Article

Study on the Stability of Produced Water from Alkali/Surfactant/Polymer Flooding under the Synergetic Effect of Quartz Sand Particles and Oil Displacement Agents

Bin Huang [1,2,*], Chen Wang [1], Weisen Zhang [1], Cheng Fu [1,2,*], Haibo Liu [3] and Hongwei Wang [3]

[1] The Key Laboratory of Enhanced Oil and Gas Recovery of Educational Ministry, Northeast Petroleum University, Daqing 163318, China; wangchen534@163.com (C.W.); zws369948219@163.com (W.Z.)

[2] Post-Doctoral Research Station of Daqing Oilfield, Daqing 163458, China

[3] Exploration and Development Research Institute of Daqing oilfield, Daqing 163712, China; liuhaibocsl@petrochina.com.cn (H.L.); yjy-whw@petrochina.com.cn (H.W.)

[*] Correspondence: huangbin111@163.com or huangbin@nepu.edu.cn (B.H.); cheng_fu111@163.com or fucheng@nepu.edu.cn (C.F.)

check for updates

Abstract: With the wide application of ASP (alkali/surfactant/polymer) flooding oil recovery technology, the produced water from ASP flooding has increased greatly. The clay particles carried by crude oil in the process of flow have a synergetic effect with oil displacement agents in the produced water, which increases the treatment difficulty of produced water. The stability of produced water is decided by the stability of oil droplets in the ASP-flooding-produced water system. The oil content, Zeta potential, interfacial tension and oil droplet size are important parameters to characterize the stability of produced water. In this paper, the changes of the oil content, Zeta potential, interfacial tension and oil droplet size of ASP flooding oily wastewater under the synergetic effect of different concentrations of quartz sand particles and oil displacement agents were studied by laboratory experiments. The experimental results show that the negatively charged quartz sand particles can absorb active substances in crude oil and surfactant molecules in the water phase and migrate to the oil–water interface, which increases the repulsion between quartz sand particles, decreasing the oil–water interfacial tension. Thus, the stability of oil droplets is enhanced, and the aggregation difficulty between oil droplets and quartz sand particles is increased. With the continually increasing quartz sand concentration, quartz sand particles combine with surfactant molecules adsorbed on the oil–water interface to form an aggregate. Meanwhile, the polymer molecules crimp from the stretching state, and the number of them surrounding the surface of the flocculation structure is close to saturation, which makes the oil droplets and quartz sand particles prone to aggregation, and the carried active substances desorb from the interface, resulting in the instability of the produced water system. The research on the synergetic effect between quartz sand particles and oil displacement agents is of great significance for deepening the treatment of ASP-produced water.

Keywords: quartz sand particle; produced water system; ASP oil displacement agent; oil–water interface; oil droplet stability

1. Introduction

At present, the water content of produced liquid in most Chinese oil fields is up to more than 90%. With the continuous decline of water production and the scattered distribution of remaining oil, it is increasingly difficult to develop oilfields, and the recovery ratio is generally 30%–40% [1].

Alkali–surfactant–polymer (ASP) flooding oil recovery technology is built on alkali–polymer flooding and surfactant–polymer flooding. ASP flooding is a method to greatly improve oil recovery [2]. It can increase the recovery ratio by more than 20% under the condition that the water cut of oil fields reaches 98%, which has become an economic and effective method to enhance oil recovery [3].

The ASP-flooding-produced water is an oily wastewater containing oil-displacing agents after the oil and water separation from the ASP-flooding-produced liquid [4]. Due to the synergy between the alkali, polymer and surfactant, ASP-flooding-produced water is difficult to treat, and some conventional oil–water separation treatment technologies become invalid in ASP-flooding-produced water [5,6]. China needs to treat 500 million m^3 of produced water from oil fields every year, and oil fields spend a lot of money on produced water treatment every year. The effect of treatment is related to the injection quality of produced water in oil fields, as well as to environmental problems [7].

In recent years, a large number of research works have been studied on the treatment of ASP-flooding-produced water at home and abroad, mainly focusing on the effects of oil displacement agents on the properties of the oil–water interface [5,6,8], the screening of chemical agents [9,10] and the improvement of treatment equipment [11,12]. Deng Shubo et al. studied the effect of oil displacement agents on the stability of ASP-flooding-produced water and found that the surfactant had the greatest influence on the stability of oil droplets, which hindered the coalescence of oil droplets and increased the difficulty of oil–water separation [6]. The Daqing oilfield institute hydration chamber has studied the oil–water separation characteristics, microstructure, interfacial properties and chemical agents of ASP-flooding-produced water and achieved good results [13,14]. Ye Qing et al. found that, in addition to the type of oil displacement agents, the pH value and salinity of the produced water also affect the oil–water separation [15]. Di et al. [16] designed a new type of ASP-flooding oil–water separator, and the experimental results showed that the oil–water separation rate could reach above 98%. Although some progress has been made in these studies, the existence of clay particles in produced water has not been considered. When the oil displacement agent flows through the formation, it will absorb the mineral substances and clay particles in the formation, carry the clay particles and combine with crude oil in the formation. The crude-oil-produced liquid is dehydrated to obtain crude oil and produced water; some clay particles can enter the produced water, making the produced water contain clay particles from formation. Clay particles have a synergy with oil displacement agents, which affects the stability of ASP-flooding-produced water, increases the treatment difficulty of ASP-flooding-produced water [17] and thus limits the popularization of ASP flooding oil recovery technology. Based on the analysis of the soil geology of Daqing oil field, it is found that quartz sand is the most common type of solid particle of the clay [18].

In this paper, simulated ASP-flooding-produced water containing quartz sand particles was prepared by a laboratory experiment. The effects of oil displacement agent concentration and quartz sand particle concentration on the stability of the produced water system were systematically studied, summarizing the influence rule of the quartz sand particles and oil displacement agent on the stability of oil droplets in ASP-flooding-produced oily water and analyzing the active mechanism of quartz sand particles and oil displacement agent on oil droplets in the produced water system.

2. Experimental Materials and Methods

2.1. Experimental Materials

Crude oil with a density of 860 kg/m^3, viscosity of 60 mPa·s and water content of less than 0.5% at 45 °C was provided by Daqing oilfield No.1 oil recovery plant (Daqing, China). The polymer was analytically pure hydrolyzed polyacrylamide (HPAM) with a molecular weight of 3 million and hydrolysis degree of 25%–30%, which was provided by Daqing oilfield oil recovery engineering (Daqing, China) research institute. The surfactant was alkyl benzene sulfonate (ORS-41), mass fraction was 50%, provided by Daqing oilfield No. 1 oil recovery plant (Daqing, China). The alkali was analytically pure NaOH with a mass fraction of 30% and was provided by Daqing oilfield oil recovery

engineering research institute (Daqing, China). Analytically pure quartz sand particles were provided by Daqing oilfield No. 1 oil recovery plant (Daqing, China). Analytically pure sodium chloride was provided by the Tianjin Damao Chemical Reagent Plant (Tianjin, China). Analytically pure sodium bicarbonate, anhydrous sodium sulfate, and anhydrous sodium carbonate were provided by the Tianjin Yaohua Chemical Plant (Tianjin, China). Analytically pure anhydrous calcium chloride and magnesium chloride were provided by the Harbin Xinda Chemical Plant (Harbin, China). Petroleum ether was provided by Shenyang Elepkes Chemical Co. Ltd (Shenyang, China). The experimental water was distilled water.

2.2. Instruments

A temperature-controlled bath box, type S501-2, was used to keep the emulsion temperature stable, from the Liaoyang Huaguang Instrument Factory (Liaoyang, China). A digital display dispersing machine, type IKAT25, was used for the preparation of different types of emulsion by uniform stirring, from the IKA company, (Staufen, Germany). An ultraviolet spectrophotometer, type TU-1901, was used for the determination of the oil content in emulsion, from Shanghai Mapda Instrument Equipment Co. Ltd (Shanghai, China). A laser particle size analyzer, type BT-9300H, was used to measure the particle size distribution of oil droplets in emulsion, from Suzhou Hinos Industrial Co. Ltd (Suzhou, China). A Zeta potentiometer, type JS94H, was used to measure the electrode potential between oil droplets, from Shanghai Zhongchen Digital Technology Instrument Co. LTD (Shanghai, China). A rotary drop ultra-low interfacial tensiometer, type XZD-5, was used for the determination of interfacial tension of the produced water system, from Beijing Hake Experimental Instrument factory (Beijing, China). The electronic balance, type BS210S, was from Shanghai Sadris Trading Co. Ltd (Shanghai, China). The micropipette, type Eppendorf, was from Eppendorf China Co. Ltd (Shanghai, China).

2.3. Preparation of Simulated ASP-Flooding-Produced Water Containing Quartz Sand Particles

According to the water quality characteristics of ASP-flooding-produced water in Daqing oilfield, the specific steps of simulated ASP-flooding-produced water containing quartz sand particles preparation were as follows:

(1) Preparation of mineralized water: refer to the salinity content of ASP-flooding-produced water in Daqing oilfield, the salinity of the mineralized water was determined; that is, the contents of NaCl, $NaHCO_3$, Na_2CO_3, Na_2SO_4, $CaCl_2$, $MgCl_2$, and other main components were, respectively, 1523, 2820, 168.7, 10.5, 56.9 and 35.5 mg/L.

(2) Preparation of oil droplet mother liquor: 0.4 g surfactant with a mass fraction of 50% and 199.6 g mineralized water were added to a 500 mL beaker, heated in a water bath to 45 °C, and then added to 200 g crude oil at 45 °C. Next, the high-speed shearing dispersing emulsifier was used to emulsify the emulsion at 20000 rpm for 10 min to produce the oil droplet mother liquor with an oil content of 50%.

(3) Next, 99.6 mL of mineralized water with different contents of oil displacement agents (alkali, polymer and surfactant) and quartz sand particles were added into a 250 mL beaker, then 0.4 g oil droplet mother liquor with a mass fraction of 50% was added. After shaking well, the simulated ASP-flooding-produced water containing quartz sand particles with an oil content of 2000 mg/L was prepared. The main indexes were an oil content < 3000 mg/L, alkali < 1500 mg/L, polymer < 800 mg/L, surfactant < 600 mg/L.

In order to introduce the processes between each measurement parameter more intuitively, we made a figure to explain the experimental set-up in the lab, as shown in Figure 1.
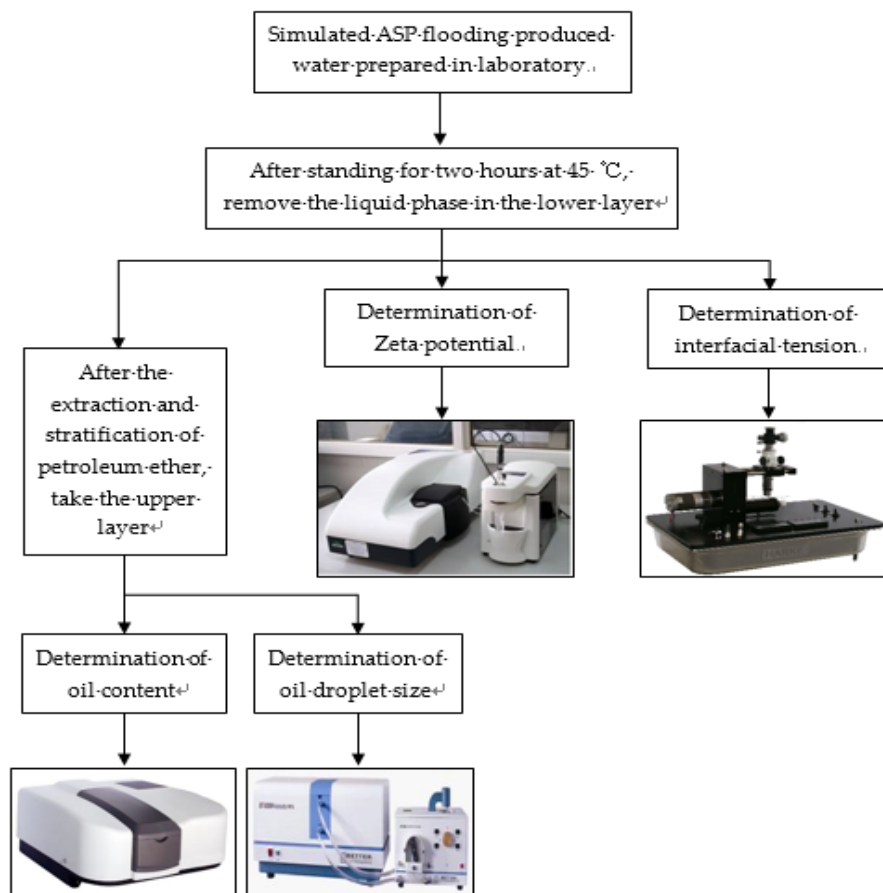
Figure 1. The experimental set-up in the laboratory.

2.4. Determination of Oil–Water Separation Characteristics

The characteristics of oil–water separation can be characterized by oil content, which is an important index to measure the stability of produced water emulsion [6]. With the increase of oil content, the stability of emulsion increases. The oil content in water is determined by ultraviolet spectrophotometry [19]. As the standard oil is crude oil, 254 nm is used as the absorption wavelength. First, the standard curve of oil content in water was drawn: 0.1 g crude oil was accurately weighed, dissolved in a 100 mL capacity bottle with petroleum ether and diluted to the scale. The oil content of the standard oil solution was 1000 mg/L. Then, 2 mL, 3 mL, 4 mL, 6 mL, 8 mL and 10 mL of the standard oil solution were transferred into the 10 mL colorimetrical cylinder by pipette; the volume was fixed with petroleum ether and shaken well. A series of samples with a known oil content was configured. We took petroleum ether as a blank, compared the colors on the ultraviolet spectrophotometer, drew the standard curve according to the measured luminosity value and corresponding oil content and took the oil content (mg/L) as the abscissa and absorbance (A) as the ordinate, as shown in Figure 2. The linear relationship in the figure is as follows:
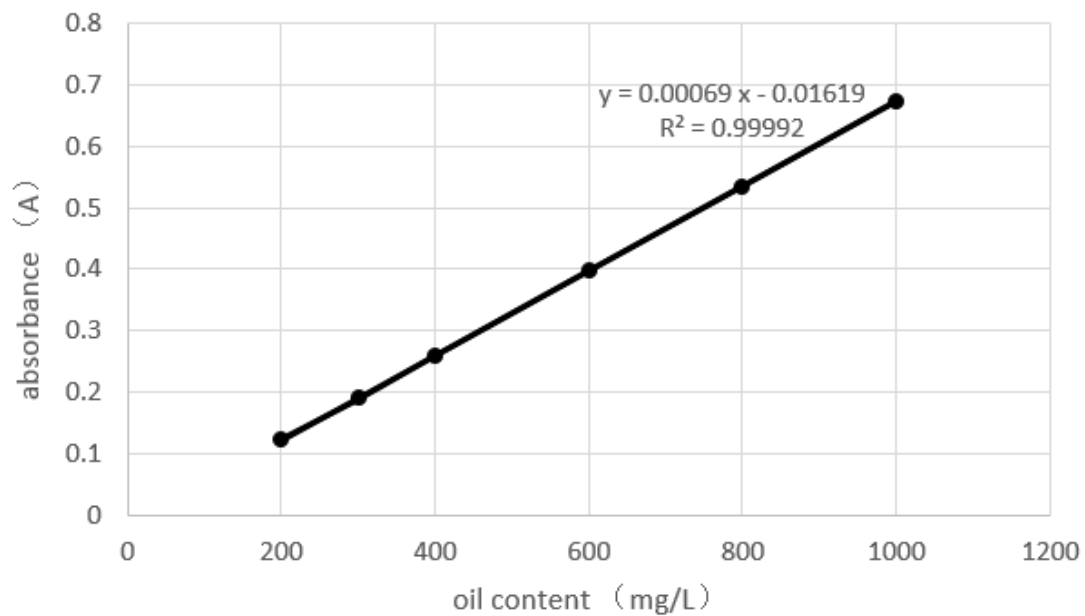
$$y = 0.00069x - 0.01619; \ R^2 = 0.99992.$$

Figure 2. The relationship between absorbance and oil content.

With petroleum ether as the reference liquid and simulated produced water containing different concentrations of quartz sand particles and oil displacement agents as the sample to be tested, the measured absorbance was substituted into the standard equation to calculate the oil content in the produced water.

2.5. Determination of Zeta Potential

According to the theory of interfacial charge [20], the oil droplets in ASP-flooding-produced water are charged. When two oil droplets approach each other, they generate electrostatic repulsion. The electrostatic repulsion must be overcome for the droplets to coalesce. Therefore, the greater the absolute value of the Zeta potential, the more difficult it is for oil droplets to coalesce and the more stable the emulsion is. Conversely, the smaller the absolute value of Zeta potential, the weaker the repulsion between oil droplets, and the more unstable the emulsion is.

After the simulated ASP-flooding-produced water containing quartz sand particles of different concentrations settled for 2 h, 5–10 mL water samples were taken out of the bottom of the reagent bottle and put into the colorimetrical cylinder as the samples to be tested. We repeated this 5 times for each sample, removed the maximum and minimum values, and the average Zeta potential values of the remaining 3 times were calculated. The relationship between system stability and Zeta potential is shown in Table 1.

Table 1. The relationship between system stability and Zeta potential.

Zeta Potential/mV	Colloidal Stability
below-70	Excellent stability
-70 to -50	Good stability
-50 to -30	General stability
-30 to -10	Begins to become unstable
-10– 0	Rapid aggregation

2.6. Determination of interfacial tension

In the stability system of emulsion, the oil–water interfacial tension is an important factor affecting its stability. The smaller the oil–water interfacial tension is, the more stable the emulsion system is. In terms of ASP-flooding-produced water, in addition to the interfacial active substances in the crude oil, the residual oil displacement agent components and the existence of clay particles will cause the change of interfacial tension [21].

First, we set the test temperature at 45 °C and the speed at 8500 r/min. Then, we injected the crude oil into the middle of the centrifuge tube by a microinjector, the centrifuge tube was put into the rotation axis of the instrument, the compression cap was tightened, and the rotation speed control was started to make the tube rotate at the set speed; the observation and reading were carried out after the tube was stabilized. Finally, the following formula was used for the calculation: $\gamma = 1.233 \times 10^3 \times \Delta\rho \times (Kd)^3 (6000/S)^{-2}$. In the formula, γ represents interfacial tension, mN/m; $\Delta\rho$ represents the oil–water phase density difference, g/cm^3; K represents amplification factor; d represents the width of the oil droplets, mm; and S represents the rotation speed, r/min.

2.7. Determination of Oil Droplet Size

The oil droplets particle size is determined by a type BT-9300H laser particle size distribution instrument. We loaded 600 mL deionized distilled water into a beaker, heated it to 45 °C and then poured it into the sample pool of the laser particle size distribution instrument, turned on the water circulation system and computer operating system and measured the background value at this time. Then, 50 mL of simulated ASP flooding oily sewage containing quartz sand particles at 45 °C was shaken well and held up for 4 hours, and an appropriate sample amount was extracted from the lower layer with a syringe, measuring the particle size distribution of oil droplets.

3. Experimental Results and Discussion

3.1. The Synergetic Effect of Quartz Sand Particles and Oil Displacement Agents on Oil–Water Separation Characteristics

The simulated ASP-flooding-produced water containing quartz sand particles was prepared in the laboratory, and the effects of different concentrations of quartz sand particles and oil displacement agents on the oil–water separation characteristics were investigated; the results are shown in the Figures 3–5 below.
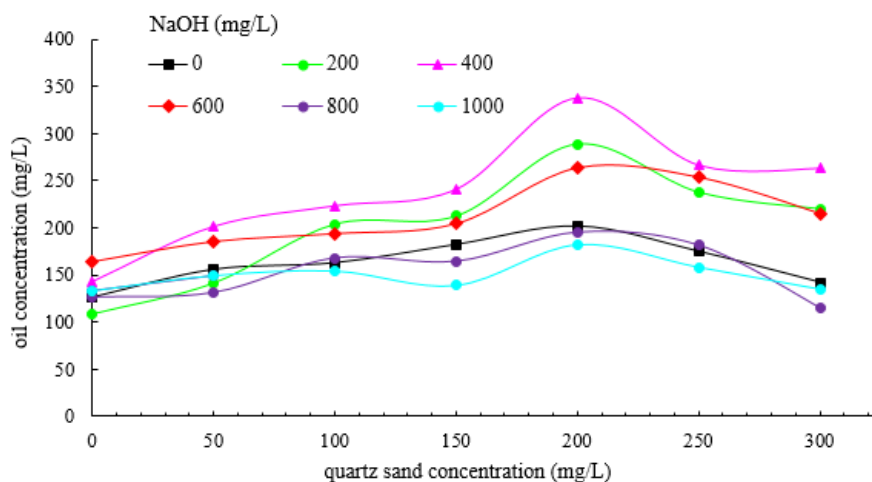

Figure 3. The synergetic effect of alkali and quartz sand particles on oil–water separation (polymer concentration 500 mg/L, surfactant concentration 200 mg/L).
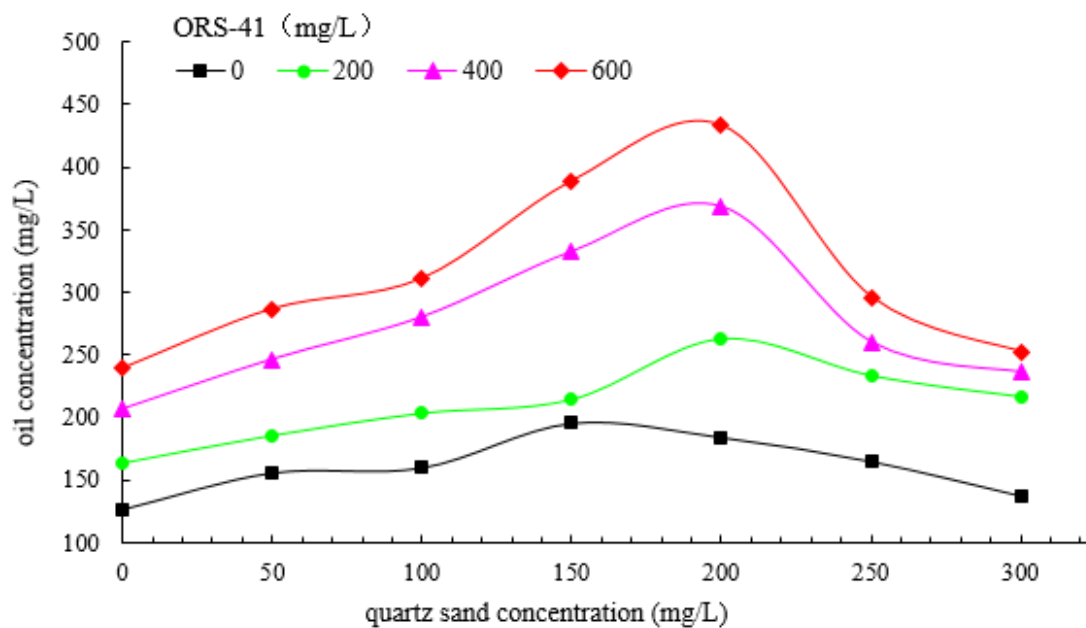
Figure 4. The synergetic effect of surfactant and quartz sand particles on oil–water separation (polymer concentration 500 mg/L, alkali concentration 600 mg/L).
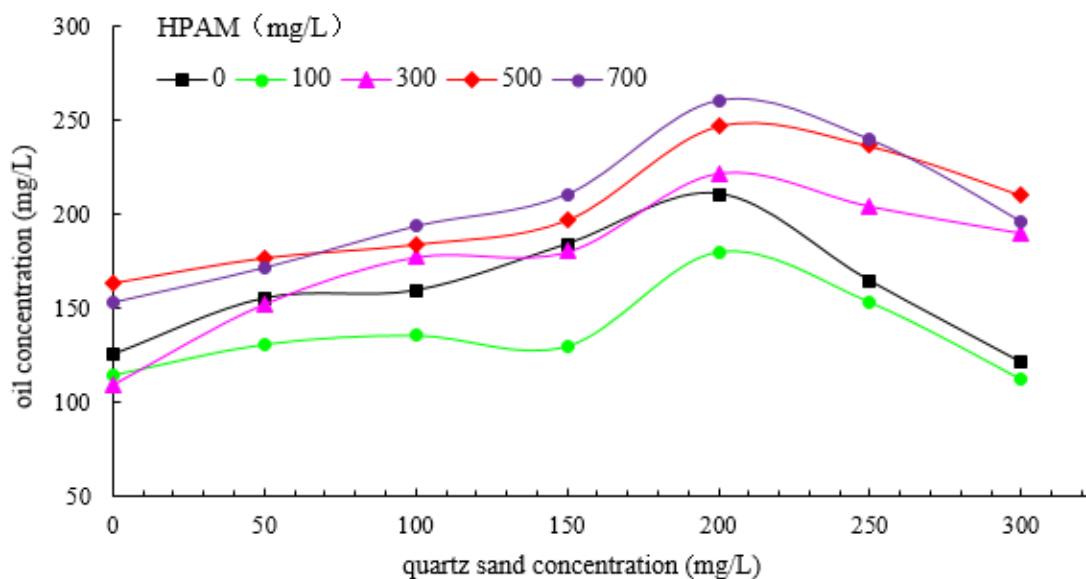

Figure 5. The synergetic effect of polymer and quartz sand particles on oil–water separation (alkali concentration 600 mg/L, surfactant concentration 200 mg/L).

3.1.1. The Synergetic Effect of Quartz Sand Particles and Alkali

When the NaOH concentration increases from 0 to 400 mg/L, the oil content increases with the increase of NaOH concentration. As the NaOH concentration continues to increase, the oil content gradually decreases; that is, the stability of oil droplets increases first and then weakens with the increase of NaOH concentration. Because there are acidic components in crude oil, they can react with NaOH to form a surfactant, and the newly generated surfactant and the original surfactant of the system will reduce the interfacial tension between oil and water, enhance the stability of oil droplets. The higher the concentration of surfactant adsorbed on the oil–water interface, the higher the oil content. When the NaOH concentration is more than 400 mg/L, NaOH has neutralized the acidic components in crude oil, there is a large amount of excess Na^+ in the water phase. Na^+ can neutralize the oil droplets' surface negative charge, reduce the oil droplets' surface negative charge density and

weaken the stability of the oil droplets [22]. At the same time, Na^+ can compress the structure of the double layer, weaken the acting force between oil droplets and facilitate the coalescence of oil droplets [23].

At first, the oil content increases with the increase of quartz sand concentration; then, the oil content decreases with the increase of quartz sand concentration because quartz sand particles are negatively charged and can be adsorbed on the oil droplets' oil–water interface, increasing the negative charge density of oil droplets' surface and enhancing the stability of oil droplets. The stability of the produced water system is the strongest when the quartz sand particle concentration is 200 mg/L. Since then, with the continuous addition of quartz sand, its concentration in the liquid phase increases continuously. Due to the action of gravity, quartz sand particles tend to aggregate, and polymer has the ability of flocculation. The aggregation of quartz sand and oil droplets can effectively promote the oil–water separation, making the produced water system unstable.

3.1.2. The Synergetic Effect of Quartz Sand Particles and Surfactant

As shown in Figure 4, the oil content increases with the increase of surfactant concentration, indicating that the surfactant can enhance the stability of oil droplets and make it difficult for small oil droplets to aggregate; this is because the surfactant can be adsorbed on the surface of oil droplets in the form of nonpolar groups sticking into oil droplets and polar groups sticking into the water, changing the surface properties of the oil droplets and making the surface of the oil droplets from hydrophobicity to hydrophilicity, thus making it difficult for oil droplets to approach each other, resulting in the increasing stability of oil droplets.

At the beginning, the oil content in the produced water increases with the increase of quartz sand concentration. When the quartz sand particle concentration is 200 mg/L, the oil content in the produced water reaches the maximum. Then, with the increase of quartz sand concentration, the oil content decreases, but the oil content is higher than the initial oil content because surfactant molecules can gather on the oil–water interface, forming a resistant film around the oil droplets that prevents them from coalescing [24]. When the quartz sand and surfactant exist in produced water at the same time, the surfactant will be adsorbed on the quartz sand particles in an aqueous phase, increasing the repulsion between the particles, hindering the coalescence of quartz sand particles and oil droplets and leading to the enhanced stability of produced water system. As the quartz sand concentration increases, the number of quartz sand particles adsorbed with surfactant molecules gradually reaches saturation and the excess quartz sand particles tend to aggregate with oil droplets, thus promoting the oil–water separation process.

3.1.3. The Synergetic Effect of Quartz Sand Particles and Polymer

It can be seen in Figure 5 that the oil content decreases first and then increases with the increase of polymer concentration; that is, the stability of oil drops decreases first and then increases. Because the polymer used in the experiment has a high molecular weight of 3 million, when the polymer concentration is low, though the addition of polymer increases the fluid film strength of oil droplets, the polymer molecules have bridging and flocculating effects, which can be adsorbed on the oil droplets' surface, causing the flocculation of dispersed oil droplets. Meanwhile, the polymer can compress the double electrode layer on the surface of oil droplets, weaken the acting force between oil droplets and reduce the stability of oil droplets. When the cover degree of polymer on the oil droplets' surface reaches 50% [25], the flocculation reaches its maximum. Then, as the polymer concentration continues to increase, on the one hand, the polymer molecules will produce a steric hindrance effect, which is not conducive to the coalescence of oil droplets [8]; on the other hand, with the increase of polymer concentration, the viscosity of the aqueous phase increases, which slows down the aggregation rate of oil droplets and enhances the stability of oil droplets.

When the quartz sand concentration is less than 200 mg/L, the oil content increases with the increase of quartz sand concentration. When the quartz sand concentration is more than 200 mg/L,

the oil content decreases with the increase of quartz sand concentration because the system salinity content is high. When the concentration of quartz sand particles is high, the polymer molecular morphology changes; it crimps from the stretching state [26]. The coverage on the surface of quartz sand particles decreases, and quartz sand particles tend to aggregate with oil droplets, thus facilitating the oil–water separation.

3.2. The Synergetic Effect of Quartz Sand Particles and Oil Displacement Agents on Zeta Potential

3.2.1. The Synergetic Effect of Quartz Sand Particles and Alkali

It can be seen in Figure 6 that when the alkali concentration increases from 0 to 400 mg/L, with the raising of alkali concentration, the Zeta potential decreases. With the further raising of alkali concentration, the Zeta potential increases, because when the alkali concentration is low, NaOH will react with acidic components to form a surface-active substance. The newly generated surface-active substance is adsorbed on the interface between oil and water, increasing the negative charge density on the oil droplets' surface and reducing the Zeta potential on the oil droplets' surface. When the alkali concentration further increases, the acidic components of crude oil are neutralized. The excess Na^+ in aqueous phase can neutralize the negative charge on the oil droplets' surface, thus reducing the negative charge density of the oil droplets' surface. At the same time, Na^+ can compress the diffuse electric double layer of the oil droplets' surface [22]. Under this joint action, the Zeta potential increases.
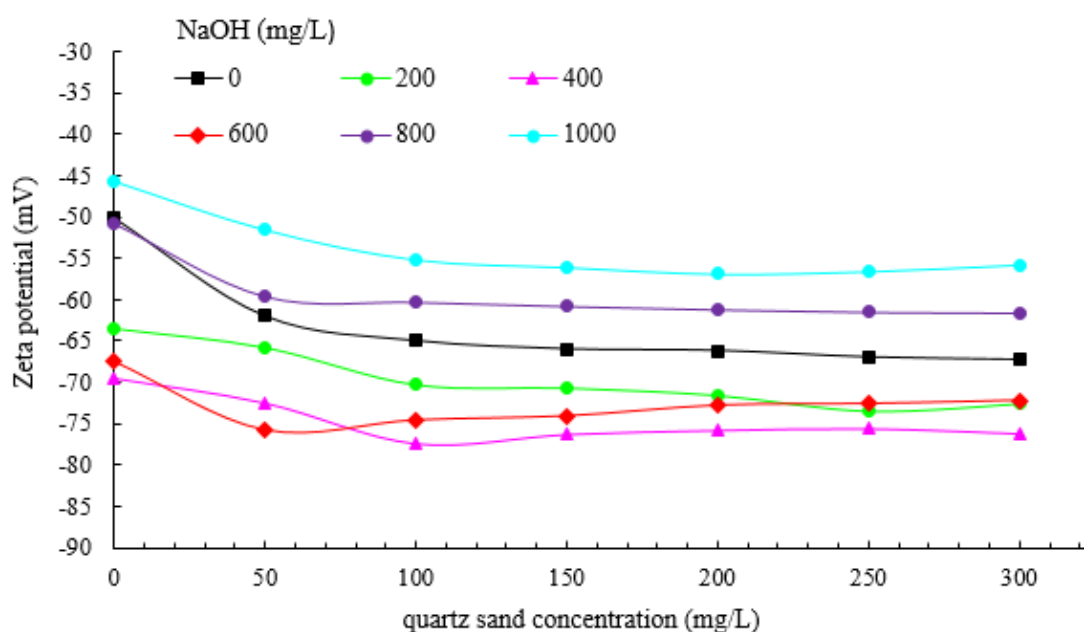

Figure 6. The synergetic effect of alkali and quartz sand particles on Zeta potential (polymer concentration 500 mg/L, surfactant concentration 200 mg/L).

When the quartz sand concentration is lower than 100 mg/L, the Zeta potential decreases gradually with the addition of quartz sand particles. With the further raising of quartz sand concentration, the Zeta potential remains almost unchanged and tends to be stable. The quartz sand particles carry negative charges and can adhere to the oil droplets' surface, increasing the negative charge density on the oil droplets' surface and increasing the electronegativity on the oil droplets' surface, and the Zeta potential decreases. When the quartz sand concentration is high, its adsorption reaches saturation, and the Zeta potential no longer changes.

3.2.2. The Synergetic Effect of Quartz Sand Particles and Surfactant

It can be seen in Figure 7 that when the concentration of alkali and polymer are constant and the concentration of surfactant is lower than 400 mg/L, the Zeta potential significantly decreases with the raising of surfactant concentration. When the surfactant concentration increases further, the Zeta potential decreases slowly. Because the surfactant can raise the negative charge density, the Zeta potential can be significantly reduced. As the surfactant concentration continues to rise, the number of surfactant molecules adsorbed on the surface of oil droplets reaches saturation, and the Zeta potential decreases at a slower rate [27].
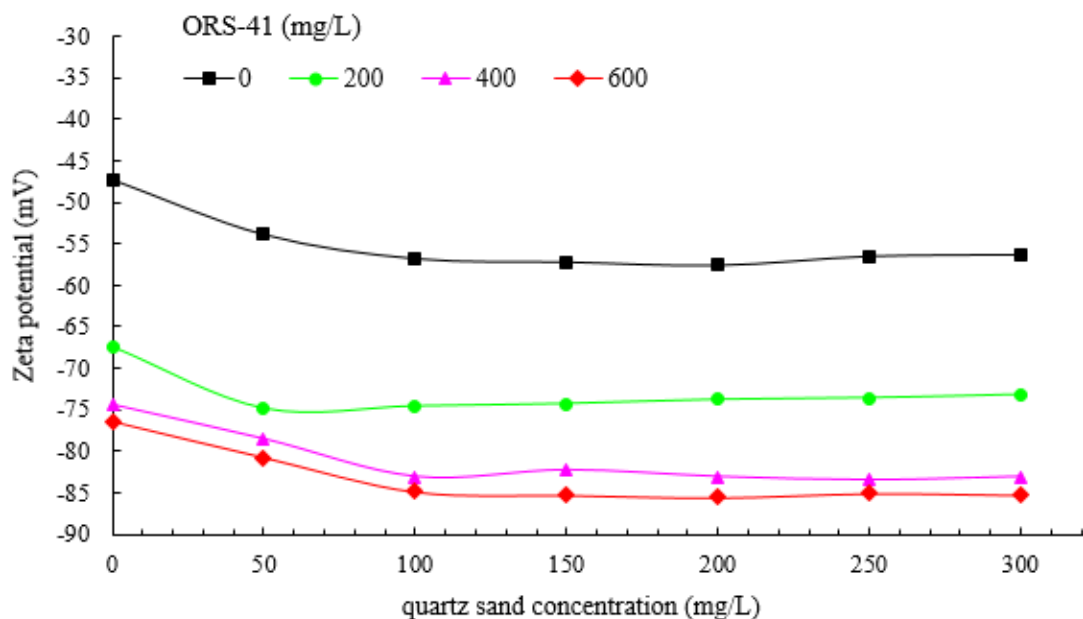

Figure 7. The synergetic effect of surfactant and quartz sand particles on Zeta potential (polymer concentration 500 mg/L, alkali concentration 600 mg/L).

When the quartz sand concentration is between 0 to 100 mg/L, the Zeta potential decreases significantly with the rise of quartz sand concentration; when the quartz sand concentration increases further, the Zeta potential remains almost unchanged. This is because, when the quartz sand concentration is low, quartz sand particles can form a flocculated structure with the surfactant, oil droplets and polymer. Quartz sand particles carry negative charges, which increases the surface negative charge density of oil droplets and decreases the Zeta potential by surrounding the surface of the structure. With the increase of the quartz sand concentration, the amount of quartz sand surrounding the surface of the structure is close to saturation, the electrostatic repulsion increases, the negative charge density increment slows down and the Zeta potential decreases slowly and tends to be stable.

3.2.3. The Synergetic Effect of Quartz Sand Particles and Polymer

It can be seen in Figure 8 that the Zeta potential of oil droplets' surface decreases gradually with the increase of polymer concentration, because polymer molecules also adsorb on the oil droplets' surface, thus increasing the negative charge density on the oil droplets' surface. However, due to the weak surface activity of polymers, the number of polymer molecules adsorbed on the oil droplets' surface is relatively low [28]; as a result, the Zeta potential decreases slowly.
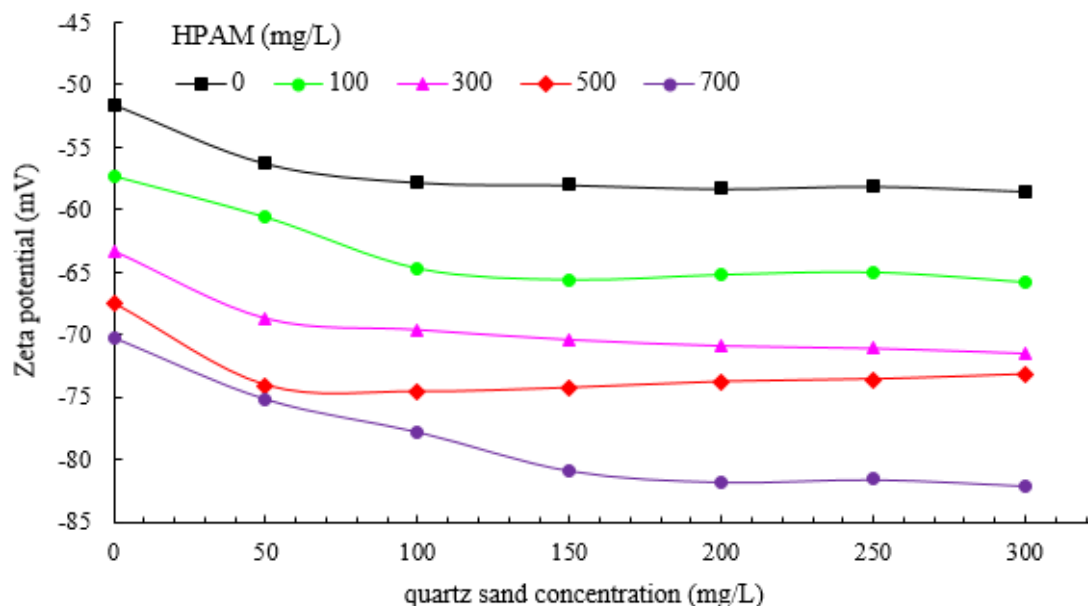
Figure 8. The synergetic effect of polymer and quartz sand particles on Zeta potential (alkali concentration 600 mg/L, surfactant concentration 200 mg/L).

At the beginning, the Zeta potential gradually decreases as the quartz sand concentration increases. When the quartz sand concentration reaches 150 mg/L, no matter how much the concentration of polymer increases, the Zeta potential basically remains unchanged. The reason is that the polymer and quartz sand particles themselves are negatively charged, which adsorb on the interface between oil and water, enhancing the electronegativity of oil droplets and reducing the Zeta potential. When the quartz sand concentration in the liquid phase is high, on the one hand, the adsorption and desorption processes of quartz sand particles on the oil droplets' surface reach dynamic equilibrium; on the other hand, the electrostatic repulsion between quartz sand particles and oil droplets increases, and the generated electrostatic repulsion enhances the stability of the emulsion system.

3.3. The Synergetic Effect of Quartz Sand Particles and Oil Displacement Agents on Interfacial Tension

3.3.1. The Synergetic Effect of Quartz Sand Particles and Alkali

It can be seen in Figure 9 that when the alkali concentration is in the range of 0 to 400 mg/L, the interfacial tension decreases with the rise of alkali concentration because the surfactant generated by the reaction of NaOH with acidic components of crude oil has the property of reducing the interfacial tension. When the alkali concentration is more than 400 mg/L, NaOH has basically neutralized the acidic components, and a large amount of excess Na^+ will freely diffuse to the oil–water interface and compress the diffuse electric double layer on the surface of oil droplets, thus increasing the oil–water interfacial tension.
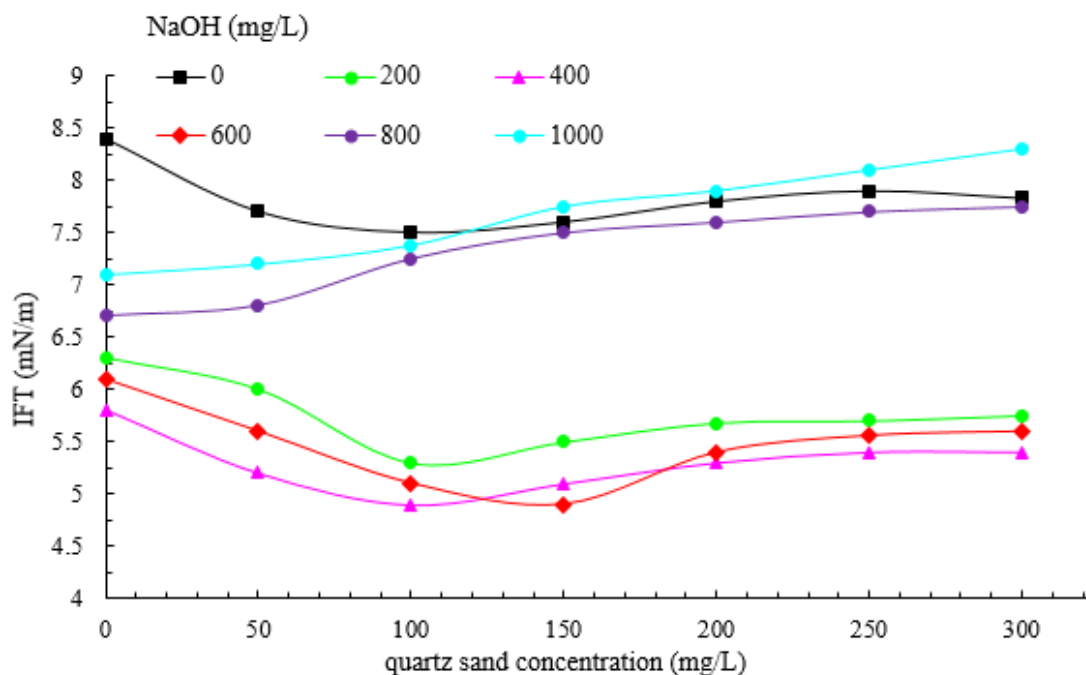
Figure 9. The synergetic effect of quartz sand particles and alkali on interfacial tension (polymer concentration 500 mg/L, surfactant concentration 200 mg/L).

When the concentration of alkali is no more than 600 mg/L and the quartz sand concentration is in the range of 0–100 mg/L, the interfacial tension decreases with the increase of quartz sand concentration. When the quartz sand concentration is more than 100 mg/L, the interfacial tension increases with the increase of quartz sand concentration. Because quartz sand particles are negatively charged, they can carry the active substances in crude oil and adsorb on the interface between oil and water of oil droplets, reducing the oil–water interface tension. When the quartz sand concentration is too high, quartz sand particles tend to aggregate, and the polymer itself has the ability of flocculation, which reduces the number of active substances adsorbed on the interface between oil and water, resulting in the increase of interfacial tension [29]. When the alkali concentration exceeds 600 mg/L, the interfacial tension increases with the increase of quartz sand concentration. Because the system's pH value is high at this time, the alkali hydrolyzes the polymer, causing a lot of polymer molecules to curl, reducing the adsorption capacity on the oil–water interface, increasing the flocculation of quartz sand particles, resulting in the desorption of the active substances from the interface, and the interfacial tension gradually increases.

3.3.2. The Synergetic Effect of Quartz Sand Particles and Surfactant

It can be seen in Figure 10 that the concentration of alkali and polymer is constant and the concentration of surfactant is between 0–400 mg/L, the interfacial tension decreases significantly with the increase of surfactant concentration. When the surfactant concentration is more than 400 mg/L, with the rise of surfactant concentration, the interfacial tension continues to decrease, but the decreased degree is smaller. This indicates that the surfactant has a great influence on the system's interfacial tension. The surfactant used in the experiment is alkyl benzene sulfonate, which has good surface activity and can be adsorbed on the oil–water interface, and the interfacial tension can be significantly reduced through the strong interaction with the oil droplets. The more surfactant molecules there are on the interface between oil and water, the lower the interfacial tension value.
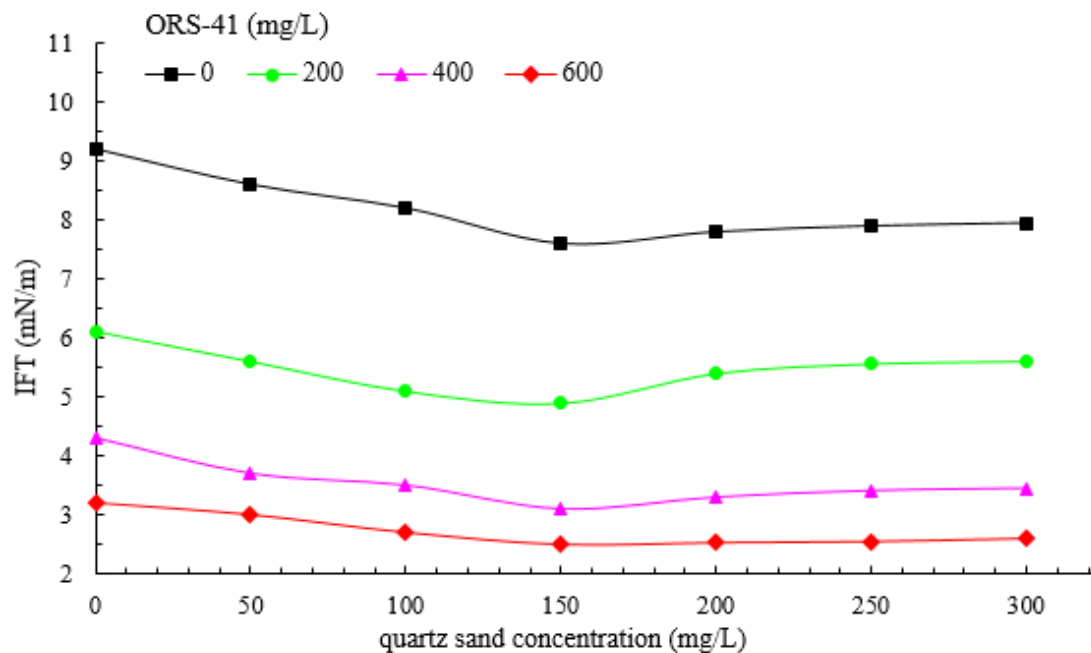
Figure 10. The synergetic effect of quartz sand particles and surfactant on interfacial tension (polymer concentration 500 mg/L, alkali concentration 600 mg/L).

At the beginning, the interfacial tension decreases with the increase of quartz sand concentration. When the quartz sand concentration exceeds 150 mg/L, the interfacial tension slightly increases with the rise of quartz sand concentration. The negatively charged quartz sand particles can carry active substances in crude oil and adsorb on the interface between oil and water of oil droplets, thus reducing the oil–water interface tension. As increasing numbers of quartz sand particles are adsorbed on the oil–water interface, a composite membrane will be formed, thus reducing the adsorption amount of surfactant molecules on the interface between oil and water. At the same time, quartz sand particles may combine with surfactant molecules to form an aggregate, which further reduces the adsorption amount of surfactant molecules and increases the interfacial tension.

3.3.3. The Synergetic Effect of Quartz Sand Particles and Polymer

When the concentration of alkali and surfactant is constant and the concentration of quartz sand is 0 mg/L, as can be seen in Figure 11, with the change of polymer concentration, the oil–water interfacial tension is basically unchanged. In other words, the polymer has little influence on the interfacial tension. However, when quartz sand particles exist, the interfacial tension decreases with the rise of polymer concentration. Because the polymer used in the experiment is high-molecular-weight polyacrylamide, which has good water solubility and can be diffused from the aqueous phase to the interface between oil and water and then adsorbed with quartz sand particles and the active substances carried by them, the interaction between quartz sand particles and polymer reduces the interfacial tension.
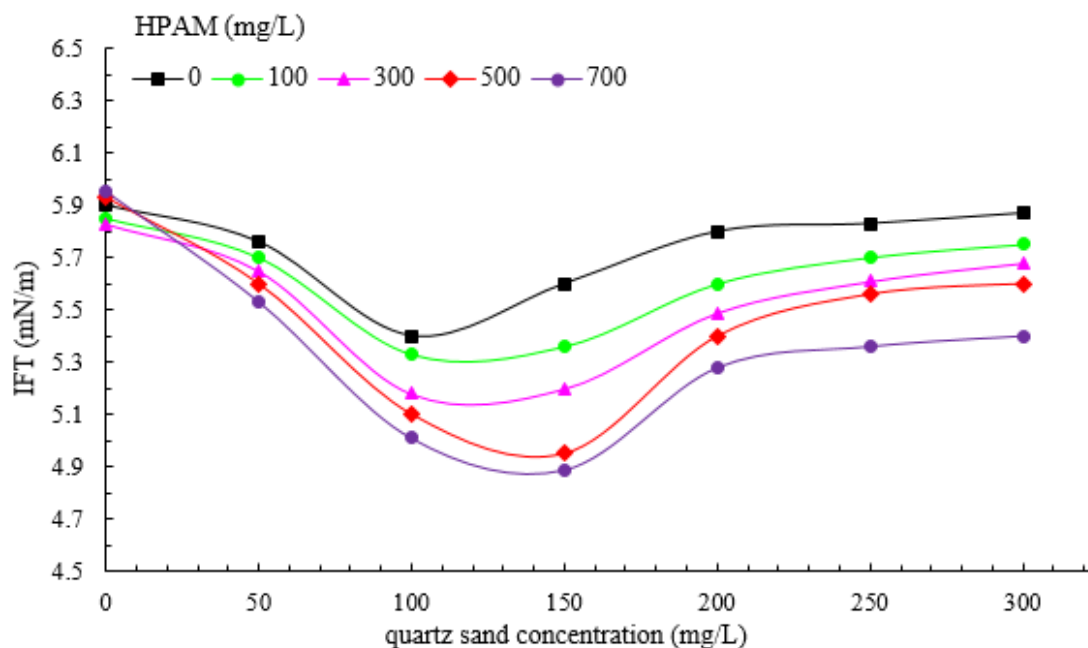
Figure 11. The synergetic effect of quartz sand particles and polymer on interfacial tension (alkali concentration 600 mg/L, surfactant concentration 200 mg/L)

For polymers of different concentrations, when quartz sand concentration is less than 150 mg/L, the interfacial tension decreases with the increase of quartz sand concentration. Because quartz sand particles can absorb the active substances in crude oil and migrate to the interface between oil and water, these active substances significantly reduce the oil–water interface tension. When the quartz sand concentration is between 100–150 mg/L, the interfacial tension reaches the minimized level, and then the interfacial tension increases with the rise of quartz sand concentration; because the area of oil–water interface is limited, when the number of quartz sand particles adsorbed on the interface between oil and water reaches saturation, the excess quartz sand particles will adsorb some surface-active substances, and accumulation and settlement occur [30], leading to the increase of interfacial tension.

3.4. The Synergetic Effect of Quartz Sand Particles and Oil Displacement Agents on Oil Droplet size

The measurement results are represented by the median diameter. In other words, the median diameter is used to represent the oil droplet size under different conditions. When there are no ASP oil displacement agents in the system, the initial particle size of oil droplets is 3.93 µm. After settling for 2 hours, the oil droplets' particle size is 4.32 µm; compared with the initial particle size, the increase in particle size is very small, indicating that only a slight coalescence has occurred in oil droplets. When the polymer concentration in the system is 500 mg/L and the alkali concentration and surfactant concentration is 0 mg/L, the particle size of the oil droplets is 8.17 µm—much larger than when there are no ASP oil displacement agents in the system—indicating that the existence of HPAM is conducive to the aggregation of oil droplets. When the NaOH concentration in the system is 600 mg/L and the polymer concentration and surfactant concentration is 0 mg/L, the oil droplets particle size is 4.10 µm—smaller than when there are no ASP oil displacement agents in the system—indicating that the existence of NaOH is not conducive to the aggregation of oil droplets, but the hindrance effect is weak. When the surfactant concentration in the system is 200 mg/L and the alkali concentration and polymer concentration is 0 mg/L, the oil droplets particle size is 3.81 µm—much smaller than when there are no ASP oil displacement agents in the system— which indicates that the existence of the surfactant is not only unfavorable to the aggregation of oil droplets but also can enhance the stability of oil droplets. The effects of different concentrations of quartz sand particles and oil displacement agents on the oil droplet size were investigated; the results are shown in the Figures 12–14 below.
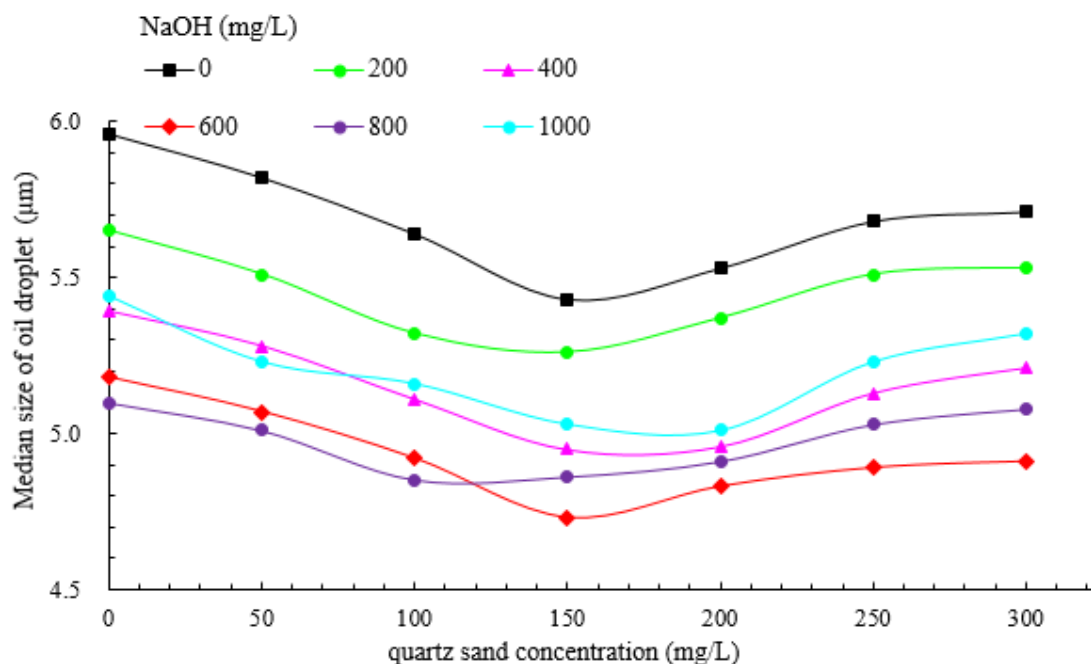
Figure 12. The synergetic effect of quartz sand particles and alkali on oil droplets size (polymer concentration 500 mg/L, surfactant concentration 200 mg/L).
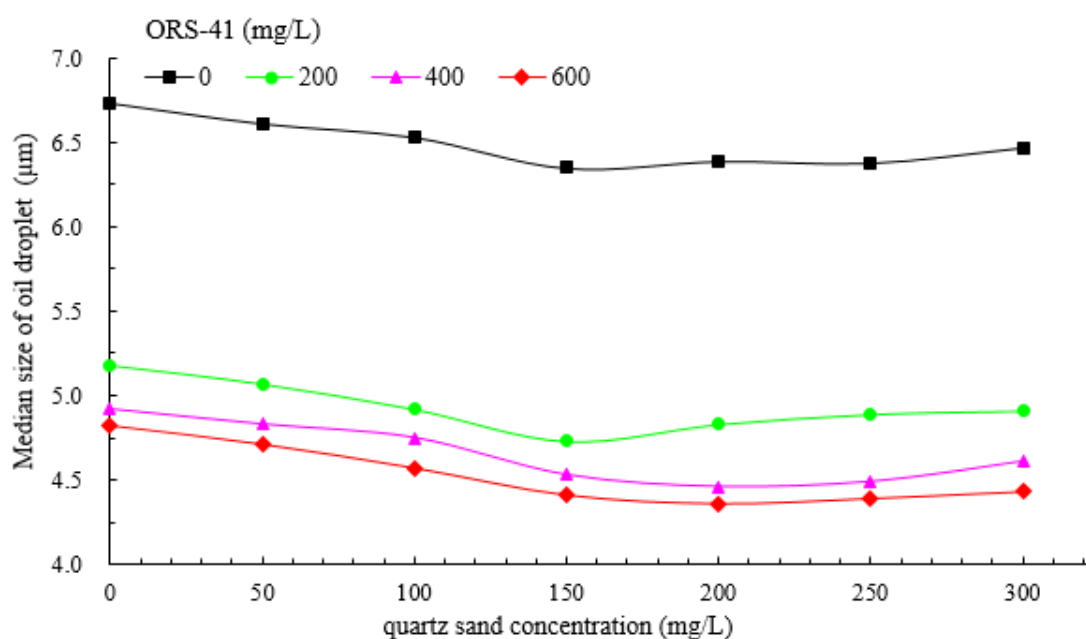

Figure 13. The synergetic effect of the quartz sand particles and surfactant on the oil droplet size (polymer concentration 500 mg/L, alkali concentration 600 mg/L).
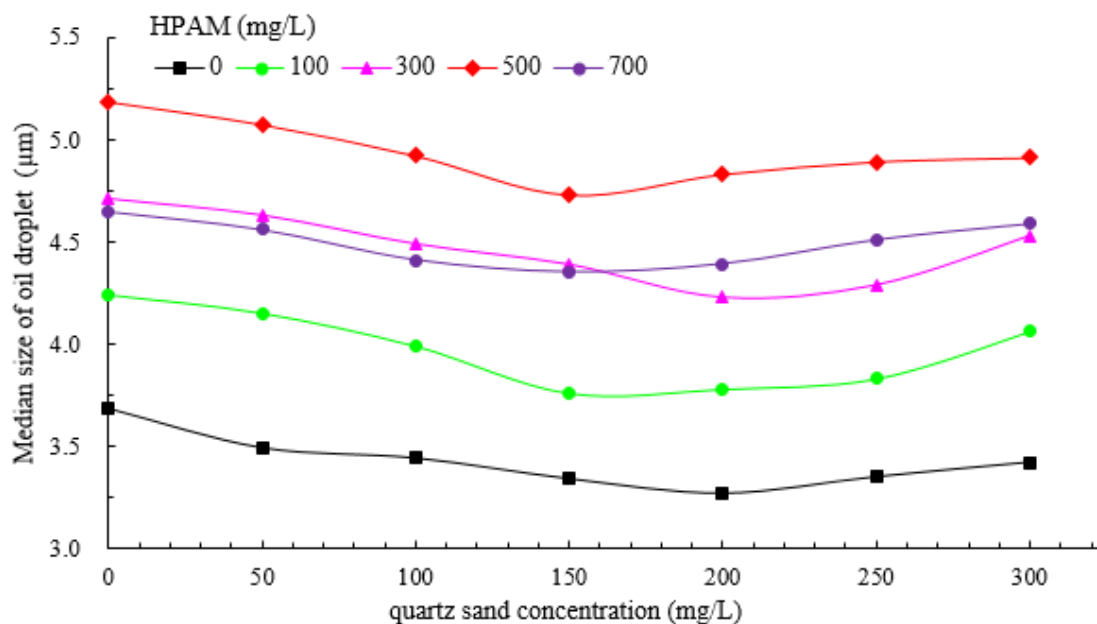
Figure 14. The synergetic effect of quartz sand particles and polymer on oil droplet size (alkali concentration 600 mg/L, surfactant concentration 200 mg/L).

3.4.1. The Synergetic Effect of Quartz Sand Particles and Alkali

When the NaOH concentration is low, the oil droplet size gradually decreases with the rise of NaOH concentration, indicating that NaOH hinders the coalescence of oil droplets at this time, because the surface-active substance generated by the reaction of NaOH and acidic components of crude oil can adsorb on the oil droplets' surface, reduce the oil–water interfacial tension and enhance the stability of oil droplets, and the oil droplets size decreases. When the NaOH concentration is more than 800 mg/L, the acidic components in crude oil are completely reacted. At this time, NaOH acts as an electrolyte, and Na^+ can compress the double electrode layer, weakening the stability of oil droplets—which is conducive to the coalescence of oil droplets—and increasing the oil droplet size.

At the beginning, the oil droplets' particle size decreases with the increase of quartz sand concentration; then, the oil droplets' particle size increases with the rise of quartz sand concentration. Negatively charged quartz sand particles adhere to the oil droplets' surface, enhancing the electronegativity on the oil droplets' surface; thus, the oil droplets' stability is enhanced, which hinders the coalescence of oil droplets. Quartz sand particles tend to aggregate with the further rise of the quartz sand concentration. The aggregation of quartz sand and oil droplets can promote the oil–water separation, and the polymer itself has the ability of flocculation, which is conducive to the increase of the oil droplet size.

3.4.2. The Synergetic Effect of Quartz Sand Particles and Surfactant

When the surfactant concentration in the system is 0, the particle size of the oil droplets is 6.73 μm—much larger than when there are no ASP oil displacement agents in the system, but smaller than that, there are only polymer oil displacement agents in the system—indicating that the flocculation effect of polymer is much stronger than the hindrance effect of NaOH on the coalescence of oil droplets. At first, the oil droplet size decreases sharply with the rise of surfactant concentration; then, the oil droplet size begins to decrease. The existence of the surfactant makes the oil droplets disperse more evenly, which weakens the flocculation effect of the polymer on the oil droplets. Meanwhile, the surfactant reduces the Zeta potential on the oil droplets' surface. Moreover the electrostatic repulsion between the oil droplets increases, thus reducing the probability of a collision and hindering the coalescence of oil droplets.

When the quartz sand concentration is low, the oil droplet size decreases with the rise of quartz sand concentration. When the quartz sand concentration is in the range of 150–200 mg/L, the oil droplet size reaches its smallest value. With the further increase of quartz sand concentration, the oil droplet size gradually increases due to the quartz sand particles and their surface-active substances adsorbing on the interface between oil and water, which is equivalent to forming a certain structured interfacial film, enhancing the stability of produced water, increasing the coalescence difficulty of oil droplet coalescence and decreasing the oil droplet size [31]. With the further increase of quartz sand concentration, the oil droplets and quartz sand particles combine to form a larger aggregated structure. The number of surface-active substances on the interface between oil and water decreases, the strength of the interfacial film weakens, and thus quartz sand particles carry part of the oil droplets, accumulate and settle, leading to the stability of produced water decreasing, promoting the oil–water separation, and increasing the oil droplet size.

3.4.3. The Synergetic Effect of Quartz Sand Particles and Polymer

The particle size of oil droplets increases first and then decreases with the rise of polymer concentration. When the polymer concentration is 700 mg/L, the particle size of oil droplets decreases, but the oil droplets size at this time is still larger than when there are no ASP oil displacement agents in the system. Due to the flocculation effects of the polymer, when the polymer concentration is low, the polymer molecules can adsorb on the oil droplets' surface, generate the bridge connection effect, combine small oil droplets together and construct the floc unit. However, the coalescence between oil droplets does not occur, and the higher the polymer concentration, the larger the flocs unit volume formed, and the more oil droplets are contained in the floc unit. With the continuous increase of polymer concentration, the viscosity of the aqueous phase also increases [32], and the movement velocity of oil droplets slows down, thus hindering the coalescence of oil droplets. At the same time, the polymer molecules cover on the oil droplets' surface, forming a steric hindrance effect. This effect is not conducive to the coalescence of oil droplets, resulting in a decrease of oil droplet size. Because the flocculation effect of the polymer weakens but still exists, and the flocculation effect of the polymer is still stronger than the effect of hindering the coalescence of oil droplets, so the particle size of oil droplets at this time is still larger than when there were no ASP oil displacement agents in the system.

When the quartz sand concentration is low, the oil droplet size decreases with the rise of the quartz sand concentration. When the quartz sand concentration is more than 200 mg/L, the oil droplet size increases gradually because quartz sand particles and their surface-active substances can adsorb on the interface between oil and water, increasing the intensity of oil–water interfacial film, and the stability of oil droplets are enhanced, which hinders the coalescence of oil droplets. Along with the continuous increase of quartz sand concentration, the aggregated structure formed by quartz sand particles and oil droplets increases, and the aggregates tend to coalescence. At the same time, the surface-active substances in crude oil are limited. When the quartz sand concentration is high, the adsorption of quartz sand particles on the surface-active substances results in a reduction of surface-active substances concentration on the interface. The formed interfacial film is weak and not sufficient to stabilize the emulsion [33]. Under the combined action of the two, the stability of the produced water system weakens and the oil droplet size increases.

4. Conclusions

In this paper, simulated ASP-flooding-produced water containing different concentrations of quartz sand particles and oil displacement agents was prepared by laboratory experiment. The oil–water separation characteristic of the produced water system was characterized by the oil content. By measuring the Zeta potential, oil–water interfacial tension and oil droplets size, the effects and mechanism of quartz sand particles and oil displacement agents on the oil droplets' stability were summarized and analyzed, as shown in Figure 15. The content described below is shown in Figure 15 intuitively from the initial state to the coalescence occurrence and coalescence finishes.
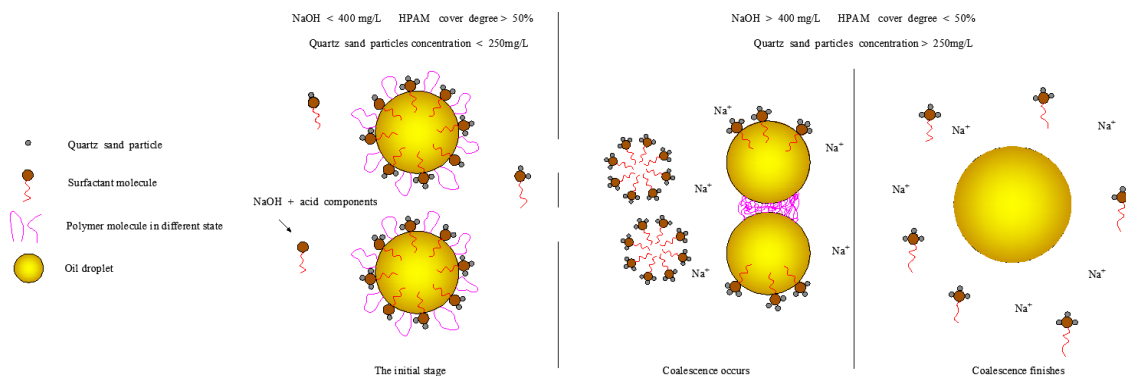
Figure 15. The mechanism of quartz sand particles and oil displacement agents on the stability of oil droplets in the alkali/surfactant/polymer (ASP)-flooding-produced water system.

When the NaOH concentration is less than 400 mg/L, with the increase of its concentration, the surface-active substances generated by the reaction of NaOH and acidic components of crude oil can adsorb on the oil–water interface; the surfactant can adsorb on the interface between oil and water in the form of nonpolar groups sticking into oil phase and polar groups sticking into water phase, changing the surface properties of the oil droplets from hydrophobicity to hydrophilicity, making it more difficult for oil droplets to coalesce. When the NaOH concentration is more than 600 mg/L, the acidic components in crude oil are all neutralized; the excess Na^+ in aqueous phase neutralizes the negative charges on the oil droplets' surface and compresses the diffuse electric double layer. Thus, the stability of the system is gradually weakened. Polymer molecules have a flocculation effect, which can adsorb on the oil droplets' surface; when the coverage degree of the polymer on the surface of oil droplets reaches 50%, the flocculation reaches its maximum. With the increase of polymer concentration, the viscosity of the aqueous phase increases. At the same time, a steric hindrance effect is generated between polymer molecules. Thus, the stability of the system is gradually enhanced.

When the oil displacement agent concentration is constant (the polymer concentration is not zero), with the increase of the quartz sand concentration, the oil content first increases and then decreases, the Zeta potential first decreases and then basically remains stable, and the interfacial tension and oil droplet size first decrease and then increase. The quartz sand particles are negatively charged, which can carry the active substances in crude oil and surfactant molecules in the aqueous phase and adsorb on the oil–water interface of oil droplets, increasing the negative charge density on the oil droplets' surface, decreasing the Zeta potential and interfacial tension, enhancing the stability of the oil droplets and increasing the difficulty of coalescence. When the quartz sand particle concentration is in the range of 150–250 mg/L, the produced water is the most difficult to deal with. When the quartz sand particle concentration is high, they adsorb or combine with surfactant molecules adsorbed on the oil–water interface to form aggregates. Thus, the adsorption capacity of surfactant molecules on the oil–water interface is decreased. The polymer molecules crimp from the stretching state. The number of polymer molecules surrounding the surface of the flocculation structure is close to saturation. Quartz sand particles tend to aggregate, and the active substances carried by them are desorbed from the interface, resulting in the produced water system becoming unstable.

Author Contributions: Conceptualization, B.H., C.W.; methodology, formal analysis, investigation and writing—original draft preparation, B.H., C.W.; writing—Review and editing, supervision and project administration, W.Z., C.F.; writing—Review and Editing, H.L., H.W. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cheng, J.; Wu, J.; Hu, J. Key theories and technologies for enhanced oil recovery of alkaline/surfactant/polymer flooding. *Acta Pet. Sin.* **2014**, *35*, 310–318.

2. Wang, D.; Cheng, J. Summary of alkali/surfactant/polymer flooding in Daqing oilfield. In Proceedings of the SPE Arctic and Extreme Environments Technical Conference and Exhibition, Houston, TX, USA, 3–6 October 1999.

3. Vladimir, A.; Eduardo, M. *Enhanced Oil Recovery*; Gulf Professional Publishing: Houston, TX, USA, 2010.

4. Li, F.; He, W.; Sun, D.; Wu, T.; Li, Y. Effect of sodium-montmorillonite particles on the stability of oil droplets in produced water from alkali/surfactant/polymer flooding. *J. Clean. Prod.* **2015**, *104*, 468–474. [CrossRef]

5. Deng, S.; Yu, G.; Jiang, Z.; Zhang, R.; Ting, Y.P. Destabilization of oil droplets in produced water from ASP flooding. *Colloids Surfaces A: Physicochem. Eng. Asp.* **2005**, *252*, 113–119. [CrossRef]

6. Deng, S.; Bai, R.; Chen, J.P.; Yu, G.; Jiang, Z.; Zhou, F. Effects of alkaline/surfactant/polymer on stability of oil droplets in produced water from ASP flooding. *Colloids Surfaces A Physicochem. Eng. Asp.* **2002**, *211*, 275–284. [CrossRef]

7. Yang, L.; Zhihua, W.; Xianglong, Z.; Hongqi, Z.; Xinpeng, L. An environmentally-friendly method for disposal of the ASP flooding produced water. In Proceedings of the SPE Arctic and Extreme Environments Technical Conference and Exhibition, Moscow, Russia, 15–17 October 2013.

8. Wang, F. Research on Oil/Water Separation Specialities and Disposal Technologies in ASP Flooding Produced Water. Ph.D. Thesis, Shanghai Jiaotong University, Shanghai, China, 2007.

9. Huang, B.; Li, X.; Zhang, W.; Fu, C.; Wang, Y.; Fu, S. Study on Demulsification-Flocculation Mechanism of Oil-Water Emulsion in Produced Water from Alkali/Surfactant/Polymer Flooding. *Polymers* **2019**, *11*, 395. [CrossRef]

10. Huang, B.; Wang, J.; Zhang, W.; Fu, C.; Wang, Y.; Liu, X. Screening and Optimization of Demulsifiers and Flocculants Based on ASP Flooding-Produced Water. *Processes* **2019**, *7*, 239. [CrossRef]

11. Etchepare, R.; Oliveira, H.; Azevedo, A.; Rubio, J. Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles. *Sep. Purif. Technol.* **2017**, *186*, 326–332. [CrossRef]

12. Al-Maamari, R.S.; Sueyoshi, M.; Tasaki, M.; Okamura, K.; Al-Lawati, Y.; Nabulsi, R.; Al-Battashi, M. Flotation, Filtration, and Adsorption: Pilot Trials for Oilfield Produced-Water Treatment. *Oil Gas Facil.* **2014**, *3*, 56–66. [CrossRef]

13. Deng, S.B.; Zhou, F.S.; Yu, G. Speciality of oil-field produced water and its treatment technology. *Industrial Water Treatment* **2000**, *20*, 10–12.

14. Zhao, L.H.; Li, B.L.; Chen, Z.X.; Ji, G.S.; Shu, Z.M. *Character of Oilfield Produced Water and Factor infLuencing on its Treatment*; Liaoning Chemical Industry: Liaoning, China, 2007; pp. 69–72.

15. Ye, Q. Research on Oil/Water Separation Characteristic and Treatment in ASP Produced Water. Ph.D. Thesis, Shanghai Jiaotong University, Shanghai, China, 2008.

16. Di, M.; Xv, C.; Zhao, S. Air floating /hydrolysis acidification /biological contact oxidation /filtration process for treatment of ASP flooding produced water. *China Water Wastewater* **2016**, *32*, 69–70.

17. Yan, N.; Masliyah, J.H. Characterization and demulsification of solids-stabilized oil-in-water emulsions Part 1. Partitioning of clay particles and preparation of emulsions. *Colloids Surfaces A Physicochem. Eng. Asp.* **1995**, *96*, 229–242. [CrossRef]

18. Guo, Q. Experimental Study on the Effect of the Wetting Property of Support Agent on the Fracturing Operation. Ph.D. Thesis, Northeast Petroleum University, Daqing, China, 2016.

19. SY/T 5329-94, Water quality standard and practice for analysis of oilfield injecting waters in clastic reservoirs. In Proceedings of the MATEC Web of Conferences, Cape Town, South Africa, 24–26 September 2018.

20. Gan, Z.; Xing, X.; Xu, Z. Effects of image charges, interfacial charge discreteness, and surface roughness on the zeta potential of spherical electric double layers. *J. Chem. Phys.* **2012**, *137*, 34708. [CrossRef] [PubMed]

21. Hong, J.S.; Fischer, P. Bulk and interfacial rheology of emulsions stabilized with clay particles. *Colloids Surfaces A Physicochem. Eng. Asp.* **2016**, *508*, 316–326. [CrossRef]

22. Huang, B.; Zhang, W.; Wang, J.; Fu, C. Effect of oil displacement agent on oil droplet stability in alkali/surfactant/polymer flooding oily wastewater. *Chem. Ind. Eng. Prog.* **2019**, *38*, 1053–1061.

23. Lakatos-Szabó, J.; Lakatos, I. Effect of alkaline materials on interfacial rheological properties of oil-water systems. *Colloid Polym. Sci.* **1999**, *277*, 41–47. [CrossRef]

24. Yarranton, W.; Urrutia, P.; Sztukowski, D.M. Effect of interfacial rheology on model emulsion coalescence II. Emulsion coalescence. *J. Colloid Interface Sci.* **2007**, *310*, 253–259. [CrossRef]

25. Nguyen, D.T.; Sadeghi, N. Stable Emulsion and Demulsification in Chemical EOR Flooding: Challenges and Best Practices. In Proceedings of the SPE EOR Conference at Oil and Gas West Asia; Society of Petroleum Engineers (SPE), Muscat, China, 16–18 April 2012; pp. 16–18.

26. Nedjhioui, M.; Moulai-Mostefa, N.; Morsli, A.; Bensmaili, A. Combined effects of polymer/surfactant/oil/alkali on physical chemical properties. *Desalination* **2005**, *185*, 543–550. [CrossRef]

27. Taylor, K.C.; Nasr-El-Din, H.A. The effect of synthetic surfactants on the interfacial behaviour of crude oil/alkali/polymer systems. *Colloids Surfaces A Physicochem. Eng. Asp.* **1996**, *108*, 49–72. [CrossRef]

28. Ling, S.; Wei-Dong, L.; Zhan-Xiang, T. Rheologic Behavior of Aqueous Solutions of Surface Active Polymer SLH-I for EOR. *Oilfield Chem.* **2008**.

29. Schorling, P.-C.; Kessel, D.; Rahimian, I. Influence of the crude oil resin/asphaltene ratio on the stability of oil/water emulsions. *Colloids Surfaces A Physicochem. Eng. Asp.* **1999**, *152*, 95–102. [CrossRef]

30. Khelifa, A.; Stoffyn-Egli, P.; Hill, P.S.; Lee, K. Effects of salinity and clay type on oil-mineral aggregation. *Mar. Environ. Res.* **2005**, *59*, 235–254. [CrossRef] [PubMed]

31. Jeon, T.Y.; Hong, J.S. Stabilization of O/W emulsion with hydrophilic/hydrophobic clay particles. *Colloid Polym. Sci.* **2014**, *292*, 2939–2947. [CrossRef]

32. Huang, B.; Hu, X.; Fu, C.; Cheng, H.; Li, Y. Experimental and numerical simulation study on the flow characteristics and optimization of structural parameters of displacement agent in partial pressure tools. *Energy Sci. Eng.* **2019**, 1–21. [CrossRef]

33. Tarimala, S.; Dai, L.L. Structure of Microparticles in Solid-Stabilized Emulsions. *Langmuir* **2004**, *20*, 3492–3494. [CrossRef] [PubMed]