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Effects of petroleum sulfonate on the OMA structure in shengli oilfield produced water*

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Abstract: ***Objective*** In order to improve the treatment efficiency of the produced water from oilfield, and investigate the mechanism of the stability of the waste water, the influence of surfactant on the oil mineral aggregate (OMA) structure and separation of oil from water was studied. ***Methods*** The effects of petroleum sulfonate on the structure of OMAs formed by montmroillonite and crude oil from Shengli oilfield were investigated by measuring the zeta potential and separation of oil and water. ***Results*** The results indicated that the zeta potential of the OMA became more negative with the increasing petroleum sulfonate concentrations to some extent, and the zeta potentials of the OMA were higher than that of the oil droplets and montmorillonite when log[(w)(TRS)/ %]changed from −3 to −1.75, but the zeta potentials of OMA were lower than that of oil droplets when log[(w)(TRS)/ %] changed from −1.75 to −0.25. In other hand there was more water incorporated into OMAs because of the enhanced hydration ability of the montmorillonite and oil droplets by adsorption the petroleum sulfonate. And as a result, the OMA floated to the upper layer accompanied by much more water which made it difficult to separate oil water from oilfield. However, water content was decreased and some oil was released from the upper layer when the concentration of the TRS was in the range of 0.3%～0.5%. It was because that the dispersive ability of the TRS increased and the oil droplet became smaller, then fewer solid fines was required to form OMA structure and the bonding force between the oil droplet and the solid fine particle was weakened when the concentration of the TRS was high enough. ***Conclusion*** The separation of oil from water become difficult because of the existence of the TRS. However, the petroleum sulfonate could be used as chemical dispersant as the concentration was high enough, and the oil can be released from the waste water.

Key words: Zeta Potential; Petroleum Sulphonate(TRS); OMA(oil mineral aggregates); Separation of oil and water; Dense phase

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石油磺酸盐对胜利油田采出水中 OMA 结构的影响

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摘　要　目的　为提高油田采出水的处理效率,研究采出水稳定性机理,考察表面活性剂对污水中 OMA 结构及油水分离的影响。**方法**　通过 zeta 电位的测定及油水分离情况,研究了石油磺酸盐对胜利油田原油与蒙脱土之间形成的 OMA 结构的影响。**结果**　在一定程度范围内,OMA zeta 电位随石油磺酸盐浓度的增加而增加,而且当 log[(w)(TRS)/ %]自−3 到−1.75 之间变化时,OMA 的 zeta 电位高于油滴及蒙脱土 zeta 电位,但当 log[(w)(TRS)/ %]处在−1.75 ～−0.25 之间时,OMA 的 zeta 电位低于油滴的 zeta 电位。另一方面,由于蒙脱土和油滴吸附了石油磺酸盐,增强了其水化作用,使得 OMA 含水量增加,导致了 OMA 携带了大量的水上浮,从而使得油水分离难度增加。然而当石油磺酸盐浓度处于 0.3%～0.5%时,石油磺酸盐浓度足够高时,由于石油磺酸盐的分散能力较强,导致了油滴变小,OMA 中结合的固体颗粒减少,使得固体颗粒与油滴之间的相互作用力降低,导致上层液油滴析出。**结论**　石油磺酸盐的存在增加了油水分离难度。但当其浓度足够高时,分散能力增强,可拆散污水中的 OMA 结构,使油析出。

关键词　Zeta 电位;石油磺酸盐;油矿物聚集体;油水分离;致富相

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In recent years with the development of the tertiary oil production the amount of produced water increases greatly, and the property of the produced water becomes more complicated and more difficult to be treated. Meanwhile, owing to the lack of the knowledge of the property and mechanism of the stability of the produced water, the technology for the treatment of the produced water has not been developed. It is necessary to study the nature of the waste water and to find the key factors which dominate the stability of the produced water.

Chemical flooding agents and solid particles are commonly found and of great importance in stabilizing the produced liquid from oilfield. Therefore, the study about the effects of surfactant and solid particles on the stability of produced liquid has attracted the interests of many researchers[1-2]. Wang[3-4] pointed out that the petroleum sulfonate promotes the stability of the crude emulsion to some extent by enhanced the interfacial film at the oil-water interface and increased the zeta potential of the oil droplets. Yan[5] believed that solid particles promote the stability of the emulsion by forming net-like structure and rigid films at the oil-water interface which prevent the oil droplets from aggregating. The studies of Bragg[6]. indicated that the oil mineral aggregates are likely to be formed by the interaction of suspended mineral fines with crude oil, and the mineral fines can stabilize oil droplets. The detailed studies[7] of OMA formation have revealed that oil associates with fine mineral particles in an aqueous medium not only as molecules adsorbed onto mineral surfaces, but also as a discrete phase to form microscopic oil-mineral aggregates. Khelifa and Stoffyn[8] et al. pointed out that the type and size of OMA was controlled by the mineral type and surface properties, quantity, viscosity and composition of the oil, and oil/mineral ratio. In addition to this conflicting results have been reported with regard to the effects of chemical dispersants on formation and fate of OMAs in both laboratory and oilfield studies[9] found that OMA formation was negligible with chemically-dispersed oil in water column, whereas Guyomarch et al. reported that significant amounts of oil were incorporated into OMAs when oils and chemical dispersants were mixed with mineral fines. Zheng[10] pointed out that the chemical dispersants could change the surface physicochemical properties of oil droplets to impair the binding of oil to mineral fines.

Petroleum sulfonate is widely used surfactant in oilfield and it is expected to affect formation and fate of the OMA existed in the produced water because the surface physicochemical properties of oil droplets and clay particles could be altered by the adsorption of the TRS on them.

1 EXPERIMENTAL

1.1 Materials

A jet fuel from a refinery without any additives was purified by silica gel adsorption before the experiments were carried out. The silica gel was heated for 10 h at 160℃ in a muffled oven and then cooled in a vacuum desiccator at room temperature before the silica gel was used.

The physical parameters of the crude oil (from Shengli Oilfield) used in this study were as follows: density 0.908 $g \cdot cm^{-3}$, acid value 3.217mg $KOH \cdot g^{-1}$ oil, and Viscosity 2078 $MPa \cdot s$ at 50℃. The crude oil in investigation was dissolved in the purified jet fuel as model oils.

The dark brown viscous petroleum sulphonate liquid was synthesized by Designing and Research Institute of Shengli Oilfield in China. The main component of the petroleum sulphonate was alkylbenzene sulphonate, and the active content of the surfactant was 48.69% by mass. The sulphonated oil content was more than 75% by mass and salt content was less than 6%. The physical parameters were as follows: solubility≥20% in water at 40℃, the pH value of 1% by mass aqueous solution is 7～9, and the ability of resistance to Ca^{2+} and Mg^{2+} ≥120 $mg \cdot L^{-1}$.

The Na-montmorillonite used in this study was obtained from the Institute of Chemistry Academy of Science. The chemical analysis of the Na-montmorillonite was shown in table 1.

Table 1 Chemical analysis of the Na-montmorillonite w %

Al_2O_3	SiO_2	K_2O	Na_2O	MgO	CaO	MnO	TiO_2	Fe_2O_3	Others
7.95	69.8	0.446	9.75	1.48	0.086	0.0078	0.0431	1.06	9.38

The water used in the experiments was distilled water and synthetic formation water, the composition of the latter is shown in table 2.

Table2 Composition of formation water

Ion	Cl^-	HCO_3^-	$Na^+ + K^+$	Mg^{2+}	Ca^{2+}
Concentration mg/L	2885.5	818.9	2064.6	20.9	66.9

1.2 Measurement of the zeta potential of OMA

The effect of TRS on the OMA structure was detected by determining the zeta potentials and the separation of oil and water from the suspension containing OMA structure.

The zeta potential measurement was conducted on a Zetaplus analyzer(Brookhaven Company, USA).

The emulsification was carried out by utilizing a CAT×120 dispering tool for 2 min at 6000 r. p. m.

The samples were prepared by using distilled water with different concentrations of petroleum sulfonate and montmorillonite mixing with the model oils(w/o ration: 100 : 1, v/v) by agitating, then the samples were left to stand for 24h for the measurement of zeta potential and the samples used to be measured were obtained from the situation below the surface 2cm to avoid obtaining the oil droplets floating to the upper layer.

1.3 Separation of oil and water measurement

The o/w emulsions were prepared by mixing aqueous phase containing the petroleum sulfonate and montmorillonite with oil phase (aqueous phase/oil phase ratio: 4 : 1, v/v). The emulsification was carried out by shaking the mixture in a 50 ml cylinder 200 times. The stability of emulsion was determined visually by measuring the changes of the dense phase volume fraction with time at 30℃.

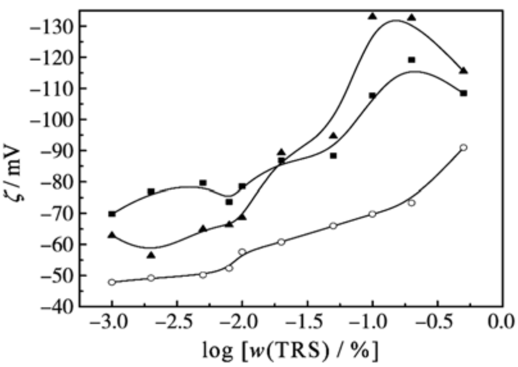
2 RESULTS AND DISCUSSIONS

2.1 Effects of the Na-montmorillonite on the OMA structure

According to the studies of Wang[6] that the OMA can be formed by crude oil droplet and montmorillonite particle, and the zeta potential of the OMA are obviously higher than that of both the model crude oil droplets and montmorillonite particles (zeta potential of montmorillonite particle existed in distilled water −38.9 mV[5]). The zeta potential of the particles increase notably as the concentrations of Na-montmorillonite increase from 0 to 300 mg · kg^{-1}, but the zeta potential is almost not changed any more as the concentration of montmorillonite increase. Because of the high zeta potential values and the strong interfacial films it is more difficult for the OMA to combine with each other or with more oil droplets. As a result the structure of the OMA should be the style of liquid OMA structure under the experiment conditions, and with the increase of the concentrations of montmorillonite, more and more solid particles were trapped by the OMA structure which led to the increase of the zeta potential of the OMA structure. The flocculates with over-trapped solid particles would be settled by the gravities when the concentration of the montmorillonite was high enough, as a result the zeta potential of the suspension measured in the experiment was not changed obviously when the concentration of the montmorillonite exceeded 300 mg · kg^{-1}.

2.2 Effects of the petroleum sulfonate on the OMA structure

The effects of petroleum sulfonate on the OMA structure was detected by measuring the zeta potentials of the OMA existed in the emulsion (Fig. 1).



■ 3% model crude oil + 200 mg·kg^{-1} Na-montmorillonite + TRS solution with distilled water; ▲ 3% model crude oil + TRS solution with distilled water; ○ 200 mg·kg^{-1} Na-montmorillonite + TRS solution with distilled water

Figure 1 Effects of petroleum sulfonate on the zeta potential of the OMA particles in the complex system

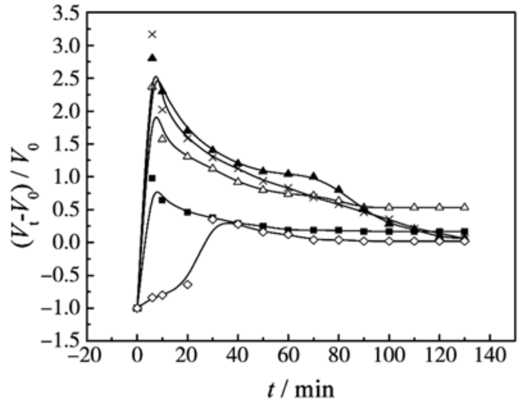
Figure 1 showed that the increasing tendency of the zeta potential of OMA particles(exist in the complex system containing montmorillonite, petroleum sulfonate and model crude oil)was similar to that of the oil droplets (in the system with TRS and model crude oil) as the increasing concentration of petroleum sulfonate. Moreover, the zeta potentials of the particles in the former system were higher than that of the latter system when the concentration of the TRS was not too high, however, it did not look like this when the concentration of the petroleum sulfonate was high enough, the zeta potential of the former particle became gradually same with that of the later particles at first and then it was lower than that of the latter as the concentration of the petroleum sulfonate increased continuously.

Moveover another phenomenon was observed during the experimental process. There was a little oil released from the suspensions in the upper layer, and the lower layer was turbid, when the concentration of the TRS was high enough.

Figure 1 also indicated that the zeta potential of the particles was decreased when the concentration of the petroleum sulphonate was high enough which might be caused by the surface conductance or by the relaxation and retardation effect on the electrophoretic mobility of the particles with high charge density.

2.3 Effects of the petroleum sulfonate on the stability of OMA and emulsion

The changes of the dense phase volume fraction were used to measure the influences of petroleum sulfonate on the stability of the emulsion (Figure 2).



Oil phase: 3% model crude oil; water phase: suspension prepared by model water with TRS and montmorillonite. The composition of the water phase of the curves: ◇ 0.05% TRS, ■ 0.01% TRS + 200mg·kg^{-1} montmorillonite; △ 0.05% TRS + 200mg·kg^{-1} montmorillonite; ▲ 0.3% TRS + 200mg·kg^{-1} montmorillonite, × 0.5% TRS + 200 mg·kg^{-1} montmorillonite

Figure 2 The dense phase volume fraction change curve with time in the complex emulsion

From figure 2 it can be seen that the slope of dense phase volume fraction change curve in the complex system was larger than that of the curve in the system only containing the TRS. It indicated that the rise rate of flocculation in the complex system was faster than the other.

Figure 2 showed that in the complex system the maximum dense phase volume fraction value increased with the increase concentration of the petroleum sulfonate, and the final stable dense phase volume fraction value also increased with the increase of the concentration at low petroleum sulfonate concentrations (0.01% ~ 0.05%). Moreover, it was higher than that of the stable value in the suspension containing montmorillonite without TRS.

During the experimental process it was observed that the final stable dense phase volume fraction value in the complex system was close to that of in the TRS system without montmorillonite when the petroleum sulfonate concentration in the range of(0.3%～0.5%). Moreover, there was some oil released from the suspension and formed the continuous oil phase in the upper layer after standing for 30 min, while there was no continuous oil phase appeared at the lower concentration of the TRS in the complex system after standing for 30 min.

These phenomena can be explained by the following reasons. OMA formed by the reaction of montmorillonite and oil droplets in emulsion was influenced by the salinity and surfactant in the aqueous solution. There might be existed a complex OMA structure between the model oil droplets and montmorillonite particles under the model water condition, and there were multiple oil droplets in one OMA structure which resulted in the fast floating of the flocculation in the complex system.

The increasing of the maximum dense phase volume fraction with the increase of the petroleum sulfonate concentration indicated that the water content increase in the upper dense phase. This might be caused by the following reasons, the adsorption of the TRS molecular on the montmorillonite and oil droplet enhanced the hydration of them and made the hydrated layer become thicker because of the strong hydrophilic ability of the TRS. As a result, with the float of OMA to the upper layer(a mixture of emulsion and suspension of the solid particle and water) of the emulsions there was more water entering the upper layer.

With the increase in the concentration of the TRS the strength of the interfacial film became stronger and the zeta potential of the colloid particles also increased when the concentration of the surfactant changed form 0.1%～0.3%[5-6], which made it more difficult for the particles existed in the dense phase to aggregate with each other. In the other hand the network structure of the OMA might be reinforced by the additional strength of the interfacial film, and moreover the increase of the concentration of TRS intensified the hydration of the montmorillonite. Therefore, there was more water was trapped by the OMA and the stable dense phase volume fraction value was higher. However, when the petroleum sulfonate concentration was high enough the zeta potential of the oil droplet and the montmorillonite particle charged more negatively, and then the dispersive action of TRS appeared and OMA structure formed by montmorillonite and oil droplet was altered and less solid particle was trapped by the OMA structure. Therefore, the strength of interfacial film and the network structure decreased and less water was trapped in the flocculation, which made it easy for the oil droplet to aggregate and a little oil to be released and the stable dense phase volume fraction to decrease.

3 Conclusions

Based on this study it can be concluded as followings:

3.1 The oil-mineral aggregates(OMA) structure was influenced by the salinity and TRS in the aqueous solution. The zeta potential of the OMA was higher than that of the oil droplet and montmorillonite particle when log[(w)(TRS)/ %] changed from −3 to −1.75, but, when log[(w)(TRS)/ %] changed from −1.75 to −0.25, the zeta potential of OMA was lower than that of oil droplet.

3.2 The dispersive ability of the TRS was enhanced when the concentration of TRS changed from 0.3%～0.5%, as a result a little oil was released form the complex system. The petroleum sulfonate could be used as chemical dispersant as the concentration was high enough.

3.3 As the concentration of TRS was in the range of 0.01%～0.3%, the adsorption of TRS reinforced the hydration extent of montmorillonite particles and oil droplets, and the water content in OMA structure increased which led to the upper dense phase holding more water (下转第 338 页)

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than that of in the system without TRS. When the concentration of TRS changed form 0.3%~0.5% the water content in the upper dense phase was reduced and the separation degree of oil and water was enhanced because of the enhanced dispersive ability of the TRS and the decreased content of the montmorillonite in OMA.

NOMENCLATURE

ζ zeta potential,mV

t separation time,min

w mass percent concentration,%

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