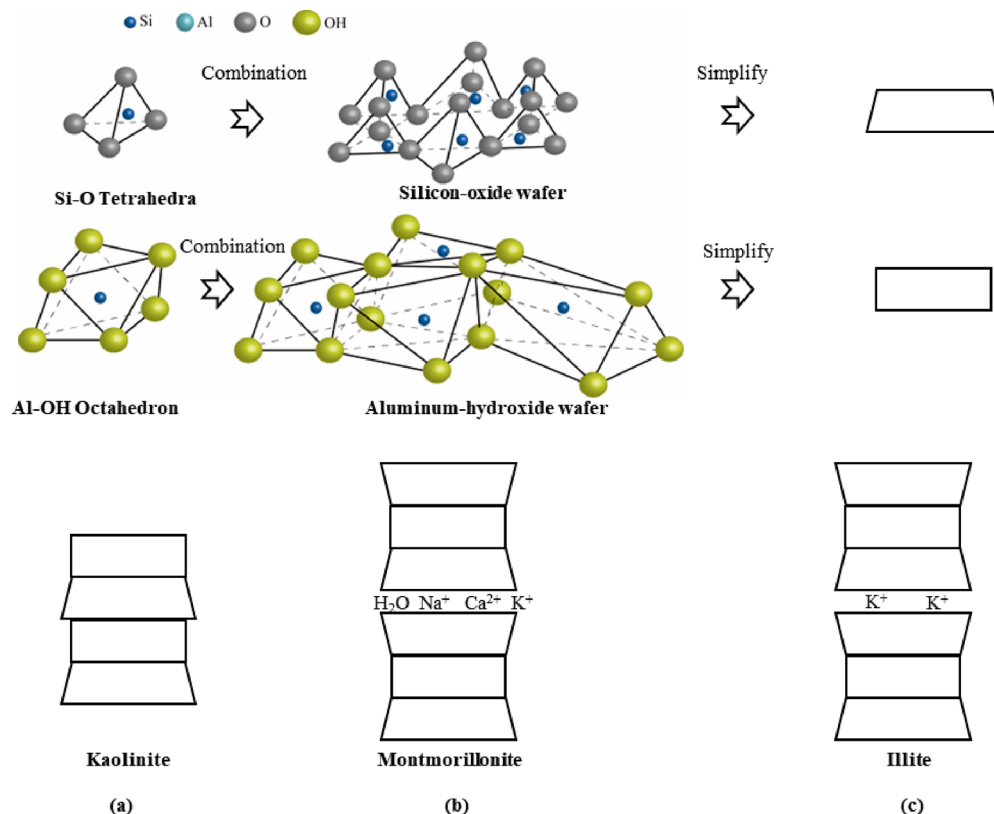


**Figure 7.** Percentage abundances of minerals in coal samples treated with clean fracturing fluid: (a) the proportion of kaolinite in TS coal samples, (b) the proportion of kaolinite in NC coal samples, (c) the proportion of montmorillonite in TS coal samples, (d) the proportion of montmorillonite in NC coal samples, (e) the proportion of Illite in TS coal samples, (f) the proportion of Illite in NC coal samples, and (g) the proportion of calcite in TS coal samples.

and water between the layers of montmorillonite; therefore, anionic VES will be adsorbed between the layers. Similarly, electrostatic repulsion will hinder the adsorption of anionic VES in clean fracturing fluid D on the surface of the Illite. To sum up, adsorption of clean fracturing fluids B, B<sub>2</sub>, and C

containing cationic VES onto the surfaces of clay minerals mainly occurs by electrostatic adsorption and aggregation layer adsorption, and aggregation layer adsorption is affected by the hydrocarbon chain length. For clean fracturing fluid containing anionic VES, adsorption onto the surfaces of clay minerals





**Figure 8.** Structural diagram of clay minerals: (a) kaolinite, (b) montmorillonite, and (c) Illite.

mainly occurs by interlayer anion adsorption and aggregation layer adsorption. Therefore, anionic VES exerts a combined effect of surface electrostatic repulsion, layer electrostatic attraction, and hydrophobic force on the surfaces of clay minerals.

The mineral contents of TS coal samples treated with clean fracturing fluids are shown in Figure 7a,c,e,g. These results indicate that clean fracturing fluid has a little effect on the mineral composition of TS coal samples; thus, the fluids in which the TS coal samples had been soaked did not show a noticeable orange color (Figure 4). The relative percentages of montmorillonite and Illite in coal samples treated with fluid B decreased slightly, mainly as a result of dissolution or removal of those minerals. The relative percentage of kaolinite in coal samples treated with clean fracturing fluids B<sub>2</sub> and C decreased. The lowest relative percentage of kaolinite was observed in coal samples treated with fluid C. Kaolinite is not easy to dissolve, indicating that fluids B<sub>2</sub> and C have a strong ability to remove kaolinite through adsorption; thus, VES with a long hydrocarbon chain has a strong ability to remove kaolinite. The addition of zwitterionic VES increases the ability of clean fracturing fluid to remove kaolinite. The relative percentage of Illite decreased in coal samples treated with clean fracturing fluid D, indicating that this fluid has strong chemical dissolution capacity and can effectively remove Illite.

The relative mineral content of NC coal samples treated with clean fracturing fluids is illustrated in Figure 7b,d,f. The kaolinite contents of the NC coal samples treated with clean fracturing fluids are markedly lower than those of the samples treated with deionized water, indicating that fluids B, B<sub>2</sub>, C, and D have a strong ability to remove kaolinite. Of these fluids, fluid B has the best cleaning effect on kaolinite (the kaolinite content of fluid-B-treated samples is 11.8% lower than that of

samples treated with deionized water). Increases of the hydrocarbon chain length of VES will reduce the ability of fracturing fluid to remove kaolinite. Even with the addition of zwitterion VES, the fracturing fluid's ability to remove kaolinite does not increase. The removal of kaolinite from the coal samples by clean fracturing fluid B resulted in an increase in the relative content of montmorillonite (7.4% more than that of the deionized-water-treated coal samples) and Illite (4.4% more than that of the deionized-water-treated coal samples). However, treatment with fluid B<sub>2</sub> only led to an increase in the relative content of Illite, indicating that this fluid dissolved or removed montmorillonite and that increasing the hydrocarbon chain length of VES will increase the adsorption of VES on montmorillonite. Clean fracturing fluid D removes kaolinite, and the relative content of Illite remained unchanged, whereas that of montmorillonite increased. As seen from Figure 7e, clean fracturing fluid D can effectively remove Illite. This finding indicates that clean fracturing fluid D containing anionic VES has a greater ability to dissolve and remove Illite than montmorillonite. This difference arises mainly because adsorption of anionic VES is blocked by the electrostatic repulsion force on the surface of montmorillonite, and the interlayer adsorption of anionic VES between montmorillonite layers is small. The electrostatic repulsion of the Illite surface has a little effect on the adsorption of anionic VES.

#### 4. CONCLUSIONS

The hydrophobic groups, ionic types, and mixing of VES can affect the performance of clean fracturing fluids. We analyzed the effects of hydrophobic chain length and mixing of different ion types of VESs on the pore changes of coal. We also assessed the elemental contents of clean fracturing fluids after



soaking of coal samples and measured the mineral composition and content in coal samples treated with clean fracturing fluids. The main conclusions of the study are as follows.

1. The greatest change in coal porosity was observed in samples treated with clean fracturing fluid B, with a porosity increase of approximately 178% for TS coal samples and ca. 109% for NC coal samples.
2. Mixed anionic and zwitterionic VES was more likely to cause clay swelling in soft coal. Adding two methylene groups to the hydrocarbon chain of VES increased clay swelling. Adding 0.1 wt % CAB (zwitterionic VES) to cationic VES fracturing fluid B can reduce the extent of clay expansion induced by the fracturing fluid.
3. Clean fracturing fluids B, B<sub>2</sub>, and C are conducive to the dissolution of calcite, pyrite, Illite, and montmorillonite. More types of dissolved minerals are present in fracturing fluids prepared with STAC containing more methylene groups. Mixing cationic and zwitterionic VES can promote the dissolution of Ca-containing minerals.
4. VES with a long hydrocarbon chain has a strong ability to remove kaolinite in the TS coal samples ( $f = 1.31$ ). The addition of zwitterion VES increased the ability of clean fracturing fluids to remove kaolinite in the TS coal samples. Clean fracturing fluid D containing anionic VES exhibited strong chemical dissolution and Illite removal capacity in the TS coal samples. Increased hydrocarbon chain length of VES reduced the ability of fracturing fluids to remove kaolinite in the NC coal samples ( $f = 0.35$ ). Even with the addition of zwitterion VES, the fracturing fluid's ability to remove kaolinite did not increase. Clean fracturing fluid B<sub>2</sub> prepared with STAC containing more methylene groups had a dissolution or removal effect on montmorillonite in the NC coal samples. Clean fracturing fluid D containing anionic VES has a greater ability to dissolve and remove Illite than montmorillonite.

## AUTHOR INFORMATION

### Corresponding Author

**Mengmeng Yang** – College of Safety and Emergency Management Engineering, Taiyuan University of Technology, Taiyuan 030024, China; Pingdingshan Tianan Coal Mining Co., LTD., Pingdingshan 467000, China; State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China;  
 orcid.org/0009-0009-2251-4583;  
 Email: yangmengmeng@tyut.edu.cn

### Authors

**Junyue Zhang** – State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China

**Liang Zhang** – State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China; School of Emergency Management, Xihua University, Chengdu 610039, China

**Shihui Gong** – State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.4c00692>

## Notes

The authors declare no competing financial interest.

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