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Catanionic Surfactant Systems for Emulsifying and Viscosity Reduction of Shale Oil

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Abstract: Shale oil resources are abundant in the second member of the Kongdian Formation, Cangdong Sag, Bohai Bay Basin, China. However, the shale oil here has high viscosity and poor fluidity, resulting in low recovery and huge difficulty in development, gathering, and transporting. This study assembled a catanionic surfactant (PSG) through electrostatic interactions between cetyltrimethylammonium bromide (CTAB) and α-olefin sulfonate (AOS) in an aqueous phase, which can be used as an effective emulsifying and viscosity-reducing agents for shale oils of Dagang oilfield. The interfacial activity and emulsification performance of PSG can be optimized by changing the molar ratio of CTAB to AOS. Notably, the PSG assembled at the molar ratio of 6:4 shows the best performance, with ultra-high surface activity and excellent salt resistance. At an oil/water ratio of 1:1 and 50 °C, an aqueous solution of 0.2% PSG can emulsify five types of shale oil, making it form shale oil-in-water (O/W) emulsion with a viscosity of less than 35 mPa·s, thereby reducing the viscosity of shale oil and improving its flowability. Importantly, shale oil and water can be separated by simple sedimentation without adding demulsifiers. This study has important guiding significance for the efficient development and transportation of shale oil.

Keywords: catanionic surfactant; shale oil; emulsify; O/W; viscosity

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1. Introduction

With the gradual decrease in conventional oil and gas resources, shale oil, as an important strategic replacement resource, has attracted extensive attention in recent years [1]. Shale oil resources are rich in China, and the recoverable resources are estimated to be between 1 billion and 1.5 billion tons [2,3]. Despite the large reserves of shale resources, China's continental shale oil is different from North American marine shale oil. Most of the oil-bearing shale has low maturity, strong reservoir heterogeneity, and developed nanopores [4–6]. Additionally, shale oil has the characteristics of large molecules, strong polarity, and high wax content [7]. Therefore, the scale-efficient development of China's shale oil still faces many challenges.

The second member of the Kongdian Formation, Cangdong Sag, Bohai Bay Basin, China is a favorable enrichment area for shale oil [8]. However, the shale oil in this area has a viscosity of 30.24–1167 mPa·s at 50 °C, a density of 0.85–0.94 g/cm^3, a pour point of 28–47 °C, and an average wax content higher than 20%, resulting in low fluidity for crude oil transportation [7]. As a result, the flowback fluid of shale oil is easy to plug into the wellbore during the lifting process, which affects the production efficiency and poses great challenges to the efficient exploitation of shale oil, especially in the process of long-distance transportation and reservoir transformation [8]. To reduce the viscosity of crude oil and improve its fluidity, researchers have proposed several key methods, such as catalytic aquathermolysis, solvent dilution, emulsification, etc. [9,10]. However, catalytic aquathermolysis is faced with the difficulty of large-scale catalyst preparation, while solvent dilution has a high cost and environmental problems. By contrast, emulsifying and viscosity reduction technology is not only cost-effective but also the most promising large-scale application [11,12].

Surfactants, as interfacial activity substances that can significantly reduce the interfacial tension of oil and water, play a vital role in emulsifying and viscosity reduction of heavy oil [13–15]. It can reduce the viscosity of crude oil by changing the properties of the oil/water interface and promoting the dispersion of the oil droplets in water [16]. Among many surfactants, catanionic surfactants show remarkable advantages in emulsifying and viscosity reduction because of their unique molecular structure and properties [17]. Catanionic surfactants not only combine the characteristics of cationic and anionic surfactants, but also show many new properties, such as a significant increase in surface activity, an improvement in temperature-resistance and salt-resistance, etc. [18–20], which makes it able to provide a stable emulsification effect under harsh environmental conditions. For example, Huang and co-workers prepared a catanionic surfactant that can obtain ultra-low oil/water interfacial tension at low concentration for the actual oil/water system of several blocks form Shengli Oilfield and Karamay oilfield, thus achieving emulsification and a viscosity reduction effect [21,22]. However, unlike heavy oil, there are rare reports on viscosity reduction of shale oil, which leads to serious technical gaps. In this study, the emulsifying and viscosity reduction of shale oil was studied in detail. CTAB and AOS in the aqueous phase were used to assemble catanionic surfactant (PSG). A small amount of PSG as an emulsifier can reverse phase high-viscosity shale oil (W/O) into low-viscosity O/W emulsion, and the demulsification rate is higher than 85% after 2 h. This surfactant can not only reduce the viscosity of initial shale oil, but also does not affect the terminal demulsification, which is expected to play an important role in shale oil lifting and pipeline transportation. Thus, this work provides a new perspective on shale oil exploitation technology and promotes the efficient development of unconventional oil and gas resources.

2. Materials and Methods

2.1. Materials and Reagents

Five kinds of shale oils (i.e., GY734H, GY735H, GY151H, GY152H, and GY512L) come from the second member of Kongdian Formation, Cangdong Sag, Bohai Bay Basin, China. Cetyltrimethyl ammonium bromide (CTAB, 99%) was purchased from Sinopharm Chemical Reagent Co., LTD, Shanghai, China. α-olefin sulfonate (AOS, 92%) was purchased from Shandong Yusuo Chemical Technology Co., LTD, Linyi, China. Its average molecular weight is 315 g/mol. Distilled water and tap water are from the laboratory. Field water is provided by PetroChina Dagang Oilfield, Tianjin, China.

2.2. Preparation of Catanionic Surfactant Systems

According to the different molar ratios of CTAB and AOS, these two surfactants were weighed in a 50 mL breaker. Then, 25 mL water was added to the beaker. A catanionic surfactant aqueous solution with a concentration of 0.2% was prepared by using a six-joint magnetic constant temperature agitator (CJJ-93, Jiangsu Jintan Huanyu Scientific Instrument Factory, Changzhou, China) at 50 °C for 30 min.

2.3. Physicochemical Properties Characterization of Shale Oil

According to the national or industry standards in Table 1, the physicochemical properties of shale oil were determined.

Table 1. Relevant standards for physicochemical characterization of shale oil.

No.	Properties	Reference Standards
1	Viscosity	SY/T0520-2008 [23]
2	Density	GB/T13377-2010 [24]
3	Wax content	SY/T0537-2008 [25]
4	Pour point	SY/T0541-2009 [26]
5	Wax appearance temperature	SY/T0522-2008 [27]

2.4. Water Quality Analysis

According to the oil and gas industry standard "Oil field water Analysis Method" (SY/T5523-2006) [28], the content of six ions and total salinity of distilled water, tap water, and field water were determined, respectively, as listed in Table 2.

Table 2. Water quality analysis results of distilled water, tap water, and field water.

Ion Content (mg/L)	Distilled Water	Tap Water	Field Water
$Na^+ + K^+$	4	20	10,183
Mg^{2+}	/	11	73
Ca^{2+}	/	38	260
$SO_4{}^{2-}$	/	/	264
$CO_3{}^{2-}$	/	/	31
$HCO_3{}^-$	6	133	411
Cl^-	3	52	15,897
Total salinity	13	254	27,119

2.5. Determination and Calculation of Critical Micelle Concentration (CMC) and Hydrophilic–Lipophilic Equilibrium Value (HLB)

According to the conductivity method [29], the CMCs of CTAB and AOS surfactants were determined by electrical conductivity (DDSJ-308A, Shanghai YiZhi Scientific Instrument Co., LTD, Shanghai, China), and then the CMC of catanionic surfactant was calculated by Clint theory (Equation (1)) [14].

$$\frac{1}{C_{12}(1+K_0)} = \frac{X_1}{C_1(1+K_0)} + \frac{X_2}{C_2(1+K_0)} \tag{1}$$

where C_{12} is the CMC of the catanionic surfactant. C_1 and C_2 are the CMCs of CTAB and AOS, respectively. X_1 and X_2 are the mole fractions of CTAB and AOS, respectively. K_0 is a constant related to the binding degree of the counterion of the micelle. Here, K_0 = 0.59 was used in the calculation [30].

According to reports in the literature, the HLB value of cationic surfactant CTAB is 15.8 [31], while the HLB value of anionic surfactant AOS can be calculated according to the method reported by Mcgowan [32]. Finally, the HLB value of the catanionic surfactant system can be calculated according to Equation (2).

$$HLB = \sum (F_i \times HLB_i) \tag{2}$$

where F_i is the mass proportion of each surfactant in the system. HLB_i is the HLB value of each surfactant.

2.6. Emulsifying and Viscosity Reduction of Shale Oil Experiment

First, according to the molar ratio of 6:4, CTAB and AOS were dissolved in 25 mL of water to assemble a catanionic surfactant (i.e., PSG) with a desired mass concentration. Then, the preheated shale oil was heated to 50 °C and gradually added into 0.2% PSG surfactant solution in a beaker, and the system was placed in a digital display constant-temperature water bath (HH, Changzhou Future Instrument Manufacturing Co., LTD, Changzhou, China) at 50 °C for 30 min. Subsequently, the mixture was stirred manually and thoroughly using a glass rod for 2 min at 50 °C to form a stable and homogeneous emulsion. The mass percentages of PSG in the water were from 0.1 % to 0.5%. The oil-to-water mass ratios were from 90:10 to 10:90.

The emulsifying and viscosity reduction rate was calculated according to Equation (3).

$$\varphi_e = \frac{\eta_0 - \eta_e}{\eta_0} \times 100(\%) \tag{3}$$

where η_0 and η_e are the viscosity of shale oil at 50 °C before and after emulsifying, mPa·s.

Finally, demulsification performance after emulsifying and viscosity reduction was evaluated. The above emulsion was poured into a 50 mL measuring cylinder with a stopper and placed in an oven at 80 °C for 2 h. The volume of water separation was observed and immediately recorded, and then the demulsification rate of shale oil emulsion was calculated according to Equation (4).

$$\varphi_d = \frac{25 - V_w}{25} \times 100\ (\%) \tag{4}$$

where V_w is the volume of water separation from shale oil emulsion after standing at 80 °C for 2 h, mL.

2.7. Morphology and Droplet Size Distribution Measurements

A drop of shale oil or emulsion was placed on the slide, and then the cover slide was covered with tweezers. The emulsified structure of shale oil was observed with a polarizing microscope (ECLIPSE 80i, Nikon, Tokyo, Japan), and photo images were taken. The average particle size of the emulsion drops was measured by instrument software (NIS-Elements D 3.0).

2.8. Viscosity Measurements

First, the sample was heated in an oven at 50 °C for 30 min, and then 5 mL was taken out and poured into the sample cup. Subsequently, the sample was heated evenly at 50 °C for 10 min. The viscosimeter (DV2TLVTJ0, BROOKFIELD, Middleboro, MA, USA) and 18# rotor was used to test the sample viscosity at 10 rpm, and the sample was measured in parallel 3 times and the average value of viscosity was recorded.

2.9. Determination of Interfacial Tension (IFT)

The ability of surfactants to reduce the interfacial tension between shale oil and water was evaluated by a rotating drop interfacial tensiometer (701, CNG, Chicago, IL, USA). The sample tube was first filled with a surfactant solution using an injection, and then a small amount of shale oil was attached to the inner wall of the sample tube with the tip of a needle. After the sample tube was installed, the interfacial tension was tested at 90 °C and 5000 rpm for 20 min. The equilibrium interfacial tension was finally obtained.

3. Results and Discussion

3.1. Physicochemical Properties of Shale Oil

The physicochemical properties of shale oil significantly affect the interface properties between oil, water, and shale, thus affecting the efficient development of shale oil. As shown in Table 3, the viscosities of the five shale oils are as follows, GY734H > GY512L > GY152H

> GY151H > GY735H, and the change in law of density and viscosity is almost the same. That is, the greater the viscosity of shale oil, the higher the corresponding density, which is like the property of heavy oil. In addition, the pour point and wax content of these shale oils are between 34 and 49 °C, and 20.24 and 30.49%, respectively. As a result, they are almost in a solid state at room temperature, resulting in no fluidity.

Table 3. Physicochemical properties of shale oil.

Property	GY151H	GY152H	GY734H	GY735H	GY512L
Viscosity at 50 °C, mPa·s	87.27	142.49	2220	58	726
Density at 20 °C, g/cm^3	0.8859	0.9016	0.9048	0.8301	0.8997
Pour point, °C	34	37	42	32	49
Wax content, %	26.40	30.49	23.54	27.12	20.24

3.2. Characterization of Catanionic Surfactant Systems

3.2.1. Oil/Water Interfacial Tension

Surfactants play a key role in interfacial tension reduction during emulsification. The surfactant molecules adsorb at the interface of crude oil and water, thus reducing the interfacial tension [33]. This phenomenon of interfacial tension reduction depends on the chemical structure and concentration of the surfactant itself, as well as the external environment, such as temperature and salinity of water [34]. As shown in Figure 1a, the oil/water interfacial tension between GY734H shale oil and surfactant aqueous solution gradually decreases with the increasing the ratio of cationic surfactant CTAB. The interfacial tension reaches the lowest value at the molar ratio of 6:4, and gradually increases when the ratio of CTAB is further increased. The same is true for GY151H shale oil, indicating that the interfacial activity of catanionic surfactants assembled by electrostatic interaction in the water phase is the strongest at the optimal molar ratio of 6:4 (CTAB/AOS). The catanionic surfactant has a double-headed and double-tailed structure, behaving like a Gemini surfactant, which can also be called "pseudogemini surfactant". Compared to conventional Gemini surfactants linked by covalent bonds, the pseudogemini surfactant assembled by electrostatic interaction has been studied extensively due to its unique characteristics, including simple synthesis procedures, multifarious aggregate structures, a strong capability to reduce oil/water interfacial tension, and so on [19,35]. As shown in Figure 1b, the oil/water interfacial tension gradually decreases with increasing the PSG surfactant concentration, The interfacial tension reaches the lowest value of 0.0287 mN /m at 0.2%, and gradually increases when the concentration is further increased. Adsorption of surfactant molecules at the oil/water interface reaches equilibrium when the surfactant concentration is further increased, so the change trend of interfacial tension becomes slow. This result shows that 0.2% is the optimal concentration of PSG surfactants, which can not only reduce the interfacial tension between shale oil and water to the lowest value, but also meet the surfactant concentration standard used in the oilfield.

Generally, as typical high-temperature reservoirs, shale reservoirs are buried deeper than conventional reservoirs. Therefore, it is crucial to study the effect of temperature on the interfacial tension between shale oil and surfactant solution. As shown in Figure 1c, the oil/water interfacial tension gradually decreases with increasing the test temperature. After fitting, it was found that there is almost a linear relationship between temperature and interfacial tension. According to the linear equation, it can be inferred that the interfacial tension can be reduced to below 10^{-3} mN/m under the temperature (120–150 °C) of the shale reservoir in the second member of Kongdian Formation, Cangdong Sag, Bohai Bay Basin, China. Furthermore, 0.2% PSG solution can still reduce the interfacial tension to less than 0.01 mN/m after aging at 150 °C for one month, indicating that it has strong high-temperature stability and can be used in shale oil reservoir conditions. Considering the salinity of field water in the actual application, the effect of water quality on the interfacial tension of oil and water was also studied. The total salinity of distilled water, tap water, and field water is 11 mg/L, 254 mg/L, and 27,119 mg/L, respectively (Table 2). As shown in Figure 1d, it can be found that the oil/water interfacial tension gradually decreases with increasing the salinity in the water phase. Surprisingly, 0.2% PSG solution after using field water can reduce the interfacial tension of GY734H shale oil to 0.0033 mN /m. For several other shale oils, the interfacial tension can also be reduced to less than 0.01 mN /m using field water (Table 4), indicating that the catanionic surfactant has ultra-high interfacial activity in field water and excellent salt resistance.

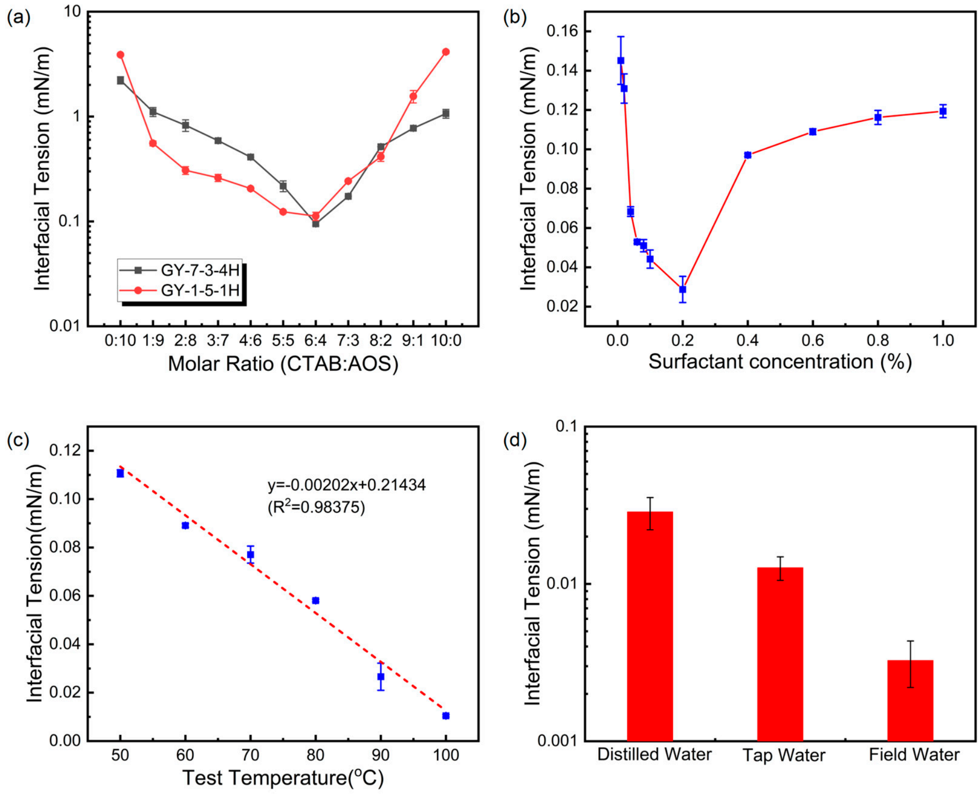

Figure 1. (**a**) Effect of surfactant molar ratio on interfacial tension between shale oil and 0.2% PSG solution at 90 °C; (**b**) effect of PSG (CTAB/AOS = 6:4, molar ratio) concentration on the interfacial tension between GY734H shale oil and water at 90 °C; (**c**) effect of temperature on the interfacial tension between GY734H shale oil and 0.2% PSG solution (CTAB/AOS = 6:4, molar ratio); (**d**) effect of water quality on the interfacial tension between GY734H shale oil and 0.2% PSG solution at 90 °C.

Table 4. Interfacial tension between shale oil and field water with or without PSG surfactant.

Shale Oils	Interfacial Tension (mN/m)	
	With Field Water	With 0.2% PSG Aqueous Solution
GY151H	9.9586	0.0049
GY152H	7.3441	0.0028
GY735H	11.4108	0.0087
GY512L	10.5533	0.0054

3.2.2. Critical Micelle Concentration

For ionic surfactants, when the concentration is less than the critical micelle concentration (CMC), it exists in the form of ions in water and has strong conductivity; while the concentration is greater than CMC, micelles gradually form [36]. Due to the large volume of micelles, their conductivity decreases compared with free ions, and the slope of the curve decreases [37].

Therefore, the CMC value can be obtained from the turning point of the curve of conductivity with surfactant concentration. As shown in Figure 2, the CMC of CTAB and AOS measured by the conductivity method is 0.8608 mmol/L and 0.5105 mmol/L, respectively, while the results reported in the literature are 0.82–1.09 mmol/L and 0.13–3.17 mmol/L, respectively [38–41], indicating that the measured results of conductivity are basically consistent with those reported in the literature. According to Clint theory, the CMC of PSG assembled by electrostatic interaction between CTAB and AOS at the optimal molar ratio (i.e., 6:4) in the water is 0.4825 mmol/L, while the experimental result is 0.4271 mmol/L. The comparison shows that the experimental and calculated values of the CMC for PSG are very close, indicating that the CMC results are credible.

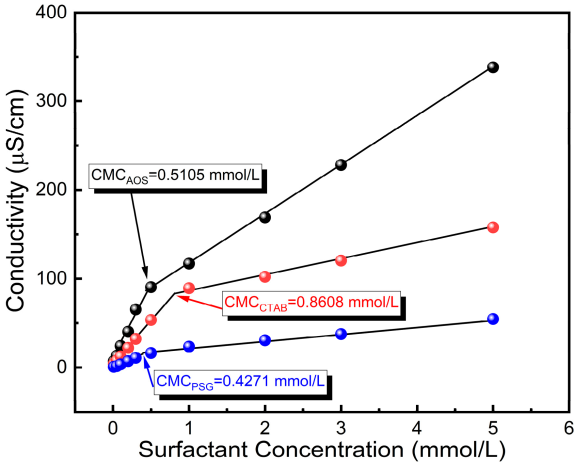

Figure 2. Relationship between surfactant concentration and solution conductivity.

3.2.3. Hydrophilic Lipophilic Balance Value

In addition to CMC, hydrophilic–lipophilic balance value (HLB) is also an important parameter of surfactants, which reflects the hydrophilic–lipophilic properties of surfactant molecules. In general, a high HLB value indicates that the surfactant has strong hydrophilicity and poor lipophilicity, and vice versa. According to reports in the literature, the HLB value of CTAB is 15.8 [31], while the HLB value of AOS is 10.4, calculated according to the method proposed by Mcgowan [32]. As a result, the HLB value of the catanionic surfactant PSG calculated by using Equation (2) is 13.8. Thus, PSG can be used as an O/W emulsifier, because the hydrophilicity of the surfactant is stronger than the lipophilicity at the HLB value of 10–15 [42,43].

3.3. Emulsifying and Viscosity Reduction of Shale Oil

3.3.1. Effect of Surfactant Molar Ratio on Emulsifying and Viscosity Reduction of Shale Oil

The molar ratio of CTAB and AOS affects the emulsifying performance by influencing the interfacial tension of shale oil and water. The effect of the mixed molar ratio of CTAB and AOS on emulsifying and viscosity reduction of shale oil was studied with the total concentration of fixed surfactant of 0.2%. As shown in Figure 3, the drainage rate of shale oil emulsion after emulsifying and viscosity reduction first decreases and reaches the lowest at 6:4, and then increases with the increasing molar ratio of CTAB, indicating that the catanionic surfactant assembled at the molar ratio of 6:4 has the strongest ability to stabilize shale oil-in-water (O/W) emulsion. Because PSG molecules can stably absorb at the interface of shale oil and water, the interfacial film strength is the strongest at this time, reducing the interfacial tension between PSG solution and shale oil. Therefore, this molar ratio was used for experiments in subsequent studies.

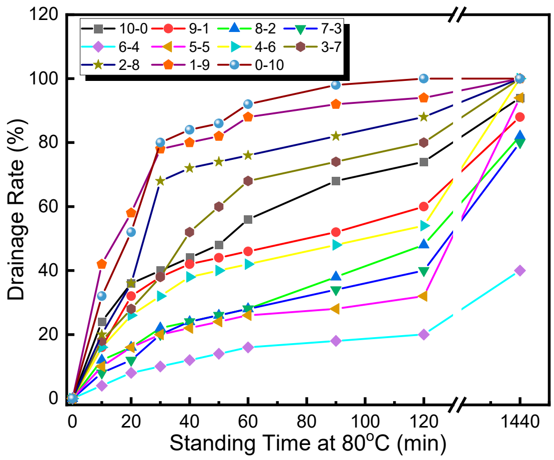

Figure 3. Effect of surfactant molar ratio on drainage rate of shale oil emulsion formed by using 0.2% PSG solution.

3.3.2. Effect of Surfactant Concentration on Emulsifying and Viscosity Reduction of Shale Oil

Surfactant concentration affects the strength of the interfacial film of the emulsion, thereby influencing the stability of the emulsion [44]. As shown in Table 5, the initial viscosity of shale oil at 50 °C is 2220 mPa·s, and it was found to be water-in-shale oil (W/O) emulsion by optical microscopy, causing poor fluidity (Figure 4a). However, when PSG aqueous solution was used as an emulsifying viscosity reducer and mixed with shale oil, something incredible happened. When the concentration of PSG is lower than 0.2%, the stability of the shale oil emulsion formed after emulsifying is very poor, and the separation of shale oil and water occurs immediately in 1–2 min, resulting in unmeasurable viscosity of the mixed system. Surprisingly, when the PSG concentration is higher than 0.2%, O/W emulsion is formed after emulsifying (Figure 4b), causing excellent fluidity. Meanwhile, the viscosity of the system is lower than 33 mPa·s, and the viscosity reduction rate is more than 99%. In addition, the drainage rate of the formed O/W emulsion after standing at 80 °C gradually decreased with increasing PSG concentration (Figure 5), indicating that the stability of the system was enhanced. Because more surfactant molecules were adsorbed at the oil/water interface, which enhanced the strength of the interface film. Interestingly, under the condition of no demulsifiers, the demulsification efficiency of the emulsion is higher than 90% after standing at 80 °C for 2 h, which can meet the requirements of the oilfield. Therefore, considering the application cost and the stability of the shale oil emulsion, 0.2% was selected as the optimal concentration for PSG in the follow-up study.

Table 5. Effect of surfactant concentration on emulsifying and viscosity reduction of shale oil.

Sample	Viscosity at 50 °C (mPa·s)	Viscosity Reduction Rate (%)	Phenomenon
Shale oil (GY734H)	2220	/	Stable W/O
Shale oil + 0.1%PGS	/	/	Unstable O/W
Shale oil + 0.2%PGS	33	98.51	O/W
Shale oil + 0.3%PGS	30	98.65	O/W
Shale oil + 0.4%PGS	28	98.74	O/W
Shale oil + 0.5%PGS	29	98.69	O/W

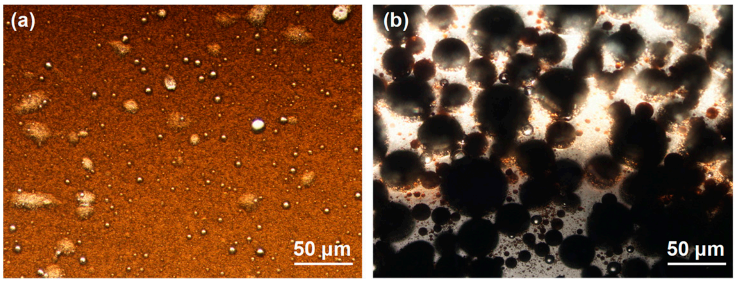

Figure 4. Micro-optical images of shale oil (**a**) before and (**b**) after emulsifying and viscosity reduction with 0.2% PSG solution.

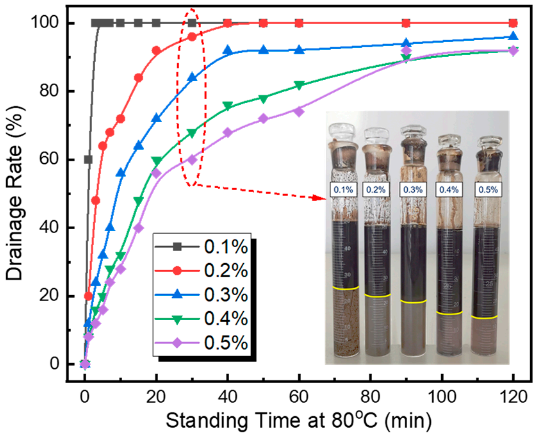

Figure 5. Effect of surfactant concentration on drainage rate of shale oil emulsion.

3.3.3. Effect of Temperature on Emulsifying and Viscosity Reduction of Shale Oil

The temperature affects the viscosity of shale oil, thereby resulting in the dispersion of shale oil in water. Therefore, the effect of temperature on emulsifying and viscosity reduction of shale oil was studied in detail. As shown in Table 6, the viscosity of the formed O/W emulsion decreased slightly with increasing the emulsification temperature, and the viscosity reduction rate was higher than 99%. Because the continuous phase is water, the emulsification temperature has little influence on the viscosity of the continuous phase in the emulsion after emulsifying and viscosity reduction. However, the increase in temperature causes the initial viscosity of shale oil to decrease, which facilitates its dispersion in water, thus promoting the emulsifying and viscosity reduction process.

Table 6. Effect of temperature on emulsifying and viscosity reduction of shale oil.

Temperature (°C)	**Viscosity at 50 °C (mPa·s)**	**Viscosity Reduction Rate (%)**	**Phenomenon**
50	33	98.51	O/W
60	32	98.56	O/W
70	31	98.60	O/W
80	28	98.74	O/W
90	25	98.87	O/W

3.3.4. Effect of Oil/Water Mass Ratio on Emulsifying and Viscosity Reduction of Shale Oil

The mass ratio of crude oil to water has a significant influence on the viscosity of the system after emulsifying. The high ratio does not facilitate the formation of a stable O/W emulsion, resulting in a higher viscosity of the system than that of initial shale oil, while the low ratio facilitates the emulsifying and viscosity reduction, increasing the cost of oil recovery due to high water consumption [12]. Therefore, the aqueous solution of 0.2% PSG was used as the emulsifier for the investigation into the effect of the oil-to-water mass ratio on the viscosity of the shale oil/water/PSG mixture. As shown in Table 7, the viscosity of emulsion formed after emulsifying first increases and then decreases with a decreasing oil/water ratio at the concentration of 0.2% PSG. The W/O emulsion is formed after emulsifying when the oil/water ratio is higher than 6:4, while the reverse phase occurs and the O/W emulsion is formed after emulsifying when the oil/water ratio is lower than 6:4. Furthermore, the viscosity reduction rate is higher than 99% when the oil/water ratio is lower than 5:5, indicating that the best oil/water ratio is 5:5 (i.e., 1:1) for emulsifying and viscosity reduction of shale oil.

Table 7. Effect of oil/water mass ratio on emulsifying and viscosity reduction.

Oil-to-Water Ratio	Viscosity at 50 °C (mPa·s)	Viscosity Reduction Rate (%)	Phenomenon
Shale oil (GY734H)	2220	/	Stable W/O
9:1	3171	−42.84	W/O
8:2	3615	−62.84	W/O
7:3	1480	33.33	O/W and O/W
6:4	365	83.56	O/W
5:5	33	98.51	O/W
4:6	28	98.74	O/W
3:7	21	99.05	O/W
2:8	15	99.32	O/W
1:9	12	99.46	O/W

3.3.5. Effect of Water Quality on Emulsification and Viscosity Reduction of Shale Oil

In oil field production, field water or brine is often readily available for the injection and preparation of chemical agents, but distilled water or fresh water is not easy to obtain. Field water contains a variety of ions, resulting in high salinity. Consequently, the effect of water quality on emulsification was studied here. As shown in Table 8, the viscosity of O/W emulsion formed after emulsifying for shale oil decreases gradually with increasing the water salinity at an oil/water ratio of 1:1. The viscosity reduction effect of field water is better than that of distilled water and tap water. Because the interfacial tension between PSG aqueous solution prepared with field water and shale oil is lower than that between distilled or tap water, and PSG molecules are adsorbed more easily at the oil/water interface in field water, thus stabilizing the emulsion. Bastian et al. found that seawater and formation water have a strongly reducing effect on oil/water interfacial tension when they investigated the influence of salinity on reservoir fluid interfacial tension [45]. Low interfacial tension is conducive to emulsification and viscosity reduction of crude oils. Therefore, the catanionic surfactant not only has outstanding salt resistance, but is also conducive to oilfield application.

Table 8. Effect of total salinity of water on emulsifying and viscosity reduction of shale oil.

Sample	Total Salinity of Water (mg/L)	Viscosity at 50 °C (mPa·s)	Viscosity Reduction Rate (%)	Phenomenon
Shale oil (GY734H)	/	2220	/	Stable W/O
Shale oil + distilled water with 0.2% PGS	13	51	97.70	O/W
Shale oil + tap water with 0.2% PGS	254	35	98.42	O/W
Shale oil + field water with 0.2% PGS	27,119	33	98.51	O/W

3.3.6. Effect of Shale Oil Type on Emulsification and Viscosity Reduction of Shale Oil

Generally, shale oils are very different in physicochemical properties, and emulsion viscosity is influenced by the characteristics of crude oils. In the experiment, to study the universality of the catanionic surfactants, five kinds of shale oil from the second member of Kongdian Formation, Cangdong Sag, Bohai Bay Basin, China were selected for emulsification and viscosity reduction experiments. It was found that O/W emulsions are formed after emulsifying the five shale oils with 0.2% PSG at an oil/water ratio of 1:1 and 50 °C, and the viscosity is lower than 35 mPa·s (Table 9). The catanionic surfactant assembled by us has excellent universality and can be used for emulsifying and viscosity reduction of various shale oils, thereby improving the fluidity of shale oil. It is beneficial to improve oil recovery and efficient gathering and transportation.

Table 9. Effect of shale oil type on emulsification and viscosity reduction.

Sample	Viscosity at 50 °C (mPa·s)		Viscosity Reduction Rate (%)	Phenomenon
	Before Emulsifying	After Emulsifying		
GY734H	2220	33	98.51	O/W
GY735H	238	35	85.29	O/W
GY151H	137	28	79.56	O/W
GY152H	142	30	78.87	O/W
GY512L	726	28	96.14	O/W

3.4. *Proposed Mechanism*

At the oil/water ratio of 1:1 and emulsifying temperature of 50 °C, the mechanism of emulsifying and viscosity reduction of shale oil with 0.2% PSG aqueous solution is proposed. As shown in Figure 6, for catanionic surfactant PSG assembled by electrostatic interactions between CTAB and AOS in an aqueous phase, the sulfonic acid group and quaternary amine group are hydrophilic parts, and the two long carbon chains are hydrophobic parts, which is like the structure of Gemini surfactants. As a result, it exhibits extremely high surface and interface activity. The initial shale oil has high viscosity due to its high wax content and a small amount of water, which forms a W/O emulsion. When PSG aqueous solution as an emulsifier is mixed manually with shale oil at 50 °C, PSG molecules are gradually adsorbed at the interface between shale oil and water, resulting in a significant reduction in interfacial tension. At this moment, the W/O emulsion is gradually reversed into O/W emulsion. Because the continuous phase is water, the viscosity of the system is significantly reduced, thus improving the fluidity of shale oil. After standing for some time, the temperature of the system decreases, and the wax crystals in the shale oil gradually accumulate, resulting in the rapid aggregation of oil droplets, and finally the separation of shale oil and water.

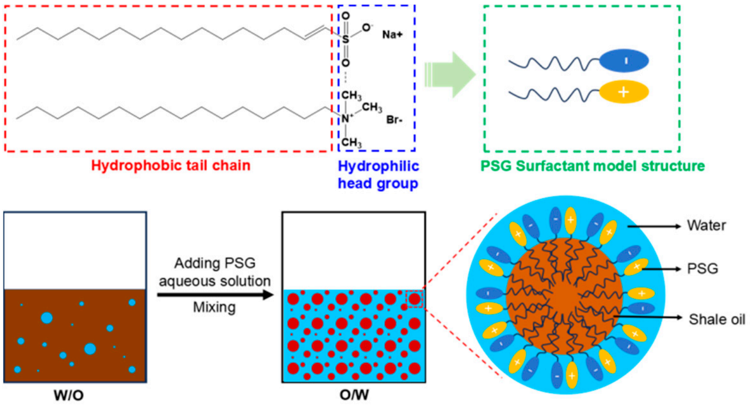

Figure 6. Mechanism of emulsifying and viscosity reduction of shale oil.

4. Conclusions

In summary, a kind of catanionic surfactant (PSG) was assembled by the electrostatic interaction between cationic surfactant CTAB and anionic surfactant AOS in the aqueous phase to reduce the viscosity of shale oil. PSG has excellent surface and interface activity, with a CMC of 0.4825 mmol/L. At the same time, its HLB value is 13.83, making it suitable for use as an O/W emulsifier. The 0.2% PSG can reduce the interfacial tension between shale oil and water to less than 0.01 mN/m in the field water with a salinity of 27,119 mg/L. Additionally, it can emulsify five kinds of shale oil to form O/W emulsions at an oil-to-water ratio of 1:1 and 50 °C, reducing the viscosity of shale oil to less than 35 mPa·s, thereby improving its fluidity. Moreover, without any additional demulsifiers, this system spontaneously separates into oil and water phases after two hours, achieving a demulsification rate higher than 85%. This work solves the problems of high viscosity and poor fluidity in shale oil and shows promising application potential in the efficient development, gathering, and transportation of shale oil. In the future, we will study the synergistic effect of this surfactant in CO_2 huff-n-puff and smart fracturing to improve shale oil recovery in Bohai Bay Basin, east China.

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