Influence of polymers on the stability of Gudao crude oil emulsions

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Abstract: The influence of different types and concentrations of polymers on the stability of Gudao crude oil emulsion was investigated by measuring the volume of water separated from the emulsions and the interfacial shear viscosity of the oil/water interfacial film. Experimental results indicate that the simulated water-in-oil emulsion with 40 mg/L of partially hydrolyzed polyacrylamide (HPAM) 3530S could be easily broken by adding demulsifier C and was readily separated into two layers. However, HPAM AX-74H and hydrophobically associating water-soluble polymer (HAP) could stabilize the crude oil emulsion. With increasing concentration of AX-74H and HAP, crude oil emulsions became more stable. Water droplets were loosely packed in the water-in model oil emulsion containing HPAM 3530S, but water droplets were smaller and more closely packed in the emulsion containing AX-74H or HAP. The polymers could be adsorbed on the oil/water interface, thereby increasing the strength of the interfacial film and enhancing the emulsion stability.

Key words: Polymer, crude emulsion, stability

1 Introduction

Polymer flooding has been used in many oilfields in China since the 1980s (Shen, 2003; Delamaide and Wang, 1994). An additional 8-12% of original oil in place (OOIP) can be recovered by polymer flooding after water flooding. However, some problems arise during polymer flooding. One of the problems is the separation of water from crude oil because the polymer used in flooding can enhance the stability of crude oil emulsions (Deng et al, 2002a; Kang et al, 1997; Li et al, 1997). In order to solve this problem, demulsification of Gudao crude emulsion formed during polymer flooding was studied, and the influence of different types and concentrations of polymers on the stability of Gudao crude emulsions was investigated.

2 Experimental

2.1 Materials

The crude oil used was from the Gudao Oilfield, with acid

number of 3.64 mg(KOH)/g(oil). The demulsifier C was PO/EO/PO triblock polyether, with mole ratio of PO/EO/PO of 1:1:2 (PO-propylene oxide, EO-epoxyethane). The demulsifier and crude oil were provided by the Shengli Engineering Design and Consulting Co. Ltd.

Hydrophobically associating polymer (HAP) was a Yan-shan Chemical Plant product, with a viscosity-average molecular weight of 1.09×10^7 and degree of hydrolysis of 25%. HAP is an anionic polymer and its molecular structure was reported in the literature (Jiang et al, 2003). The partially hydrolyzed polyacrylamide (HPAM) was a Pfizer product, named HPAM 3530S, having a viscosity-average molecular weight of 1.70×10^7 and degree of hydrolysis of 26%. Polymer AX-74H was a Mitsui Chemicals Inc., Japan product, having a viscosity-average molecular weight of 1.99×10^7 and degree of hydrolysis of 25%.

Other chemicals used in the experiments, such as NaCl, NaHCO₃, MgSO₄, CaCl₂ and KCl were commercially available, analytical reagents. The simulated formation water used had a salinity of 5,705 mg/L, and its major ion composition is listed in Table 1.

Table 1 Major ion composition of simulated formation water

Ion	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	Na ⁺ + K ⁺	Mg ²⁺	Ca ²⁺
Concentration, mg/L	3068.3	400.2	89.9	2038.1	28.3	80.2

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2.2 Experimental methods

2.2.1 Measurement of emulsion stability

The polymer solution was prepared by dissolving the polymer in simulated formation water.

The water-in-oil (W/O) emulsion was prepared by adding 8 ml of polymer solution to 12 ml crude oil. The volume ratio of crude oil to water was 60:40. After standing for 20 minutes at room temperature, the mixture was sheared with a stirrer for 160 seconds to obtain polymer-containing W/O emulsion, in which the concentration of polymer was in the range of 0-120 mg/l.

Demulsification of W/O emulsion was carried out by adding 0.1 ml of 60 mg/l demulsifier C into 20 ml the emulsion. After being mixed evenly, the emulsion was transferred to a graduated cylinder with a stopper and then was put in a water bath at 50 °C for demulsification.

The volume of water separated from the emulsion was measured with time and the separation rate of water, $V_t/V_0 \times 100$, was calculated. V_t is the volume of water separated from W/O emulsion at time t and V_0 is the total volume of water used for preparing the W/O emulsions. The emulsion stability was evaluated by measuring the value of water separation rate.

2.2.2 Microscope observation

The microstructures of the W/O emulsions made up of 60% by volume of model oil (a mixture of 10% by weight Gudao crude oil and 90% by weight jet fuel) and 40% by volume of polymer solution were observed with XS-18 microscope (Jiangnan Optoelectronics Co. Ltd.). In the water-in-model oil emulsion, the concentration of polymer was 40 mg/L.

2.2.3 Measurement of interfacial shear viscosity

The interfacial shear viscosity of water-in-model oil emulsion was measured with a SVR-S interfacial viscoelasticity meter (Kyowa Kagaku Co., Japan) at 30 °C.

3 Results and discussion

3.1 Influence of polymers on W/O emulsion stability

Fig. 1 is a plot of volume percent water separated as a function of time for one control emulsion without any polymers and three emulsions containing different polymers of HPAM 3530S, AX-74H and HAP, respectively. The concentration of polymer in the emulsions was 40 mg/L. Fig. 1 shows that there existed significant difference in the stability of W/O emulsions containing different polymers. Polymers AX-74H and HAP could improve the stability of W/O emulsions, with only a small amount of water separated from the emulsions. However, HPAM 3530S could reduce the stability of emulsion, and a large amount of water was separated from the emulsion.

Droplet size distribution was observed under microscope for the prepared water-in-model oil emulsions, as shown in Fig. 2. The water-in-model oil emulsion containing HPAM 3530S, was an unstable emulsion, in which water droplets were unevenly dispersed in the oil phase, and the model oil was present as large oil drops without containing any water.

Fig. 1 Influence of different polymers on emulsion stability

However, the water droplets formed a closely packed layer on the microscope slide if the water-in-oil emulsion contained AX-74H and HAP respectively and water droplets were smaller, compared with the emulsion without any polymer. This phenomenon indicates that the emulsions containing AX-74H or HAP were more stable. However, the water droplets were unevenly dispersed in the emulsions containing HPAM 3530S, indicating lower stability of the emulsion than the emulsion without any polymer.

The molecular weights of these three polymers used in the experiments were different. HAP had the smallest molecular weight (Ren et al, 2006). The molecular weight of AX-74H was significantly higher than those of other polymers. The solution of polymer of higher molecular weight would have higher viscosity, therefore the friction between water droplets and model oil in the emulsion containing such a polymer would increase and consequently the sedimentation resistance to water droplets would rise (Deng et al, 2002b). As a result, the amount of water separated from emulsion containing AX-74H decreased.

Interfacial tension of the emulsion system containing HAP was lower than that of the system containing HPAM 3530S, because of the existence of a small amount of surfactant in HAP (Taylor and Nasr-El-Dinb, 1998). The interfacial energy would decrease with decreasing interfacial tension. This was advantageous to reducing thermodynamic instability and the formation of more well-dispersed water droplets in oil. The stability of emulsion, in turn was increased and demulsification became more difficult.

3.2 Influence of polymer concentration

W/O emulsions with different polymer concentrations were prepared with the same volume ratio of crude oil to water. Fig. 3 illustrates that the amount of water separated from emulsions containing AX-74H or HAP decreased as the concentration of polymer in the emulsion increased, the separation rate of water changed quickly when the concentration of polymer in the emulsion was lower than 20 mg/L. This indicates that the polymer concentration could influence the emulsion stability significantly. The separation

(a) Emulsion without any polymer

(b) Emulsion containing HPAM 3530S

(c) Emulsion containing AX-74H

(d) Emulsion containing HAP

Fig. 2 Photograph of emulsions with or without polymers

rate of water from the emulsion containing HPAM 3530S decreased when the polymer concentration in the emulsion was lower than 20 mg/L and increased when the polymer concentration in the emulsion was higher than 20 mg/L. Approximately 55% by volume of water could be separated from the emulsion when the concentration of HPAM 3530S in the emulsion was higher than 40 mg/L.

The emulsion containing AX-74H or HAP was more stable than the emulsion containing HPAM 3530S when the polymer concentration in the emulsion was higher than 40 mg/L.

Fig. 3 Influence of polymer concentration on emulsion stability

3.3 Influence of polymer on interfacial shear viscosity

The stability of W/O emulsion is dominated by the strength of oil/water interfacial film, and the strength of interfacial film can be characterized by the interfacial shear viscosity. The higher the interfacial shear viscosity, the stronger the film, and the more stable the emulsion (Li et al, 2002a, 2006). Fig. 4 shows the interfacial shear viscosity of the film between model oil and water in the presence of polymers (HPAM 3530S, AX-74H, and HAP). The interfacial shear viscosity of the film between model oil and water rose sharply with AX-74h concentration, and was significantly higher than that of the film between model oil and water in the presence of HPAM 3530S. In this study, polymers AX-74H and HPAM 3530S were both partially hydrolyzed polyacrylamide, but AX-74H had a higher relative molecular weight than 3530S. When polymers were adsorbed on the interface between model oil and water, the polymer and the interfacial active components, such as asphaltene, resin fractions in crude oil would form a strong interfacial film (Li et al, 2007; Cao et al, 2004). This film prevented the coalescence of water droplets, therefore the emulsion was stable (Li et al, 2002b; Dicharry et al, 2006). Polymer AX-74H had a higher molecular weight than HPAM 3530S, the emulsion containing AX-74H was more stable than the emulsion containing HPAM 3530S under the experimental

conditions (Figs.1 and 3). This phenomenon might be caused by the synergistic effect of polymer and demulsifier C.

Fig. 4 also shows that the interfacial shear viscosity of the interfacial film between model oil and water increased with increasing HAP concentration, and Fig. 3 shows that the water separation rates of emulsions containing HAP and AX-74 decreased with increasing polymer concentrations. HAP had a different molecular structure from HPAM, but it had the same effect on the interfacial shear viscosity and the stability of the emulsions.

Fig. 4 Influence of polymer concentration on interfacial shear viscosity of the film between model oil and water

4 Conclusions

1) Demulsifier C could easily break W/O emulsion with 40 mg/L of HPAM 3530S, but the rate of demulsification and the water separation rate decreased for W/O emulsions with 40 mg/l of polymer AX-74H or HAP.

2) After adding 0.1 ml of 60 mg/L demulsifier, the rate of separation of water from the emulsion initially decreased, then increased with the increase in HPAM 3530S concentration in the emulsion, and finally leveled off with increasing 3530S concentration. The emulsion was the most stable, with the least amount of water separated, when the HPAM 3530S concentration in the emulsion was in the range of 12 to 20 mg/L.

3) The rate of demulsification and the water separated from the emulsion decreased significantly with increasing concentration of AX-74H or HAP when 0.1 ml of 60 mg/L demulsifier was added into the emulsion.

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