

Experimental Research on the Performance of a Wetting Agent Based on Compound Acidification in Low-Porosity and Hard-to-Wet Coal Seams

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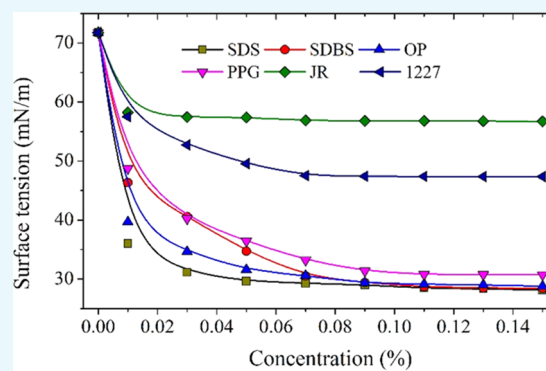
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ABSTRACT: To improve the wetting performance of the composite acid solution in the deep coal seam, in this paper, the surface tension and contact angle characteristics of the compound acid wetting agent are studied, then the composition of the wetting agent is developed and evaluated based on nuclear magnetic resonance. The research indicates that surfactants can reduce the surface tension of water, and the surface tension tends to decrease with the increase in the surfactant concentration. The critical micelle concentration of the anionic surfactant sodium dodecyl sulfate (SDS) solution is only 0.025%, and the corresponding critical surface tension is 30.63 mN/m. The wetting agent material based on the composite acid solution includes the acid HCl, HF, the anionic surfactant SDS, and the inorganic salt NaCl, the composition of which is 8%, 8%, 0.025%, and 0.6 mol/L, respectively. The total wetting rate of the composite acid-containing HCl + HF + SDS + NaCl is the largest, reaching 64.30%, which has good wettability inside the coal and can be a comprehensive intrusion into the internal structure of coal pores.



1. INTRODUCTION

Due to its own physical and chemical properties, mine dust has the hazards of reducing the service life and accuracy of equipment, decreasing the visibility of the production site, being prone to spontaneous combustion, and causing occupational diseases (pneumoconiosis) for long-term dust-exposed personnel.^{1–4} Coal mine dust not only menaces the safe production of mines but also seriously endangers the physical and mental health of workers.^{5–8} In recent years, the prevention and control of dust hazards in China have gradually received attention. In the past 10 years, there have not been a hundred deaths caused by dust explosions; however, this does not mean that coal mine dust prevention and control work has been at the forefront of the world.^{9–11} On the contrary, the dust hazards are still very serious. The number of people suffering from pneumoconiosis is the highest in the world due to the long-term work of Chinese coal miners in a high concentration of dust environment.

Chemical wetting dust suppression is one of the most effective methods to improve coal seam water injection, and the most typical method is to add a surfactant.^{12–14} The surfactant is a special chemical substance, one end is connected to a hydrophilic group, and the other end is connected to a hydrophobic group. When it is mixed with some liquids, the gas–liquid and solid–liquid interfacial tension of the liquid can change significantly.¹⁵ Cheng et al. obtained the best surfactant

and its suitable concentration for coal seams by comparing the moisture absorption growth rate of coal samples in the selected best surfactant solution and pure water through contact angle test experiments, providing a scientific basis for coal seam water injection.¹⁶ Wang et al. proposed an active magnetized water technology for dust reduction based on the synergistic theory of surfactants and magnetization.¹⁷ Through the solution wetting performance test, the study found that the surface tension and contact angle of active magnetized water were reduced by 60% compared with pure water, and the dust removal efficiency is increased by 40%, which improves the underground working environment. Ni et al. studied the effects of [Bmim][Cl] (1-butyl-3-methylimidazole chloride) ionic liquid and anionic surfactant–NaCl system solution on the wettability of coal dust. The results showed that adding NaCl to the sodium dodecyl sulfate (SDS) solution reduced the contact angle and enhanced the wetting effect.^{18–21} Khasanov et al. constructed the continuity seepage equation of water in the coal and studied the degree of hydrophilicity of the added

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surfactant solutions to coal dust.²² The results showed that the combination of anionic and nonionic surfactants and the addition of a certain amount of inorganic salt can significantly enhance the wettability of the solution to the coal dust. Jin et al. used wetting chemical dust suppressants to remove dust as a means of dust control, conducted a systematic study on wet chemical dust suppressants, and compared the moisture absorption and moisturizing capabilities of various hygroscopic materials and several surface activities.²³ For the wetting ability of the agent, calcium chloride, magnesium chloride, and Triton X-100 were selected as the base and auxiliary materials of the dust suppressant, in which the formula was studied and optimized.

At present, the research on chemical wetting and dust suppression is mainly focused on the development of wetting agents, especially chemical wetting agents containing different types of active agents, which have a good promotion effect on the prevention and control of mine dust, to a certain extent, the coal dust control technology has been deepened and improved. However, with the deepening of China's mining depth, the hard-wetting of coal seams makes it difficult for coal seam water injection to inject water into low-porosity coal seams, which seriously affects its dust control effect. At the same time, through previous studies, it was found that more minerals are distributed in the coal.²⁴ Therefore, this paper proposes a composite acid wetting technology. To develop the wetting capability of the composite acid solution deeply, physical experimental methods are used, such as researching the surface tension change law and contact angle change characteristics of the composite acid liquid wetting agent, developing a high-quality composite acid liquid wetting agent, determining the composition of the wetting agent, and evaluating the wetting performance of the composite acid liquid wetting agent based on nuclear magnetic resonance.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Wetting Agent Raw Material Selection. According to the classification of acid liquid and surfactant, in the development process of the composite acid wetting agent in this paper, two acids were selected: HCl and HF; six surfactants of anionic, nonionic, and cationic were selected; and NaCl inorganic salt was chosen. Both concentrations of HCl and HF were 8%, and the concentrations of NaCl were 0.3, 0.6, and 0.9 mol/L. Surfactant additives were formulated into eight different concentrations of solutions with concentrations of 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13, and 0.15%. Surfactants are divided into three categories, including anionic surfactants, cationic surfactants, and nonionic surfactants. The six types of surfactants selected in this article include three types of surfactants. To make the results more convincing and scientific, this article selects eight concentrations, which are representative. The surfactants used in the experiment are shown in Table 1.

2.2. Coal Sample Preparation. The coal from Xiaojihan Coal Mine in Yulin City, Shanxi Province, was crushed, and the coal powder below 200 mesh was screened, and the mass was determined to be 2 g. The coal dust was evenly spread on the tablet press liner, and boric acid was filled between the liner and the mold. A certain pressure was maintained for 1 min to make a cylindrical coal sample.

2.3. Measurement of Solution Surface Tension and Contact Angle. The DSA optical droplet morphology analysis system is used to measure the surface tension of

Table 1. Types of Experimental Surfactants

surfactant names	abbreviation	types
sodium dodecyl sulfate	SDS	anion
sodium dodecylbenzene sulfate	SDBS	anion
OP emulsifier	OP	nonionic
poly(propylene glycol)	PPG	nonionic
cationic cellulose	JR	cation
dodecyl dimethyl benzyl ammonium chloride	1227	cation

different concentrations of surfactants and compound solutions.^{25–27} The contact angles formed by all solutions and coal samples are measured using fixed and continuous dynamic tracking.²⁸

3. RESULTS AND DISCUSSION

3.1. Variation Law of Surface Tension of Compound Acid with Different Proportion. **3.1.1. Surface Tension and Critical Micelle Concentration (CMC) of Surfactants.** Adding surfactants to the composite acid solution can positively change the wettability of coal. It is related to the structure and properties of the surfactant added to the compound solution.²⁹

The molecular structure of surfactants is generally composed of polar groups and nonpolar groups.^{30,31} Polar groups are easily soluble in water and have hydrophilic properties and are called hydrophilic groups; nonpolar groups are insoluble in water and are called hydrophobic groups. When the surfactant concentration is low, the surface tension of the solution can drop sharply. Conversely, when the concentration increases beyond a certain value, the surface tension hardly changes.^{32–34} At this time, the surfactant molecule encloses the hydrophobic group inside and hardly contacts with water, and the molecular aggregate composed of the hydrophilic group facing the water is called a micelle. The point at which the properties of the surfactant change with concentration, the concentration at which micelles begin to form in solution, is called the critical micelle concentration. The corresponding surface tension is called critical surface tension (CST) and is usually expressed as σ_c . The CMC can indicate the efficiency of surfactants in reducing the surface tension of the solution. The smaller the corresponding critical micelle concentration, the higher the efficiency.³⁵ At the same time, the smaller the σ_c is, the better the surfactant's ability to reduce the surface tension of the solution is.³⁶

From the perspective of simplifying research methods and saving material costs, the surface tension method is used to determine the CMC of surfactants.³⁷ At eight different concentrations, the surface tension of six surfactant solutions is measured by the hanging drop method. The proportions of surfactant additives shown in Table 2 are 0.01, 0.03, 0.05, 0.07, 0.09, 0.111, 0.13 and 0.15%.

Therefore, the changes of different surfactant solutions with increasing concentrations are shown in Figure 1.

As shown in Figure 1, anionic surfactants SDS and sodium dodecylbenzene sulfonate (SDBS), nonionic surfactants OP and PPG, and cationic surfactants JR and 1227 can all reduce the surface tension of the entire system. Moreover, when the concentration of the solution gradually increases, the surface tension is negatively correlated to decrease. When the surfactant concentration is less than 0.03%, the surface tension decreases greatly. When the concentration exceeds a fixed value, the decreasing trend of surface tension is gentle. Among

Table 2. Relationship between the Surface Tension and Concentration (mN/m)^a

surfactants	concentrations (%)								
	0	0.01	0.03	0.05	0.07	0.09	0.11	0.13	0.15
SDS	71.78	36.02	32.16	29.67	29.31	29.01	28.45	28.34	28.16
SDBS	71.78	46.34	40.60	34.71	30.53	29.42	28.68	28.52	28.42
OP	71.78	39.67	34.63	31.58	30.56	29.32	29.12	29.01	28.79
PPG	71.78	48.74	40.23	36.43	33.19	31.38	30.78	30.76	30.74
JR	71.78	58.23	57.45	57.40	56.87	56.81	56.80	56.78	56.71
1227	71.78	57.51	52.72	49.56	47.53	47.41	47.39	47.36	47.36

^aThe solution with a concentration of 0% is pure water.

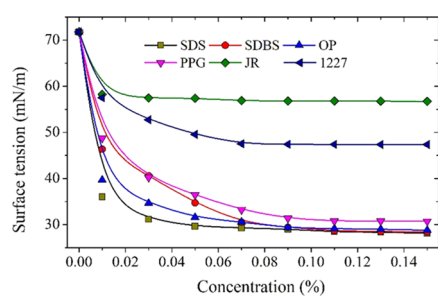


Figure 1. Changes of surface tension with the concentrations.

them, under the same concentration conditions, the surface tension of the anionic surfactant SDS solution and the cationic surfactant JR solution has the largest and smallest declines, respectively. At a concentration of 0.15%, the surface tension of the former is 28.16 mN/m, and the surface tension of the latter is 56.71 mN/m.

Taffarelz explored the method of solving the CMC of a surfactant,³⁸ drawing a graph of the surface tension of the surfactant solution with the concentration change and drawing two straight lines in the decreasing and smoothing trend of the surface tension. The concentration corresponding to the intersection of the two straight lines is the critical micelle concentration of the solution. According to this method, the CMC of the SDS and OP solution are shown in Figures 2 and 3.

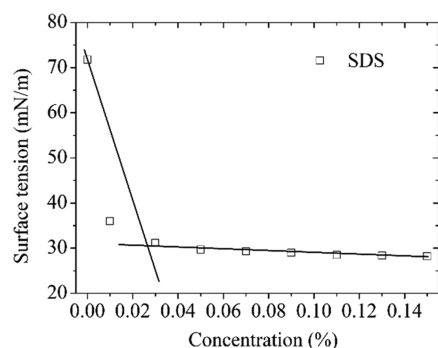


Figure 2. Relationship between the surface tension of SDS solution and its concentration.

From Figures 2 and 3, the CMCs of the SDS solution and the PPG solution are 0.025 and 0.040%, respectively. Different solutions of the corresponding concentrations are configured, and the CST is measured to be 30.63 and 37.93 mN/m, respectively. Using the same method, the CMC and CST of the six solutions are shown in Table 3.

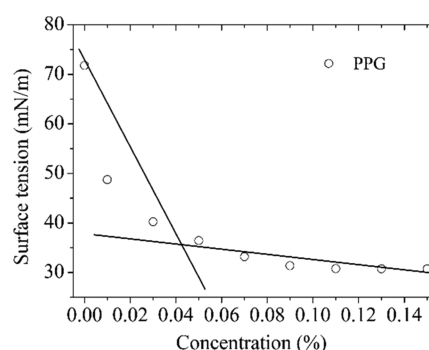


Figure 3. Relationship between the surface tension of PPG solution and its concentration.

It can be seen from Table 3 that when all solutions reach the CMC, they are all less than 0.06%. Among them, the CMC of anionic and nonionic surfactant solutions is less than that of cationic surfactants, indicating that anionic and nonionic surfactants are more effective in reducing the surface tension of the solution than cationic surfactants. Among them, the CMC of the SDS solution is the lowest, only 0.025%, and the corresponding CST is 30.63 mN/m, indicating that it has the highest efficiency in reducing the surface tension of the solution.

3.1.2. Variation of Surface Tension of Compound Acid with Different Proportions. The six selected surfactant solutions are proportioned with two acid solutions. The surfactant concentration is its critical micelle concentration. The concentration of HCl solution and HF solution are both 8%. The solution numbers and proportions are shown in Table 4.

The pendant drop method is used to measure the surface tension of different surfactant composite acids, as shown in Table 5.

It can be concluded from Table 5 that the surface tension of the composite acid solution containing surfactants is significantly reduced, indicating that the coal wetting effect has been significantly improved. Simultaneously, the surface tension of the composite-acidified solution containing anionic and nonionic surfactants is less than that of the pure acid solution, while the composite acid solution containing a cationic surfactant is greater than that of the pure acid solution, which shows that different types of surfactants have different effects on the wetting of coal by acid.

3.2. Variation Characteristics of the Contact Angle Formed by Different Proportions of Composite Acid Solution and Coal. During the wetting process, the wetting edge formed by the coal surface and water, that is, the contact angle, reflects the size of the attraction between water

Table 3. Critical Micelle Concentration and Critical Surface Tension of Different Surfactants

surfactant	SDS	SDBS	OP	PPG	JR	1227
CMC (%)	0.025	0.029	0.038	0.040	0.023	0.059
CST (mN/m)	30.63	35.45	34.36	37.93	59.79	50.15

Table 4. Number and Proportion of Different Surfactant Compound Solutions

solution numbers	material abbreviation	proportion (%)
1#	HCl	8
2#	HCl + HF	8 + 8
3#	HCl + HF + SDS	8 + 8 + 0.025
4#	HCl + HF + SDBS	8 + 8 + 0.029
5#	HCl + HF + OP	8 + 8 + 0.038
6#	HCl + HF + PPG	8 + 8 + 0.040
7#	HCl + HF + JR	8 + 8 + 0.023
8#	HCl + HF + 1227	8 + 8 + 0.059

molecules and coal molecules. As can be seen in Figure 4, the contact angle refers to the angle θ formed from the solid–liquid interface through the liquid itself to the gas–liquid interface in the solid–liquid–gas interface system. The contact angle between the compound liquid and the coal surface is a significant measurement of wettability. The easier the solution is to diffuse on the solid surface, the smaller the contact angle value of the solution with the coal sample, the stronger the wetting effect. The smaller the θ value, the better the wetting performance. When $\theta \leq 90^\circ$, the surface of the solid is hydrophilic, and the liquid is easier to wet the solid at this time. When $90^\circ < \theta \leq 180^\circ$, it is called adhesion wetting. At this time, the solid surface is hydrophobic and not easy to wet solids.

Therefore, it is necessary to reduce the contact angle of the composite acid solution on the coal surface as much as possible, increase the contact area of the composite acid solution and the coal surface, and increase the wetting range and wetting effect of the coal. Because inorganic salts can reduce the surface tension of the solution, the inorganic salt NaCl is added to the composite acid solution containing the active agent to further reduce it. The result is that the contact area between the solution and the coal surface increases, thereby reducing the contact angle between the solution and the coal sample. Table 6 shows the proportion of NaCl composite acid solution with different concentrations.

The DSA analysis system can accurately capture the images of the instantaneous contact angle between the solid and liquid, and the fastest shooting is 50 frames/s. Through this system, the dynamic contact angle of the NaCl-containing composite acid solution on the coal surface is obtained. Figures 5–8 show pictures of part of the time (1, 10, 20 s).

The contact angles of all of the composite acids A#, B#, C#, and D# on the coal surface decrease with time, as shown in Figures 5–8. Because with the increase of time, the solution gradually spreads on the coal sample to increase the contact area. The contact angle formed by the composite acid A# with the coal sample is the largest, the initial contact angle is 58.6° , and it reaches equilibrium after 20 s, and the contact angle is

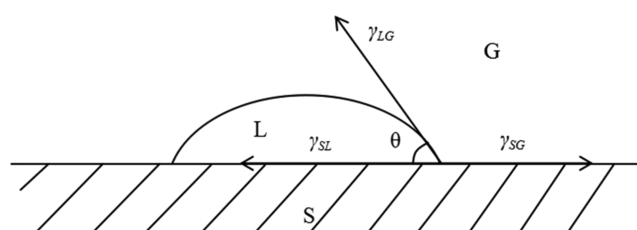


Figure 4. Contact angle of solution droplets and coal.

Table 6. Number and Ratio of Composite Acid Solution Containing NaCl

solution numbers	material abbreviation	proportion
A#	HCl + HF + SDS	8% + 8% + 0.025%
B#	HCl + HF + SDS + NaCl	8% + 8% + 0.025% + 0.3 mol/L
C#	HCl + HF + SDS + NaCl	8% + 8% + 0.025% + 0.6 mol/L
D#	HCl + HF + SDS + NaCl	8% + 8% + 0.025% + 0.9 mol/L

reduced to 36.2° . In the HCl + HF + SDS + NaCl composite acid solution, increasing the concentration of the NaCl solution reduces the dynamic contact angle and equilibrium contact angle formed by the composite solution with the coal sample. When the NaCl concentration in the composite acid solution is 0.3 mol/L, the equilibrium contact angle formed decreases from 36.2 to 27.3° . Because of the electrostatic force between NaCl and SDS, the thickness of the double electron layers of the ion head is compressed so that the repulsive force between them is weakened, and the SDS molecules are more likely to accumulate on the surface of the solution. At the same time, the counterion in NaCl has a neutralizing effect on the charges of part of the hydrophilic groups in SDS, which reduces the phase potential and the surface tension. After that, the increase in the concentration of the inorganic salt NaCl affects the continuous decrease of the contact angle. When its concentration increased to 0.6 and 0.9 mol/L, the equilibrium contact angles formed decreased to 21.1 and 16.2° , respectively. Therefore, adding a specific concentration of NaCl to the HCl + HF + SDS composite acid can reduce the contact angle, thereby improving the wetting performance of the composite acid to coal.

Figure 9 shows the dynamic change curve of the contact angle of the four composite acid solutions on the coal surface with time, which can be used to more intuitively study the dynamic contact angle formed by the composite acid solution.

Observing Figure 9 shows that the contact angles formed by all of the composite acid solutions with the coal samples decrease with the increase of time. The contact angle decreased rapidly from the initial stage to a slow drop and

Table 5. Surface Tension of Composite Acid Containing Different Surfactants

solution numbers	1#	2#	3#	4#	5#	6#	7#	8#
surface tension (mN/m)	47.23	38.94	24.97	29.34	28.67	31.18	52.24	47.92

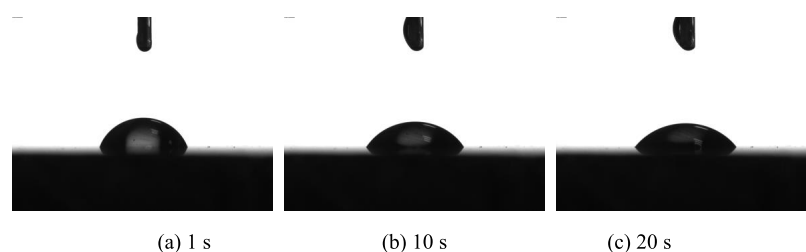


Figure 5. Dynamic contact angle formed by the A# solution and coal sample.

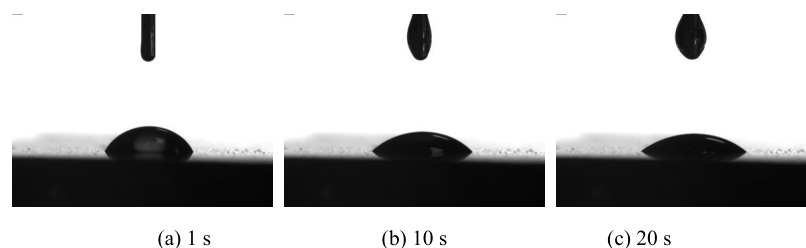


Figure 6. Dynamic contact angle formed by the B# solution and coal sample.

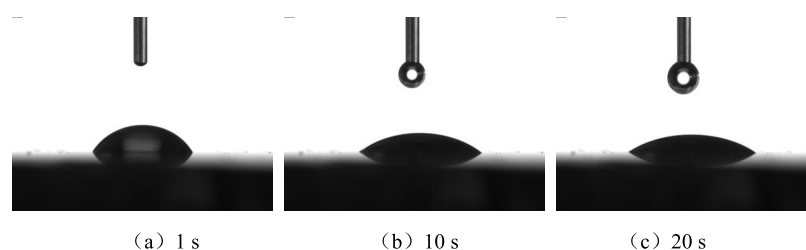


Figure 7. Dynamic contact angle formed by the C# solution and coal sample.

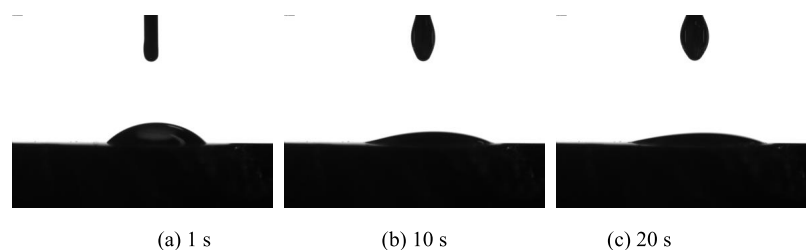


Figure 8. Dynamic contact angle formed by the D# solution and coal sample.

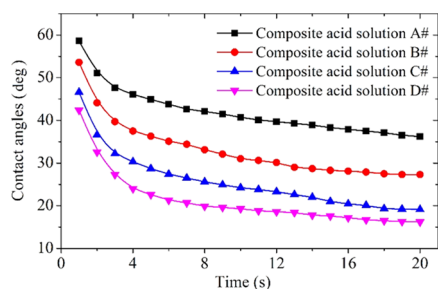


Figure 9. Dynamic change curve of the contact angles with time.

reached equilibrium after 20 s. Due to the increasing concentration of NaCl, the equilibrium contact angles of the four composite acid solutions on the coal surface decreased to 36.2, 27.3, 21.1, and 16.2°, respectively, indicating that the addition of NaCl to the composite acid solution weakened the surface shrinkage of the liquid, which increases the contact area

between the composite acid and the coal surface, and promotes the coal wettability of the composite acid liquid.

3.3. Determination of Wetting Agent Composition Based on Compound Acid. The wetting performance of the wetting agent of the composite acid liquid on the coal surface mainly depends on two aspects. The first is that the smaller the contact angle formed by the compound solution with the coal sample, the better the wetting performance of the solution; the second is that the lower the surface tension of the solution itself, the stronger the wetting ability.

By studying the surface tension and contact angle characteristics of different surfactant types and concentration solutions, it is concluded that compared with pure water, the composite acid-containing HCl + HF + SDS has the largest reduction in surface tension. At the same time, the use of inorganic salt NaCl as an additive can effectively reduce the equilibrium contact angle. However, when the NaCl concentration in the compound solution reaches saturation, the surfactant ion head no longer interacts with the inorganic salt ions. Therefore, when adding a higher concentration of NaCl solution to the

composite acid solution, the equilibrium contact angle changes gently. As shown in Figure 9, the NaCl concentration is selected as 0.6 mol/L. To sum up, the wetting agent material based on the composite acid solution includes acid solution HCl, HF, anionic surfactant SDS, and inorganic salt NaCl, the composition of which is 8%, 8%, 0.025%, and 0.6 mol/L, respectively.

3.4. Wetting Performance Evaluation of Composite Acid Solution Based on Nuclear Magnetic Resonance.

3.4.1. Evaluation Method of Wetting Performance of Composite Acid Solution. By injecting saturated acid liquid into the coal seam, the composite acid liquid migrates into the coal body and wets the coal body. That is, the wetting in the coal seam is produced by the movable fluid in the pore-fracture system of the coal seam. The more the moving fluid, the better is its potential wetting effect. Since the source of the T_2 signal amplitude of nuclear magnetic resonance is hydrogen protons, the more the hydrogen protons, the larger the T_2 signal amplitude, indicating that the more the movable fluid inside the coal body, the greater the water content of the coal body. Therefore, the wetting performance of the composite acid can be evaluated by comparing the T_2 distribution of the fully saturated four composite acids and the coal samples after centrifugation.

Prepare a cylindrical coal sample with a diameter of 30 mm and a length of 60 mm for use. At the same time, four composite acid solutions a#, b#, c#, and d# were prepared. The composite acid solution ratio is shown in Table 7. The NM-

Table 7. Proportion of Four Kinds of Compound Acid

solution numbers	material abbreviation	proportion
a#	HCl	8%
b#	HCl + HF	8% + 8%
c#	HCl + HF + SDS	8% + 8% + 0.025%
d#	HCl + HF + SDS + NaCl	8% + 8% + 0.025% + 0.6 mol/L

VSD vacuum saturation device was used to dry-pump the prepared coal sample for 480 min and wet-pump for 240 min, as shown in Figure 10. After that, the nuclear magnetic resonance test was performed and the T_2 distribution was inverted. The saturated acid liquid coal sample was centrifuged for 30 min at a speed of 10 000 rpm using a TG16-WS high-speed centrifuge, as shown in Figure 11, the NMR test was



Figure 10. NM-VSD vacuum saturation device.



Figure 11. TG16-WS high-speed centrifuge.

performed again, the T_2 distribution was inverted, the two T_2 distribution results were compared, and the wetting performance of the composite acid solution was analyzed.

The peak area enclosed by the T_2 curve and the abscissa of the coal sample under the conditions of saturated four complex acid solutions is defined as the water-bearing area S_1 ; the peak area enclosed by the T_2 curve and the abscissa of the coal sample after centrifugation is defined as the immovable fluid area S_2 ; and the movable fluid area S is equal to the water-bearing area S_1 minus the immovable fluid area S_2 . The composite acid wetting rate of the coal sample is defined as $\eta = (S_1 - S_2)/S_1 = S/S_1$. The greater the wetting rate, the better the composite acid wetting performance.

3.4.2. Evaluation of Wetting Performance of Composite Acid Solution Based on Nuclear Magnetic Resonance.

Figure 12 shows the T_2 distribution curves of the coal sample after being saturated with four composite acid solutions and centrifugation. In Figure 12, three relaxation peaks can be observed in the distribution range of the transverse relaxation time T_2 , and the position interval of the three relaxation peaks is: the first relaxation peak is 0.05–5 ms; the second relaxation peak is 5–100 ms; and the third relaxation peak is 100–600 ms. T_2 has a certain relationship with the specific surface area. The smaller the pore size of the porous medium, the shorter the transverse relaxation time T_2 . Therefore, through this special connection, it can be known that the aperture corresponding to the third relaxation peak is the largest, and the aperture corresponding to the first relaxation peak is smaller than the second and third relaxation peaks, respectively. After centrifuging the coal sample, the coal sample saturated with the compound solution showed that the third relaxation peak of the T_2 distribution disappeared and the peak area became 0; both the first and second relaxation peaks are reduced, and the peak area is reduced accordingly. It can be concluded that after the coal sample is centrifuged for 30 min, the most effective wetting is the third relaxation peak in the T_2 spectrum, and the acid in the pores is all movable fluid. For the second relaxation peak, there is a lot of loss of composite acid in the related pores, only a small part of the immovable fluid, the wetting effect of the pores of the composite acid at this stage is less than the pores corresponding to the third relaxation peak; the decrease in the area of the first relaxation peak is the smallest, indicating that the corresponding pores have less movable fluid and are basically immovable fluids. Therefore, the composite acid has the worst wetting effect in the pores corresponding to the first relaxation peak.

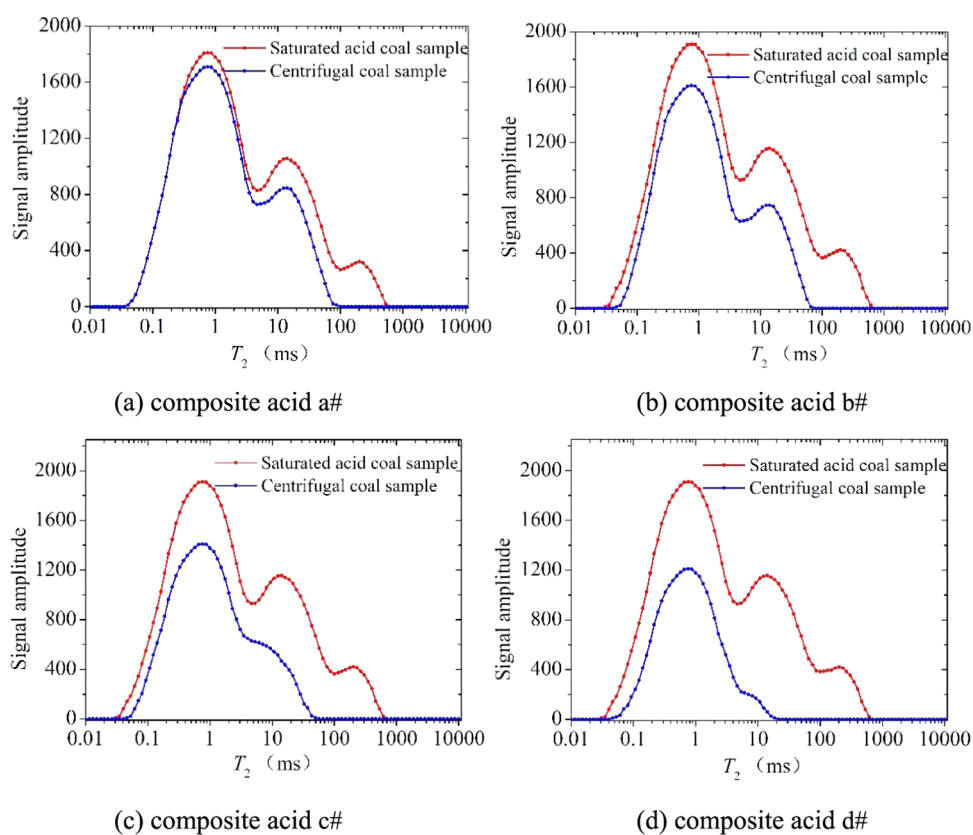


Figure 12. T_2 distribution curves when saturated with four compound acid solutions and after centrifugation.

Table 8. Peak Area Statistics of T_2 Distribution before and after Sample Centrifugation

solution numbers	material abbreviation	wetting parameter	peak area value			
			first relaxation peak	second relaxation peak	third relaxation peak	total relaxation peak
a#	HCl	S_1	9985.67	6283.55	2497.13	18 766.35
		S_2	8285.45	4861.94	0	13 147.39
		η (%)	17.03	22.62	100	29.94
b#	HCl + HF	S_1	10 001.46	6687.98	2591.45	19 280.89
		S_2	7890.98	4774.83	0	12 665.81
		η (%)	21.10	28.61	100	34.31
c#	HCl + HF + SDS	S_1	10 211.13	7145.67	2697.13	20 053.93
		S_2	6874.21	3536.56	0	10 410.77
		η (%)	32.68	50.51	100	48.09
d#	HCl + HF + SDS + NaCl	S_1	10 471.45	7687.43	2909.72	21 068.60
		S_2	6275.34	1245.53	0	7520.87
		η (%)	40.07	83.80	100	64.30

Based on accurate quantitative analysis, statistics of the water-bearing area S_1 , the area of immovable fluid S_2 , and the wetting rate of the composite acid solution η are used to quantitatively evaluate the wettability of various composite acid solutions. The wet effect is shown in Table 8.

It can be seen from Table 8 that after the coal sample is centrifuged, within the pore range, the wetting rate of the composite acid in the macropores corresponding to the third relaxation peak is the highest, reaching 100%, followed by the second relaxation peak. It is the smallest in the first relaxation peak. The four composite acidification solutions produced different wetting rates in the coal pores. Specifically, a single HCl produced the lowest wetting rate, with an overall wetting rate of 29.94%. Especially at the first relaxation peak, the wetting rate in the corresponding pores is only 17.03%. The

overall wetting rate of compound acid d# is the largest, reaching 64.30%, the pore wetting rate in the second relaxation peak reaches 83.80%, and the wetting rate of the third relaxation peak is 100%. It can be concluded that the wetting agent based on the composite acid solution has good wettability inside the coal and can be a more comprehensive intrusion into the internal structure of coal pores. In microporosity and low-permeability coal seams, it is difficult to inject water into the coal seam. However, most studies have found that due to the large number of mineral elements embedded in the coal, acid can be injected into the coal seam.³⁹ The acid liquid reacts with the minerals in the coal to dissolve the minerals and increase the porosity of the coal seam, thereby increasing the wettability of the coal seam.

4. CONCLUSIONS

In this paper, the surface tension change law and contact angle characteristics of the compound acid liquid wetting agent are studied, a high-quality compound acid agent is developed, the composition of the wetting agent is determined, and the wetting performance of the composite acid solution is evaluated based on nuclear magnetic resonance. The main conclusions are as follows:

- (1) Under the same concentration conditions, the surface tension of the anionic surfactant SDS solution and the cationic surfactant JR solution have the largest and smallest decrease, respectively. When the concentration of the former is 0.15%, the corresponding surface tension is 28.16 mN/m; when the concentration of the latter is 0.15%, the corresponding surface tension is 56.71 mN/m.
- (2) When CMC is reached, the concentration of all surfactants is less than 0.06%. Among them, the anionic surfactant SDS solution has the lowest CMC, only 0.025%, and the corresponding CST is 30.63 mN/m, which has the highest efficiency in reducing surface tension.
- (3) The addition of inorganic salt NaCl to the composite acid solution correspondingly weakened the ability of the liquid to shrink. The wetting agent material based on the composite acid solution includes the acid HCl, HF, the anionic surfactant SDS, and the inorganic salt NaCl, the composition of which is 8%, 8%, 0.025%, and 0.6 mol/L, respectively.
- (4) The wetting rate of a single HCl solution is the smallest, with a total wetting rate of 29.94%. The overall wetting rate of the composite acid-containing HCl + HF + SDS + NaCl is the largest, reaching 64.30%. The wetting agent based on the composite acid solution has good wettability inside the coal sample and can penetrate the internal structure of coal pores more comprehensively.

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Notes

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