Interaction of Cationic Surfactants with Anionic Polymers for Improving Oil Production

Introduction

Surfactants and polymers are widely used in chemical flooding to increase the oil production (Green and Willhite 1998). Polymer increases the viscosity of injected fluid which decreases the water/oil mobility ratio, while surfactant reduces the interfacial tension between crude oil and the injection fluid (Lake 1989). These lead to higher oil production potential.

Surfactants used for chemical flooding were usually anionic surfactants such as sulfate, sulfonates and carboxylates with different hydrophobic chains (Hirasaki et al. 2011, Negin et al. 2017). This is due to most chemical flooding applications were in sandstone reservoirs (Sheng 2010, Guo et al. 2018, Alvarado and Manrique, 2010). Sandstone is composed of quartz (SiO₂) grains cemented together with a variety of minerals. As a result, the rock surface of sandstone is negatively charged. The adsorption of anionic surfactants on sandstone is low due to electrostatic repulsion. Polymers used were also negatively charged such as partially hydrolyzed polyacrylamides (Needham and Doe 1987, Zhu et al. 2015) and sulfonated polyacrylamides (Moradi-Araghi et al. 1987, Levitt et al. 2008).

Different from the sandstone rock with negative surface charge, the carbonate rock is a class of sedimentary rocks composed of carbonate minerals which is positively charged at moderate pH condition. This surface charge difference affects chemical selection. Due to the large molecular weight, anionic polymers show low adsorption on oppositely charged carbonate rocks (Cao et al. 2015). However, anionic surfactants exhibit high adsorption on carbonate rock surfaces. To reduce the adsorption, cationic surfactant is preferred (Austad and Standnes 2003).

It is essential to develop chemical formulations for carbonate reservoirs since over 60% of the world-wide hydrocarbon reserves are held in carbonate reservoirs (Jordan and Wilson 1994, Han et al. 2013). This work studied the possibility of surfactant-polymer (SP) mixture using cationic surfactant and anionic polymer for carbonate reservoir.

The properties between 4 anionic polymers, including partially hydrolyzed polyacrylamides, sulfonated polyacrylamides and hydrophobic associating polymers, and 2 cationic surfactants with different self-assembly behaviours, were tested to evaluate their potential for chemical flooding. Compatibility tests of the oppositely charged polymer and surfactants in brine were performed, and the salinity effect was investigated. Meanwhile, rheology measurements were conducted to look into the effect of cationic surfactants on different anionic polymers.

Method

Cationic surfactants were selected because of their low adsorption on carbonate rocks. Anionic polymers with different structures including partially hydrolyzed polyacrylamides HPAM-S4H and HPAM-S5H, sulfonated polyacrylamides SPAM-A5V and hydrophobic associating polymer APAM-G2L were used to study the structure effect on interaction between anionic polymer and cationic surfactant. Cationic surfactants used were CAS-1 with spherical micelles and CAS-B with wormlike micelles in solution. CAS-B was also called as viscoelastic surfactant (VES). Compatibility tests of polymer and surfactant mixtures were conducted in distilled water and brines with different salinities to study the salinity effect on the interaction between anionic polymers and cationic surfactants. The effect of cationic surfactants on polymer viscosity at different temperatures was investigated using a Rheometer with double wall concentric cylinder geometry.

Compatibility of Cationic Surfactant and Anionic Polymers

Compatibility of chemicals in injection brine is essential to determine whether the chemicals can be successfully used for field application. The formation of precipitation or insoluble particles will significantly reduce the efficiency of chemical solutions as well as cause reservoir formation damage. Table 1 summarizes the compatibility results of cationic surfactant CAS-1 with different anionic
polymers. The compatibility results were recorded by the compatibility codes of A: clear solution; B: slightly hazy solution; C: hazy solution; and D: precipitation. Two oppositely charged chemicals are usually not compatible with each other due to strong electrostatic interaction. As expected, the mixtures of anionic polymers and cationic surfactants precipitated in deionized water due to the charge neutralization. The compatibility became better and the solution turned to be transparent in high salinity injection water (IJW) with total dissolved solid of 57,670 ppm. This is attributed to the shielding of polymer and surfactant charges by the salts, which diminishes the electrostatic interaction between the chemicals. All the systems showed good compatibility in injection water.

The critical salinity for good compatibility of CAS-1 with APAM-G2L, HPAM-S4H and HPAM-S5H was 0.4×IJW (23,068 ppm), while the mixture of CAS-1 and sulfonated polyacrylamides SPAM-A5V still precipitated at this salinity. The latter mixture became soluble until salinity reached 0.6×IJW (34,600 ppm).

**Table 1 Compatibility results of cationic surfactant CAS-1 with polymers in different salinities at 25°C ([polymer] = [surfactant] = 0.2%)**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>0.25 x IJW</th>
<th>0.4 x IJW</th>
<th>0.6 x IJW</th>
<th>0.8 x IJW</th>
<th>IJW</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPAM-A5V</td>
<td>D</td>
<td>D</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>APAM-G2L</td>
<td>C</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>HPAM-S4H</td>
<td>D</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>HPAM-S5H</td>
<td>C</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

**Rheological Properties of Cationic Surfactant and Anionic Polymers**

The polymer solution viscosity is a key parameter to evaluate the potential for improving oil production. The effect of cationic surfactants CAS-1 and CAS-B on viscosity of anionic polymers with different structures was studied in IJW at 25°C and 90°C. CAS-1 forms spherical micelles in solutions above critical micellar concentration. CAS-B is a viscoelastic surfactant with a shear thickening behavior at moderate shear rates, indicating the formation of wormlike micelles (Berret et al. 1998, Muller et al. 2003).

Figures 1 and 2 show the effect of cationic surfactant CAS-1 on viscosity of different polymers at 25°C and 90°C. Relative viscosity ($\eta_r$) was calculated to better evaluate the interaction between anionic polymer and cationic surfactants:

$$\eta_r = \eta_o/(\eta_o - \eta_s)$$

where $\eta_o$ is the viscosity of SP mixture, $\eta_s$ is the viscosity of surfactant solution, $\eta_o$ is the viscosity of polymer solution, and $\eta_b$ is the viscosity of brine.

For partially hydrolyzed polyacrylamides HPAM-S4H and HPAM-S5H, CAS-1 increased the mixture viscosity at 25°C, and this effect diminished at 90°C. For sulfonated polyacrylamides SPAM-A5V, CAS-1 slightly increased the viscosity at 25°C, and decreased the viscosity at 90°C. When applied with the hydrophobic associating polymer APAM-G2L, CAS-1 decreased the solution viscosity at both 25°C and 90°C in. These results suggest that the polymer side chain and temperature affect the properties of surfactant-polymer mixtures.

When mixing the cationic viscoelastic surfactant CAS-B with different anionic polymers, significant viscosity increase was observed at 25°C. For the mixture of CAS-B and hydrophobic associating polymer, the solution viscosity was several times higher than the sum of polymer viscosity and surfactant viscosity at high temperature of 90°C. This is due to the entanglement between polymers molecules and wormlike micelles.
Figure 1 Relative viscosity results of 2000 ppm cationic surfactant CAS-1 with polymers of different concentrations in IJW at 25°C.

Figure 2 Relative viscosity results of 2000 ppm cationic surfactant CAS-1 with polymers of different concentrations in IJW at 90°C.

Conclusions

In this work, the compatibility and rheology properties of several oppositely charged SP mixtures were studied, using anionic polymers with different structures and 2 cationic surfactants with different self-assembly properties. High salinity diminishes the electrostatic interaction between anionic polymers and cationic surfactants, which improves the compatibility and make it possible to apply oppositely charged surfactant and polymer in high salinity reservoir condition. For partially hydrolyzed polyacrylamides, both cationic surfactants with spherical (CAS-1) or wormlike (CAS-B) micelles showed positive effect on viscosity. For sulfonated polyacrylamides, cationic surfactant CAS-1 slightly reduced the viscosity at high temperature. CAS-1 significantly reduced the viscosity of hydrophobic associating polymer, while CAS-B increased the viscosity. These results suggest that the anionic polymer side chain and self-assembly structures of cationic surfactants play an important role in the performance of polymer-surfactant mixtures, which should be taken into account in the design of optimal formulations.
References


