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Research Article

Alkali/Surfactant/Polymer Flooding in the Daqing Oilfield Class II Reservoirs Using Associating Polymer

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Hydrophobically modified associating polyacrylamide (HAPAM) has good compatibility with the Daqing heavy alkylbenzene sulfonate surfactant. The HAPAM alkali/surfactant/polymer (ASP) system can generate ultralow interfacial tension in a wide range of alkali/surfactant concentrations and maintain stable viscosity and interfacial tension for 120 days. The HAPAM ASP system has good injectivity for the Daqing class II reservoirs (100–300 $\times 10^{-3}$ μm^2) and can improve oil recovery by more than 25% on top of water flooding. In the presence of both the alkali and the surfactant, the surfactant interacts with the associating groups of the polymer to form more micelles, which can significantly enhance the viscosity of the ASP system. Compared with using HPAM (Mw = 2.5 MDa), using HAPAM can reduce the polymer use by more than 40%.

1. Introduction

ASP flooding is the chemical flooding method that gives the highest oil recovery rate [1–5]. Despite the controversies on its technical and economic feasibilities [6, 7], pilot on-site experiments and examination of its industrial application are continuously carried out [8–12]. The technical issues of ASP flooding mainly include (1) formation damage due to the use of strong base, (2) scale buildup in the injection and production equipment, and (3) difficulties in processing the produced fluid [13–15]. In addition, compared with the already industrialized polymer flooding technology, ASP flooding is considerably more costly [10], mainly because the used polymer has poor resistance against alkali. Currently, new trends in ASP flooding include (1) the use of alkali-resistant polymer to reduce costs [16]; (2) developing weak-alkali ASP flooding system to alleviate problems associated with using strong base [17]; (3) developing ASP flooding system suitable for reservoirs with low/medium permeability. Field test indicated that hydrophobically modified associating polyacrylamide (HAPAM) can be a suitable flooding agent for high-temperature high-salinity reservoirs due to its excellent characteristics in temperature, salt, and shear resistance and so forth, [18]. Nevertheless, the ASP flooding system based on HAPAM has not been reported yet. This paper describes the latest research progress on using strongly basic ASP flooding system consisting of the HAPAM associating polymer at the Daqing Class II reservoirs (100–300 $\times 10^{-3}$ μm^2).

2. Experimental

2.1. Materials. HAPAM (Figure 1) was synthesized according to the literature [19] using 0.5% mol/mol cetyl dimethylallyl ammonium chloride (C_{16}DMAAC) as the hydrophobic monomer. The synthesized HAPAM has an intrinsic viscosity of 1388 mL/g and a hydrolysis degree of 24.5% (w/w).

HPAM (average molecular mass, 25,000 kDa; hydrolysis degree, 21.6% w/w) was provided by Daqing Refining and Chemical Company. C_{16}DMAAC was supplied by Southwest Petroleum University. Other reagents were purchased from Chengdu Kelong Chemical Reagents Corporation (China). All reagents were used as received without further purification. Heavy alkylbenzene sulfonate and the crude oil (ρ = 0.85 g/cm^3) were obtained from the Daqing oilfield.

To simulate the injected water in the pilot test, inorganic salts were added to distilled water and the solution was used

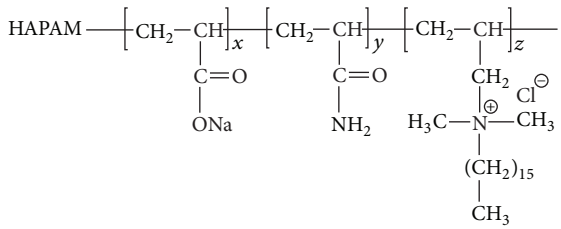

Figure 1: The structure of HAPAM.

Table 1: Composition of the simulated injection water.

Ion style	Ion concentration (mg L^{-1})
K^+ and Na^+	1044.87
Ca^{2+}	56.51
Mg^{2+}	24.90
HCO_3^-	2351.91
SO_4^{2-}	148.12
Cl^-	256.46
Total dissolved substance (TDS)	3882.77

in the subsequent experiments. The composition and salinity of the simulated injection water are given in Table 1. No precipitate was present in any formation water.

2.2. Solution Preparation. The stock solution of the surfactant or polymer (5000 mg/L) was prepared by dissolving the surfactant or polymer in brine. The ASP dilute solution was prepared by mixing the stock solutions to obtain the desired surfactant and polymer concentrations.

2.3. Measurement of Oil/Water Interfacial Tension. The oil/water interfacial tension between the solution and crude oil was measured using a Texas-500C spinning drop tensiometer (Bowing, USA) for 30 min at 45°C. The instrument could automatically record the interfacial tension with an image monitoring device and an image acquisition software.

2.4. Measurement of Viscosity. Solution viscosity was measured using a Brookfield DV-III viscometer (Brookfield, USA) at 45°C with a shear rate of 7.34 s^{-1}.

2.5. Injectivity Test. The cores saturated with brine were inserted into three core holders connected in series, each having a test point. The flooding solutions were injected into the cores at a constant rate of 1.0 mL/min until the pressure stabilized. Subsequently, brine was injected into the cores that had absorbed the polymer and the surfactant, and the experiment was finished when the pressure drop stabilized across the cores. All tests were run at 45°C. The pressures were recorded by a data terminal.

2.6. Core Flooding Test. Crude oil was injected continuously with a positive-displacement pump and an air bath held at 45°C until no more water was produced. Water flooding was then started until initial oil saturation was reached. Afterwards, chemical flooding was carried out by injecting a 0.3 PV displacement plug and then flooding with chase water

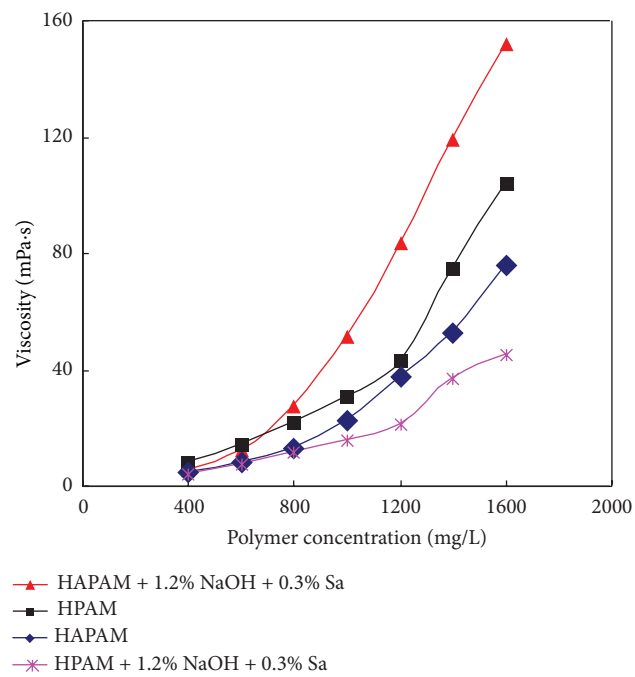

Figure 2: Viscosity-concentration curves of four flooding systems.

until the water cut of the produced fluid approached 98%. The oil recoveries and water cuts were calculated every 0.15 PV during the experiment.

3. Results and Discussion

3.1. Viscosity Enhancement. Figure 2 shows that, in the presence of alkali and surfactant, the HAPAM ASP flooding system has significantly better viscosity than using HPAM (Mw = 2.5 MDa) and can reduce the polymer use by more than 40%.

3.2. Compatibility between the Associating Polymer and the Surfactant. Figures 3 and 4 show the interfacial tension of the ASP systems containing HAPAM and HPAM, respectively.

The experimental comparison of the dynamic interfacial tension of the two ASP flooding systems is shown in Figure 5.

The results in Figures 3 and 4 indicate that the associating polymer HAPAM has better compatibility with heavy alkylbenzene sulfonate than HPAM and can enable ultralow interfacial tension in a wide alkali/surfactant concentration range. Figure 5 shows that HAPAM can quickly generate ultralow interfacial tension with heavy alkylbenzene sulfonate and remain stable for 120 min.

3.3. Aging Stability of HAPAM ASP Flooding System. Figure 6 shows that, within an aging period of 120 days, the viscosity of the HAPAM ASP system was always greater than 40 mPa·s and the interfacial tension remained stable.

3.4. Conductivity in Porous Media. The injectivity and conductivity of the sample were evaluated by the core flow experiment using three cores connected in series. The water

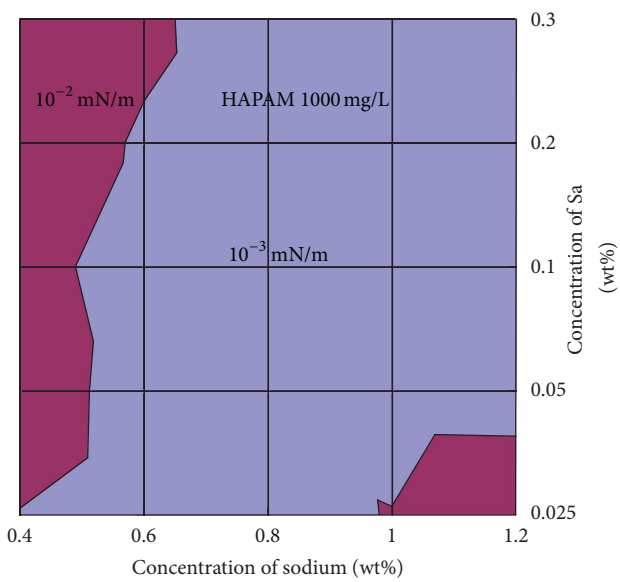

Figure 3: Interfacial tension of the ASP flooding system containing HAPAM.

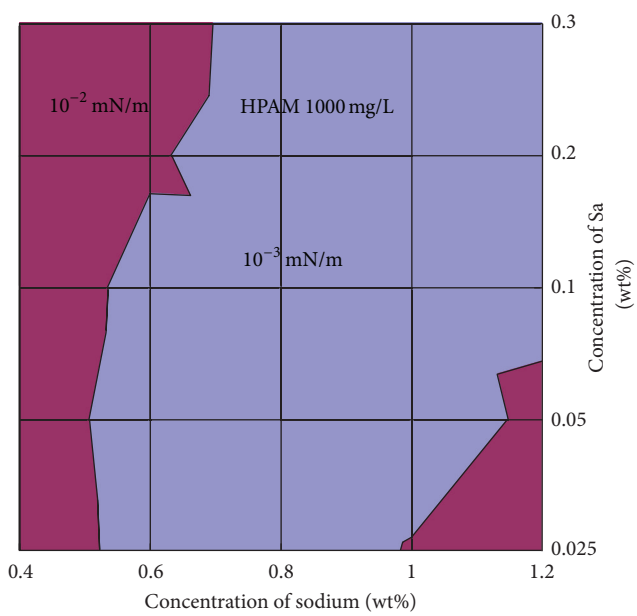

Figure 4: Interfacial tension of the ASP flooding system containing HPAM.

permeability of the three cores was $249 \times 10^{-3}\ \mu m^2$, $270 \times 10^{-3}\ \mu m^2$, and $256 \times 10^{-3}\ \mu m^2$, respectively, the concentration of the associating polymer was 1000 mg/L, the surfactant concentration was 0.3%, and the NaOH concentration was 1.2%.

Figure 7 shows that the HAPAM ASP system can penetrate into the $200 \times 10^{-3}\ \mu m^2$ core. The pressure gradient between the measurement points is relatively uniform, which suggests good pressure-conduction performance.

3.5. Core Flooding Experiment. Core flooding experiment was carried out using the HAPAM ASP system (1000 mg/L

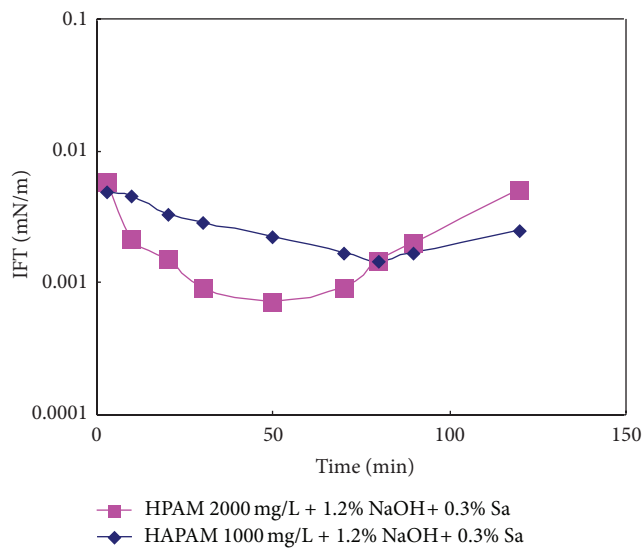

Figure 5: Dynamic interfacial tension of the two ASP systems.

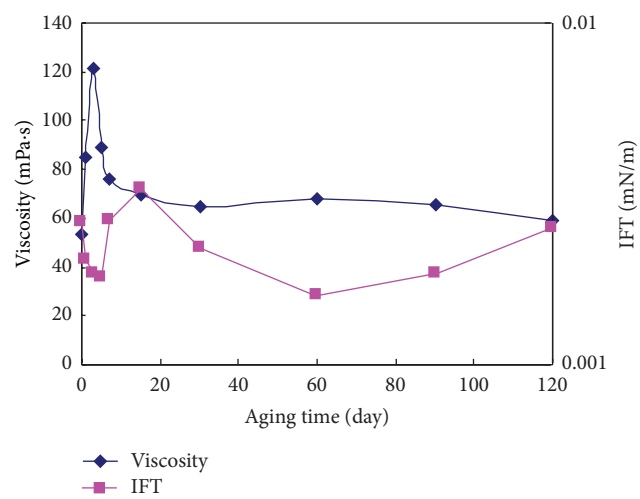

Figure 6: Variation of viscosity and interfacial tension with time.

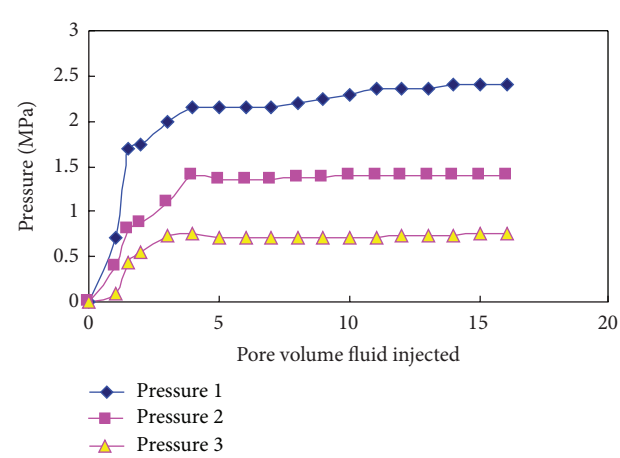

Figure 7: Conductivity of the HAPAM ASP flooding system in porous medium.

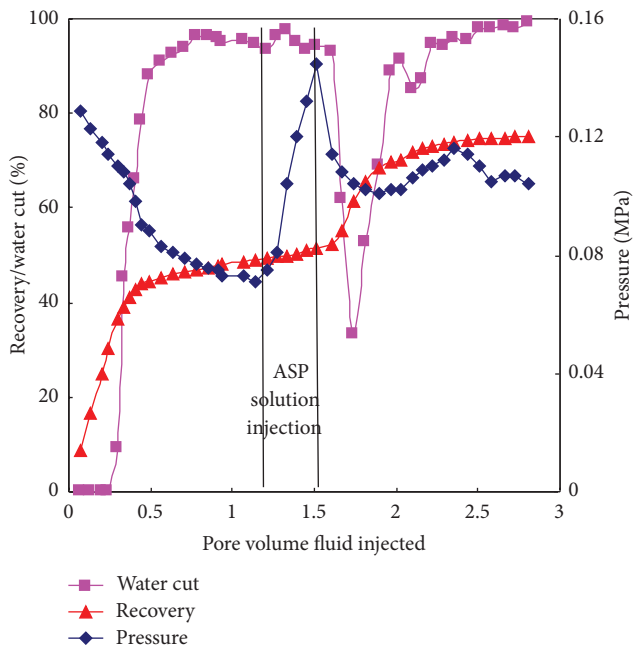

Figure 8: Flooding curve of the ASP flooding system.

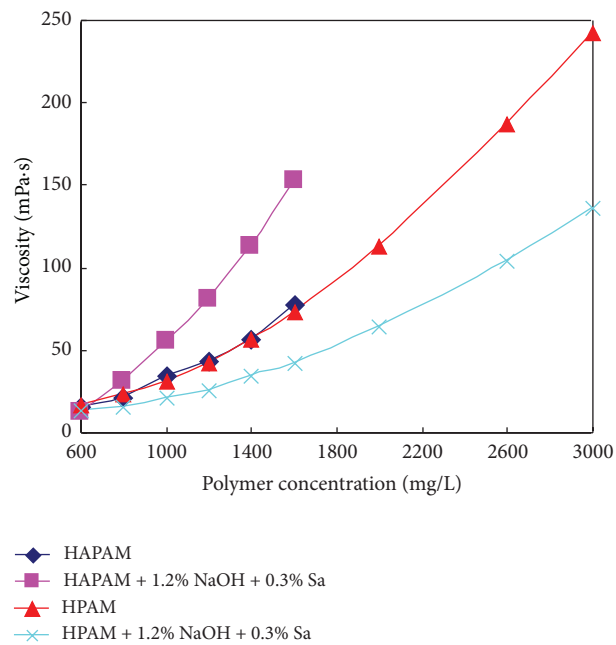

Figure 9: Viscosity-concentration curves of four flooding systems (in on-site injection water).

associating polymer HAPAM + 1.2% NaOH + 0.3% heavy alkylbenzene sulfonate) and 30 cm homogeneous square cores ($184 \times 0^{-3}\ \mu m^2$). The experimental results are shown in Figure 8.

The results in Figure 8 show that using 0.3 PV ASP flooding fluid can further improve oil recovery by 26% on top of water flooding.

3.6. Performance of ASP System under Field Conditions. The on-site injection water and surfactant were used to further investigate the performance of the HAPAM ASP flooding system.

The mother liquor was prepared at 20°C for a dissolution time of 2 h using on-site water of the oil production plant and the on-site dehydrated crude oil. The surfactant (effective content 50%) and NaOH were all on-site industrial products.

3.6.1. Viscosity. The ASP systems containing HAPAM and HPAM (Mw = 2.5 MDa) were prepared. The polymer concentration was 1000 mg/L, the surfactant concentration was 0.3%, and the NaOH concentration was 1.2%. The change of the different systems with the concentration is shown in Figure 9.

Figure 9 shows that, after the addition of base and surfactant, the HAPAM ASP system has clearly better viscosity under field conditions compared with other systems.

3.6.2. Interfacial Tension. The interfacial tension was measured at a fixed HAPAM concentration of 1000 mg/L and varying concentrations of surfactant and base. The experimental results are shown in Figure 10.

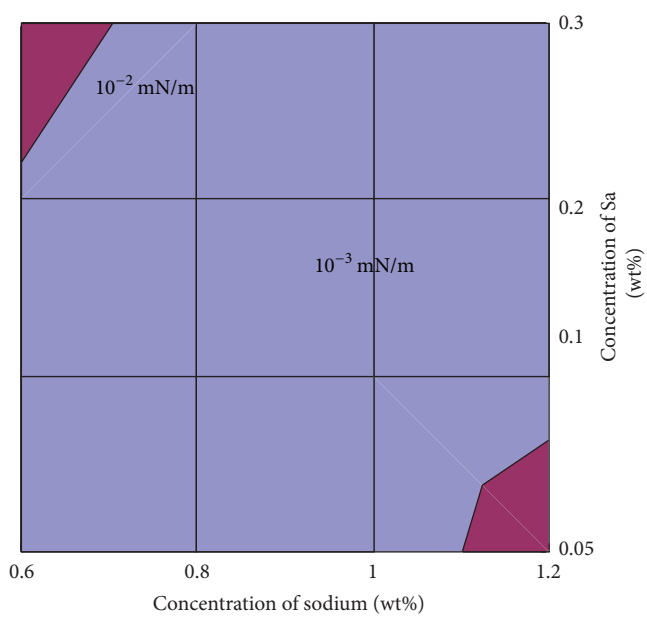

Figure 10: Interfacial tension of the HAPAM ASP system (in on-site injection water).

3.7. Discussions on the Viscosity Enhancement of the HAPAM ASP System. The prominent feature of the HAPAM ASP system is that, in the presence of both the base and the surfactant, the viscosity of the ASP system is significantly higher than that of the polymer solution alone, indicating a viscosity enhancing effect of the associating polymer under the given conditions. In this paper, the mechanism of this viscosity enhancement is analyzed and discussed (see Figure 11).

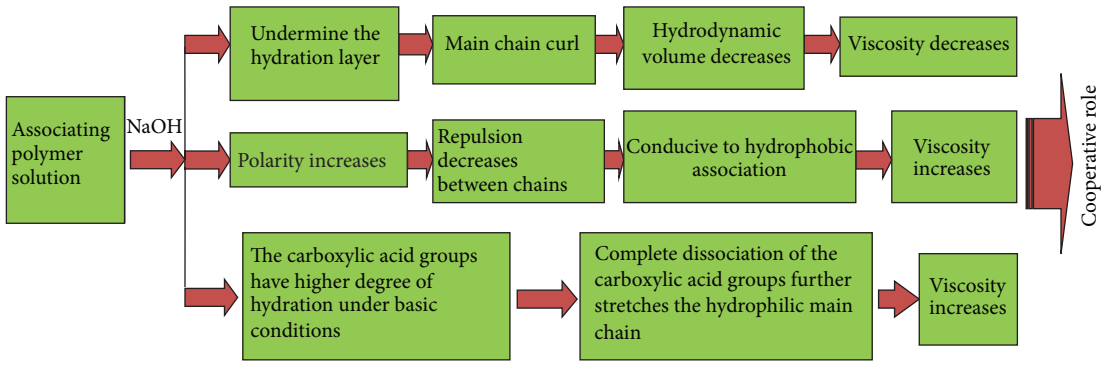

Figure 11: The effect of alkali on the viscosity of the associating polymer solution.

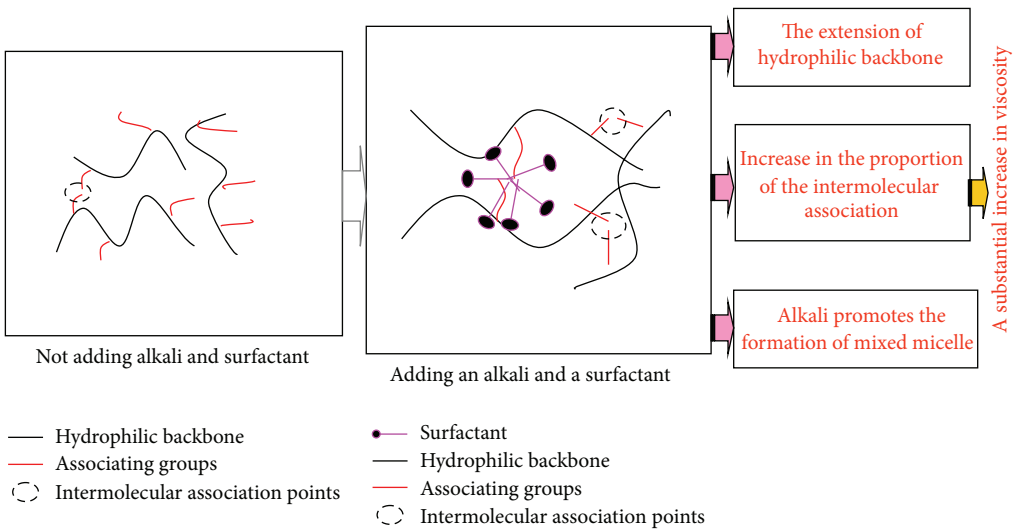

Figure 12: The effect of alkali mixed surfactant on the status of the associating polymer solution.

Because the base can promote the hydrolysis of the amide groups on the main chain of the associating polymer [20], it has less influence than NaCl on the viscosity of the associating polymer solution.

In the presence of both the base and the surfactant, the viscosity of the resulting ASP system is increased substantially. This is mainly because, under basic conditions, the carboxylic acid groups on the hydrophilic main chain have a higher hydration degree, the carboxylic acid groups are completely dissociated, and the molecular chain is more extended. Consequently, the surfactant interacts with the associating groups to form more intermolecular associating micelles, which substantially increases the solution viscosity (see Figure 12). This viscosity enhancement is closely related to the type and composition of the surfactant. Because the heavy alkylbenzene sulfonate surfactant used in this study has a very complicated composition, the mechanism of viscosity enhancement in the ASP system needs to be further studied.

4. Conclusions

The associating polymer HAPAM has good compatibility with the Daqing surfactant. The HAPAM ASP flooding system has good interfacial tension. After the addition of base and surfactant, the viscosity of the HAPAM ASP flooding system is increased significantly. Compared with using the HPAM polymer (Mw = 2.5 MDa), using HAPAM gives much better viscosity and can reduce polymer use by more than 40%. The core series injection experiment shows that the HAPAM ASP flooding system has good injectivity for the Daqing class II reservoirs ($100–300 \times 10^{-3}\ \mu m^2$). The pressure gradient is uniform between the measurement points. The oil recovery can be improved by more than 25% on top of water flooding. Under basic conditions, the carboxylic acid groups on the hydrophilic main chain have a higher hydration degree, the carboxylic acid groups are completely dissociated, and the molecular chain is more extended. This promotes the interaction between the surfactant and the associating groups to form more intermolecular associating micelles, which substantially increase the solution viscosity.

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