



Multifunctional Surfactant: Integration of Fracturing Fluid Flooding

MENG CUN¹, JINCHENG MAO^{1*}, JIZHEN TIAN¹, MINGJIN CAI², XIAOJIANG YANG^{1*},
CHONG LIN¹, ZIGAO HUANG¹

¹State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, P. R. China

²Exploration and Development Research Institute Tarim Oilfield of CNPC, Kuerle 841000, China

Abstract: Significant research focus has recently been directed toward energy-saving and emission-reduction practices, as well as the unique benefits of an integrated working fluid in the oilfield industry. Surfactants cannot be widely used in engineering practice due to cost constraints. At the same time, there is no proper solution to the flowback liquid problem. SY-JS, a multifunctional surfactant, was developed to broaden the application of surfactants in the oilfield industry. It still meets the field operation requirements of a good fracturing fluid thickener with a shear rate of 170 s^{-1} at 140°C and salinity (NaCl or KCl) of 12-13%. When the fracturing fluid has finished its job and returns to the ground, the molecular structure of the surfactant in the flowback fluid was found to be complete after laboratory evaluation of the fracturing and oil displacement integrated working fluid systems. Surfactants with an intact molecular structure should retain their distinct lipophilic and hydrophilic properties. When groundwater and produced water are compounded and re-injected into the reservoir for oil displacement, 0.2 percent anionic surfactant B1-12 is used to balance the charge and reduce interfacial tension. The rock's contact angle can be reduced by 56.95 percent, and the recovery rate can be increased by 6%. Based on these findings, the surfactant's dynamic self-healing mechanism was proposed. Furthermore, the capillary force, interfacial tension, and wettability were combined to propose wettability determines capillary force direction and interfacial tension determines capillary force magnitude. Furthermore, it provides favorable evidence that interfacial tension does not always reach ultralow levels during reservoir exploitation.

Keywords: energy-saving and emission-reduction, multifunctional surfactant, fracturing fluid thickener, surfactant compound, dynamic self-healing, flooding

1. Introduction

It is worth noting that surfactant as a fracturing fluid thickening agent and oil-displacing agent with enhanced oil recovery has been a hot topic in the petroleum industry in recent years [1-3]. The main agents used for thickening or strengthening foams in conventional water-based and foam fracturing fluid systems are macromolecular polymers, such as guar gum, which easily form insoluble residues under formation conditions. As a result, the concept of clean fracturing fluid has piqued the interest of many researchers, and its importance stems from the fact that fracturing fluids are broken after fracturing. Fracturing fluids do not affect the permeability of the rock matrix or fracture conductivity. Schlumberger invented a new clean fracturing fluid based on self-assembly theory in 1997 [4, 5]. Surfactant molecules aggregate in aqueous solutions when they come into contact with counter ions, forming wormlike micelles (WLM). Meanwhile, wormlike micelles join together to form a three-dimensional (3D) network structure, which increases the viscoelasticity of the fluid. To ensure the fracturing fluid's sand-carrying capacity. At the same time, the molecular weight of viscoelastic surfactant is only a few 100–1000, which is 3-5 orders of magnitude lower than that of conventional polymers, resulting in almost no residue of VES clean fracturing fluid after gel breaking [6]. However, as oil resources are developed, more low-permeability tight reservoirs require further improvement for more complex production environments. A fracturing fluid must maintain a certain viscosity during the construction process and

*email: jcmiao@swpu.edu.cn, 815675989@qq.com

thoroughly break the gel after the construction to carry the proppant in the construction and flow back smoothly. The main requirement for fracturing fluids is stability, especially with the continuous development of high-temperature reservoirs. Temperature resistance has emerged as the main standard for assessing the quality of clean fracturing fluids. High temperatures degrade the wormlike micelles and 3D network structure formed by VES self-assembly, resulting in fluid viscosity loss. Clean fracturing fluid (VES) is typically composed of a surfactant and a counterion. Through shielding, a small amount of counterion weakens the electric repulsion between the surfactant's hydrophilic groups and promotes micellar aggregates. There is a binding force between counterions and surfactant hydrophilic groups. The surfactant will become dehydrated if the binding force is too strong. As a result, too many counterions will easily precipitate the surfactant. As a result, salt tolerance is another requirement of clean fracturing fluid, and viscosity change is the most important feature of a fracturing fluid system [7, 8]. It should be noted that, according to the introduction of relevant research reports and current field investigations, cost-ineffectiveness is regarded as one of the primary factors limiting the widespread popularization and application of VES fracturing fluid. According to rough commercial statistics, the cost of VES fracturing fluid is 5-30 times that of traditional guar gum fracturing fluid. Although recent studies have reduced the cost of clean fracturing fluids to some extent, they continue to be more expensive than traditional polymer-fracturing fluids, which has a significant impact on the large-scale application of VES fracturing fluid.

The issue of fracturing fluid treatment and reuse is becoming more prominent. It was once thought that industrial sewage was one of the "most difficult to treat." According to numerous studies, after each fracturing operation, approximately 30-60% of the fracturing fluid will flow back to the surface, forming fracturing flowback fluid. The backflow liquid contains a variety of complex components, including organic matter, soluble salts, and various additives, and it transports a variety of pollutants, including sludge, suspended solids, and oil. If such sewage is directly discharged without effective treatment, it will result in a significant waste of water resources while also polluting the surrounding shallow groundwater and surface water systems, affecting human health. As a result, one of the most pressing issues is the resource treatment of fracturing flowback fluid.

The use of surfactants in the oil industry also includes tertiary oil recovery [9, 10]. Primary and secondary oil recovery results are usually unsatisfactory, tertiary oil recovery is carried out. The addition of a suitable surfactant to the injected water can reduce the tension at the oil-water interface and change the wettability of the rock. The oil film on the rock surface can be separated better after surfactant treatment, and mixed water injection can make the remaining oil bound by formation displacement, greatly improving oil recovery. Surfactant is a type of chemical oil displacement agent that has a wide range of applications and can significantly improve oil recovery [11, 12].

However, in addition to meeting these fundamental requirements as oil-displacing agents, we must also consider the reservoir environment. Surfactants are widely used in the manufacture of ordinary reservoirs. as more complex reservoirs are developed, ordinary surfactants will be unable to meet production demands. They are not suitable for special reservoirs, such as high-salt and high-temperature reservoirs. therefore, new surfactants suitable for special conditions must be researched and developed. These new surfactants have a high economic value (cost-effectiveness) and can produce high oil displacement efficiency values when used in low concentrations, which is important for expanding the application range of chemical flooding [7, 9, 13, 14].

Simultaneously, in response to the call for "green environmental protection and recycling," SY-JS was synthesized, a multifunctional surfactant. The surfactant can be reused through "dynamic self-healing" when stimulated by counterions. In addition, we altered the stimulation technology design concept. We used gel breaking and reuse of clean fracturing fluid as the oil displacement agent. The integrated operation concept of "pressure injection and production" is adopted," which organically combined single-well clean fracturing fluid technology with the production of three chemical additives, resulting in a set of continuous development technology.

SY-JS, a multifunctional surfactant, was selected for the following reasons:

(1) It is technically and economically feasible to avoid the bondage caused by repeatedly adding chemical reagents during operation.

(2) The "rigid-flexible combination" design concept is used in the molecular structure design, with a large sterically hindered rigid group cyclohexane and an ultra-long hydrophobic tail chain of unsaturated bonds to improve temperature resistance. The use of "double cations" to increase surfactant hydration layer improves salt resistance.

(3) The system has low damage, shear resistance, good sand-carrying performance, high oil displacement efficiency, and cost-effectiveness.

(4) It saves energy and reduces emissions, which reduces flowback fluid treatment problems.

(5) It broadens the use of surfactants in the petroleum industry.

2. Materials and methods

2.1. Material

Epichlorohydrin, N, n-dimethylcyclohexamine and propyl mustard dimethylamine were purchased from Shanghai McLean Biochemical Technology Co., Ltd. (Shanghai, China). Ethylene glycol butane, kerosene and ethyl acetate are provided by Shanghai Aladdin Biochemical Technology Co., Ltd. B1-12 was purchased from Shanxi Xinshi Chemical Co., Ltd. These chemicals are chemical grade and can be used without further purification. Deionized water was prepared in the laboratory and used in all experiments.

2.2. Proton nuclear magnetic resonance (NMR) spectrum

The structure of SY-JS was detected by ^1H NMR spectroscopy. Figure 1 shows the ^1H NMR (400 MHz, CDCl_3) SY-JS proton spectrum: 0.86 (t, 3H, CH_3), 1.31 (t, 28H, $\text{CH}_3(\text{CH}_2)_6$), 1.48–1.52 (m, 8H, $(\text{CH}_2)\text{CH}_2\text{C}=\text{OH}_2\text{CH}=\text{CHCH}_2(\text{CH}_2)_3$), 2.0 (t, 8H, $\text{N}+2\text{CH}_3\text{CHCH}_2\text{CH}_2(\text{CH}_2)_3$, $(\text{CH}_2)\text{C}=\text{O}$), 2.18 (t, 6H, $(\text{CH}_2)\text{CH}=\text{CH}, \text{C}=\text{ONH}(\text{CH}_2)_2$), 3.22–3.92 (m, 18H, $(\text{CH}_2)\text{N}+(\text{CH}_3)_2(\text{CH}_2)\text{CHOH}(\text{CH}_2)\text{N}^+(\text{CH}_3)_2$), 5.12 (s, 1H, $(\text{CH})\text{OH}$), 5.43 (s, 2H, $(\text{CH}=\text{CH})$), and 7.92 (s, 1H, $\text{C}=\text{O}(\text{NH})$). The same number of hydrogen atoms in the target product molecule was found in the NMR spectrum, and the hydrogen atoms at different displacements were mapped to the corresponding positions in the molecular structure. These proved the consistency of the synthesized product and the target product.

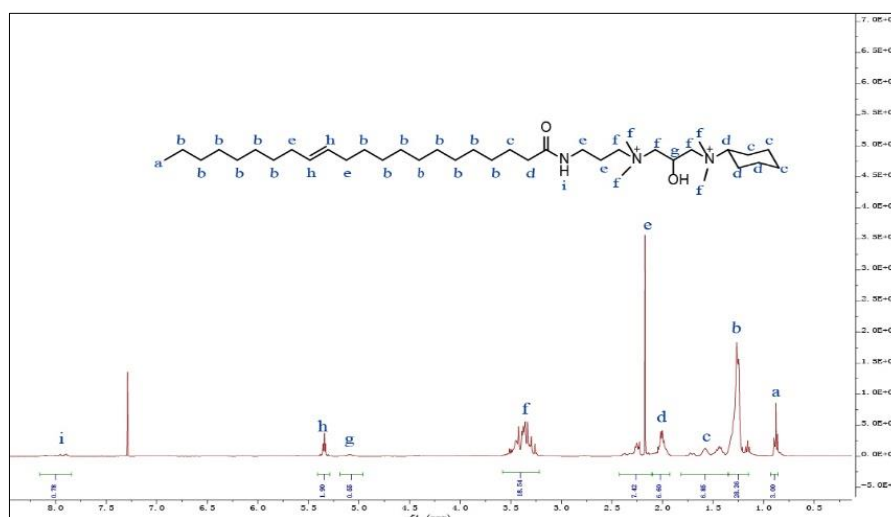


Figure 1. ^1H NMR spectra in CDCl_3

2.3. Measurement

The ^1H nuclear magnetic resonance (^1H NMR) spectra of SY-JS is obtained using a BRUKER AVANCE III HD 400 MHz spectrometer (Bruker, Karlsruhe, Germany). The interfacial tension measurements were conducted using a KRUSS DSA30S tensiometer (Kruss, Hamburg, Germany). The

interface parameter integrated measurement system (KRUSS DSA30S, Kruss, Germany) measured the contact angles. Scanning electron microscope (SEM) micrographs were obtained from a Quanta 450 scanning SEM (FEI, Hillsboro, OR, USA). Rheological properties were evaluated using a HAAKE MARS III Rheometer (Thermo Scientific, Munich, Germany).

3. Results and discussions

3.1. Fracturing fluid performance test

Surfactants use as thickeners of clean fracturing fluids in deep wells and high-temperature wells remain difficult. Temperature and shear stability are critical parameters for evaluating fracturing fluid systems, as they determine the bearing capacity of the proppant [15, 16]. The rheological properties of the surfactant solution are unique. When the surfactant concentration exceeds the critical micelle concentration, the long hydrophobic chain extends into the aqueous phase, causing the viscoelastic surfactant molecules to aggregate to form spherical micelles with the long-chain hydrophobic group as the core and the hydrophilic group extending into the solvent, as shown in Figure 2a. The space occupied by the surfactant micelles decreases and the repulsion between micelles increases as the concentration of the viscoelastic surfactant increases and the solution properties change. At the same time, spherical micelles begin to deform and merge into linear or rod micelles with less space. The rod-shaped micelles continue to merge to form longer vermicular micelles. Because of the hydrophobic effect, these micelles entangle and form a spatial crosslinked network structure. When micelles are exposed to high temperatures, they curl and shrink as a result of the thermal movement of molecules. At the same time, the shape and spatial network structure of micelles will be cut and destroyed by the action of high-speed shearing. The most obvious symptom is a decrease in apparent viscosity.

As a result, to ensure that the solution system has good viscoelasticity and shear viscosity. Not only can the addition of appropriate additives improve the interaction between ions and molecules in the VES fluid, but also it can improve the microstructure and rheological behavior of micelles [17].

As illustrated in Figures 2b and c. According to the results of the above analysis, 3 % SY-JS + 12wt% KCl and 3%SY-JS + 12wt% NaCl have good viscoelasticity and microstructure. The shear and heat resistances were measured using a rheometer at 140°C for 120 min at a shear rate of 170 s⁻¹. The viscosity of the test solution after 120 min was about 30 MPa·s, which meets industry standards and indicates that the fracturing fluid has high-thermal shear stability and meets the requirements of high-temperature operation in deep wells [18, 19].

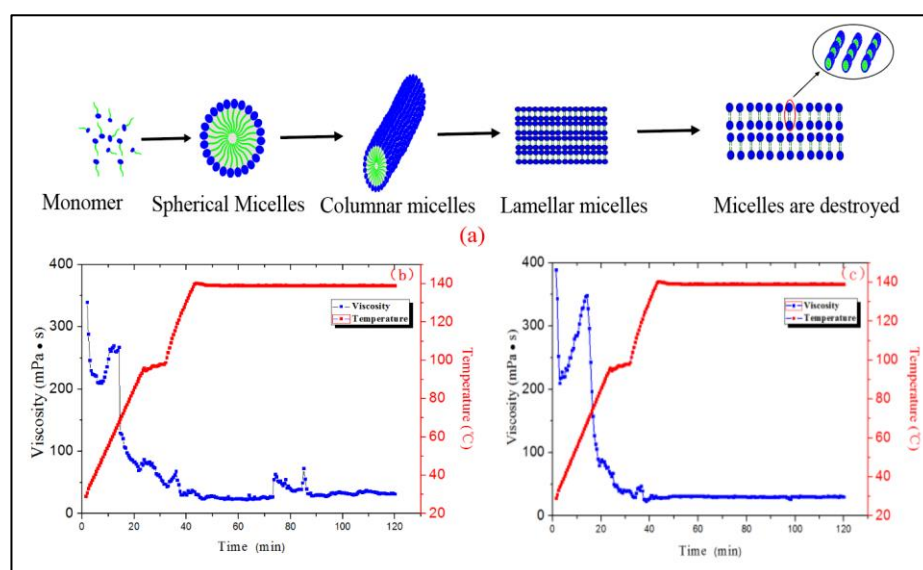


Figure 2. Rheological test and mechanism diagram

3.2. Preparation and optimization of gel breaker

To achieve the best oil displacement effect with the backflow fluid, the fracturing fluid gel must be optimized. The fracturing site's backflow fluid is mixed with formation water, crude oil, microorganisms, and other impurities. The experiment used a gel breaker prepared in the laboratory to accurately evaluate the oil displacement performance of the gel breaker's oil displacement agent and to eliminate other possible interfering factors.

To better simulate the field flowback fluid's real-world situation, ethylene glycol butyl ether was added to the clean fracturing fluid formula and heated in a water bath at 90°C for 2 h to accelerate gel breaking. Table 1 displays the experimental results. In comparison to the experimental data, when the kerosene dosage is 2%, the viscosity of the gel breaker reaches its lowest value and the gel is completely broken.

Table 1. Optimal selection of gel breaking-experiment at 90°C

Kerosene amount	Breaker viscosity at different times (mPa·s)		
	30 min	60 min	90 min
1%	7.22	5.32	2.31
1.5%	6.55	4.67	2.66
2%	4.33	3.22	1.96

3.3. Feasibility study on recycling of backflow liquid

The stability of the surfactant molecular structure in a complex environment is a critical requirement for fracturing fluid flowback fluid flooding. Conventional polymer-fracturing fluids use crosslinking agents to form chemical crosslinking gels, forcing the fracturing fluid system to become a gel system. Discovered through indoor research, Micelles will undergo reversible changes after exposure to complex conditions. Surfactants are interesting because of their low molecular weight and hydrophobic aggregation of molecules. The ability to form aggregates will persist if the molecular structure is stable.

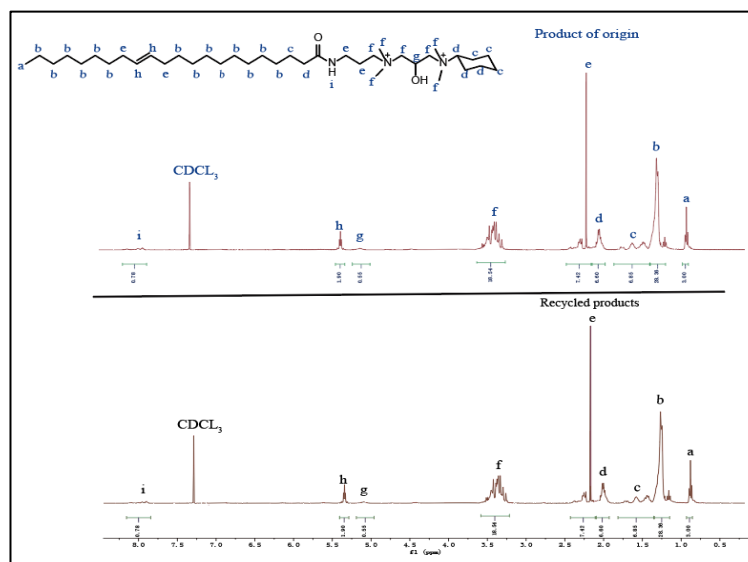


Figure 3. Comparison of NMR-H spectra of the gel breaker and original products

The product's spectrum after gel breaking is completely consistent with that of the original product, as shown in Figure 3, indicating that the molecular structure of the gel breaking and original products are consistent. The presence of molecular structure implies that each functional group in the molecular structure continues to have related effects. Simultaneously, the wetting function, reduced interfacial tension, and emulsifying function of the surfactant can all be used normally.

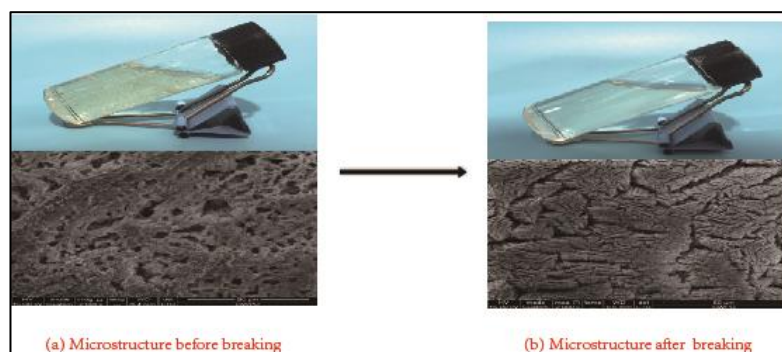


Figure 4. Comparison of the microscopic appearance of gel breaker and original products

We observed the micromorphology before and after the gel breaker to fully explain the theory that "the destruction of surface activity is reversible" (Figure 4). The results show a clear shift from a to b. The spatial network structure of the surfactant was visible before gel breaking, but it vanished after gel breaking. As a result, when a surfactant is used as a thickener in a high-temperature, high-salt, and even high-shear environment, only the spatial structure is irreversibly destroyed.

3.4. Oil displacement performance test

3.4.1. Wetting test

Wettability is the key to testing the flooding performance of surfactants. Wetting refers to the process of replacing one type of liquid on the surface with another [20, 21]. When the rock surface is hydrophilic rock and in contact with the surfactant solution, an adsorption layer with hydrophilic end groups facing the rock and hydrophobic chains facing outward will be formed on the rock surface. Simultaneously, the solid surface becomes an oil-wet surface, and wetting reversal occurs. When the rock surface is oil-wet, an adsorption layer forms with nonpolar (hydrophilic end) and polar (hydrophobic end) groups toward the solid and outside forms, respectively. This is one of the causes of surfactant flooding in many oil-wet reservoirs.

The contact angle is one of the most effective methods for determining wettability. The contact angle is the angle formed by the liquid and the solid surface as a result of the incomplete expansion. Figure 5 depicts the relationship between contact angle and wetting. If the solid is hydrophilic, the contact angle is 90° ; otherwise, it is hydrophobic.

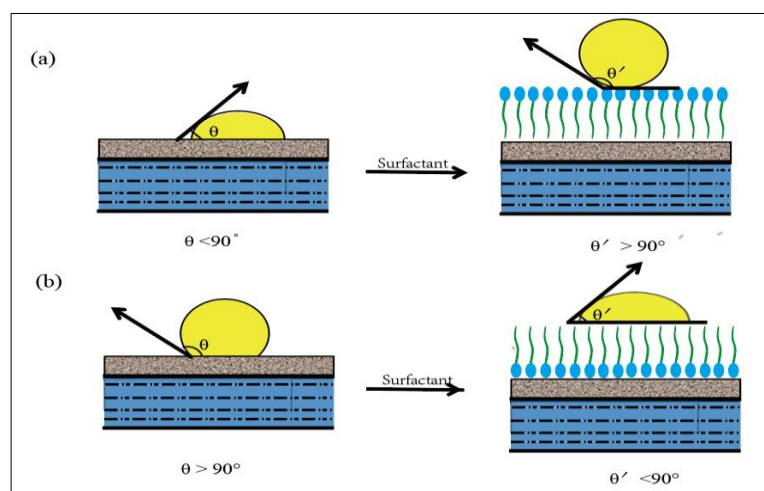


Figure 5. Action diagram of wettability

The water contact angle of crude oil on the core slice after adsorption of the surfactant was measured using the core slice-soaking method in this study. As the control group, sandstone core slices were soaked in a 3wt percent ammonium chloride solution for 48 h before being oven-dried. The mixing of the breaker and formation water was then simulated. To measure the wetting angle, the previous breaker was diluted to five solutions of 0.1 percent, 0.2 percent, 0.3 percent, 0.4 percent, and 0.5 percent, which were then compared to the blank group. The outcomes are depicted in Figure 6 and Table 2.

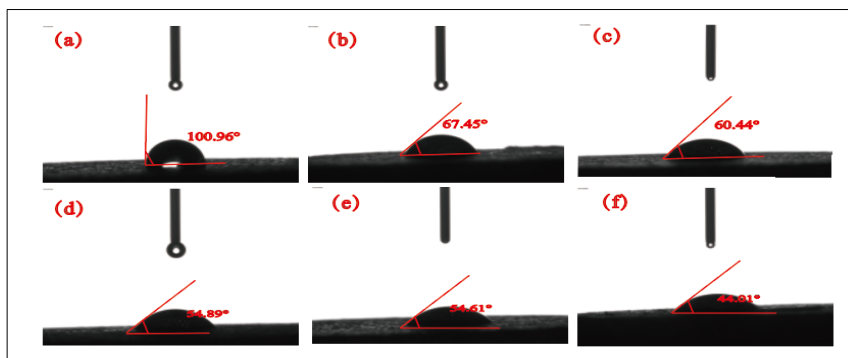


Figure 6. Wetting test results display

Table 2. Experimental data of wetting angle

Group	(a)	(b)	(c)	(d)	(e)	(f)
Concentration	0	0.1%	0.2%	0.3%	0.4%	0.5%
Wetting Angle	100.96	67.45	60.44	54.89	54.61	44.01

Surprisingly, the contact angle decreases as SY-JS concentration increases, according to the experimental results. The smaller the contact angle, the easier it is for the liquid to wet the solid. The experimental results show that when the solution concentration reaches 5%, the wetting effect is the best. The surfactant is spread on the solid surface, as shown in Figure 6(f), indicating that the surfactant's hydrophobic chain is toward the solid surface, the hydrophilic head group is toward the rock surface, and the contact angle decreases from 100.96° to 44.01°. The hydrophilicity increases, the lipophilicity decreases, and the wetting reversal occur during the process. At the same time, the adhesion of oil to the rock surface is reduced, and it is easily displaced. As a result, surfactant flooding in oil-wet reservoirs significantly improves oil recovery.

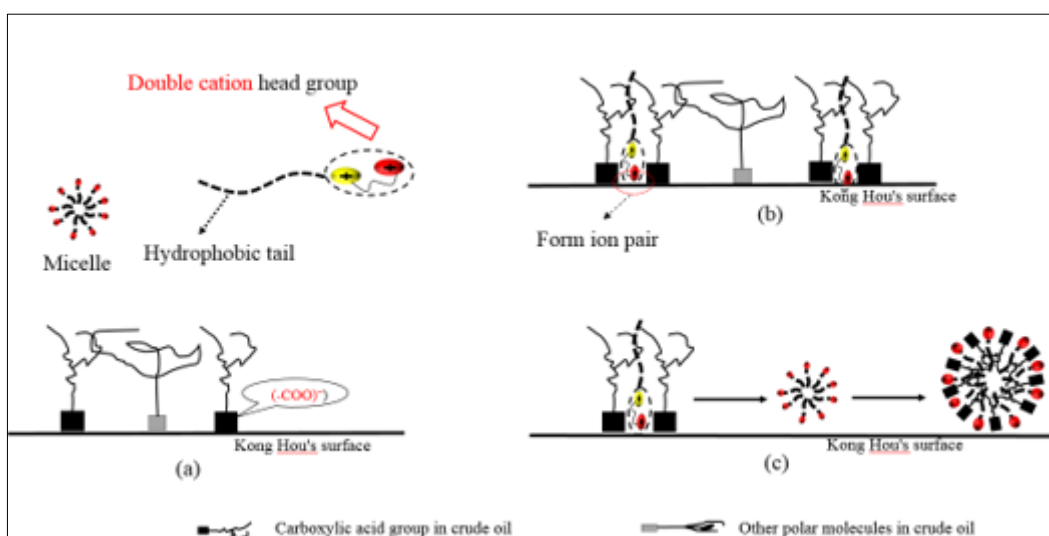


Figure 7. Wetting mechanism of SY-JS

Such remarkable wetting reversal ability necessitated a molecular structure investigation by our research team to unravel the mysterious mechanism. Standnes and Austad [22] investigated the wettability of surfactants, revealing their thorough understanding. They proposed that electrostatic attraction can cause carboxylic acid groups in crude oil and cationic head groups in cationic surfactants to form ion pairs. Desorbed ion pairs from the solid surface can be solubilized into micelles. As a result, the wettability of the solid surface improves. We presented our findings based on their understanding (Figure 7). The molecular structure of SY-JS multifunctional surfactant contains a double cation structure, which increases electrostatic attraction, forms more ion pairs, and increases the number of solubilizing micelles. Rock's hydrophilicity is enhanced. The crude oil and asphaltene adsorbed in the rock migrate from the rock's surface to the solution's interior during the flowback fluid displacement process, this will improve oil recovery.

3.4.2. Interfacial tension test

Interfacial tension can be regarded as the contraction force acting on the liquid interface per unit length. The interfacial tension is caused by the directional adsorption of the surfactant between two immiscible liquids. In Petroleum Engineering, the spread factor and displacement efficiency of oil displacement agents are the most important parameters among many decisive factors affecting oil recovery. Generally, increasing the number of capillaries improves the displacement efficiency, whereas reducing the oil-water interface increases the number of capillaries. Oil and water occur in underground reservoirs. thus, according to Darcy's formula, the viscosity is converted to that of water μ_w . The product of seepage velocity v_o . Capillary number N_C is expressed by the following equation (1), where ΔP is the pressure difference applied to the oil drop and L is the length of the oil drop, σ is the capillary force [23].

$$N_C = \frac{\Delta P/L}{\sigma} = \frac{\mu_w v_o}{\sigma} \quad (1)$$

The worth the relative influence of driving force and flow resistance in the process of oil-water two-phase flow, the interaction of viscous and capillary forces, is represented by N_C . It is responsible for determining the micro-distribution of the oil-water two-phase liquid in the reservoir rock pore media. It also determines the state of movement, the position of detention, and the size of oil droplets in different capillaries. N_C is directly related to the start of flow and migration. The greater the N_C , the lower the residual oil saturation and the greater the displacement efficiency. Surfactant flooding is based on this trend. As a result, to reduce the interfacial tension and eliminate capillary formation action, the adhesion work required to displace crude oil should be reduced and the oil displacement efficiency should be improved.

The oil-displacing agent in this example contains surfactants, NaCl or KCl, alcohols and other liquids. Because the laboratory's separation function cannot remove these mixtures, these substances may affect the surface tension of the flowback fluid. However, in order to accurately test the displacement performance of the backflow liquid mixture, we measured its interfacial tension.

The temperature of the backflow solution was found to have a significant effect on the interfacial tension of SY-JS during testing. As a result, we devised the following design scheme to test the interfacial tension at temperatures of 70°C, 80°C, and 90°C, rotation speeds of 6000 rpm, 0.5 percent concentration, and backflow times of 60, 70, 80, and 90 min, The experimental result diagram is shown in Figure 8a.

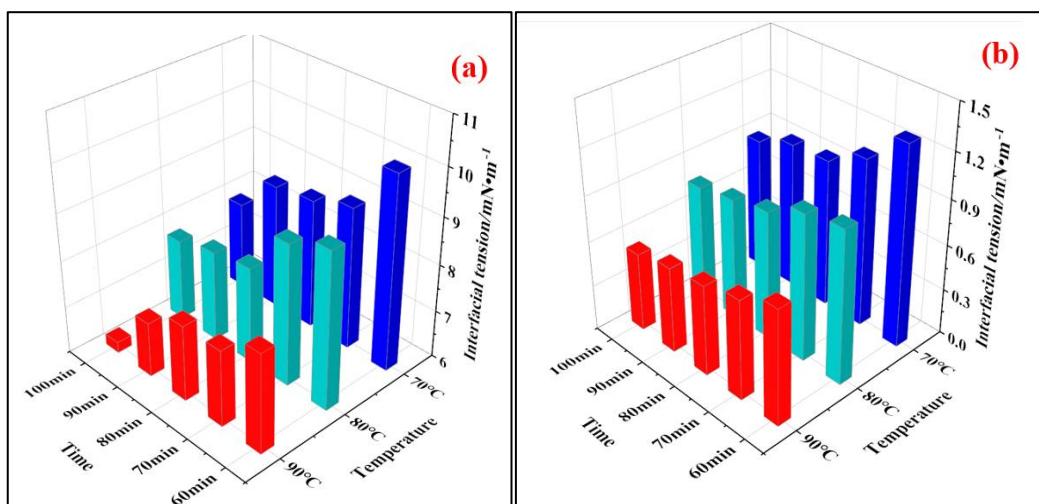


Figure 8. Interfacial tension tests of a SY-JS flowback and b SY-JS compound flowback liquids

Generally, the interfacial tension is 10^{-1} - 10^{-3} $\text{mN} \cdot \text{m}^{-1}$ is low surface tension, whereas 10^{-3} $\text{mN} \cdot \text{m}^{-1}$ or lower is considered ultralow interface tension. The results show that the interface tension decreases as temperature and backflow time increase, but it is not lower than the standard low surface tension at 90°C and 100 min.

It is proposed that adding ethylene glycol butyl ether to accelerate gel breaking and counter ions and kerosene to simulate the real underground environment affects interfacial tension under laboratory conditions.

To reduce the flowback fluid's interfacial tension as much as possible and achieve a better oil displacement effect, our team tried several anionic surfactants, including 0.2 percent B1-12, which can achieve lower interfacial tension when combined with 0.5% SY-JS. The two are well-matched, and their synergistic effect reduces interfacial tension to the low interfacial tension standard. The critical micelle concentration of the surfactant in the composite system and its content differ, as does the distribution proportion of the surfactant adsorbed on the oil-water interface. The interaction of the surfactant, oil, and water molecules at the oil-water interface in the mixed solution can be regarded as a unified equilibrium relationship, according to the well-known equilibrium theory. The adsorption of surfactant molecules results in the formation of a thin surfactant layer at the interface of the aqueous surfactant solution and crude oil. The interfacial tension is reduced to a minimum when the surfactant distribution ratio reaches a certain value [24]. Furthermore, the Jamin effect occurs in low-permeability reservoirs, increasing capillary resistance and injection pressure while decreasing recovery. The combination of 0.5% SY-JS and anionics surfactant B1-12 can reduce oil droplet emission power through the pore throat. Oil droplets can change shape more easily, and the flowback liquid's oil displacement efficiency can be improved.

Figure 8 depicts the experimental results of SY-JS and anionic (b). At 90°C for 100 min, the interfacial tension reaches $0.52 \text{ mN} \cdot \text{m}^{-1}$, which is within the range of low interfacial tension and can achieve a good oil displacement effect. Thus, if the reservoir wettability and oil-water interfacial tension are properly matched, oil recovery can be maximized without pursuing ultralow oil-water interfacial tension blindly. Because anionic surfactants are relatively expensive, the surfactant restriction is reduced, the application cost is reduced, and a theoretical reference is provided for improving oil recovery in the future by changing the wettability of the reservoir. It also provides a theoretical foundation for future improvements in oil recovery by changing the interfacial tension.

Many researchers also stated that while lowering the interfacial tension test (IFT) is important, IFT should not be reduced to an ultralow value to improve the recovery of tight reservoirs [25]. The surfactant's penetration rate is limited by ultralow IFT, which limits oil production. When the wettability

of the surfactant solution changes, the recovery decreases as the IFT decreases. More research is needed for the surfactant method of the tight oil reservoir.

Furthermore, because wettability determines the direction of the capillary force, multifunctional surfactants can reverse the wettability of the rock surface. When the injection pressure is small, the direction and size of the capillary force are important factors in oil displacement efficiency. It is hypothesized that interfacial tension influences the capillary force's action mechanism. Figure 9 depicts the capillary force's action mechanism.

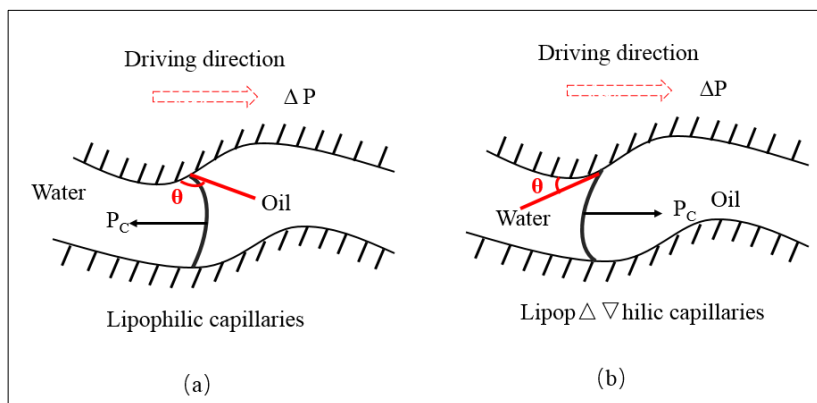


Figure 9. Capillary force mechanism

Because of the different shape and direction of the curved liquid level at the oil-water interface of an oil-water bearing reservoir, the direction of the capillary force produced by the result is different. The direction of the capillary force P_C and the pressure difference in the water flooding displacement is also different, as shown in Figure 10a. The driving direction of P is the inverse of the resisting capillary force P_C , which is incompatible with hydraulic drive. In contrast, in Figure 10b, P_C (the power) and the pressure difference of water flooding displacement P are both pointing in the same direction. Furthermore, the multi-kinetic surfactant SY-JS causes a wetting reversal on the surface of oil-bearing rock, and capillary force is the power that promotes oil displacement by the backflow liquid.

Interfacial tension characterizes the contraction force at the liquid interface. The capillary force describes the additional surface effect produced on the liquid surface, and the two have a direct relationship. The size of the interfacial tension determines the capillary force, according to the basic formula (2) of capillary equilibrium theory.

$$P_c = \frac{2\sigma\cos\theta}{r} \quad (2)$$

where P_C represents the capillary force, σ is the oil-water interfacial tension, θ is the wetting contact angle, and r represents the capillary radius. The capillary force is the driving force in wetting reversals on the rock surface, and the interfacial tension does not reach the ultralow interfacial tension level, which is good for oil extraction. It also provides a theoretical foundation for some researchers to propose that as IFT decreases, the recovery factor decreases. It also explains the theory that wettability determines the direction of the capillary force and interfacial tension determines the magnitude of the capillary force.

3.4.3. Oil displacement efficiency test of flowback fluid

The core displacement experiment is the most direct way to assess the effect of a composite system on recovery. The physical simulation displacement effect test of the composite flooding system in SY/t6424-2000 is used to conduct the core displacement experiment. The displacement device is depicted in Figure 10.

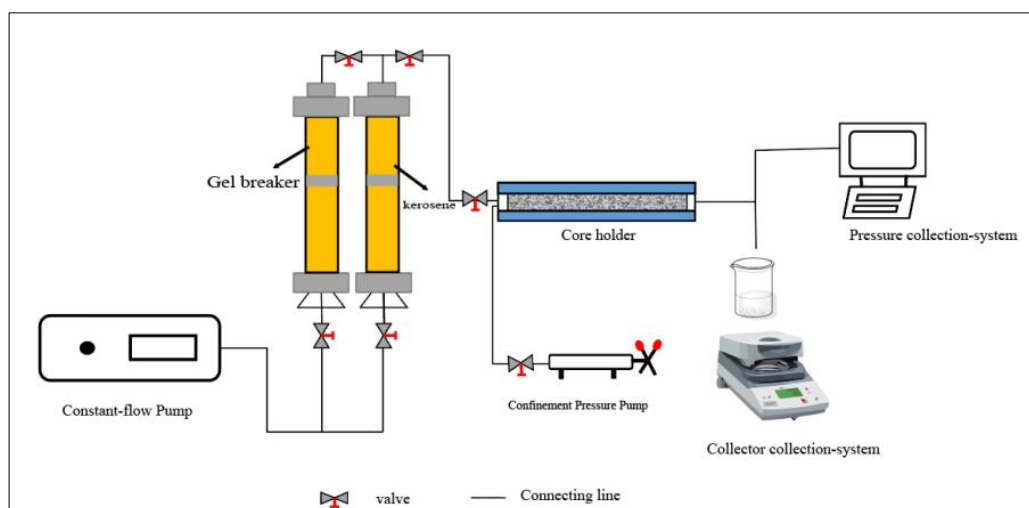


Figure 10. Flowback fluid-flooding unit

Two groups of artificial cores were selected by the core experiment of group A. The permeability of group A is $14.1 \times 10^{-3} \text{ um}^2$, and its core size dimension ($d \times L$) is $2.53 \text{ cm} \times 98 \text{ cm}$. Water flooding experiment was conducted on the core, and SY-JS flowback fluid and anionic surfactant were prepared after the water flooding experiment. The experimental results are shown in Figure 11.

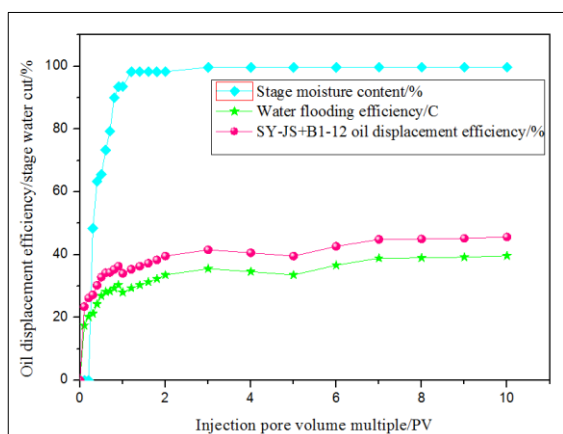


Figure 11. Comparison of oil displacement experimental results

When water flooding is performed on the core, the results show that the average oil displacement efficiency is 29.51 percent. The oil displacement was increased by 6.0 percent on average by using SY-JS fracturing fluid gel breaker and anionic 0.5 percent B1-12 composite system. Following fracturing, the flowback fluid is adjusted to allow the fracturing fluid to replace the conventional oil displacement agent after gel breaking, thereby directly promoting oil displacement and improving crude oil recovery. Finally, the SY-JS oil displacement fracturing fluid has dual fracturing and oil displacement effects. The process and mechanism of multifunctional surfactant fracturing oil displacement are summarized in the preceding research, and the mechanism diagram (Figure 11) can be obtained. This mechanism diagram summarizes surfactant gelation, breaking, recovery, regelation, and recycling.

When the surfactant concentration exceeds that of the micelle, aggregates form and a network structure forms due to the promotion of counterions in the formation. When the surfactant enters the reservoir and comes into contact with the oil or gas, these substances are incorporated into the micelle, and the wormlike micelle structure expands and disintegrates into small spherical micelles, reducing the fluid's viscoelasticity. As a result, the fracturing fluid completes its mission and returns to the ground, where it injects into the formation via the proportioning of oilfield-produced water. despite the destruction of the micelles, the surfactant's molecular structure remained intact throughout the

experiment. Furthermore, the monomer of the surfactant in the solution is gathered at the interface. The synergistic effect of the two, with gel breaking and gelation, rearranges the charge, resulting in "physical dynamic crosslinking" and the formation of micelle aggregates.

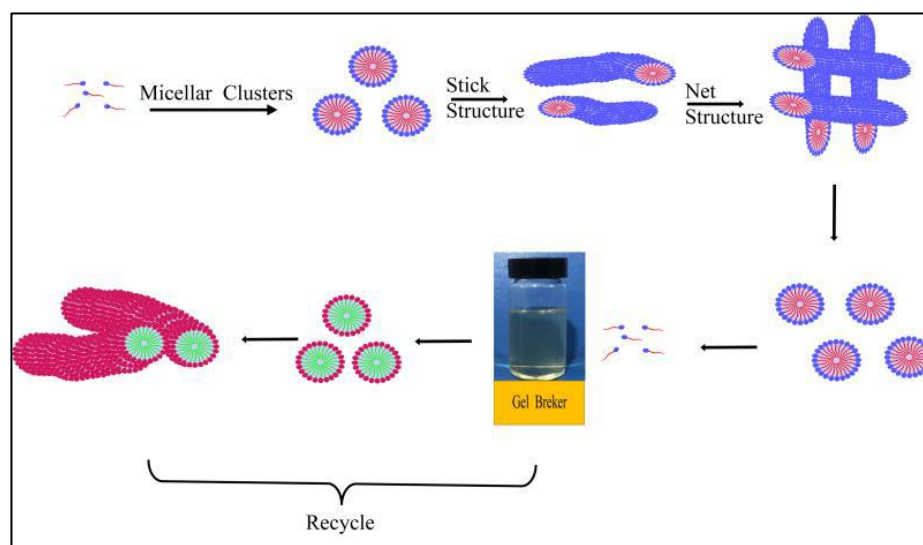


Figure 12. Clean fracturing fluid flowback fluid-flooding process and mechanism diagram

3.4.4. Core damage experiment of gel breaker flowback fluid

To study the formation damage and adsorption of gel breaker flooding, the core damage experiment of flowback fluid formula was carried out. The breaker formula is 0.2% kerosene+0.5%SY-JS+0.2%B1-12+ Deionized water. The core size is 25 mm ×80mm. The porosity ranges between 1.15% and 15.3%, the average porosity is 8.38%, and the average permeability is less than 5 md. The experimental results are shown in Table 3.

Table 3. Core damage test results

Sample	Gel breaking time (h)	Broken fluidviscosity (mPa s)	Residue (mg/L)	Kerosene permeability (mD)	Regained permeability (mD)	Permeability recovery rate (%)
Flowback liquid	1.96	4.62	48	9.22	7.82	89
SY/T6376-2008	≤12	≤5	≤100	/	/	≥80

Clay minerals usually have unsaturated charges. According to the principle of electrical neutrality, the surface of clay minerals must adsorb the same amount of different ions to achieve electrical balance. Cations in clay minerals dissociate in water to form diffusion bilayers, while SY-JS surfactant-containing double cations can better prevent the dissociation of cations and reduce adsorption. The experimental results show that its adsorption capacity is far lower than the fracturing fluid standard, and the core damage rate is low.

4. Conclusions

We successfully designed and synthesized SY-JS, a multifunctional surfactant that can be used as an integrated fracturing and oil displacement-working fluid, in this study. The "physical dynamic repair" theory of surfactant in the field of oil fracturing and oil displacement was proposed through various fracturing fluid and oil displacement performance tests. The molecular structure remains after gel breaking at high temperatures and salt. Component repair is formed again as a result of the synergistic



effect with anionic surfactant to play the surfactant's oil displacement function. The following conclusions are possible.

The clean fracturing fluid formula for the rheological test is 3 percent SY-JS + 12 percent NaCl solution and 3 percent SY-JS + 12 percent KCl solution. Clean fracturing fluid met field construction requirements at a shear rate of 170 s^{-1} at 140°C .

It was discovered through the wettability test and core displacement experiment that the flowback fluid of the SY-JS clean fracturing fluid can reverse rock wettability. Based on the water flooding, oil recovery can be increased by 6% when the flowback liquid containing 0.5% SY-JS is compounded with 0.2% anionic surfactant B1-12.

In the field of surfactant wettability, the mechanism of SY-JS surfactant causing wetting reversal on the rock surface is proposed, which enriches the surfactant's wetting mechanism.

The theory of "wettability determines the direction of the capillary force, and the interfacial tension determines the magnitude of the capillary force" proves that low interfacial tension is not beneficial to oil displacement by combining the capillary force, wettability, and interfacial tension.

Finally, the multifunctional surfactant SY-JS surfactant can be used in clean fracturing fluid for reservoir reconstruction and can be used to readjust the flowback fluid of the clean fracturing fluid to replace the conventional oil displacement agent for direct oil displacement mechanism analysis, and put forward the function of "dynamic physical surfactant repair." Finally, the SY-JS surfactant is thought to have dual effects on fracturing and oil displacement. Furthermore, it provides a new concept for the widespread use of surfactants in the oil industry as well as a direction for integrating oilfield-working fluid.

Acknowledgments. The research is partly supported by China Postdoctoral Science Foundation (2019M650250), National Natural Science Foundation of China (Grant Nos. 41902303), National High Technology Research & Development Program (2016ZX05053, 2016ZX05014-005-007) and Sichuan Province Regional Innovation Cooperation Project (2020YFQ0031).

References

1. ALAGIC, E., SKAUGE, A., Combined Low Salinity Brine Injection and Surfactant Flooding in Mixed Wet Sandstone Cores[J]. *Energy & Fuels*. 2010, 24(6): 3551-3559.
2. EDIN, ALAGIC, ARNE, et al., Combined Low Salinity Brine Injection and Surfactant Flooding in Mixed-Wet Sandstone Cores[J]. *Energy & Fuels*. 2010.
3. RAMIREZ, W. F., FATHI, Z., Optimal Injection Policies for Enhanced Oil Recovery: Part 2- Surfactant Flooding[J]. 1984.
4. FU, D., CHEN, Y., XIAO, Z., et al., Viscoelastic Surfactant Fluids Stable at High Brine Concentration and Methods of Using Same[P].
5. KABIR-UD-DIN, NAQVI, ANDLEEB, et al., Effect of surfactant structure on the mixed micelle formation of cationic gemini-zwitterionic phospholipid systems[J]. *Colloids & Surfaces A Physicochemical & Engineering Aspects*. 2015.
6. LIU, G. J., LI, X. R., ZHENG, L. J., Preparation and Property Evaluation of Anionic Clean Fracturing Fluid[J]. *Advanced Materials Research*. 2013, 602-604: 1238-1242.
7. ZHANG, W., MAO, J., YANG, X., et al., Development of a sulfonic gemini zwitterionic viscoelastic surfactant with high salt tolerance for seawater-based clean fracturing fluid[J]. *Chemical Engineering Science*. 2019, 207: 688-701.
8. FU, D., CHEN, Y., XIAO, Z., et al., Viscoelastic surfactant fluids stable at high brine concentration and methods of using same[P].
9. YANG, X., MAO, J., MAO, J., et al., The Role of KCl in Cationic Gemini Viscoelastic Surfactant Based Clean Fracturing Fluids[J]. *Colloids and Surfaces A Physicochemical and Engineering Aspects*. 2020, 606: 125510.
10. FU, D., DISMUKE, K., DAVIES, S., et al., Viscoelastic fluids for oilfield uses[P].

11. JAMALOEI, B. Y., KHARRAT, R., Analysis of Microscopic Displacement Mechanisms of Dilute Surfactant Flooding in Oil-wet and Water-wet Porous Media[J]. *Transport in Porous Media*. 2010, 81(1): 1-19.
12. RAMIREZ, W. F., FATHI, Z., Optimal Injection Policies for Enhanced Oil Recovery: Part 2- Surfactant Flooding[J]. 1984.
13. YANG, X., MAO, J., MAO, J., et al., The Role of KCl in Cationic Gemini Viscoelastic Surfactant Based Clean Fracturing Fluids[J]. *Colloids and Surfaces A Physicochemical and Engineering Aspects*. 2020, 606: 125510.
14. YANG, Z., JM, A., JZ, A., et al., Preparation of a novel sulfonic Gemini zwitterionic viscoelastic surfactant with superior heat and salt resistance using a rigid-soft combined strategy[J]. *Journal of Molecular Liquids*., 318.
15. CHEN, X., HUANG, F., Research Progress of Temperature-Resistant and Salt-Tolerant Surfactants for Enhanced Oil Recovery[J]. *Petrochemical Technology*. 2010.
16. LUO, S. C., ZI-JING, Y. U., NIU, G., et al., Study on the Temperature-resistant and Salt-tolerant Surfactant BHJ-2 for EOR[J]. *Fine Chemicals*. 2016.
17. MENG, C. A., JM, A., HLS, B., et al., Development of a novel temperature-resistant and salt-resistant double-cationic surfactant with "super thick hydration layer" for clean fracturing fluid[J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*., 617.
18. NAGARAJAN, R., Molecular packing parameter and surfactant self-assembly: The neglected role of the surfactant tail[J]. *Langmuir*. 2002, 18(1): 31-38.
19. AHMADI, M. A., SHADIZADEH, S. R., Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks: Static and dynamic conditions[J]. *Fuel*. 2015, 159(nov.1): 15-26.
20. SOMASUNDARAN, P., ZHANG, L., Adsorption of surfactants on minerals for wettability control in improved oil recovery processes[J]. *Journal of Petroleum Science & Engineering*. 2006, 52(1-4): 198-212.
21. MAESTRO, A., GUZMÁN, E., SANTINI, E., et al., Wettability of silica nanoparticle-surfactant nanocomposite interfacial layers[J]. *Soft Matter*. 2012, 8(3): 837-843.
22. MAESTRO, A., GUZMÁN, E., SANTINI, E., et al., Wettability of silica nanoparticle-surfactant nanocomposite interfacial layers[J]. *Soft Matter*. 2012, 8(3): 837-843.
23. CAMPANELLI, J. R., WANG, X., Dynamic Interfacial Tension of Surfactant Mixtures at Liquid-Liquid Interfaces[J]. *Journal of Colloid & Interface Science*. 1999, 213(2): 340.
24. LUND, R., PIPICH, V., WILLNER L, et al., Structural and thermodynamic aspects of the cylinder-to-sphere transition in amphiphilic diblock copolymer micelles[J]. *Soft Matter*. 2011, 7(4): 1491-1500.
25. ALTAMIRANO, R. H., RIVERA, L. Z., CERVANTES, V. M., et al., Composition based on geminals zwitterionics liquids as wettability modifiers in enhanced oil recovery processes[P]

Manuscript received: 7.09.2021