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Influences of water treatment agents on oil-water interfacial properties of oilfield produced water

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Abstract: The emulsion stability of oilfield produced water is related to the oil-water interfacial film strength and the zeta potential of the oil droplets. We investigated the effects of water treatment agents (corrosion inhibitor SL-2, scale inhibitor HEDP, germicide 1227, and flocculant polyaluminium chloride PAC) on the stability of oilfield produced water. The influence of these treatment agents on oil-water interfacial properties and the mechanism of these agents acting on the oilfield produced water were studied by measuring the interfacial shear viscosity, interfacial tension and zeta electric potential. The results indicated that the scale inhibitor HEDP could increase the oil-water interfacial film strength, and it could also increase the absolute value of the zeta potential of oil droplets. HEDP played an important role in the stability of the emulsion. Polyaluminum chloride (PAC) reduced the stability of the emulsion by considerably decreasing the absolute value of the zeta potential of oil droplets. Corrosion inhibitor SL-2 and germicide 1227 could decrease the oil-water interfacial tension, whereas they had little influence on oil-water interfacial shear viscosity and oil-water interfacial electricity properties.

Key words: Water treatment agents, oil-water interfacial properties, emulsion stability, oilfield produced water

1 Introduction

Water flooding is one of the primary methods for increasing the ultimate recovery and the profit in development of oilfields, and the quality of the injection water is critical to achieve highly-efficient development of the oilfields. However, repeated use of injection water leads to increases of the concentration of complicated components of the oilfield produced water, which consists of solid impurities, oil suspensions, dissolved gases, salts, and organic compounds. It brings new problems to the treatment of oilfield produced water (Wang, 1999; Deng et al, 2000; Lin et al, 2012), such as poor treatment effectiveness, a significant increase in the treatment cost, and pollution of drainage and injection water. These problems affect not only the further improvement of oil recovery due to the increase in the cost of oil production, but also the environment and ecological balance. Therefore, treatment of oilfield produced water is an urgent issue of significant importance, and the oil-water interfacial properties are the key factors influencing the stability of the suspension and emulsion (Tsamantakis et al, 2005; Opawale et al, 1998).

The presence of wastewater treatment agents inevitably influences the interfacial properties of the oilfield produced water (Santini et al, 2010; Allenson et al, 2011; Chen et al, 2007). To investigate the effect of water treatment agents on the stability of the oilfield produced water, the oil-water interfacial properties and the mechanism of these agents acting on the oilfield produced water are studied in this paper. This study can provide a basis and guidance for efficient treatment of oilfield produced water; it also has practical significance for the selection of oilfield wastewater treatment agents.

2 Materials and methods

2.1 Materials and instruments

Reagents

Crude oil, and oilfield produced water which was used as a reference for preparation of simulated oilfield produced water in laboratory, were from the Shengli oilfield (China); Kerosene (the interfacial tension of the kerosene treated by silicone was 46.61 $mN \cdot m^{-1}$).

Corrosion inhibitor SL-2 (maleic anhydride copolymer); scale inhibitor HEDP (hydroxyethylidene diphosphonic acid); germicide 1227 (dodecyl benzyl dimethyl ammonium chloride); flocculant PAC (polyaluminium chloride). All these water treatment agents were obtained from Shandong Taihe Water Treatment Co., Ltd. (China), and all these water treatment agents (technical pure) were used as received.

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Instruments

SVR-S interfacial viscoelastic meter (Kyowa Hakko Co., Japan); DataPhysics SCAT interfacial tensiometer (DataPhysics, Germany); Zetasizer Nano-ZS nanoparticle size and zeta potential analyzer (Malvern Instruments Ltd, UK), CAT-120 high-speed stirrer (CAT Company, Germany).

2.2 Methods

2.2.1 Preparation of simulated crude oil

The 10 wt% simulated crude oil was prepared by using silicone-treated kerosene as solvent, crude oil from Shengli Oilfield as solute, and the solution was ultrasonically dispersed for 5 min.

2.2.2 Preparation of simulated oilfield produced water

The properties of oilfield produced water usually change and its stability can be destroyed at laboratory conditions, therefore, in this work, simulated oilfield produced water was prepared and used in the experiments to obtain reproducible results.

The simulated oilfield produced water was prepared according to the ionic and crude oil compositions of Shengli Oilfield produced water. The ionic compositions of Shengli Oilfield produced water are shown in Table 1.

Table 1 Ion compositions of produced oilfield water from Shengli Oilfield

Ion component	Na^++K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-
Concentration, mg·L^{-1}	6026	101	340	9890	502

The simulated oilfield produced water was prepared by adding 2 wt% dehydrated crude oil into the water containing the same ions composition as the produced water from Shengli Oilfield, and the solution was emulsified for 120 s using a high-speed stirrer at a rotating rate of 18,000 r·min^{-1}, and then it was kept standing for 1 h. The oil-in-water emulsion in the lower layer was the prepared simulated oilfield produced water.

2.2.3 Preparation of simulated oilfield produced water containing water treatment agents

In the oil production process, the oilfield produced water is usually re-injected to the oil well after being treated with various water treatment agents. In order to study the influence of various water treatment agents on the stability of oilfield produced water, simulated oilfield produced water with different water treatment agents was prepared as follows:

Simulated oilfield produced water (prepared by the method in 2.2.2, with more 2 wt% oil added) with different concentrations (0, 20, 40, 60, 80, 100, and 120 mg·L^{-1}) of water treatment agents (SL-2, HEDP, 1227, or PAC) was prepared, and then stirred uniformly. The lower layer of the prepared solution was the simulated oilfield produced water containing water treatment agents.

2.2.4 Determination of interfacial tension

The interfacial tension between the simulated oil (oil phase) and simulated oilfield produced water (aqueous phase with crude oil) were determined at 30 °C by the Wilhelmy plate method with a Dataphysics SCAT interfacial tensiometer.

2.2.5 Determination of interfacial shear viscosity

The interfacial shear viscosity between the simulated crude oil and simulated oilfield produced water was measured at 30 °C using a SVR-S interfacial viscoelastic meter (Kyowa Hakko Co., Japan).

2.2.6 Determination of zeta potential

The zeta potentials of oil droplets in emulsions were measured using a Zetasizer Nano-ZS nanoparticle size and zeta potential analyzer. The emulsions were prepared using the same method in 2.2.2. The emulsions samples were obtained from a depth of 2 cm below the liquid level of the prepared emulsion after it standing for 24 h (in order to obtain a more stable system) to avoid floating oil. The testing temperature was 30 °C.

3 Results and discussion

3.1 Influence of water treatment agents on oil-water interfacial tension

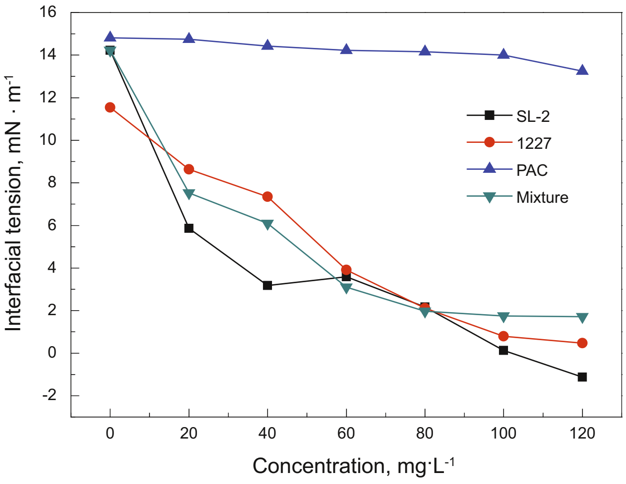
Various concentrations of water treatment agents SL-2, 1227, PAC, and scale inhibitor HEDP and a mixture of these four treatment agents (SL-2, 1227, PAC, and HEDP, with a molar ratio of the four agents of 1:1:1:1, the total concentration of the mixture is 2,000 mg/L) were used to investigate their influences on oil-water interfacial tensions. The results are shown in Fig. 1.

Fig. 1(a) shows that the oil-water interfacial tension decreased significantly with increasing concentration of SL-2 or 1227; when the concentration of SL-2 or 1227 reached 120 mg·L^{-1}, the oil-water interfacial tensions of the two systems were both less than 1 mN·m^{-1}, indicating that SL-2 and 1227 had relatively higher interfacial activity than the other two water treatment agents HEDP and PAC. Fig. 1(a) also indicates that the oil-water interfacial tensions varied only slightly when the PAC concentration was in the range of 20-120 mg·L^{-1}.

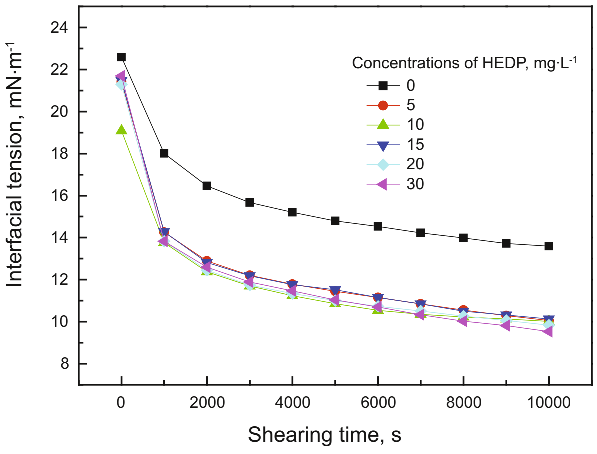
SL-2 is a cationic imidazoline organic corrosion inhibitor, which has a similar molecular structure to surfactants, thus it can be easily adsorbed at the oil-water interface and reduce oil-water interfacial tension (Li et al, 2011). Germicide 1227 is a cationic surfactant which can also be easily adsorbed at the oil-water interface and substantially reduce oil-water interfacial tension by forming a composite membrane with surfactants in crude oil (Binks et al, 2011).

Dispersing flocculant PAC in water can form positively charged mononuclear and multinuclear complex compounds through hydrolyzation (Li et al, 2002); some of the positively charged complex compounds diffuse to the oil-water interface and are characteristically absorbed onto the electric double layer at the oil-water interface. These adsorbed complex compounds can neutralize some of negative charges on the oil-water interface, hence influence the interfacial adsorption of the active components in crude oil. However, with no interfacial activity and limited concentration of the complex ions at the oil-water interface, these complex compounds have little effect on oil-water interfacial tension.

Fig. 1 (b) shows that HEDP can reduce oil-water interfacial tension to some extent, which was relatively



(a) Effect of SL-2, 1227, PAC and the mixture of SL-2, 1227, PAC on oil-water interfacial tensions at different concentrations



(b) Effect of HEDP on oil-water interfacial tensions at different concentrations

Fig. 1 Effect of water treatment agents on oil-water interfacial tensions

smaller than that using SL-2 and 1227. Furthermore, the influence of HEDP on oil-water interfacial tension changed slightly with its concentration.

The metallic elements, such as calcium, magnesium, iron, etc., in Shengli crude oil are primarily in the form of naphthenates, fatty acid salts and phenates (Guo et al, 2007), and the majority of these compounds are oil-soluble interfacial active substances (Zhu and Wang, 1998). Calcium naphthenate in crude oil is a compound formed by ionic bonds. It can be absorbed at the oil-water interface and exist in the following ionization equilibrium: $(RCOO)_2Ca \rightleftharpoons Ca^{2+} + 2RCOO^-$. HEDP can form stable complexes through chelating with Ca^{2+}, Mg^{2+} and other multivalent metal ions (Li and Lin, 2006; Huang et al, 2002), destroying the above ionization equilibrium, subsequently, leading to an increase of free $RCOO^-$, and an enhancement of the hydrophilicity and adsorption capacity of $RCOO^-$ on the oil-water interface resulting in a decrease of oil-water interfacial tension. However, due to the limited amounts of multivalent metal ions in crude oil, the oil-water interfacial tension changed very little with increasing concentration of HEDP.

Fig. 1(a) also indicated that the oil-water interfacial tension significantly decreased with increasing concentrations of the water treatment agent mixture. Among the four treatment agents in the mixture, SL-2 and 1227 had a stronger capability for reducing the interfacial tension than the other two agents. Therefore, the decrease of the oil-water interfacial tension was mainly attributed to these two agents (SL-2 and 1227).

3.2 Influence of water treatment agents on oil-water interfacial shear viscosity

The influence of various concentrations (20-120 mg·L^{-1}) of SL-2, 1227, PAC, HEDP and the mixture of the four treatment agents on oil-water interfacial shear viscosity were investigated. It was found that the varying trends of these agents influencing oil-water interfacial shear viscosity were similar at different concentrations. An example of the influence of water treatment agents on oil-water interfacial shear viscosity at a concentration of 30 mg·L^{-1} is shown in Fig. 2(a).

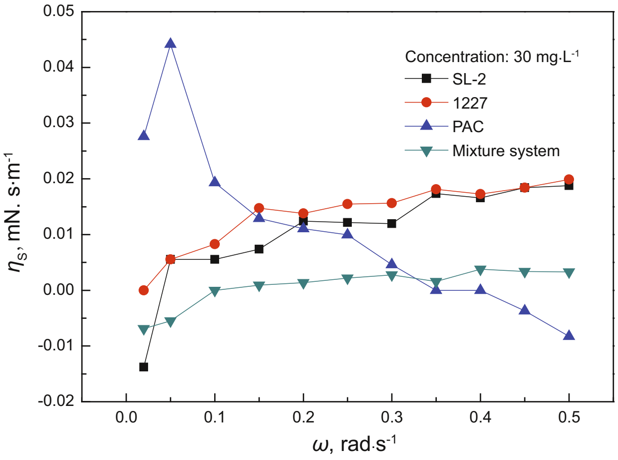
Fig. 2(b) and Fig. 2(c) show the change of interfacial shear viscosity at different shear rates and concentrations of HEDP.

As shown in Fig. 2(a), the oil-water interfacial shear viscosity increased with increasing shearing rate when SL-2 and 1227 were added to the aqueous phase (oilfield produced water), and the increase of the oil-water interfacial shear viscosity with 1227 was slightly greater than that with SL-2. The interfacial shear viscosity decreased with increasing shearing rate as PAC was added to the oilfield produced water.

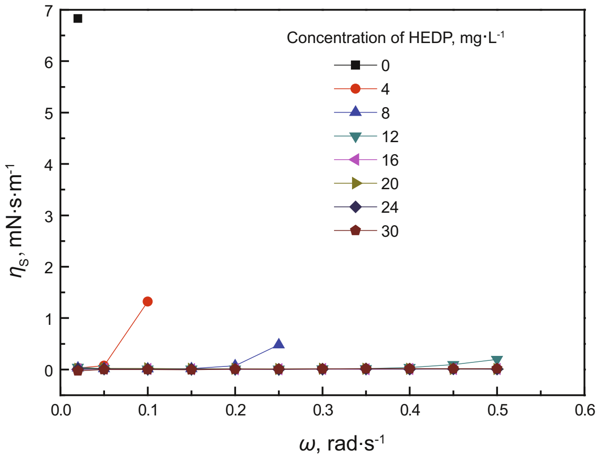
SL-2 can be easily adsorbed on the oil-water interface reducing interfacial tension and forming complexes with active materials on the interface through electrostatic interaction, resulting in a slight enhancement of interfacial film strength. At the same time, the adsorption of SL-2 on the oil-water interface can also decrease the adsorption amount of macromolecule active components of crude oil, resulting in a slight decrease in oil-water interfacial shear viscosity. As a result, SL-2 has little effect on oil-water interfacial shear viscosity.

1227 can slightly enhance oil-water interfacial film strength by forming a composite membrane with surfactants in crude oil, and the interfacial shear viscosity can also increase slightly.

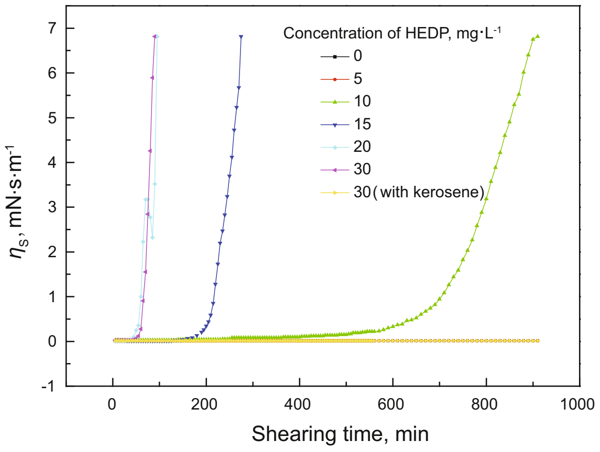
When PAC was dispersed in water, positively charged mononuclear and multinuclear complex compounds would be formed due to the hydrolyzation of PAC, and some positively charged complex compounds diffusing to the oil-water interface would be characteristically adsorbed in the interface electric double layer. This influences the interfacial adsorption of active components in crude oil and the oil-water interfacial shear viscosity. In addition, the charge neutralization decreased the electroviscous effect in the shearing process, resulting in a significant decrease of the interfacial shear viscosity. For the mixture of SL-2, 1227, PAC and HEDP, the interfacial shear viscosity decreased slightly with the addition of the mixture of treatment agents, as shown in Fig. 2(a).



(a) Effect of SL-2, 1227, PAC and the mixture on oil-water interfacial shear viscosity at a concentration of 30 mg·L^{-1}



(b) Effect of different concentrations of HEDP on oil-water interfacial shear viscosity at various shear rates



(c) Effect of different concentrations of HEDP on the oil-water interfacial shear viscosity with time

Fig. 2 Effect of water treatment agents on the oil-water interfacial shear viscosity

The reason is that interaction among various components exists and the mutual influence between the mixture and the interfacial active components (Ortiz et al, 2012).

Fig. 2(b) shows that HEDP had little influence on oil-water interfacial shear viscosity at low concentrations (4-8 mg·L^{-1}), and the interfacial shear viscosity changed little with variations of shear rate. However, at higher concentrations (12-24 mg·L^{-1}), the oil-water interfacial shear viscosity rapidly increased with increasing shear rates. The interfacial shear viscosity reached 6.83 mN·s·m^{-1} when the HEDP concentration was 30 mg·L^{-1}, and the shear rate was 0.02 rad·s^{-1}.

Fig. 2(c) shows that at low HEDP concentrations (0 and 5 mg·L^{-1}), the oil-water interfacial shear viscosity almost unchanged with time, indicating that HEDP had little effect on interfacial shear viscosity at low concentrations. However, at high concentrations (10-30 mg·L^{-1}), the interfacial shear viscosity increased sharply with time and with increasing concentration of HEDP.

At low concentration, HEDP first formed stable complexes with Ca^{2+} and Mg^{2+}, resulting in a small amount of HEDP diffusing to the oil-water interface. Therefore, it had little effect on oil-water interfacial shear viscosity. With an increase in the HEDP concentration, the amount of HEDP diffusing to the oil-water interface increased and the HEDP on the oil-water interface forms hydrogen bonds with the carboxylic acid active components in crude oil, resulting in an enhancement of interfacial film strength.

The HEDP on oil-water interface can also chelate with polyvalent metal ions in crude oil, these polyvalent metal ions in crude oil are absorbed to the oil-water interface, and form a chelating membrane, as shown in Fig. 3 (Lu et al, 2002). Because HEDP is active in the formation of interfacial films and with increasing extent of reaction, the interfacial shear viscosity increased with time.

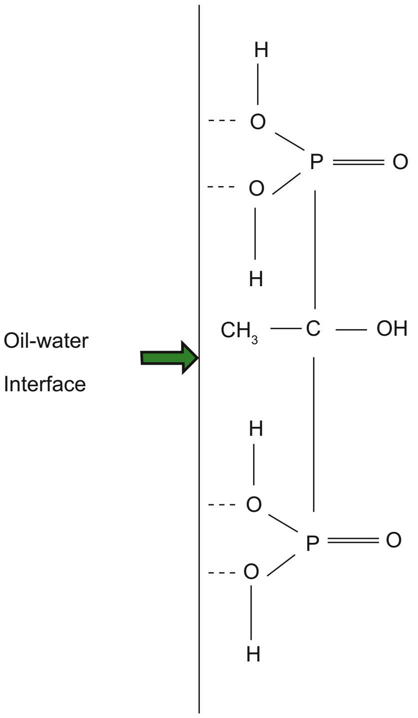


Fig. 3 Film forming mechanism of HEDP

Table 2 The zeta potentials of suspensions with water treatment agents at different concentrations

Water treatment agents	Zeta potential at different concentrations			
	0 mg·L^{-1}	20 mg·L^{-1}	60 mg·L^{-1}	120 mg·L^{-1}
SL-2	-20.6	-18.1	-14.2	-6.6
HEDP	-20.6	-21.0	-23.1	-25.0
1227	-20.6	-19.0	-16.1	-7.5
PAC	-20.6	-10.6	-2.9	-1.3
Mixture of the four water treatment agents	-20.6	-12.0	-9.6	-5.2

In addition, due to the chelation of HEDP with polyvalent metal ions, the amount of free RCOO$^-$ absorbed on the oil-water interface increased enhancing the dipole-dipole interaction among the active components on the interface, and resulting in an increase of interfacial shear viscosity.

When the HEDP concentration in the aqueous phase was 30 mg·L^{-1}, and kerosene was used as oil phase, due to low concentration of Ca^{2+} and Mg^{2+} ions in kerosene, there was little reaction between HEDP and the Ca^{2+} and Mg^{2+} ions on the oil-water interface, and the change of interfacial shear viscosity with time was consistent with that when the HEDP concentration was 0 or 5 mg·L^{-1}, and simulated oil was used as the oil phase.

As shown in Fig. 2(a), the interfacial shear viscosity of HEDP was the highest among the four agents at the same concentration (30 mg·L^{-1}). HEDP plays an important role in the stability of the emulsion.

3.3 Influence of water treatment agents on zeta potential

Table 2 presents the influence of water treatment agents at different concentrations on the zeta potential of oil droplets at a temperature of 30 °C.

As shown in Table 2, the absolute value of the zeta potential of the HEDP system increased with increasing concentration, whereas the absolute value of zeta potential of systems with other four water treatment agents decreased with increasing concentration of water treatment agents. The reason was that HEDP can chelate with polyvalent metal ions in aqueous phase, weakening the compression capability of polyvalent metal ions on the interface electrical double layer, and leading to an increase of the diffusion layer thickness, resulting in an increase of the absolute value of the zeta potential. In addition, the chelation of HEDP with polyvalent metal ions led to an increase of free RCOO$^-$ and an increase of negative charges on the oil-water interface, also resulting in an increase of the absolute value of the zeta potential.

Corrosion inhibitor SL-2 and germicide 1227 are both cationic surfactants, and they can be absorbed on the interface electrical double layer and neutralize some of surface charges with opposite potentials, resulting in a decrease of absolute value of the zeta potential by compressing the electrical double layer.

Polyaluminum chloride (PAC) can form positively charged mononuclear and multinuclear complex compounds through hydrolyzation. Positively charged complex compounds diffusing to oil-water interface can be characteristically adsorbed on the interface electric double layer and neutralize some of the negative charges on the oil-water interface, resulting in a sharp decrease of the absolute value of zeta potential. PAC can reduce the stability of emulsion by considerably decreasing the absolute value of zeta potential of oil droplets.

4 Conclusions

1) The scale inhibitor HEDP has little influence on oil-water interfacial tensions, whereas it has a significant influence on the oil-water interfacial shear viscosity because of its enhancement of the strength of the oil-water interfacial membrane. HEDP can also increase the zeta potential on the surface of the oil droplets. The presence of scale inhibitor increases the stability of produced water and causes the treatment of produced water to be more difficult.

2) PAC had little effect on oil-water interfacial tension and interfacial shear viscosity, but it reduced the stability of the emulsion by considerably decreasing the absolute value of the zeta potential of oil droplets.

3) SL-2 and 1227 decrease oil-water interfacial tensions significantly, whereas they have little influence on oil-water interfacial shear viscosity and oil-water interfacial electricity properties. SL-2 and 1227 have no significant effect on the emulsion stability of oilfield produced water.

4) The decrease of interfacial tensions in the mixture system primarily depended on corrosion inhibitor SL-2 and germicide 1227, whereas the changes in interfacial viscosity were primarily induced by scale inhibitor HEDP. The change of surface electrical properties was primarily attributed to flocculant PAC.

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