Stability Dynamic Characteristic of Oil-in-Water Emulsion from Alkali–Surfactant–Polymer Flooding

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ABSTRACT: The relationship model between the droplet lifetime and interface properties is established to characterize the stability of oil droplets, and then, the influence of the alkali–surfactant–polymer (ASP) concentration on the lifetime is analyzed by theoretical calculations. The stability dynamic characteristics of oil-in-water (O/W) emulsions from ASP flooding were evaluated using the emulsion stability model (Civan model) based on two-phase separation. The effect of ASP on dynamic characteristics of the emulsion was explored by analyzing film strength qualitatively and measuring interfacial tension and ζ potential. The results showed that the Civan model was suitable to evaluate the stability of the O/W emulsion and to obtain the corresponding dynamic characteristics. The O/W emulsions became more stable with the increasing alkali concentration first at a low alkali concentration (c_{NaOH} < 200 mg/L) and then became less stable with the increasing alkali concentration at a high alkali concentration (c_{NaOH} > 200 mg/L). The stabilities of O/W emulsions were improved with the increasing concentrations of the surfactant and polymer. The mechanism of stabilization of the O/W emulsion by ASP is as follows. The surface-active substances formed by the reaction of alkali and acidic substances in the oil phase, together with surfactants, adsorb at the oil–water interface, reducing the interfacial tension and increasing the strength of the oil–water interface film. The polymer only increases the strength of the interface film by increasing the viscoelasticity of the oil–water interface film.

1. INTRODUCTION

Petroleum has been an important strategic resource in the world. With the ever-increasing energy competition today, how to improve oil recovery is a concern of the petroleum industry. After years of exploitation, most of China’s oilfields have entered the late stage of high water content. The crude oil from water flooding is decreasing year by year, and the current recovery rate is generally only 30−40%. The application of recovery enhancement technology is a necessary stage of oilfield development, and it is also an effective method for old oilfields to suppress the decline in the production and maintain stable production.1−4

The alkali–surfactant–polymer (ASP) flooding is a technology that greatly enhances oil recovery based on binary floods such as alkaline−polymer flooding and surfactant−polymer flooding. The ASP flooding has been studied in the Daqing oilfield since the 1980s and has gradually achieved continuous innovation breakthroughs in theoretical research, system formulations, and industrialization application. In 1997, five pilot field experiments were carried out in the Daqing oilfield. The field test results showed that ASP flooding can increase oil recovery by 20% compared with water flooding.5,6

In 1998, the world’s first industrial test of ASP flooding was carried out in the Daqing oilfield, which further verified the oil displacement effect of ASP flooding under the conditions of large well spacing, multiple good groups, and multiple oil layers. It provides a theoretical and practical basis for the large-scale popularization and application of ASP flooding technology in the Daqing oilfield. In 2000, five industrial field experiments were carried out in the Daqing oilfield to continue to verify that ASP flooding can increase oil recovery by 20% compared with water flooding. In 2014, the technology and management system of ASP flooding was established, industrial applications were promoted, and large-scale commercial applications and complete sets of output conditions were available.7,8 At present, a relatively supporting technical system has been formed to achieve the goal of increasing oilfield recovery and improving development effects and has become a new point of output growth.

The geological reserves suitable for ASP flooding in China are about 83 × 10⁸ t. As far as the Daqing oilfield is concerned, the reserves are approximately 14 × 10⁹ t. The ASP flooding...
production reached 4.63 million tons in 2020, and the annual output has been increasing year by year since 2014, as shown in Figure 1.9−12

Figure 1. ASP flooding oil production in the Daqing oilfield.

The ASP flooding has been identified as the leading technology for maintaining the output. However, the residual alkali, surfactant, and polymer in the produced water cause serious emulsification and separation difficulties, which severely restrict the large-scale promotion of ASP flooding technology.13 To break up oil-in-water (O/W) emulsions, a variety of demulsification techniques have been applied for oil−water separation, such as chemical methods,14 physical methods,15 biological methods,16 and mechanical methods including gravity demulsification,17 microwave demulsification,18 thermal demulsification,19 electric demulsification,20 air flotation,21 ultrasonic demulsification,22 and membrane technology.23,24 These conventional methods often exhibit low efficiency when handling O/W emulsions from ASP flooding. Due to the residue of ASP, the O/W emulsions from ASP flooding have the characteristics of large viscosity, small particle size, and strong interfacial film. This makes it difficult for oil droplets to coalesce and grow up, which becomes a bottleneck restricting the implementation of demulsification. Therefore, it is of great significance for oil−water separation to study the effects of ASP on the stabilization of emulsions. In this study, we investigate the stability dynamic characteristic of O/W emulsions using the lifetime model and Civan model. We investigate the role of ASP in the emulsion stability and the interface properties to provide quantitative insight into the microscopic mechanism of emulsion stabilization by ASP.

2. RESULTS AND DISCUSSION

2.1. Lifetime Model of an O/W Interfacial Film. An emulsion is a highly dispersed system where work needs to be done to disperse the dispersed phase and store it at the oil−water interface in the form of surface energy. The process of increasing surface free energy is not spontaneous, but the reverse process (that is, the process of automatically merging droplets to reduce the surface area) is spontaneous, so emulsions are thermodynamically unstable.25 Under the same dispersion conditions, to reduce the instability of the emulsion, it is necessary to reduce the oil−water interfacial tension, which can be achieved by adding surfactants. The surfactant added to the oil−water system not only reduces the surface tension but also adsors at the interface and forms an interface film with a certain strength, which protects the dispersed phase and makes it difficult to merge after colliding with each other.26 Solid particles suspended in oil−water systems are also good emulsifiers. A particle emulsifier is the same as the usual surfactants. Adsorption reduces the interfacial area and hence lowers the free energy of the system. Furthermore, unlike surfactants, such particles need not be amphiphilic—the only requirement is that they should be partially wetted by both fluids.27 Due to ionization, adsorption, or friction between the droplets and the medium, most of the stable O/W (or W/O) droplets are charged, so the droplets can repel each other when they are close, which prevents them from merging and improves the stability of the emulsion.28 The increase in the viscosity of the external phase of the emulsion can reduce the diffusion coefficient of the droplets and reduce the collision frequency and coalescence rate, which is conducive to the stability of the emulsion. The size and distribution of emulsion...
droplets have a great influence on the stability of the emulsion. Generally, the narrower the droplet size range, the more stable the emulsion is.\textsuperscript{29} In addition, the phase state and stability of surfactant-stabilized emulsions are affected easily by salinity. Generally speaking, monovalent metal soaps can emulsify oil and water into O/W emulsions. Adding high-valent metal ions, such as Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Al\textsuperscript{3+}, Cr\textsuperscript{3+}, etc., will compress the diffuse electric double layer at the oil−water interface, reduce the strength and thickness of the interface film, and reduce the stability of the emulsion. At the same time, after the concentration of high-valent metal ions dominates, the emulsifier exhibits the hydrophobicity of the high-valent metal soap, which makes the emulsion phase invert to the W/O type.\textsuperscript{30}

The produced water from ASP flooding contains a large amount of surfactants, polyacrylamide, alkali, and oil. The oil−water interface of the simulated emulsion prepared in this experiment mainly absorbs sodium dodecylbenzene (SDBS) and HPAM, and the adsorption method is as follows: (1) SDBS molecules are arranged on the interface to form an interface film, and the hydrophilic groups interact with the carboxyl anion or amide anion in the HPAM chain, thus part of HPAM molecules can be aligned on the oil−water interface (Figure 2, adsorption form 1). (2) The lipophilic groups of −CH\textsubscript{2}− in the HPAM chain can connect with the oil phase, and the hydrophilic groups of −COOH and −CONH\textsubscript{2} dissolve in the water phase. In this adsorption form, HPAM molecules can adsorb on the oil−water interface (Figure 2, adsorption form 2). Also, amphiphilic HPAM and SDBS can bond together through hydrophobic forces, electrostatic interactions, hydrogen bonds, etc., to strengthen the interface layer. The interface structure of the O/W emulsion is shown in Figure 2.\textsuperscript{31−35}

The O/W emulsion from ASP flooding is a multiphase dispersion system, and the key to its instability is the aggregation of suspended oil droplets into larger droplets. As shown in Figure 3, when the suspended oil droplets move randomly and approach each other, they will be subject to buoyancy and intermolecular forces (van der Waals attraction, electrostatic repulsion, steric hindrance, etc.). Due to the two forces, the collision of droplets will produce three results: (1) droplet rebound, (2) droplet flocculation, and (3) interfacial film breakage and droplet coalescence. The difficulty of coalescence of oil droplets mainly depends on the strength of the interfacial film of the oil droplets. Usually, greater interfacial strength can lead to a longer lifetime of the interfacial film, and it is less likely that the oil droplets coalesce. However, the strength of the interfacial film is not easy to be measured, and the film lifetime can be used to characterize the stability of the oil droplets. The factors affecting the lifetime of the interface film are divided into two categories: one is the chemical substance in the system such as alkali, surfactant, polymer, and salt, and the other is the nature of the oil droplet itself, that is, the size of the oil droplet.\textsuperscript{36,37}

The interfacial film of oil droplets is elastic and easily deforms by applying an external force. When the oil droplets are close to each other, external forces such as buoyancy play a leading role, and the oil droplets remain spherical, as shown in Figure 4a. When the distance between oil droplets is shortened, the intermolecular forces play a dominant role and the interface where the oil droplets are close to each other will sink inward. Thus, an interface film will be formed between the oil droplets, as shown in Figure 4.

When the emulsion droplets approach each other driven by a certain external force, the life of the interfacial film can be calculated from eq 1:\textsuperscript{37}

\[
\tau = \int_{h_c}^{h_a} \frac{dh}{V}
\]

(1)

From the literature, eq 2 was obtained

\[
\tau = \frac{9\eta}{2g\Delta \rho} \ln a = \frac{9\eta \ln(10)h_c}{2g\Delta \rho} a + \frac{3\eta a^2}{4\sigma h_c} = \frac{15\eta a}{2\sigma}
\]

\[
+ \frac{9\eta g \Delta \rho}{144\sigma^2 h_c^2} a^5 - \frac{25\eta g \Delta \rho}{4\sigma^2} a^3
\]

(2)

Based on eq 2, it can be found that the oil droplet size, oil−water interfacial tension, and viscosity will affect the life of the interfacial film.

2.1.1. Influence of the Droplet Size on the Lifetime of the O/W Interfacial Film. To more intuitively study the influence of the size on the lifetime of the interfacial film, we organize the formula and reassign A−F

\[
A = \frac{9\eta}{2g\Delta \rho}, \quad B = \frac{9\eta \ln(10)h_c}{2g\Delta \rho}, \quad C = \frac{3\eta a^2}{4\sigma h_c}, \quad D = \frac{15\eta a}{2\sigma}, \quad E = \frac{9\eta g \Delta \rho}{144\sigma^2 h_c^2}, \quad F = \frac{25\eta g \Delta \rho}{4\sigma^2}
\]

Then, the mathematical relationship between the lifetime and the droplet radius is derived as shown in eq 3

Figure 3. Possible results of the collision of two emulsion droplets in connection with the droplet−droplet interaction.

Figure 4. Morphological changes during the approach of oil droplets: (a) droplets are spherical and (b) droplets deform to form a flat film.
\[
\tau = A \ln \frac{a}{\Delta} - B \frac{1}{a} + Ca^2 - Da + Ea^3 - Fa^4
\]  

(3)

where \( \tau \) is the lifetime of a single droplet, \( \sigma \) is the interfacial tension, \( g \) is the gravitational acceleration, \( \Delta \rho \) is the density difference, \( a \) is the droplet radius, \( h_i \) is the distance between the droplets, and \( \eta \) is the viscosity of the film phase. According to ref 16, \( h_i = 5 \text{ nm} \), \( g = 9.8 \text{ m/s}^2 \), \( \Delta \rho = 200 \text{ kg/m}^3 \), and the experimental \( \eta = 1.33 \text{ mPa s} \) and the calculations for \( A - F \) can be performed. Moreover, the mathematical relationship between the lifetime of the liquid film and the radius of the droplet is shown in Figure 5.

![Figure 5](https://pubs.acs.org/journal/acsodf)

Figure 5. Calculated lifetime, \( \tau \), of O/W drops approaching from below a water–oil interface in the Taylor regime and Reynolds regime (other lines) as a function of the droplet radius, \( a \).

The various curves in Figure 5 correspond to different values of the interfacial tension (\( \sigma \)). The left-side branches of the curves correspond to the Taylor regime (nondeformed droplets), and the right-side branches correspond to the Reynolds regime (formation of the film between the droplets). In the Taylor regime, the lifetime of the O/W droplet decreases with the increase in the radius of droplets. In the case of a larger radius (the Reynolds regime), the lifetime increases with the increasing radius of droplets. This is exactly the opposite trend to that of the Taylor regime. There is a minimum value in the curve of \( \tau \) vs \( a \), which was proposed in ref 38.

2.1.2. Influence of Alkali on the Lifetime of the O/W Interfacial Film. It can be found from eq 1 that the influence of alkali on the lifetime of the interfacial film cannot be directly analyzed by this model. However, it can be found that the effect of alkali on the interfacial film of oil droplets has two main aspects: first, the alkali can react with the acidic substances in the crude oil to form surfactant; thus, high strength of the interfacial film can be obtained. Second, as the alkali concentration continues to increase, the ions electrolyzed will compress the electric double layer at the interface of the oil droplet, weaken the strength of the interface film of the oil droplet, and reduce the lifetime of the interfacial film.

2.1.3. Influence of Surfactant on the Lifetime of the O/W Interfacial Film. It can be found from eq 1 that the influence of interfacial tension on the film lifetime of oil droplets can be directly analyzed by this model. Surfactants have the effect of reducing the interfacial tension of oil and water, which is the main reason for the stable existence of oil droplets in water. The interfacial tension of oil and water in the produced water from ASP flooding mainly depends on the concentration of surfactants. Therefore, interfacial tension can be used to reflect the effect of the surfactant concentration on the film lifetime. We organize eq 1 and reassign \( A - E \):

\[
A = \frac{9\eta \ln a}{2g\Delta \rho} - \frac{9\eta \ln(10h_i)}{a}, \quad B = \frac{3\eta a^2}{4h_i}, \quad C = 15a\eta, \quad D = \frac{9\eta \Delta \rho a^3}{144h_i^2}, \quad E = \frac{25\eta \Delta \rho a^3}{4}
\]

Then, the mathematical relationship between the film lifetime and the interfacial tension is derived and is shown in eq 4

\[
\tau = A + \frac{B - C}{\sigma} + \frac{D - E}{\sigma^2}
\]  

(4)

where \( \tau \) is the lifetime of a single droplet and \( \sigma \) is the interfacial tension. According to the literature, \( h_i = 5 \text{ nm} \), \( g = 9.8 \text{ m/s}^2 \), \( \Delta \rho = 200 \text{ kg/m}^3 \), and the experimental \( \eta = 1.33 \text{ mPa s} \). Taking the sizes of oil droplets as 1, 2, 3, 4, and 5 \( \mu \text{m} \), the values of \( A - F \) can be calculated. Furthermore, the mathematical relationship between the film lifetime and the interfacial tension is shown in Figure 6.

![Figure 6](https://pubs.acs.org/journal/acsodf)

Figure 6. Calculated lifetime, \( \tau \), of O/W drops approaching from below a water–oil interface in the Taylor regime and Reynolds regime (other lines) as a function of the interfacial tension.

It can be seen from Figure 6 that the lifetime of the O/W droplet increases with the decrease in the interfacial tension, which shows that the stability of the O/W droplet increases with the increasing concentration of the surfactant. As the interfacial tension decreases, the lifetime of the O/W droplet changes greatly. In the case of smaller \( \sigma \) (interfacial tension, the left-hand side branches of curves in Figure 6), the film lifetime increases sharply with the decrease in the interfacial tension, which shows that the concentration of surfactants greatly affects the film lifetime of the O/W droplet. At the same time, it was also found that with the increase in the droplet size, the influence of surfactants on the film lifetime gradually weakened, and the reduction range gradually became smaller.
2.1.4. Influence of Polymers on the Lifetime of the O/W Interfacial Film. As eq 1 deforms and reassigns A–E, the mathematical model of the film lifetime and viscosity can be described as eq 5
\[
A = \frac{9\ln a}{2g\Delta \rho a}, \quad B = \frac{9\ln(10k_c)}{2g\Delta \rho a}, \quad C = \frac{3a^2}{4\sigma h_c}, \quad D = \frac{15a}{2\sigma}, \quad E
\]
\[
= \frac{9g\Delta \rho a^5}{144\sigma^2 h_c^2}, \quad F = \frac{25g\Delta \rho a^3}{4\sigma^2}
\]
\[
\tau = (A - B + C - D + E - F)\eta \tag{5}
\]
Taking the size of the oil droplet as 2, 3, 4, and 5 μm, the values of A–F can be calculated, and the mathematical relationship between the film lifetime and viscosity is shown in Figure 7.

![Figure 7. Calculated lifetime, τ, of O/W drops approaching from below a water–oil interface in the Taylor regime and Reynolds regime (other lines) as a function of the viscosity.](image)

It can be seen from Figure 7 that the film lifetime increases with the increase in the viscosity in the water phase, that is, the lifetime increases with the increase in the polymer concentration, and the stability of the oil droplet increases with the polymer concentration. At the same time, it can also be found from Figure 7 that the smaller size of the oil droplet can result in a longer lifetime, which shows that the larger size of the oil droplet makes it break easily.41,42

2.2. Quantitative Theoretical Model of Emulsion Stability. The stability of emulsions is a key parameter in the petroleum industry for the separation of oil and water. The stability of emulsions was studied generally by experiments. Only a few studies described quantitative theoretical analyses.43 These works provide valuable insight into the mechanism of emulsion formation and a method to determine and interpret the key parameters of emulsion formation, including the reaction order, rate constant, and half-life.

Based on the stability model established by Civan, the influence of alkali, surfactant, and polymer on oil droplet dynamics has been analyzed. According to the stability model, the instantaneous demulsification rate can be calculated by eq 6
\[
dX\frac{dt}{dX} = k_d(X_f - X)^n \tag{6}
\]
where X is the demulsification rate of the emulsion at time t, X_f is the maximum demulsification rate of the emulsion, and n is the reaction order during the demulsification process of the emulsion, n = 0.4.44 The initial state is defined as X = 0 and dt = t, and eq 6 is organized as eq 7
\[
(X_f - X)^{1-n} = X_f^{1-n} - (1-n)k_d(t - t_d) \tag{7}
\]
where t_d is the delay time of emulsion instability, a plot of X_f^{1-n} – (X_f – X)^{1-n} vs t – t_d should yield a linear correlation, and the slope of m is equal to (1 – n)k_d. Therefore, the rate constant of emulsion instability (k_d) can be defined as eq 8
\[
k_d = \frac{m}{(1-n)} \tag{8}
\]
The half-life of the O/W emulsion from ASP flooding can be determined using eq 9 by combining eqs 7 and 8
\[
(t - t_d) = \frac{X_f^{0.6} - (0.5X_f)^{0.6}}{0.6k_d} \tag{9}
\]

2.2.1. Effect of Alkali on the Stability Dynamic Characteristic of Emulsions. The emulsions used in the tests were prepared by mixing water samples containing 200, 400, 800, and 1200 mg/L NaOH; 0.1% SDBS; and 450 mg/L HPAM and emulsifying them for 10 min with a speed of 1500 rpm. The bottle tests with 100 mL of emulsions were used to measure the water separation rate at different settling times. Based on the water separation rate, we can acquire the scatter plot of X_f^{1-n} – (X_f – X)^{1-n} with t – t_d. Therefore, the slope m can be obtained by linear fitting of scattered points, as shown in Figure 8.

![Figure 8. Straight-line plot of the present data of the fraction of separated water from various emulsions vs time with different alkali additions.](image)

According to eq 8, the instability rate of the O/W emulsion from ASP flooding can be calculated. Finally, according to eq 9, the half-life of oil droplets can be calculated. The results are shown in Table 1.

2.2.2. Effect of Surfactant on the Stability Dynamic Characteristic of Emulsions. The emulsions used in the tests were prepared by mixing water samples containing 0.025%,

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0.5%, 0.1%, and 0.2% SDBS, 200 mg/L NaOH, and 450 mg/L HPAM at 1500 rpm for 10 min. The calculation steps are the same as above, and the results are shown in Figure 9 and Table 2.

Table 1. Effect of the NaOH Concentration on the Instability Rate and Half-Life of O/W Emulsion

| concentration (mg/L) | (1 − n)k₁ | k₂ (h⁻¹) | (t − t₀)₁/₂ (h) |
|----------------------|------------|----------|-----------------|
| 200                  | 0.0804     | 0.1340   | 2.8144          |
| 400                  | 0.0794     | 0.1324   | 2.8920          |
| 800                  | 0.0778     | 0.1296   | 2.9438          |
| 1200                 | 0.0762     | 0.1270   | 3.1269          |

2.2.3. Effect of the Polymer on the Stability Dynamic Characteristic of Emulsions. The emulsions used in the tests were prepared by mixing water samples containing 150, 300, and 450 mg/L HPAM; 0.1% SDBS; and 200 mg/L NaOH and emulsifying them for 10 min with a speed of 1500 rpm. The calculation steps are the same as above, and the results are shown in Figure 10 and Table 3.

Table 2. Effect of Surfactant on the Instability Rate and Half-Life of the Oil–Water Emulsion

| mass percentage (%) | (1 − n)k₁ | k₂ (h⁻¹) | (t − t₀)₁/₂ (h) |
|---------------------|------------|----------|-----------------|
| 0.025               | 0.1132     | 0.1887   | 2.1226          |
| 0.05                | 0.1102     | 0.1837   | 2.1333          |
| 0.1                 | 0.0842     | 0.1070   | 2.4333          |
| 0.2                 | 0.0501     | 0.0845   | 2.4510          |

2.3. Microscopic Mechanism of the Influence of ASP on the Stability of O/W Emulsions. The stability of O/W emulsion from ASP flooding is related to many factors, such as the composition and ratio of the two phases, particle size and distribution, temperature, viscosity, and properties of the interfacial film. Among them, the interfacial properties including interfacial film strength, ζ potential, and interfacial tension play a vital role in the stability of the emulsion.35–47

2.3.1. Influence of ASP on O/W Interfacial Strength. It can be seen from Table 1 that with the increase in the NaOH concentration, the instability rate of the O/W emulsion gradually decreases and the half-life of instability gradually increases. The reason is that NaOH reacts with acidic substances in the oil phase to form certain surfactants, which improves the strength of the interfacial film.39 The influence of surfactants on the oil–water interface film is shown in Figure 6 and Table 2. With the increase in the surfactant concentration, the lifetime of the O/W droplet and the half-life of instability increase and the instability rate constant decreases, indicating that the increase in the surfactant enhances the strength of the oil–water interface film of the emulsion. This is because the increased surfactants are arranged more closely at the oil–water interface, increasing the strength of the interface film.26 The influence of the polymer on the oil–water interface film is shown in Figure 7 and Table 3. With the increase in the HPAM concentration, the lifetime of the interfacial film and the instability rate of the oil–water emulsion gradually decrease and the half-life of droplet demulsification increases, which shows that the increase in the polymer concentration improves the strength of the oil–water interface film. This is due to the adsorption and orientation of a high concentration of polymers at the interface between the solution and the oil phase, forming a tightly arranged oil–water interface film, which increases the viscoelasticity of the oil–water interface film, thereby improving the strength of the film.38,49

2.3.2. Influence of ASP on the Interfacial Tension. The interface between two immiscible fluids has high interfacial tension, which produces droplets of one liquid dispersed in a second immiscible liquid, forming an inherently unstable system. The interfacial tension reflects the adsorption of active substances at the interface. Therefore, the study of interfacial tension can explain the influence of ASP on the oil–water interfacial film, and then, dynamic characteristics of the emulsion are further discussed.59

As shown in Figure 11a, the interfacial tension first decreases and then slightly increases with the increase in the NaOH concentration.

Figure 10. Straight-line plot of the present data of the fraction of separated water from various emulsions vs time with different surfactant additions.

Table 3. Effect of HPAM on the Instability Rate and Half-Life of the Oil–Water Emulsion

| concentration (mg/L) | (1 − n)k₁ | k₂ (h⁻¹) | (t − t₀)₁/₂ (h) |
|----------------------|------------|----------|-----------------|
| 150                  | 0.1033     | 0.1722   | 2.2244          |
| 300                  | 0.0862     | 0.1436   | 2.3354          |
| 450                  | 0.0587     | 0.0977   | 2.4223          |

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concentration. This is because NaOH can react with acidic substances in the oil phase, which can adsorb at the oil–water interface and decrease the interfacial tension. When the concentration of NaOH is higher than 200 mg/L, all acidic substances react, and NaOH has no obvious effect on the interfacial tension. As shown in Figure 11b, the interfacial tension decreases as the surfactant concentration increases. When the surfactant content is less than 0.1%, the interfacial tension decreases sharply. While continuing to increase the surfactant content, the interfacial tension slowly decreases. This is because 0.1% surfactant can make the oil–water interface adsorption saturated. As shown in Figure 11c, as the polymer concentration increases, the oil–water interfacial tension remains unchanged, which shows that the polymer has a small effect on the interfacial tension. Furthermore, the lower interfacial tension also benefits from the salinity of the oil–water system, which increases the activity of the surfactant molecules and helps reduce the interfacial tension.28

2.3.3. Influence of ASP on ζ Potential. The ζ potential is the main parameter describing the interface charge of the dispersed droplets. Its absolute value characterizes the magnitude of the charge on the surface of the droplets. It is related to the structure of the charge layer and reflects the strength of the charge repulsion between the dispersed droplets. It is generally believed that a larger ζ potential led to a more stable emulsion.17 The influence of ASP on the ζ potential is shown in Figure 12.

As shown in Figure 12a, as the NaOH concentration increases, the ζ potential first decreases and then rises slightly. The reason may be that the anionic surfactant generated by sodium hydroxide and acidic substances in the oil sample increases the negative charge density at the oil–water interface and the ζ potential decreases at low concentrations.31 As the concentration of sodium hydroxide increases, sodium ions play a dominant role in the compression of the interfacial diffusion double layer, thereby increasing the ζ potential. As shown in Figure 12b,c, surfactants and polymers have similar effects on the ζ potential. As their concentrations increase, the ζ potential decreases. This is mainly because both the surfactant molecules and polymer molecules adsorbed at the oil–water interface are negatively charged. As their concentrations increase, the repulsive force between the charges increases, making the polymers tightly arranged at the oil–water interface. The ability of oil droplets to coalesce decreases, which leads to an increase in the absolute value of the ζ potential, and the influence of surfactants is greater.

3. CONCLUSIONS

The influence of the alkali, surfactant, and polymer concentration on the stability of droplets was analyzed using a lifetime model of the O/W interfacial film. The dynamic characteristics of the O/W emulsion from ASP flooding conform to the emulsion stability model based on two-phase separation, which is closely related to the properties of the oil–water interface. While the strength of the oil–water interfacial film increases with the increasing alkali concentration at a low alkali concentration ($c_{\text{NaOH}} < 200 \text{ mg/L}$), the rate constant $k_d$ decreases and the emulsion stability increases. While the strength of the oil–water interfacial film decreases with the increasing alkali concentration at a high alkali concentration ($c_{\text{NaOH}} > 200 \text{ mg/L}$), the rate constant $k_d$ increases and the emulsion stability decreases. Furthermore, the strength of the oil–water interfacial film decreases with the increasing surfactant and polymer concentration, the rate constant $k_d$ decreases, and the stability of the emulsion increases. The mechanism of stabilization of the O/W emulsion by ASP can be described as follows: alkali and surfactants reduce the interfacial tension and increase the interfacial strength, and the polymer only increases
the strength of the interface film by increasing the viscoelasticity of the oil–water interface film.

4. EXPERIMENTAL SECTION

4.1. Chemicals and reagents. Sodium hydroxide (NaOH) was purchased from Lianying Quanrui Reagent Co., Ltd., China. SDBS was purchased from Aladdin Chemistry, Shanghai, China. Polyacrylamide (HPAM, Mw ~ 5 × 10^6, 99%) was obtained from Zibo Jinxiang Chemical Reagent Factory. Sodium carbonate (Na2CO3), calcium chloride (CaCl2), sodium chloride (NaCl), sodium sulfate (Na2SO4), sodium bicarbonate (NaHCO3), and magnesium chloride hexahydrate (MgCl2·6H2O) were purchased from Macklin Chemical Reagent, Shanghai, China. All chemicals are of analytical grade and directly used without further treatment.

4.2. Emulsion Preparation. The water samples used in the experiment are prepared according to the analysis data of the produced water from ASP flooding. The total salinity is 4600 mg/L, and the salt content is shown in Table 4.

A model O/W emulsion was obtained by mixing diesel containing 200 mg/L NaOH, 0.1% SDBS, and PAM with deionized water (V_diesel/V_water = 3:4) and emulsifying it for 10 min with a speed of 1500 rpm.

4.3. Emulsion Test and Performance Evaluation. To evaluate the stability of the oil–water emulsion from ASP flooding, the tubes with stoppers were filled with 50 mL of the model emulsion. To record the volume of the water layer every 0.5 h and calculate the water separation ratio W_d, the formula in eq 10 is used

\[
\text{water separation [%]} = \left(\frac{\text{separated water volume}}{\text{added sample volume} + \text{original water in emulsion}}\right) \times 100\%
\]  

\[\text{eq 10}\]

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Notes

The authors declare no competing financial interest.

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