



A Comprehensive Review on Applications of Polymeric Surfactants for Chemical Enhanced Oil Recovery



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Abstract

The decline in conventional oil reserves encouraged oil producers to exploit heavy and unconventional oils, which in many situations requires application of chemical enhanced oil recovery (CEOR) on extracting and recovering the hydrocarbons. Available CEOR methods, although they are well established, new challenges always there, and hence, new CEOR techniques are always emerge. Recently researchers suggest polymeric surfactants which represent a very attractive EOR fluid due to their ability of increasing the water viscosity while simultaneously decreasing the interfacial tension. This paper reviews the research conducted in the previous three decades on testing the ability of using the polymeric surfactants solutions in EOR applications.

Keywords: Polymeric surfactants; Chemical enhanced oil recovery; Surface activity; Rheological properties

Introduction

During enhanced oil recovery stage, chemical solutions prepared in water are injected into oil reservoirs to displace the trapped oil. The most commonly used chemical enhanced oil recovery (CEOR) processes are: [a] polymer flooding; in which a water soluble polymer is used to increase the water viscosity, [b] surfactant-polymer (SP) flooding; is a process in which a combination of polymer and surfactant are injected, the surfactant used to decrease the oil-water interfacial tension (IFT), and [c] alkali-surfactant-polymer flooding (ASP); in which a relatively cheap inorganic base which function same as the costly surfactant is injected along with the previous combination to decrease the high cost of the process [1-5], the alkali also decreased the loss of surfactant due to its adsorption onto both sandstone and carbonate particles [6,5].

So the main mechanism for enhancing the oil recovery are the increase in water viscosity and the increase in IFT between water and oil phases [7,6]. In some CEOR methods (e.g.: SP or ASP flooding), the main objective is to combine the two mentioned mechanisms (i.e.: increase in the water viscosity and decrease in the IFT), and hence, increasing the efficiency of the process. In such processes, the interaction of the fluids (i.e.: polymer and

surfactant) with each other, adsorption of surfactant onto the rock or its solubilization in oil, and chemical degradation due to high reservoir temperature or high salinity limits the field application for such chemicals [8-11]. For these reasons, the so called polymeric surfactant (which combines the positive effects of surfactants and polymers in a single component) becomes an attractive CEOR alternative. In this paper, the different requirements of polymeric surfactant as a CEOR fluid will be discussed, and the research work done in the last three decades will be summarized.

Requirements of Polymeric Surfactants for CEOR

Polymeric surfactants are macromolecules with structure combines both hydrophobic and hydrophilic parts. This macromolecular nature enables the polymeric surfactants (compared to traditional surfactants) to have a much larger variety of both simple and complex structures. The chemical structure of polymeric surfactants confers them very interesting interfacial and rheological properties. Some polymeric surfactants respond to the change in external parameters (e.g.: solution pH, temperature, and electrolytes concentration) by

changing their hydrophobicity. For all these properties and characteristics, polymeric surfactants attract a lot of interest in different important applications including but not limited to: agriculture, water purification, pharmacology, electronic, cosmetics, and enhanced oil recovery.

The rheological properties of the CEOR fluids are very important since they control the mobility ratio between the displacing and displaced fluids by tuning the viscosity of the water phase, which is the main mechanism for polymers as explained in the introduction. While in surfactant flooding, formation of a stable emulsions between oil and the displacing solution in flow conditions, and hence, the balance between the Laplace pressure and the viscous force acting on a drop in a laminar flow field is the most important objective [12,13]. The capillary number (N_c), which is a dimensionless ratio between the viscous and capillary forces, is a very important factor for CEOR processes efficiency evaluation since it gives an indication about the residual oil in place [1,14]. According to Darcy's equation, the N_c could be represented as in e.q. 1.

$$N_c = (v \cdot \eta_c) / \gamma \quad \text{Eq. 1}$$

Where η_c denotes the continuous phase viscosity, v and γ represents the Darcy velocity and IFT, respectively. The typical N_c for water flooding is in the range of (10^{-8} to 10^{-7}), which is suggested to increase by more than 2 to 3 times in order to be able to produced substantial amount of the trapped oil, so the suggested chemical most have a considerably low IFT (IFT of less than 10^{-1} mN/m) [15-17].

In addition to the ability of the polymeric surfactants to simultaneously decrease the oil-water system IFT and to increase the displacing solution viscosity, which all contribute positively on the N_c , segregation of the injected fluids at harsh reservoir conditions could be avoiding using the polymeric surfactant which is a single component and not a mixture [14,18].

Based on the above discussion, the choice of the appropriate system is not trivial. For example, the slow equilibration of polymeric surfactant micelles as explained by Theodoly et al. [19] could lead to very low surface activity, and hence, decrease the possibility of migration of the macromolecules to the interface [19, 20-24].

Polymeric Surfactants for CEOR

Several amphiphilic polymers have been suggested as CEOR fluids by e.g: [25- 32] Theodoly et al. [19], but many of these publications did not confirmed the effectiveness of the suggested fluid for the claimed application. In the following section, some of the publications in which the suggested fluid is evaluated in them of identify few papers in which viscosity, surface properties and salt effects will be discussed.

Yahya & Hamad [33] considered optimization of both the rheological properties and interfacial behavior for water soluble copolymers solutions consist of sodium maleate/1-dodecene

and sodium maleate/1-hexadecene. They reported that the copolymers (which are characterized by hydrophobic moieties) exhibit a moderate surface and interfacial activities, due to their unique structure.

Oligomeric polyesters performance as a CEOR fluid has been evaluated through the measurements of surface and interfacial tension. Oligomeric polyesters exhibited a considerably low IFT in the range of 10^{-3} to 10^{-4} mN/m for alkane carbon number (6-9), which makes them a good candidate for enhance oil recovery [34].

Abu-Sharkh et al. [35] prepared modified water-soluble block copolymers by aqueous micellar copolymerization of acrylamide and relatively small quantity of N-phenethylacrylamide (2-3 mole %). The block copolymers enhanced the thinking properties due the intermolecular hydrophobic associations, as indicated by the increase in the solution viscosity with the increase in the concentration of the polymer. The increase of the concentration of the polymer also decreased the interfacial tensions of water/n-decane system as a result of the strong adsorption of the copolymer at the interface.

The interfacial activity for polymeric surfactants seems to be highly dependent on the nature and structure of the hydrophobic groups. copolymer of acrylamide, or AM Shaikh et al. [26], benzyl AM Yahaya et al. [35], and phenyl AM Abu-Sharkh et al. [36] exhibit different interfacial and surface behaviors. It was clear that the interfacial and surface activates are lower for higher conformational freedom of the monomers. One of the most important outcome of the studies conducted by Shaikh et al. [26], Abu-Sharkh et al. [37], Yahaya et al. [35], Abu-Sharkh et al. [36] is that the viscosity and/or the interfacial activity did not affect by addition of NaCl, and in some cases the presence of NaCl enchases the surface activity which is so desired for CEOR processes.

Zhao et al. [38] reported that introducing of only 1% of hydrophobic acrylates in a polyacrylamide significantly increased the water/oil emulsion stability, and hence, work as polymeric surfactant. Evaluation of the polymeric surfactants performance as a CEOR solutions through core food experiments is not common in the literature. Maia et al. [39] compared the performance of polyacrylamide (HPAM) and a hydrophobic ally modified polyacrylamide (HMPAM) in enhancing the oil recovery from Botucatu sandstone. The authors reported that, the HMPAM system has better salt and thermal degradation resistance, it was also able to increase the solution viscosity efficiently. These properties make the HMPAM system a good candidate for high permeability systems. Lai et al. [40] also confirmed the ability of the HMPAM to increase oil recovery greater than 14% under 5000mg/L NaCl at 65 °C.

In a very recent study Co et al. [41] compared the performance of the traditional HPAM, with a modified HPAM with (1 to 5%) surfactant like monomer (i.e.: functionalized

polymeric surfactant (FPS)). Core flood tests results showed that the FPS system was able to increase the ultimate oil recovery by 5% greater than that recovered by traditional HPAM even when FPS even has mobility ratio less than the traditional HPAM. This is attributed to the fact that the surfactant-like monomers enhance the microscopic displacement efficiency by creating an oil-water emulsion by pulling the water-soluble polymer toward the interface of oil and water phases. In this study, the authors also explained the positive effect of the low IFT (10-1mN/m) on the oil recovery.

Conclusion

Theoretically, the polymeric surfactants with the surface and interfacial activities as well as its viscos effect could be an effective alternative for the currently available CEOR techniques. The fact that all the desired characteristics for the CEOR fluids are available for a single component, compared the current practice of mixing different chemical, and hence, separation and loss of part of the components, could shift the researchers to

dig more into characterizing and optimizing the performance of polymeric surfactants for CEOR processes.

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