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**Department of Earth Science and Engineering**

**Centre for Petroleum Studies**

A laboratory study of polymer rheology in bulk and in sandstone cores  
with application to German oilfields

**By**

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**A report submitted in partial fulfilment of the requirements for  
the MSc and/or the DIC.**

**September 2012**

## **DECLARATION OF OWN WORK**

I declare that this thesis

**“A laboratory study of polymer rheology in bulk and in sandstone cores with application to German oilfields”**

is entirely my own work and that where any material could be construed as the work of others, it is fully cited and referenced, and/or with appropriate acknowledgement given.

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# A laboratory study of polymer rheology in bulk and in sandstone cores with application to German oilfields

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## Abstract

Viscosity is the key rheological parameter in polymer floods, since the main design criterion is to ensure a favourable mobility ratio. New polymers are being developed with enhanced properties to improve the cost-effectiveness of polymer floods. Of these innovative polymers, hydrophobically associative polymers (HAP) have a structure that gives them interesting thickening properties and a greater resistance to salinity. In this paper, the rheological behaviour of a newly developed HAP is studied both in bulk and through Bentheimer sandstone core plugs. The salinity of the brine was varied from 0.5 wt% to 15 wt% NaCl and the permeability of the plugs from 500 mD to 2 D, to be consistent with German oilfields conditions. Throughout this study, comparisons were made with two commercially available polymers, a co-polymer of ATBS and acrylamide polymer (2-acrylamido-2-methyl propane-sulfonic acid or AMPS) and a polysaccharide polymer (PSP).

All polymers showed a shear-thinning behaviour in bulk. The results were well matched with the Carreau model. HAP and AMPS showed similar elastic behaviours; PSP gave a higher elastic response at comparable concentration and salinity. In porous media, HAP and AMPS had very different behaviours compared to their behaviour in bulk. HAP showed a shear-thinning behaviour with viscosity levels 30 times those observed in bulk at low shear rates which is due to retention. Salinity increased the apparent viscosity of HAP due to the intensification of hydrophobic interactions in high polar salty environments. AMPS showed two different viscosity regimes. (1) At low shear rates, the polymer solution had a Newtonian behaviour with values higher than bulk due to retention. (2) At higher shear rates, a shear-thickening behaviour occurred; this is due to the expansion – contraction transition of the polymer molecules in elongational flow which onsets the dilatancy. The results were predicted from the bulk data, using the Carreau model parameters, with the unified apparent viscosity model. PSP displayed a shear-thinning behaviour with viscosity values very similar to the bulk viscosity when using a 22.91 cm long core.

Injectivity of AMPS is compromised due to the mechanical degradation of the polymer occurring at high shear rates. The shear reversibility of HAP, its high viscosity levels at low shear rates and its high molecular weight make this polymer a favourable candidate for field polymer flooding, though its high retention may be an issue. PSP is also very resistant to mechanical degradation. Further investigations are needed at reservoir conditions to determine the feasibility of polymer floods with the studied polymers.

## Introduction

The use of polymers in water flooding is widely recognised as a technically and commercially proven process of enhanced oil recovery (EOR). Adding polymers to the water flood increases the viscosity and reduces the mobility ratio with the reservoir oil. Most common polymers used for EOR purposes are partially hydrolysed polyacrylamides (HPAM) and biopolymers such as Xanthan (Lake, 1987).

Currently, the focus is on the development of new EOR polymers with enhanced properties. The aims are (1) to reduce the costs of polymer floods by lowering the quantities of polymer needed, (2) to extend the range of suitable reservoirs in terms of salinity, and (3) to achieve higher oil recovery. Among those innovative polymers are AMPS, or 2-acrylamide-2-methyl propane-sulfonic copolymers, and hydrophobically associative polymers or HAP. The literature has been extensively reviewed by Taylor *et al.* (1998) for the performance of HAP.

AMPS can offer significantly advantages over common HPAM. Its sulfonated functionality increases the resistance of the polymer to salinity. This functionality interacts less with divalent cations so that the polymer molecules stay soluble in aqueous solution at high salinities. AMPS are also more resistant to hydrolysis (the conversion of amide groups ( $\text{CONH}_2$ ) into carboxyl groups ( $\text{COO}^-$ )) than HPAM. They are still affected by ionic shielding.

HAP have significantly higher viscosities at low shear rates. They do not merely rely on the thickening effect by molecular weight. The hydrophobic interactions between the polymer chains form a 3D associative polymer network which increases the viscosity of the solution. HAP have also a high tolerance to salt due to the intensification of hydrophobic interactions in high polar salty environments. They are still affected by ionic shielding but at a lesser extent than AMPS. In addition, HAP have a lesser sensitivity to mechanical degradation. This is due to the hydrophobic interactions dominating the viscosifying effect over the molecular weight. When shear stress is applied, the intermolecular associations are ruptured but leaving the polymer

backbone intact. As the shear stress is ceased, the associative polymer network is reformed and the viscosity goes back to its original level.

The rheology of EOR polymers is an important parameter. Its study both in bulk and in porous media is essential as it is important to relate the bulk properties to those in porous media. Studies have been reported extensively in literature for common AMPS, HAP and biopolymers (Cannella *et al.*, 1988, Kim *et al.*, 2010; Seright *et al.*, 2011a) but do not cover very high salinities, typical of many oilfield settings. Bulk rheology, through viscometry and oscillation tests, is the first step to understanding the polymer's shear-thinning behaviour, i.e. viscosity decrease with increasing shear rate, and the influence of parameters like salinity and concentration. These tests can characterize the viscous and elastic behaviour of the polymer separately.

Understanding the polymer rheology in porous media is essential as solutions behave differently when flowing through the pore space. Due to the acceleration and deceleration of the fluid upon entering and leaving individual pores, molecules of viscoelastic polymers continuously expand and contract (Fig. 1). This phenomenon induces a shear-thickening behaviour, i.e. a viscosity increase with increasing shear rate, at high shear rates which significantly improves the sweep efficiency (Han *et al.*, 1995; Wang *et al.*, 2000). Associative polymers have been shown to display either shear-thinning or shear-thickening behaviours in porous media (Bock *et al.*, 1988). Polysaccharides like Xanthan have a shear-thinning behaviour that is closely similar to that in a rheometer (Cannella *et al.*, 1988).

Those behaviours are affected by several parameters including polymer concentration, salinity, permeability and geometry of the porous medium. German fields have salinities up to 18-20% and permeability ranging from 0.2 to 2 Darcy. There is a need to study the behaviour of polymer solutions in those conditions which are not usually found in the literature.

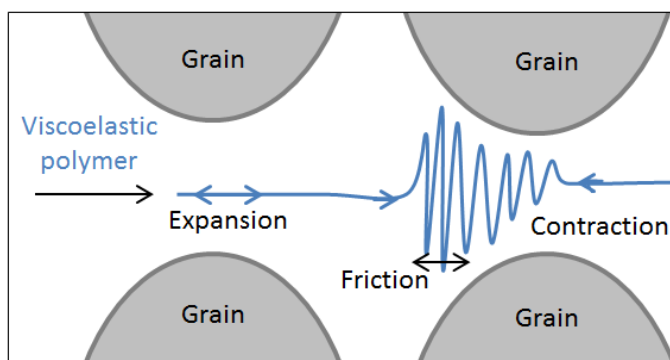


Fig. 1 – Schematic picture of viscoelastic flow in porous media.

## Literature review

Sandiford and Pye were the first to establish that polymer flooding improved oil recovery, compared to conventional water flooding, by lowering the mobility ratio between flood water and reservoir oil (Sandiford, 1964, Pye, 1964). Many additional studies have been carried out in the laboratory and in the field. Ranges of the most important parameters for polymer flooding success based on field operations have been reported (Jewett *et al.*, 1970; Du *et al.*, 2004).

The viscoelastic effects of polymer solutions were first studied in the mid-1960s. Marshall established that viscoelastic fluids when flowing through a porous medium showed an increased pressure drop to values well above those expected for purely viscous fluids (Marshall *et al.*, 1966). This was confirmed by further laboratory studies and a critical velocity was defined at which the viscoelastic fluids deviate from viscous flow in porous media (Wissler, 1971; Gogarty *et al.*, 1972). Gogarty further showed that elastic effects were dependent on the concentration and the medium used. He provided a basis for detecting viscoelastic fluids with a visco-inelastic power-law analysis (Gogarty *et al.*, 1972).

The study of polymer elasticity through core flooding tests as well as bulk rheology tests became a research focus. The shear-thickening behaviour (elastic behaviour) at high flow rates of polyacrylamides was demonstrated as well as its dependence on permeability, temperature, polymer molecular weight and concentration (Heemskerk *et al.*, 1984). The description of flow behaviour in cores of viscoelastic polyacrylamide solutions was further studied and approximated using two power-law coefficients and the critical flow rate (Heemskerk *et al.*, 1984).

Recently, an apparent viscosity model that accounts for both shear-thinning and shear-thickening behaviour of polymer solutions in porous media was developed over a wide range of flow velocities (Delshad *et al.*, 2008). These behaviours can be predicted from rheometer-measured shear and oscillatory viscosities. Databases of viscoelastic properties for EOR polymers were developed over a wide range of polymer concentration, salinity, hardness and temperature, therefore providing new data on fundamental flow properties (Lee *et al.*, 2009; Kim *et al.*, 2010).

In more recent studies where the influence of polymer rheology on polymer flooding is discussed, improvement of displacement efficiency at both micro and macro scales is assigned to elasticity (Han *et al.*, 1995; Wang *et al.*, 2000). This was confirmed by Urbissinova *et al.* who studied the effect of elasticity alone on displacement efficiency (Urbissinova *et al.*, 2010).

Studies of polymer solutions at high salinities have appeared in the literature only recently. They mostly investigate stability and transport properties of new polymers which are especially designed for high salinities (Vermolen *et al.*, 2011;



Kulawardana *et al.*, 2012). This paper studies the rheological properties, both in bulk and in sandstone cores, of a newly developed polymer which is design to withstand harsher environments, a HAP polymer. Throughout this study, comparisons are made with two commercially available polymers, a AMPS and a PSP. The aims were to establish whether the HAP (1) performed better in a high salinity environment and (2) was more suitable for application in German oilfields compared to commercially available polymers.

**Polymer rheology theory**

Polymer solutions are non-Newtonian fluids, i.e. their viscosity is not constant and is dependent on the shear strain applied to the solution. The study of polymer rheological properties is essential to determine how polymers behave both in bulk and in porous media prior to their injection in the field.

**Bulk rheology properties:** Viscosity is the key rheological parameter of polymer solutions as the aim of the polymer flooding process is to increase the viscosity of the water in order to reduce the mobility ratio with the reservoir oil. The mobility ratio is defined as the ratio of the displacing phase mobility to the displaced phase mobility:

$$M_r = \frac{\lambda_p}{\lambda_o} = \frac{(k/\eta)_p}{(k/\eta)_o} \dots\dots\dots (1)$$

where the subscripts p and o refer to polymer and oil respectively, k is the rock permeability and  $\eta$  the viscosity. For non-Newtonian fluids the viscosity is defined as the ratio of shear stress to shear rate, with the viscosity being dependent of the shear rate:

$$\tau = -\eta(\dot{\gamma}) \frac{dv}{dr} = -\eta(\dot{\gamma}) * \dot{\gamma} \dots\dots\dots (2)$$

where  $\dot{\gamma}$  is the shear rate and  $\tau$  the shear stress. Several correlations have been proposed to describe the relationship between the polymer viscosity and the shear rate. The simplest model is the power-law model:

$$\eta(\dot{\gamma}) = K\dot{\gamma}^{n-1} \dots\dots\dots (3)$$

where K and n are respectively the power-law coefficient and index. For non-Newtonian fluids,  $0 < n < 1$ . Equation 3 is only valid in the shear-thinning region of the viscosity curve. To incorporate the entire shear rate range, the Carreau model (Carreau, 1972) can be used (Fig. 2(a)):

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty) [1 + (\lambda\dot{\gamma})^\alpha]^{-\frac{N-1}{\alpha}} \dots\dots\dots (4)$$

where  $\eta_0$  and  $\eta_\infty$  are respectively the low and high viscosity plateau values,  $\lambda$  is a time empirical constant,  $\alpha$  is usually taken as 2 and N is an empirical constant. Meter *et al.* (1964) proposed a similar model:

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{1 + (\frac{\dot{\gamma}}{\dot{\gamma}_{1/2}})^{N_1 - 1}} \dots\dots\dots (5)$$

where  $\dot{\gamma}_{1/2}$  is the shear rate at which the viscosity is the average of  $\eta_0$  and  $\eta_\infty$ , and  $N_1$  is an empirical constant.

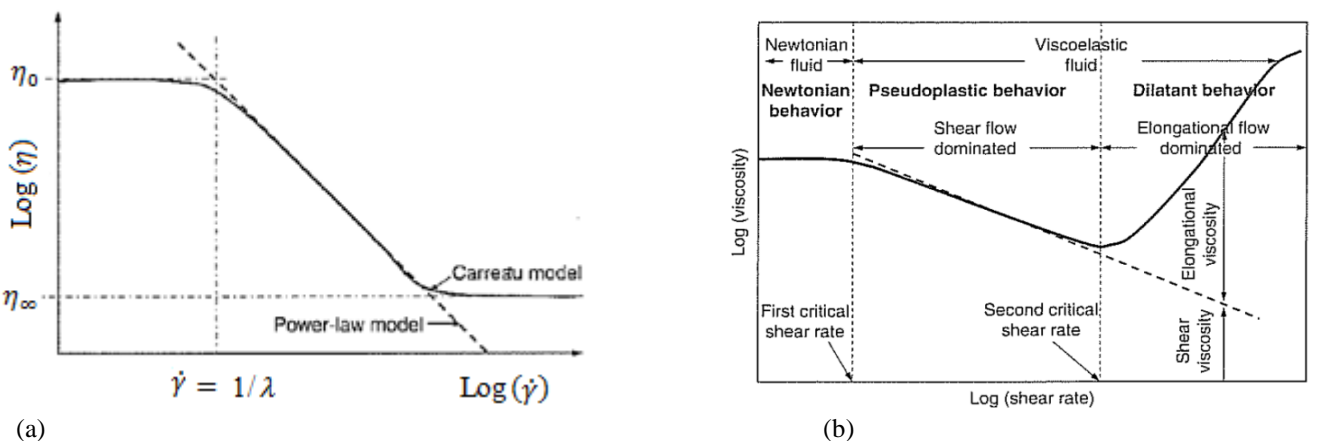


Fig. 2 –Schematic description (a) of bulk viscosity models and (b) of viscoelastic models (from Sheng, 2011).

**Viscoelastic properties:** Viscoelastic fluids exhibit both viscous and elastic characteristics when submitted to deformation. Properties like shear strain are measured with varying angular frequency,  $\omega$ , or deformation. Oscillatory properties like the elastic and viscous modulus and the complex viscosity are calculated from these measurements. The polymer sample is placed in a Couette device which is a pair of concentric cylinders, one of which is fixed. The sample is put in the narrow gap between the cylinders and the free cylinder is rotated (Fig. 3). The flow set-up between the two cylinders is almost a simple shear flow. The rotation is a simple harmonic motion, which is defined as follows, along with the shear rate:

$$\gamma(t) = \gamma_0 \sin(\omega t) \dots\dots\dots (6)$$

$$\dot{\gamma}(t) = \omega \gamma_0 \cos(\omega t) \dots\dots\dots (7)$$

where  $\gamma_0$  is the maximum amplitude of the shear strain. In the linear viscoelastic region, the shear stress is defined as follows:

$$\tau(t) = \int_{-\infty}^t G(t-t')\dot{\gamma}(t)dt' = \int_{-\infty}^t G(t-t')\omega \gamma_0 \cos(\omega t') dt' \dots\dots\dots (8)$$

where  $G$  is the relaxation modulus of the fluid. This integral can be transformed by changing variables using  $s = t - t'$ :

$$\begin{aligned} \tau(t) &= \int_0^\infty G(s)\omega\gamma_0 \cos(\omega(t-s)) ds = \gamma_0 \left[ \omega \int_0^\infty G(s) \sin(\omega s) ds \right] \sin(\omega t) + \gamma_0 \left[ \omega \int_0^\infty G(s) \cos(\omega s) ds \right] \cos(\omega t) \\ &= \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)] \dots\dots\dots (9) \end{aligned}$$

where  $G'$  is the elastic or storage modulus and  $G''$  the viscous or loss modulus. Viscoelastic fluids produce this two-component stress response when they undergo deformation because some of the energy is stored elastically and some is dissipated. The moduli can be expressed as a complex modulus,  $G^*$ , (Equation 10) and the viscosity as a complex viscosity,  $\eta^*$ , (Equation 11).

$$G^* = G' + iG'' \dots\dots\dots (10)$$

$$\eta^* = \eta' + i\eta'' = \frac{G'}{\omega} + i \frac{G''}{\omega} \dots\dots\dots (11)$$

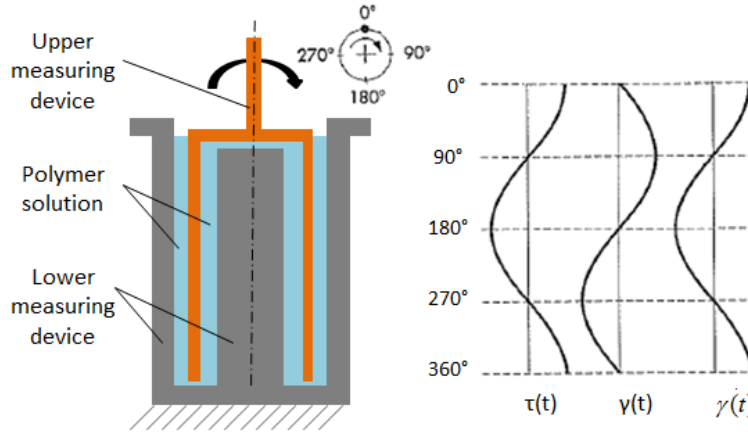


Fig. 3 – Oscillation tests with a Couette device (right diagram from Mezger, 2006).

**Apparent rheology properties**

**Apparent viscosity.** The apparent viscosity,  $\eta_{app}$ , is the viscosity of the polymer solution applied to porous media flow. It can be estimated using Darcy’s law:

$$\eta_{app} = \frac{k_f \Delta P}{uL} \dots\dots\dots (12)$$

where  $k_f$  is the flushed permeability,  $u$  the volumetric flow rate or Darcy velocity and  $\Delta P$  the pressure drop across the porous medium.

**Apparent or effective shear rate.** The effective shear rate in the porous medium is usually represented in the form of Equation 13:

$$\gamma_{eff} = C \left( \frac{3n+1}{4n} \right)^{\frac{n}{n-1}} \left( \frac{u}{\sqrt{k_f \phi}} \right) \dots\dots\dots (13)$$

where  $n$  is the power-law index,  $C$  the shear rate coefficient,  $u$  the Darcy velocity,  $k_f$  the flushed permeability and  $\phi$  the porosity. Cannella *et al.* (1988) reported that  $C = 6.0$  fits their experimental data of Xanthan biopolymer core floods. However, Wreath *et al.* (1990) noticed that for hydrolysed polyacrylamides polymers,  $C$  is dependent on permeability and porosity of the medium.

**Unified apparent viscosity model.** The previous viscosity models only account for the shear-thinning behaviour of the polymer solutions. To capture the more complex rheological behaviour of HPAM polymers – shear-thinning at low flow rates, shear-thickening at medium flow rates and degradation at high flow rates – Delshad *et al.* (2008) proposed a unified apparent viscosity model (UAV) for the entire range of flow rates (Fig. 2 (b)). The model is based on the assumption that the apparent viscosity of the polymer solution is the sum of the shear-dominating viscosity and the elongational-domination viscosity (Equation 14). The Carreau model is used for the shear-thinning region.

$$\eta_{app} = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \left[ 1 + (\lambda \gamma_{eff})^{\alpha} \right]^{\frac{N-1}{\alpha}} + \eta_{max} \left[ 1 - \exp(-(\lambda_2 \tau_r \gamma_{eff})^{n_2-1}) \right] \dots \dots \dots (14)$$

where  $\eta_{max}$  is the viscosity plateau value beyond which degradation occurs,  $\lambda_2$  is an empirical constant,  $\tau_r$  is the relaxation time and  $n_2$  is the shear-thickening index.

## Polymer solution preparation

**Polymers:** Three polymer types were used in this experimental study: an hydrophobically associative polymer, a co-polymer of ATBS and acrylamide (2-acrylamide-2-methyl propane-sulfonic acid) and a polysaccharide polymer. Hereafter, these polymers will be referred to as HAP, AMPS and PSP respectively. These coded names were used to minimise commercial implications. Polymer properties are given in Table 1. All polymers were provided as dry powders.

**Table 1 – Polymers used in this study**

Description	Anionicity	Mw	Concentration range
HAP	High*	Very high*	150 ppm – 1000ppm
AMPS	Medium*	Low*	250 ppm – 1000ppm
PSP	Low*	High	500 ppm – 1000 ppm

\* from SNF Floerger

**Brine:** Simple brine solutions were prepared with a concentration of NaCl ranging from 0.5 wt% to 15 wt%. All solutions were filtered through 0.2  $\mu\text{m}$  filters. Studies of polymer behaviour at salinities above 10 wt% NaCl are necessary to represent German oilfields.

**Polymer solution preparation:** All solutions were prepared by adding the polymer at a given concentration directly to the brine. The polymer powder was sprinkled onto a vortex shoulder of brine created by a magnetic stirrer or rotating blades to individually wet the polymer particles. Care was taken to avoid lumping of the powder. Compared with AMPS, HAP took longer to dissolve in the brine. PSP needed high shear, provided by rotating blades, to dissolve into brine. After dissolution, all solutions were filtered with a 5  $\mu\text{m}$  pore size filter (AMPS and PSP) or a 12  $\mu\text{m}$  pore size filter (HAP) to eliminate suspended particles.

## Rheological characterisation of polymer solutions

An Anton Paar rheometer (Physica MCR 301) equipped with a Couette measuring system was used to carry out the rheological measurements (Fig. 3). The rheometer has a torque resolution of 0.1 mNm, and a normal force resolution of 0.5 mN. The rheometer was calibrated every two days to ensure the measurements' accuracy. Two types of rheological measurements were made: rotation and oscillation tests. The measurements were conducted at 25°C.

**Rotation tests:** Rotation tests were carried out to study the shear viscosity of the polymer solutions as a function of the shear rate. Tests were made with a range of shear rates from 0.01 to 10,000  $\text{s}^{-1}$ . To acquire a reproducible measurement, a constant shear of 30 Pa, 20 Pa for PSP solutions, was applied to the system for 5 minutes. The shear viscosity results shown are the one obtained after the 5 minutes shearing. The measurements were conducted twice for all samples. The results showed good repeatability.

Fig. 4 compares the shear viscosity of the three polymers at 500 ppm concentration and 0.5 wt% NaCl. Figs. 5 to 7 show the dependence of shear viscosity on salinity at 1000 ppm for AMPS, HAP and PSP respectively. The viscosity of HAP solutions showed a strong dependence on the polymer relaxation time (Fig 8(a)). To be able to compare results, the viscosity measured right after the 5 minutes shearing was chosen. HAP solutions also showed a hysteresis effect (Fig 8(b)). The same procedure was carried out for all measurements to ensure that the hysteresis effect did not affect the results. This involved

applying the same shear to all solutions and conducting the viscosity measurements directly after shearing.

The time for the polymer molecules to relax (relaxation time) was measured. Polymer solutions were submitted to a constant shear of 20 Pa for 5 minutes. The viscosity versus time was then recorded at a constant shear rate of  $10 \text{ s}^{-1}$ . The results are displayed in Fig. 9 for a polymer concentration of 500 ppm and a salt concentration of 5 wt%.

**Oscillation tests:** Oscillation tests were carried out to measure the viscoelastic properties of the polymer solutions. Two types of oscillation tests were conducted: amplitude sweeps and frequency sweeps.

Amplitude sweeps were carried out to identify the linear viscoelastic response (LVR) range of a solution. The tests were performed at constant frequency, 1 Hz, and at varying amplitudes through a wide range of deformations. For this study, the deformation range was taken from 1% to 10,000%. The LVR range for the different samples was then determined (Fig. 10). As shown in Fig. 10, the viscosity of the three samples is not clearly dependent on the deformation applied for a range of deformations up to 80% for AMPS, 15% for HAP and 30% for PSP. At higher deformations, the viscosity decreases rapidly. This decrease of viscosity indicates the limit of the linear range of the solutions.

The LVR ranges of the samples being determined, the frequency sweep tests were implemented. Frequency sweeps are used to investigate time-dependent shear behaviour since the frequency is the inverse of time. They were performed at constant deformation, taken within the linear range determined earlier, and at varying frequencies. The frequency range was taken from 0.1 to 100 Hz. Results for the different samples are shown in Figs. 12 to 15 as a function of the angular frequency. Fig. 12 compares the elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) of the three polymers studied at 500 ppm polymer concentration and 0.5 wt% NaCl. Figs. 13, 14 and 15 show the dependence on salinity of AMPS, HAP and PSP respectively at 1000 ppm polymer concentration.

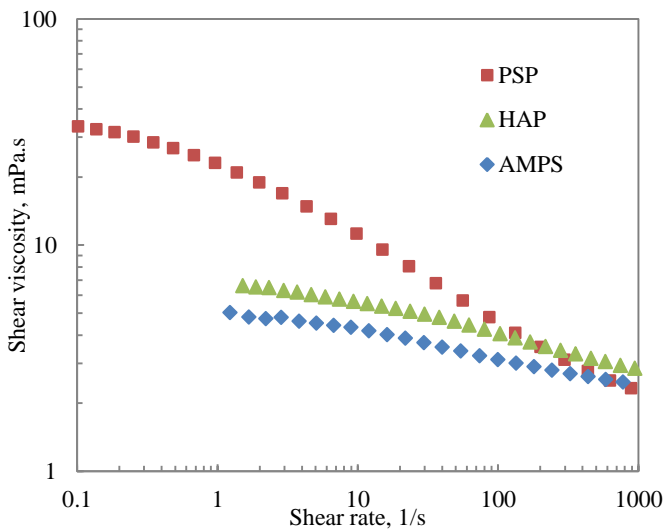


Fig. 4 – Rotation tests for AMPS, HAP and PSP at 500 ppm polymer concentration and 0.5 wt% NaCl.

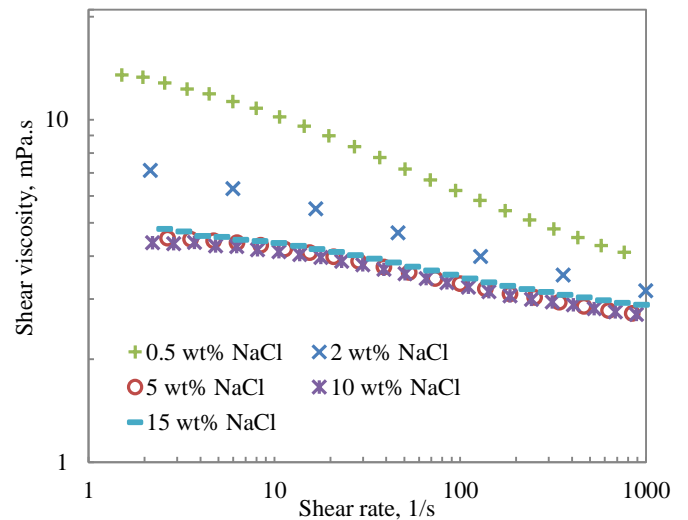


Fig. 5 – Rotation tests for AMPS - Salinity dependence with 1000 ppm polymer.

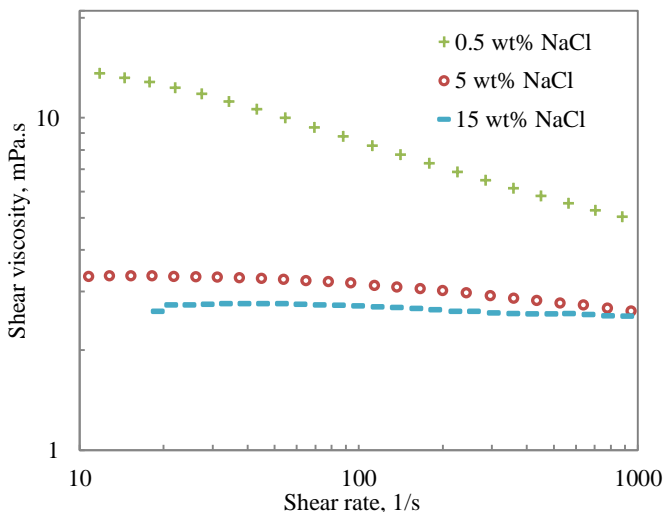


Fig. 6 – Rotation tests for HAP - Salinity dependence with 1000 ppm polymer.

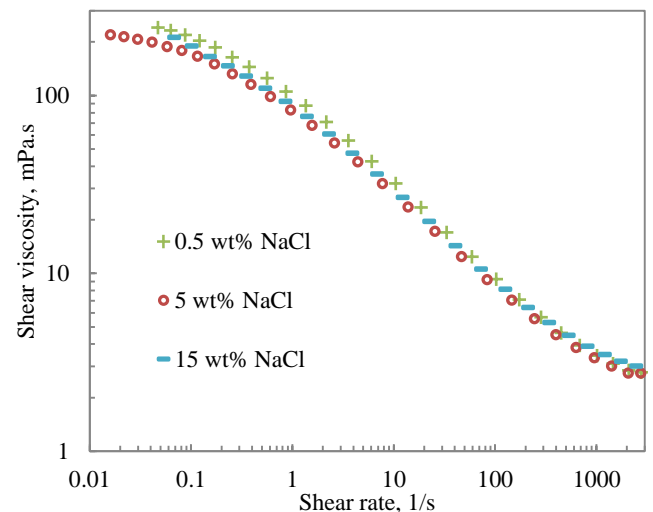


Fig. 7 – Rotation tests for PSP - Salinity dependence with 1000 ppm polymer.

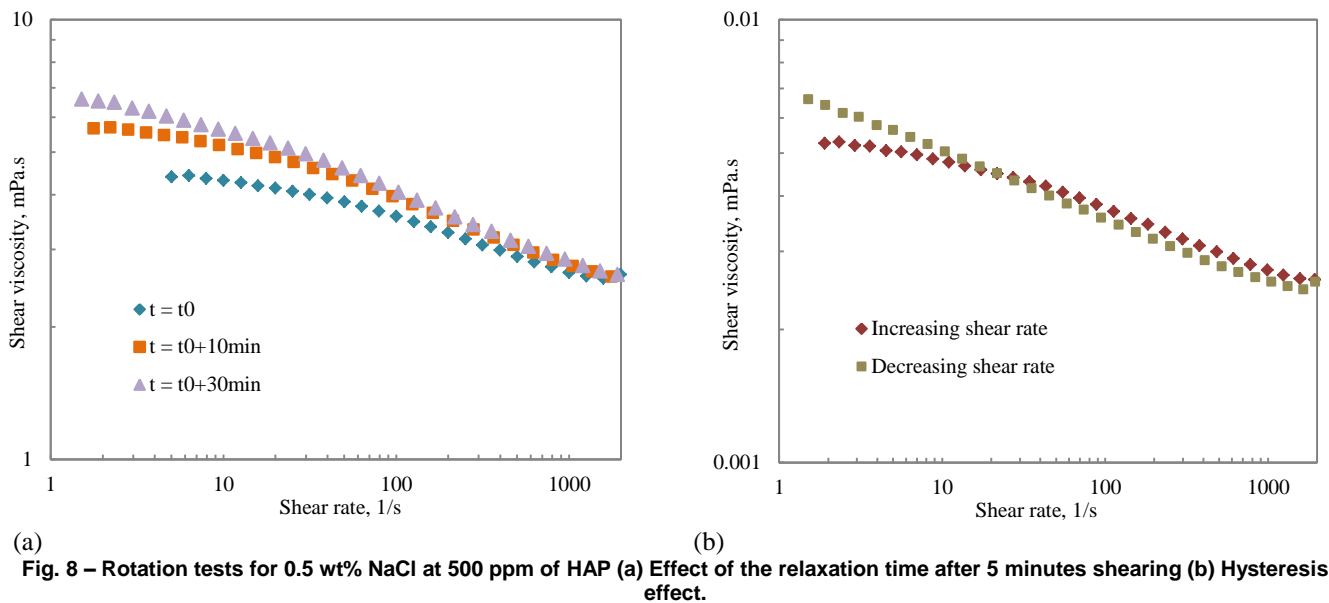


Fig. 8 – Rotation tests for 0.5 wt% NaCl at 500 ppm of HAP (a) Effect of the relaxation time after 5 minutes shearing (b) Hysteresis effect.

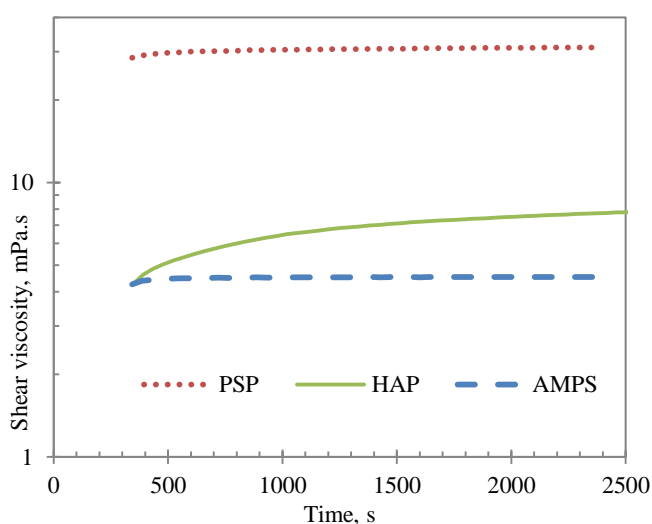


Fig. 9 – Relaxation of polymer after 5 minutes shearing at 20 Pa for AMPS, HAP and PSP at a shear rate of  $10 \text{ s}^{-1}$ .

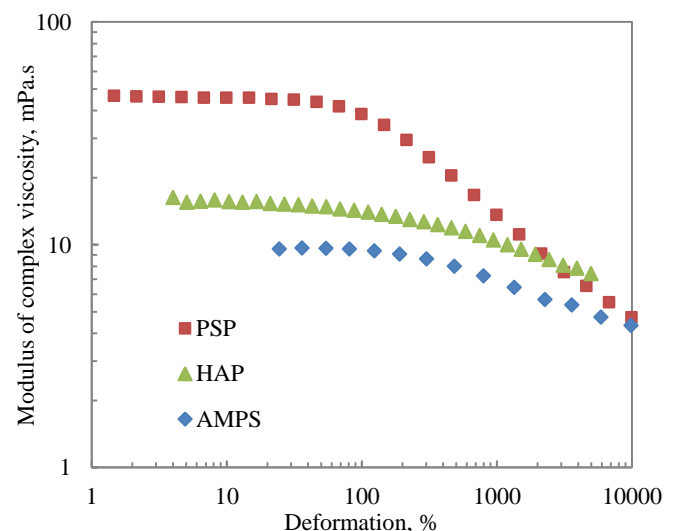


Fig. 10 – LVR range at 0.5 wt% NaCl and 1000 ppm polymer for AMPS, HAP and PSP.

**Discussion:** All polymers displayed a shear-thinning behaviour, i.e. a viscosity decrease with increasing shear rate. When the shear rate increases, the polymer molecules coil up causing the viscosity to decrease. The results were matched with the Carreau model (Equation 4). Examples of good matches are shown in Figs. 17 and 20.

**Discussion of results.** A polymer concentration increase relates to an increase in shear viscosity. AMPS has a medium anionicity – it has some anionic carboxyl groups along its chain. These negatively charged groups cause repulsion between polymer molecules inducing the latter to elongate and align with other molecules. This results in an increase of the hydrodynamic volume and of the viscosity at high concentration. HAP contains hydrophilic and a small fraction of hydrophobic monomers. Because of the hydrophobicity, two kinds of associations are possible: intermolecular and intramolecular. The first causes the viscosity of the solution to increase and the second the viscosity of the solution to decrease. With increasing concentration, stronger associations between molecules occur increasing the polymer solution viscosity (Sheng, 2011). PSP is a very branched polymer (Fig. 11) and when its molecules are aligned, the solution becomes more rigid and the viscosity increases (Lake, 1987).

The viscosity of HAP is higher than AMPS (Fig. 4). Because of conformation of flexible coils, the viscosity of AMPS solutions cannot be very high in saline water even with high molecular weight polymers. HAP on the other hand has a strong association of molecules due to the hydrophobic groups which results in a 3D network structure and a high solution viscosity. In aqueous solutions, HAP exists in single molecules. The association is weak and the viscosity close to AMPS's. This is observed for AMPS and HAP at 500 ppm and 0.5 wt% NaCl. When the concentration of HAP reaches a certain level called the

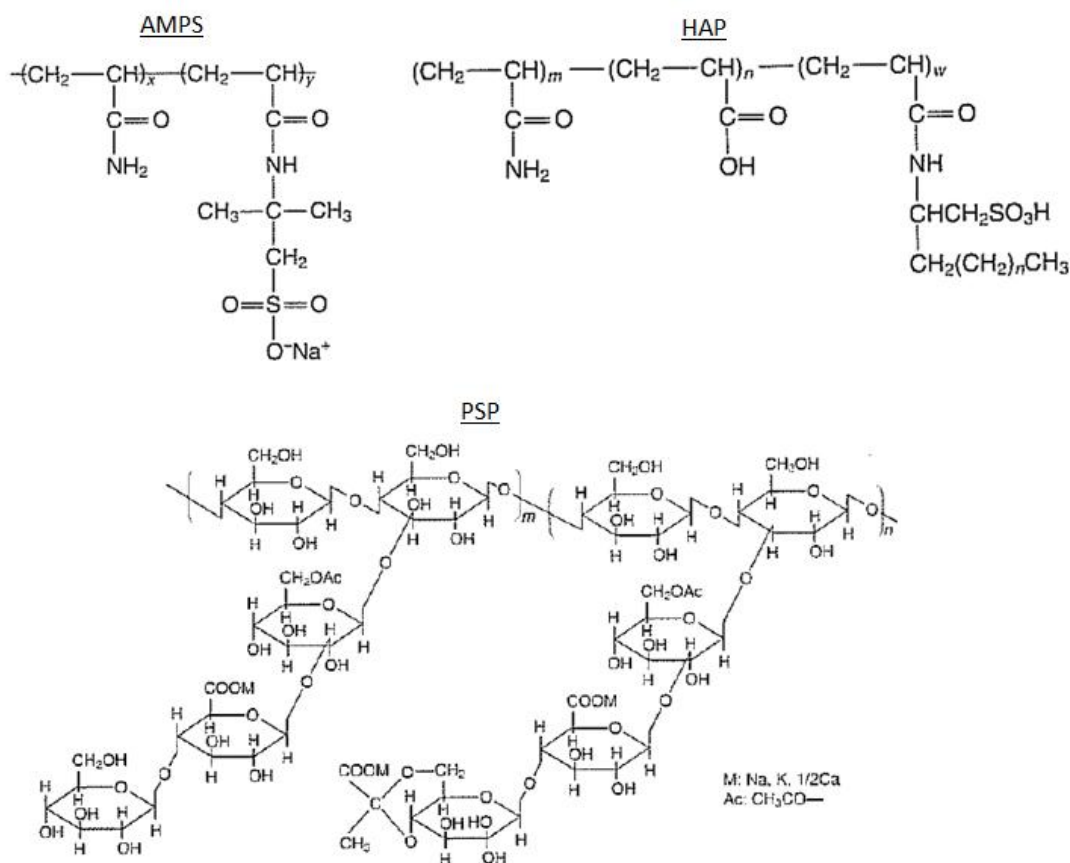


Fig. 11 – Chemical structure of AMPS, HAP and PSP (from Sheng, 2011).

critical associating concentration, the associations become stronger and the viscosity increases above that of AMPS (Luo *et al.*, 2006). So the critical associating concentration for HAP at 0.5 wt% NaCl is around 500 ppm.

The dependence on salinity varies with the polymer type as shown in Figs. 5, 6 and 7. AMPS exhibits a decrease of shear viscosity with increasing salinity up to 5 wt% NaCl. Any further increase in salinity gives similar viscosity results. This can be explained by the  $Na^+$  ions shielding the negatively charged groups of the polymer molecules. The molecules coil up causing the viscosity to decrease. When all the anionic groups are shielded, increasing the salinity of the solution has little effect, as observed (Lake, 1987). HAP has a similar behaviour compared to AMPS. The presence of salt shields the anionic groups causing molecule repulsion which compresses the molecule chains and therefore increases the intramolecular associations and decreases the solution viscosity (Wang *et al.*, 1999). AMPS was less affected by salinity than HAP. Salinity has very little impact on PSP, and only at low shear rates. Polysaccharide molecules have a low number of anionic groups and are therefore not affected by increasing salinity (Lake, 1987).

HAP shear instability (Fig. 8) can be explained by the damage of the polymer network structure at high shear rates. This causes the loss of viscosity. When the shear rate is reduced, the network structure is restored and the viscosity increases (Luo *et al.*, 2001).

As shown in Figs. 12 to 15, the viscous modulus of all polymers increases with angular frequency. This is due to the coiling up of the polymer modules which increases viscosity. The elastic modulus increases with angular frequency before sharply decreasing due to some inertia effects. Elastic and viscous moduli dependence on polymer concentration was analysed. Both moduli increased with a polymer concentration increase. This can be explained by the decrease of the distance between polymer molecules when the polymer concentration is increased. Van der Waals forces become larger and it becomes more difficult for the polymer molecules to deform (Sheng, 2011).

The dependence on salinity is shown in Figs. 13, 14 and 15. AMPS exhibits a decrease of elastic and viscous moduli with increasing salinity. It was observed that any increase of salinity above 5 wt% NaCl gives similar results for the viscous modulus; and the elastic modulus is within a range of 0.001 and 0.004 Pa. The dependence of viscous modulus with salinity for HAP solutions is a similar than for AMPS. The elastic behaviour of HAP is fairly constant with increasing salinity. This is due to the fact that both polymers have a high anionicity which makes them sensible to divalent ions. HAP was considerably less affected by salinity than AMPS. Salinity has very little impact on PSP and only at low shear rates – polysaccharides have a low anionicity.

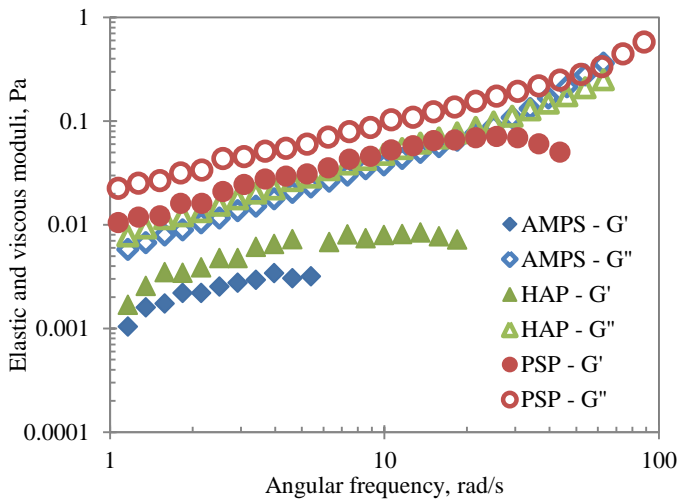


Fig. 12 – Dynamic frequency tests for AMPS, HAP and PSP at 500 ppm polymer concentration and 0.5 wt% NaCl.

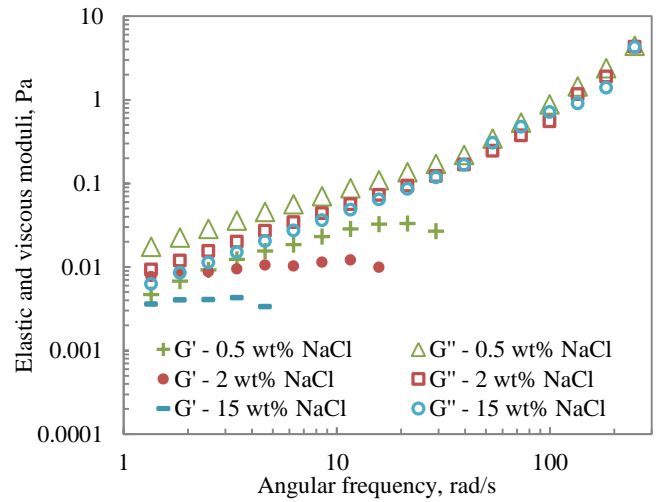


Fig. 13 – Dynamic frequency tests for AMPS - Salinity dependence with 1000 ppm polymer.

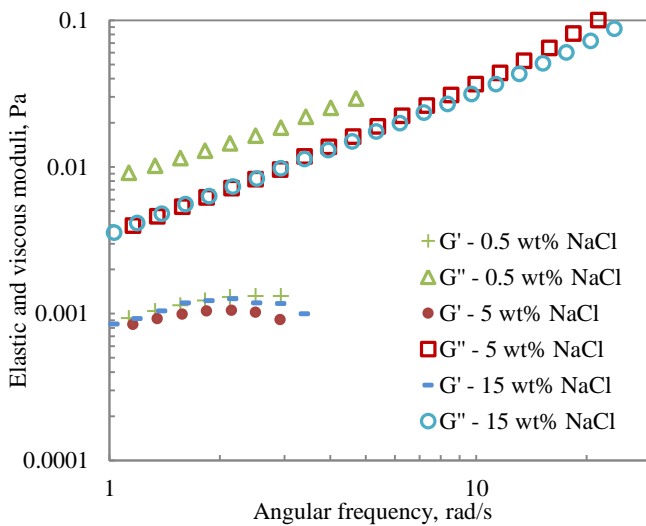


Fig. 14 – Dynamic frequency tests for HAP - Salinity dependence with 1000 ppm polymer.

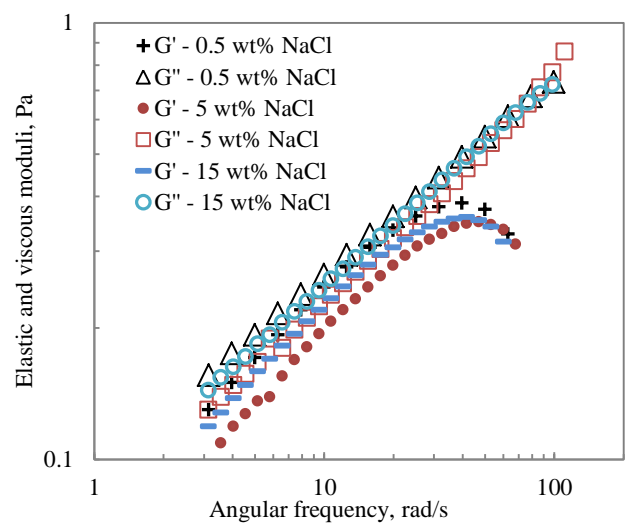


Fig. 15 – Dynamic frequency tests for PSP - Salinity dependence with 1000 ppm polymer.

**Core flooding experiments**

Polymer flood tests were conducted in Bentheimer sandstone plugs (type Gildehaus) to investigate the effects of the permeability of the porous media and the salinity of the brine on the polymer viscosity.

**Experimental set-up:** The experimental set-up (Fig. 16) consisted of 2 serial mounted coreholders, a 2-syringes pump and two pressure transducer cells to measure the pressure drop across the plug – 0.2 bar and 5 bar. The 0.2 bar transducer gave the possibility to measure low values accurately. The first core acted as a filter to prevent the formation of a filtration cake on the second core on which the measurements were conducted. The first plug was always chosen with a lower permeability than the second plug to trap more of the particles that may cause a filtration cake on the second plug. The pump provided a maximum pressure of 5 bar. Measures of pressure drops were recorded on a plotter.

**Core flooding experiments:** Small plugs were used for the tests with permeabilities varying from 500 mD to 2 D. Dimensions can be found in Table 2. A new plug was used for each experiment. All experiments were conducted at 20°C. The salinity of the brine ranged from 5 wt% to 15 wt%. The polymer concentration used was 500 ppm for AMPS and PSP. 150 ppm was used for HAP to have comparative viscosity levels with the other polymers. Due to its high molecular weight, HAP at a concentration of 500 ppm gave viscosity values above 260 mPa.s at low shear rates in porous media.

The plugs were fitted inside a Hassler cell with a rubber sleeve with an overburden pressure of 20 bar. Air was evacuated from the plug using a vacuum pump. The plugs were then saturated with degassed brine and the pore volume measured, from which the porosity of the plug was estimated. The pressure drop across the plug was measured while flooding it with brine at



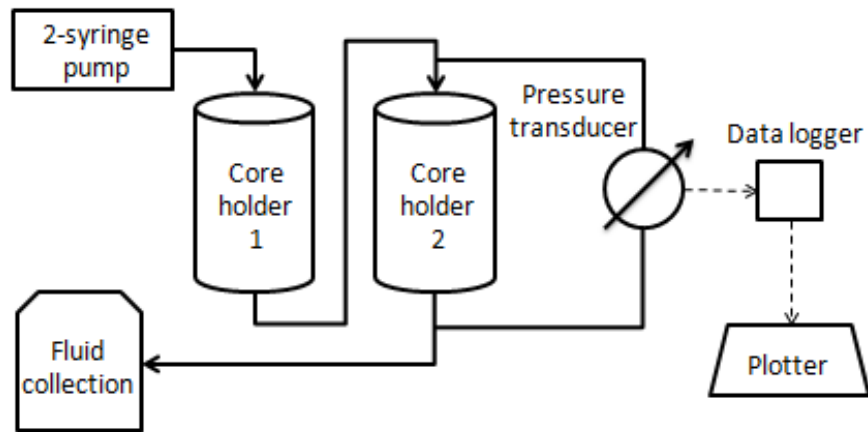


Fig. 16 – Schematic representation of the experimental set-up.

different rates for greater accuracy. The permeability of the plug was calculated using Darcy's law (Equation 12). The permeability measurements were conducted twice for every sample. The results showed good repeatability. The viscosity of the brine was measured using an Anton Paar AMVn viscometer.

The plug was then entirely flooded with degassed polymer solution at constant flow rate until a steady-state pressure drop was reached. This required the injection of 27PV to 45PV for AMPS, 29PV to 50PV for HAP and 13PV to 44PV for PSP. Varying flow rates from 1 to 2,000 ml/h were then applied while recording the pressure drop across the plug. The apparent viscosity of the polymer solutions was calculated using Darcy's law (Equation 12).

The results are shown in Figs. 17 to 22. For all experiments, the apparent viscosity correlated well with the parameter  $u(1 - \phi)/\sqrt{\phi k}$ , where  $u$  is the Darcy velocity,  $\phi$  the porosity and  $k$  the permeability. This parameter is based on a capillary-bundle model of porous media and has been used widely in the literature (Heemskerk *et al.*, 1984; Cannella *et al.*, 1988; Wreath *et al.*, 1990; Seright *et al.*, 2011a and b). To make the results match with the bulk viscosity data, shear rates were divided by respectively 80 and 60 for AMPS and PSP. Those are strictly empirical factors.

**Retention:** Retention includes mechanical trapping, hydrodynamic retention and adsorption (Zaitoun *et al.*, 1987). In most cases, only the adsorption is considered irreversible due to the polymer adsorption on the rock. Adsorption was estimated by flooding brine after the polymer flood to eliminate all polymer particles that were not adsorbed irreversibly by the rock. Brine was flooded at 2 ml/min until the pressure drop across the plug was stabilised. The rock permeability was then measured at different flow rates for greater accuracy. The permeability measurements were conducted twice for every sample. The results showed good repeatability. Table 2 gives the residual permeability reduction factor,  $F_{krr}$ , for each experiment.  $F_{krr}$  is defined as the ratio of the rock permeability to water before polymer flood to the rock permeability to water after polymer flood.

Table 2 – Summary of experiments

Experiment (* with filtration cake)	Solution	NaCl content (wt%)	Core length / diameter (cm) / (cm)	Porosity	Permeability (mD)	Permeability after polymer flood (mD)	$F_{krr}$
1*	AMPS (at 500 ppm)	5	4.72 / 3.00	0.21	2169	1085	2.00
2		5	4.90 / 3.00	0.22	1543	896	1.72
3		5	4.67 / 2.99	0.18	1161	519	2.24
4		5	3.90 / 3.01	0.12	469	262	1.79
5		5	22.91 / 2.95	0.23	2698	731	3.69
6*		10	4.95 / 3.00	0.23	1403	920	1.53
7		10	4.96 / 3.01	0.22	1696	1018	1.67
8*		15	4.73 / 3.00	0.23	1472	792	1.86
9		15	4.90 / 3.00	0.22	1564	890	1.76
10	HAP (at 150 ppm)	5	22.91 / 2.94	0.24	2385	-	-
11		5	4.34 / 3.01	0.20	979	292	3.35
12		5	3.82 / 3.01	0.13	508	125	4.07
13		10	4.54 / 3.01	0.21	1415	322	4.40
14	15	4.35 / 3.01	0.21	1257	217	5.79	
15	PSP (at 500 ppm)	5	4.70 / 3.01	0.21	1647	671	2.45
16		5	22.91 / 2.95	0.23	2124	1091	1.95
17		10	4.61 / 3.01	0.21	1536	713	2.15
18		15	4.88 / 3.00	0.24	1412	873	1.62



Table 2 shows that  $F_{krr}$  for HAP is much higher than for AMPS or PSP. This result suggests that pore plugging or higher polymer retention has occurred for HAP. This was also observed by Seright *et al.* (2011b) and Dupuis *et al.* (2011).  $F_{krr}$  for HAP also increases with salinity.

**Discussion of core flooding experiments:** The behaviour of the polymer solutions is different in porous media compared to bulk. For AMPS, two different results are presented. The first set of experiments showed the formation of a filter cake on the inlet side of the core and a shear-thinning behaviour was observed at low shear rates (Fig. 17 (a)). The experiments were carried out a second time using the double-core set-up to prevent this effect. A Newtonian-like behaviour was then observed (Fig. 17 (b)). This phenomenon has also been observed by Seright *et al.* (2011a). The shear-thinning behaviour of such polymers at low shear rates in porous media may be an experimental artefact due in part to a polymer molecular weight that is too high to propagate without forming an internal or external filter cake. Since that, once the filtration issue was removed, AMPS no longer showed a shear-thinning behaviour, this behaviour appears to be an experimental artefact. Furthermore, Seright *et al.* demonstrate that if such behaviour is observed, it attenuates with increasing salinity. The fact that the experiments in this study have been conducted at high salinity reinforces the previous conclusion.

Eliminating the filtration issues reduced the previously obtained apparent viscosity at low shear rates. For the parameter  $u(1-\phi)/\sqrt{\phi k}$  ranging from 0.1 and 0.5 cm/h.mD<sup>0.5</sup>, the apparent viscosity has a slight shear-thickening behaviour instead of an expected Newtonian behaviour. To test the assumption that this behaviour is due to the use of short cores, an experiment with a 22.91 cm long core was carried out. The results are shown in Fig. 17(b) (open diamonds). A Newtonian behaviour was observed with a viscosity 2.4 higher than the bulk. This is consistent with literature reports that the viscosity of viscoelastic polymers can be higher in porous media than in bulk (Pye, 1964; Seright *et al.*, 2009) due to polymer retention in the rock. Table 2 shows that  $F_{krr} = 3,69$  for this experiment which implies high retention.

At higher shear rates, a shear-thickening behaviour occurs. When flowing in porous media, viscoelastic polymers deform to adjust to the flow field, i.e. to rapid changes of pore throat diameters. Figs. 12 and 9 show respectively that AMPS has some elasticity and that its relaxation time is small. When flowing from one pore throat to another, the polymer molecules have then the time to go back to their original state after being deformed by entering the pore. So the molecules will undergo a series of expansions and contractions (Fig. 1). These expansions increase the viscous friction and onsets the shear-thickening behaviour. At very high shear rates, the apparent viscosity should decrease due to degradation and rupture of the polymer chains (Seright *et al.*, 2009). This last effect was not seen due to experimental equipment's limitation. The results were predicted from the bulk data with the unified apparent viscosity model (Equation 14). An example of good match is shown in Fig. 17 (b).

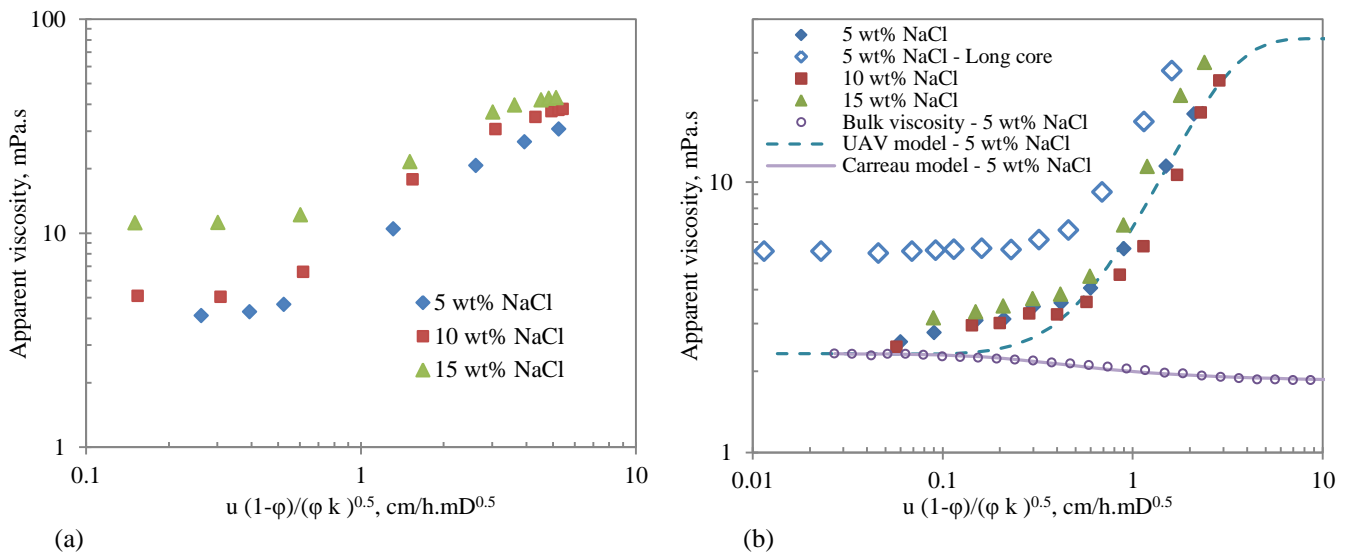


Fig. 17 – Influence of salinity on the apparent viscosity of AMPS at 500 ppm in 1.5 D cores (a) with filtration cake and (b) without filtration cake.

HAP displayed a shear-thinning behaviour (Fig. 19). Figs. 12 and 9 show respectively that HAP has some elasticity and that its relaxation time is high. So when flowing through a pore throat, the polymer chains are expanded and they do not have the time to go back to their original state before going through the next throat. The molecules remain elongated with little friction between them which explains the shear-thinning behaviour (Fig. 18). A second argument is that the polymer network structure is damaged at high shear rates. This reduces the viscosity of the solution and conceals any viscoelastic effects.

HAP displayed very high apparent viscosity at low shear rates, roughly 30 times higher than the bulk viscosity. This phenomenon can be due partly (1) to the use of short cores, (2) and/or to retention (Seright *et al.*, 2011b). To assess the impact

of the core length on the apparent viscosity, an experiment with a 22.91 cm long core was carried out. The results displayed in Fig. 19 (open diamonds) show that the apparent viscosity levels do not decrease. High apparent viscosity levels are then potentially expected deeper into the formation.

If the high apparent viscosity was due to retention, apparent viscosity values should vary with permeability. If it is assumed that small permeable cores have smaller pores and pore throats, pore plugging is expected to be more important in less permeable cores. Fig. 22 shows that this is the case. The residual permeability reduction factors obtained also show that retention may be high (Table 2).

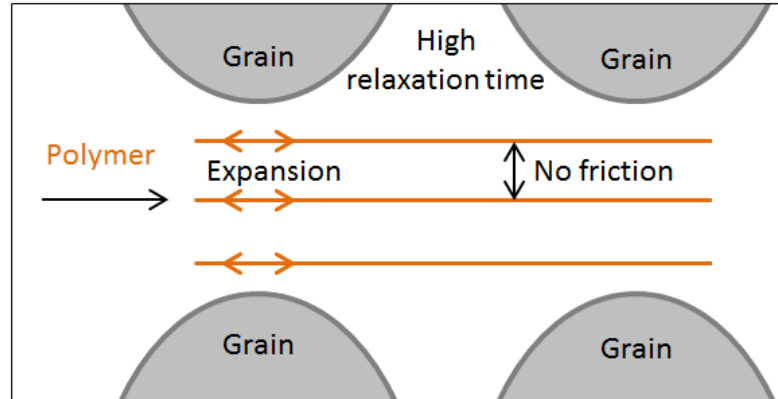


Fig. 18 – Schematic description of shear-thinning behavior in porous media.

PSP has also a shear thinning behaviour in porous media (Fig. 20) despite a high elastic modulus (Fig. 12). PSP has a rigid structure due to its large number of branches (Fig. 11) and its relaxation time is small (Fig. 9). The polymer chains cannot deform themselves much which explains the shear-thinning behaviour. The results matched well with the bulk viscosity data as it has been shown previously in the literature (Cannella *et al.*, 1988; Seright *et al.*, 2011a).

At low velocities, the porous media data depart from the bulk data. To test the assumption that this is due to the use of short cores, an experiment with a 22.91 cm long core was carried out. The results are shown in Fig. 20 (open diamonds). At low velocity, the apparent viscosity exhibit a power-law behaviour and the previous effects are not observed. A plateau was still expected at this range of velocities instead of the power-law behaviour because of the viscosity plateau observed in the bulk data. Seright *et al.* (2011a) studied this phenomenon with Xanthan and concluded it was due to a polymer component that was not expected to propagate very far into the formation. It would be necessary to use internal pressure taps in order to exclude the effect at the core inlet which may be responsible for the lack of plateau at low shear rates.

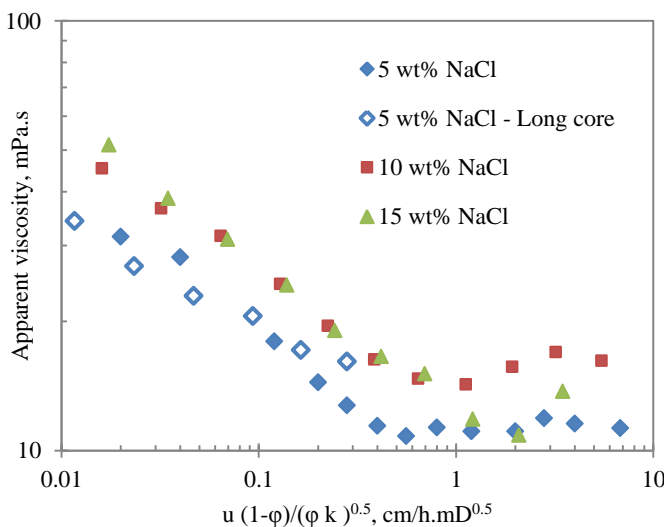


Fig. 19 – Influence of salinity on the apparent viscosity at 500 ppm of HAP in 1.5 D cores – without filtration cake.

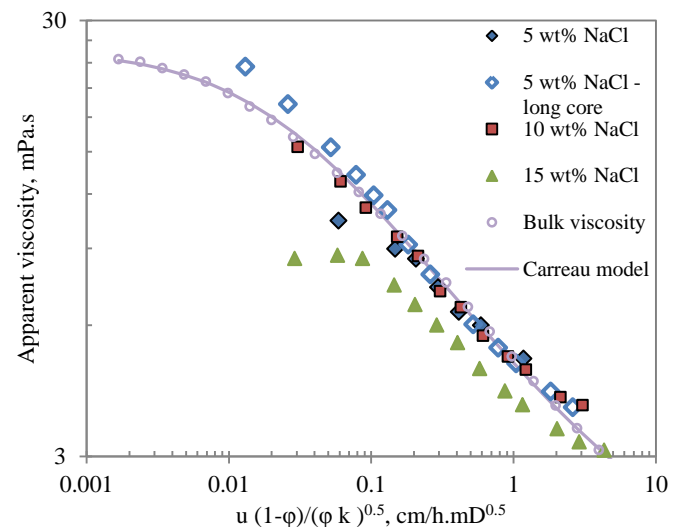


Fig. 20 – Influence of salinity on the apparent viscosity of PSP at 500 ppm in 1.5 D cores – without filtration cake.

**Influence of salinity.** As shown in Fig. 17(b), the apparent viscosity increases with salinity for AMPS. The apparent viscosity is similar for salinities of 5 wt% and 10 wt%. This shows that the addition of salt can enhance intermolecular

associations. For HAP, apparent viscosity increases with salinity up to 10 wt% NaCl and then stabilises for higher salt contents (Fig. 19). This increase in apparent viscosity with salinity can be explained by the increase of the polarity of the solvent which increases the hydrophobic interactions of the polymer chains. This effect offsets the ionic shielding repulsion increasing the viscosity of the solution. PSP is very little affected by salinity in porous media up to 10 wt% NaCl (Fig. 20) due to its low anionicity. At 15 wt% NaCl, the apparent viscosity decreases slightly.

**Influence of permeability.** As shown on Fig. 21, the apparent viscosity of AMPS is fairly similar for permeabilities of 1D and 1.5 D. It decreases though when lowering the permeability to 500 mD. This is due to the inaccessible pore volume (IPV). It is assumed that the size of pores and pore throats decrease with permeability. Then, at low permeabilities, the polymer molecules cannot flow through all the pores due to their size. So, the polymer travels faster through the less permeable core and the viscosity is lowered. Apparent viscosity increases with decreasing permeability for HAP (Fig. 22). This is due to the high retention of HAP in sandstone cores (see Table 2). Retention overcomes the IPV effect and the polymer travels slower. This delay increases the apparent viscosity.

The influence of permeability on the apparent viscosity of a similar polysaccharide to PSP has been studied by Cannella *et al.* (1988). He reported that in Berea sandstone cores with permeabilities ranging from 100 mD to 740 mD the apparent viscosity had similar values.

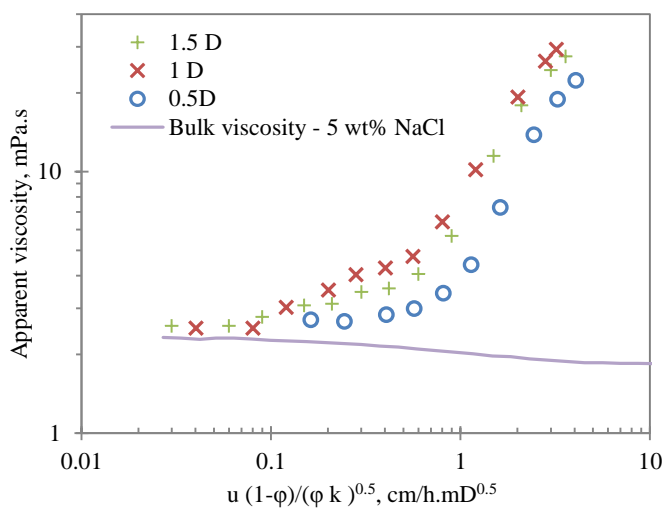


Fig. 21 – Influence of permeability on the apparent viscosity of AMPS at 5 wt% NaCl.

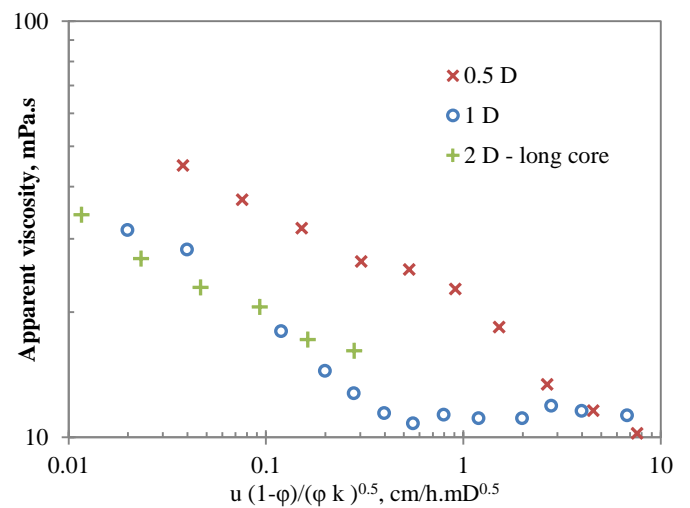


Fig. 22 – Influence of permeability on the apparent viscosity of HAP at 5 wt% NaCl.

**Application to German reservoirs:** The polymers presented in this paper were studied as potential candidates for polymer floods in German oilfields. Several polymer properties can affect injectivity such as polymer behaviour in porous media and mechanical degradation (Seright *et al.*, 2009). Injectivity is defined as the ratio of the injection rate by the downhole pressure difference between the well and the formation.

When polymer solutions are injected into a well with no fractures, the maximum shear rate occurs when the polymer solution enters the formation. The shear rate will decrease thereafter. In porous media, the shear rate can be calculated using Equation 15 which is derived from the Hagen-Poiseuille equation for flow in capillary tubes:

$$\dot{\gamma} = \frac{4\beta v}{\sqrt{8k/\phi}} \dots\dots\dots (15)$$

where  $\beta = 2.5$ ,  $v$  is the velocity,  $k$  the water permeability and  $\phi$  the porosity. For a perforated well with 6 perforations per foot, with a flow rate of 150 m<sup>3</sup>/d over a 10 meter interval with a permeability of 2 Darcy, a porosity of 0.22, a well radius of 7'' and a perforation diameter of 3''1/2, the maximum shear rate is approximately 1.7 x 10<sup>3</sup> s<sup>-1</sup>. This corresponds to a value of 21.2 cm/h.mD<sup>0.5</sup> for the parameter  $u(1 - \phi)/\sqrt{\phi k}$ . This is obtained by dividing the shear rate by 80 to match the results as explained previously. This value is well beyond the shear-thickening range of AMPS where mechanical degradation would certainly occur (Fig. 17(b)). Higher concentrations of AMPS will then be necessary to counteract the viscosity loss due to mechanical degradation while injecting. This issue overthrows the displacement efficiency advantages of shear-thickening behaviour (Han *et al.*, 1995; Wang *et al.*, 2000; Urbissinova *et al.*, 2010).

On the contrary, HAP and PSP are more resistant to mechanical degradation due to their shear-thinning behaviours. Polysaccharides are known to be very resistant to mechanical degradation (Sorbie, 1991). HAP displays a shear reversibility

that is very beneficial in terms of injectivity. The shear-thinning behaviour lowers the viscosity at high shear rates which improves injectivity at the well bore. Further away in the formation, the shear rate is reduced and the viscosity is restored. HAP has very high viscosity levels at low shear rate which is favourable for displacement efficiency. However, HAP displays high retention in sandstone cores which will increase the amount of polymer needed. It also has a sharp increase in viscosity with polymer concentration which may cause issues in the performance of polymer floods in the field if small errors in concentration are made.

### Conclusions and Future Work

The rheological properties (both in bulk and in sandstone cores) of a newly developed hydrophobically associative polymer, HAP, were studied. Comparisons were made with two commercially available polymers, a copolymer of ATBS and acrylamide (AMPS) and a polysaccharide polymer (PSP).

- In porous media, AMPS showed two different viscosity regimes when the filtration effects were removed. At low shear rates, when flowing through a 22.91 cm long core, the polymer solution had a Newtonian behaviour with values higher than bulk due to retention. At higher shear rates, a shear-thickening behaviour occurred; this is due to the expansion – contraction transition of the polymer molecules in elongational flow which onsets the dilatancy.
- HAP showed shear-thinning behaviour in porous media, with viscosity levels 30 times higher than in bulk at low shear rates, which is partly due to retention. Experiments in 22.91 cm long cores gave similar results; high apparent viscosity levels are then potentially expected deeper in the formation.
- PSP displayed a shear-thinning behaviour with viscosity values very similar to the bulk viscosity when using 22.91 cm long cores.
- In Bentheimer cores, salinity increased the apparent viscosity of HAP due to the intensification of hydrophobic interactions in high polar salty environments.
- For AMPS, apparent viscosity decreased with permeability due to inaccessible pore volume; if lower permeability implies smaller pores, the polymer molecules cannot enter all the pores due to their size and travel faster through the core. On the contrary, apparent viscosity of HAP increased with decreasing permeability due to high retention.
- Injectivity of AMPS is compromised due to the mechanical degradation of the polymer occurring at high shear rates. The shear reversibility of HAP, its high viscosity level at low shear rates and its high molecular weight make HAP a favourable candidate for field polymer flooding. Though its high retention may be an issue. PSP is also very resistant to mechanical degradation.

Further studies need to be conducted to determine the feasibility of polymer floods with the studied polymers. These include temperature and stability studies, as well as oil recovery experiments at reservoir conditions.

### Nomenclature and abbreviations

C	=	Shear rate coefficient
F <sub>krr</sub>	=	Residual permeability reduction factor
G	=	Relaxation modulus of fluid, Pa
G'	=	Elastic or storage modulus, Pa
G''	=	Viscous or loss modulus, Pa
G*	=	Complex modulus, Pa
k	=	Permeability, D
k <sub>f</sub>	=	Flushed water permeability, D
K	=	Power-law coefficient
L	=	Length of core, m
Mr	=	Mobility ratio
n	=	Power-law index
n <sub>2</sub>	=	Shear-thickening index
N, N <sub>1</sub>	=	Empirical constants
ΔP	=	Pressure drop across the core, Pa
u	=	Darcy velocity, m/s
v	=	Velocity, m/s
α	=	Empirical constant
β	=	Constant equal to 2.5
η	=	Viscosity, Pa.s
η <sub>0</sub>	=	Low viscosity plateau, Pa.s
η <sub>∞</sub>	=	High viscosity plateau, Pa.s

$\eta^*$	=	Complex viscosity, Pa.s
$\eta'$	=	Real part of complex viscosity, Pa.s
$\eta''$	=	Imaginary part of complex viscosity, Pa.s
$\eta_{app}$	=	Apparent viscosity, Pa.s
$\eta_{max}$	=	Viscosity plateau beyond which degradation occurs, Pa.s
$\gamma$	=	Shear strain
$\gamma_0$	=	Maximum amplitude of shear strain
$\dot{\gamma}$	=	Shear rate, 1/s
$\dot{\gamma}_{eff}$	=	Effective shear rate, 1/s
$\dot{\gamma}_{1/2}$	=	Shear rate at which the viscosity is the average of $\eta_0$ and $\eta_{\infty}$ , 1/s
$\lambda$	=	Time empirical constant, s
$\lambda_2$	=	Empirical constant
$\lambda_o$	=	Oil mobility, m <sup>2</sup> /Pa.s
$\lambda_p$	=	Polymer mobility, m <sup>2</sup> /Pa.s
$\omega$	=	Angular frequency, rad/s
$\tau$	=	Shear stress, Pa
$\tau_r$	=	Relaxation time, s
$\phi$	=	Porosity

AMPS	=	Co-polymer of ATBS and acrylamide
ATBS	=	2-acrylamido-2-methyl propane sulfonic acid polymer
EOR	=	Enhanced oil recovery
HAP	=	Hydrophobically associative polymer
HPAM	=	Partially hydrolysed polyacrylamide
IPV	=	Inaccessible pore volume
LVR	=	Linear viscoelastic region
Mw	=	Molecular weight
PSP	=	Polysaccharide polymer
UAV	=	Unified apparent viscosity model

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## APPENDICES

### Appendix A1: Critical Literature Review, milestones table

**Table A1.1 – Polymer flooding milestones**

Paper number	Year	Title	Authors	Contribution
SPE 844	1964	Laboratory and field studies of water floods using polymer solutions to increase oil recoveries	B.B. Sandiford	1. First to identify polymer characteristics (water solubility) to have an influence on the flooding results 2. First to show that polymer flooding improves sweep efficiency and microscopic displacement efficiency compared to water flooding alone
SPE 845	1964	Improved Secondary Recovery by Control of Water Mobility	D.J. Pye	First to use polymers to increase water viscosity in order to lower mobility ratio in water flood with conclusive results in improving oil recovery
SPE 1687	1966	Flow of viscoelastic fluids through porous media	R.J. Marshall, A.B. Metzner	First to show the viscoelastic effect of an increased pressure drop to values well above those expected for purely viscous fluids
SPE 2545	1970	Polymer flooding - A current appraisal	R.L. Jewett, G.F. Schurz	First to examine ranges of some of the more important parameters for polymer flooding success based on field reports
IECF i160039 a012	1971	Viscoelastic effects in the flow of non-Newtonian fluids through a porous medium	E.H. Wissler	First to account quantitatively for the elongational stresses developed in viscoelastic flow through porous media.
SPE 4025	1972	Viscoelastic effects in polymer flow through porous media	W.B. Gogarty, G.L. Levy, V.G. Fox	First to provide a basis for detecting viscoelastic fluids with a visco-inelastic power-law analysis
SPE 12652	1984	Quantification of viscoelastic effects of polyacrylamide	J. Heemskerk, R. Janssen-van Rosmalen, R.J. Holtslag, D. Teeuw	First to show schematically that polyacrylamide exhibits elastic properties at high flow rates
SPE 30013	1995	The viscoelastic behaviour of HPAM solutions in porous media and its effects on displacement efficiency	Han Xian-Qing, Wang Wei-Ying, Xu Ying	First explain how the viscoelastic properties of polymers play an important role in improving the oil displacement efficiency
SPE 63227	2000	Viscous-Elastic Polymer Can Increase Microscale Displacement Efficiency in Cores	Wang Demin, Cheng Jiecheng, Yang Qingyan, Gong Wenchao, Li Qun, Chen Fuming	First to show that elastic properties of polymers are responsible for the increase in micro-scale displacement efficiency
SPE 113620	2008	Mechanistic interpretation and utilization of viscoelastic behavior of polymer solutions for improved polymer-flood efficiency	M. Delshad, D.H. Kim, O.A. Magbagbeola, C. Huh, G.A. Pope, F. Tarahhom	First to develop an unified apparent viscosity model that accounts for both shear-thinning and shear-thickening behaviour of polymer solutions in porous media over a wide range of flow velocities
SPE 124798	2009	Development of a comprehensive rheological property database for EOR polymers	S. Lee, D.H. Kim, C. Huh, G.A. Pope	First to develop a databases of viscoelastic properties for EOR polymers
SPE 133471	2010	Effect of elasticity during viscoelastic polymer flooding: a possible mechanism of increasing the sweep efficiency	T.S. Urbissinova, J.J. Trivedi, E. Kuru	First to show the effect of elasticity alone on displacement efficiency of polymer floods

## Appendix A2: Critical Literature Review, paper summary

### SPE 844 (1964)

Laboratory and field studies of water floods using polymer solutions to increase oil recoveries

Authors: B.B. Sandiford

#### Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

1. First to identify polymer characteristics (water solubility) to have an influence on the flooding results.
2. First to show that polymer flooding improves sweep efficiency, microscopic displacement efficiency or a combination of these mechanisms compared to water flooding alone.

#### Objective of the paper:

To show that by adding a water-soluble polymer to flood water there is an increase in the efficiency of oil displacement.

#### Methodology used:

1. Laboratory tests: unconsolidated sand-pack flood experiments with linear and radial systems. Polymer slugs were injected preceding or following water. Oil recovery was measured.
2. Field studies: small slugs of polymer solution injected during regular water flood. Increased oil recovery was looked for in the nearby producing wells.

#### Conclusion reached:

1. Adding partially hydrolysed polyacrylamide to flood water increases oil recovery.
2. Laboratory data show that low-concentration solutions of this polymer will increase the recovery of oil ranging from very low to very high viscosity in a non-linear or in a heterogeneous system and high viscosity oil in any system.
3. Field tests also indicate that flooding with low-concentration partially hydrolysed polyacrylamide solutions has possibilities of commercial application to a variety of fields.

#### Comments:

Milestone paper.

This paper takes into account economical parameters of polymer flooding.



**SPE 845 (1964)****Improved Secondary Recovery by Control of Water Mobility**

Authors: D.J. Pye

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

1. First to use polymers to increase water viscosity in order to lower mobility ratio in water flood with conclusive results in improving oil recovery.
2. First to define the apparent viscosity using Darcy's law and the resistance factor.

Objective of the paper:

To study the impact of the solution mobility on areal sweep, permeability distribution and displacement efficiency.

Methodology used:

1. Areal sweep efficiency: models using compressed glass wool as the porous media; areal coverage values at a given mobility ratio are measured.
2. Permeability distribution: two-core experiment using parallel sand-packed tubes; oil produced was measured.
3. Displacement efficiency: typical equilibrium-type experiment where a fixed water-oil ratio was injected into a core to equilibrium and the resulting saturation determined by radio tracer techniques according to Jennings (1958).

Conclusion reached:

In view of the laboratory and field experimental data obtained, this process appears to hold promise to the oil producing industry as a means of increasing recovery and reducing production costs.

Comments:

Milestone paper.

**SPE 1687 (1966)**

Flow of viscoelastic fluids through porous media

Authors: R.J. Marshall, A.B. Metzner

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

First to show the viscoelastic effect of an increased pressure drop to values well above those expected for purely viscous fluids.

Objective of the paper:

To define the conditions under which the Deborah number characteristic of the flow process may become large enough to cause significant deviations from the usual drag coefficient-Reynolds number relationships for purely viscous fluids flowing through porous media under non-inertial conditions.

Methodology used:

1. Non-Newtonian fluid model by Christopher and Middleman (1965) and using a capillary model to define a base equation to measure the deviations in pressure drop due to viscoelastic effects.
2. Experimental: porous medium of a sintered bronze porous disc. Porosity and permeability were determined using the model above. Shear stress-shear rate curves were obtained using either a capillary tube or a cone-and-plate viscometer. Normal stress measurements were obtained using both a rheogoniometric device and a capillary thrust apparatus.

Conclusion reached:

1. The analysis of flow in converging channels suggest that dramatic increases in the pressure drop to values well above those expected for purely viscous fluids should be found at Deborah number levels of the order of 0.1 to 1.
2. The dependence of the observed effects of the homogeneity of the porous medium and their effects on the flow uniformity would appear to be important and require further study.

Comments:

Milestone paper.

**SPE 2545 (1970)**

Polymer flooding - A current appraisal

Authors: R.L. Jewett, G.F. Schurz

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

First to examine ranges of some of the more important parameters for polymer flooding success based on field reports.

Objective of the paper:

To present basic conditions and test results for a large number of polymer flood projects and to examine the ranges of some of the more important parameters within which success has been achieved.

Methodology used:

1. Gathering a list of reservoir and fluid properties for 61 polymer flood projects between 1964 and 1969 – represents more than 95% of all the polymer injected to date as a mobility control agent in flooding.
2. All projects are classified as:
  - Successful: Project is complete and information on the test, substantiating economic recovery, has been published; the initial pilot has been concluded and the polymer flood has now expanded to a commercial application; the project started as a commercially scaled venture, the polymer slug has been or will soon be completely injected, and performance to date is encouraging.
  - Unsuccessful Projects: these projects are considered unsuccessful because no expansion is contemplated.
  - Unsuitable Reservoirs: substantial gas cap; reservoir underlain by extensive bottom water or contiguous to unconfined aquifer; severe injectivity problems; extensive fracturing or extremely high-permeability thief zones; pay zone not isolated.
  - Recently Initiated Projects: data not sufficient to permit evaluation.
3. Ranges of conditions were developed for successful projects.

Conclusion reached:

1. On the basis of the results from a substantial number of field projects, polymer flooding has been found to be successful, as defined, over broad ranges of reservoir conditions and fluid characteristics.
2. The proper selection and design of a polymer flood requires calculation procedures that are sophisticated enough to account for the many variables involved.

Comments:

Milestone paper.

**IECF i160039a012 (1971)**

Viscoelastic effects in the flow of non-Newtonian fluids through a porous medium

Authors: E.H. Wissler

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

First to account quantitatively for the elongational stresses developed in viscoelastic flow through porous media. This provides a basis for experimental study of viscoelastic effects in polymer solutions.

Objective of the paper:

To provide an analytical basis for experimental study of viscoelastic effects in polymer solutions.

Methodology used:

1. Derivation of Darcy's law for flow of a power-law visco-inelastic fluid.
2. Third-order perturbation analysis of flow of a viscoelastic fluid through a converging-diverging channel.
3. Analysis of the flow of a power-law fluid through the same system.

Conclusion reached:

1. Viscoelastic effects can be important in certain cases. When they are, the actual pressure gradient will exceed the purely viscous gradient.
2. A reasonably accurate analysis can be performed for the flow of a visco-inelastic power-law fluid through a converging-diverging channel. This should provide a convenient basis for detecting viscoelastic effects in fluids.

Comments:

Milestone paper.

**SPE 4025 (1972)**

Viscoelastic effects in polymer flow through porous media

Authors: W.B. Gogarty, G.L. Levy, V.G. Fox

Contribution to laboratory studies of polymer flooding for EOR:

Good. This paper distinguished between viscous and elastic behaviours.

Objective of the paper:

To investigate how viscous fluids behave while flowing through unconsolidated porous media and to develop a modified form of Darcy's law for viscoelastic liquids.

Methodology used:

1. Capillary device: used to characterize the elastic response of polymer solutions. The end effects were calculated from an equation suggested by LaNLeve and Bogue,  $\Delta P_T = \Delta P_D + \Delta P_E$ , where  $\Delta P_D$  is the pressure loss resulting from developed flow;  $\Delta P_E$  is the total pressure loss due to end effects.
2. Flow in porous media: pressure drops across the test cell (filled with tight packs of glass beads) were measured from taps placed inside the ends of the core at different flow rates. The apparent viscosity was determined from the experimental data using Darcy's law with the flushed permeability.
3. Modified Darcy's equation: derived from Blake-Kozeny equation developed for a packed bed by considering the porous media as a bundle of capillary tubes and on capillary results.

Conclusion reached:

1. Fluids which exhibit elasticity deviate from viscous flow above some critical velocity in porous flow.
2. For the fluids studied in this work, the elastic exponent,  $m$ , determined from capillary experiments decreases at the same rate as power law index,  $n$ , decreases. This indicates that more elasticity is experienced as the polymer solution becomes more non-Newtonian.
3. The geometry of the porous media significantly affects elastic responses. The critical shear rate at which elastic effects are first noticed is significantly lower for the irregular sand and binary mixtures of glass beads than for regular glass spheres.
4. A narrow range of concentration of CMC and carbopol exists where elastic effects are first noticed. Below this concentration range, viscous forces control; above elastic effects occur.
5. A modified form of the non-Newtonian Darcy equation has been developed to predict the viscous and elastic pressure drop versus flow rate relationships for flow of the elastic CXC solutions in beds of different geometry.

Comments:

The paper shows clearly that the medium used conditions elastic effects. For instance, the elastic component is absent with steady state flow in the capillary device; but it is present during steady state flow in porous media due to the acceleration and deceleration of the fluid upon entering and leaving individual pores.

**SPE 12652 (1984)**

## Quantification of viscoelastic effects of polyacrylamide

Authors: J. Heemskerk, R. Janssen-van Rosmalen, R.J. Holtslag, D. Teeuw

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

First to show schematically that polyacrylamide exhibits elastic properties at high flow rates.

Objective of the paper:

To study the separate effect of viscous and elastic responses of polyacrylamide solutions, especially their shear thickening behaviour beyond a critical flow rate with varying reservoir parameters.

Methodology used:

Core flooding experiments using field sandstone core plugs and sandpacks made of industrial sand. The steady shear viscosity and the viscoelasticity were measured using a rotation viscometer and an oscillation rheometer.

Conclusion reached:

1. For the flow of polyacrylamide solutions in consolidated and unconsolidated sandstones, the onset of shear thickening in terms of a critical flow rate shifts towards higher values with increasing permeability, temperature and decreasing molecular weight and concentration of the polymer.
2. The concept of the Deborah number can only be used to give a first estimate of the critical flow rate.
3. From oscillation rheometry, separating viscous and elastic effects, a practical fluid relaxation time can be derived, which is indicative of the critical flow rate of non-linear polymer solutions.
4. The excess pressure drop due to viscoelasticity is dependent on the fluid characteristics.
5. The description of flow behaviour in cores of viscoelastic polyacrylamide solutions can be approximated using two power-law coefficients and the critical flow rate.

Comments:

Milestone paper.

**SPE 18089 (1988)**

Prediction of xanthan rheology in porous media

Authors: W.J. Canella, C. huh, R.S. SerightContribution to the understanding of physical phenomena in polymer flooding:

Good. This paper shows that the Newtonian behaviour of xanthan at low shear rates is dependent on concentration, temperature and measurement type. It also shows the flow behaviour of the polymer at the pore scale.

Objective of the paper:

1. To compare the rheology of xanthan in porous media and viscometers and relate the two by developing apparent shear rate equations.
2. Modelling a porous medium with a network of capillary tubes to assess connectivity of flow channel influence the apparent viscosity with a power law fluid.

Methodology used:

1. Core flooding with a wide range of polymer concentrations, effective brine permeabilities, residual oil saturations, temperatures and rock lithologies. Viscosity and pressure drop measurements – apparent viscosities determined with Darcy's law.
2. Calculation of the apparent viscosity using an equation derived from the effective medium theory applied to the capillary tube network:

$$\mu_{app} = \frac{K}{\lambda^{3n+1}} \left( \frac{3n+1}{4n} \right)^n \left( \frac{\sqrt{2}\varepsilon u}{\sqrt{k\phi}} \right)^{n-1}$$

Conclusion reached:

1. An apparent shear rate equation has been developed to relate porous media and viscometer measurements.
2. At low shear rates, polymer concentration and temperature have an impact on the rheology (Newtonian behaviour vs power law) and discrepancies arise between porous media and viscometer measurements. New equations were developed for porous media.
3. Biomodel network modelling showed that most of the polymer flow occurs almost without any branching of the flow channels, even though the paths may be tortuous. The flow through the narrower channels is negligible and only the connectivity of the wider channels is important.

Comments:

For conclusion 3), the study was conducted with a pore structure limited to the bimodal distribution of pore sizes. Studies with more realistic distribution of pore sizes should be done to explain the experimental results in a more quantitative manner.

**SPE 30013 (1995)**

The viscoelastic behaviour of HPAM solutions in porous media and its effects on displacement efficiency

Authors: Han Xian-Qing, Wang Wei-Ying, Xu Ying

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

First explain that the viscoelastic properties of polymers play an important role in improving the oil displacement efficiency.

Objective of the paper:

To study the viscoelastic behaviour of HPAM solutions and its effects on oil recovery through core flooding tests and mathematical modelling.

Methodology used:

1. Displacement efficiency: core flooding tests at irreducible water saturation. A comparison between the displacement efficiencies by water flood and by polymer flood was made under identical conditions. Three groups of oil displacement test were performed with cores of different permeabilities.
2. Residual oil saturation: de-oiling tests with 40 cores of different permeability were performed at various injection rates.
3. Mathematical model: 1-D numerical simulation with and without taking the viscoelastic property into account respectively. The rheological behaviour of polymer solution is described by Ellis model and viscoelasticity model respectively.

Conclusion reached:

1. According to the values of the critical velocities determined experimentally, it was shown that viscoelastic effects occur within the common flow rate range in oil reservoir.
2. Comprehensive Han's index can be used to evaluate the viscoelastic characteristics of polymer solution under various reservoir conditions.
3. The viscoelastic property of polymers plays an important role improving oil displacement efficiency. Polymer flood displacement efficiency reaches its maximum when the viscoelastic property of polymer solutions is brought into full play.
4. The empirical equation can be used to predict the relative increment of displacement efficiency under various conditions.

Comments:

Milestone paper.



**SPE 63227 (2000)****Viscous-Elastic Polymer Can Increase Microscale Displacement Efficiency in Cores**

Authors: Wang Demin, Cheng Jiechens, Yang Qingyan, Gong Wenchao, Li Qun, Chen Fuming

Contribution to the understanding of polymer flow in inhomogeneous reservoirs:

First to show that elastic properties of polymers are responsible for the increase in micro-scale displacement efficiency.

Objective of the paper:

To show that viscoelastic polymer flooding increases the recovery at a micro scale.

Methodology used:

1. Core flooding experiments with the following sequence: water-glycerine-HPAM or water-HPAM-glycerine. The recovery of the three chemicals was recorded.
2. Polymer drive experiments with three types of residual oil: in “dead ends”, in pores and “dragged”/”stripped” into threads.
3. Viscoelastic properties measurement with oscillation tests.
4. Pressure cores analysis with cores obtained in an area already polymer flooded.

Conclusion reached:

1. The results in the lab and field show that HPAM solution flooding can increase micro-scale displacement efficiency. The quantitative results will be different for different fluids and reservoir conditions.
2. Work in the lab show that the main reason HPAM fluid can increase micro-scale displacement efficiency in cores is because the fluid has elastic properties.
3. In order to obtain better technical and economical results by chemical flooding, the salinity of the make-up water should be as low as possible and the molecular weight of the polymer and concentration of the fluid as high as possible, care should be taken to avoid polymer degradation.
4. By developing new types of polymers that exhibit higher elastic properties in their fluid state and in different condition (high salinity, high temperature and high shear rate), much more crude oil from reservoirs in the world could be recovered.
5. The behaviour of the flow of viscoelastic fluids through porous medium is quite different from that of fluids with no elasticity. Many results obtained by work on the flow of Newtonian Fluids through porous medium, when used on viscoelastic fluid flow, needs to be re-evaluated.

Comments:

Milestone paper.

**SPE 113620 (2008)**

Mechanistic interpretation and utilization of viscoelastic behaviour of polymer solutions for improved polymer-flood efficiency

Authors: M. Delshad, D.H. kim, O.A. Magbagbeola, C. huh, G.A. Pope, F. Tarahhom

Contribution to the understanding of physical phenomena in polymer flooding:

First to develop a correlation of the shear-thinning and shear-thickening behaviour of polymers over the entire range of flow velocities. These behaviours can be predicted from rheometer-measured shear and oscillatory viscosities.

Objective of the paper:

To develop a correlation of the shear-thinning and shear-thickening behaviour of HPAM polymers over the entire range of flow velocity from rheometric measurements of viscosity only.

Methodology used:

1. Apparent viscosity model for full velocity range composed of:
  - a shear-viscosity-dominant part represented by the Carreau equation and
  - a elongational-viscosity-dominant part represented in terms of Deborah number (Hirasaki and pope, 1974).
2. Models for polymer molecule's relaxation time:  $G'$  and  $G''$  cross-over point model and Rouse model
3. Validation of the above models with rheometer data (bulk viscosity and oscillatory properties) coreflood experiments and published data of Yuan (1981).
4. Implementation and validation of viscosity model in UTCHEM: the apparent viscosity is modelled using Meter's equation.

Conclusion reached:

1. An apparent viscosity model that accounts for both shear-thinning and shear-thickening behaviour of polymer in porous media was developed and was tested by history matching polymer core flood results.
2. The viscoelastic model successfully fit the apparent viscosity over a wide range of Darcy velocity for several polymer solutions.
3. The viscoelastic model was implemented in UTCHEM and successfully history-matched published oil recovery polymer flood laboratory results.

Comments:

Milestone paper for viscoelastic models.

**SPE 124798 (2009)**

Development of a comprehensive rheological property database for EOR polymers

Authors: S. Lee, D.H. Kim, C. Huh, G.A. Pope

Contribution to the understanding of polymer flow in porous media:

Not much on the theory side because the paper summarises work done by others but it quantifies the effects of the main parameters on shear viscosity.

Objective of the paper:

Develop a comprehensive compilation of rheological data and polymer parameters for currently available EOR polymers.

Methodology used:

1. Carreau model for theoretical determination of influence parameters on the shear viscosity
2. Viscosity measurements using TA Instruments advanced rheometric expansion system for experimental measurements with Martin equation for correlation

Conclusion reached:

1. Shear viscosity of polymer solution depends not only on the shear rate but also on the polymer concentration, salinity, hardness and temperature.
2. Martin's equation accurately quantifies the effects of polymer and salts concentration on shear viscosity.

Comments:

Only the shear viscosity side is approached. There is need for a database on the oscillation test side of polymer rheology.

**SPE 129971 (2010)**

Development of a viscoelastic property database for EOR polymers

Authors: D.H. Kim, C.H. Ahn, C. Huh, G.A. Pope

Contribution to the understanding of polymer flow in porous media:

Good. This paper provides valuable rheology data of common polymers and the data needed to use Delshad *et al.* (2008) apparent viscosity model.

Objective of the paper:

To develop a viscoelastic property database for the EOR polymers so that the model parameters for the shear-thickening portion of the apparent viscosity model of Delshad *et al.* (2008) can be obtained.

Methodology used:

1. Apparent viscosity model by Delshad *et al.* (2008).
2. Generalised Maxwell model employed to estimate the relaxation time of the polymer solution.
3. Dynamic rheological measurements made on polymers to confirm the above models.

Conclusion reached:

1. Empirical correlations that relate the characteristic relaxation time with process variables such as polymer concentration, salinity, divalent ion content and temperature have been established.
2. When compared to the relaxation time values obtained from the  $G'$  and  $G''$  data measured for specific reservoir conditions, the empirical correlations provided quite satisfactory predictions of the relaxation time, with input of these reservoir parameters.
3. The predicted relaxation time, when employed into the apparent viscosity model of Delshad *et al.* (2008), allows a reasonable prediction of the shear-thickening behaviour of the polymers studied.

Comments:

Sequel to Lee *et al.* (2009)

**SPE 133471 (2010)**

Effect of elasticity during viscoelastic polymer flooding: a possible mechanism of increasing the sweep efficiency

Authors: T.S. Urbissinova, J.J. Trivedi, E. Kuru

Contribution to laboratory studies of polymer flooding for EOR:

Good. This paper clearly shows the effect of elastic behaviour of polymer alone on recovery.

Objective of the paper:

To study the effect of elasticity alone of polymer-based fluids on the microscopic sweep efficiency.

Methodology used:

Use of two polymers with similar shear viscosity but significantly different elastic characteristics.

1. Rheological characterisation of polymer solution: viscometry tests, oscillation tests (elastic and viscous modulus) – distinction between elastic and viscous properties.
2. Polymer flooding experiments: porous media of solid glass beads, water used as the flowing medium and Darcy's law for radial steady-state flow for permeability measurements. Polymer solutions were injected into the radial core by using a constant rate pump, with pressure measurements throughout the experiment. The effluent fluids were collected and the resulting oil recovery was recorded.

Conclusion reached:

1. Wider molecular weight (MWD) distribution of the polymer solution increases the elastic properties of the solution.
2. The sweep efficiency of polymer floods could be improved by optimizing the MWD of the polymer solution.
3. Later breakthrough time and higher recovery observed when flooding the polymer solution with higher elasticity can be attributed to elastic properties of the polymer solution.

Comments:

Milestone paper.

**SPE 129200 (2011)**

New insights into polymer rheology in porous media

Authors: R.S. Seright, T. Fan, K. Wavrik, R. de Carvalho Balaban

Contribution to the understanding of polymer flow in porous media:

Good because this paper resolves discrepancies in the literature about the rheology behaviour of two major polymer used in EOR.

Objective of the paper:

To clarify about the rheology of xanthan and hydrolysed polyacrylamide (HPAM) solutions in porous media at low velocities.

Methodology used:

Core flooding with variation of injection rate and measurement of resistance factor.

Conclusion reached:

1. At low velocities in short cores with sufficiently low permeability, fresh xanthan solutions show shear thinning whereas viscosity predict Newtonian behaviour. This is due to a polymer component that propagates at a lower rate than the remainder of the polymer solution.
2. In short cores with sufficiently low permeability, shear thinning can be observed for fresh HPAM solutions at low fluxes. This phenomenon can be eliminated or reduced by increasing the flow rate or by passing the solution through a few feet of rock at low flux.
3. Under the conditions where HPAM is used for EOR, the extent of shear thinning is very low especially compared to the shear thickening phenomenon that appears at high fluxes.

Comments:

This paper gives conditions at which shear-thinning behaviour may occur or not for HPAM solutions at low flow rates. Methods are also given to determine if the behaviour observed in an experimental artefact.

**SPE 141355 (2011)****Rheology of a new sulfonic associative polymer in porous media**

Authors: R.S. Seright, T. Fan, K. Wavrik, H. Wan, N. Gaillard, C. Favéro

Contribution to the understanding of polymer flow in porous media:

Good because this paper presents and explains the rheology of a new associative polymer.

Objective of the paper:

To establish (1) whether the associative polymer provided higher resistance factors in porous media compared to HPAM, (2) whether these enhanced resistance factors are expected to propagate deep into the formation and (3) the resistance to mechanical degradation of the associative polymer compared to HPAM.

Methodology used:

1. Core flooding experiments in Berea sandstone cores and porous-polyethylene cores.
2. Core flooding experiments in 78cm, 157cm and 122cm long cores with internal pressure taps.
3. Core flooding experiments with reinjection of effluent submitted at a 2,500 psi/ft pressure gradient.

Conclusion reached:

1. In Berea sandstone and porous polyethylene cores, low-flux resistance factors for fresh associative polymer were at least twice those that HPAM.
2. After exposure to 2,500 psi/ft pressure gradient, associative polymer solutions experienced 19-35% viscosity loss, whereas HPAM solutions experienced 5-17% viscosity loss.
3. Those higher than expected resistance factors are expected to propagate deep into the reservoir.
4. The associative polymer appears to contain a species that propagates through porous rock at rates comparable to those for HPAM and a second species that moves much more slowly and creates much higher resistance factors.

Comments:

Very clear approach to explain the behaviour of the associative polymer and its difference from the bulk viscosity.

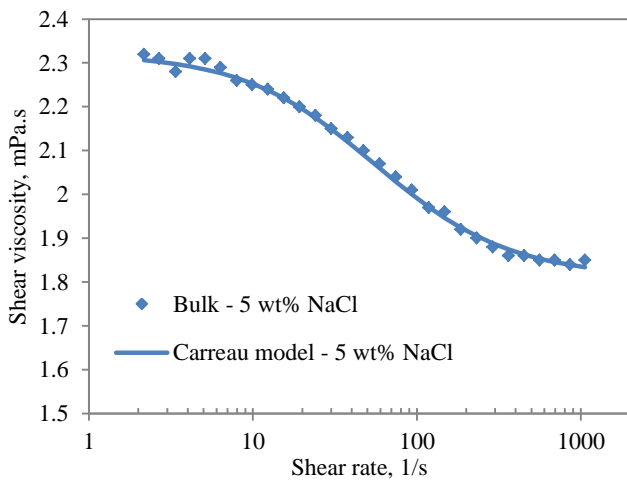
### Appendix B: Carreau model parameters

The bulk viscosity measurements can be fitted with the Carreau model (Equation 4). Equation 4 is reminded below. The best fit model parameters for AMPS, HAP and PSP solutions at 500 ppm are summarized in Table B1. Figs. B1 to B3 compare the measurements with the Carreau model for AMPS, HAP and PSP respectively.

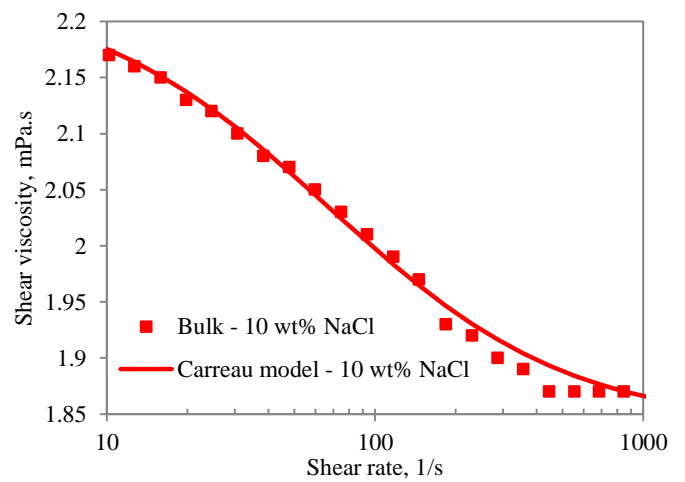
$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})[1 + (\lambda\dot{\gamma})^{\alpha}]^{\frac{N-1}{\alpha}} \dots\dots\dots (4)$$

**Table B1 – Carreau model parameters**

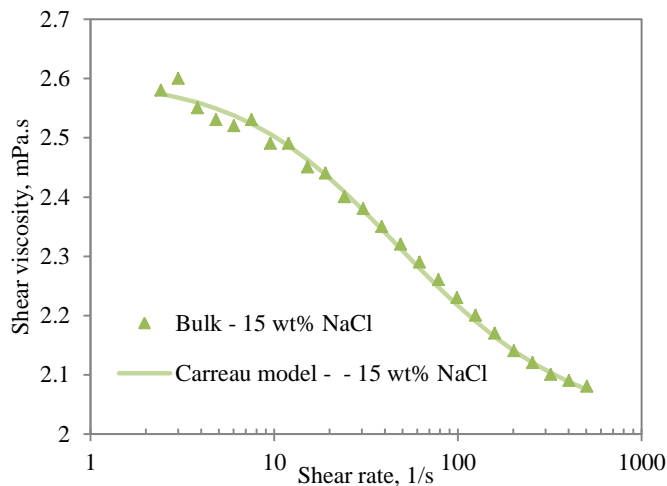
Polymer	NaCl concentration	$\eta^0$ (mPa.s)	$\eta^{\infty}$ (mPa.s)	$\lambda$ (s)	$\alpha$	N
AMPS	5 wt%	2.3	1.8	0.020	1.10	0.005
	10 wt%	2.2	1.8	0.014	0.95	0.005
	15 wt%	2.6	2.0	0.030	1.05	0.25
HAP	5 wt%	1.8	1.7	0.035	2.40	0.12
	10 wt%	2.4	1.9	0.037	1.10	0.20
	15 wt%	1.5	1.4	0.050	0.90	0.10
PSP	5 wt%	25.8	1.2	0.750	0.84	0.51
	10 wt%	31.0	1.2	0.900	0.75	0.52
	15 wt%	28.5	1.8	0.800	0.68	0.47



(a)



(b)



(c)

**Fig. B1 – Viscosity versus shear rate for AMPS at 500 ppm (a) at 5 wt% NaCl (b) at 10 wt% NaCl (c) at 15 wt% NaCl.**



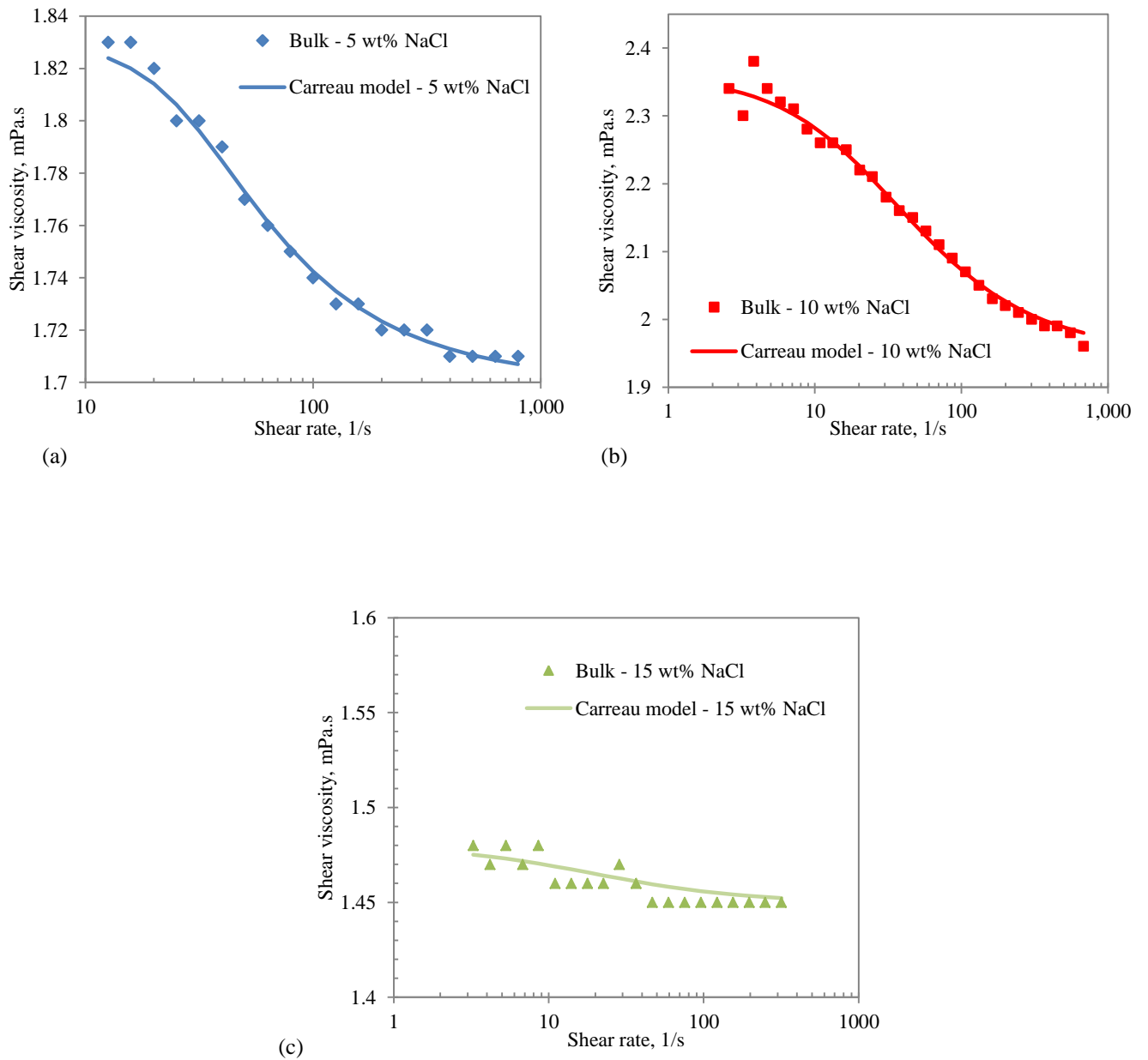


Fig. B2 – Viscosity versus shear rate for HAP at 500 ppm (a) at 5 wt% NaCl (b) at 10 wt% NaCl (c) at 15 wt% NaCl.

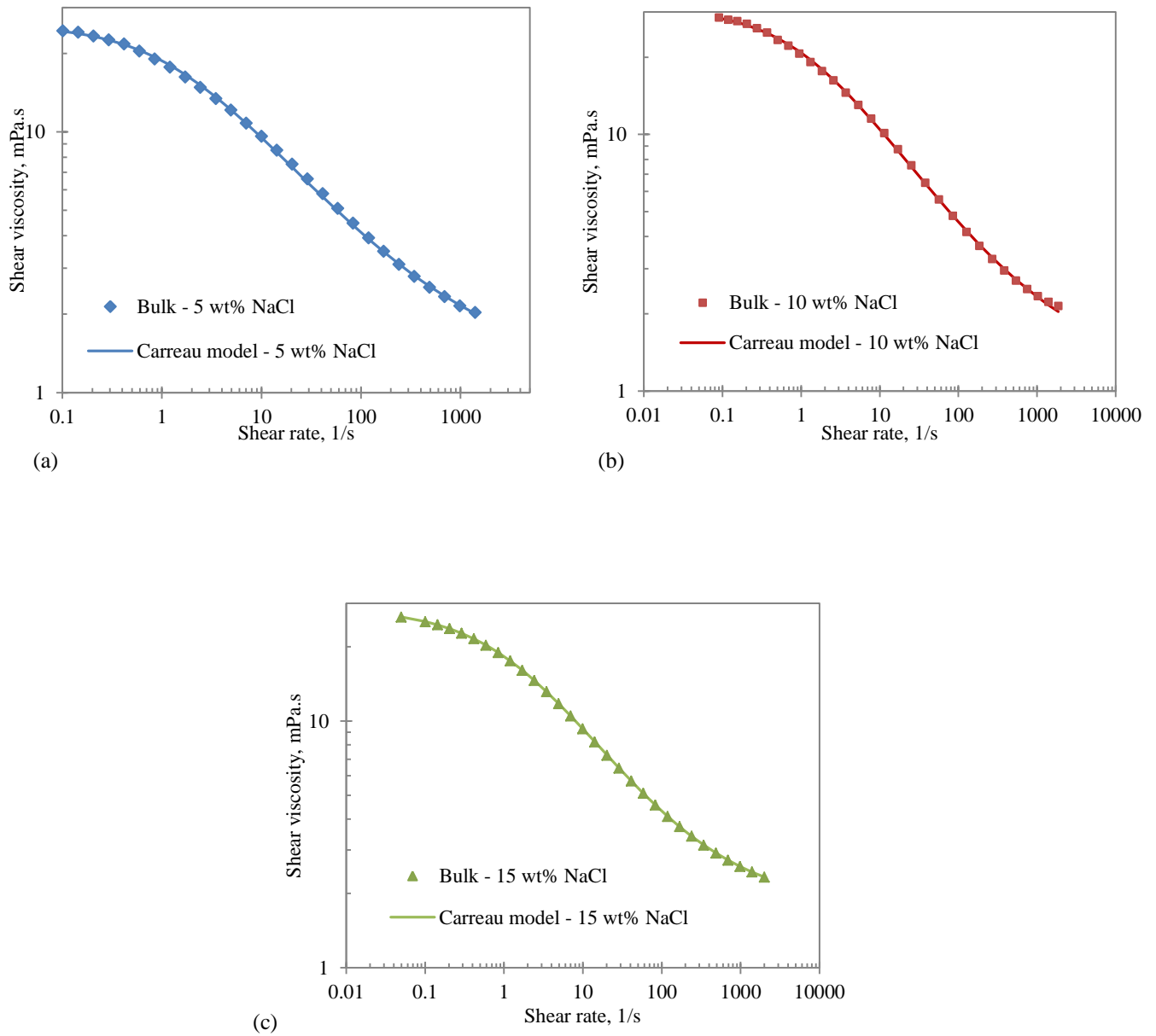


Fig. B3 – Viscosity versus shear rate for PSP at 500 ppm (a) at 5 wt% NaCl (b) at 10 wt% NaCl (c) at 15 wt% NaCl.

## Appendix C: Additional data on rotation and oscillation tests results

- Good repeatability of viscosity results

To acquire a reproducible measurement, a constant shear of 30 Pa, 20 Pa for PSP solutions, was applied to the system for 5 minutes. The shear viscosity results shown are the one obtained after the 5 minutes shearing. The measurements were conducted twice for all samples. The results showed good repeatability.

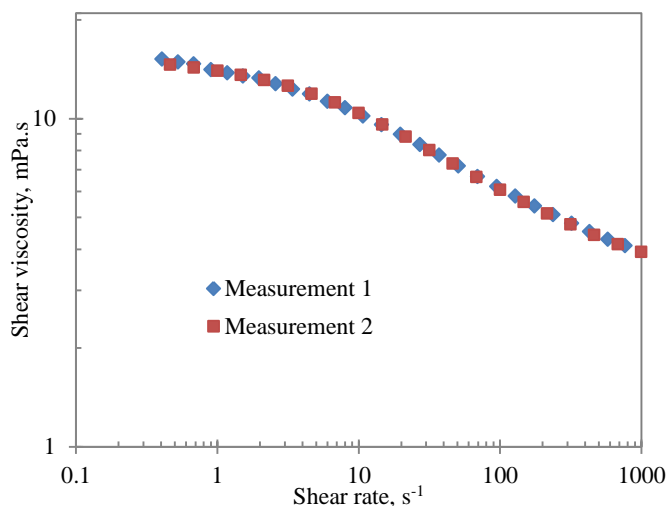


Fig. C1 – Viscosity measurement repeatability for AMPS (1000 ppm, 0.5 wt% NaCl).

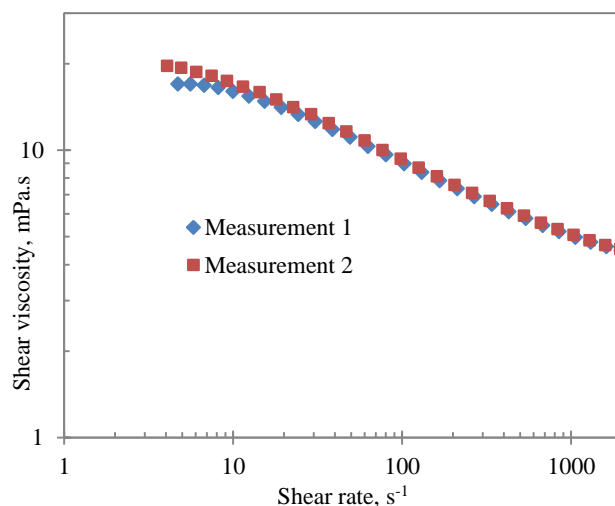


Fig. C2 – Viscosity measurement repeatability for HAP (1000 ppm, 0.5 wt% NaCl).

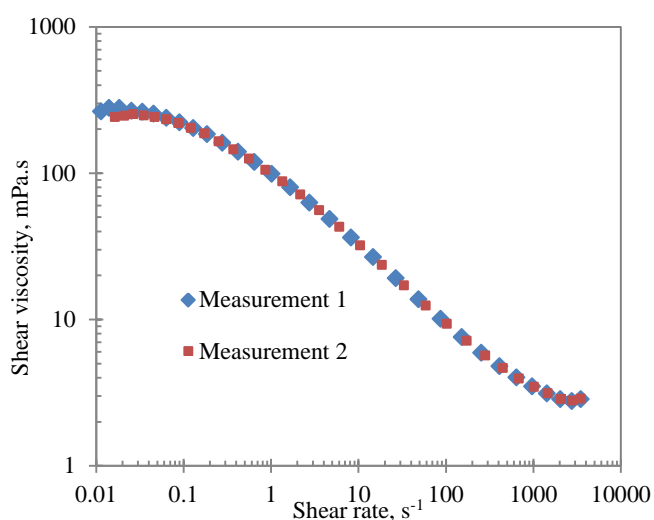
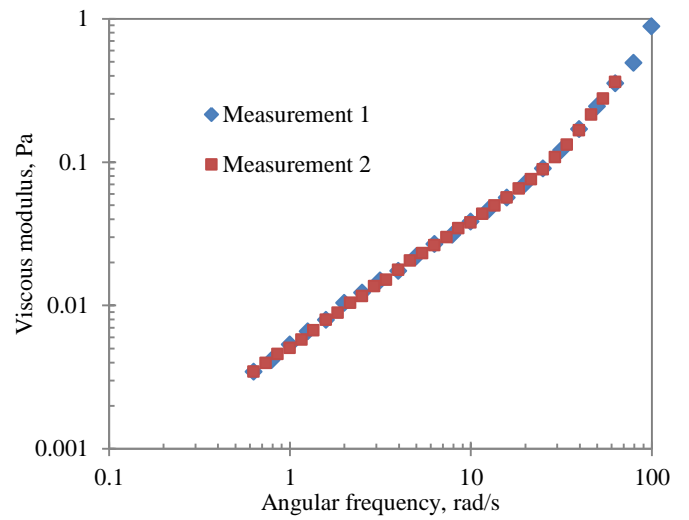
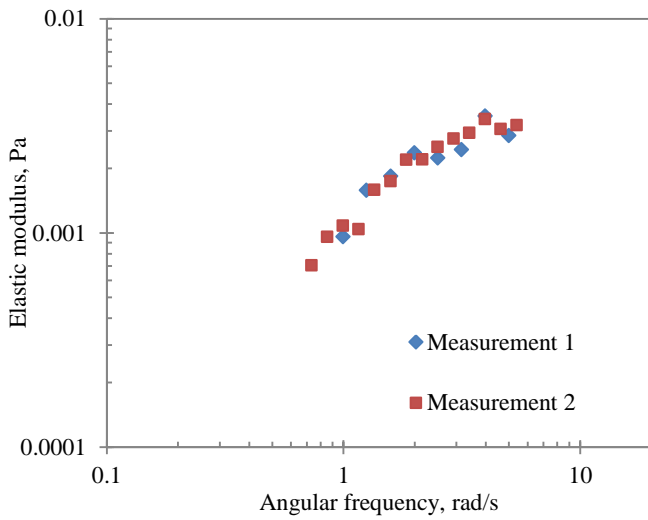
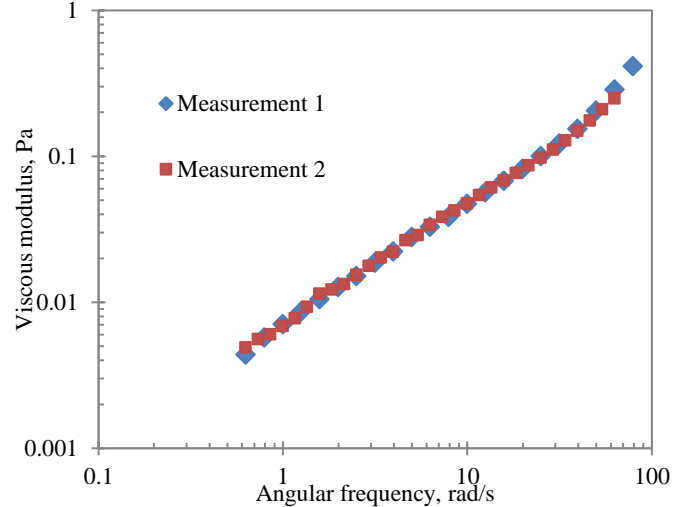
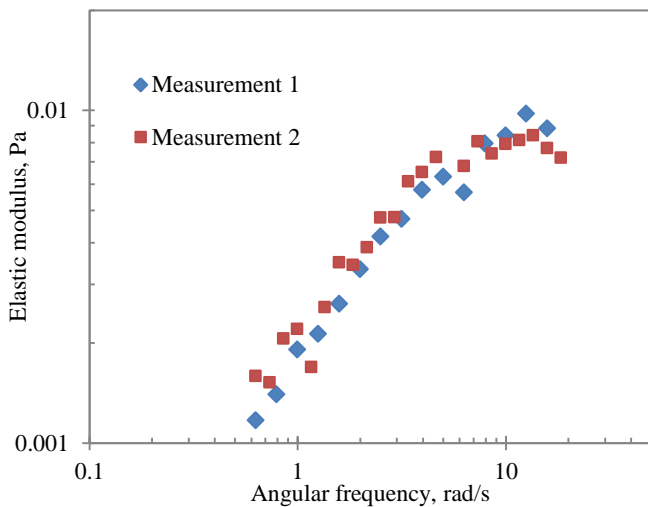


Fig. C3 – Viscosity measurement repeatability for PSP (1000 ppm, 0.5 wt% NaCl).

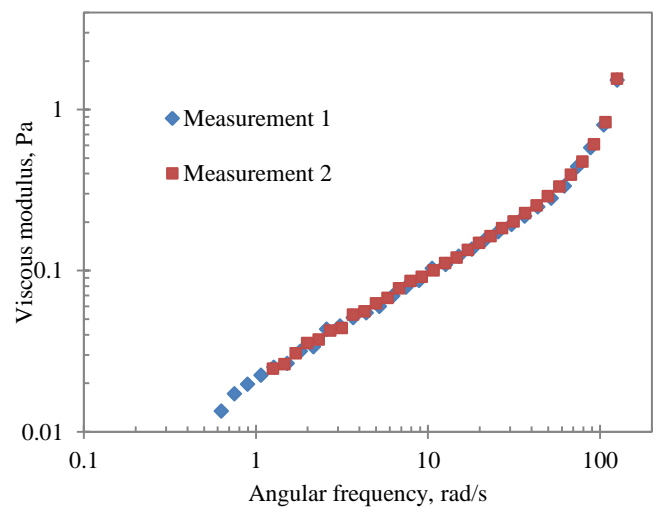
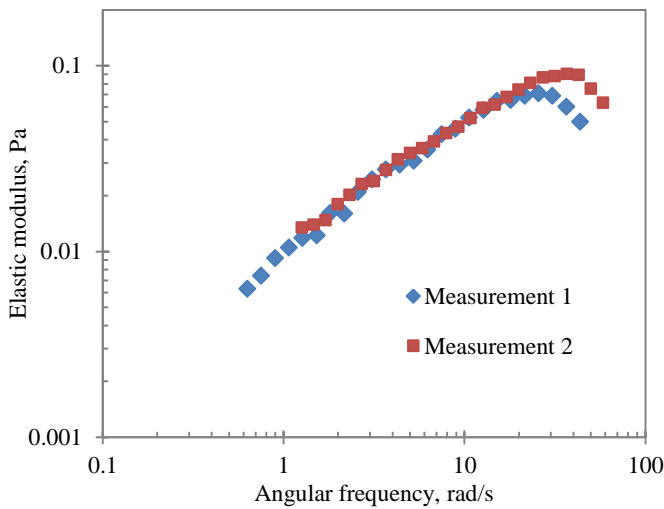
- Good repeatability of oscillation tests results



**Fig. C4 – Repeatability of oscillation measurements for AMPS (500 ppm, 0.5 wt% NaCl).**



**Fig. C5 – Repeatability of oscillation measurements for HAP (500 ppm, 0.5 wt% NaCl).**



**Fig. C6 – Repeatability of oscillation measurements for PSP (500 ppm, 0.5 wt% NaCl).**

- Polymer concentration influence on shear viscosity

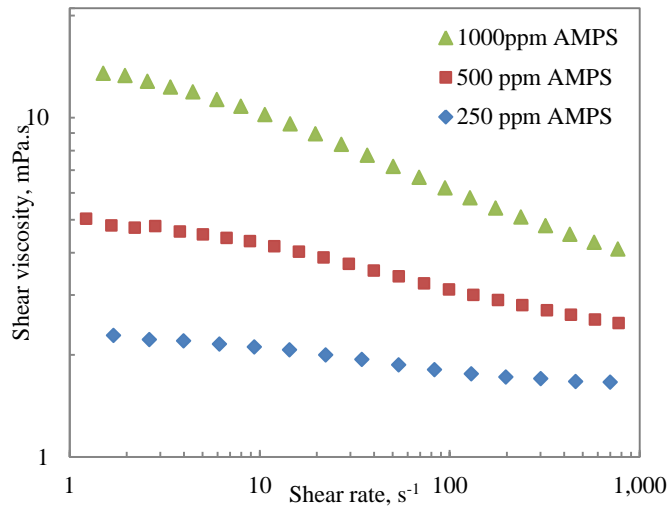


Fig. C7 – Rotation tests for AMPS - Polymer concentration dependence at 0.5 wt% NaCl.

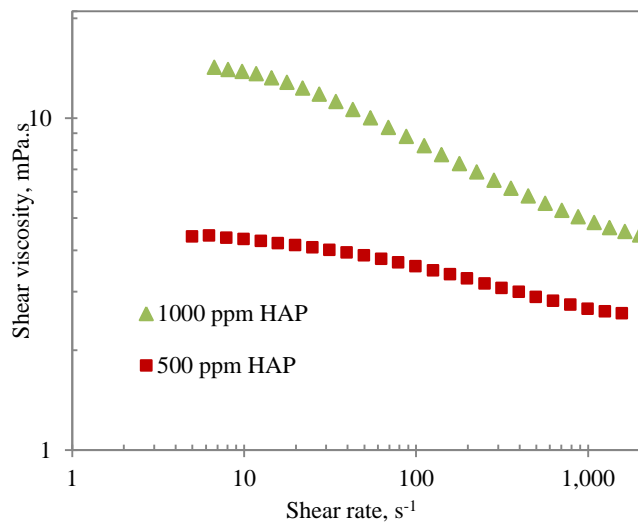


Fig. C8 – Rotation tests for HAP - Polymer concentration dependence at 0.5 wt% NaCl.

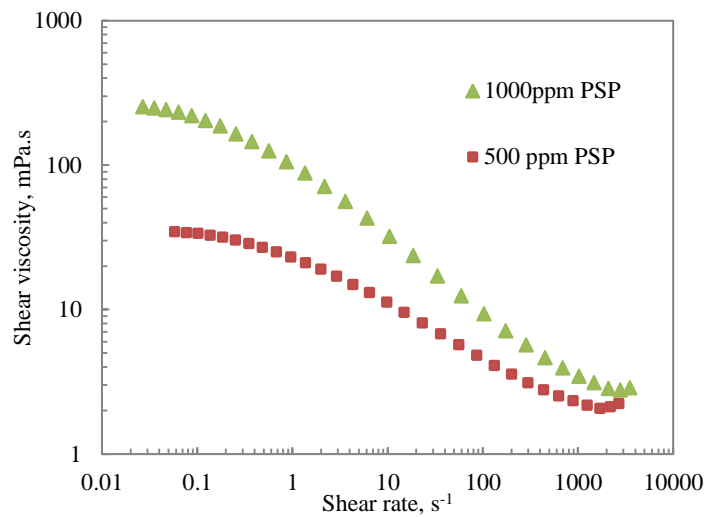


Fig. C9 – Rotation tests for PSP - Polymer concentration dependence at 0.5 wt% NaCl.

• Polymer concentration influence on elastic and viscous moduli

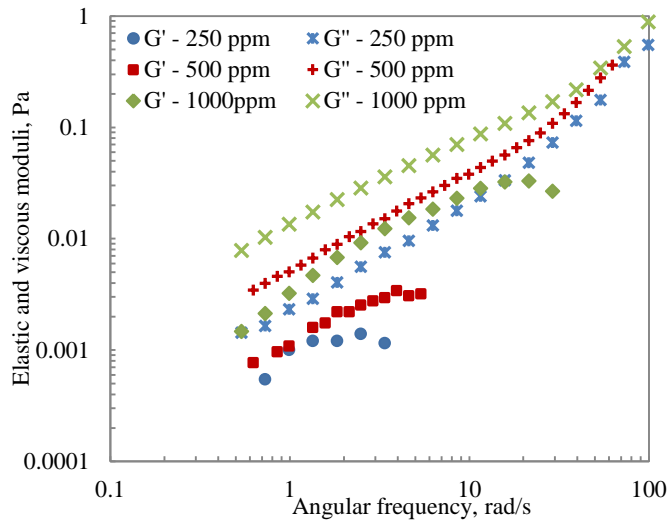


Fig. C10 – Dynamic frequency tests for AMPS - Polymer concentration dependence at 0.5 wt% NaCl.

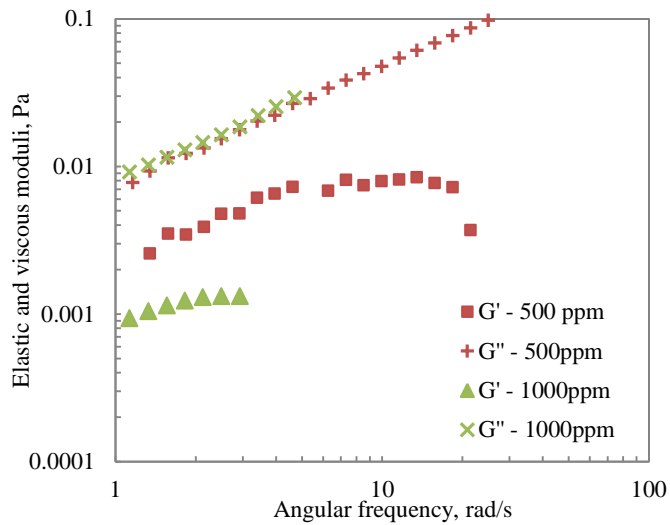


Fig. C11 – Dynamic frequency tests for HAP - Polymer concentration dependence at 0.5 wt% NaCl.

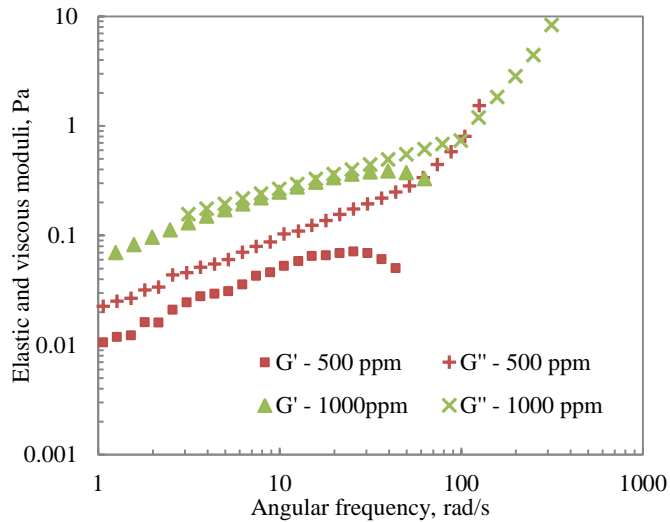


Fig. C12 – Dynamic frequency tests for PSP - Polymer concentration dependence at 0.5 wt% NaCl.

## Appendix D: Calculation of core plug porosity and absolute permeability



Fig. D1 – Example of Gildehaus sandstone core plug.

- Porosity data

**Table D1 – Porosity data**

Experiments	Core data			Calculations	
	Length (cm)	Diameter (cm)	Pore volume (ml)	Volume (cm <sup>3</sup> ) = L*π*(D/2) <sup>2</sup>	Porosity (%) =PV/V
1	4.72	3.00	6.93	33.36	20.8
2	4.90	3.00	7.66	34.64	22.1
3	4.67	2.99	6.03	32.79	18.4
4	3.90	3.01	3.44	27.75	12.4
5	22.91	2.95	34.48	156.06	22.7
6	4.95	3.00	7.88	34.99	22.5
7	4.96	3.01	7.73	35.29	21.9
8	4.73	3.00	7.53	33.43	22.5
9	4.90	3.00	7.68	34.64	22.2
10	22.91	2.94	37.56	155.53	24.1
11	4.34	3.01	6.23	30.88	20.2
12	3.82	3.01	3.49	27.18	12.8
13	4.54	3.01	6.81	32.31	21.1
14	4.35	3.01	6.38	30.95	20.6
15	4.70	3.01	7.16	33.36	21.5
16	22.91	2.95	35.23	156.59	22.5
17	4.61	3.01	7.01	32.80	21.4
18	4.88	3.00	8.36	34.49	24.2

- Permeability data

The permeability of the plugs was calculated using Darcy’s law (Equation 12) which is reminded below. The pressure drop across the plug was measured while flooding the plug with brine at different flow rate for more accuracy.

$$k = \frac{q\mu L}{A\Delta P} \dots\dots\dots (12)$$

The steps to determine k are shown below for Experiment 2. The brine viscosity is shown in Table D2.

**Table D2 – Brine viscosity data**

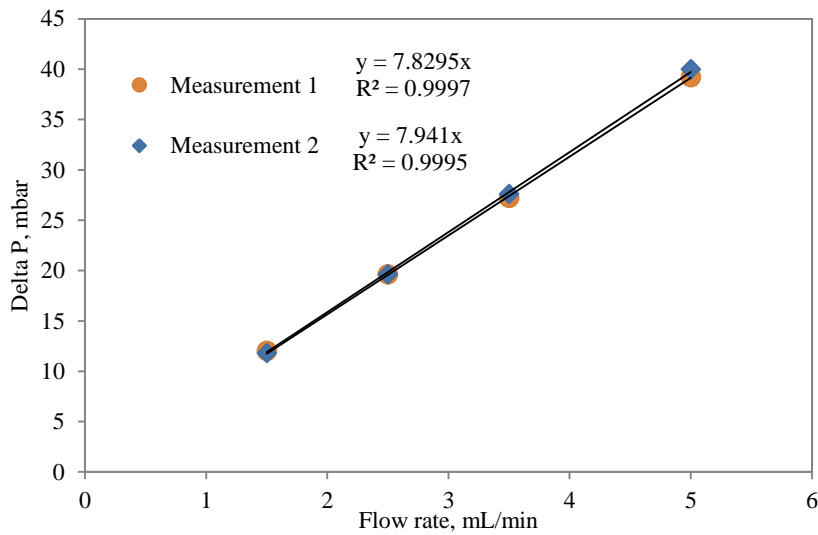
Brine at 5 wt% NaCl	1.045	mPa.s
Brine at 10 wt% NaCl	1.130	mPa.s
Brine at 15 wt% NaCl	1.204	mPa.s

Experiment 2

Length	4.90	cm
Cross section	7.07	cm <sup>2</sup>
Water viscosity	1.045	mPa.s

Slope	7.83	-
Rock permeability	1543	mD

Flow rate (ml/min)	Pressure drop (mbar) Measure 1	Pressure drop (mbar) Measure 2
1.5	12	11.8
2.5	19.6	19.6
3.5	27.2	27.6
5	39.2	40



**Fig. D2 – Determination of rock permeability**



## Appendix E: Unified apparent viscosity model parameters

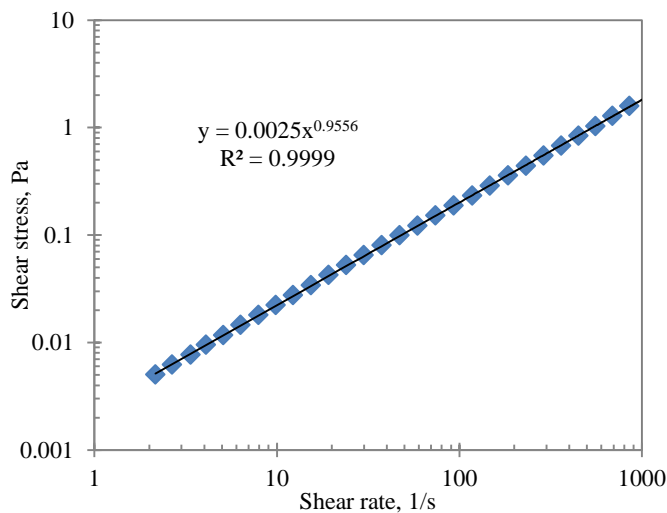
The unified apparent viscosity (UAV) model was used to predict the apparent viscosity of AMPS from the bulk rheology measurements (Equation 14). The model parameters of Equation 14 are summarised in Table E1. The parameters of the first part of the equation are the same used for the Carreau model in Appendix B. The effective shear rate was calculated using Equation 13. The values of C and n used are given in Table E1. The power-law index n is determined by plotting the shear stress versus the shear rate on a log-log plot. Fig. E1 shows an example of the determination of n for AMPS at 500 ppm and 5 wt% NaCl. Equations 13 and 14 are reminded below. Figs. E2 and E3 compare the measurements with the UAV model for different brine salinities and core permeabilities.

$$\dot{\gamma}_{eff} = C \left( \frac{3n+1}{4n} \right)^{\frac{n}{n-1}} \left( \frac{u}{\sqrt{k_f \phi}} \right) \dots\dots\dots (13)$$

$$\eta_{app} = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \left[ 1 + (\lambda \dot{\gamma}_{eff})^{\alpha} \right]^{\frac{N-1}{\alpha}} + \eta_{max} \left[ 1 - \exp(-(\lambda_2 \tau_r \dot{\gamma}_{eff})^{n_2-1}) \right] \dots\dots\dots (14)$$

**Table E1 – UAV model parameters for AMPS**

NaCl concentration	Permeability (Darcy)	C	n	$\mu^{max}$ (mPa.s)	$\lambda_2 * \tau_r$	n2
5 wt%	1.5	0.9	0.96	32	0.0047	2.8
10 wt%	1.5	0.9	0.96	32	0.0045	3.2
15 wt%	1.5	0.9	0.95	28	0.007	3.5
5 wt%	1.0	1.0	0.96	40	0.004	2.6
5 wt%	0.5	1.4	0.96	25	0.0042	3.2



**Fig. E1 – Determination of the power-law index for AMPS 500 ppm solution at 5 wt% NaCl.**

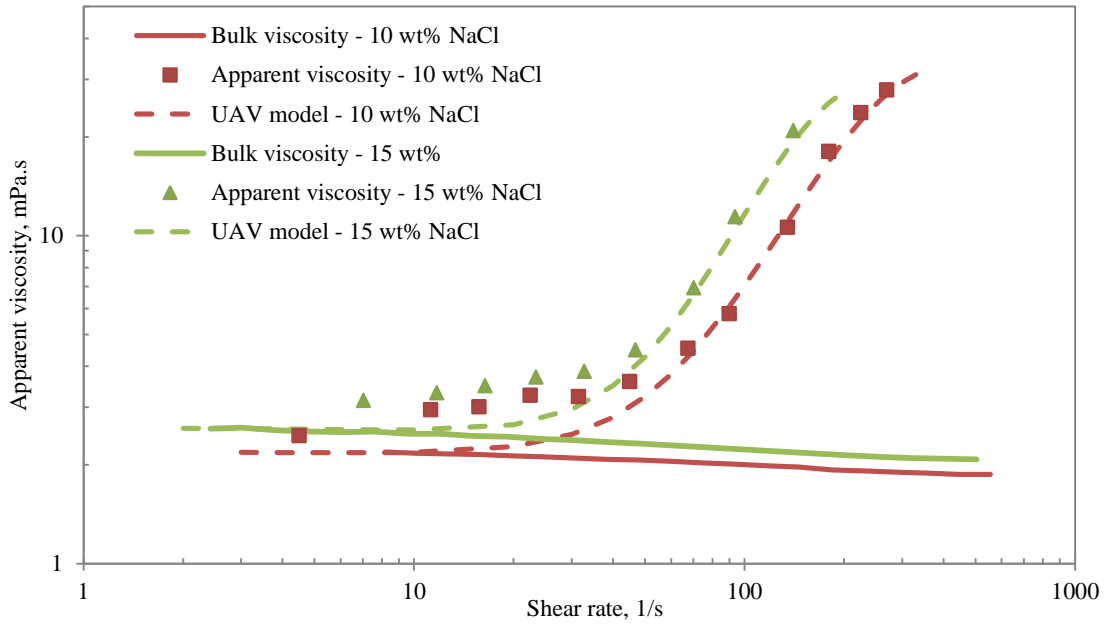


Fig. E2 – Apparent viscosity versus shear rate for AMPS at 500 ppm - 10 wt% NaCl and 15 wt% NaCl.

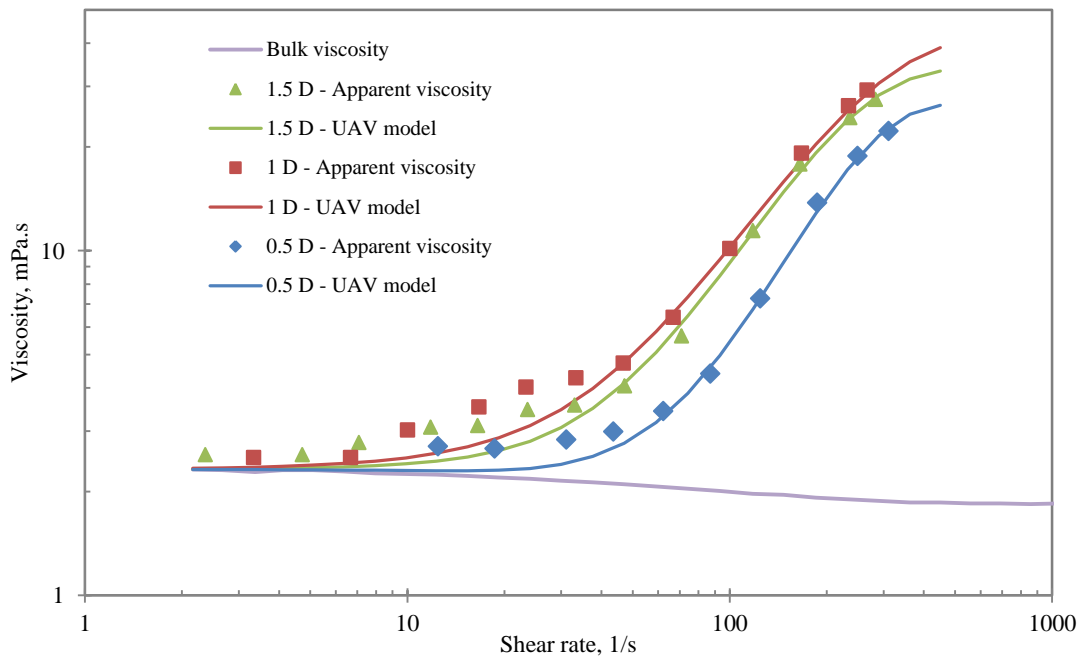


Fig. E3 – Apparent viscosity versus shear rate for AMPS at 500 ppm and 5 wt% NaCl for different core permeabilities.