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Research Article

Mechanism of Surfactant Enhancement of CO_2 Displacement Recovery in Interlayer Shale Oil Reservoirs

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Aiming at the problem that few studies have been conducted on the combination of multiple media in enhanced oil recovery (EOR), the physical simulation experiment of surfactants + CO_2 (SPC) was carried out to analyze the influence of surfactant on the CO_2 displacement effect of interlayer shale oil reservoir. The results show that when the displacement flow volume (DFV) reaches 20 PV, the oil displacement efficiency (ODE) of SPC displacement is 0.42~3.00% higher than that of CO_2 displacement. The ODE of small pore displacement can be increased by 1.51~3.61%. And the relative displacement content (RDC) ratio of free oil of tight shale oil reservoir can be increased by 7.10~20.54%. When the DFV is 5 PV, the ODE can be improved more significantly. It shows that the efficiency of small pore displacement can be increased by 1.74~2.33%. It also indicates that the ODE can be increased by 7.03% of the ultralow permeability shale oil reservoir. And the RDC ratio of free oil of tight shale oil reservoir can be increased by 10.34~21.50%. Surfactant can improve the wettability of the reservoir and make the rock sample wet. This research can help to understand the influence of surfactant on CO_2 displacement effect and reveal the mechanism of SPC displacement improving the ODE of interlayer shale oil reservoir, providing theoretical basis for the effective development of interlayer shale oil reservoir.

1. Introduction

The successful exploration and development of shale oil in North America has made shale oil become an important unconventional oil and gas resource in the world, and also promoted the development of shale oil theory in China [1–3]. The pore structure of Chang 7 reservoir in Ordos Basin is relatively complex, with wide distribution of nanoscale pores. As the occurrence characteristics and production rules of crude oil are different from those of conventional reservoirs, it is difficult to be extracted. Practice also shows that there are problems such as rapid energy decline, low production capacity, and difficulty in water injection of actual development [4–7]. Therefore, it is necessary to replenish the formation energy and use synergistic methods to improve the displacement environment. Gas injection can be used as an effective method to replenish formation energy. Zhang et al. [8] have shown that viscosity reduction, swelling, and miscibility can be achieved during CO_2 displacement, replenishing formation energy, and improving oil recovery. Lan et al. [9] believed that the mechanism of CO_2 EOR in shale reservoir includes pressurization, dissolution, extraction, expansion, adsorption displacement, reduction of capillary force, and diffusion. Yang et al. [10] studied the feasibility of nitrogen huff and puff in shale reservoirs by means of laboratory core displacement and numerical simulation. The results show that nitrogen

Table 1: Basic parameters of Chang 7 shale reservoir samples.

No.	Horizon	Depth/m	Permeability/mD	Porosity/%	Length/cm	Diameter/cm
1	Yanchang	2429.20-2429.40	0.068	9.27	3.264	2.526
2	Yanchang	2442.80-2443.00	0.137	9.22	4.227	2.521
3	Yanchang	2336.20-2336.45	0.036	8.74	3.328	2.522
4	Yanchang	2429.20-2429.40	0.068	9.27	4.109	2.529
5	Yanchang	2442.80-2443.00	0.137	9.22	3.239	2.524
6	Yanchang	2336.20-2336.45	0.036	8.74	3.829	2.519

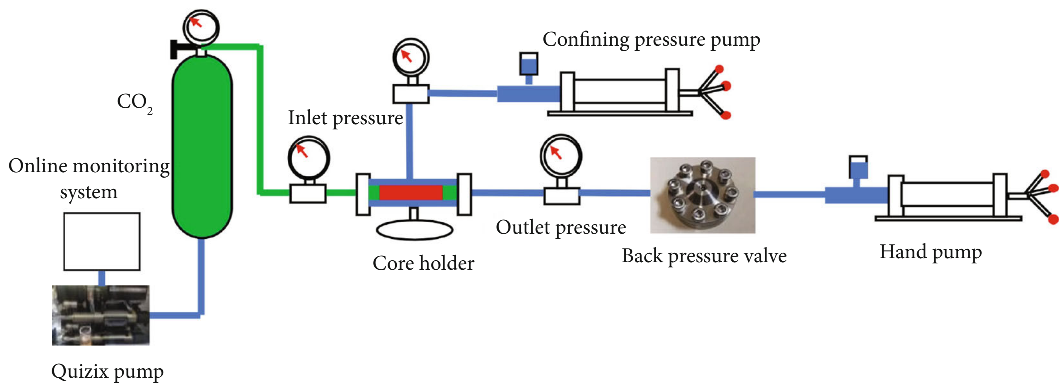


Figure 1: Experimental connection device.

has a good energy-enhancing effect and can significantly improve the ODE. Thakur et al. [11] found that the good pressurization effect of natural gas can induce the extension of fractures in the formation and increase the degree of communication between artificial fractures and natural fractures, expanding the sweep efficiency. However, some studies have also shown that gas injection is prone to gas channeling and cannot mobilize a large amount of crude oil in the matrix [12]. Under the condition that a single medium cannot effectively enhance the oil recovery, a combination of multiple mediums is required to enhance the oil recovery. Qinhong et al. [13] believed that due to the large amount of organic matter in shale reservoirs, the wettability of the matrix is mostly oil-wet or neutral, and the improvement of wettability through wetting inversion can improve the imbibition recovery rate. Alverez et al. [14] improved ODE by surfactant, mainly through improving wettability and oil-water interfacial tension. Khoa et al. [15] believed that surfactant system can enter the kerogen containing pores of shale matrix, change the wettability of organic pores and displace hydrocarbons trapped in organic matter. Cai et al. [16] have shown that organic solvents can improve the wettability of shale matrix and promote the flow of crude oil from matrix to fractures, enhancing oil recovery. Dordzie and Dejam [17] reviewed the reports on surfactant enhancing fractured carbonate reservoirs, showing that fines migration could either promote EOR or reduce recovery based on the occurrence of formation damage. It can be seen from the above survey that domestic and foreign scholars have conducted a series of studies on EOR with different media, but there are few studies on the combination of multiple media to enhance interlayer shale oil recovery. Based on this, this research is aimed at the interlayer shale oil

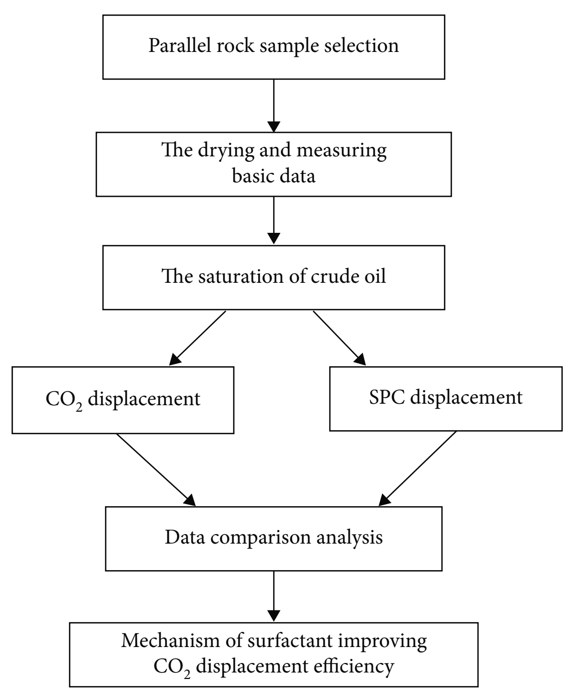


Figure 2: The steps of the work.

reservoir of Yanchang Formation in the Ordos Basin, Changqing, to carry out experimental research on SPC displacement. First, experimental equipment was set up, and then two groups of parallel rock samples were carried out SPC displacement and CO_2 displacement experiments, respectively. The experimental results of the two groups were analyzed by

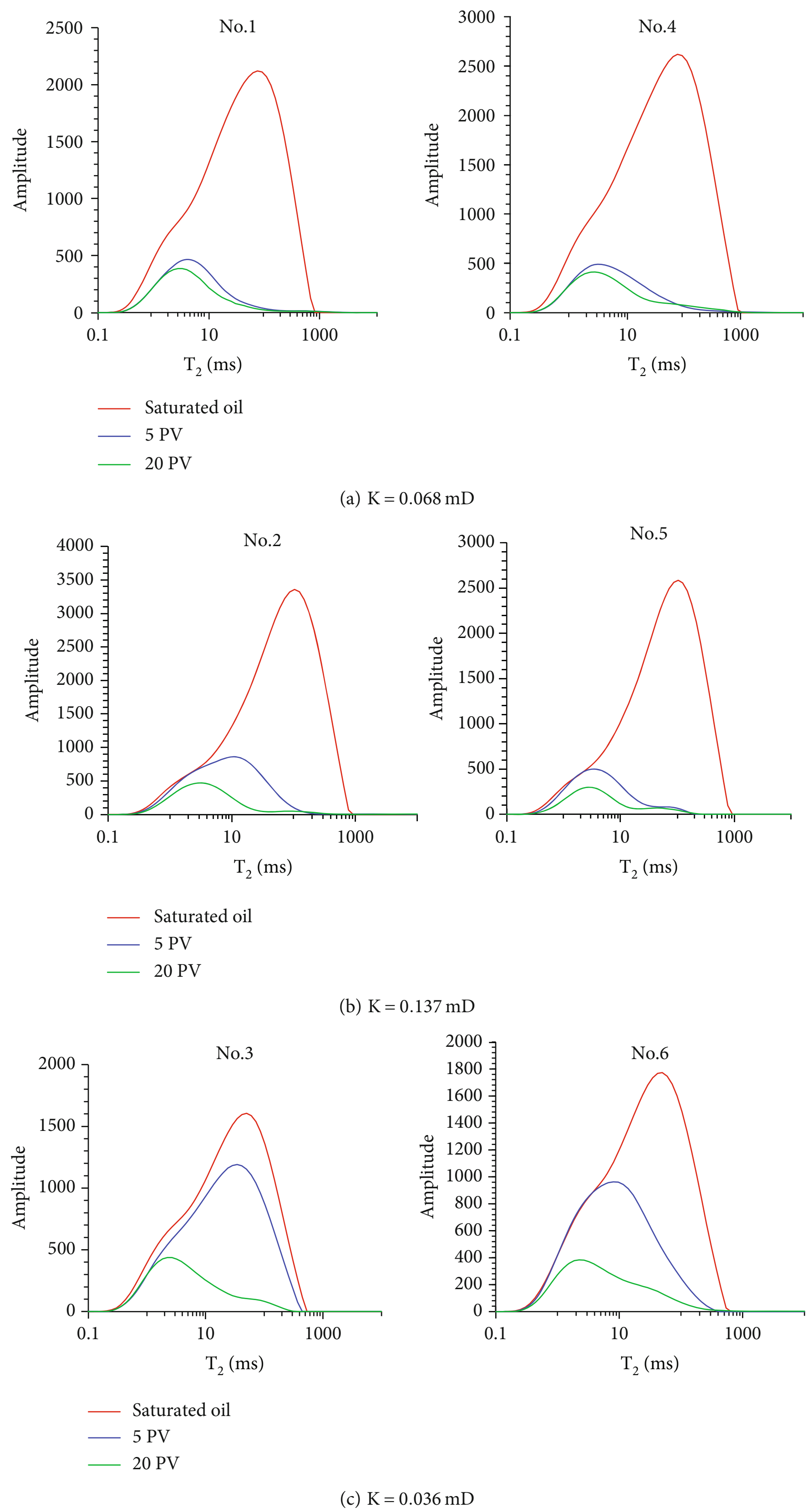


FIGURE 3: NMR spectra of rock samples during displacement with different media.

analogy, and finally the mechanism of EOR by SPC displacement was revealed. Through the analysis of microscopic production rules of rock samples under different media displacement, it reveals the mechanism of SPC displacement to improve oil recovery and provides a theoretical basis for the effective development of interlayer shale oil.

2. Experimental Samples and Equipment

2.1. Experimental Samples

(1) The interlayer shale of the Yanchang Formation in the Ordos Basin was selected as the experimental samples. The geological characteristics are mainly shallow lacustrine delta front deposition, the enrichment of thin interlayer "sweet spot" and the micromigration within the source [18–23]. The sampling depth was between 2300 m and 2450 m. The rock type was gray-brown oil spot fine sandstone. The core parameters are shown in Table 1. Rock samples No.1, No.2, and No.3 are parallel samples of No.4, No.5, and No.6, respectively

(2) The purity of CO_2 used in the experiment was above 99.95%.

(3) Crude oil. It was extracted from shale oil reservoir of Yanchang Formation in Changqing Oilfield, Ordos Basin. The density of crude oil measured at room temperature and Atmospheric pressure is 0.78 g/cm^3, and the viscosity is 2.5 mPa·s. The oil viscosity was measured at 70°C and 18 MPa to simulate the Changqing reservoir temperature and the actual formation pressure. The experiment was conducted under the condition of constant temperature 65°C, which effectively simulated the reservoir temperature condition. The experimental results can more effectively illustrate the actual production and recovery of oil

(4) Surfactant name: NM-207, an anionic and negative nonionic composite surfactant (ANNCS). The product appearance is translucent emulsion, and the overall color is white. The density is 0.95~1.05 g/cm^3. The diameter is 30~50 nm, and the viscosity is 6.3 mPa·s at room temperature of 25°C. At present, its chemical composition cannot be precise. Be limited by it, its influence on CO_2 displacement cannot be analyzed from the aspect of chemical research

2.2. Experiment Equipment. It includes core displacement system, nuclear magnetic resonance (NMR) instrument, quizix displacement pump and online monitoring system, core holder, intermediate container, thermostat, back pressure valve, high temperature and high pressure gradient field NMR core analyzer, contact angle meter, and interfacial tension meter. The specific connection is shown in Figure 1. The quizix displacement pump used in this study has an online monitoring system that allows visual observation of displacement velocity and flow volume. As a result, it can more accurately determine whether the displacement state is stable and how much DFV remains than conventional displacement pumps. In other words, the calculation results are more accurate and the equipment is more advanced.

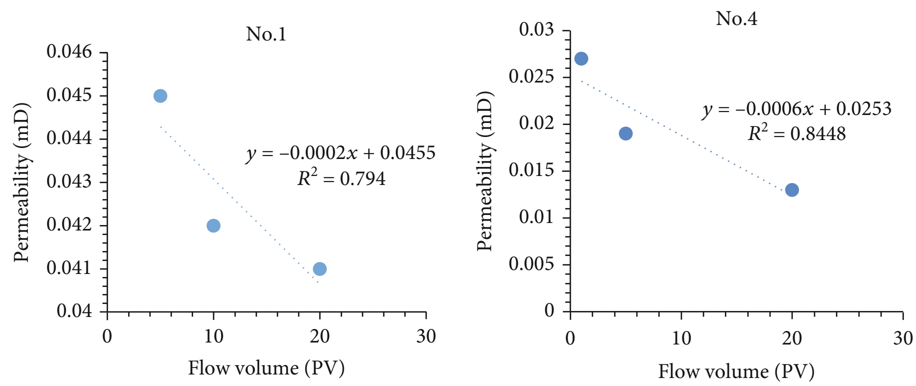
Table 2: ODE and pore proportion in different media of rock samples.

(a) CO_2

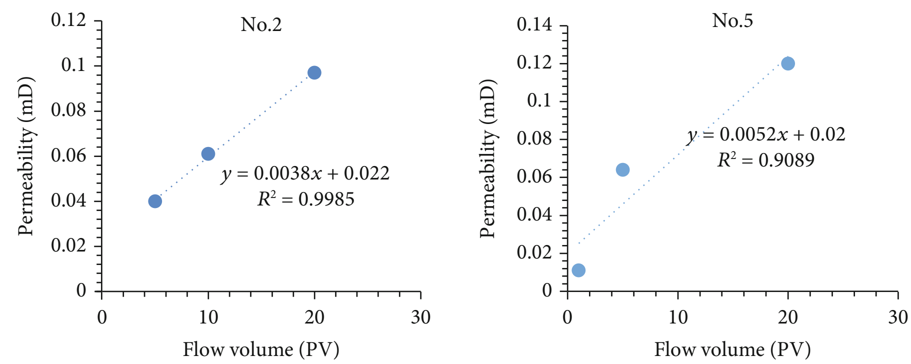
No.	Flow volume/PV	Pore throats	Absolute ODE contribution/%	ODE/%
1	5	Small pore	14.45	84.21
		Medium pore	42.93	
		Macropore	27.38	
	20	Small pore	16.32	87.44
		Medium pore	43.61	
		Macropore	27.51	
2	5	Small pore	2.66	74.34
		Medium pore	34.44	
		Macropore	37.24	
	20	Small pore	8.67	89.88
		Medium pore	42.94	
		Macropore	38.28	
3	5	Small pore	4.77	25.15
		Medium pore	11.93	
		Macropore	8.45	
	20	Small pore	14.29	77.85
		Medium pore	45.16	
		Macropore	18.40	

(b) Surfactant + CO_2

No.	Flow volume/PV	Pore throats	Absolute ODE contribution/%	ODE/%
4	5	Small pore	16.19	85.02
		Medium pore	41.42	
		Macropore	27.41	
	20	Small pore	17.83	87.86
		Medium pore	42.87	
		Macropore	27.16	
5	5	Small pore	4.99	83.99
		Medium pore	41.47	
		Macropore	37.54	
	20	Small pore	10.64	91.22
		Medium pore	42.97	
		Macropore	37.60	
6	5	Small pore	6.70	57.81
		Medium pore	33.52	
		Macropore	17.59	
	20	Small pore	17.90	80.85
		Medium pore	44.43	
		Macropore	18.53	



(a) K = 0.068 mD



(b) K = 0.137 mD

FIGURE 4: Correlation between DFV and permeability of rock samples.

3. Experimental Procedure and Method

3.1. Experimental Procedure

(1) The drying of rock samples. Six samples were placed in a drying oven and dried at 90°C for 24 h. The cores were weighed and the T_2 spectrum of the dried samples was measured

(2) The measurement of porosity and permeability. The permeability was tested by nitrogen, and the porosity was tested by helium

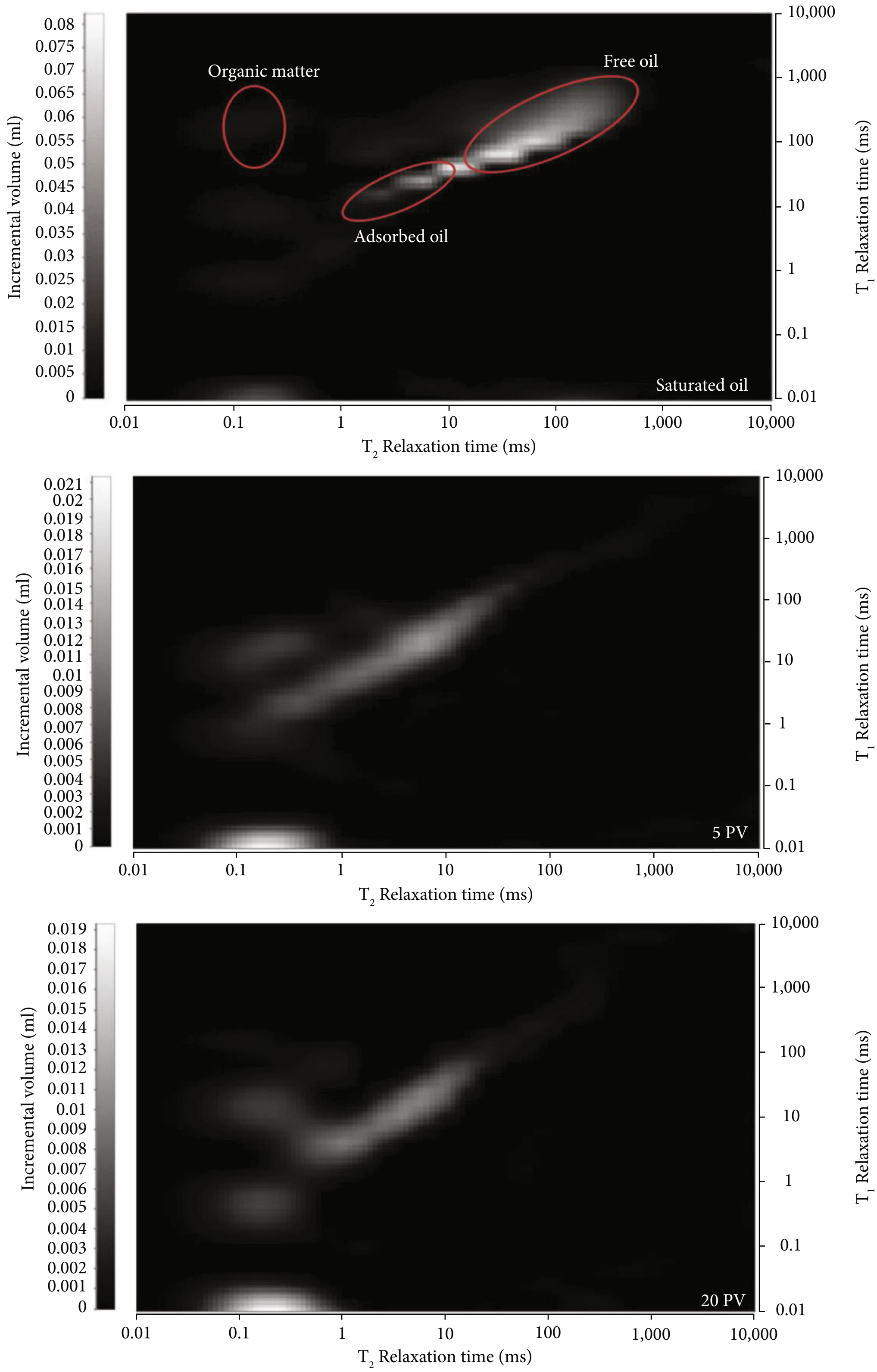
(3) The saturation of crude oil. The samples were vacuumized for 24 h and pressurized to saturate with kerosene. Then, the samples saturated with kerosene were displaced by crude oil at the displacement pressure of 4 ~ 8 MPa, the confining pressure of 6 ~ 15 MPa, and the DFV was 2 ~ 3PV. The NMR T_2 spectrum of the core after saturated crude oil was measured

(4) CO_2 displacement. The saturated crude oil samples were displaced by CO_2 under the conditions of inlet pressure 20 MPa, outlet pressure 19 MPa, confining pressure 24 MPa, and constant temperature 65°C. Rock samples No.4, No.5, and No.6 were wetted with surfactant for half an hour before displacement, and then the NMR T_2 spectrum and two-dimensional NMR T_1-T_2 spectrum of rock samples under different DFV were measured. The PV is the flow volume, which means the pore throat volume of the rock sample, and its unit is mL. The working steps are shown in Figure 2

3.2. Experimental Method. NMR can be used as an approximate nondestructive technique to measure the microscopic pore structure characteristics of shale reservoirs. It analyzes the properties of pore fluids by observing the hydrogen nuclei signals in the rock pores, and obtains parameters related to the physical properties of the reservoir. And the dynamic fluid parameters are calculated to describe and evaluate the entire reservoir. For 2D NMR spectroscopy, the fluid in its natural state has a T_1/T_2 value of 1. When constrained by pore space, the T_1/T_2 values of fluids with different properties will change. For unconventional oil reservoirs, the components of movable oil and nonmovable oil (such as bitumen and kerogen) are different in the T_1/T_2 schematic diagram. Therefore, two-dimensional spectroscopy is an important means to evaluate reservoir pore structure and fluid [24–27].

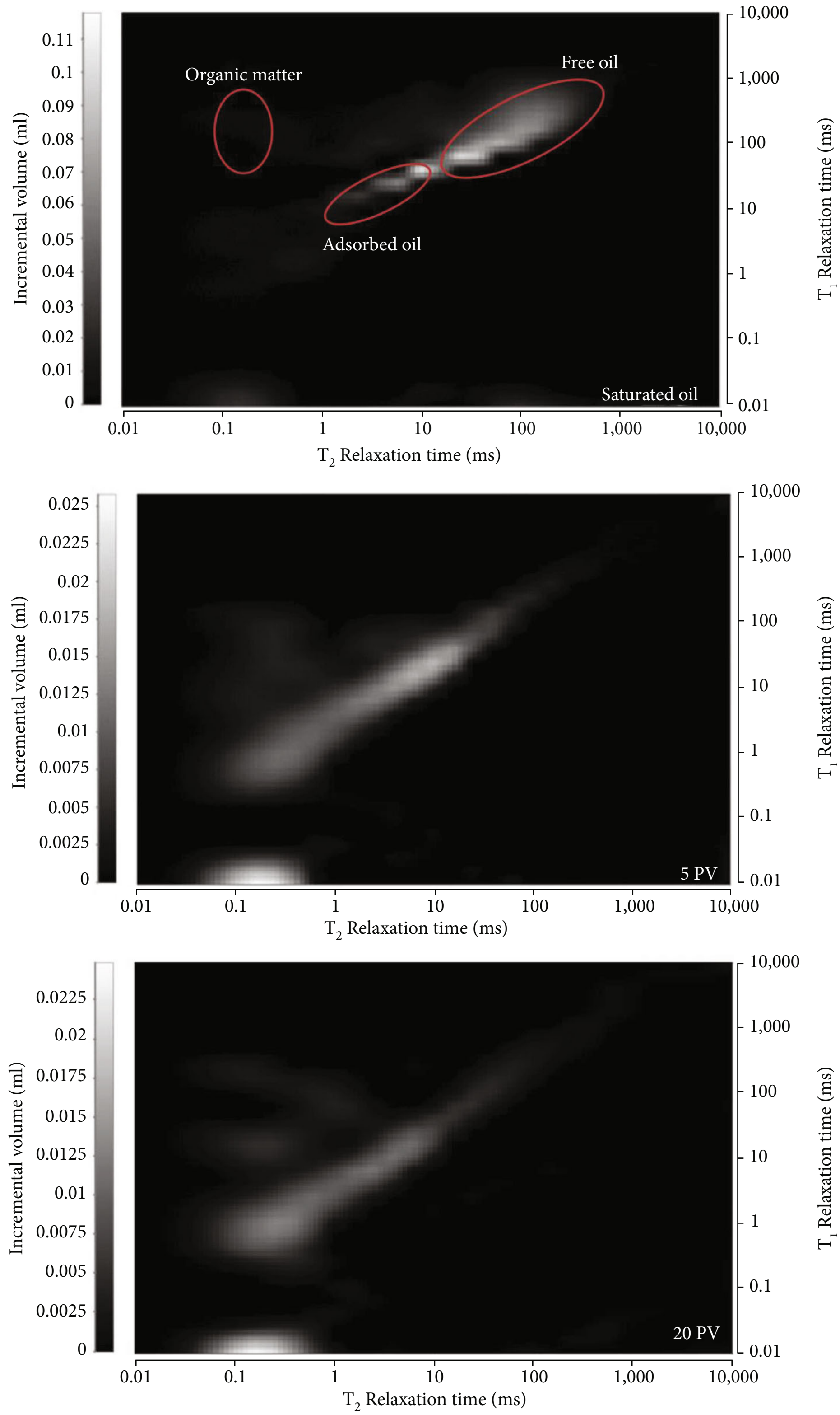
4. Results and Discussions

4.1. One-Dimensional NMR Analysis. Figures 3(a), 3(b), and 3(c) show the NMR T_2 spectrum of six rock samples under different media displacement. Table 2 shows the ODE and the contribution of absolute ODE in different pore-throat



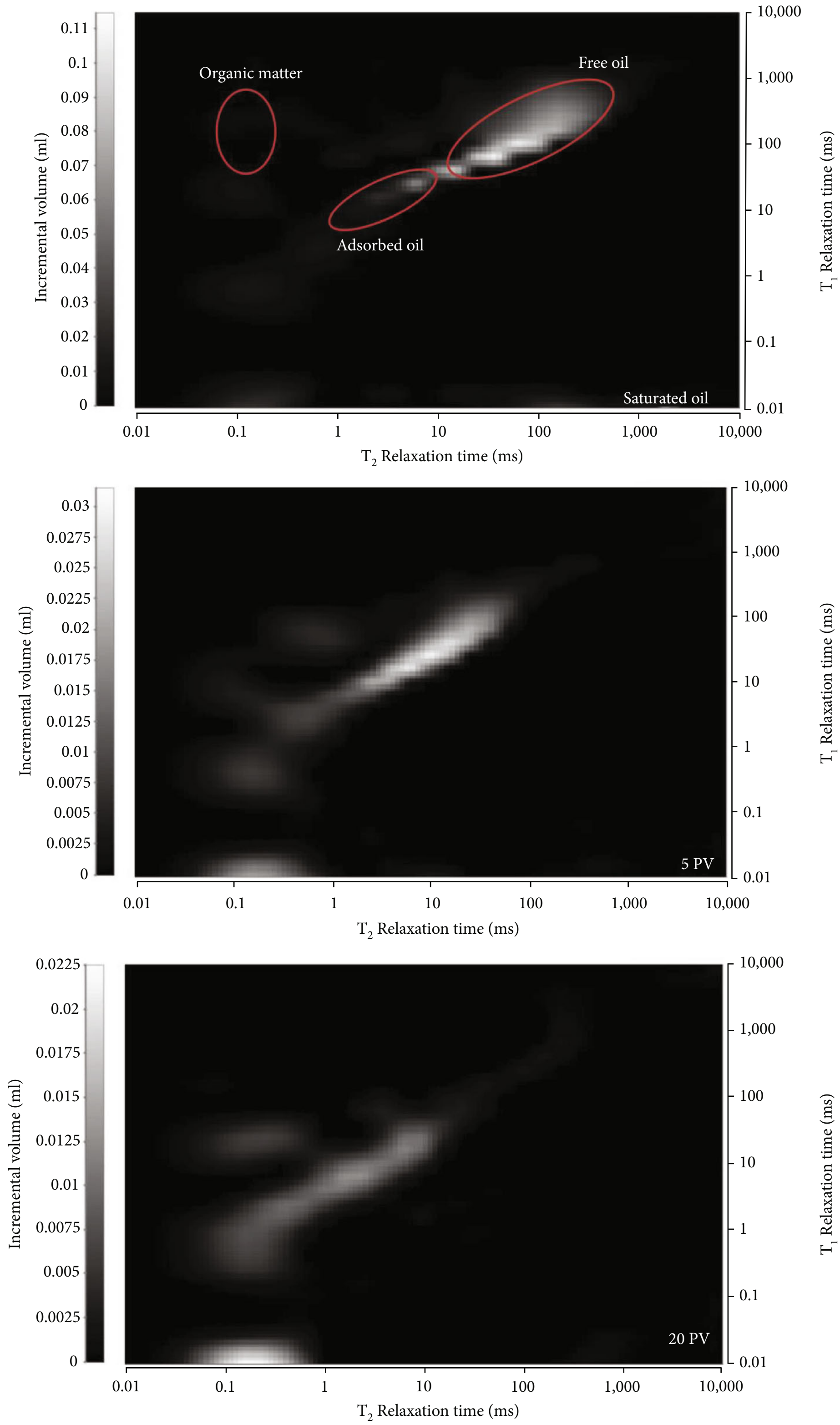
(a) No.1 (K = 0.068 mD)

Figure 5: Continued.



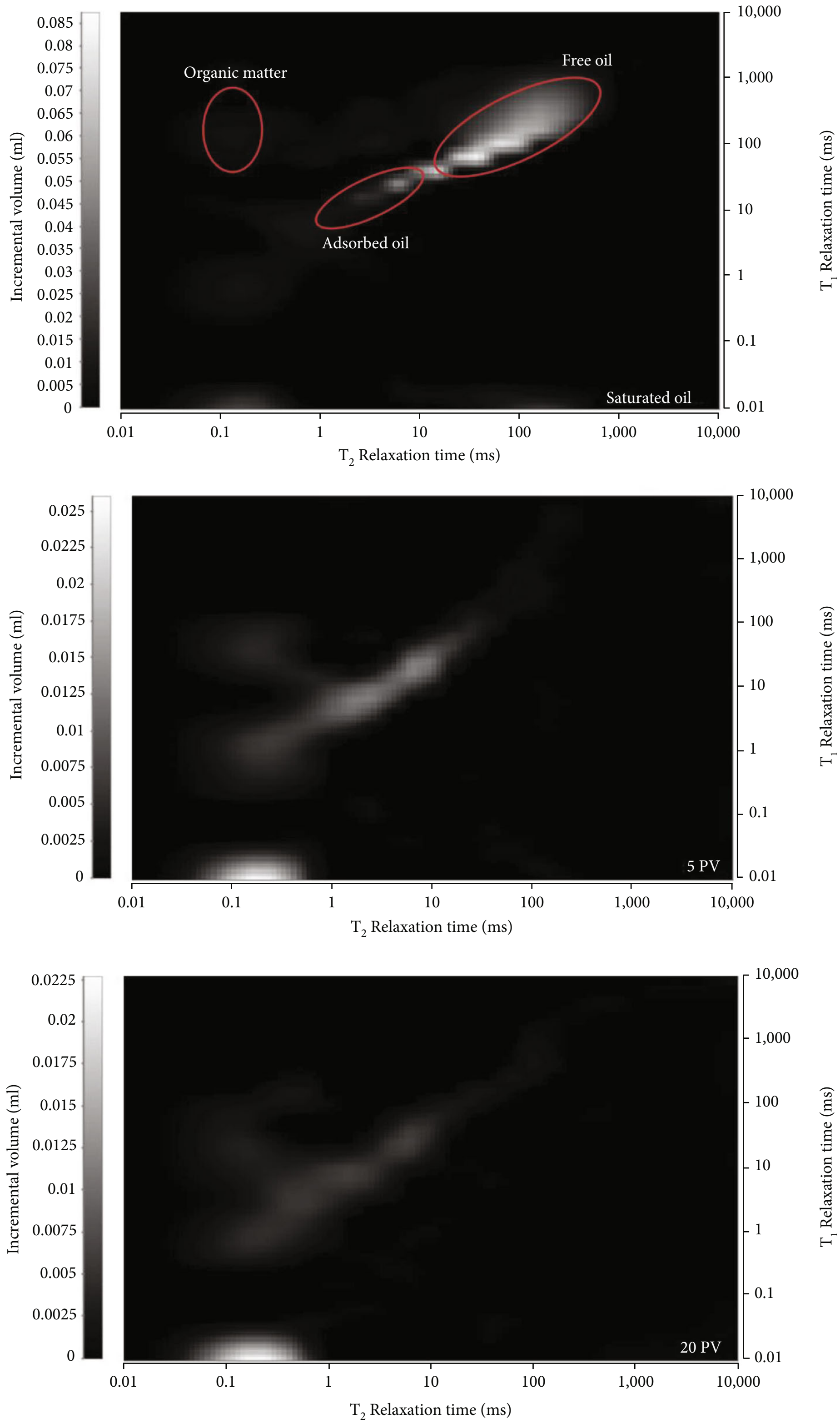
(b) No.4 (K = 0.068 mD)

FIGURE 5: Continued.



(c) No.2 (K = 0.137 mD)

Figure 5: Continued.



(d) No.5 (K = 0.137 mD)

Figure 5: T_1-T_2 2D NMR spectra of parallel rock samples at different displacement stages.

intervals. Based on the research of domestic scholars [28–30], the relaxation time of 0.1 ~ 10 ms is considered as small pore throat, 10~100 ms is considered as medium pore throat, and the relaxation time greater than 100 ms is considered as macropore throat. Figure 3 shows that with the continuous increase of DFV, the peak value gradually shifts to the left. It

Table 3: Classification criteria of NMR T_1-T_2 spectral signals in different occurrence states.

Scope	Occurrence states
$T_2 > 33$⊠$T_1 > 33$	Free oil
$T_2 < 33$⊠$T_1 < 100$	Adsorbed oil
$T_2 < 1$⊠$T_1 > 10$	Organic matter

is also shown in Table 2 that under the two displacement media, the medium pore throat and macropore throat contribute the main ODE, and the small pore throat contributes less. For the parallel samples of No.1 and No.4, No.2 and No.5, and No.3 and No.6, when the DFV is 20 PV, the ODE of SPC is 0.42%, 1.34%, and 3.00% higher than that of CO_2 displacement, respectively. And the contribution of the absolute ODE of small pore throats is 1.51%, 1.97%, and 3.61% higher, respectively. When the DFV reaches 5 PV, the ODE of SPC displacement is 0.81%, 9.65%, and 32.66% higher than that of CO_2 displacement, respectively. And the contribution of SPC displacement absolute ODE of small pore throats is 1.74%, 2.33%, and 1.93% higher, respectively. For the parallel samples of No.2 and No.5, the medium pore ODE of SPC displacement is 7.03% higher than that of CO_2 displacement. It can be seen that the ODE of SPC displacement is higher than that of CO_2 displacement, and it is more obvious when the DFV is 5 PV. SPC displacement has a more obvious effect on improving the ODE of small pore throats of tight shale oil reservoirs ($K < 0.1$ mD). For ultralow permeability shale oil reservoirs ($0.1\text{ mD} < K < 1.0\text{ mD}$), the improvement effect of medium pore throat ODE is more obvious. When the DFV is from 5 PV to 20 PV, the decrease of SPC displacement curve is smaller than that of CO_2 displacement, and the displacement time is shortened.

4.2. Variation of Permeability of Rock Samples with DFV under Different Media Displacement. Figure 4 shows the correlation between DFV and permeability under different displacement media of parallel rock samples. It can be seen from the Figure 4 that for tight shale oil reservoirs with permeability less than 0.1 mD, the permeability is negatively correlated with the DFV, and the SPC displacement can reduce the permeability decrease rate. For ultralow permeability shale oil reservoirs with permeability between 0.1 mD and 1.0 mD, permeability is positively correlated with DFV. The permeability after SPC displacement is higher than that after CO_2 displacement, and the surfactant can improve the reservoir.

4.3. Quantitative Analysis of Occurrence State by Two-Dimensional NMR. Figure 5 shows the NMR T_1-T_2 spectra of parallel samples displaced by different media. According to the research of domestic scholars [31–36], the T_1-T_2 spectrum of the occurrence state of the rock sample is divided, and the classification standards are shown in Table 3. The different occurrence states of the rock samples were quantitatively characterized, as shown in Table 4. According to Table 4, when the DFV is 5 PV, the RDC of free oil of sample No.4 is 10.34% higher than that of sample No. 1. The RDC of free oil of sample No.2 and No.5 is 91.77% and 83.33%, respectively. And the RDC of free oil of sample No.6 is 21.5% higher than that of sample No.3. When the DFV is

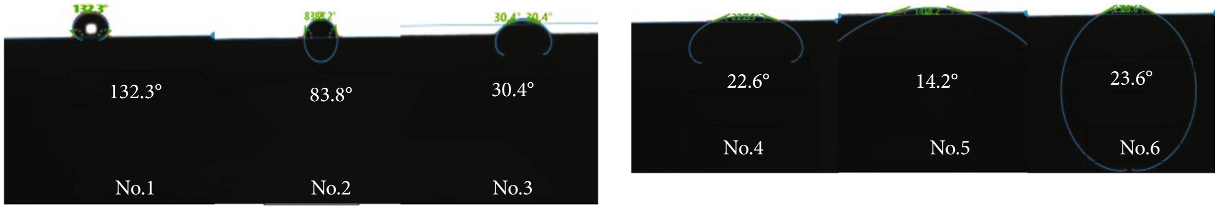
Table 4: Displacement effect of parallel rock samples under different DFV.

(a) CO_2

No.	Occurrence	Relative content ratio after saturated crude oil/%	Flow volume/PV	RDC/%
1	Free oil	49.95	5	66.26
			20	63.11
	Adsorbed oil	33.64	5	12.90
			20	16.61
	Organic matter	4.55	5	2.39
			20	2.06
2	Free oil	62.40	5	91.77
			20	79.64
	Adsorbed oil	29.59	5	0.93
			20	10.50
	Organic matter	3.26	5	2.17
			20	0.37
3	Free oil	40.51	5	57.50
			20	58.17
	Adsorbed oil	50.71	5	15.87
			20	30.87
	Organic matter	6.03	5	1.55
			20	0.63

(b) Surfactant + CO_2

No.	Occurrence	Relative content ratio after saturated crude oil/%	Flow volume/PV	RDC/%
4	Free oil	51.69	5 PV	76.60
			20 PV	70.21
	Adsorbed oil	33.33	5 PV	3.06
			20 PV	11.51
	Organic matter	3.68	5 PV	0.35
			20 PV	0.48
5	Free oil	61.82	5 PV	83.33
			20 PV	74.79
	Adsorbed oil	28.35	5 PV	4.82
			20 PV	14.63
	Organic matter	4.09	5 PV	0.07
			20 PV	1.62
6	Free oil	40.67	5 PV	79.00
			20 PV	78.71
	Adsorbed oil	53.21	5 PV	11.86
			20 PV	13.07
	Organic matter	5.98	5 PV	3.63
			20 PV	5.83



(a) Contact angle with water

(b) Contact angle with water after soaking with surfactant

FIGURE 6: Wetting angle of rock sample.

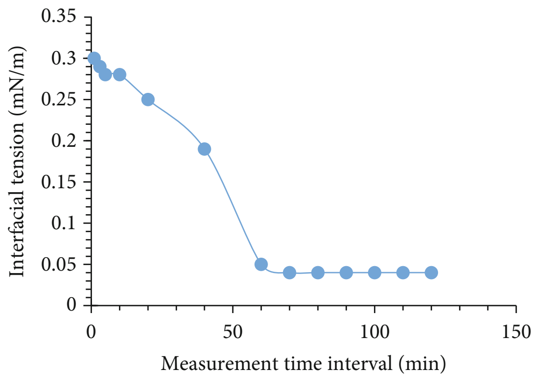


FIGURE 7: Change curve of interfacial tension between surfactant and crude oil with measurement time.

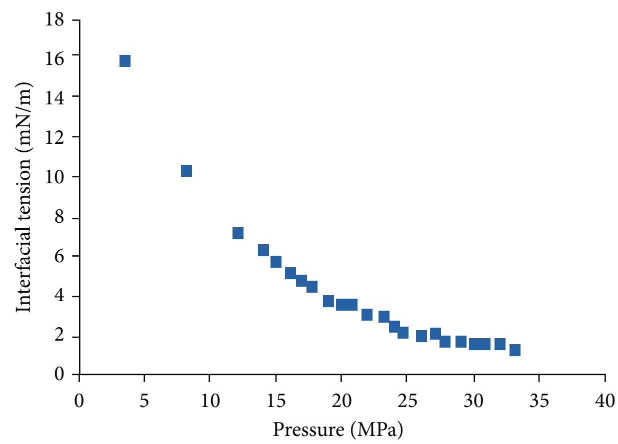


FIGURE 8: Interfacial tension between CO_2 and crude oil [37].

20 PV, the RDC of free oil of sample No.4 is 7.10% higher than that of sample No.1. The RDC of free oil of sample No.2 and No.5 is 79.44% and 74.79%, respectively. And the RDC of free oil of sample No.6 is 20.54% higher than that of sample No.3. In conclusion, SPC displacement can improve the RDC of free oil of tight shale oil reservoirs, and the effect is more obvious when the DFV is 5 PV. Besides, the ratio of free oil to adsorbed oil of RDC of sample No.4 is larger than that of sample No.1. The ratio of free oil to adsorbed oil of RDC of sample No.6 is larger than that of sample No.3, and the ratio of free oil to adsorbed oil of RDC of sample No.5 is smaller than that of sample No.2. This verifies that SPC displacement can improve the free ODE of tight shale oil reservoirs and improve the adsorbed ODE of ultralow permeability shale oil reservoirs. In addition, when the DFV increases from 5PV to 20PV, the ratio of free oil to adsorbed oil decreases, indicating that the adsorbed ODE increases with the increase of DFV. When the DFV is 20PV, the RDC of organic matter of sample No.5 is 1.25% higher than that of sample No.2. And the RDC of organic matter of sample No.6 is 5.20% higher than that of sample No.3. This indicates that at a larger DFV, surfactants can enter the kerogen-containing pores of shale matrix and displace the hydrocarbon in organic matter.

4.4. Measurement of Contact Angle and Interfacial Tension. Figures 6(a) and 6(b) are schematic diagrams of the contact angles of parallel samples. The contact angles of No.1, No.2, and No.3 rock samples with water are 132.3°, 83.8°, and 30.4°, respectively. And their wettability is oil-wet, neutral, and water-wet, respectively. The contact angles with water after soaking with surfactant of No.4, No.5, and No.6 rock samples were 22.6°, 14.2°, and 23.6°, respectively. It can be seen that the surfactant can change the wettability of the rock sample, making the rock sample appear water-wet. For the No.2 rock sample with better physical properties, the better the wettability improvement effect of surfactant is. Therefore, SPC displacement has a stronger stripping effect on the oil film than CO_2 displacement.

Figure 7 shows the change curve of the interfacial tension between the surfactant and the crude oil with the measurement time under the temperature of the reservoir, and the interfacial tension is below 0.3 mN/m. When the measurement time was 70 min, the interfacial tension reached a stable state of 0.04 mN/m. According to the research of domestic scholars [37], Figure 8 shows that the interfacial tension between CO_2 and crude oil at reservoir temperature is about 4 mN/m. Compared with it, the interfacial tension between surfactant and crude oil is very small, and the effect of seepage resistance is also small.

5. Summary and Conclusions

In the research, the effect and mechanism of ANNCS surfactant on ODE of the interlayer shale oil reservoir of Yanchang Formation in Ordos Basin, Changqing Oilfield were studied. By comparing the SPC displacement and CO_2 displacement experiments, the following conclusions were obtained.

(1) The ODE of SPC is higher than that of CO_2 displacement, and the effect is more obvious when the DFV

is 5 PV. SPC displacement can improve the ODE of small pores of tight shale oil reservoirs and medium pores of ultralow permeability shale oil reservoirs. Besides, it can also shorten the displacement time

(2) SPC displacement can reduce the decrease rate of permeability of tight shale oil reservoir. For ultralow permeability shale oil reservoirs, the permeability of SPC displacement is higher than that of CO_2 displacement. Surfactants can change the wettability of rock samples and make them all appear wet. SPC has stronger stripping effect on oil film than CO_2 displacement

(3) SPC displacement can improve the RDC of free oil of tight shale oil reservoirs and improve the adsorbed ODE of ultralow permeability shale oil reservoirs. With the increase of DFV, the adsorbed ODE also increases. At high DFV, surfactants can enter the kerogen-containing pores of the shale matrix and displace the hydrocarbons in the organic matter

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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