Hydrophobically Associating Polymers for Oilfield Applications

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This paper is to be presented at the Petroleum Society’s 8th Canadian International Petroleum Conference (58th Annual Technical Meeting), Calgary, Alberta, Canada, June 12 – 14, 2007. Discussion of this paper is invited and may be presented at the meeting if filed in writing with the technical program chairman prior to the conclusion of the meeting. This paper and any discussion filed will be considered for publication in Petroleum Society journals. Publication rights are reserved. This is a pre-print and subject to correction.

Abstract

Recent developments in water-soluble hydrophobically associating polymers are examined with particular emphasis on their use for oilfield applications. These polymers have potential for use in EOR, acidizing, drilling fluids, completion fluids and profile modification. They have also been reported to selectively reduce water permeability in sandstones, and have been used as drag-reducing agents.

Associating polymers are very similar to conventional water-soluble polymers used in the oil industry, except that they have a small number of hydrophobic groups incorporated into the polymer backbone. At levels of incorporation of less than 1 mol%, these hydrophobic groups can significantly change polymer performance.

Factors that affect the rheology and adsorption of associating polymers are discussed. These factors include the hydrophobe type, content and distribution in the polymer, the polymer molecular weight, and the brine composition.

This paper provides an evaluation of the current state of this technology.

Introduction

Water-soluble polymers are used in the oilfield in polymer flooding\(^1\), in drilling and completion fluids\(^2\), in acid stimulation treatments\(^3\), as drag reducing agents\(^4\) and in profile modification\(^5\).

These water-soluble polymers are usually acrylamide copolymers, partially hydrolyzed polyacrylamide (HPAM), or biopolymers such as xanthan or guar gum\(^6\).

Water-soluble hydrophobically associating polymers (AP) are water-soluble polymers that contain a small number (less than one mole percent) of hydrophobic groups attached directly to the polymer backbone (Figure 1). In aqueous solutions, these hydrophobic groups can associate to minimize their exposure to the solvent, similar to the formation of micelles by a surfactant above its critical micelle concentration (CMC) (Figure 2). Polymer association can result in solution properties not available with conventional water-soluble polymers.

The potential for using hydrophobically associating polymers in the oilfield was extensively reviewed in 1998\(^7\). In that work, Taylor and Nasr-El-Din examined the synthesis, characterization, stability and rheology of acrylamide-based...
associating polymers for improved oil recovery. A number of significant developments have occurred since that time. More associating polymers have become commercially available, and new applications for their use in the oilfield have been reported.

Discussion

Synthesis and Characterization

Taylor and Nasr-El-Din reviewed synthesis and characterization(8). Yabin et al.(9) synthesized hydrophobically associating acrylamide polymers for oilfield applications and studied their solution properties as a function of electrolyte concentration, temperature and shear rate. Feng et al.(10,11) have reported in detail on the synthesis, characterization and properties of hydrophobically associating polyacrylamides. Eoff et al.(12,13) prepared associating polymers based on polydimethylaminoethyl methacrylate. This polymer was modified to introduce n-alkyl groups containing 10, 16 or 18 carbons and was used extensively in the field.

Adsorption Behaviour

The adsorption behaviour of associating polymers is unique. Water-soluble polymers like polyacrylamide commonly reach a plateau adsorption level on surfaces(14). In contrast, adsorption of hydrophobically associating polymers increases with increasing concentration and a plateau adsorption level is not reached(13,14). This behaviour has been attributed to associative adsorption of polymer chains onto previously adsorbed layers of polymers(14). Figure 3 shows how this adsorption may occur. With polyacrylamide, adsorption occurs until the surface is covered (a). With the associating polyacrylamide (b), hydrophobic interaction leads to additional adsorption and multilayer formation(14). This layer is more tightly bound to the surface than with non-associating polyacrylamides(14).

Rheology

The rheology of associating polymers is affected by molecular weight, degree of hydrolysis, hydrophobe type, degree of incorporation of hydrophobe, and distribution of hydrophobe(8,15-18). The critical concentration, c*, can be used to divide the rheological behaviour of associating polymers into a dilute region and a semi-dilute region(19). At concentrations below c*, intramolecular hydrophobic associations within the polymer dominate the behaviour of the polymer. Above c*, intermolecular associations between polymers become much more important to the polymer rheology. The value of c* is approximately equal to the reciprocal of the intrinsic viscosity(20).

As the hydrophobe content is increased, intrinsic viscosity will generally decrease due to an increase in intramolecular association. At the same time, the Huggins constant will increase(21). Increasing intramolecular association leads to an increase in bulk viscosity above c*. Below c*, a decrease in viscosity results as intramolecular association increases. Figure 4 shows the effect of hydrophobe concentration on the reduced viscosity of acrylamide/dodecyl methacrylate copolymers.

Increasing the alkyl chain length of the hydrophobic group greatly increases intramolecular association above c*. Introducing a phenyl group in the hydrophobe monomer significantly enhances the viscosity, especially at high hydrophobe concentrations(22).

Increasing polymer molecular weight generally increases the solution viscosity(8).

Increasing the degree of hydrolysis of the polymer generally increases the intrinsic viscosity and also decreases the Huggins constant due to an improvement in polymer-solvent interaction(22).

McCormick et al.(23) showed that a copolymer of acrylamide and N-decylacrylamide exhibited an increase in reduced viscosity with increasing temperature. Varadaraj showed that associating polymer/surfactant mixtures could exhibit constant or increasing viscosity as temperature was increased from 20 to 60°C in brine solutions(24). Thermo-reversible associating polymer gels have been reported by Varghese et al.(25) that reversibly swell as temperature is changed.

These results show that changes in temperature can have a large effect on the rheology of associating polymers by changing their aggregation behaviour.

Solubility of associating polymers is an important consideration in oilfield applications, since a lack of solubility can lead to formation damage. The solubility of an associating polymer decreases by increasing the hydrophobe content, by increasing the hydrophobe chain length, or by increasing the molecular weight. This decrease in solubility can be counteracted to some extent by increasing the ionic character of the associating polymer. This can be done by hydrolyzing the amide groups of a polyacrylamide, or by copolymerization with sulfonate-containing monomers(26).

Feng et al.(20) reported on the effects of NaCl on the rheology of water-soluble hydrophobically modified polyacrylamides. This effect is extremely important to the behaviour of these polymers in oilfield fluids, because of variations of salinity found in oilfield brines. Apparent viscosity and reduced viscosity were measured as a function of NaCl content. Hydrophobically associating polyacrylamide and hydrolyzed polyacrylamide were prepared by post-modification and contained 0.8 mol% of a C-8 alkyl group. Increasing salinity resulted in a decrease in reduced viscosity for both modified polymers in the dilute region. In the semi-dilute region above c*, the reduced viscosity increased as the salinity increased for hydrophobically modified polyacrylamide. The hydrophobically modified hydrolyzed polyacrylamide showed a minimum in reduced viscosity as the salinity was increased. Increasing the aging time significantly increased the viscosity of the polymer solutions.

Yabin et al.(9) examined the rheology of hydrophobically associating polymers used for EOR as a function of electrolyte concentration, temperature and shear rate. They prepared acrylamide copolymers with a range of hydrophobe chain lengths, hydrophobe concentrations, and degree of hydrolysis. Results were in agreement with previous trends.

Varying surfactant concentration can have a significant effect on the rheology of associating polymers. Iliopoloulos et al.(20) and Magny et al.(27) examined the interactions between sodium dodecyl sulphate and hydrophobically modified poly(sodium acrylate) containing either 1 or 3 mole percent of octadecyl or dodecyl associating groups. A maximum in solution viscosity occurred very near the critical micelle concentration of the surfactant. Viscosity was increased by up to 5 orders of magnitude. At the critical micelle concentration, the micelles can effectively cross-link the associating polymer if more than one hydrophobic group from different polymer chains is incorporated into a micelle. Above the CMC, the number of micelles per polymer-bound hydrophobe increases, and the micelles can no longer effectively cross-link the polymer. As a result, viscosity decreases. This shows that the rheology of associating polymers can be very sensitive to changes in surfactant concentration.
Young et al.\textsuperscript{(28)} found that sodium dodecyl sulphate (SDS) increased the viscosity of hydrophobically modified hydroxybutyl guar gum (HMHBG) up to a factor of 10, depending on the SDS concentration (Figure 5). Maximum viscosity was observed with 0.008 mol/dm\textsuperscript{3} of SDS. At higher concentrations, viscosity decreased to values nearly identical to unmodified hydroxybutyl guar gum.

**Conformance Control**

Eoff et al.\textsuperscript{(12)} developed and applied hydrophobically modified polymers for the treatment of water production problems. They showed that hydrophobically modified acrylamide copolymers can selectively reduce water production relative to oil in core flood testing. This type of polymer system is known as a relative permeability modifier. Results from 25 case histories of application of this method in sandstone reservoirs were recently reported by Dalrymple et al.\textsuperscript{(29)} The system was reported to have an 88\% success rate at reducing water production.

Zhao et al.\textsuperscript{(30)} used associating polymers to treat water production problems in the Zhongyuan oilfield in China. However, no details of the polymer type or structure were provided. Associating polymers were injected with a cross-linker and pH modifier into high salinity formations as a shear-thinning gel.

**Acid Diversion**

Associative polymers have been used to achieve fluid diversion during an acid stimulation treatment\textsuperscript{(33)}. Polymers based on dimethylaminoethyl methacrylate were investigated, with hydrophobic groups of C10, C16 or C18. This associating polymer produces a very low viscosity in the acidizing fluid, but reacts with the formation surface to reduce aqueous phase permeability. It is claimed that permanent water permeability reduction occurs in sandstone formations. Coreflood testing in sandstone and carbonate cores showed that the C16 modified polymer demonstrated the highest level of permeability reduction.

Use of associating polymers for simultaneous acid diversion and water control in carbonate reservoirs was reported by Al-Taq et al.\textsuperscript{(31)} Experimental studies included coreflood experiments on reservoir cores at downhole conditions. Extensive lab testing showed that the associative polymers had no significant effect on the relative permeability to oil, but relative permeability to water was significantly reduced. The associative polymer was used during a matrix acid treatment of a damaged well and included stages of associative polymer and 20 wt\% HCl with additives. Post-treatment production data showed that the oil rate increased by 11-fold while the water rate decreased by 3-fold. The overall result was a reduction in water-cut from 75 to 14 vol\%. PLT testing confirmed that the associative polymer had diverted acid to the oil zone.

**Polymer Flooding**

Yabin et al.\textsuperscript{(9)} conducted coreflood experiments with associating polymers. Experiments carried out at high salinities showed a significant improvement over conventional hydrolyzed polyacrylamide corefloods. The associating polymer was a partially hydrolyzed copolymer of acrylamide and a cationic hydrophobic monomer. It had improved salinity and temperature tolerance compared to HPAM.

Varadaraj et al.\textsuperscript{(24)} patented a composition containing a hydrophobically associating polymer and a surfactant for use in polymer flooding. By varying polymer and surfactant concentration in a brine, viscosity could be varied from 20 to 2,500 mPa.s, and that viscosity of their compositions remained relatively constant from 20 to 60°C.

Adsorption is a concern with polymer flooding and has limited this application.

**Drilling and Completion Fluids**

Young et al.\textsuperscript{(28)} proposed a hydrophobically modified guar gum for use in completion fluids. Audibert-Hayet et al.\textsuperscript{(32)} reported on hydrophobically modified natural polymers for use as non-damaging drilling fluids.

Young et al.\textsuperscript{(28)} examined a hydrophobically modified hydroxybutyl guar gum (HMHBG) with potential for completion applications. The modified polymer contained 1 to 2 w/w\% of randomly distributed C-16 alkyl groups and had an average molecular weight of 2.2 millions. They compared the rheology of HMHBG with guar, hydroxypropyl guar (HPG) and hydroxybutyl guar (HBG). The hydrophobically modified polymer showed much higher values of low-shear viscosity than the corresponding non-associating hydroxybutyl guar.

Extensional viscosity of the HMHBG was approximately double the value of the unmodified HBG.

Audibert-Hayet et al.\textsuperscript{(32)} studied hydrophobically modified polymers for use in non-damaging fluids. The modified guar gum dramatically improved the control of fluid loss. A thin, impermeable filter cake formed on the rock surface during drilling to reduce fluid loss. This filter cake was easily removed at low pressure differentials during flowback of the well.

The hydrophobically modified polymer described by Audibert-Hayet et al.\textsuperscript{(32)} is designed to be used in conjunction with a biopolymer and calcium carbonate as a fluid loss additive. The adsorption properties of the modified polymer are more important than its rheological properties. The authors speculate that the hydrophobic interactions include not only the hydrophobic groups of the polymer, but also hydrophobic particles present in the drilling fluid. The sum of these interactions contributes to the fluid loss control of the system.

Hydrophobically modified hydroxyalkyl guar gums have shown several useful properties. These include an increase in viscosity and suspending properties\textsuperscript{(28)}, good salt tolerance, and an improvement in fluid loss control\textsuperscript{(33)}.

**Drag Reducing Agents**

The potential for hydrophobically associating polymers as drag reducing agents was originally proposed by Mumick and McCormick\textsuperscript{(33)}. However, no significant additional work has been reported in this area.

**Conclusions**

Recent developments in the use of water-soluble hydrophobically associating polymers in the oilfield were examined.

In oilfield applications, the adsorption behaviour of associating polymers can be more important than the rheology. This is particularly true in non-damaging completion fluids and in profile modification. A better understanding of adsorption behaviour has been a major driving force in current application of these polymers.

New applications in acid diversion and conformance control have been developed and applied successfully in the field.

The strong interaction between surfactant and associating polymer is of interest in applications requiring high viscosity.

Future promising applications include gels for conformance control and continued use for modification of water relative permeability.
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FIGURE 1: Associating Acrylamide Copolymer

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} = \text{O} & \quad \text{C} = \text{O} \\
\text{NH}_2 & \quad \text{OH} \\
\end{align*}
\]

\[R^1 = \text{hydrophobic group (ie } C_8 - C_{20})\]
\[R^2 = \text{H or CH}_3\]

FIGURE 2: Two-Dimensional Representation of Interactions of Hydrophobes in an Associating Polymer.
FIGURE 3: Possible Structures of adsorbed layer for polyacrylamide (a) and for hydrophobically modified polyacrylamide (b). Polymer chains adsorbed only by hydrophobic interactions in (b) are depicted by the dashed lines. (from Volpert et al.\textsuperscript{(14)})

FIGURE 4: Reduced Viscosity of Acrylamide/Dodecyl Methacrylate Copolymers. Hydrophobe Concentration in mole\%. (from Flynn and Goodwin\textsuperscript{(35)})
FIGURE 5: Apparent viscosity measured at 20°C, a shear rate of 2 s⁻¹ and a polymer concentration of 0.5 wt%. (from Young et al.²⁸)