

Rheology of Hydrophobically Associating Polymers for Oilfield Applications

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ABSTRACT

Water-soluble hydrophobically associating polymers are examined with particular emphasis on their rheology for oilfield applications. The incorporation of a small amount (less than 1 mol%) of hydrophobic groups into the polymer backbone of a water-soluble polymer dramatically alters the rheological properties of the resulting material. Associating polymers have potential for use in mobility control, drilling and completion fluids and profile modification.

INTRODUCTION

Water-soluble polymers are used in the oilfield in polymer flooding,^{1,2} in drilling and completion fluids,³ in acid stimulation treatments,^{4,5} as drag reducing agents⁶ and in profile modification.⁷

These water-soluble polymers are usually acrylamide copolymers, partially hydrolyzed polyacrylamide (HPAM), or biopolymers such as xanthan or guar gum.^{1,2}

The rheology of HPAM⁸ and biopolymers⁹ for enhanced oil recovery has been studied in detail.

Biopolymers such as xanthan are not easily shear-degraded and are not sensitive to an increase in salinity or divalent ion concentration. As a result, they are used in drilling fluids and at high salinities. In contrast, acrylamide polymers are easily shear degraded and their viscosity is significantly reduced as salinity or divalent

ion concentration increase. Acrylamide polymers are more commonly used at lower salinities, up to an equivalent of 1 wt% sodium chloride.

Water-soluble hydrophobically associating polymers are water-soluble polymers that contain a small number (less than one mole %) of hydrophobic groups attached directly to the polymer backbone. 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. As a result of association, the hydrodynamic size of the polymer increases and the solution viscosity increases.

Water-soluble hydrophobically associating polymers were extensively reviewed by Taylor and Nasr-El-Din in 1998.¹⁰ In that work, they examined the synthesis, characterization, stability and rheology of acrylamide-based associating polymers for improved oil recovery.

Further studies of the rheology of associating polymers for oilfield applications have been reported since 1998. Young et al.¹¹ proposed a hydrophobically modified guar gum for use in completion fluids. Audibert-Hayat et al.¹² reported on hydrophobically modified natural polymers for use as non-damaging drilling fluids. Yabin et al.¹³ synthesized hydrophobically associating acrylamide polymers for oilfield applications and studied their solution properties as a function of electrolyte

concentration, temperature and shear rate. Eoff et al.¹⁴ developed and applied hydrophobically modified polymers for the treatment of water production problems. These recent studies will be discussed in more detail later in this paper.

The rheology of associating polymers is affected by molecular weight, degree of hydrolysis, hydrophobe type, degree of incorporation of hydrophobe, and distribution of hydrophobe.^{10,15-17}

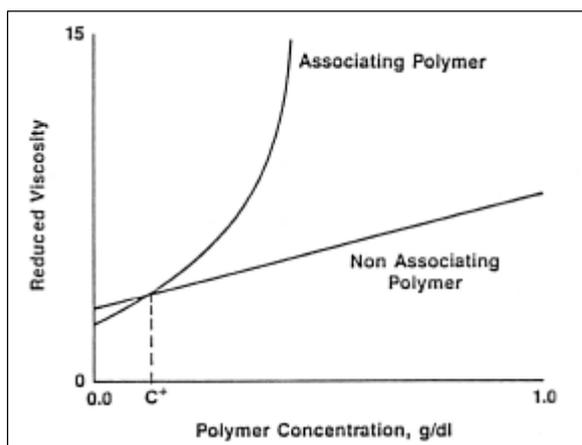


Figure 1. Critical aggregation concentration, c^* , of an associating polymer (from Schulz and Bock.¹⁸)

The critical concentration, c^* , is shown in Figure 1. 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 critical concentration can be used to divide the rheological behaviour of associating polymers into a dilute region and a semi-dilute region. The value of c^* is approximately equal to the reciprocal of the intrinsic viscosity.¹⁹

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 is decreased by increasing the hydrophobe content, by increasing the hydrophobe chain length, or by increasing the molecular weight. This

decrease in solubility can be countered to some extent by increasing the ionic character of the associating polymer. This can be done by hydrolyzing amide groups of a polyacrylamide, or by copolymerization with sulfonate-containing monomers.¹⁰

The factors that affect the rheology of associating polymers can be summarized as follows:

Hydrophobe Content

As 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.²⁰ Increasing intermolecular association leads to an increase in bulk viscosity above c^* . Below c^* , a decrease in viscosity results as intramolecular association increases.

Hydrophobe Type

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.²¹

Molecular Weight

Increasing molecular weight generally increases the solution viscosity.¹⁰

Degree of Hydrolysis

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.²¹

Temperature

McCormick et al.²² showed that a copolymer of acrylamide and N-decylacrylamide exhibited an increase in reduced viscosity with increasing temperature. In contrast, Taylor et al.²³ showed that the viscosity of certain

associating polymers showed a transition temperature at which viscosity dropped dramatically (Figure 2).

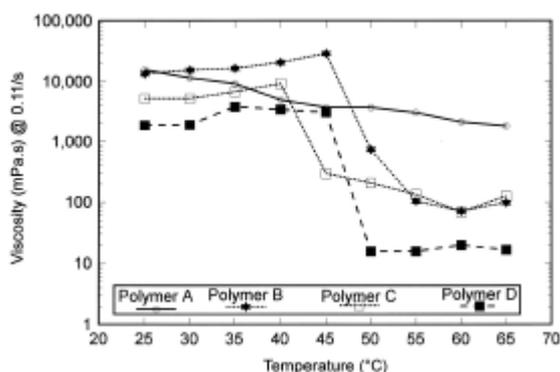


Figure 2. Effect of temperature on viscosity of associating polymers (0.1 g/dL). A: 25 mol% HPAM, 0.2 mol% polyoxyethylene(10)lauryl ether. B: 25 mol% HPAM, 0.2 mol% dodecyl methacrylate. C: 30 mol% HPAM, 0.75 mol% N-n-octylacrylamide. D: 30 mol% 2-acrylamide-2-methylpropane sulfonate, 0.75 mol% N-n-octylacrylamide.

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

Chemical Interactions

The addition of salts or surface-active agents can have a significant effect on the rheology of associating polymers. In general, the viscosity of associating polymers increases with increasing salt concentration, especially at higher polymer concentrations. Increased salinity enhances aggregation of the hydrophobic groups. It also decreases the solubility of the associating polymer. As a result, viscosity will increase up to a certain salinity, after which viscosity will drop and precipitation or gelation of the polymer may occur.

Low concentrations of cross-linking species such as iron (III) can greatly increase the viscosity of associating polymer solutions or result in gelation. This is of concern in

oilfield fluids where iron (III) commonly occurs in the presence of steel tubing.

Varying surfactant concentration can have a very significant effect on rheology of associating polymers. Iliopoloulos et al.²⁴ and Magny et al.²⁵ 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.

Recent Studies

Young et al.¹¹ 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 million. 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 comparable non-associating hydroxybutyl guar.

Young et al.¹¹ found that sodium dodecyl sulphate (SDS) increased the viscosity of HMHBG up to a factor of 10, depending on the SDS concentration. Maximum viscosity was observed with 0.008 mol/dm³ of SDS. At higher concentrations, viscosity decreased

to values nearly identical to unmodified HBG.

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

Feng et al.¹⁹ 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^* , 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.

Audibert-Hayet et al.¹² 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.

Hydrophobically modified hydroxyalkyl guar gums have shown several useful properties. These include an increase in viscosity and suspending properties,¹¹ good salt tolerance, and an improvement in fluid loss control.²⁶

The hydrophobically modified polymer described by Audibert-Hayet et al.¹² 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.

Eoff et al.¹⁴ showed that hydrophobically modified acrylamide copolymers can selectively reduce water production in core flood testing. It is possible to reduce water production from a reservoir rock without significantly reducing the production of oil. This type of polymer system is known as a relative permeability modifier. The adsorption properties of the polymer are much more important than its rheological properties. In addition to the testing as relative permeability modifiers, the hydrophobically modified polymers studied by Eoff et al.¹⁴ showed that at a constant shear rate, the viscosity would rapidly increase after a period of time. This effect was shear rate dependent.

Yabin et al.¹³ 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.

SUMMARY AND CONCLUSIONS

Factors that affect the rheology of water-soluble hydrophobically associating polymers for oilfield applications were discussed. Recent work in the field was summarized.

Molecular weight, degree of hydrolysis, hydrophobe type, hydrophobe content, temperature and salinity can all significantly affect the rheology of associating polymers.

Interactions of hydrophobic groups with surfactants, with hydrophobic particles in

solution or with rock surfaces can also have important effects on solution rheology.

It is important to mention that 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.

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