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Wormlike Micellar Solution: Alternate of Polymeric Mobility Control Agent for Chemical EOR

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Abstract: In Alkaline-Surfactant-Polymer (ASP) flooding, mobility control is one of the important factors for improving tertiary oil recovery. It is achieved by using polymeric mobility control agent such as partial hydrolyzed polyacrylamide (HPAM). However, polymer is highly degradable when subjected to high temperature; high salinity and high shear rates. These limitations of polymer adversely restrict the extension of ASP in such reservoirs conditions. In order to overcome these limitations, Wormlike Micellar (WLM) solution can be studied as a potential alternative. This study presents a review on application of WLM solution as mobility control agent for chemical EOR. It discusses the current limitations with existing polymers, comparison between WLM and polymers.

Key words: Polymeric mobility, EOR, worm like, polymer

INTRODUCTION

The high oil prices and technology advancement during past years has created new opportunity on chemical EOR methods. In which different combinations of chemicals (alkaline, surfactant and polymer) have been used (Hirasaki *et al.*, 2008). At present, Alkaline-Surfactant-Polymer (ASP) flooding is known as the most effective technique of it. Whereby, alkali reacts with crude oil and forms natural surfactant inside the reservoir. It is also used as inhibitor to reduce the adsorption of surfactant on rock formation. The surfactant mainly reduces the interfacial tension between crude oil and displacing fluid. Polymer in turn, is able to augment the viscosity of displacing fluid for mobility control-thus leading towards ultimate efficiency of oil recovery (Watkins, 2009; Alvarado and Manrique, 2010).

China, in this case, has conducted the major part of study on ASP flooding, after a number of experiments; China has recovered 18-23% of additional oil beyond water flooding (Wang *et al.*, 1999; Li *et al.*, 2003; Berger and Lee, 2006). The researchers were satisfied since the conditions of reservoir (Daqing oil field; low temperature and low salinity) were favorable to ASP flooding. In fact, reservoirs chosen as the candidates for this method are frequently differ at high salinity and high temperature. In these variations, ASP chemicals were found inefficient for displacement of oil (Flaaten, 2007).

Responding to that, advance research was conducted. In which, sulfonate group of anionic surfactants and metabolate in alkaline were introduced to show the greater stability of these chemicals. Whereas, polymers are still seems to be highly degradable.

Therefore, the use of polymer is only effective in a polymer friendly reservoir environment and it lacks a wider application in harsh reservoir conditions, where some are looking at the challenges for ramping the past and some in future opportunity for doing so now. Responding this, a source for a robust alternative, technically capable of being applied into these challenging characteristics is needed. Thus, the study is presenting, a surfactant based alternative viscoelastic WLM solutions that can suppress these limitations in polymer as mobility control agent.

MOBILITY CONTROL AGENT IN CHEMICAL EOR

The oil left behind water flooding is trapped into a porous media or because water is bypassed some ways due to reservoir heterogeneity. To remobilize that oil, mobility ratio is therefore a focal concept in each method of chemical EOR (Sorbie, 1991). Mathematically, it is a ratio between mobility of displaced fluid and displacing fluid. The mobility ratio will be favorable if it is less than or equals to one. In general, mobility is expressed as the permeability of fluid divide by its flowing viscosity. In

that case, to modify mobility ratio, water viscosity is only a parameter that can be altered. Since, it is impractical to change the viscosity or permeability of crude oil inside the reservoir (Selle, 2005). For this, the typical water-soluble polymers are used to increase the viscosity of water as described below.

EOR polymers: Xanthan gum (biopolymer) and partially hydrolyzed polyacrylamides (HPAM) are the most frequently engaged polymers in chemical EOR. Xanthan polymer is formed from the polymerization of saccharides and a biopolymer. Meanwhile, HPAMs are the co-polymers of acrylic acid and acrylamides. Xanthan polymers are rigid in molecules and quite resistant to mechanical degradation. In HPAM, permanent shear losses of viscosity takes place near wellbore but not for xanthan (Luo *et al.*, 2006). However, the bacterial attack inside the reservoir comes to be a serious constraint for biopolymers. Hence, the application of the biocides and surface handling is necessary that is by using them along with the injected solutions to avoid the biological degradation of these polymers. This makes the process quite expensive and economically unfeasible. Considering this, HPAMs are the most widely used polymers for mobility control. These polymers undergo partial hydrolysis, creating the negatively charged carbon chain of scattering carboxyl functional groups (--COO--). These charges then yields the chain extension which leads to increase the viscosity of solution (Sorbie, 1991). China has conducted major part of study on HPAM, where 20% of average additional oil recovery is reported beyond water flooding.

LIMITATIONS OF POLYMERIC MOBILITY CONTROL AGENT

The reservoirs frequently differ in characteristics. For instance, salinity of formation brine can be higher than 200,000 mg L⁻¹, temperature from 70-120°C and shear rates more than 1000 1 sec⁻¹ (Puerto *et al.*, 2010). In these variations, HPAM polymers attribute to severe loss of viscosity which makes an operation failure. For example the polymers were employed in German fields at temperature (20-70°C) and salinity (20-20000 ppm). It is reported as the polymer could not sustain appropriate viscosity of injectants in situ reservoir. Thus the project partially became successful. Further this discussion elaborated in following contents.

Degradation due to shear rates: The main source of shearing which can take place are various stages of injection process from surface to sub-surface. For

example, the use of shearing device for polymer preparation, injection with pump, flow from chokes, flow from down hole valves or perforations and sand face has yielded the maximum difference of pressure. In HPAM polymer's, the viscosity loss due the mechanic shearing from preparation facilities until wellhead can be 77%. In subsequent, it is severely considered near well bore (Maerker, 1975). Then, degradation by porous media inside reservoir is mainly due to longer distances through different pore geometry at different permeability and so on. The normal range of shear rate in porous media is under 20 sec⁻¹ (Lee *et al.*, 2009).

Degradation due to salinity: The salts, when they are dissolved in the solution of polymer, a number of positive charged ions are produced. Thereby salt shields the negative charges and condense the chain that sharply reduce the viscosity of solution (Sorbie, 1991; Sheng, 2010). Recently, a comprehensive rheological property database has been developed on variety of polymers. In which, HPAM 3330s solution polymer was reported with remarkable loss of viscosity, when tested with NaCl and CaCl₂ (Lee *et al.*, 2009). Thus, the SNF FLOERGER commercial manufacturing company of HPAM reveals that HPAM polymers are not capable of withstanding reservoir conditions above 35000 ppm NaCl including divalent salts of 1000 ppm (SNF FLOERGER, 2013). Apart from these limitations, as mentioned earlier that HPAM polymer solution still has to compromise the considerable loss of viscosity.

Degradation due to temperature: HPAM polymer undergoes a destructive hydrolysis under high temperatures. The hydrolysis is associated to the percentage of acrylate groups formed from acrylamides. Thus, acrylate group increases the negative charges on carbon chain. At initial stage, a hydrolytic reaction increases the viscosity of aqueous polymer solution. Then insufficient acrylamides makes HPAM chemically unstable (Sheng, 2010). For HPAM, the typical values of hydrolysis lies in range of 30-35% (Muller, 1981). Another significant cause of hydrolysis is the presence of divalent salts. If calcium is maintained below 200 ppm, then HPAM is feasible at 100°C, otherwise precipitates if the fraction of acrylate groups becomes higher than the range (Seright *et al.*, 2010). Therefore, HPAM is limited at temperatures of above 60°C under the anaerobic conditions of water with calcium less than 20 ppm (Sorbie, 1991; SNF FLOERGER, 2013). Overall, it is concluded that HPAM polymer limits several potential applications of chemical EOR in warmer reservoirs above 60°C with salinity higher than 35000 ppm of NaCl including divalent ions of 1000 ppm.

WORMLIKE MICELLES AS AN ALTERNATIVE TO POLYMER

Wormlike micelles are highly viscoelastic self-assemble aggregates resulted from surfactant molecules in an aqueous solution. When these aggregates grow and entangle each other, the aqueous solution becomes viscoelastic. Due to these remarkable rheological properties much like polymers, they have been studied for more than 20 years in variety of applications. Therefore, various compositions of WLM are reported upon the addition of salt, counter-ion or co-surfactant in an aqueous surfactant. But here, it is necessary to emphasize the chemistry and rheology in general. By this way, WLM can be greatly understood and compared with polymer, to become alternative mobility control agent in chemical EOR.

Chemistry of WLM solutions: The surfactant molecule consists of head and tail group. The head, in this case, refers to hydrophilic and ionic-ally charged while tail refers to hydrophobic and neutral in charge. Figure 1 presents the schematic of a cationic surfactant molecule. The zigzag is showing hydrocarbon tail which is covalently bonded with sphere which is positively charged head group. The head of that molecule can vary from positive to negative or neutral in charge, depending upon the type of surfactant i.e., ionic or nonionic.

The fundamentals of surfactant suggest that these molecules will tend to saturate the interface between two liquids in aqueous solution. At Critical Micelles Concentration (CMC) of surfactant, the molecules will arrange themselves in depth of aqueous part. Such as; the tails become close together and heads facilitate their contact with water (Esumi and Ueno, 2003; Zana and Kaler, 2007). The process of such aggregation is called micellization as shown in Fig. 2.

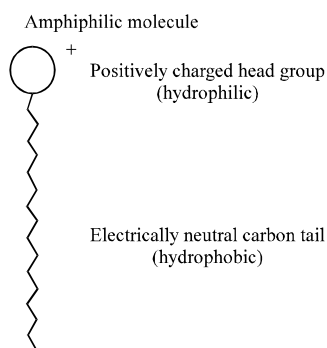


Fig. 1: Amphiphilic molecule of cationic surfactant (Handzy, 2005)

Here, basic morphology is sphere. The morphology of these aggregates can differ on addition of counter-ions i.e., organic or inorganic salt or co-surfactants. The counter-ions shield the electrostatic repulsive forces between head-head of surfactant molecules. Thus, the area of head group will be affected, to incorporate different morphology of micelles (Yang, 2002). Here, WLM are discussed which are owing to cylindrical morphology. It is often induced when spherical micelles merge themselves by energy of end-cap. Further, one dimensional growth of these cylindrical micelles achieve WLM structures as shown in Fig. 3 (Walker, 2001).

Rheology of WLM solutions: The WLM are viscoelastic thread like surfactant aggregates. At more elevated concentrations, these threads partly coincide and establish an entanglement which is resulting in viscoelastic solution greatly resembling with the entangled polymers (Fig. 4). The phenomenon of viscoelasticity in WLM solutions can be described when the shear forces are applied on it. They involve both viscous flow and elastic deformation. The definition of viscous flow can be irreversible deformation and can be maintained while applying shear stress. The molecule under the forces displaced or deformed will not attend the original positions. However, upon removing that stress, the surfactant molecules will come to original position of micellar equilibrium.

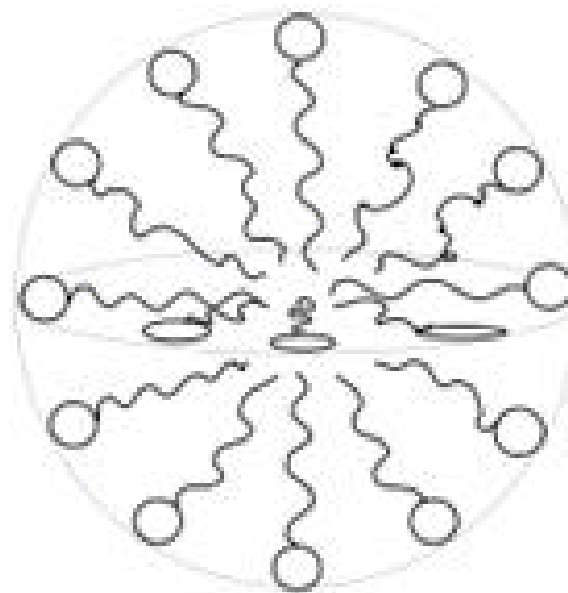


Fig. 2: Spherical micellar transition into wormlike micellar (Handzy, 2005)

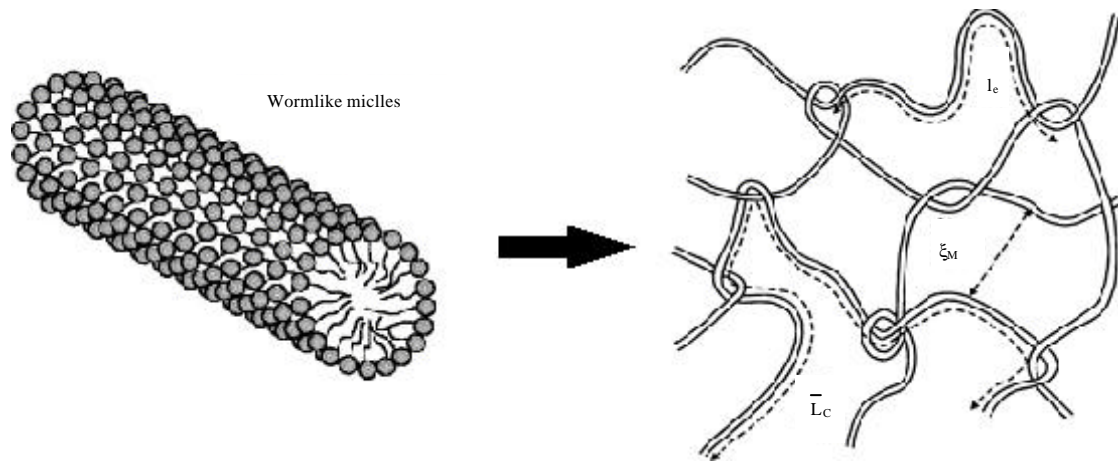


Fig. 3: Entanglement of WLM micelles (Schubert, 2003)

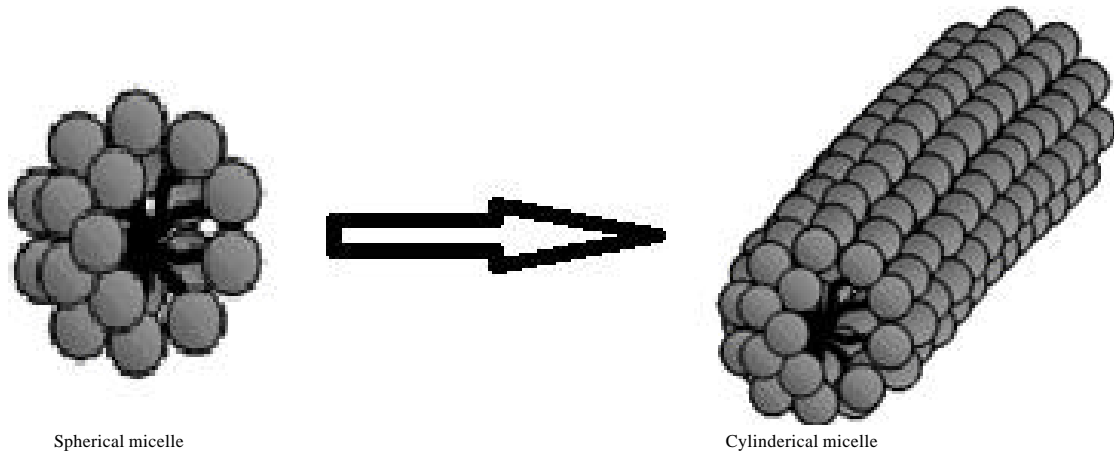


Fig. 4: Transition of spherical micelles into cylindrical micelles

Table 1: Examples of WLM compositions

Surfactant	Salt/Co-surfactant	References
Hexadecyltrimethylammonium bromide	Sodium nitrate, sodium chloride or sodium bromide	Kuperkar <i>et al.</i> (2008)
Sodium oleate	Octadecyldecyltrimethylammonium bromide	Ziserman <i>et al.</i> (2009)
Sodium dodecyl sulfate or sodium dodecyl trioxyethylene sulfate	Sodium oleate	Ishizuka <i>et al.</i> (2009)
Polyoxyethylene dodecyl ether	Polyoxyethylene cholesteryl ether	Acharya and Kunieda (2003)
Sodium dodecyl sulfate	Tetradecyl dimethylammonium propane sulphonates+sodium chloride	Lopez-Diaz and Castillo (2010)

The WLM consists of a number of physical attractions or repulsions between molecules which can continuously break and reform regarding time as shown in Fig. 5. This continuing dynamics of reversible breakup and reformation process is dependent on shear rates, temperature and concentration of surfactant or salt in composition. Therefore, wormlike micellar solution is considered to be an equilibrium polymer. Thus, this phenomenal network imparts viscoelastic WLM solutions (Rehage and Hoffmann, 1991; Cates and Candau, 1990).

Examples of WLM solutions: There are variety of compositional systems that are composed of different surfactant types such as anionic, cationic, non-ionic and in mixed formulation i.e., ionic-ionic (a-b), ionic-nonionic (d), ionic-zwitterionic (e) and nonionic-zwitterionic systems. Based on types few relevant examples are given in Table 1.

Industrial applications: The remarkable viscoelastic properties of WLM solutions have been largely exploited

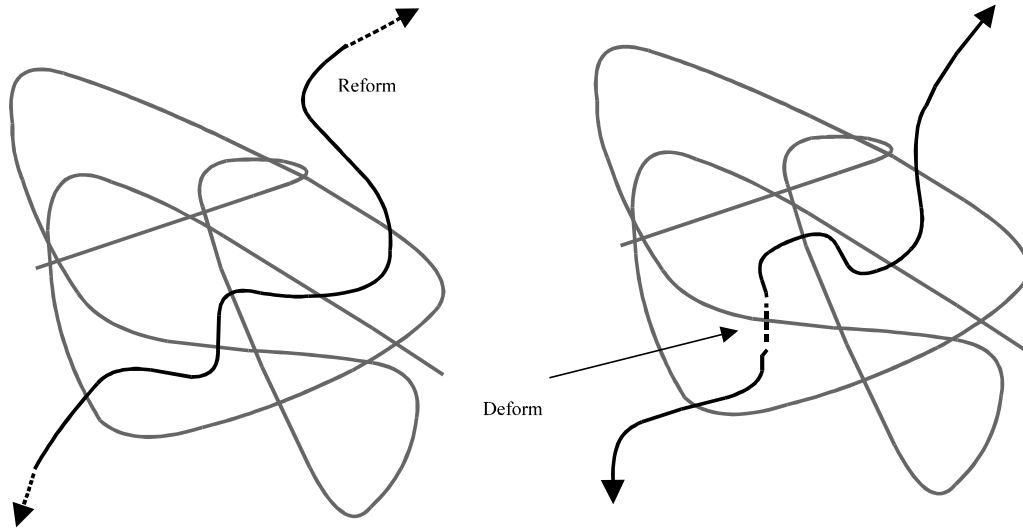


Fig. 5: Reformation and deformation phenomena of WLM (Miller, 2007)

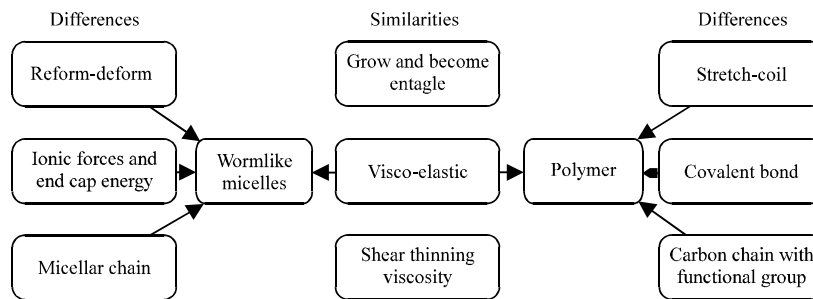


Fig. 6: Comparison between WLM and polymer

in the oil industry. In oil fields, traditional polymers are used like guar or hydroxyl ethylene cellulose as fluid thickening. The polymer-based fluid leaves residues and clog pores in the proppant pack of wells. It has been resolved faster when WLM were used in well completion, well stimulation, gravel packing and in coiled tubing cleanout process. WLM solutions are also used as the reversible viscoelastic thickening fluids for oil-well drilling process. Apart from oil field, the reversible WLM fluids have been expanded to heating and cooling plant installations to replace highly shear-degradable polymers (Zana and Kaler, 2007). These remarkable viscoelastic properties of WLM solutions are largely exploited in home-care products, hard-surface cleaners or drain-openers as well as in personal care products such as shampoos, body soaps and so on.

COMPARISON BETWEEN WLM AND POLYMER

Similarities: This rheological behavior of WLM solutions shows strong similarity with polymer solutions.

Thus, the ability of WLM solutions that can modify their morphology in flowing conditions are subjected to great interest in various applications of non-linear flow conditions (Rehage and Hoffmann, 1991). Thus the chains can be reformed and deformed to impart viscoelastic properties in solution. To illustrate this, high shear rates will disturb the equilibrium of WLM structure that yields the typical shear thinning of viscous solution. In WLM solutions, an increase in concentration of salt or surfactant often observes the increase in maximum viscosity (Zana and Kaler, 2007). It is typically concerned to the growth and entanglement of cylindrical micelles. In this case, if the branching of micelles increases, the viscosity will be reduced (Schubert, 2003; Ishizuka *et al.*, 2009). In short, Fig. 6 shows the schematic of general comparing between WLM and polymer.

Differences: It is deemed essential to know that micelles do not refer to molecules. Different from polymers, no chemical bond will be found between neighboring amphiphiles and organic salt. The structure of WLM is

different from polymer, such as micellar chain comprising electrostatic forces which can reform and deform rather than permanent breakdown or coiling carbon chain under changing shear rates or temperature fluctuations (Walker, 2001; Yang, 2002).

This, furthermore, is also able to break into smaller micelles or even join with other micelles in order to form a longer micelle. This is called as ionic forces which are persistently happened in the fluid and even in equilibrium conditions (Cates and Candau, 1990). Thereby, the micellar chain length is unknown unlike polymeric chain of carbons. In which, individual molecules are free and able to leave or join a new micellar pool of free molecules. Comparatively speaking, the second advantage of WLM solutions is mainly composition. It is formed in surfactant upon mixing salts or co-surfactants i.e., salt being an ingredient, increases the viscosity of solution (Berret, 2006). However, in HPAM polymer based solution, salt causes remarkable loss of viscosity (Sheng, 2010).

SUMMARY

The research industry is seeking a number of profitable and technical strategies to resolve the limitations of polymer at high temperature, high salinity and high shear rate reservoirs. This study, in turn, has succeeded in ascertaining WLM solution an alternative to polymer with highly stable viscoelastic properties in such reservoir conditions. Unlike polymeric structure, salt is main ingredient in WLM composition. However, in HPAM polymer based solution, salt is the main cause of deleterious viscosity. The WLM chain comprises of electrostatic forces which can reform and deform rather than permanent breakdown or coiling carbon chain under changing shear rates or temperature fluctuations. This is because WLM solutions can be an alternative source of becoming viable mobility control agent. It can be capable of suppressing the limitations of polymer at reservoir conditions of extended salinity, temperature and shear rates.

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