Performance evaluation of a novel viscosity-reducing agent for heavy oil

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Abstract. Heavy oil has high viscosity, high content of resins-asphaltenes and poor fluidity, which makes it difficult to produce. In the early research, a novel viscosity-reducing agent with high molecular weights and various active groups was synthesized in the laboratory. Ion composition analysis of wastewater and heavy oil viscosity test of Jinchai 27 well were carried out. The emulsifying and viscosity reducing properties of a novel viscosity-reducing agent for heavy oil under low shear condition were evaluated by water content change of emulsion phase and viscosity reduction rate. The results showed that under 50 °C and low shear (10~20s⁻¹) condition, the viscosity-reducing agent solution had a fast emulsifying speed for the heavy oil. The O/W emulsion with good emulsion stability formed after about 60min shear. The viscosity reduction rate for the heavy oil was above 90%. The emulsion micrographs showed that the emulsion was highly dispersed and the particle size was uniform with diameter of 2 microns or even lower. The viscosity value of viscosity-reducing agent solution with concentration higher than 1200 mg/L could reach 25.0mPa.s under 8.0s⁻¹ shear rate and 50°C, which indicated that it had a certain thickening property. Artificial core flooding experiments showed that viscosity-reducing agent flooding could increase heavy oil recovery by more than 10% compared with water flooding.

1. Introduction

For heavy oil reservoirs, oil recovery with water flooding was very low because of high viscosity, high density and poor fluidity of crude oil[1][2]. For example, 70% oilfields in Bohai Sea were heavy oil ones, and the actual average oil recovery with water flooding was only 20.2%[3]. Although polymer flooding and combination flooding technologies in conventional crude oil production had been widely used and succeeded in greatly enhancing recovery, such chemical flooding technologies were rarely used in heavy oil reservoir production. The main technical principle of polymer flooding was to increase water phase viscosity, oil-water mobility ratio and sweep efficiency by using high molecular weight polymers such as anionic polyacrylamide. However, crude oil viscosities in most heavy oil reservoirs were more than 100 mPa.s. Polymer flooding couldn’t significantly improve oil-water mobility ratio and sweep efficiency, resulting in ineffective or inefficient circulation of injected water.

In recent years, much attention has been paid to improving the heavy oil development effect with water flooding by emulsifying and viscosity reducing agents [4]. The key was to develop heavy oil emulsifying viscosity-reducing agent of O/W type with highly activity [5]. Study showed that the emulsion formed by small molecular emulsifiers such as sodium dodecyl sulfonate (SDBS) was poor
in stability and easy to reverse into W/O emulsion with high viscosity. Compound of polymer/alkali/surfactant had better emulsifying performance. However, polymers and surfactants were easily separated by chromatographic effect in formation [6], which resulted in decrease of oil emulsifying and washing effect.

A novel viscosity-reducing agent for heavy oil had been developed in the early research, which had a backbone based on acrylamide structure units and branched chain containing various highly active and functional groups such as non-ionic polyether and hydrophobic groups. The active groups could greatly improve the surface activity of the copolymer, emulsifying and dispersing properties. The performance of viscosity-reducing agent was studied by oil viscosity reduction and oil recovery improvement.

2. Materials and experiments

2.1. Materials

The experimental oil was heavy oil from Jincai 27 well in Liaohe oilfield. The experimental water was wastewater from Jincai in Liaohe Oilfield, and its ion composition was0.67mg/L Ca\(^{2+}\), 0.09mg/LMg\(^{2+}\), 17.9mg/LK\(^{+}\), 587mg/L Na\(^{+}\), 213mg/L Cl\(^{-}\), 42.4mg/LSO\(_4^{2-}\), 33.9mg/L CO\(_3^{2-}\) and 1070.0 HCO\(_3^{-}\). The metal ion concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The concentration of SO\(_4^{2-}\) and Cl\(^{-}\) ion was analyzed by ion chromatography. And the concentration of CO\(_3^{2-}\) and HCO\(_3^{-}\) was analyzed by acid-base indicator titration.

Viscosity-reducing agent for heavy oil was synthesized by micellar copolymerization of active monomers such as polyether, sulfonate monomer, hydrophobic monomers and acrylamide with potassium persulfate, sodium bisulfite and azo initiator by. The backbone of its molecular structure was formed by the terminal alkenyl groups of various monomers and the branched chain was made of various active segments with hydrophobic and hydrophilic properties. The FTIR of the viscosity-reducing agent was showed in Figure 1. The peaks at 3416cm\(^{-1}\) and 3196cm\(^{-1}\) confirmed the –NH\(_2\) groups. And the peaks at 1672cm\(^{-1}\) indicated the existence of C=O groups. The C-O-C group could be confirmed by appearance of 1196 cm\(^{-1}\) and 837 cm\(^{-1}\) peak. And the peaks at 1119 cm\(^{-1}\) confirmed the –SO\(_3^{2-}\) groups. The peak at 1557cm\(^{-1}\) indicated the existence of phenyl group. And the peaks at 2924 cm\(^{-1}\), 2855 cm\(^{-1}\) and 1452 cm\(^{-1}\) confirmed the –CH\(_2\)– groups. The FTIR showed that the viscosity-reducing agent was a copolymer containing various active groups.

![Figure 1. FTIR of the viscosity-reducing agent for heavy oil.](image-url)
2.2. Evaluation method of emulsifying and viscosity reducing performance for heavy oil
Solution of viscosity-reducing agent was prepared with oilfield sewage. And quantitative 0.1% solution was mixed with dehydrated crude oil at a ratio of 4:6 (volume ratio, v/v) and placed in a plugged glass tube. The initial oil phase volume \( V_1 \) and initial water phase volume \( V_2 \) were recorded. The plugged glass tubes were placed in an oscillator at 50°C temperature and sheared at low speed (shear rate 10-20s\(^{-1}\)), recording the volume of remaining water phase \( V_3 \). The water content of emulsion phase \( W \) could be calculated by \( (V_2-V_3) \times (V_1+V_2-V_3) \times 100\% \). When the emulsion was completely emulsified, the water content of emulsion was 60%. According to the oscillating time and water content of emulsion phase, the emulsifying speed of heavy oil could be analysed. After heavy oil and water were completely emulsified, the emulsion viscosity was measured at 50°C with MCR301 viscometer of Anton Paar Co.Ltd.

2.3. Microscopic analysis for heavy oil emulsion
The heavy oil emulsion was evenly coated on the slide surface, and then placed on the carrier platform of Leica DM2500 transmission microscope. By adjusting the eyepiece and objective lens to a certain magnification, the state and dispersion of heavy oil emulsion were observed through computer software matched with the microscope and taken photos. And the oil droplets size could be measured by computer software.

2.4. Flooding performance evaluation of viscosity-reducing agent for heavy oil
Heavy oil, field sewage in Liaohe oilfield and artificial cores were used to investigate the oil displacement effect of viscosity reducer. The core was saturated with heavy oil at 50°C and water flooding was carried out until the water cut of produced fluid reached 98%. Then viscosity-reducing agent solution flooding was carried out until the water cut of produced fluid reached 98%. The oil recovery rates of water flooding and viscosity-reducing agent were calculated respectively.

3. Results and analysis
3.1. Effect of shear rate and temperature on oil sample viscosity
Figure 2 showed heavy oil viscosity at different shear rates (0-100S\(^{-1}\)) and Figure 2 showed heavy oil viscosity at different temperature (25-60°C). The viscosity of heavy oil sample was 629.2mPa.s at 50°C and shear rates of 20s\(^{-1}\).

![Figure 2. Viscosity of heavy oil in Jinccai 27 well of Liaohe under different shear rates (a) and temperature (b).](image-url)
The heavy oil viscosity was affected seriously by temperature. The heavy oil viscosity mainly came from heavy components such as asphaltenes and resins. The resins and asphaltenes formed aggregates in a certain way. When heavy oil flowed, its viscosity increased because it need to overcome the interaction between asphaltenes aggregates through hydrogen bonds and molecular entanglement. At higher temperature, some asphaltenes aggregates were broken and the cohesion and viscosity of heavy oil decreased.

3.2. Emulsifying and viscosity reducing performance of viscosity-reducing agent

The emulsifying and viscosity reducing performance of viscosity-reducing agent were investigated by the water content change in emulsion phase, the emulsion type and viscosity reduction rate [7]. The results were shown in Table 1 and Figure 3. The experimental results showed that PAM (polyacrylamide) samples had slow emulsifying speed low viscosity reduction rate. The small molecule viscosity-reducing agent had high emulsifying speed and poor emulsion stability. The novel viscosity-reducing agent had fast emulsifying speed and good O/W emulsion stability. Its viscosity reduction rate for heavy oil (viscosity 629.1mPa.s) could reach more than 90% at 50 °C and low shear condition. In addition, water in heavy oil emulsification will gradually separate after 24 hours resting. This was beneficial to the produced liquid treatment, which could be further enhanced by air flotation [8].

Table 1. Emulsifying and viscosity reducing effect of viscosity-reducing agent for heavy oil.

| Test items                          | Blank | Polymer A | Viscosity-reducing agent1a | Viscosity-reducing agent2b | Viscosity-reducing agent3c |
|------------------------------------|-------|-----------|---------------------------|---------------------------|---------------------------|
| Water content in emulsion phase    |       |           |                           |                           |                           |
| 0min                               | 0.00% | 0.00%     | 0.00%                     | 0.00%                     | 0.00%                     |
| 2 min                              | 1.41% | 3.52%     | 21.63%                    | 5.98%                     | 3.32%                     |
| 6 min                              | 1.41% | 3.57%     | 26.82%                    | 16.61%                    | 7.71%                     |
| 14 min                             | 1.41% | 3.58%     | 32.98%                    | 20.85%                    | 16.10%                    |
| 30 min                             | 1.41% | 7.10%     | 46.60%                    | 34.72%                    | 24.12%                    |
| 50 min                             | 4.60% | 15.62%    | 49.10%                    | 37.40%                    | 26.62%                    |
| 95 min                             | 5.86% | 38.40%    | 58.96%                    | 57.98%                    | 54.32%                    |
| 145 min                            | 11.20%| 42.30%    | 59.62%                    | 58.90%                    | 56.10%                    |
| Emulsion type                      |       |           |                           |                           |                           |
| W/O                                | /     | /         | <40%                      | 92.1%                     | 90.2%                     | 80.2%                     |
| W/O or O/W                         |       |           |                           |                           |                           |
| O/W                                |       |           |                           |                           |                           |
| O/W                                |       |           |                           |                           |                           |
| O/W                                |       |           |                           |                           |                           |

Note: (1) The polymer A was commercial hydrophobic modified polyacrylamide used for oil displacement agent (2) Viscosity-reducing agent1a, 2b and 3c were self-made viscosity-reducing agents with average molecular weight of 12.5 million, 8.1 million and 4.3 million respectively.

Heavy oil has high viscosity and poor fluidity, which was mainly related to much resins and asphaltenes components [9]. Resins and asphaltenes were polycyclic aromatic hydrocarbons with large molecular weight and strong polarity, which formed a highly ordered three-dimensional structure with high stability and viscosity [10]. After mixing the viscosity-reducing agent with heavy oil, the active groups such as polyether could reduce interfacial tension between oil and water. Under low shear conditions, the resins-asphaltenes aggregates were dismantled and dispersed into the water phase as small oil droplets, forming an oil-in-water emulsion with low viscosity [11]. The high surface steric hindrance of aqueous solution of viscosity-reducing agent was conducive to the emulsion stability.
3.3. Microscopic analysis of heavy oil emulsion

Figure 3. Appearance of heavy oil before and after emulsification with viscosity-reducing agents (Samples from left to right were blank, viscosity-reducing agent3, viscosity-reducing agent2, Polymer A and viscosity-reducing agent1).

Figure 4. Microscopic comparison of heavy oil before and after emulsification with viscosity-reducing agent.

3.3. Microscopic analysis of heavy oil emulsion

Figure 4 compared the microscopic picture of heavy oil before and after emulsification with viscosity-reducing agent. It could be seen the heavy oil was dispersed highly into water phase. It was considered that heavy oil was a colloidal system with asphaltenes as dispersing phase, resins as plastic solvent and saturated hydrocarbons as dispersing medium. Asphaltenes were layered materials stacked by polyaromatic hydrocarbons through π-π bonds. It contained heteroatoms such as S, O, N and metal atoms such as Ni and V. Asphaltenes had the characteristics of high density, high polarity and high aromaticity. Resins and asphaltenes formed supramolecular aggregates through association effect, which increased the oil system viscosity [12].

It was concluded that polyether segment was hydrophilic and hydrophilic. And polyether segment could be aligned at the oil-water interface, which promoted the emulsification and dispersion of oil droplets into water [13]. In addition, steric hindrance effect could improve the stability of O/W emulsion. The synergistic effect of nonionic polyether chain and sulfonate segment could produce better emulsifying, dispersing and solubilizing effects on heavy oil [14]. In addition, the hydrophobic groups on the viscosity-reducing agent molecule could interact with heavy components of heavy oil and destroy the association structure, which ultimately reduced heavy oil viscosity [15].

3.4. Oil displacement efficiency of viscosity-reducing agent solution

Firstly, the thickening property of the viscosity-reducing agent was investigated. The viscosity-reducing agent (8.1 million molecular weight) was prepared into water solution with 400-1600 mg/L concentration by field sewage. The apparent viscosity was measured by LVDV II viscometer produced by Brookfield Company at 25°C. The results were shown in Table 2. It could be seen that the viscosity of viscosity-reducing agent solution increased with the increase of viscosity-reducing agent concentration. When viscosity-reducing agent concentration was higher than 1200 mg/L, the solution viscosity was higher than 25.0 mPa.s. It showed that the viscosity-reducing agent not only had the emulsifying and viscosity reducing effect of heavy oil phase, but also had a strong thickening ability to water phase, which could improve the sweeping ability of injection fluid [16].

| Concentration (mg/L) | 400 | 800 | 1000 | 1200 | 1400 | 1600 |
|----------------------|-----|-----|------|------|------|------|
| Viscosity (mPa.s)    | 9.1 | 15.6| 19.5 | 25   | 31   | 38   |

Core flooding test of viscosity-reducing agent was carried out with heavy oil and field sewage in Liaohe oilfield. The viscosity of heavy oil was 629.2 mPa.s and sewage salinity was 2000.0 mg/L. The artificial core was 25 mm*300 mm (diameter*length) and air permeability was 750 mD. The experimental steps of oil flooding test were as follows: Firstly, the core was saturated with heavy oil at 50°C. Next, mass of saturated oil and initial oil saturation were calculated. Then core water flooding was carried out and oil recovery rate of water flooding was calculated when water content in displacement fluid reached 98%. Next, flooding of viscosity-reducing agent solution was carried out and oil recovery rate was calculated when water content in displacement fluid reached 98%. Results (Table 3) showed that the oil recovery rate of viscosity-reducing agent solution flooding could be increased by more than 10% than water flooding.

| Core Number | Chemical Agent         | Initial oil saturation | Oil recovery rate | Raise Value |
|-------------|------------------------|------------------------|-------------------|-------------|
|             |                        |                        | Water flooding    | Chemical Flooding |                  |
| 1-1^a       | Viscosity-reducing agent | 86.2%                  | 15.8%             | 29.2%       | 13.4%         |
| 1-2^a       | Commercial PAM         | 85.3%                  | 16.2%             | 22.3%       | 6.1%          |

4. Conclusions

(1) The ion composition of wastewater and viscosity of heavy oil from Jincai 27 well in Liaohe oilfield were analyzed. The viscosity of heavy oil was 629.1 mPa.s at 50°C.

(2) The emulsifying and viscosity reducing test were carried out. Results showed that under 50°C and low shear rate, the viscosity-reducing agent could emulsify the heavy oil quickly, form the oil in water emulsion with good stability. The viscosity reduction rate of the heavy oil reached the maximum of 90%.

(3) Micrographs showed that the heavy oil emulsion was highly dispersed and had a uniform particle size, with a particle size of 2 microns or even lower, indicating that the viscosity-reducing agent had excellent emulsifying and dispersing properties.

(4) When the concentration of viscosity-reducing agent was higher than 1200 mg/L, the viscosity of its aqueous solution could reach up to 25.0 mPa.s, indicating that it had a certain thickening property. Core flooding experiments showed that amphiphilic polymer solution flooding could increase heavy oil recovery by more than 10% compared with water flooding. The new viscosity-reducing agent has high application potential in heavy oil production.
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