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Preparation of nano emulsion with high salt resistance

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Abstract: In this paper, the high salt shale reservoir as the research object, through the combination of microemulsion dilution method and pseudo-ternary phase diagram to screen the salt resistance of good nano emulsion. In the system, D-limonene was used as the oil phase, and the surfactant CAB-35 and AOS were selected by pseudo-ternary phase diagram method as the surfactant in the ratio of 1:1, and then mixed with n-butanol in the ratio of 1:1 to obtain the best microemulsion effect. The nano emulsion system was prepared by diluting the microemulsion. By testing the interfacial tension, the optimum preparation conditions of nano emulsion were screened. The results showed that the nano emulsion prepared by dilution under the condition of 5:5 oil/water ratio of microemulsion system had the best ability to reduce the interfacial tension between oil and water.

Keywords: Surfactant; Microemulsion; Nano emulsion.

1. Introduction

At present, the most commonly used imbibition oil recovery is surfactant[1, 2] and nano fluid[3], because the use of surfactant imbibition oil recovery, there are a large number of surfactants adsorbed in the near well zone, but not into the formation, so that its imbibition displacement ability is greatly reduced[4-6]. However, when solid nanoparticles flow through small pores in shale, they are easy to cause blockage and damage to the formation. Nano-emulsion has the function of changing formation wettability of surfactant, and has the advantages of small adsorption capacity near the well zone[7], and can pass through small pores through deformation without causing damage to the formation[8, 9]. Therefore, nano-emulsion has become a key technology for imbibition to improve recovery efficiency of shale formation.

However, nano emulsion does not have thermodynamic stability, so energy input is needed in the preparation process of nano emulsion. Due to the difference of input energy in the process of preparing nano emulsion, the preparation methods are mainly divided into two kinds, one is high energy emulsification method, the other is low energy emulsification method. The cost of equipment used in high-energy emulsification method is relatively high, and the maintenance cost required in the daily use process is also relatively high. Therefore, the production cost of nano-emulsion prepared by this method is too high, and it is not suitable for mass production[10]. The preparation of nano emulsion by low energy emulsification method is mainly to use the characteristics of surfactant, oil and water three components, by changing the system composition, temperature and other conditions, so as to change the spontaneous curvature of the surfactant, only need to use a simple preparation process, can make it spontaneously form nano emulsion[11]. Common low energy emulsifying methods include: phase transition temperature method, phase transition component method, microemulsion dilution method. Because the microemulsion dilution method has no strict requirements on the stirring rate in the dilution process, it can be prepared at any time when it is needed. Because of the advantages of simple operation and low cost, this method is easier to mass production. In addition, microemulsion has good thermodynamic stability, and its stability will not change during long-term placement, which can greatly improve the shortcomings of low stability of nano-emulsion in long-term placement. Therefore, in this paper, microemulsion dilution method is used to prepare nano-emulsion, and HLB method is combined with ternary phase diagram method to screen out the best formula.

2. Experimental methods

2.1. Screening of surfactants

Because limonene is similar to aromatic solvent in structure and solubility, it has a good effect on dissolving precipitates in crude oil, which can dissolve wax, asphalt, keratin and other substances in crude oil, reduce the viscosity of crude oil and increase the fluidity of crude oil in the formation. Therefore, D-limonene is selected as the oil phase. Several groups of mixed emulsifiers were selected, which were composed of two surfactants in a certain ratio. The concentration of NaCl in the fixed aqueous phase was 10wt%, the organic solvent was n-butanol, and the ratio of emulsifier to alcohol was 1:1, and the HLB value of the emulsifier was the same as that of the emulsified system (D-limonene).

According to Formula 2-2 and Formula 2-3, continue to calculate the mixture ratio of surfactants. As shown in Table.1, make its HLB value the same as that of emulsion system (D-limonene), and mix according to the calculated amounts of surfactants, auxiliary surfactants and organic solvent alcohol. Pour it into a centrifuge tube with a total oil and water volume of 5g, and the oil-water ratio is 1:9, 2:8, … 8:2, 9:1 respectively. While shaking, drop it, observe the turbidity of the solution, stop dropping until the solution reaches a clear state, and stand for 15min without delamination to obtain microemulsion, and record the amount of emulsifier added.

$$HLB=\sum HLB\times X_i \quad (1)$$

$$\sum X_i=1 \quad (2)$$

Where HLB is the HLB value of the compounded emulsifier; HLBi is the HLB value of a single surfactant; Xi is the mass fraction of each surfactant.

According to the amount of emulsifier, oil and water added in the experiment, the percentage of each in the system is calculated, and the three-element phase diagram is drawn according to the data.

Table 1. Mixture ratio of different surfactants

emulsifier	CAB-35+ Tween80	CAB-35+ AEO-9	CAB-35+ APG-10	CAB-35+ AOS	CAB-35+ SDBS
Compounding ratio	1:2	7:10	6:11	1:1	1:2

2.2. Screening of alcohols

The two surfactants selected above are selected as emulsifiers, and the emulsifiers are mixed with different alcohols according to the ratio of 1:1. The mixture ratio of surfactants is calculated by Formula 2-2 and Formula 2-3, so that the HLB value is the same as that of emulsified system (D- limonene). According to the calculated surfactant and co-surfactant, the total amount of oil and water is 5g, and the oil-water ratio is 1:9,2:8, …, 8:2, 9:1. Shake evenly when adding, and observe the turbidity of the solution until the solution reaches a clear state, stop adding, and stand for 15min without delamination to obtain microemulsion, and record the addition amount of emulsifier.

According to the amount of emulsifier, oil and water added in the experiment, the percentage of each in the system is calculated, and the three-element phase diagram is drawn according to the data.

2.3. Alcohols to surfactant ratio screening

Km is the mass ratio of alcohol to surfactant. Select the above two surfactants and alcohol as emulsifiers, mix the composite surfactants and alcohol in the ratio of Km=1, 1.5, 2 and 2.5, and then continue to calculate the composite ratio of surfactants through formulas 2-2 and 2-3 to make the HLB value the same as that of the emulsion system. Pour it into a centrifuge tube with a total oil and water volume of 5g, and the oil-water ratio is 1:9, 2:8, … 8:2, 9:1 respectively. While shaking, drop it, observe the turbidity of the solution, stop dropping until the solution reaches a clear state, and stand for 15min without delamination to obtain microemulsion, and record the amount of emulsifier added.

According to the amount of emulsifier, oil and water added in the experiment, the percentage of each in the system is calculated, and the three-element phase diagram is drawn according to the data.

2.4. Effects of different oil-water ratios on nano-emulsion

The microemulsions prepared with different oil-water ratios were diluted with simulated formation water at a dilution concentration of 0.5wt%, respectively, to prepare nano-emulsions. The interfacial tension between the microemulsions and kerosene was tested, and the influence of the microemulsions with different oil-water ratios on the nano-emulsions was judged by the size of the interfacial tension.

3. Results and discussions

3.1. Screening of surfactants

Due to the different affinity of surfactants to oil and water, the composition addition amount of microemulsion formed is different. Therefore, the area of microemulsion in the ternary phase diagram is also different. The area of microemulsion can reflect the solubility and stability of the microemulsion system. Jones[12] proposed that the larger the microemulsion region formed in the emulsifier system, the greater the application value of the system in EOR, the higher the solubilization content of the system and the better its stability.

It can be seen from Fig.1 that the microemulsion area of CAB-35+AOS is the largest, so the emulsification effect is the best when CAB-35+AOS is selected as the surfactant in the emulsifier.

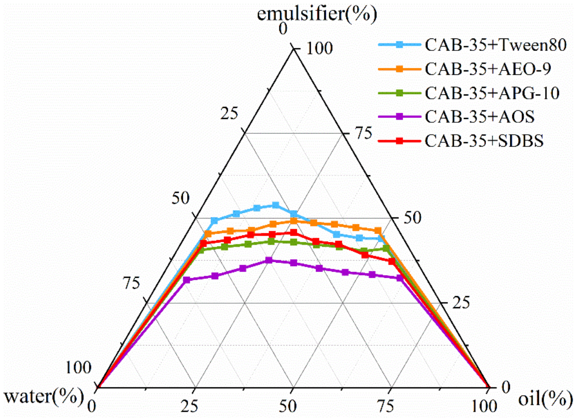

Fig.1 Screening of surfactants

3.2. Screening of alcohols

As can be seen from Fig.2, the microemulsion area of n-butanol is the largest, so the emulsification effect is the best when n-butanol is selected as the cosurfactant in the emulsifier. This indicates that the addition of cosurfactants (alcohols) can soften the oil-water interfacial film, and the ability to soften the oil-water interfacial film is better with the increase of the carbon chain length of alcohols. As the carbon chain length increases, the volume of alcohol molecules also increases. However, when the carbon chain length exceeds the carbon chain length of n-butanol, the molecular volume is too large, leading to the increase of the resistance of its embedding into the interfacial film. As a result, the flexibility of the oil-water interface film is reduced and the rigidity is enhanced, which is not conducive to the bending of the oil-water interface film, and thus it is not easy to form microemulsion. Therefore, the best cosurfactant of the microemulsion system is n-butanol.

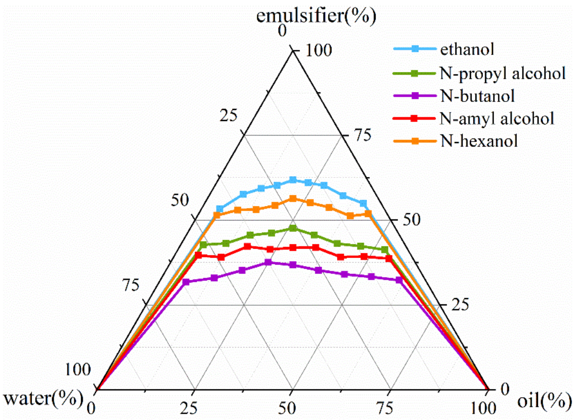

Fig.2 Screening of alcohols

3.3. Alcohols to surfactant ratio screening

Km refers to the mass ratio of alcohol to surfactant. It can be seen from Fig.3 that the microemulsion area is the largest when the ratio of alcohol to surfactant is 1:1, and the addition of alcohol can change the concentration of surfactant in the oil-water phase. When Km is less than 1, more alcohols will be distributed in the oil-water interface film with the increase of alcohol concentration. More alcohols are involved in the formation of the oil-water interface film, thus improving the stability of the oil-water interface. When Km=1, alcohols can just be completely embedded into the surfactant, and the solubilization space of the microemulsion system formed at this time is the largest, so the microemulsion region formed at this time is the largest, and the emulsification effect is the best. However, when Km is greater than 1, the alcohol distributed in the oil-water interface film has reached saturation. As the alcohol concentration continues to increase, excessive alcohol cannot enter the oil-water interface film and thus dissolves into the oil phase or the water phase, changing the composition of the oil phase and the water phase. As a result, the balance of the oil-water interface film is destroyed and the stability of the oil-water interface is reduced. And when excessive alcohol enters the water phase or the oil phase, the association phenomenon between alcohol molecules and surfactant molecules will occur, which causes the oil-water interface structure to become loose, resulting in the instability of the system. Therefore, when the ratio of alcohols to surfactants is 1:1, the microemulsion obtained by the combination has the best emulsification effect.

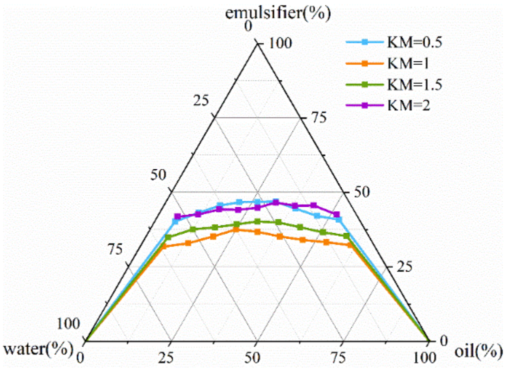

Fig.3 Alcohols to surfactant ratio screening

3.4. Effects of different oil-water ratios on nano-emulsion

The interfacial tension between oil and water is shown in Fig.4. As the oil-water ratio of microemulsion decreases, the interfacial tension decreases first and then increases. The nanoemulsion prepared by diluting the oil-water ratio of 5:5 and 4:6 has the lowest interfacial tension, and the nanoemulsion prepared by diluting the oil-water ratio of 5:5 has the lowest interfacial tension. Only 0.0118 mN/m.

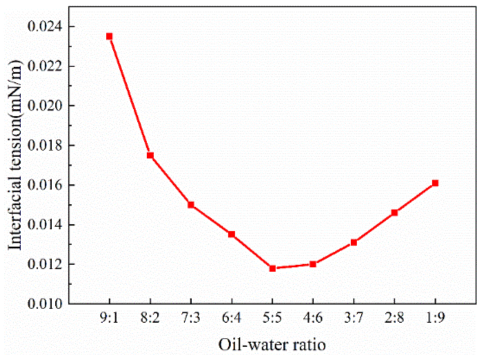

Fig.4 Interfacial tension of nanoemulsion formed by dilution of microemulsion with different oil-water ratio

4. Conclusion

(1) According to the combination of HLB value method and pseudo-ternary phase diagram, the optimal emulsifier formula of microemulsion system was selected as the surfactant: CAB-35 and AOS, and the co-surfactant: n-butanol, and the mixing ratio of the three was 1:1:1.

(2) The microemulsion prepared with different oil-water ratios was diluted, and the interfacial tension of the diluted nanoemulsion was measured. With the decrease of the oil-water ratio, the ability to reduce the interfacial tension of the diluted nanoemulsion showed a trend of decreasing first and then increasing. When the oil-water ratio of the microemulsion was 5:5, The nano emulsion obtained by dilution has the best effect on reducing interfacial tension.

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