Formulation Optimize of Anion - nonionic Gemini Mixed Surfactant System for Microemulsion Flooding in Low Permeability Reservoirs

Tian Lv[1, a] and Yuanhang Wang[2, b]

[1]Northeast Petroleum University, Daqing 163000, China;

[2]The Eighth Brigade of Testing Technology Services Branch Company, Daqing 163000, China.

[a]adlvtian@126.com, [b]wangyuanhang27@163.com

Abstract

Anion-nonionic Gemini mutiple surfactant has a good ability of heat resistance, salt resistance and the ability of calcium and magnesium ions resistance, and does not have chromatographic separation , so this kind of surfactant has huge potential in tertiary oil recovery. Since the complex system has better oil displacement efficiency and heat and salt resistance than the components alone, and it can improve the solubility and long-term thermal stability of the system, so anion-nonionic Gemini mutiple surfactant is chosen for microemulsion formulation optimize. In this paper, Winsor phase diagram method is used to study the effect of surfactant concentration, salinity, alcohol type, and alcohol concentration on microemulsion phase behavior and interfacial tension, and then select the best microemulsion formula[3-6]. Then surfactant and different types of microemulsion are used to do the flooding experiment in cores of low permeable oil fields. And by analyzing the results, it can be found that the middle phase microemulsion improve the oil recovery most.

Keywords

Anion-nonionic Gemini mutiple surfactant, formulation optimize, phase volume, interfacial tension.

1. Introduction

At present, salt-based anionic surfactant is mainly used in domestic and international oilfield, the interfacial activity of the surfactant is high and the absorbance in the formation is small, but its brine tolerance is poor[1,2]. The application of cationic surfactants in oilfield has been curbed because it can be easily absorbed and deposited, its poisonousness is large and it is hard to produce ultra-low interfacial tension. Although amphoteric ionic surfactant has a better performance, but it is hard to apply in the oilfield because of its higher cost of production[3,4]. Non-ionic surface is used under some restrictions because it is active with strong ability of tolerance to salt and hard water, it has good emulsifying properties and displacement characteristics, but some non-ionic surfactants is sensitive to temperature, and it has affection to environmental pollution[5,6]. Anion-nonionic surfactant is a kind of hybrid surface agent, it can not only keep the respective advantages of anionic and nonionic surfactant, but also can prevent the chromatographic fractionation[7,8], namely it contains both anionic hydrophilic group and nonionic hydrophilic group in the same molecular structure of surfactant, thus greatly improving the salt tolerance and temperature tolerance[9,10]. So this article choose Anion-nonionic Gemini mutiple surfactant to research the microemulsion flooding.

At the same time, the low permeable oilfields has important significance in the development of oil and gas fields in our country, it has the characteristic of low permeability, low abundance and low individual well production capacity. The distribution of low permeability oil and gas resources in China is wide, it contains more oil and gas and has more reservoir types, and it has the characteristc that the gas is upper, the oil is lower, and the sea phase contains gas most, the land phase contains both oil and gas. The reserve volume of low permeable oilfields have a high proportion of discovered reserves and accounts for more than two-thirds of the national reserves, its development potential is tremendous[11]. Now most of low permeability oilfield has come to the stage of tertiary oil recovery, the microemulsion flooding is a method of tertiary oil recovery also. Microemulsion is the spontaneous formation of the thermodynamic stability system under a appropriate proportion which is made up of water, oil, surfactant, and cosurfactant. Compared with the common emulsion, the appearance of microemulsion is stable and transparent, and the droplet size is small (10~100nm). Because microemulsion can mix with both oil and water within a certain range to eliminate the interfacial tension between oil and water, so its efficiency of displacement and enhanced oil recovery is better[12]. Zhou Bingling has mentioned that middle phase microemulsion can be solubilized in both oil and water, its efficiency of improving oil recovery is the best[13]. Mahesh Budhathoki has also noted that the phased optimal parameters can be obtained in middle phase microemulsion, but they did not form contrast experiments[14]. This article selecte a middle phase microemulsion formulation, and compared with the upper phase microemulsion and lower phase microemulsion, so as to verify the middle phase microemulsion enhance the oil recovery most.

2. Experiment Equipments and Reagents

The instruments used in the experiment includes spinning drop interfacial tension equipment (US Texas-500 type), constant pressure and speed pump, core holder, piston containers, vacuum pumps, pressure gauges, incubators. The Reagents used in the experiment includes Anion-nonionic Gemini mutiple surfactant, anhydrous ethanol, butannol, hexanol, pentanol, propanol, distilled water. The core, crude oil and formation water used in the experiments are all taken from a low permeability peripheral Daqing oil field.

3. Experimental Method

The crude oil are used as the oil phase, and use absolute ethyl alcohol to three times recrystallize anion-nonionic Gemini mutiple surfactant. Then make it dry at 60 ℃, then dry it in vacuum to a constant weight. After the alcohol redistilled, choose the middle distillate. The water used in the experiment is three times distilled water.

The study steps of phase diagram are as follows: the whose total volume is 10ml. Take a specified amount of NaCl solution and alcohol, the remaining volume filled with equivoluminal oil and water. The aqueous phase is a solution with different range of surfactant concentration. When they were well mixed later, put it in the incubator at 40±0.1℃ until the volume of each phase were unchanged, and write down each phase volume. Draw the diagram of phase volume and surfactant concentration, which is called the diagram of phase behavior. And then keep other components unchanged, draw the diagram of phase volume and salinity, phase volume and alcohol concentration.

4. Determination of Surfactant Concentration

Keep the concentration of butanol at 4%, and NaCl at 5%, change the concentration of the surfactant, the diagram of surfactant concentration and phase volume can be gotted. As shown in Fig. 1.

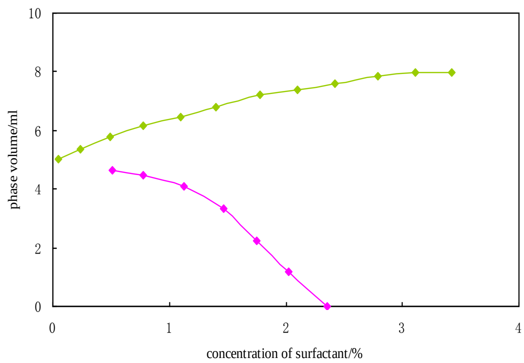

Fig. 1 Relationship between surfactant concentration and phase volume

Figure 1 shows that when the concentration of surfactant is less than 0.5%, the remaining oil and the lower phase microemulsion phase are in two-phase equilibrium. When the surfactant concentration is higher than 0.5%, the middle phase microemulsion formed, but the phase volume is pretty small. In the system of the three-phase region, surfactant gathered in the middle phase, so when the surfactant concentration increased, the amount of solubilization of oil and water are increased , it will also appear that the middle phase volume increased. The middle phase disappeared until the surfactant concentration is greater than 2.3%, and the upper phase and aqueous phase are in two-phase equilibrium.

In order to determine the optimize concentration of surfactant, microemulsion with different kinds of surfactant concentration is prepared, to which joined the crude oil to measure the interfacial tension between the microemulsion and the crude oil. The relationship is shown in Fig. 2.

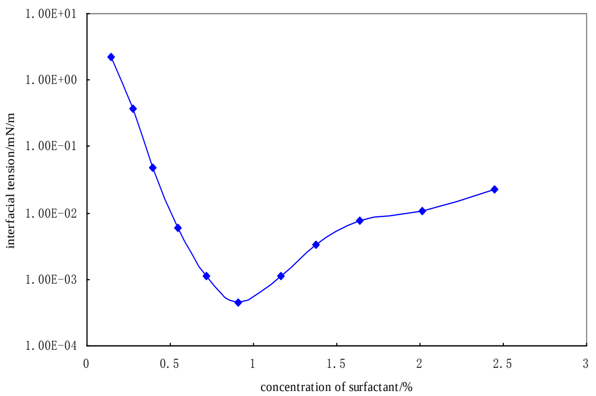

Fig.2 Relationship between surfactant concentration and interfacial tension

According to the experimental results, it can be concluded that the results is best when the concentration of surfactant is 0.9%. So the concentration of the surfactant was 0.9% in the following experiments.

5. Determination of Alcohol Type

Based on the experimental results above, the surfactant concentration is 0.9% and alcohol concentration is 4%, keep the system temperature at 40℃, change the concentration of NaCl solution, and use propanol, butannol, pentanol, hexanol as the cosurfactant respectively. Then conduct salinity scanning on the system, the phase behavior diagram is shown in Fig. 3.

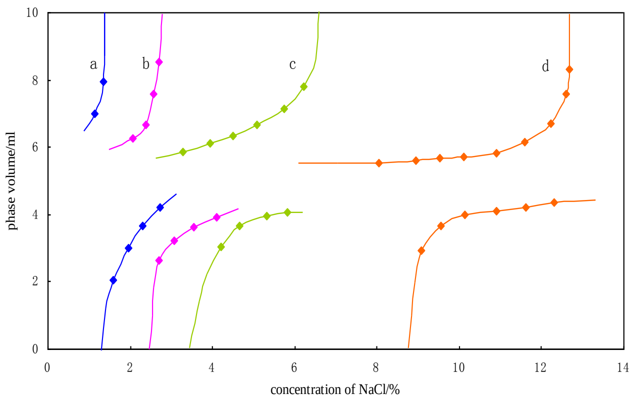

Fig.3 Relationship between NaCl concentration and phase volume under different alcohol

It can be concluded from Figure 3 that, with the increase of the hydrocarbon chain of alcohols in the system, the salinity content needed to form the middle phase microemulsion is decreased. From butannol to propanol, its needed salinity content reduced from 8.7% to 1.5%. The reason is that with the increasing of hydrocarbon chain of alcohol, the hydrophobic effect between alcohol and surfactant is enhanced, it is conducive to the formation microemulsion. After the solubilization of oil, the density of microemulsion is reduced, causing that microemulsion enrich phase separate from lower microemulsion phase[15], then the middle phase microemulsion is gotten.

After the formation of the middle phase microemulsion, more salt is needed for the hydrophilic propanol, in order to force all the surfactants into the oil phase. So that the middle phase was destroyed, and translated to the equilibrium between upper phase microemulsion and the residual aqueous phase. However, for the higher carbon number alcohols, due to their increase of lipophilic , the middle phase can be destroyed as long as the addition of a small amount of salt. It also shown that with the increase of the hydrocarbon chain length, the salinity width value decrease, which is, the difference value of salinity to the formation and disappearance of middle phase microemulsion in a certain system .Thus we have difficulty in controling the quantity of alcohol to form middle phase microemulsion, so we choose butanol in the following experiment[16] .

6. Determination of Salt Concentration

From line c in Figure 3 ,it can be known that , when the salinity is less than 2.6% ,it will form a single-phase microemulsion. From 2.6% to 3.5% is a two-phase equilibrium of lower phase microemulsion and the residual oil phase. From 3.5% to 6.2% is a three phase balance of the residual oil phase and middle phase microemulsion and the residual aqueous. From 6.2% to 6.6% is the two-phase equilibrium of the residual aqueous and upper phase microemulsion.

The transform of phase behavior shows that in low salility (2.6% - 3.5%) is the two-phase equilibrium of lower phase microemulsion and the residual oil phase. When the salinity increases, microemulsion aggregation number increases, improve the oil solubilization capacity of the system. And the increase of salt content compress the electric double layer of microemulsion droplets also. Then reduce the repulsion between the droplets, it is benifit for the proximity and coalescence between droplets. Due to the increase of the density difference, microemulsion enriched phase separate from lower phase, then we get the three phase balance of aqueous phase, oil phase and middle phase microemulsion. When salinity increase to 6.6%, it will force more and more surfactant get into oil phase, and gradually form the upper phase microemulsion. As the following increase of the amount of NaCl , the amount of the surfactant in middle phase microemulsion is gradually reduced, until it is destroyed, showing the two-phase equilibrium of the upper phase microemulsion and the residual water phase.

The interfacial tension between microemulsion system and oil is measured under different sodium chloride concentration, and the relationship between microemulsion system and oil is shown in Fig. 4.

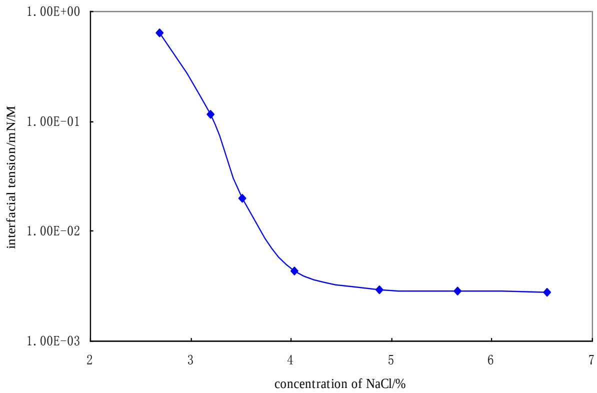

Fig. 4 Relationship between NaCl concentration and interfacial tension

According to the experimental results above, it can be seen that when the concentration of sodium chloride is 3.8%, the result is better and the consumption is reasonable when it comes to economic factors. So we determine the optimal formula of sodium chloride concentration is 3.8%

7. Determination of Alcohol Concentration

In the aqueous phase, keep the concentration of NaCl is constantly 3.8%, the concentration of the surfactant is 0.9%, then study the effect of the concentration of butanol on the phase behavior, and the phase diagram is shown in Fig. 5.

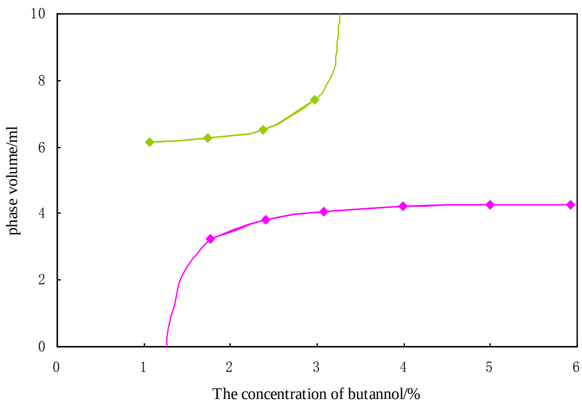

Fig.5 Relationship between the concentration of butanol and phase volume

Fig.5 shows the effect of butanol concentration on the phase behavior. When the alcohol concentration is less than 1%, the system occurred emulsification, it is difficult to be separated, at this time the weight ratio of butanol and surfactant is 3:2, the ratio of molar is 5:1. This phenomenon indicates that in microemulsion formation process, butanol not only has an effect on the droplet film, but also is distributed to oil and water phase to improve the two-phase properties. It is conducive to the reduce of interfacial tension and the formation of microemulsion.

Similarly, the charge density of the membrane consists of butanol molecule decreased, it is conducive to the droplet approach and coalescence. In addition, because of the exist of the composite membrane, its mechanical strength increased, and it is conducive to increase the oil solubilization capacity. These factors, also can make microemulsion enrichment phase become middle phase microemulsion from lower phase microemulsion. When the butanol concentration is higher than 3.3%, a large amount of oleophylic butanol is distributed to the oil phase, so that a large amount of the surfactant is also distributed to the oil phase and form the upper phase microemulsion, at the same time the middle phase microemulsion disappeared.

By comparing the Fig.1 and Fig.5, we know that when the middle phase microemulsion occur formation and disappearance, the molar ratio between the butanol and the surfactant is connected with the adding order. From Fig.5 we know that, for the system containing 0.9% surfactant at the beginning, the molar ratio when the middle phase microemulsion formation and disappearance is respectively 6.45 and 8.82. From Fig.1, for the system contains 4% butanol at the beginning, the molar ratio is 29.4 and 3.67. The reason is that in Fig.5, anion-nonionic Gemini mutiple surfactant micelle is formed first, adding butanol can form a composite film on the droplet interface and then become microemulsion. But in Fig.1, butanol has been distributed into water phase and oil phase, improve the properties of two-phase, and make the surfactant form into microemulsion in a lower concentration(0.5%). These facts indicate that, changing the oil-water two-phase properties through butanol, can reduce the surfactant dosage to form the middle phase microemulsion[17].

According to the experimental results above, the interfacial tension of oil and water is measured under different concentration of butanol. The results were shown in Fig. 6.

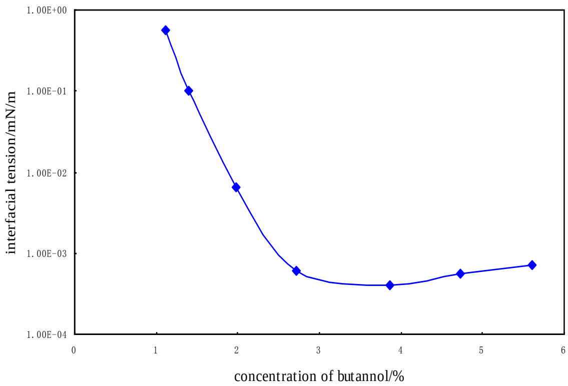

Fig. 6 The relationship between the concentration of butanol and interfacial tension

As shown in the figure above, the optimal concentration of butanol is 2.7%. So the formula of the optimum medium phase microemulsion is 0.9% anion-nonionic Gemini mutiple surfactant /2.7% butanol /3.8% NaCl solution /crude oil.

8. Oil Displacement Effect Experiment

Based on the results above, we select the following four oil displacement system:

(1) Optimal middle phase microemulsion system: 0.9% surfactant/2.7%butanol/3.8%NaCl solution/crude oil

(2) Upper phase microemulsion system: 0.9% surfactant/1%butanol/3.8%NaCl solution/crude oil

(3) Lower phase microemulsion system: 0.9% surfactant/4%butanol/3.8%NaCl solution/crude oil

(4) Surfactant system: 1.5% surfactant

Oil displacement experiment is conducted in cores that taken from a low permeable oil fields in the peripheral field of Daqing. First, saturate oil into the cores, and then conduct water flooding to 98% water content, write down water flooding efficiency. Then inject into all kinds of microemulsion or surfactant, let stand for 48h, then conduct subsequent water flooding until the oil can't move out, determine the ultimate oil recovery efficiency. The experimental results are shown in Table 1.

Table 1. Results of oil displacement experiment

Cores	Permeab-ility /$10^{-3}\mu m^2$	Porosity /%	Oil saturation /%	Experimental formulation	Water flooding efficiency/%	Enhanced efficiency/ %	Ultimate efficiency/ %
1	34.2	21.5	67.9	Water flooding+0.3PV middle phase microemulsion+48 h+subsequent water flooding	34.5	12.8	47.3
2	33.4	22.3	64.5	Water flooding+0.3PV lower phase microemulsion+48 h+subsequent water flooding	33.7	10.5	44.2
3	31.5	21.1	66.3	Water flooding+0.3PV upper phase microemulsion+48 h+subsequent water flooding	33.4	9.8	43.2

4	38.5	20.1	70.4	Water flooding+0.3PV surfactant+48h+subsequent water flooding	33.4	6.3	39.7

According to the experimental results, it can be found that after water flooding, inject optimal middle phase microemulsion system can improve oil recovery efficiency most, and the effect is also the best.

9. Conclusion

(1)When the concentration of anion-nonionic Gemini mutiple surfactant is less than 0.5% will form upper phase microemulsion, 0.5% to 2.3% form middle phase microemulsion, more than 2.3% form lower phase microemulsion, the optimized concentration was 0.9%.

(2)With the increase of the hydrocarbon chain of alcohol, the amount of the salt to form middle phase microemulsion decrease, but the salinity wide value also decrease, so the optimized alcohol is butanol.

(3)When the concentration of NaCl is 2.6% to 3.5% will form lower phase microemulsion, 3.5% to 6.2% form middle phase microemulsion, 6.2% to 6.6% form upper phase microemulsion. And when the concentration is 3.8%, the interfacial tension reduces most.

(4)Inject alcohol first then add surfactant can reduce the amount of surfactant to form middle phase microemulsion.

(5)The recovery efficiency of surfactant, upper phase microemulsion, lower phase microemulsion and middle phase microemulsion flooding improve 6.3%, 9.8%, 10.5% and 12.8% respectively. The results show that the effect of middle phase microemulsion is best.

References

[1] H.X. Luan: *Reseach on Synthesisi and Properties of Anion-nonionic Gemini surfactant* (Ph.D., Northeast Petroleum University, China 2013),p.32.

[2] L.F. Chen, Y.Z. Shang and H.K. Liu: Effect of the spacer group of cationic gemini surfactant on microemulsion phase behavior, Journal of Colloid and Interface Science, Vol. 2 (2006) No. 5, p.644.

[3] G.Z. Li, S.E. Song and X.W. Wang: The Formation and Characteristic of Middle Phase Mieroemulsion(I) Effect of Alcohols and Surfactant, Chinese Journal of Chemical Physics, Vol. 4 (1991) No. 4, p.296-301.

[4] K. Kanan, M. Al-Jabari, I. Kayali: Phase behavioral changes in SDS association structures induced by cationic hydrotropes, Arabian Journal of Chemistry, Vol. 4 (2012) No. 6, p.32–35.

[5] Q.L. Zhao: *Studies on Synthesis and Properties of Gemini Surfactants* (MS., Wuhan University, China 2005),p.121.

[6] J.C. Zhang, S.T. Gao: Displacement Effect Efficiency of Microemulsion with Daqing Died Oil in Core, Oilfield Chemistry, Vol. 7 (1990) No. 1, p.61-67.

[7] Q.S. Yuan: The Dynamic Interfacial Tension Characteristics and Influencing Factors Research, Petroleum Geology and Recovery Efficiency, Vol. 10 (2003) No. 3, p.67-69.

[8] H.S. Zou, J.L. Chen and W.B. Chen: Stability Analysis of Water-in-Oil Microemulsion System, Journal of South China University of Technology (Natural Science Edition), Vol. 36 (2008) No. 3, p.32-36.

[9] W.X. Wu, H.X. Luan and W. Ding: Thermodynamics for Micellization of Anionic-Nonionic Gemini Surfactants, Petrolchemical Technology, Vol. 42 (2013) No. 1, p.39-46.

[10] T.T. Zhou: Synthesis, *Surface and Aggregation Properties of Nonionic Poly(ethylene Oxide) Gemini Surfactants* (MS., Haerbin Engineering University, China 2007),p.64-66.

[11] D.P. Li: Introduction of Low Permeability Oilfield Development, Petroleum Geology and Oilfield Development in Daqing, Vol. 16 (1997) No. 3, p.36-40.

[12]B. Mahesh, T.P. Hsu: Design of an optimal middle phase microemulsion for ultra high saline brine using hydrophilic lipophilic deviation (HLD) method, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 488 (2016) No. 5, p.36-45.

[13]B.L. Zhou, H. Kon and J. Zhang: Oil Flooded Efficiency Research in Middle Phase Microemulsion, Chemical Engineer, Vol. 27 (2015) No. 11, p.35-37.

[14]Q.L. Jiang, Y.C. Xin and Y.L. Wang: The Phase Behavior and Stability of Oil Emulsion by Microemulsion Flooding, Journal of Jilin Institute of Chemical Technology, Vol. 17 (2000) No. 2, p.32-36.

[15]M.G. Aarra, H. Hoiland and A. Skauge: Phase Behavior and Salt Partitioning in Two- and Three-Phase Anionic Surfactant Microemulsion Systems: Part I, Phase Behavior as a Function of Temperature, Journal of Colloid And Interface Science, Vol. 16 (1999) No. 10, p.201-215.

[16]J.L. Chai, J.R. Zhao, X.D. Yang: Studies on the phase behavior of the microemulsions formed by sodium dodecyl sulfonate, sodium dodecyl sulfate and sodium dodecyl benzene sulfonate with a novel fishlike phase diagram, Colloids and Surfaces, Vol. 42 (2007) No. 2, p.31–35.

[17]C. Tongcumpou, E.J. Acosta, L.B. Quencer: Micro emulsion formation and detergency with oily soils: I. Phase behavior and interfacial tension[J]. Journal of Surfactants and Detergents, Vol. 32 (2003) No. 2, p.16–18.