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Effect of partially hydrolyzed polyacrylamide on emulsification stability of wastewater produced from polymer flooding

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ABSTRACT

In this work, the effect of partially hydrolyzed polyacrylamide (HPAM) on the oil–water interfacial properties of produced water from polymer flooding (PWPF) was investigated. In addition, this study investigated the effects of three fiocculants (polyaluminium chloride PAC, cationic polymer FO4800SH, and nonionic polymer 402) on the stability of PWPF. The experimental results demonstrate that the addition of HPAM enhances the emulsion stability by increasing viscosity, zeta potential, interfacial tension and interfacial dilational viscoelasticity. The molecular weight and hydrolysis degree of HPAM have no significant influences on these properties. The stability of PWPF can be enhanced by increasing HPAM concentration. Dependency of frequency and concentration was observed for the interfacial dilational viscoelasticity. With the addition of HPAM, the dilational viscoelasticity not only increases with HPAM concentration but runs through a maximum at a concentration of 300 mg/L. As the oscillating frequency increases, the dilational modulus and dilational elasticity increase but the dilational viscosity decreases. The three flocculants can reduce the stability of the emulsion by considerably decreasing the absolute value of zeta potential of oil droplets. FO4800SH has a greater ability than PAC and 402 to separate oil from the emulsion. But the demulsification efficiencies of the three flocculants are not satisfactory because of the presence of HPAM residue. Further research is needed to find more efficient methods to achieve excellent performance of oil–water separation towards PWPF.

1. Introduction

As many oilfields are in their mid- or final stage of production, technologies for tertiary oil recovery have been well developed worldwide, especially in China (Zhou et al., 2013). Polymer flooding is one of the most effective tertiary oil recovery techniques. During this process, water soluble polymers are added to flooding water and then injected into reservoirs. Polymer flooding increases water viscosity and oil/water mobility ratio, and thereby enhances oil recovery. Polymer flooding has been proven to be an effective means to enhance oil recovery for middle/high water-cut oilfields (Gao, 2011). In this respect, partially hydrolyzed polyacrylamide (HPAM) has become the most widely used polymer for enhanced oil recovery because of its low-price, good viscous properties, and well-known physicochemical characteristics.

Currently, polymer flooding has been applied on a large scale to offshore oilfields and has produced remarkable results in enhancement of oil recovery (Horowitz et al., 2010; Kang et al., 2011). Nevertheless, the application of polymer flooding in the offshore environment is quite complex and encounters some technical challenges due to limited space and the absence of fresh water source on the platform (Zhou et al., 2007). One of these challenges is to efficiently treat produced water. Produced water, designated the wastewater generated after separation from oil using three-phase separators, is the largest waste stream generated in crude oil production (Lu and Wei, 2011). Nowadays, a large part of produced water is injected back into the stratum for reuse, and the rest is discharged into the surrounding environments. Produced water typically contains dispersed oils, soluble organics, salts, metals, and treatment chemicals (Fakhru'l-Razi et al., 2009). Thus, produced water must be properly treated before reinjection into the stratum or discharge into the environment to prevent stratum, environmental and ecological damages (Fakhru'l-Razi et al., 2009). In addition, polymer residue may concentrate in produced water because of continuous reuse of produced water for preparing polymer flooding solution (Fang et al., 2014). The increasing content of polymer residue in produced water would

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Nomenclature

HPAM	partially hydrolyzed polyacrylamide
PWPF	produced water from polymer flooding
PAC	polyaluminium chloride
MW	molecular weight
HD	hydrolysis degree
SS	suspended solid

make the separation of oil from water more and more difficult. Thereupon, effective treatment on produced water from polymer flooding (PWPF) is necessary and important for the environmental protection and the sustainable development of offshore oilfields.

PWPF is more difficult to treat than wastewater from water flooding, because the polymer can tightly bound with the oil and water and its electrostatic/steric effects can stabilize oil–water emulsions (Fang et al., 2014; Zhang et al., 2014). Deng et al. (2002a) investigated the properties of oil-in-water emulsions based on Daqing crude oil and they found that demulsification was an effective method to accelerate oil–water separation for the produced water. Recently, Wang and co-workers have investigated the influences of HPAM on the stability of water produced from alkaline/surfactant/polymer flooding (Wang et al., 2011). They found that, with increasing HPAM concentration, the emulsion stability of produced water initially decreased and then increased. More recently, Ma et al. (2013) demonstrated that the emulsification stability of PWPF was positively correlated with the addition amount of HPAM in the wastewater.

It was deemed that the most applicable and effective method for PWPF treatment is flocculation–demulsification (Deng et al., 2002a; Wang et al., 2011; Ma et al., 2013; Fang et al., 2014; Zhang et al., 2014). It is now generally recognized that the stabilization mechanisms of produced water include interfacial tension stability, interfacial film stability, double-layer stability, space stability, and solid particle stability (Wang et al., 2012). All these studies have given us insight into the problems relating to emulsion stability and PWPF treatment. It should be noticed that most of these studies were conducted using fresh crude oil and fresh HPAM for preparing stimulated wastewater. However, there is a significant difference in the property between fresh crude oil/HPAM and the oil/HPAM presenting in actual PWPF. This is because actual PWPF has undergone repeated shear, degradation and ageing in the stratum. In addition, existing studies were mainly limited to the effect of zeta potential and viscosity. Thus, a comprehensive study is needed on the impact of HPAM on oil–water interfacial properties of PWPF.

In land oilfields, benefiting from the limitless space, PWPF can be efficiently treated through the continuous optimization of water treatment reagents and process equipments. Thus, the treatment difficulty of PWPF is not prominent and the effluent can basically meet reinjection and discharge index. In offshore oilfields, however, limited spacing of platform does not allow big volume installation for PWPF treatment, so development of fast treatment process is necessary (Chen et al., 2015). After long-term development of oil production, many offshore oilfields enter late high water-cut stage, resulting in continuous increment in PWPF output. In this respect, therefore, there is a need to improve the performance of existing treatment technologies, to develop highly efficient treatment processes and water treatment chemicals suitable for offshore platforms.

In this study, based on LD10-1 oilfield in Bohai Bay (China), simulated PWPF was prepared and the effect of HPAM on the emulsion stability was investigated in terms of apparent viscosity, oil droplet size distribution, zeta potential, interfacial tension, and interfacial dilational viscoelasticity. Furthermore, the treatment performance of three flocculants was investigated on actual PWPF collected from LD10-1 oilfield.

2. Materials and methods

2.1. Materials

Commercial grade polyaluminium chloride (PAC) (purity:30 wt% Al_2O_3) was obtained from Zhengzhou Runquan Chemical Plant, China. A commercial grade of cationic flocculant (code: FO4800SH) was obtained from S.N.F. company (France). It is the copolymer of acrylamide and acryloyl oxygen ethyl trimethylammonium chloride, with an average molecular weight (MW) of $6–8 \times 10^6$ g/mol and a cationic degree of 80%. A nonionic flocculant (code: 402) produced by CNOOC EnerTech-Drilling & Production Co., Ltd (Tianjin, China) was used in this study. This flocculant is the copolymer of ethylene oxide and propylene oxide. HPAM, produced by Dagang oilfield Bohong Petrochemical Co., Ltd. (Tianjin, China), has MW of 2.5×10^7 g/mol and hydrolysis degree (HD) of 26%. The actual PWPF was collected from a gravity settling tank of LD10-1 oilfield in Bohai Bay, China. The mineral composition of the wastewater is listed in Table 1.

2.2. Preparation of simulated PWPF

According to the quality of formation water in LD10-1 oilfield, mineral water was prepared firstly based on the mineral composition of the actual PWPF.

To stimulate actual conditions as much as possible, oil extracted from the actual PWPF was used for preparing simulated PWPF. For this reason, the actual PWPF was extracted twice with petroleum ether, and then the extract was passed through anhydrous calcium chloride. Afterwards, the filtrate was dried at 60 °C and the oil sample was obtained. The density and apparent viscosity of oil were 0.945 g/cm^3 and 107.3 mPa s, respectively, at 65 °C.

HPAM stock solution (5000 mg/L) was prepared using mineral water. One part of the solution was irradiated by a 500 W high-pressure mercury lamp. After 3, 5 and 10 min of irradiation, the irradiation was stopped, and HPAM samples with MW of 3.55×10^6, 1.55×10^6 and 6.5×10^5 g/mol was obtained, respectively. Similarly, raw HPAM was hydrolyzed further into different HD (36% and 46%) under alkaline conditions by adding NaOH. The pH was adjusted to the initial value (7.6) using 5 M H_2SO_4 solution.

The preparation process of simulated PWPF is as follows: 300 mL of mineral water with different volumes of aged or hydrolyzed HPAM solution were added to a 1-L beaker. The mixture was stirred at 60 °C in a water bath for 1 h. Then 204 mg of the

Table 1
Characteristics of the actual PWPF used in this study.

Parameter	Value
pH	7.6
K^+ (mg/L)	34.6
Na^+ (mg/L)	3058.7
Ca^{2+} (mg/L)	276.1
Mg^{2+} (mg/L)	156.9
CO_3^{2-} (mg/L)	14.5
HCO_3^- (mg/L)	311.5
SO_4^{2-} (mg/L)	85.3
Cl^- (mg/L)	5436.9
Salinity (mg/L)	9374.2