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Research on the emulsification of weak-base ternary compound system and its effect on oil displacement efficiency

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ABSTRACT:
This paper researches the emulsification of weak-base ternary compound system and its effect on oil displacement efficiency, taking the drug concentration and oil recovery as the evaluation indexes, guided by reservoir engineering and physical chemistry, by means of chemical analysis and physical simulation. Results show that, after ternary compound system mixes with crude oil, surfactant and alkali dissolves into oil, while polymer can not. With the increase of oil-water ratio and reaction time, the distribution coefficient of alkali and surfactant in oil phase becomes larger. However, the mechanism of the two is different. The crude oil component, emulsification, alkali and polymer all have impact on the distribution of surfactant in crude oil. Compared with polymer flooding, the injection pressure of weak-base ASP flooding is higher, water cut is lower, and oil recovery increases.

Keyword: weak-base ternary compound system; distribution coefficient; crude oil component; physical simulation; emulsification; recovery degree; mechanism analysis

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ASP flooding technology is widely used because of its large increase in recovery degree, simple technology and strong reservoir adaptability. At present, field tests of ASP flooding have been carried out in Daqing Oilfield in China, and obtained obvious effects of increasing oil and reducing water cut [1-3]. In Daqing Oilfield, the strong alkaline ternary composite system is mainly used in the early flooding stage (The base is NaOH, the surfactant is heavy alkylbenzene petroleum sulfonate, and the polymer is partially hydrolyzed polyacrylamide.) Because strong alkali can interact with reservoir rock skeleton and cement, the reaction products are dissolved at high pH value. When the reaction product moves with the produced fluid to the oil well production system, the pH of the produced fluid decreases due to alkali consumption, and the calcium and magnesium plasma which is originally in the dissolved state will precipitate on oil tubes, and well pumps, resulting in the diameter of the pipeline to decrease, the flow resistance increases, the pump barrel wears up or the pump is stuck, and finally the production system is difficult to work normally [4-6]. Therefore, the scaling problem is one of the technical problems that plague the large-scale promotion and application of the strong alkali ternary composite system. In recent years, petroleum scientists have developed a weak base ternary system(The base is Na_2CO_3, the surfactant is petroleum sulfonate, and the polymer is partially hydrolyzed polyacrylamide) , The field test has achieved obvious effect of increasing oil and reducing water cut [7].

Compared with the strong base ternary composite system, the research on the weak base ternary composite system started late, and there are many technical problems to be solved further. This paper takes reservoir engineering and physical chemistry as theoretical guidance, chemical analysis and physical simulation as technical means, oil displacement agent concentration and recovery degree as evaluation indexes, the experimental study on the mass concentration distribution of oil displacement agent and its influence on oil displacement effect has been carried out, after the emulsification of weak alkali ASP system with crude oil. This is of great significance to the popularization and application of weak alkali ASP flooding in Daqing Oilfield and the improvement of oil production effect.

I. EXPERIMENT CONDITION

1.1 Experimental Materials

The polymer is a partially hydrolyzed polyacrylamide dry powder produced by Daqing Refining and Chemical Company(HPAM) , the effective content is 90%, the relative molecular weight is 2500 × 10^4, the surfactant is petroleum sulfonate, the effective content is 39%, and the alkali is Na_2CO_3. The experimental oils were dehydrated and degassed crude oil from the wellheads of the Daqing Lamadian Oilfield, Xingshugang Oilfield and Sartu Oilfield. The water used in the experiment was Daqing Oilfield injected sewage. The water quality analysis is shown in Table 1.

Table 1 Water quality analysis

Ionic composition	Cationic mass concentration ($mg\cdot L^{-1}$)			Anion mass concentration ($mg\cdot L^{-1}$)				Degree of mineralization($mg\cdot L^{-1}$)
	Ca^{2+}	Mg^{2+}	$K^{+}+Na^{+}$	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	
Sewage	44.37	14.95	1648.34	0.00	2349.27	1289.14	11.82	5357.89

The cores are quartz sand epoxy resin cementing inhomogeneous core, including 2 permeability layers. The water permeability are $200\times10^{-3}\mu m^2$ and $500\times10^{-3}\mu m^2$ respectively at 20℃. Geometric dimensions of core appearance: height × width × length = 4.5 × 4.5 × 30cm, and the thickness of each layer is 2.25cm.

1.2 Experimental apparatus

Warning mixer, 2500r/min, Electrolux Electric Co. LTD; Lu-418h high speed rotating centrifuge, Tianmei Scientific Instrument Co.LTD；722 grating spectrophotometer, Beijing Zhuoli Han Optical Instrument Co.LTD；Ux-300 energy dispersive X-ray fluorescence spectrometer, Spike Analytical Instruments ； GCMS-QD2010SE Gas chromatography-mass spectrometry, Shimadzu, Japan；Core displacement experimental apparatus.

1.3 Scheme design and experimental principles

1) Distribution law and influence factors of oil displacement agent in oil-water phase

The weak alkali ternary composite system (the mass fraction of polymer is 0.2%, the mass fraction of alkali is 1.2%, and the mass fraction of surfactant is 0.3%) was prepared by injecting sewage and mixed with crude oil at the volume ratio of 4:6, 5:5, 6:4, 7:3, 8:2 And 9:1, and the mixture was heated to 45 ℃, and then the emulsification experiment was carried out. The emulsion was kept at 65 ℃ for 24 h, and then centrifuged after gravity separation. The surfactant concentration in water phase was determined by two-phase titration, alkali concentration by acid-base titration and polymer concentration by starch cadmium iodide. The partition coefficient λ of oil displacement agent in oil-water phase is $\lambda = C_0/C_w = (C - C_w)/C_w$, where C is the initial concentration of oil displacement agent in water phase， C_0 is the concentration of oil displacement agent in oil phase， and C_w is the concentration of oil displacement agent in water phase.。

2) Effect of emulsification on improving recovery

Scheme 2-1：water flooding 98% + 0.7PV polymer flooding (the mass fraction of the polymer is 0.2%) + subsequent water flooding 98%.

Scheme 2-2: water flooding 98% + 0.7PV weak alkali ASP flooding (polymer mass fraction is 0.2%, alkali mass fraction is 1.2%, surfactant mass fraction is 0.3%) + subsequent water flooding 98%.

During the experiment, the injection rate is 1mL/min ， and the pressure recording interval was 30min .

II. RESULT ANALYSIS

2.1 Distribution law and influencing factors of oil displacement agent in oil-water phase

2.1.1 Distribution law of oil displacement agent concentration

Weak alkali ternary composite system is mixed with crude oil from Daqing Lamadian, Xingshugang and Saertu oil fields in volume ratios of 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1, after stirring for 1min, 3min and 5min, the concentration of surfactant and alkali in the water phase were detected, and calculated the partition coefficient of surfactant and alkali in the oil phase, as shown in Table 2. (Because the polymer has good water solubility, almost all of them exist in the water phase, the amount of adsorbed on the oil-water interface is small, and it is difficult to migrate to the oil phase, so the distribution coefficient of polymer in the oil phase is very low.)

It can be seen from table 2 that the partition coefficients of surfactant and alkali in oil phase vary with the physical properties of crude oil. The distribution coefficient of surfactant and alkali is the largest in Lamadian Oilfield, followed by Saertu Oilfield, and Xingshugang Oilfield is the smallest. After emulsified with crude oil, surfactant molecules will enter into the oil phase by physical mixing due to the existence of oleophilic groups in the surfactant molecular chain. With the increase of the volume ratio of crude oil to polymer, the migration and dispersion of surfactant molecules from aqueous phase to oil phase gradually increases, which leads to the increase of partition coefficient.

Alkali saponified with colloidal, asphaltic components and many polar oxygen, sulfur, nitrogen, and other organic compounds in crude oil to form surfactant such as naphthenic acid and fatty acid, which are conducive to the formation and stability of emulsion [8]. With the decrease of the volume ratio of ternary to crude oil, the contact range of alkali and crude oil is enlarged, the reaction between alkali and crude oil is more sufficient, the consumption of alkali in oil phase increases, and the distribution coefficient of alkali increases.

2.1.2 Discussion on the difference of action mechanism between oil displacement agent and crude oil in each oilfield

The n-alkane component analysis of the extracted oil in Lamadian, Saartu and Xingshigang oilfields is shown in Table 3.

Table 2 The distribution coefficient of surfactant and alkali in oil phase

Ternary to crude oil volume ratio	Mixing time (min)	Satreu crude oil		Xingshugang crude oil		Lamadian crude oil	
		Surfactant distribution coefficient	Alkali distribution coefficient	Surfactant distribution coefficient	Alkali distribution coefficient	Surfactant distribution coefficient	Alkali distribution coefficient
4:6	1	0.28	0.08	0.25	0.03	0.29	0.22
	3	0.32	0.09	0.29	0.04	0.36	0.24
	5	0.42	0.10	0.39	0.08	0.45	0.25
5:5	1	0.20	0.07	0.19	0.02	0.23	0.20
	3	0.29	0.07	0.26	0.03	0.35	0.21
	5	0.32	0.08	0.31	0.06	0.41	0.24
6:4	1	0.16	0.06	0.14	0.02	0.17	0.17
	3	0.26	0.06	0.25	0.02	0.30	0.19
	5	0.28	0.07	0.29	0.05	0.36	0.23
7:3	1	0.14	0.05	0.10	0.01	0.15	0.15
	3	0.20	0.05	0.11	0.02	0.23	0.16
	5	0.21	0.06	0.16	0.05	0.33	0.17
8:2	1	0.07	0.04	0.06	0.01	0.09	0.05
	3	0.12	0.04	0.08	0.01	0.16	0.09
	5	0.17	0.05	0.10	0.04	0.20	0.10
9:1	1	0.03	0.02	0.01	0.01	0.06	0.04
	3	0.07	0.03	0.04	0.01	0.13	0.06
	5	0.08	0.04	0.06	0.02	0.15	0.07

Table 3 The relative content of the n-alkanes component in raffinate

Oil field	Relative content(%)		$\sum C_{21}$after/$\sum C_{21}$before	Main peak carbon
	C_{10}~C_{20}	C_{21}~C_{40}		
Satreu	46.4	53.6	1.15	nC_{22}
Xingshugang	42.3	57.7	1.36	nC_{21}
Lamadian	31.2	68.8	2.21	nC_{23}

(Notes: "After $\sum C_{21}$/Before$\sum C_{21}$" is the ratio between the relative content of n-alkanes (C_{21}~C_{40}) and (C_{10}~C_{20}))

It can be seen from table 3 that the ratio of relative content of n-alkanes (C_{21}~C_{40}) to (C_{10}~C_{20}) in Saertu oilfield and Xingshugang oilfield is 1.15 and 1.36, while that of Lamadian oilfield (C_{21}~C_{40}) to (C_{10}~C_{20}) is 2.21, and the main peak carbon of crude oil is nC_{23}. It shows that the content of heavy components in n-alkanes of extracted oil in Lamadian Oilfield is relatively high, and the carbon chain distribution range is wide. According to the principle of similar phase solubility, surfactants are easier to enter the oil phase. Therefore, the distribution coefficient of surfactant in Lamadian crude oil is large.

2.1.3 Distribution law of surfactant in oil-water phase

(1) Effect of mixing time

The weak alkali ternary composite system was mixed with Daqing Xingshugang oilfield crude oil by volume ratio of 5:5，After stirring for 1min, 3min, 5min, 7min, 9min and 11min, the concentration of surfactant in the aqueous phase was tested. The influence of stirring time on the distribution coefficient of surfactant in oil phase was shown in Fig. 1.

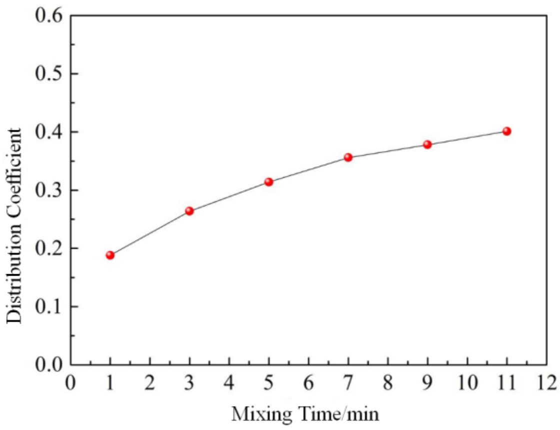


Fig.1 The effect of stirring time on the distribution coefficient of surfactant in oil phase

It can be seen from Fig. 1 that under the same volume ratio of ternary to crude oil, with the increase of stirring time, the surfactant had more sufficient contact with crude oil in the ternary composite system, the migration and dispersion of surfactant molecules from water phase to oil phase increases, the content of surfactant in water phase decreases, and the partition coefficient in oil phase becomes larger.

(2) Effect of emulsification

The weak alkali ternary composite system was mixed with Daqing Xingshugang oilfield crude oil at the volume ratio of 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1, and the surfactant concentration in the aqueous phase after a certain time was tested. (Considering the influence of non emulsification on the distribution coefficient of surfactant, the sample was poured into the measuring cylinder and placed in the constant temperature box at 45 ℃ for a certain time, and the surfactant concentration in the aqueous phase was tested), The effect of emulsification on the partition coefficient of surfactant in oil phase is shown in Fig. 2.

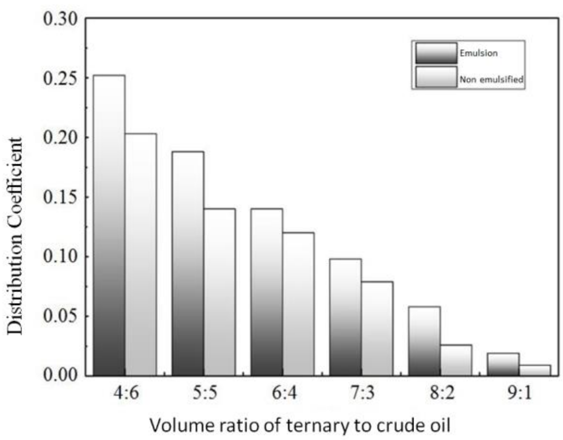


Fig.2 The effect of emulsification on the distribution coefficient of surfactant in oil phase

It can be seen from Fig. 2 that the distribution coefficients of emulsified and non emulsified surfactants have the same trend in oil phase. When the volume ratio of ternary to crude oil is the same, the distribution coefficient of non emulsified surfactant is less than that of emulsified surfactant. Because in the emulsification process, the contact area between surfactant solution and crude oil increases, and the adsorption and retention amount of surfactant at the oil-water interface becomes larger, which reaches a new equilibrium, thus increasing the distribution coefficient of surfactant in the oil phase [9].

(3) The influence of strong base and weak base

The strong alkali ternary composite system (alkali was NaOH) and the weak alkali ternary composite system (alkali was Na_2CO_3) were prepared by sewage (the mass fraction of polymer was 0.2%, the mass fraction of alkali was 1.2%, and the mass fraction of surfactant was 0.3%). The strong alkali and weak alkali ternary composite system were mixed with Daqing Xingshugang oil field crude oil at the volume ratio of 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1, and the surfactant concentration in the aqueous phase was tested after stirring for a certain time. The influence of strong base and weak base on the partition coefficient of surfactant in oil phase is shown in Fig.3.

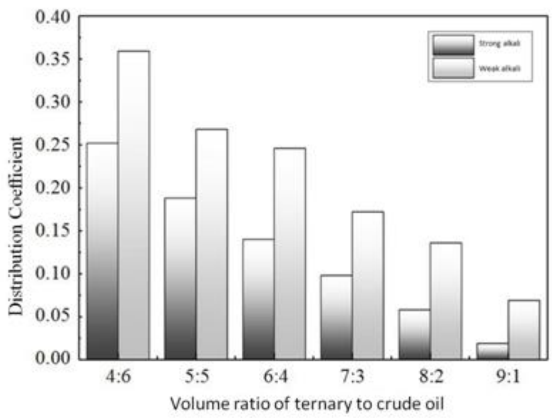
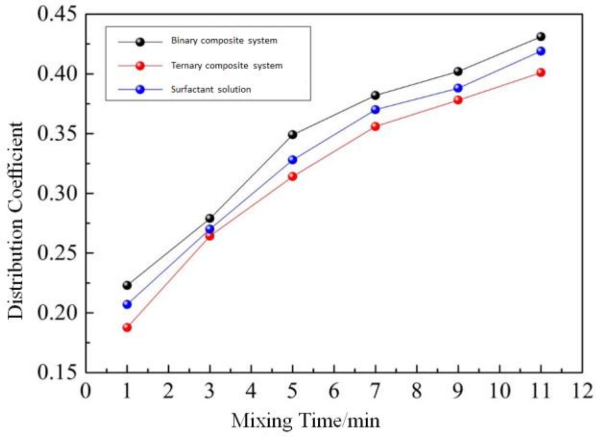


Fig.3 The effect of strong base and weak base on the distribution coefficient of surfactant in oil phase

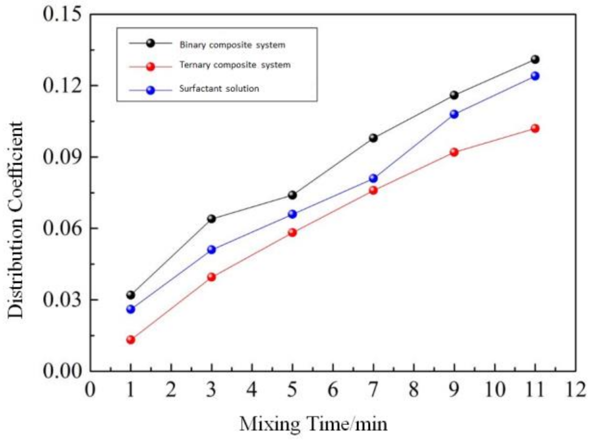
It can be seen from Fig. 3 that with the increase of the volume ratio of ternary to crude oil, the distribution coefficient of surfactants in the strong alkali and weak alkali ternary system decreases continuously. Under the same volume ratio of ternary to crude oil, the partition coefficient of surfactant in oil phase in strong alkali ternary system is greater than that in weak base ternary system.

(4) Influence of alkali and polymer

The "AS" binary composite system (the mass fraction of alkali is 1.2%, and the mass fraction of surfactant is 0.3%), the "ASP" ternary composite system(The mass fraction of polymer is 0.2%, the mass fraction of alkali is 1.2%, and the mass fraction of surfactant is 0.3%) and the surfactant solution (the mass fraction of surfactant is 0.3%) were prepared by sewage, and then mixed with the crude oil of Daqing Xingshigang Oilfield by volume ratio of 5:5 and 9:1 respectively. After stirring for 1min, 3min, 5min, 7min, 9min and 11min, the surfactant concentration in the aqueous phase was tested. The influence of alkali and polymer on the partition coefficient of surfactant in oil phase is shown in Fig. 4.



(a) The ratio of ternary to crude oil by volume is 5:5



(b) The ratio of ternary to crude oil by volume is 9:1

Fig.4 The distribution coefficient of surfactant in oil phase

It can be seen from Fig. 4 that under the same volume ratio of ternary to crude oil and stirring time, the distribution coefficient of surfactant in the oil phase is the lowest in the "ASP" ternary composite system, followed by the surfactant solution, and the "AS" binary composite system is the largest. Both alkali and polymer can affect the partition coefficient of surfactant in oil and water. On the one hand, alkali increases the ionic strength in the aqueous phase, leading to the enhancement of the repulsive force of the surfactant in the aqueous phase, thus forcing the surfactant to dissolve into the oil phase. On the other hand, the polymer enhances the apparent viscosity of the system, greatly slows down the diffusion rate of surfactant, while the adsorption of polymer molecules at the oil-water interface increases the strength of the interfacial film and hinders the diffusion of surfactant molecules into the oil phase. At the same time, the non-polar part of the surfactant can be combined with the macromolecular chain of the polymer to form an association complex, which reduces the distribution capacity of the surfactant in the oil phase [10-12]. For the ternary composite system, the influence of polymer is greater than that of alkali, resulting in the partition coefficient of surfactant in oil phase is less than that of surfactant solution.

2.2 Effect of emulsification on improving recovery

(1) Experimental results of recovery degree

The weak alkali ASP flooding experiment was carried out on two-dimensional longitudinal heterogeneous core. The experimental results of recovery degree are shown in Table 4. As can be seen from Table 4, compared with plan 2-2, the recovery degree of "Plan 2-1" increased by 21.7%, while that of "plan 2-2" increased by 28.3%, with a difference of 6.6%. It can be seen that the recovery degree of weak alkali ternary compound flooding increases greatly, which will be further described in the subsequent dynamic characteristics analysis.

(2) Experimental dynamic characteristics

The relationship between injection pressure, water cut, recovery degree and PV number in the experimental process of scheme 2-1 and scheme 2-2 is shown in Fig. 5.

Table 4 The recovery date

Parameter / Scheme	Slug size (PV)	permeability measured with wate K ($\times 10^{-3}\mu m^2$)	Work viscosity (mPa·s)	Oil saturation (%)	Recovery degree(%)		
					Water flooding	Combination flooding	Value added
2-1	0.7	351	40	68.5%	33.5	55.2	21.7

2-2	0.7	348	40	68.2%	33.2	61.5	28.3

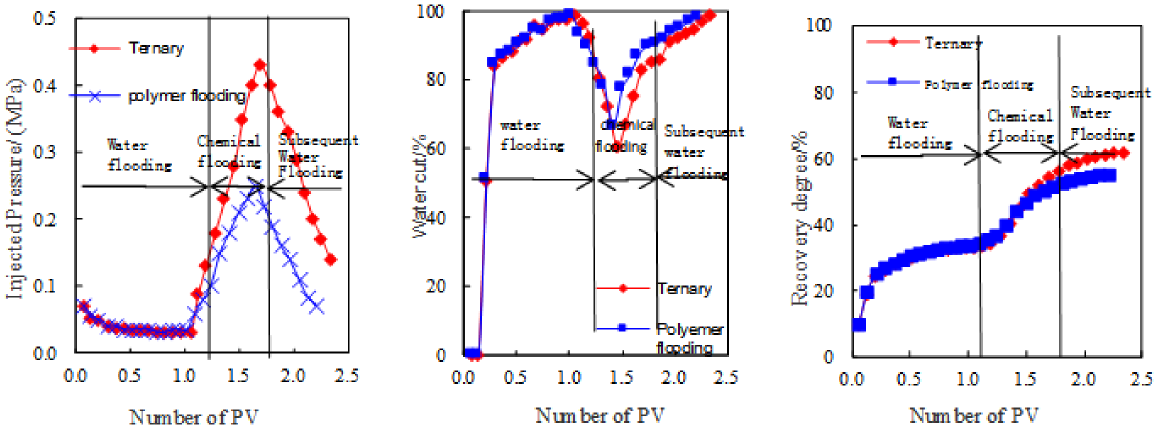
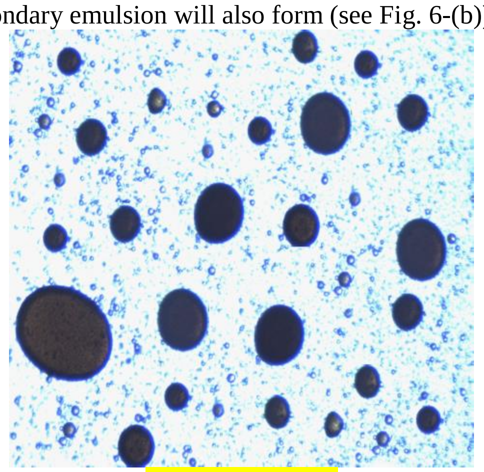


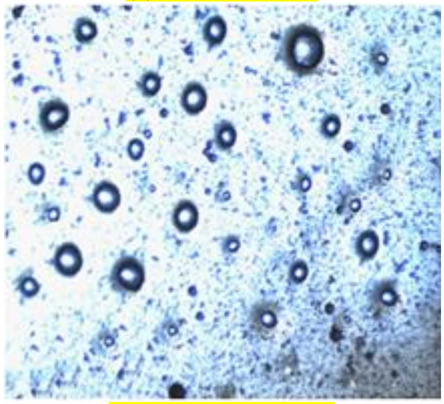
Fig.5 The relationship between injection-pressure, water cut, recovery percent and pore volume

It can be seen from Fig. 5 that compared with polymer flooding, the weak alkali ASP flooding has higher injection pressure, lower water cut and higher recovery degree. The main role of emulsification on oil displacement is emulsification carrying and profile control. The reason for the emulsification is that petroleum sulfonate and Na_2CO_3 in the weak alkali ternary composite system generate ultra-low interfacial tension in the formation pores, which makes the eroded oil form O/W emulsion flows easily, thus improving the oil washing efficiency. The profile control mechanism of emulsion is mainly the high viscosity emulsion in the process of displacement, which preferentially enters into the high permeability layer. When the emulsion migrates in the high permeability layer, its permeability reduces due to the effects of blocking aggregation, adsorption, etc. These has a certain blocking effect on these layers. On the other hand, the emulsion flows into the low permeability layer and displace the remaining oil in the low permeability layer, which can improve the heterogeneity to a certain extent. In other words, emulsification in the oil displacement process is conducive to the expansion of sweep efficiency [13]. At the same time, in the case of weak alkali ternary system and polymer system with equal consistency and viscosity, the effect of expanding sweep volume due to polymer adsorption retention in both systems can be considered to be the same. As the oil/water emulsion formed by ultra-low interfacial tension, the oil droplets passing through the tiny pore throat in the seepage process will produce Jamin effect, which leads to the increase of seepage resistance, changes the flow direction of injection fluid, expands the swept volume and enhances the oil recovery.

The emulsion type of the produced liquid was water-in-oil type, which was analyzed by micro observation method (see Fig. 6- (a)). Its size was smaller and the size distribution was uniform. When the shearing effect of the core is strong, W/O/W type secondary emulsion will also form (see Fig. 6-(b)).



(a) O/W emulsion



(b) W/O/W emulsion

Fig.6 Emulsion type of produced liquid

III. CONCLUSION

(1) After contacting with crude oil, some surfactants and alkali in the ternary composite system will transfer into the oil phase, but the polymer is difficult to enter. With the increase of oil-water volume ratio and contact time, the partition coefficients of alkali and surfactant in oil phase increase, but their action mechanisms are different.
(2) Crude oil composition is an important factor affecting the distribution of surfactants in oil and water. The content of heavy components in crude oil of Lamadian oilfield is relatively high, and the distribution range of carbon chain is wide. According to the principle of similar phase solubility, surfactants are easier to enter the oil phase.
(3) Under the condition of the same oil-water volume ratio, the distribution coefficient of the non-emulsified surfactant is less than that of the emulsified surfactant, and the distribution coefficient of the strong alkali ternary composite system is greater than that of the weak alkali ternary composite system. Both alkali and polymer affect the distribution of surfactant in oil and water.
(4) Compared with polymer flooding, weak alkali ASP flooding has higher injection pressure, lower water cut and higher recovery degree.

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