In Situ Prepared Microemulsion-polymer Flooding in Enhanced Oil Recovery—A Review


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In Situ Prepared Microemulsion-polymer Flooding in Enhanced Oil Recovery—A Review

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Microemulsion could be formed in situ through simultaneous injection of surfactant, cosurfactant, and brine into the reservoir. The formed microemulsion is expected to propagate toward the production well and along its way sweep significant amounts of the remaining hydrocarbon in the reservoir. There are numerous reports on in situ prepared microemulsion flooding in the literature. The interest in in situ prepared microemulsion flooding research activities is expected to increase tremendously in the near future because of its high potential in maximizing hydrocarbon recovery in enhanced oil recovery activities. The authors summarize major articles relevant to in situ prepared microemulsion flooding with application of various polymers in the flooding. They also discuss critically and extensively the effect and function of polymers and their role in the microemulsion flooding. This review opens new horizons for future research on in situ prepared microemulsion-polymer flooding in enhanced oil recovery processes by systematically organizing and comparing data in the literature. The data and information presented would be very useful to researchers conducting work related to enhanced oil recovery with microemulsion polymer flooding.

Keywords: enhanced oil recovery, chemical flooding, in situ, microemulsion, polymer

1. INTRODUCTION

Hydrocarbon in reservoirs is produced by means of primary, secondary, and tertiary recovery. Primary recovery entails producing the hydrocarbon by natural means while secondary recovery involves the injection of water to maintain the reservoir pressure. Tertiary recovery or enhanced oil recovery (EOR) involves the application of various processes, mainly to boost production. Such processes include gas injection, chemical flooding, thermal processes, and microbial EOR. Microemulsion-polymer flooding is considered one of the most promising chemical EOR methods because it leads to significant hydrocarbon production.

In in situ prepared microemulsion flooding, a definite surfactant formulation is injected into reservoirs. During its propagation through the reservoir, surfactant is mixed with the reservoir oil and brine. As a result, a microemulsion slug is produced downhole and called in situ prepared microemulsion flooding. The injection can be accompanied with excess water (or brine) and cosurfactant to improve the performance and stability of the microemulsion formed in the reservoir. However, no oil is augmented to the injected fluid because the addition of oil results in the formation

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of microemulsion outside of the reservoir (i.e., on the surface). This method is called preprepared microemulsion flooding. On the other hand, if the mixture of oil and surfactant without brine were used as the injected fluid, the injection fluid is neither efficient nor economical, because the purpose of EOR is to apply a mechanism that helps free trapped globules of oil effectively and economically.

In both in situ prepared microemulsion flooding and surfactant flooding, surfactant is the essential component of the injection fluid. However, they are different in two aspects. First, the concentrations of the aqueous surfactant solution are different. Second, the interfacial tensions between the aqueous and oleic phases are not the same. In surfactant flooding, the concentration of the surfactant in the injected aqueous phase is lower than the critical micelle concentration (CMC) of the surfactant. The interfacial tension (IFT) between the aqueous and oleic phases in the reservoir is not low enough to be classified as ultra-low for making microemulsion. However, in in situ prepared microemulsion flooding, two requirements need to be satisfied. First, the surfactant concentration has to be higher than the CMC of the surfactant because microemulsion would be formed whenever the surfactant concentration is above the CMC point at which the monomers of surfactant would form micelle. Second, the interfacial tension between the oleic and aqueous phases should be kept at or lower than $10^{-2}$ to $10^{-3}$ mN/m.

In situ prepared microemulsion-polymer or micellar-polymer flooding is a process of injecting a surfactant mixed with other chemicals into an oil reservoir to reduce the interfacial tension. As previously mentioned, two types of chemicals may accompany the surfactant: brine and cosurfactants such as alcohols. An in situ prepared microemulsion-polymer process starts with injection of a preflush brine into the oil reservoir to reduce reservoir salinity. Then a slug composed of surfactant, brine, and cosurfactant is injected into the reservoir. This slug, with the trapped oil in the reservoir, will form a microemulsion slug in situ. The slug is followed by the injection of a dilute solution of water-soluble polymer, which is injected into the oil reservoir to displace the microemulsion slug. The dilute solution slug ranges in volume between 0 and 100% pore volume (PV). It is often called thickened drive. The final injected slug is the chasing (driving) fluid, which is usually water to push all of the injected fluids.

The objective of having polymer in a microemulsion flooding is not only solely to ensure a stable drive. In certain cases a polymer is also added to the injected chemicals to control the mobility of the in situ microemulsion formed. The oil recovery efficiency is quite high when the injection fluid contains a polymer because of the two different natures of polymer and surfactant: surfactant reduces the interfacial tension, the polymer reduces the mobility of the microemulsion.

To have an effective in situ prepared microemulsion-polymer flooding to mobilize residual oil, it is essential to select a proper surfactant capable of forming an efficient microemulsion in situ as well as a compatible polymer, which can displace the microemulsion well. A well-designed microemulsion would lower the interfacial tension of oil and water even after its dilution during its movement through the reservoir. Consequently, numerous of surfactants were studied for different reservoir conditions (Minssieux, 1987; Sanz and Pope, 1995; Babadagli, 2006; Zhao et al., 2008; Wang et al., 2010).

It is the objective of this article to summarize research work in the literature on in situ prepared microemulsion flooding based on the open literature data. This paper also provides further information about polymers used in microemulsion flooding both as a stable displacing fluid and mobility control agent.

2. IN SITU PREPARED MICROEMULSION FLOODING WORKS

Designing a surfactant with the ability to form a microemulsion is a function of few parameters such as the type of surfactant, capability of cosurfactant, and salinity of the brine. The process in designing a surfactant to have a microemulsion has been reported in the literature numerous times in which
various types and concentrations of surfactant(s) and cosurfactant(s) were involved. It is almost impossible to simultaneously compare the behavior and efficiency of these processes because of the different types of core, types of oil, salinity of formation brine, and operating conditions such as temperature. However, a comprehensive review article would open new horizons in the progression of novel research areas. Table 1 is a summary of the most notable attempts carried out in situ prepared microemulsion flooding. In the comment/remark column, we have summarized significant remarks, observations, or criticism pertaining to the specific reference or article. In short the following useful information could be obtained from Table 1:

- Anionic surfactants were often employed in in situ prepared microemulsions techniques and often produce promising results (Glinsmann, 1979; Bae and Petrick, 1981; Gupta, 1982; Sanz and Pope, 1995; Austad and Taubøl, 1995a; Austad and Taubøl, 1995b; Taubøl et al., 1995; Austad et al., 1997; Levitt et al., 2006; Bouabboune et al., 2006; Zhao et al., 2008). These surfactants could significantly reduce the IFT of the fluid system tested. IFT values as low as 10⁻³ were measured and reported.
- Surfactant retention in porous media has been a serious issue in the application of anionic surfactants (Glinsmann, 1979; Bae and Petrick, 1981; Gupta, 1982; Austad et al., 1997). Therefore, different techniques were used to eliminate or reduce the surfactant retention or recover the surfactant after its adsorption. Among the techniques tested were injection of sacrificial agents prior to the microemulsion slug (Glinsmann, 1979), injection of a desorbing nonionic agent after the microemulsion slug (Minssieux, 1987), and injection of xanthan simultaneously with the microemulsion (Austad et al., 1997).
- Another challenge often observed during in situ prepared microemulsion flooding is the formation of emulsions or macroemulsions (Kraft and Pusch, 1982; Bragg et al., 1982; Sanz and Pope, 1995). It is apparent that the formation of any other phases other than oil, water, and microemulsion is undesirable in a chemical flooding because the viscosity of the microemulsion phase will be increased tremendously (Kraft and Pusch, 1982). Gels, liquid crystals, and macroemulsions are some example of undesirable phases that may be formed during chemical flooding with the application of incompatible surfactant(s) or cosurfactant(s). Therefore, it was necessary to design a screening strategy to select the most appropriate surfactant to minimize the occurrence of the undesirable phase (Sanz and Pope, 1995).
- The viscosity of in situ microemulsion is very critical because it directly affects the mobility of the injected phase. Issues related to extreme magnitude of mobility values (too high and too low) of the microemulsion have been reported (Gupta, 1982; Kraft and Pusch, 1982). The performance of a formulated microemulsion strongly depends on its viscosity (Levitt et al., 2006).
- To keep the IFT between the oleic and aqueous phases ultralow and at the same time reduce the side-effect of anionic surfactant, combination of anionic and nonionic surfactants were often used in the formulation of in situ prepared microemulsion under specific conditions (Kraft and Pusch, 1982; Nelson, 1983; Minssieux, 1987).
- Although nonionic and zwitterionic surfactants were rarely used in in situ prepared microemulsion flooding before the 20th century, efficient nonionic and zwitterionic surfactants were recently synthesized and used without any combination with other surfactants. The flooding was stable and effective even at high temperature and high salinity (Iglauer et al., 2009; Wang et al., 2010; Dwarakanath et al., 2008).
- Many cosurfactant(s) have been used with various surfactants to assist the surfactant to immensely lower the IFT and increase the efficiency of oil displacement (Glinsmann, 1979; Bae and Petrick, 1981; Kraft and Pusch, 1982; Gupta, 1982; Bragg et al., 1982; Nelson, 1983; Levitt et al., 2006; Bouabboune et al., 2006; Zhao et al., 2008; Dwarakanath et al., 2008; Iglauer et al., 2009). However, in some research studies, cosurfactant was not injected with the surfactant.
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Cosurfactant</th>
<th>Brine</th>
<th>Comment/Remark</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum sulfonates (from Witco</td>
<td>Isobutanol (IBA)</td>
<td>Brine (NaCl + KCl + CaCl₂ + MgCl₂ + Na₂SO₄) TDS: 1,175 and 807 ppm</td>
<td>Sodium tripolyphosphate and sodium carbonate were used as sacrificial agents to reduce surfactant adsorption in porous media. At optimum salinity conditions, surfactant retention was minimized and oil recovery was maximized.</td>
<td>Glinsmann, 1979</td>
</tr>
<tr>
<td>Chemical Co.)</td>
<td>Anionic</td>
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<td>Surfactant retention was almost the same in different salinities. High recovery efficiency was observed at lower-salinity systems because of the ion exchange and the change in composition of microemulsion during the flood. Maximum oil recovery was obtained at a salinity below the optimal salinity.</td>
<td>Bae and Petrick, 1981</td>
</tr>
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<tr>
<td>Aqueous surfactant slug size: 0.1 PV</td>
<td>1-pentanol (from Union Carbide Corp.)</td>
<td>Brine (NaCl concentrations of 8.0, 12.0, and 16.0 g/kg)</td>
<td>In the absence of cosurfactant, ultra low IFT was obtained within a narrow temperature range (53–57 °C). However, addition of the suitable cosurfactant led to the formation of a stable microemulsion in a wider range of temperature. The most important challenge of the work was the formation of emulsions during the flooding process; under these conditions the viscosity of the emulsion exceeds the viscosity of the polymer buffer following it, gives rise to fingering effect.</td>
<td>Kraft and Pusch, 1982</td>
</tr>
<tr>
<td>Petrostep 465 and 420 (from Stepan Chemical Co.)</td>
<td>Anionic</td>
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<tr>
<td>Aqueous surfactant slug size: 0.1 PV</td>
<td>Isopropyl glycol</td>
<td>Brine from a Northwest German Dogger-β reservoir TDS: 226795 ppm</td>
<td>The microemulsion formulation was not desirable for two reasons. First, the mobility of the micellar fluid was too high. Therefore, early sulfonate breakthrough was observed. Second, a large amount of surfactant was needed because three events occurred; Some of the surfactant adsorbed on the rock surfaces. Others were mostly partitioned to oil phase and were carried out with the produced oil. Some were trapped inside the core with the trapped oil.</td>
<td>Gupta, 1982</td>
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<tr>
<td>Fatty alcohol carboxylate (BW 1109)</td>
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<tr>
<td>25% nonionic + 75% anionic</td>
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<tr>
<td>Aqueous surfactant slug size: 0.3 PV</td>
<td>IPA</td>
<td>Brine (12,000 ppm NaCl + Sloss fresh water) TDS: 214 ppm</td>
<td>It was observed that with the new microemulsion, preflushing was not required before the microemulsion slug although the salinity of the formation water was relatively high. The pilot test of the formulation was technically successful; however, problems related to the formation of oil-water emulsion and bacterial degradation of biopolymer were observed.</td>
<td>Bragg et al., 1982</td>
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<tr>
<td>Mahogany AA sulfonate</td>
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<tr>
<td>Anionic</td>
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<tr>
<td>Aqueous surfactant slug size: 0.3 PV</td>
<td>Isopropanol</td>
<td>Loudon formation brine TDS: 100432 ppm</td>
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<tr>
<td>A surfactant (manufactured by Exxon)</td>
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<td>NM</td>
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</table>

(Continued on next page)
### TABLE 1
In Situ Prepared Microemulsion Flooding Review (continued)

<table>
<thead>
<tr>
<th>Microemulsion Composition</th>
<th>Surfactant</th>
<th>Cosurfactant</th>
<th>Brine</th>
<th>Comment/Remark</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous surfactant slug size: 0.4 PV</td>
<td>73.3% Petrostep® 450 (a petroleum sulfonate from Stepan Chemical Co.) + 19.8% Neodol® 25-3S (an alcohol ethoxysulfate from Shell Chemical Co.)</td>
<td>Aqueous surfactant slug size: 0.4 PV</td>
<td>Isobutyl alcohol</td>
<td>— Aqueous surfactant slug size: 0.4 PV</td>
<td>Nelson, 1983</td>
</tr>
<tr>
<td>Synthetic sulfonate + 2 ethoxylated fatty alcohols</td>
<td>Anionic + nonionic</td>
<td>Synthetic Brine (NaCl, KCl, MgCl₂, and CaCl₂)</td>
<td>TDS: 29220 ppm</td>
<td>Combination of anionic and nonionic surfactants in this formulation was useful for microemulsion flooding in reservoirs with high brine salinity at moderate temperature. However, a high level of surfactant retention in the reservoir rock was observed from this formulation. To recover the surfactant, a desorbing nonionic agent was implemented behind the microemulsion slug.</td>
<td>Minssieux, 1987</td>
</tr>
<tr>
<td>Ethoxylated sulfonate, internal olefin sulfonate + a petroleum sulfonate</td>
<td>Anionic</td>
<td>Brine (10% NaCl)</td>
<td>—</td>
<td>The alcohol-free formulation of microemulsion consists of three sulfonate surfactant seems to result in very efficient flooding, even when a small amount was injected. The surfactant was formulated based on a proposed screening strategy to minimize the formation of gels, liquid crystals, and macroemulsion during the chemical flood. However, the formulation seems to works well only for specific conditions tested and it cannot be generalized to other conditions.</td>
<td>Sanz and Pope, 1995</td>
</tr>
<tr>
<td>Aqueous surfactant slug size: 0.13 and 0.03 PV</td>
<td>Alkyl-o-xylene sulfonate (RL-3011) (from Exxon)</td>
<td>Anionic</td>
<td>Brine (2.1 and 2.7% NaCl)</td>
<td>Phase transition could be promoted through the application of polymer gradient (specifically for xanthan rather than polyacrylamides). Oil recovery was almost the same with the use of salinity gradient as well as polymer gradient.</td>
<td>Austad and Taugbøl, 1995a</td>
</tr>
<tr>
<td>Aqueous surfactant slug size: 0.5–2.5 PV</td>
<td>Alkyl-o-xylene sulfonate (RL-3011) (from Exxon)</td>
<td>Anionic</td>
<td>Brine (2% NaCl)</td>
<td>The addition of polymer to the injection fluid was shown to significantly decrease oil recovery.</td>
<td>Austad and Taugbøl, 1995b</td>
</tr>
<tr>
<td>Aqueous surfactant slug size: 0.5 PV</td>
<td>Alkyl propoxy-ethoxy sulfate</td>
<td>Anionic</td>
<td>Synthetic Brine</td>
<td>The addition of xanthan to the injection fluid resulted in higher oil recovery and lower surfactant retention.</td>
<td>Taugbøl et al., 1995</td>
</tr>
<tr>
<td>Aqueous surfactant slug size: 0.5 PV</td>
<td>Alkyl propoxy-ethoxy sulfate</td>
<td>Anionic</td>
<td>Synthetic sea water</td>
<td>Addition of xanthan to the injection fluid reduced the adsorption of surfactant both in long-term floods and in small-slug floods at surfactant concentration below CMC. In contrast, the presence of xanthan in the injection fluid for large slug floods did not alter the adsorption of surfactant.</td>
<td>Austad et al., 1997</td>
</tr>
</tbody>
</table>
Aqueous surfactant slug size: 0.5–2.36 PV
Propylene oxide (PO) surfactants  Sec-butanol (SBA)  Anionic  
Among the tested PO surfactants, the surfactants that have branched hydrophobes Levitt et al., 2006 in their structure are known to be the most suitable, yield high-performance, and have low-cost anionic surfactants which exhibited low surfactant retention because the formulated microemulsion has low viscosity.

Aqueous surfactant slug size: 0.5 PV
An anionic surfactant  Pentanol alcohol  Brine  
Comparison of the flooding efficiency of pre-prepared microemulsion flooding and surfactants (in situ microemulsions) flooding showed that pre-prepared microemulsions are more capable and efficient than in situ microemulsions. Bouabiboune et al., 2006

Aqueous surfactant slug size: 0.25 PV
Ethoxylated nonylphenol, t-octylphenoxypoly-ethoxylethanol (IGEPAL), sulfonated sodium salt, dodecyl trimethyl ammonium bromide  —  Brine (3% NaCl)  
Different kinds of surfactants were tested in naturally fractured chalky carbonate reservoirs. Injection of anionic or cationic surfactants above CMC resulted in higher oil recovery. However, the injection of anionic-nonionic blend reduced the recovery although the surfactant concentration was kept above CMC and the reported IFT was low. For the injection of pure nonionic surfactants, IFT plays the most critical role. The nonionic surfactant solution with concentration below CMC resulted in lower IFT, and consequently higher oil recovery and vice versa. Babadagli, 2006

Aqueous surfactant slug size: (primary surfactant injection)
Heavy internal olefin sulfonate  n-pentanol + SBA  Brine (1.9% NaCl + 1% Na₂CO₃)  
The formulated in situ microemulsions were identified to be applicable in high temperature and/or heavy paraffinic crude oils. They are economical and efficient at low concentration when properly formulated. Zhao et al., 2008

Aqueous surfactant slug size: 0.1 PV
An AMPS copolymer (by SNF)  IPA  Water  
An optimal cosolvent/electrolyte gradient was obtained from experimental methods combined with computer simulations. The formulated microemulsion provides very high efficiency in the oil displacement process. Dwarakanath et al., 2008

Aqueous surfactant slug size: 0.15 and 0.1 PV
Alkyl polyglycoside surfactants  1-octanol (from Aldrich)  Brine (2 wt% NaCl)  
The IFT and phase behavior of APG surfactants were reported to be independent of salinity and temperature. Alcohol chains of cosurfactants and an optimum ratio of cosurfactant/AGP were optimized to make a lower IFT. It was shown that the IFT decreases with an increase in alkyl chains of APG. Iglauer et al., 2009

Aqueous surfactant slug size: 0.25 PV
Betaine surfactant  —  Water  
The new surfactant is able to produce ultralow IFT at very low concentration even in the absence of alkali, salts, alcohol, cosurfactants, and cosolvents. The new formulation is stable at high salinity and high temperature with acceptable adsorption. Wang et al., 2010

Aqueous surfactant slug size: 0.35 PV
and consequently it has not been applied in the formulation of the microemulsion, which was prepared in situ (Minssieux, 1987; Sanz and Pope, 1995; Austad and Taugbol, 1995a; Austad and Taugbol, 1995b; Taugbol et al., 1995; Austad et al., 1997; Babadagli, 2006; Wang et al., 2010). It was believed that the applied surfactant was very effective in reducing the IFT. Therefore it was not necessary to use any cosurfactant or cosolvent (Wang et al., 2010). Furthermore, other researchers stated that the elimination of alcohols from the microemulsion formulation was necessary to keep the process economical because of the high cost of alcohols (Sanz and Pope, 1995).

In designing a strategy of in situ microemulsion flooding, manipulation of three different gradients could be used. Such gradients are polymer gradient (Austad and Taugbol, 1995a; Taugbol et al., 1995; Austad et al., 1997), salinity gradient (Glinsmann, 1979, Bae and Petrick, 1981; Austad and Taugbol, 1995a), and cosolvent gradient (Dwarakanath et al., 2008). All of these techniques led to an improvement in the efficiency of oil displacement. However, polymer gradient might have a contrary effect on the oil recovery efficiency in some special cases (Austad and Taugbol, 1995b).

Although preprepared microemulsion flooding was shown to be more efficient than in situ prepared microemulsion flooding to enhance oil recovery (Bouabboune et al., 2006), continuous progress and development has been seen recently in the application of various surfactants for in situ microemulsion flooding (Zhao et al., 2008; Dwarakanath et al., 2008; Iglauer et al., 2009; Wang et al., 2010). Therefore, it was expected that novel surfactants would be synthesized in the near future that would increase the efficiency of a microemulsion flooding.

3. POLYMER SLUG AS A THICKENED DRIVE

In microemulsion flooding, just as in other chemical flooding methods, the microemulsion slug is followed by a polymer slug. The viscosity of the aqueous phase will be increased by the addition of polymer. Thus the mobility of the aqueous phase decreases and fluid mobility ratio reduces accordingly. Unlike surfactant flooding, residual oil saturation, with a few exceptions, will not be decreased with the presence of polymer (Wang et al., 2000). However, it will increase the flood sweep efficiency to a great extent. Polymer flooding is useful when the water-flooding mobility ratio is high, and the reservoir is completely homogeneous, or a combination of the two occurs (Lake, 1989).

A polymer flood is desirable when the following conditions apply: it is economical, stable to mechanical shear during pumping and injection operations, highly resistant to bacterial attack, stable in the presence of salts and other chemicals, thermally stable, meets environmental requirements, and demonstrates minimum retention and plugging in porous media.

3.1 Preferred Commercial Polymers in Chemical Flooding

Polyacrylamide and polysaccharide are two commercial polymers commonly used in enhanced oil recovery (Sorbie, 1991). Partly hydrolyzed polyacrylamide (HPAM) is the first group of polymers widely used in EOR processes (Lake, 1989). Like the anionic surfactant, HPAM is negatively charged. Shupe (1981) tested the effect of pH, dissolved oxygen, salinity, and hardness on HPAM polymer stability. Xanthan gum, which is a bacterial polysaccharide, is the commonly used polysaccharide. Unlike HPAM, the structure of xanthan gum is more rigid and it is relatively nonionic. These properties make it invulnerable to hardness and salinity. Xanthan gum is also known to have high resistance to shear or mechanical degradation. However, it is susceptible to bacterial degradation.
### TABLE 1
Comparison of HPAM and Xanthan, Two Common Commercial Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPAM</td>
<td>It is much cheaper</td>
<td>High shear rates irreversibly degraded high molecular weight HPAM (Sorbie, 1991)</td>
</tr>
<tr>
<td></td>
<td>It is compatible with anionic surfactant</td>
<td>An increase in salinity or hardness decreases the viscosity of HPAM sharply (Nasr-El-Din et al., 1991)</td>
</tr>
<tr>
<td></td>
<td>It has relatively high resistance to bacterial attack</td>
<td>This polymer precipitates in the presence of high concentrations of divalent ions (Zaitoun and Potie, 1983)</td>
</tr>
<tr>
<td></td>
<td>It exhibits permanent permeability reduction</td>
<td>For maximizing its penetration in the reservoir, a high concentration of the polymer is used for the injection (Wang et al., 2003)</td>
</tr>
<tr>
<td>Xanthan</td>
<td>Because of its rigid structure, it is not readily shear-graded</td>
<td>There is high susceptibility to its biodegradation</td>
</tr>
<tr>
<td></td>
<td>It is not sensitive to an increase in salinity or divalent ion concentration (Nasr-El-Din and Noy, 1992)</td>
<td>Its manufacturing process may result in cellular debris which can cause problems during its injection</td>
</tr>
<tr>
<td></td>
<td>It is compatible with nonionic surfactants</td>
<td>It is more expensive</td>
</tr>
</tbody>
</table>

### TABLE 2
Polymers Used in Micellar Fluid

<table>
<thead>
<tr>
<th>Name of Polymer</th>
<th>Type of Microemulsion Flooding</th>
<th>Properties of Polymer Solution</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pusher 700™</td>
<td>In situ prepared</td>
<td>1600 ppm Pusher 700™ + brine (12000 ppm NaCl)</td>
<td>Gupta, 1982</td>
</tr>
<tr>
<td>Flocon 4800®</td>
<td>Pre-prepared</td>
<td>90.67% of microemulsion 750 ppm Flocon 4800® + brine (1.7% NaCl)</td>
<td>Puerto and Reed, 1983</td>
</tr>
<tr>
<td>Pfizer Flocon 4800®</td>
<td>Pre-prepared</td>
<td>1000 ppm Flocon 4800® (a biopolymer) + brine (104604 ppm total dissolved solids)</td>
<td>Maerker and Gale, 1992</td>
</tr>
<tr>
<td>Pfizer Flocon 4800®</td>
<td>Pre-prepared</td>
<td>Development of polyacrylamide</td>
<td>Purwono and Murachman, 2001</td>
</tr>
<tr>
<td>Xanthan and HPAM (or Alcoflood 1175A)</td>
<td>In situ prepared</td>
<td>Flocon 4800® xanthan gum (a biopolymer) + brine (104000 ppm total dissolved solids)</td>
<td>Bragg et al., 1982</td>
</tr>
<tr>
<td>Xanthan, polymer AN 125</td>
<td>In situ prepared</td>
<td>500 ppm Xanthan (from Statoil) or HPAM (from Allied Colloids) + brine (1.8–2.1 wt% NaCl)</td>
<td>Austrad and Taugbøl, 1995a</td>
</tr>
<tr>
<td>Flopaam 3330S</td>
<td>In situ prepared</td>
<td>500 ppm Xanthan (from Bioferm Statoil) + 1000 ppm polymer AN 125 (from Floerger) + brine (synthetic sea water)</td>
<td>Austad et al., 1997</td>
</tr>
<tr>
<td>AN 125</td>
<td>In situ prepared</td>
<td>2000 ppm Flopaam 3330S HPAM (from SNF) + brine (45000 ppm NaCl + 1375 ppm CaCl₂)</td>
<td>Levitt et al., 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500 ppm AN 125 polymer (from SNF Floerger) + brine (1.9 wt% NaCl)</td>
<td>Zhao et al., 2008</td>
</tr>
<tr>
<td>Name of Polymer(s)</td>
<td>Type of Microemulsion Flooding</td>
<td>Properties of polymer slug</td>
<td>Reference</td>
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</table>
| HPAM              | Preprepared                    | High-molecular-weight, partially hydrolyzed polyacrylamide (from Dow Pusher<sup>®</sup>) + fresh water  
Viscosity of solution: 32 cp at 6 rpm | Holm, 1971 |
| XC                | Preprepared                    | 1000 ppm Biopolymer + brine (1% NaCl) | Healy et al., 1975; Healy and Reed, 1977 |
| —                 | Preprepared                    | Biopolymer solution containing 8% of the formation brine (120000 ppm total dissolved solids and 3000 ppm divalent cations) | Nelson and Pope, 1978 |
| Kelzan<sup>TM</sup> and Pfizer 1035<sup>TM</sup> | Preprepared | 1000 ppm Kelzan<sup>TM</sup> or 750 ppm Pfizer 1035<sup>TM</sup> biopolymer + brine (104752 ppm total dissolved solids) | Glover et al., 1979 |
| Kelzan SS-4000    | Preprepared                    | Improved Xanflood biopolymer (from Kelco) + brine (0.9%wt NaCl in deionized water) | Meyers and Salter, 1980 |
| Pusher 700<sup>TM</sup> | Preprepared | 3.5 kg/m³ Pusher 700<sup>TM</sup> (a kind of polyacrylamide) in 10.6 kg/m³ NaCl  
Viscosity of solution: 26.5 cp at 22.5 sec<sup>−1</sup> | Willhite et al., 1980 |
| PAM               | Preprepared                    | 1700 ppm polyacrylamides + Chateaurenard water (400 ppm total dissolved solids)  
Viscosity of solution: 55 cp at 10 sec<sup>−1</sup> | Putz et al., 1981 |
| Flocon 4800<sup>®</sup> Xanflood | Preprepared | 1000 ppm Flocon 4800<sup>®</sup> in 1.7% NaCl | Puerto and Reed, 1983 |
| Kalgon and Pusher 500 | Preprepared | 500 ppm Kalgon or Pusher 500 polymer + brine (1% NaCl) | Sayyoun et al., 1991 |
| —                 | Preprepared | A polymer + brine (89300 ppm total dissolved solids)  
Viscosity of solution: 35 cp at 11 sec<sup>−1</sup> | Osterloh and Jante, 1992 |
| —                 | In situ prepared               | 1125–4150 ppm polymer + brine (0.4–3.9% NaCl)  
Viscosity of solution: 40 cp at 6 rpm | Glinsmann, 1979 |
| Kelzan<sup>TM</sup> MF | In situ prepared | 1500 ppm Kelzan<sup>TM</sup> MF biopolymer + brine (0.8–1.6% NaCl) | Bae and Petrick, 1981 |
| HEC               | In situ prepared               | 3000 ppm HEC + brine (226795 ppm total dissolved solids)  
Viscosity of solution: 20 cp at 10 sec<sup>−1</sup> | Kraft and Pusch, 1982 |
| Pfizer Flocon 4800<sup>®</sup> | In situ prepared | Xanthan biopolymer + brine (less than 104000 ppm total dissolved solids)  
Viscosity of solution: 35 cp at 11 sec<sup>−1</sup> | Bragg et al., 1982 |
| Xanflood<sup>®</sup> | In situ prepared | 1600–1800 ppm Xanflood<sup>®</sup> biopolymer (from Kelco Corp.) + brine (2.5 wt% NaCl)  
| Rhodoflood AD27 MV | In situ prepared | 1500 ppm Rhodoflood AD27 MV (a kind of polyacrylamide) + water  
Viscosity of solution: 6.44 cp at 26 sec<sup>−1</sup> | Bouabboune et al., 2006 |
| AN 125            | In situ prepared               | 2500 ppm AN 125 polymer (from SNF Floerger) + brine (1 wt% NaCl) | Zhao et al., 2008 |
| Alcoflood 1235    | In situ prepared               | 250 ppm Alcoflood 1235 (from Ciba Corp.) + brine (1 wt% NaCl) | Iglauer et al., 2009 |
| Flopaam 3330S     | In situ prepared               | 2000 ppm Flopaam 3330S + brine (with salinity of 0.2 meq/mL)  
Viscosity of solution: 17.9 cp | Roshanfekr et al., 2009 |
after injection into the reservoir. A full and detailed comparison of these two traditional polymers is given in Table 2.

### 3.2 New Generation of Polymers in Chemical Flooding

Some of the disadvantages of traditional polymers are also presented in Table 2. Wang et al. (2003) recommended the application of a new weak gel for chemical flooding. The weak gel system could reduce the problem of permeability contrast in a heterogeneous reservoir and improve the injection profile. Synthesizing an efficient polymer did not stop at this stage. Modified polysaccharide was introduced by Kjøniksen et al. (2008). Although the polymer acted as a powerful viscosifying agent at low concentration, it was found to be sensitive to salt. As a result, further development in designing optimal polymer systems was needed. In another recent work, Levitt and Pope (2008) concluded that high-viscosity polymers are more suitable for high-salinity reservoirs. It is also suggested that at calcium concentration higher than 200 ppm, sodium metaborate, or copolymers such as sodium 2-acrylamide-2-methylpropane sulfonate (AMPS) could be used to increase calcium tolerance.

### 3.3 Polymers in Microemulsion Flooding

Polymers used in microemulsion flooding can be divided into two groups. The first group refers to polymer that accompanies the microemulsion slug as one of its components. The polymer is added to the microemulsion slug to alter the rheology of the microemulsion from being thixotropic to being pseudoplastic (Maerker and Gale, 1992). As a result, the microemulsion slug becomes less mobile and fewer problems related to viscous fingering are observed. The second group of polymers in microemulsion flooding refers to polymers that drive the microemulsion slug as a separate slug. This polymer is usually diluted with brine. It is also known as a mobility buffer slug or a polymer-thickened drive. Tables 3 and 4 summarize the applications of the two different groups of polymers, respectively, both in preprepared and in situ prepared microemulsion flooding processes. Tables 3 and 4 show that the concentration of the applied polymers in micellar fluid is between 500 ppm (Austad and Taugbøl, 1995a) to 2,500 ppm (Zhao et al., 2008). However, in a system in which a uniform polymer slug is used as the driving fluid, the concentration range of polymer is maintained between 250 ppm (Iglauer et al., 2009) to 4,150 ppm (Glinsmann, 1979).

### 4. CONCLUSIONS

The success of microemulsion flooding for improving oil recovery depends on proper selection of chemicals in formulating the microemulsion. During the past 40 years, various in situ prepared microemulsion formulations have been reported in enhanced oil recovery processes. In this review we summarize the most noble and notable research work significant to in situ prepared microemulsion flooding and it compares different aspects of the microemulsion preparation and flooding. This comprehensive review and organized literature data will facilitate researchers in understanding the existing literatures on in situ prepared microemulsions.

The following are some possible future studies on in situ microemulsion flooding:

- Synthesis of a novel surfactant or improving the molecular structure of the existing commercial surfactants to improve their ability to produce microemulsion with super-low IFT.
- Application of cosurfactants other than alcohols and studying their effect on the efficiency of the microemulsion flooding.
• Investigation of the nature of preflushing and postflushing slugs injected before and after the microemulsion slug to reduce surfactant retention and consequently increase oil recovery.
• Design of a new and effective injection strategy in addition to polymer gradient, salinity gradient, and cosolvent gradient to enhance oil recovery.

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