

# Petroleum production: polymers in.

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## **Polymer in Petroleum Production**

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### **Abstract**

Polymers are widely used in oil and gas industry for a range of petroleum production applications. Their viscoelastic and solution thickening properties have particularly made them a chemical of choice for petroleum production applications. This chapter explores and discusses various types of polymers used in the oil and gas industry for petroleum production applications. The chapter focusses on chemical treatment optimisation, water shut for enhanced hydrocarbon production and reduced water production and enhanced oil recovery, and provides a treatise of rheological characterisation methods and models for these polymers.

### **1.0 Introduction to Petroleum Production Operations**

Petroleum production operation encompasses all the technical and engineering activities that take place during the production phase of an oilfield to maintain existing level of production or improve production. It involves all activities involved in the process of hydrocarbon flow from the reservoirs into the well, through the well and out into the surface facilities. The aim of production operation is therefore to ensure optimum production of hydrocarbon from the composite production system based on the modelled inflow performance relationship (IPR) and vertical lift performance (VLP) through proactive operational and engineering management of the entire production system. This includes management of the reservoirs, wells and surface facilities; diagnosis of any production limiting problems and design and implementation of engineering and/or management solutions to solve these problems.

Activities such as sand control, mineral scale control and treatment, wax, hydrate and asphaltene control and treatment, well production testing, production logging, well perforation, enhanced oil recovery, improved oil recovery, acidizing, hydraulic fracturing, acid fracturing, water shut off, reservoir pressure maintenance, gas lift etc. are classified as Petroleum Production Operation. Broadly, these activities can be categorised into stimulation, chemical treatment, water control, enhanced oil recovery and artificial lift

operations. Polymers are extensively used in all of these operational categories except artificial lift to achieve production optimisation objectives. The following sections explore the application of polymer in each of the broad categories of activities outlined above.

## **1.1 Oilfield Production Operations**

### **1.1.1 Chemical treatment**

Reservoir pressure maintenance is often necessary in reservoirs where pressure has declined to a level below that which can support optimum production from such reservoirs. In offshore environments, the water used for pressure maintenance may be sourced either from surrounding sea water or from wells drilled in water acquirers (Kokal, Raju and Biedermann 1999). The water sourced from sea water may not be compatible with the reservoir formation water at the time of injection, leading to a range of mineral scale precipitation; on the other hand, the aquifer water may contain high concentrations of CO<sub>2</sub> and may cause pitting corrosion in water source well tubings (Rosser et al 1999). Furthermore, there may be challenges associated with growth of SRB (sulphate-reducing-bacteria) which reduces sulphate to hydrogen sulphide (H<sub>2</sub>S). CO<sub>2</sub> and H<sub>2</sub>S can contaminate hydrocarbon fuel and can form corrosive acids in the presence of water. In order to prevent issues related to reservoir pressure maintenance using water, the affected components of the production systems are often treated with chemical inhibitors (scale inhibitors, corrosion inhibitors and biocides) via a placement technique called squeeze to control the precipitation of scales, initiation of corrosion and growth of SRB. The squeeze placement allows the chemical to be bull-headed into the affected areas of the production system for effective treatment. Chemical placement by bull-heading may however be challenging in complex systems such as in heterogeneous formation rocks where permeability varies substantially from one zone to the other. To overcome this problem, shear thinning polymer such Xanthan and HEC are used as part of the chemical component to allow for diversion of the chemical doses into less permeable zones which otherwise may not receive enough chemical to treat the problems in that zone.

### **1.1.2 Water Shut-off**

High water production with the hydrocarbon fluid is often a problem in highly fractured reservoirs at the early stage of their life-cycle, mature reservoirs that are nearing the end of their natural production phase or economic life and reservoirs that are underlain by strong aquifers with thin horizontal layers separating them. Water production is not desirable owing to operational, environmental and cost implications (Canbolat and Parlaktuna 2012). Operational issues relate to the technicalities of lifting, handling, cleaning and disposing the large amounts of water usually produced with the hydrocarbon

fluids; environmental implications relates to the need to meet the stringent national and international environmental regulations guiding the disposal of produced water whilst cost implications relate to the loss in hydrocarbon production and costs of treating the water. A range of techniques are used to control or remediate high water production including polymer injection, cement squeeze and mechanical barriers such as open-hole packers, liners and ICDs. Cement squeeze and mechanical barriers techniques have however been proven to be generally ineffective and unsuccessful (Johnson 2001). Polymer gel injection technology, on the other hand, is a reliable method of controlling water production in these types of reservoir. Polymer gel injected into the water zone reduces the permeability to water thereby restricting the flow of water into the well. Polymer gel treatment has been proven to be very effective in lowering water production from high water producing wells; for example a decrease of median WOR from 82 to 7 in naturally fractured carbonate reservoirs after 274 gel treatments was reported by Seright, Lane and Sydansk 2001

### **1.1.3 Enhanced Oil Recovery**

Hydrocarbon recovery from a reservoir will take place in three stages over its life-cycle; these are primary recovery stage, the secondary recovery stage and the tertiary recovery stage. During the primary recovery stage, the natural energy of the reservoir supplied by fluid and rock expansion in form of solution gas drive, water or aquifer drive, gas cap drive etc. drives the flow of the hydrocarbon from the reservoir through the well to the surface. At the secondary recovery stage, the natural energy drive of the reservoir has declined to a level that it can no longer support further optimum production from the reservoir and requires gas or water injection through the reservoir gas cap or underlying aquifer respectively to maintain the reservoir pressure and optimum production from the reservoir. Tertiary production stage, on the other hand, starts when all the hydrocarbon that can be produced from the primary and secondary production stage has been produced and the remaining trapped hydrocarbon can only be produced through modification of the reservoir fluid and rock flow related properties such as viscosity and wettability through heat application, microbial modification of fluid, gas injection and chemical injection. Chemical injection or flooding involves injection of chemicals such as polymer, foam, surfactant etc. to modify either the fluid or the rock surface to enhance the release and flow of hydrocarbon trapped in network of small pores.

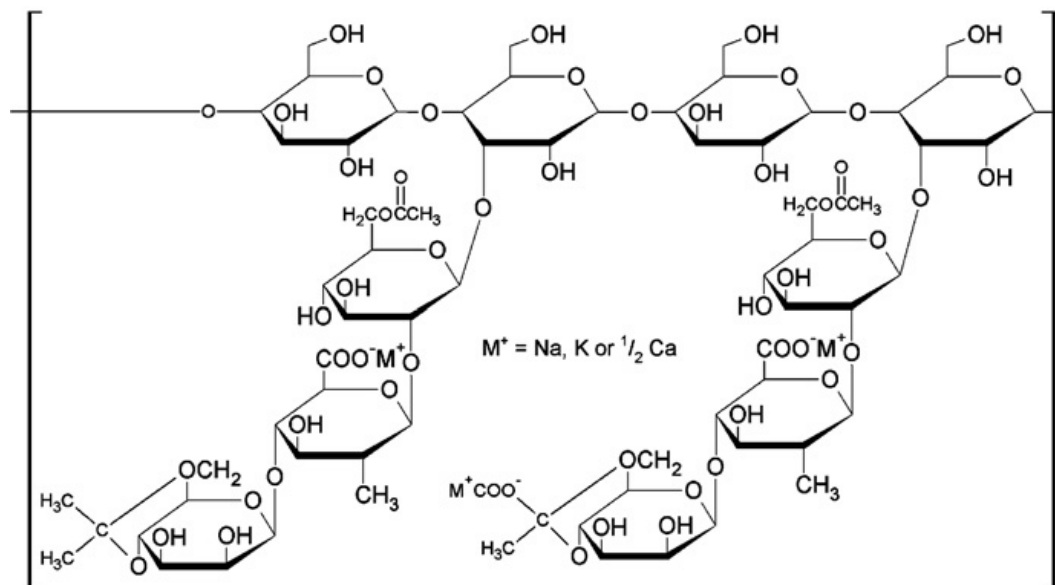
### **1.2 Types of Polymers Commonly Used in Petroleum Production Operations**

Many types of polymers are commonly used in the oil and gas industry including Xanthan gum, Polyacrylamide (PAM), Partially Hydrolysed Polyacrylamide (HPAM), Hydrogel and Hydroxyl Ethyl Cellulose (HEC). However, partially hydrolysed polyacrylamides (HPAM)

and xanthan gums are commercially and technically attractive polymers used in EOR processes (Lake, 1989) and chemical placement (Stalker 2009).

### 1.2.1 Xanthan gum

Xanthan gum falls into the family of natural polysaccharides. It is highly soluble in cold and hot water because of the polyelectrolyte nature of the xanthan molecule (García-Ochoa et al., 2000). Solutions of xanthan are highly viscous even in very low concentrations. Xanthan solutions are shear-thinning, or pseudoplastic (i.e. viscosity decreases as shear rate increases), and is less sensitive to changes in salinity and mechanical degradation in comparison to polyacrylamide (Kohler and Chauveteau, 1981; García-Ochoa et al., 2000). Xanthan gum has molecular weight ranging from 2 to 50 x 10<sup>6</sup> g/mol; and its viscosifying ability lies in both the molecular weight and in the rigidity of the polymer chains (García-Ochoa et al., 2000). Figure 1 shows a typical structure of xanthan gum. It has been shown (Zaitoun and Kohler, 1987) that molecules of xanthan gum adsorb flat on rock surfaces without significant increase in adsorbed layer thickness. Zaitoun and Kohler (1987) observed a higher retention level with flexible polyacrylamide on same rock surfaces; and attributed these adsorption discrepancies between the two polymers to the differences in their functional groups. Specifically, flexible polyacrylamide has greater formation damage potential than xanthan gum.

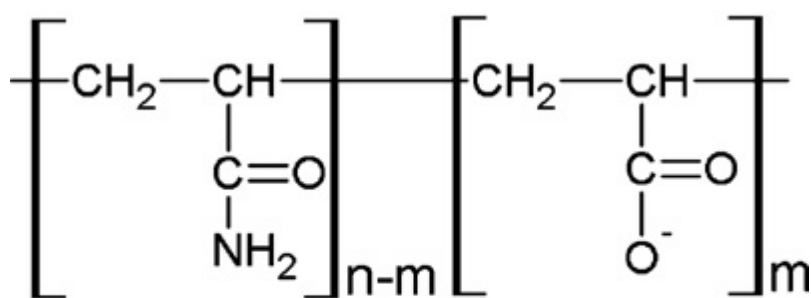


**Figure 1 - Chemical structure of xanthan gum (Wever et al., 2011).**

### 1.2.2 Hydrolysed polyacrylamide (HPAM)

HPAM is a synthetic, high-molecular weight, water-soluble, low-cost polymer which has undergone partial hydrolysis; hence the name 'partially hydrolysed polyacrylamide' (HPAM). It is a more widely used EOR polymer than xanthan gum since it can tolerate the

high mechanical forces present during the flooding of a reservoir (Lake, 1989). HPAM has a degree of hydrolysis between 25 to 35% (Lake, 1989; Borthakur et al., 1995). The ability of HPAM to viscosify is due to its high molecular weight as well as the electrostatic repulsion between polymer coils and between polymeric segments in the same coil (Lake, 1989). It has been reported to exhibit both pseudoplastic (Lake, 1989; Borthakur et al., 1995) and dilatant (Seright et al., 2009;) behaviours. HPAM degradation is by physical breakdown; and microbial attack has been reported to be difficult with HPAM (Seybold, 1994). This is due to, perhaps, its very high molecular weight. HPAM exhibits permanent or irreversible permeability reduction in porous media (Lake, 1989). Figure 2 shows the chemical structure of HPAM (Wever et al., 2011).

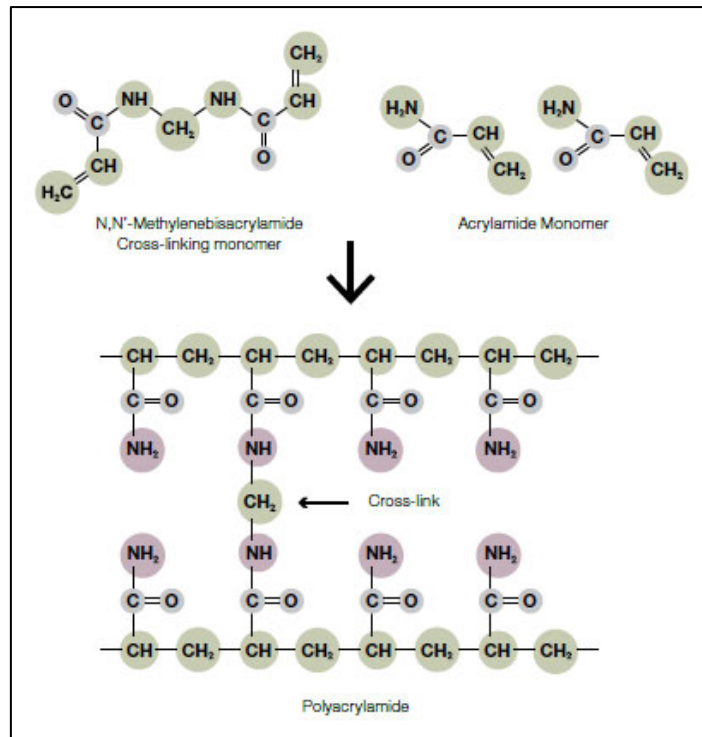


### Hydrolyzed polyacrylamide

**Figure 1 - Chemical structure of partially hydrolysed polyacrylamide (Wever et al., 2011)**

#### 1.2.3 Polyacrylamide (PAM)

Polyacrylamide is a polymer formed by the polymerisation of acrylamide monomers crosslinked at intervals by N,N'-Methylenebisacrylamide Cross-linking monomer (see Figure 3). It is hydrophilic and can swell when soaked with water or contract when ridden of water. It is a high molecular weight polymer with molecular weight greater than  $1.0 \times 10^6$  g/mol. Salinity of the polymer solution may somehow affect its temperature dependent stability; for instance at normal salinity, it is stable up to 90°C whilst at high sea water salinity, it is only stable up to 62°C. However, the effect of salinity on PAM viscosity can be minimised or controlled by hydrophobic modification (Chang et al. 2006; Hurlock 2001) which involves the hydrophobic association of low molecular weight polymer with it. Aside temperature and salinity, a number of other factors can also affect the stability of PAM; these include pH, Ferrous and Ferric iron salts, surfactants, Biocide etc. (Shupe 1981). PAM is used extensively in EOR to increase the viscosity of the injected volume and in drilling applications as fracturing fluid and drilling fluid additives to modify the rheology and improve cuttings carrying efficiency of the fluid.



**Figure 3 – Crosslinking of polyacrylamide by N,N'-Methylenebisacrylamide** (Chang et al. 2006; Hurlock 2001)

#### 1.2.4 Hydrogel

This is an hydrophilic polymer material which can hold large amount of water in its networks (Ahmed 2013) without dissolving in the water owing to the physical or chemical crosslinkage of the hydrophilic polymer chains (Schacht 2004). Structurally, they are characterised by two or multi-component systems consisting of three-dimensional network of polymer chains with water filling the space between macromolecules. One major characteristic of hydrogels that makes them suitable for oil and gas field applications is their ability to absorb and retain water. Hydrogels can be produced naturally or in synthetic polymerisation and cross-linking reactions. The synthesis can be achieved through copolymerisation of hydrophilic monomers and poly-functional co-monomers acting as cross-linkers; cross-linkage of low molecular weight hydrophilic polymers or oligomers and chemical cross-linkage of hydrophilic polymers result in the formation of a hydrogel (Schacht 2004). Hydrogels are typically used for conformance control during the enhanced oil recovery water flooding (Tongwa and Baojun 2015). High permeability zones in reservoir intervals such as areas with fracture networks can impact negatively on water-flooding performance and effectiveness. Hydrogels are therefore usually injected into such high permeability zones to seal them up and divert water flood to low permeability zones with substantial amount of difficult-to-sweep oil. In the early days of hydrogels application in the oil and gas industry for the control of conformance problems, the technology used

was such that the Hydrogels were injected into the reservoir and crosslinked in-situ (Tongwa and Baojun 2015). This technology however had to give way for a new preformed gel technology owing to some disadvantages such as selective injectivity, potential damage to low permeability zones, dispersion and dilution of gelant, syneresis, dehydration and inadequate control of gelation time (Young et al. 1988; Asghari 1999; Bryant et al. 1996; Willhite et al. 1986). The preformed gel technology has been further improved through a novel application and incorporation of nanomaterials such as calcium montmorillonite (Tongwa and Baojun 2015).

### **1.2.5 Hydroxyethyl Cellulose**

Hydroxyethyl Cellulose (HEC) is a non-ionic water soluble polymer with hydroxyethyl groups attached to the polymer structure; it is soluble in both hot and cold water, hence its wide application in the oil and gas industry for a range of oil and gas field operations such as EOR, workover, completion and fracturing. In particular because of its high solubility, it is widely used in EOR projects as a viscosifier, and in mobility control (Abbas et al 2013).

### **1.3 Polymer Applications in Petroleum Production: Principles and Procedure.**

A polymer is an organic chemical substance composed of giant molecules formed by the union of many smaller molecules (Ezell et al., 2010). Polymers vary in function and basic properties and are classified as natural (e.g. starch, biopolymers, and guar gum), modified-natural (e.g. cellulose (CMC, HEC), carboxymethyl starch) and synthetic (e.g. polyacrylate, polyacrylamide cationic polymers). Polymers are non-toxic, high viscosifying, degradable materials which do not cause environmental problems. These unique characteristics make them one of the best materials for production operations. In petroleum production, polymers lubricate and reduce friction in drill-hole in concentrations of about 0.1-0.4 %w/w; while in EOR, they reduce water mobility by increasing viscosity and decreasing absolute permeability in concentrations of about 0.05-0.2 %w/w (García-Ochoa et al., 2000).

### **1.4 Rheological Characterisation of Polymer Solution for Petroleum Production Application**

Rheological systems can either be Newtonian or non-Newtonian. Viscosity is the most important property of polymers in EOR operations as well as other applications. However, a lot of factors can affect polymer viscosity. In this section, the effects of shear rate, salinity, active polymer concentration, pH, hardness and temperature on polymer viscosity performance is discussed.



### 1.4.1 Polymer Viscosification Mechanism

While in solution, the underlying principle of how polymers viscosify is still not quite understood. However, energy dissipation arising from the interaction of molecules is one physical interpretation of viscosity. It has been proposed (Flory, 1953; Flory and Flory, 1956) that it is the interaction between long polymer chains and the solvent molecules that govern the viscosifying effects of polymers and that the mechanisms is related to the frictional effects observed in sedimentation and diffusion. The long polymer chains exhibit many motional patterns while interacting along its entire length with molecules of the solvent (Mezzomo et al., 2002; Sorbie, 1991). This leads to more energy dissipation and higher viscosity tendencies compared with liquids made of smaller molecules. It was noted (Sorbie, 1991; Sorbie et al., 2007) that polymers can increase water viscosity by factors of 10-100 even at low concentrations of a few hundred parts per million (ppm). The energy dissipation rate ( $\dot{Q}$ ) within simple shear flow is given by Eqn. (1) (Sorbie, 1991):

$$\dot{Q} = \mu \dot{\gamma}^2 \quad (1)$$

Where;  $\dot{Q}$  directly depends on viscosity of the fluid ( $\mu$ ) and on the square of the shear rate ( $\dot{\gamma}$ ).

### 1.4.2 Polymer Bulk Viscosity Theory

Viscosity has been well established to be the most important parameter for characterizing polymers (Stavland et al., 2010). Viscosity of a polymer solution is measured with viscometer; this is known as the bulk viscosity. The theory of polymer bulk viscosity is well known (Flory, 1953; Flory and Flory, 1956; Sorbie, 1991; Zitha, 2001; Stavland et al., 2010). The polymer viscosity,  $\mu$  increases non-linearly (Figure 4) as both the intrinsic viscosity,  $[\mu]_0$ , and polymer concentration,  $C_p$  increase up to the second order (Zitha, 2001); as given by Eqn. (2):

$$\mu = \mu_{sol} \left( 1 + [\mu]_0 C_p + k' [\mu]_0^2 C_p^2 \right) + O^3 \quad (2)$$

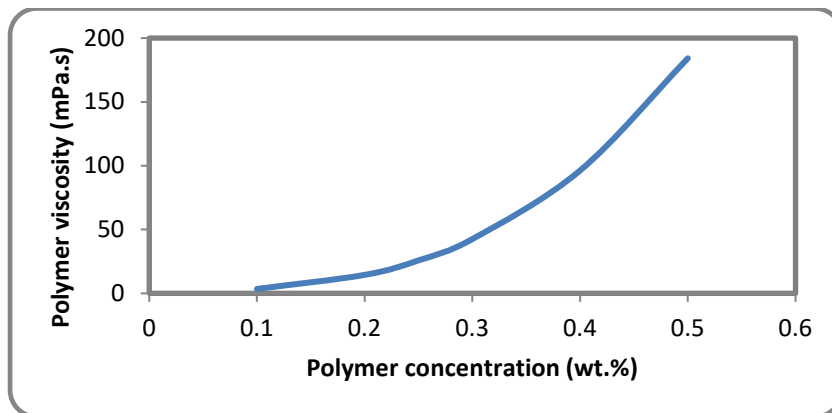
where,

$\mu_{sol}$  = solvent viscosity,

$O^3$  = third order polymer concentration

$k'$  = Huggins parameter which describes solvent quality.

- $k' < 0.4$ : good<sup>1</sup> solvent conditions
- $k' > 0.4$ : poor solvent conditions



**Figure 4 - Effect of concentration on polymer viscosity**

The intrinsic viscosity is a measure of the size of a polymer molecule in solution, and consequently, a measure of its thickening ability (Lake, 1989). The intrinsic viscosity is a function of the polymer molecular weight; this is expressed in Mark-Houwink equation (Bird et al., 1977) given as Eqn. (3):

$$[\mu]_0 = K M_w^a \quad (3)$$

Where,

$M_w$  = polymer molecular weight

$K$ ,  $a$  = empirical constants for a given polymer at a given temperature in a particular solvent. Note:  $3.0 \times 10^{-5} \leq K \leq 700 \times 10^{-5}$  = and  $0.5 \leq a \leq 1.0$  (Sorbie, 1991).

For a given molecular weight, chemical structure, shear rate, chain branching, temperature, type of solvent, and charge are the factors that affect polymer intrinsic viscosity.

### 1.4.3 Polymer Molecular Radius

When in solution, the hydrodynamic radius of polymer is known as its radius of gyration ( $R_g$ ). This parameter is difficult to measure experimentally in the laboratory. However, theoretical models have been developed to estimate this hydrodynamic parameter (Flory, 1953) depending on the macromolecular condition of the polymer in dilute solution. For

instance, HPAM is a flexible, long linear chains structure; and so in order to neutralize electrostatic repulsion between carboxylate groups, the conformation of HPAM in high saline water are coils. For example, for 20 g/L NaCl salinity, HPAM macromolecular conformation is slightly an expanded coil (Chauveateau, 1981). The Flory-Fox hydrodynamic radius of gyration equation,  $R_g$ , for this case is given by Eqn. (4):

$$R_g = \left( \frac{M_w [\mu]_0}{\Phi} \right)^{1/3} \quad (4)$$

Where,

$R_g$  = radius of gyration which characterises polymer coil in dilute solution

$\Phi$  = universal constant =  $2.1 \times 10^{21}$  dl/g.mol.cm<sup>3</sup>

$[\mu]_0$  = polymer intrinsic viscosity, cm<sup>3</sup>/gm

For rigid, rod-like or hard sphere conformation of Xanthan gum, the radius of the molecular coil in a dilute solution can be determined from (Einstein 1953, 1955) equation for the viscosity of an infinite dilute suspension of hard spheres:

$$r_M = \left( \frac{30 M_w [\mu]_0}{\pi A} \right)^{1/3} \quad (5)$$

Where,

$r_M$  = radius of molecular coil in dilute solution

A = constant = Avogadro's number,  $7.023 \times 10^{23}$  molecules/mol

$M_w$  = polymer molecular weight, g/mol.

#### 1.4.4 Non-Newtonian Viscosity-Shear Rate Relationships

All polymers are shear-thinning, i.e. their viscosities decreases with increasing shear rates (Lake, 1989). Shear-thinning behaviour of polymers has been established and proved (Bird et al., 1987) as an intramolecular effect that occurs due to the polymer extensional and orientational character while in solution. A set of well-established expressions from the literature can be used to express their viscosity-shear rate relationships. Some of the proposed analytical expressions for viscosity vs. shear rate in simple shear flow include but not limited to the power-law and the Carreau models.

#### 1.4.4.1 The Power-law (Ostwald-de Waele) Model

The Power-law model is the most widely used analytical form of viscosity-shear rate relationship which describes the pseudoplastic region of the polymer viscosity curve. This model is given by Eqn. (6) (Bird, 1960):

$$\tau(\dot{\gamma}) = K \dot{\gamma}^n \quad (6)$$

and in terms of apparent viscosity, Eqn. (7):

$$\mu(\dot{\gamma}) = K \dot{\gamma}^{n-1} \quad (7)$$

Where,

$\tau$  =shear stress

$\dot{\gamma}$  =rate of deformation (or shear rate)

$\mu$  =fluid viscosity

K=constant known as fluid consistency coefficient (cp.sec<sup>n-1</sup>)

n=dimensionless constant known as flow behaviour index ( $0.4 \leq n \leq 1$  for shear-thinning fluids).

#### 1.4.4.2 Carreau Model

Carreau equation (Carreau, 1972; Bird et al., 1987a) covers and combines the power-law region and the two Newtonian regions of the viscosity curve. Therefore, it has a better application compared with the power-law model (Eqn. 8). It is written as (Cannella et al., 1988):

$$\mu_{sh} = \mu_{\infty} + (\mu_p^0 - \mu_{\infty}) [1 + (\lambda \dot{\gamma}_{eff})^\alpha]^{(n-1)/\alpha} \quad (8)$$

Where,

$\mu_{sh}$  = apparent shear viscosity in porous media.

$\mu_p^0$  = polymer viscosity at zero shear rate.

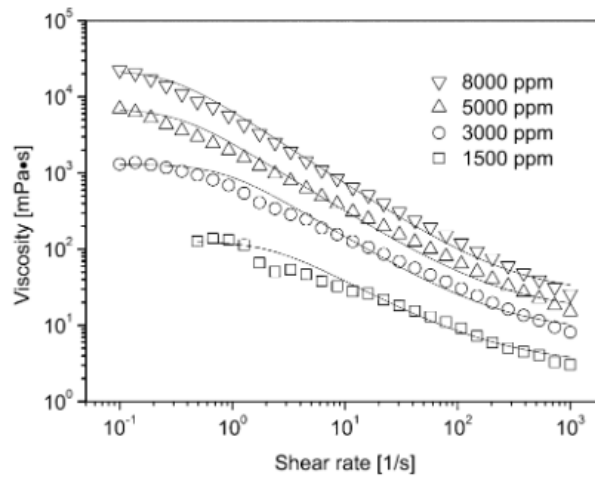
$\mu_{\infty} = \mu_w$  = viscosity at infinite shear rate.

$\lambda$  = time constant (i.e. relaxation time for realignment of polymer rods in a shear flow field) is found from the measurements of bulk viscosity

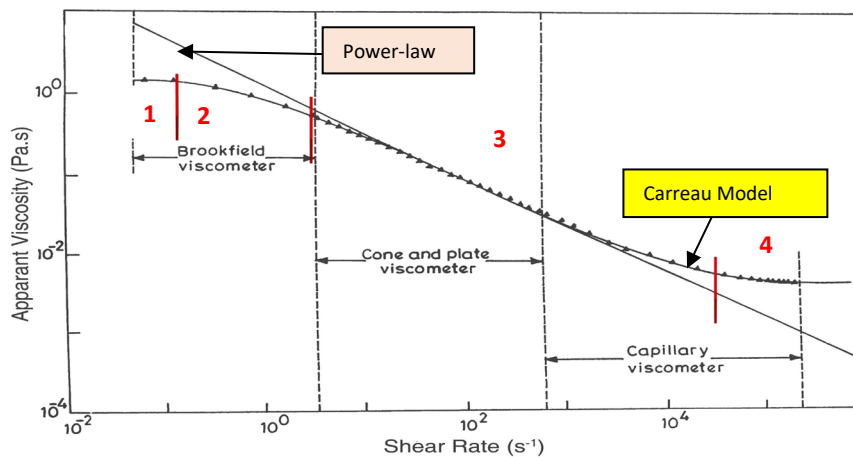
$\dot{\gamma}_{eff}$  = rate of deformation; called effective shear rate in shear flow.

$n$  = dimensionless constant known as the shear-thinning index that depends on the polymer concentration.  $0.4 \leq n \leq 1$  for viscous, pseudoplastic or shear-thinning fluids.

Figure 5 shows shear-thinning behaviours of Xanthan gum solution (Jang et al 2015); while Figure 6 is a comparison of Power-law and Carreau models for polymer solutions (Chhabra et al., 2001).



**Figure 5 - Shear-thinning behaviour of Xanthan gum solution (Jang et al, 2015)**



**Figure 6 - Comparison of Power-law and Carreau Model for polymer solution (Chhabra, 2010).**

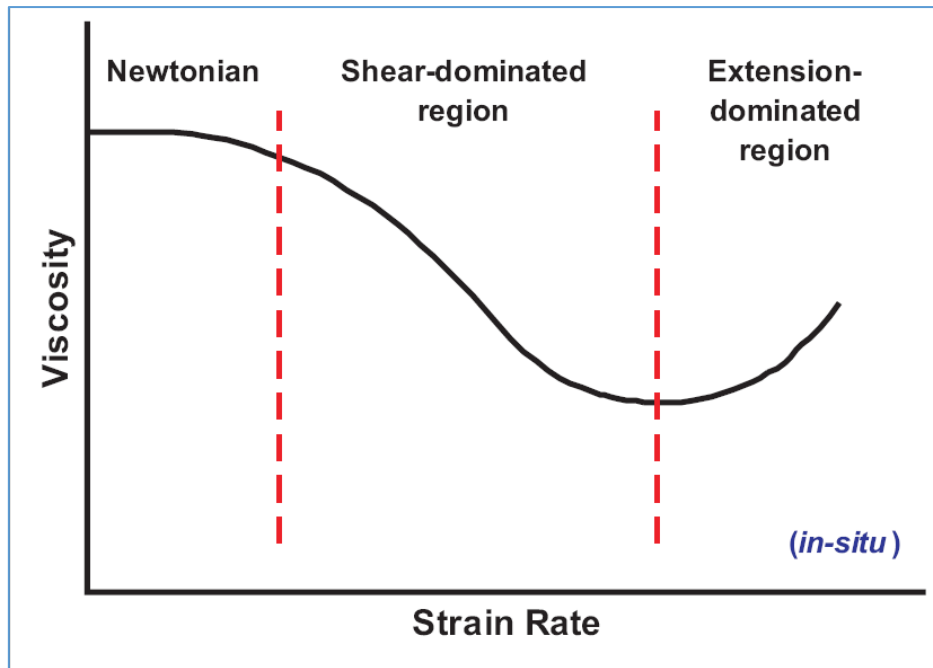
Figure 5 shows that viscosity increases with concentration and decreases with shear rate. The ability of the Carreau model to account for both low and high regions of the viscosity curve is demonstrated by Figure 6. There are four distinguishable regions in this figure:

1. Constant-viscosity region in which the behaviour of the solution is Newtonian. This region is associated with low shear rates and/or low concentration.

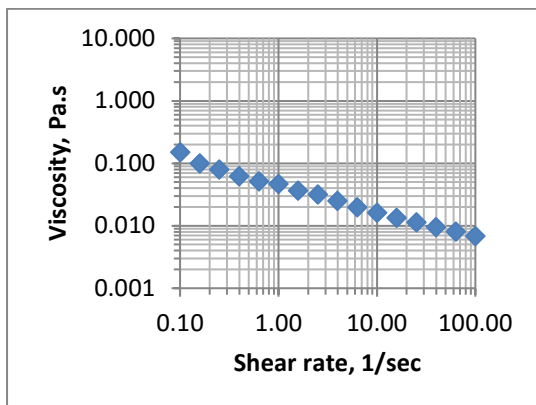
2. Transition region, which correspond to the polymer molecules undergoing deformation due to the effect of the increasing shear rate.
3. Region in which the viscosity decreases as the shear rate increases. The greater the shear, the more the molecular chains orient in the direction of flow. The behaviour of the solution is pseudoplastic.
4. Transition region, which corresponds to high degrees of shear. For HPAM, this is a region of shear-thickening (viscosity increases with shear rate) which has been attributed to the changes in the molecular conformation involving the formation of additional links between two chains.

#### **1.4.5 Dependence of Viscosity on Shear Rate**

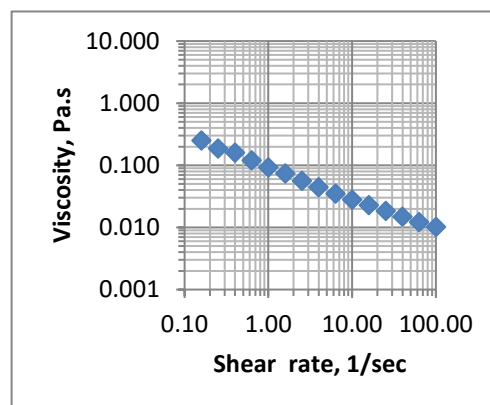
In order to attempt a discussion on the effect of shear on viscosity, an explanation of the reason for general flow curve is required. How liquid behaves or responds to stress is referred to as 'viscous' response. At low shear rate, Brownian diffusion randomizes. At this low shear region, viscosity is almost independent of shear (Newtonian region). As the shear is gradually increased, shear field aligns particles or molecules along streamlines resulting in shear thinning (Figure 7). As the shear is further increased, turbulent flow push particles out of alignment causing particles to bang into one another destroying order and causing increase in viscosity (shear thickening). Figures 8 to 11 show the effect of shear rate on viscosity of samples FP3630 S and FloComb C3525 in 0.1% NaCl. The application of shear causes structure breakdown, hence reduction in chain sizes under high shear leading to reduction in viscosity. The figures show a decreasing viscosity with increasing shear rate. The non-linear trend in the sample viscosity profiles is expected of typical non-Newtonian fluids. The combined curve of Figure 11 shows proportionate increase in viscosity with concentration. As the shear rate increases, the polymer solution viscosity reduces. As the shear rate increases further, the effect of concentration of polymer also vanishes.



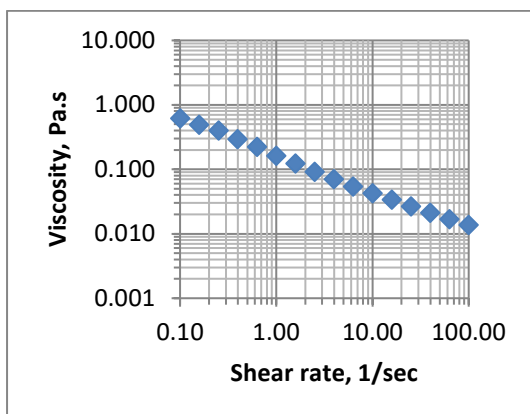
**Figure 7 - Effect of shear on the shape of general flow curve.**



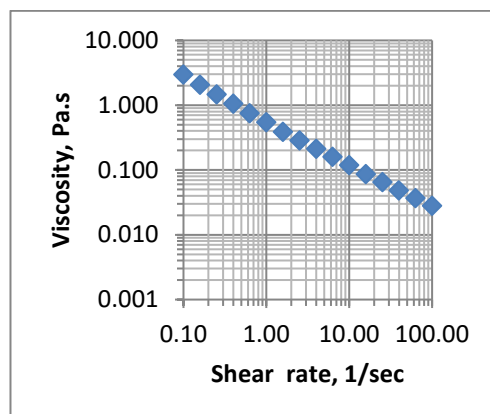
(a)



(b)

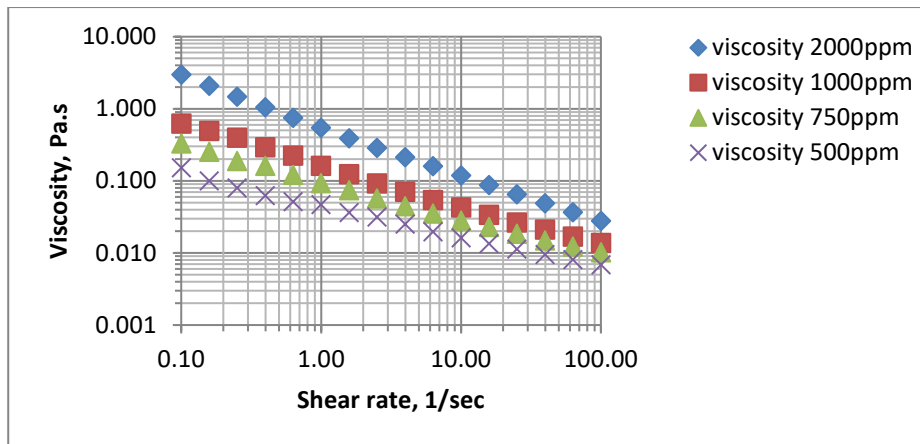


(c)

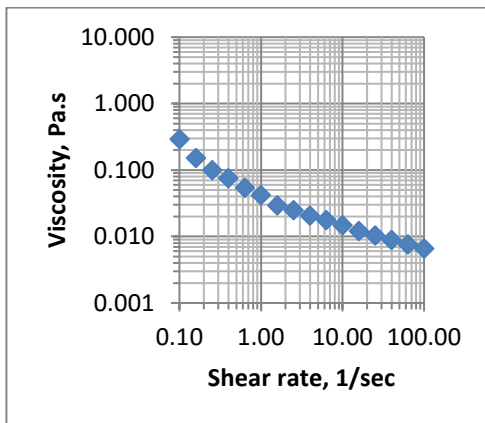


(d)

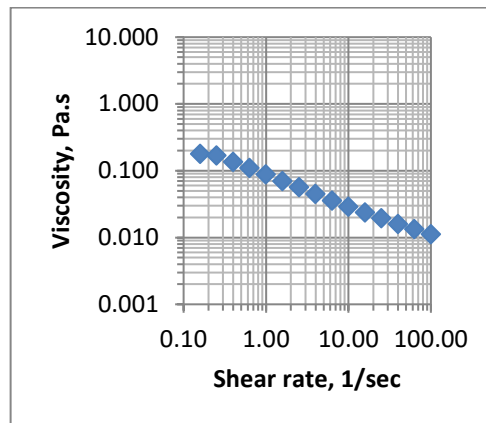
**Figure 8 - Dependence of viscosity on shear rate for FP3630 S: (a) 500ppm, (b) 750ppm, (c) 1000ppm, (d) 2000ppm in 0.1% NaCl, pH=8.2 and 25 °C**



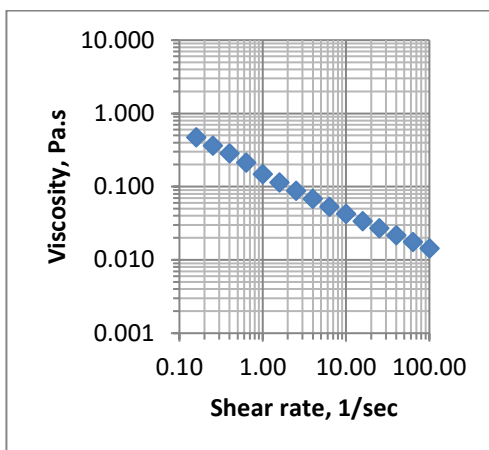
**Figure 9 - Effect of shear rate on viscosity of FP3630 S solution at different concentrations in 0.1% NaCl, pH=8.2 and 25 °C**



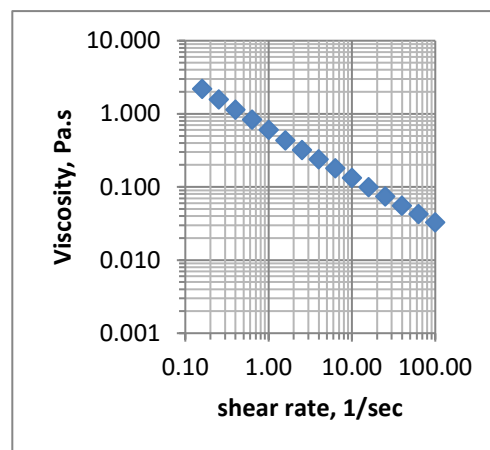
(a)



(b)



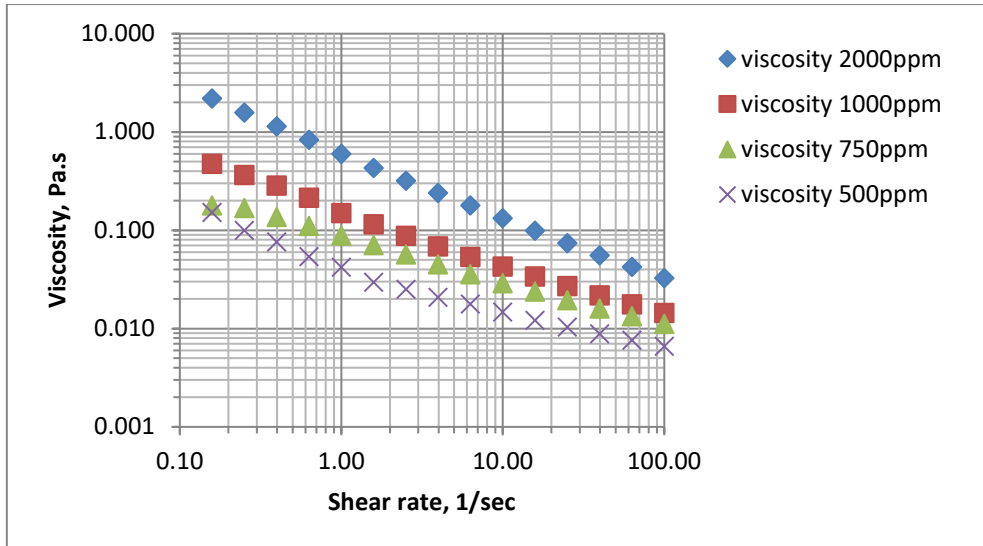
(c)



(d)

**Figure 10 - Dependence of viscosity on shear rate for FloComb C3525: (a) 500ppm, (b) 750ppm, (c) 1000ppm, (d) 2000ppm in 0.1% NaCl, pH=8.2 and 25 °C**

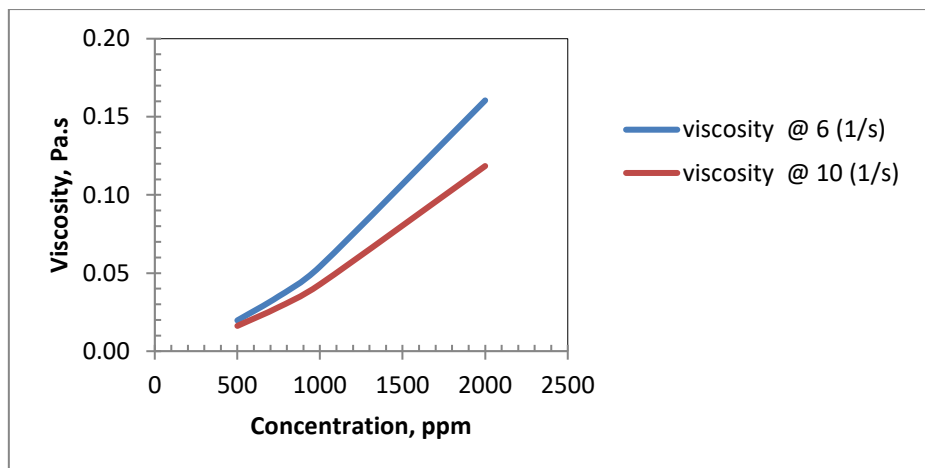




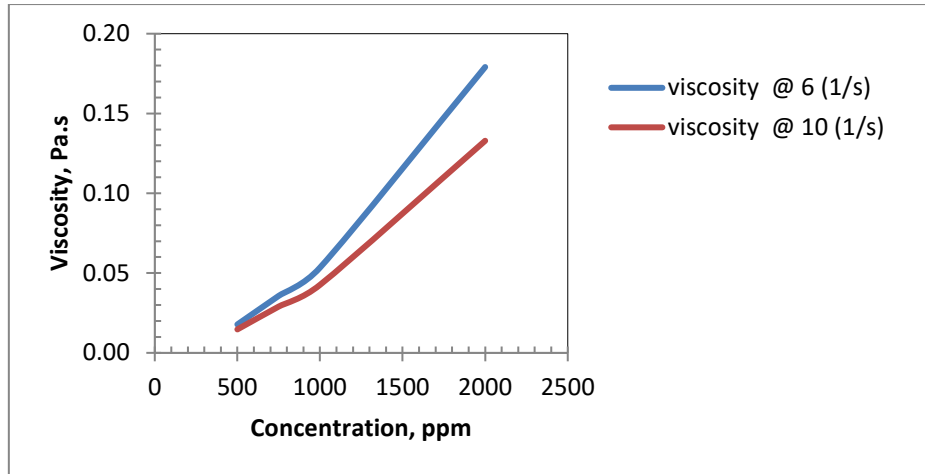
**Figure 11 - Effects of shear rate on viscosity of C3525 solution at different concentrations in 0.1% NaCl, pH=8.2 and 25 °C**

#### 1.4.6 Relationship of Polymer Concentration and Viscosity

Figure 12 shows that the viscosity of dilute solutions increases non-linearly with concentration for samples FP3630 S and FloComb C3526. At low polymer concentrations (the so-called dilute region), intramolecular associations dominate leading to a reduction in the hydrodynamic volume, and hence the reduction in viscosity. On the other hand, the solution transits to the semi-dilute region (at higher concentration) where intermolecular associations dominate. The resulting transient network causes a significant increase in viscosity (Wever et al., 2011).



(a)

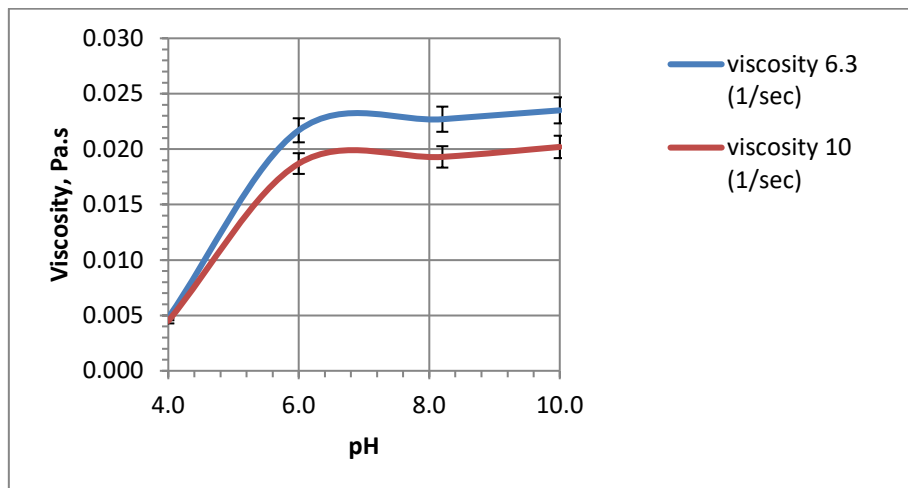


(b)

**Figure 12 - Plot of polymer concentration vs. viscosity @ shear rates of  $6 \text{ s}^{-1}$  and  $10 \text{ s}^{-1}$ : (a) FP3630 S (b) FloComb C3525 in 0.1% NaCl, pH=8.2 and  $25 \text{ }^\circ\text{C}$**

#### 1.4.7 Effect of pH on Viscosity

Figure 13 shows that solution viscosity increases gradually to a maximum as pH increases from 4 to 10. The observed behavior is due to the neutralization effects of the carboxylic groups which cause intramolecular electrostatic repulsion, thus chain extension (dominant at low pH); and disruption of intermolecular associations resulting from intermolecular electrostatic repulsion (dominant at high pH) (Zhang et al., 2008). Furthermore, polyanions are known to have low viscosity at low pH and high viscosity at high pH (Wever et al., 2011).



**Figure 13 - Effects of pH on viscosity of 750 ppm of sample FP3330 S in 0.1% NaCl measured at  $25 \text{ }^\circ\text{C}$  and pH=8.2**

#### 1.4.8 Effect of Temperature on Viscosity

Temperature is an important variable in translating laboratory measurement of oil and gas related operations (e.g., EOR) to reservoir conditions. The viscosity of polymer solution is quite sensitive to temperature. At a low shear rate, the polymer solution apparent viscosity ( $\mu_p$ ) decreases with temperature according to the Arrhenius equation (Eqn. 9)

$$\mu_p = A_p \exp\left(\frac{E_a}{RT}\right) \quad (9)$$

where,

$A_p$ =frequency (or pre-exponential) factor

$E_a$ = activation energy of the polymer solution

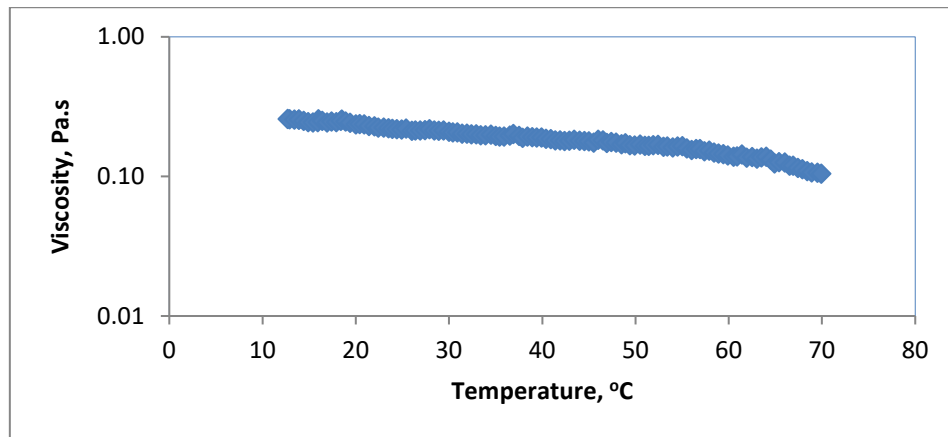
$R$ =universal gas constant

$T$ =absolute temperature.

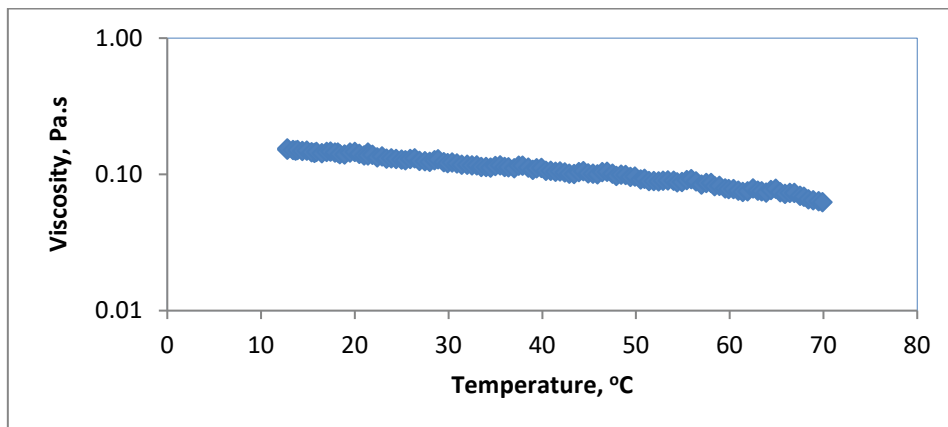
Equation (9) shows that the viscosity decreases rapidly as the temperature increases. The plausible explanation for the mechanism is that as the temperature increases, the activity of the polymer chains and molecules is enhanced, and the friction between the molecules is reduced; thus, the resistance to flow is reduced, and consequently the viscosity decreases. Different polymers have different  $E_a$ . Polymers with higher  $E_a$  are more sensitive to temperature. For example, HPAM has two  $E_a$ s: (1) at temperature less than 35 °C,  $E_a$  is low, and the viscosity does not change appreciably as the temperature increases; (2) at temperature greater than 35 °C,  $E_a$  is high, and the viscosity is more sensitive to temperature variations. Furthermore, it is presumably believed that random scission of the polymer chain is the principle mechanism of polymer decomposition in-situ (i.e., primarily as a result of polymer decomposition by random scission cleavage of the backbone) (Lange and Huh, 1994). According to the random scission model, the polymer molecular weight distribution (MWD) changes due to thermal degradation. Specifically, higher molecular weight ( $M_w$ ) polymer components degrade to lower  $M_w$  components, causing loss of polymer viscosity. In reservoir condition, since particle/molecular adhesion force is sensitive to temperature, shear resistance is also temperature dependent (Civan, 2007).

Figures 14 to 17 show that polymer solution viscosity decreases as temperature increases because an increase in temperature causes a decrease in the association strength of the hydrophobes. Furthermore, Figures 14 and 15 show that viscosity dependence on temperature is a linear function of time. The figures also show a pronounced viscosity oscillation as temperature increases further. Sample FP3630 S is more temperature stable compared with the other; the order of temperature stability (FP3630 S>C3525>FP3330

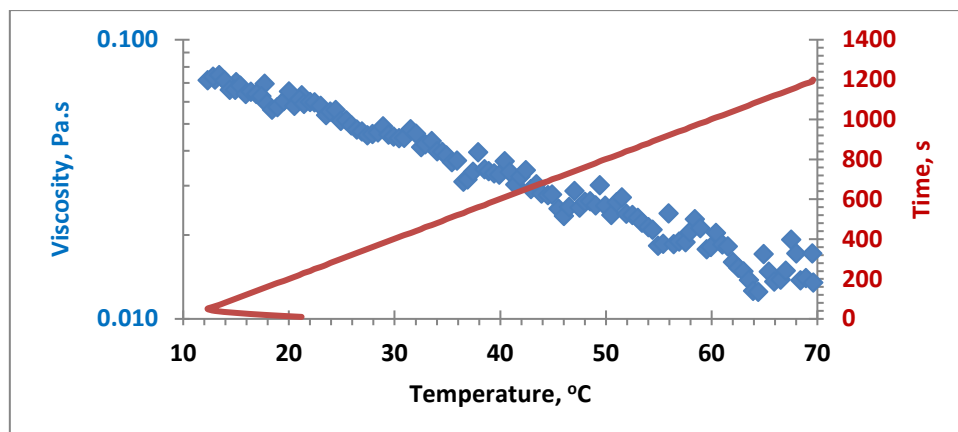
S) is shown in a combined curve of Figure 17 for the three polymers. The plausible explanation for this observation is that FP3630 S has a reticular structure with tendency to reduce the effect of temperature on its chain to a certain possible extent (Wever et al., 2011). The same explanation is applicable to C3525 over FP3330 S.



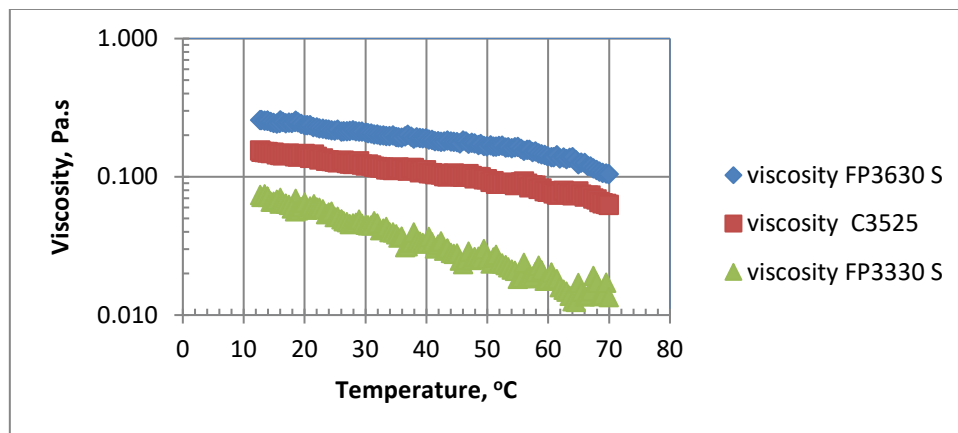
**Figure 14 - Viscosity as function of temperature for 1000 ppm of FP3630 S at pH=8.2 and at constant shear rate of  $1 \text{ s}^{-1}$  from 10 °C to 70 °C**



**Figure 15 - Viscosity as function of temperature for 1000 ppm of FloComb C3525 at pH=8.2 and at constant shear rate of  $1 \text{ s}^{-1}$  from 10 °C to 70 °C**



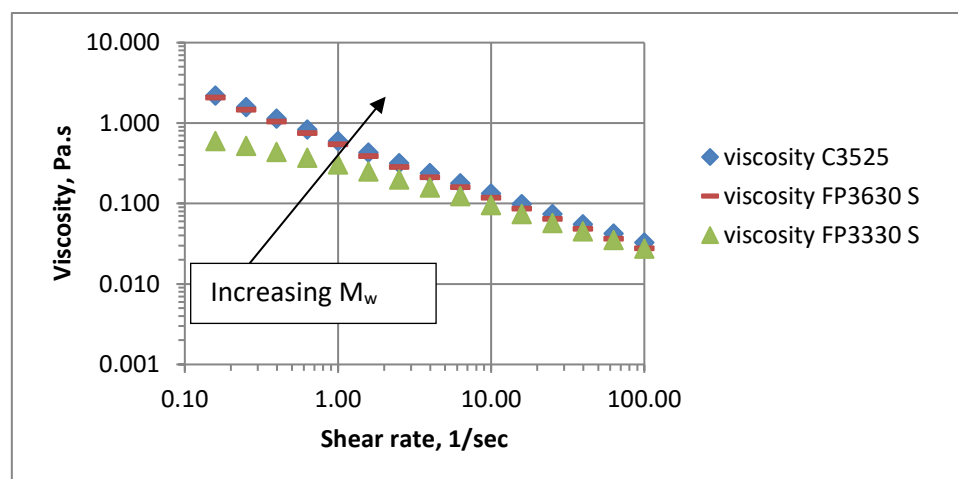
**Figure 16 - Viscosity as function of temperature for 1000 ppm of FP3330 S at pH=8.2 and at constant shear rate of  $1 \text{ s}^{-1}$  from  $10 \text{ }^\circ\text{C}$  to  $70 \text{ }^\circ\text{C}$**



**Figure 17 - Effect of temperature on viscosity for 1000 ppm of three samples at pH=8.2. The temperature ramp test was performed over a range of  $10 \text{ }^\circ\text{C}$  to  $70 \text{ }^\circ\text{C}$  at constant shear rate of  $1 \text{ s}^{-1}$**

#### 1.4.9 Effect of molecular weight

A material viscosity in the low shear plateau is related to the polymer molecular weight ( $M_w$ ); therefore, the higher the  $M_w$ , the higher the viscosity plateau (zero-shear viscosity). Figure 18 shows that polymer C3525 and FP3630 S (with almost similar  $M_w$ ) have higher molecular weight and higher viscosity than FP3330 S.

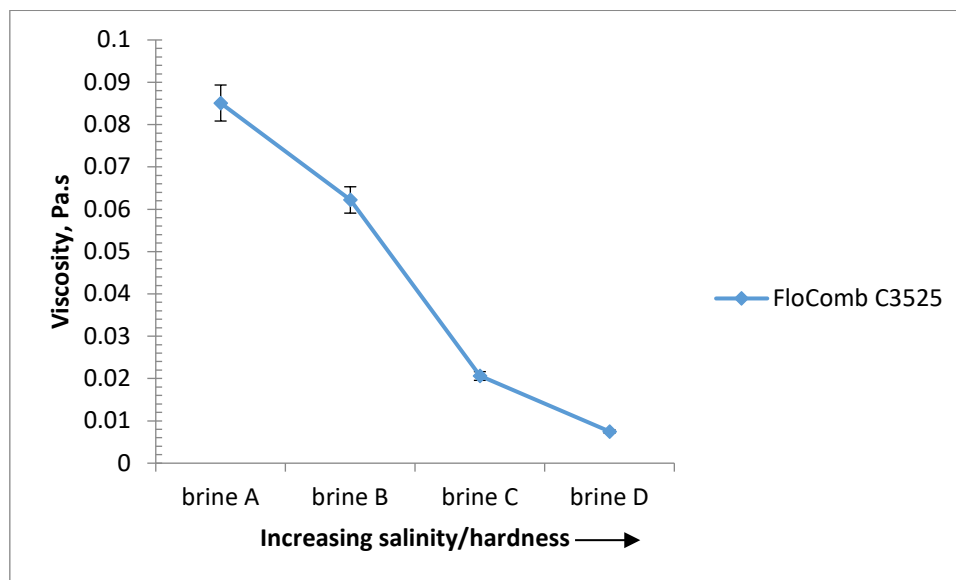


**Figure 18 - Effect of molecular weight on viscosity for three samples (750 ppm each) in 0.1% NaCl brine, pH of 8.2 and test temperature of  $25 \text{ }^\circ\text{C}$ . Shear rate range of  $0.1\text{-}100 \text{ s}^{-1}$  typical of field project was applied to the samples.**

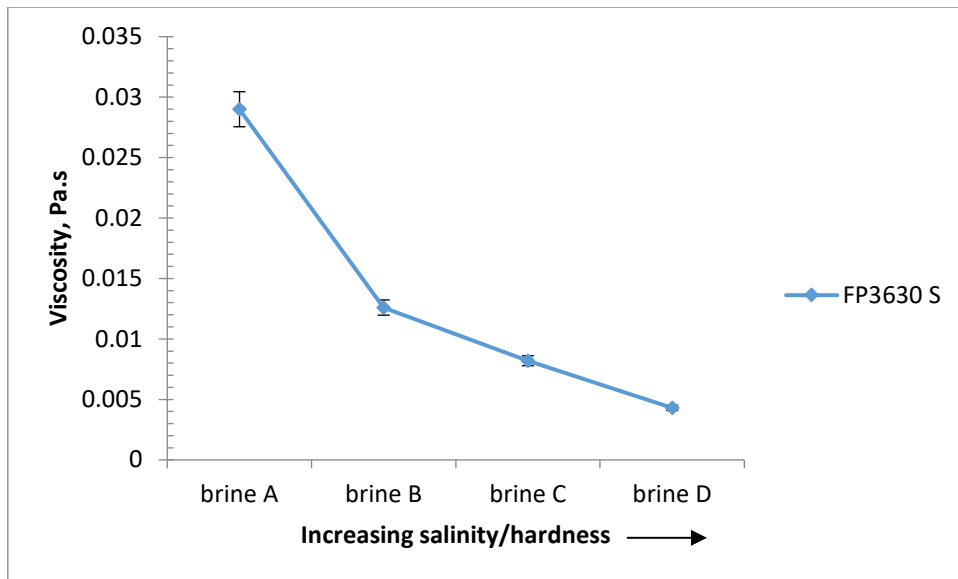
#### 1.4.10 Effects of Salinity and Hardness on Viscosity

Salinity refers to the presence of the major dissolved inorganic solutes, essentially  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , in aqueous samples. Salinity is quantified in terms of total concentration or content of such soluble salts (TDS). On the other hand **hardness** is the poly-valent-cation concentration of water (generally  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) or a measure of the quantity of divalent ions (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc.) in water, usually reported in mg/L or ppm. Hardness can be a mixture of divalent salts (referred to as total hardness); however,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are the most common sources of hard water. Hardness is measured by chemical titration.

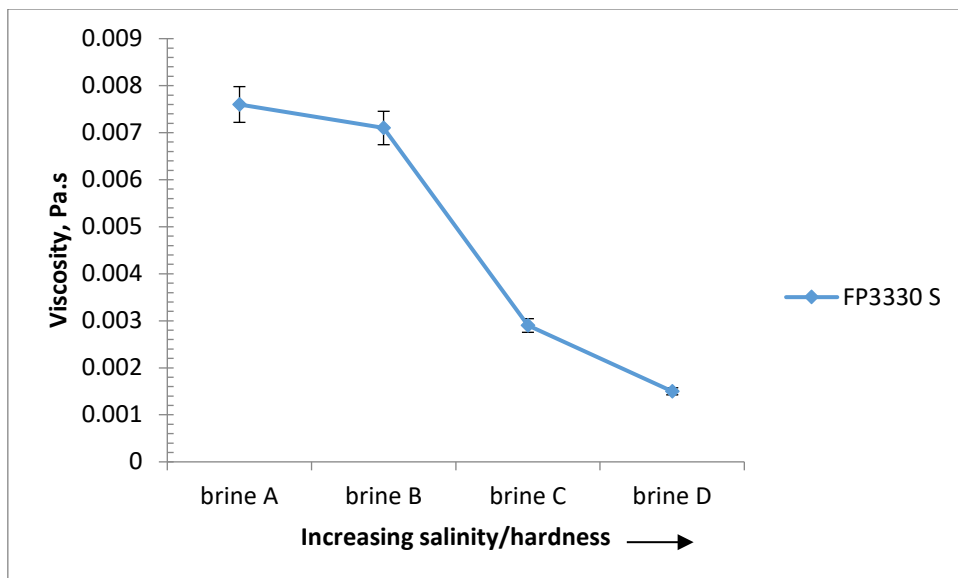
Figures 19 to 22 show the steady state flow procedure results at  $7.3 \text{ s}^{-1}$  for two polymers. Figure 19 shows that as the brine salinity increases, the viscosity reduces for C3525; the trend is similar for FP3630 S shown in Figure 20. However, FP3330 S shows a higher level of viscosity loss with increasing brine salinity concentration (Figure 21). The shielding effect of the charges on the polymer causes a reduction in electrostatic repulsion and thus less significant expansion of polymer coils in solution. This, in turn, leads to lower hydrodynamic volume which translates to reduction in viscosity. Furthermore, the polyion-metal complexes formed by the  $\text{Ca}^{2+}$  have greater effect on solution viscosity reduction (Wever et al., 2011). Figure 22 shows combined plots of the effect of salt concentrations on the viscosity of the three polymers. The figure shows that FloComb C3525 exhibits lower viscosity loss with increasing calcium ion concentration.



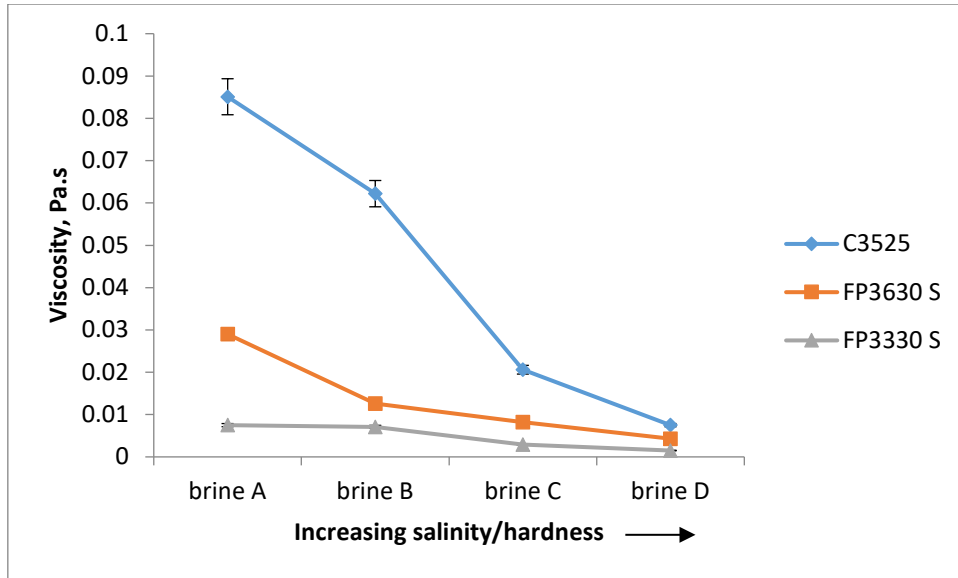
**Figure 19 - Effect of salinity and hardness on viscosity of 750 ppm of FloComb C3525 solution of pH=8.2 measured at constant shear rate ( $7.3 \text{ s}^{-1}$ ) and  $25 \text{ }^\circ\text{C}$**



**Figure 20 - Effect of salinity and hardness on viscosity of 750 ppm of FP3630 S solution of pH=8.2 measured at constant shear rate ( $7.3 \text{ s}^{-1}$ ) and  $25 \text{ }^{\circ}\text{C}$**



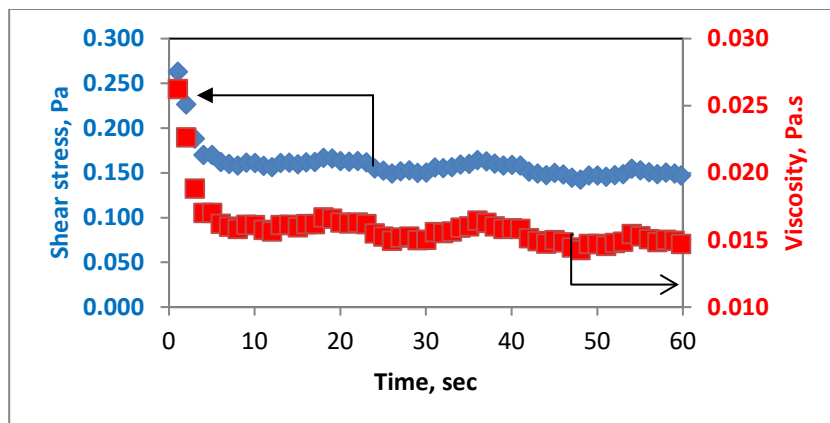
**Figure 21 - Effect of salinity and hardness on viscosity of 750 ppm of FP3330 S solution of pH=8.2 measured at constant shear rate ( $7.3 \text{ s}^{-1}$ ) and  $25 \text{ }^{\circ}\text{C}$**



**Figure 22 - Effect of salinity and hardness on viscosity of 750 ppm for the three samples solutions of pH=8.2 measured at constant shear rate ( $7.3 \text{ s}^{-1}$ ) and  $25 \text{ }^\circ\text{C}$ . This result confirms the manufacturer's claim that FloComb C3525 is calcium tolerant as it has lower viscosity loss as calcium ion concentration increases**

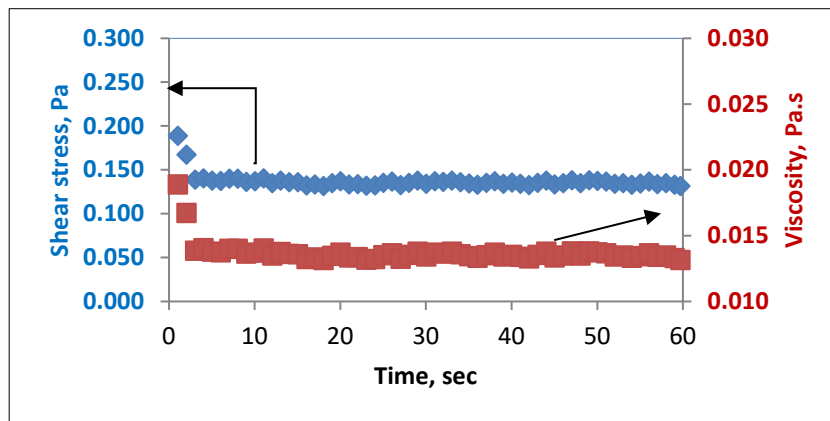
#### 1.4.11 Peak Hold Testing

Peak hold test is a controlled shear rate single point testing method used to examine the flow behaviour of polymer under constant shear rate. The test is usually carried by ramping up shear rate to a predetermined value and holding it constant for period of time. Figures 23 to 25 show the results of the peak hold tests on two polymers at a peak rate of  $10 \text{ s}^{-1}$ . The figures show stress overshoot and gradual relaxation to steady state viscosity, a trend typical of viscoelastic fluids. The steady state viscosity at  $10 \text{ s}^{-1}$  is about  $0.0148 \text{ Pa}\cdot\text{s}$  for FP3630 S (Figure 23) and  $0.013 \text{ Pa}\cdot\text{s}$  for C3525 (Figure 24). Figure 25 shows that sample FP3630 S has higher steady state viscosity than C3525.

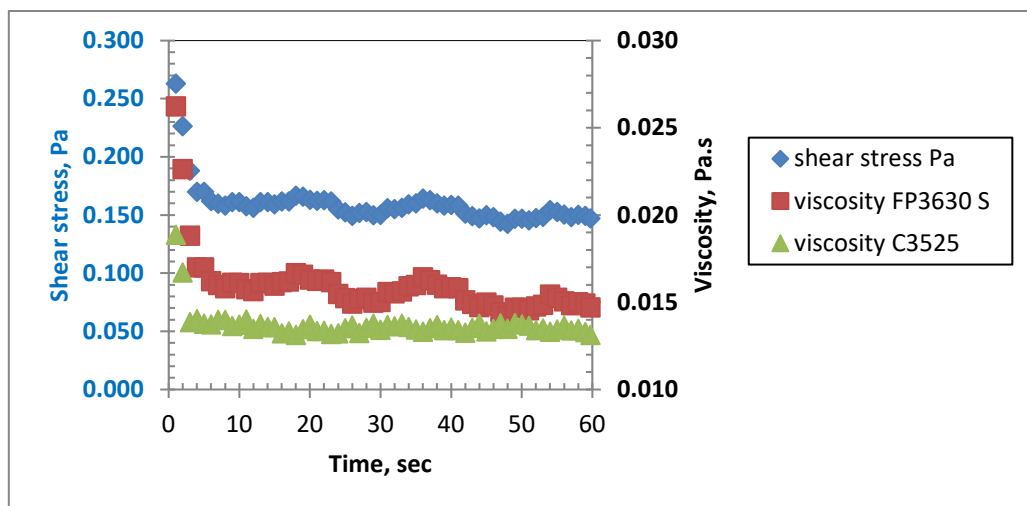


**Figure 23 - Peak hold testing of 750 ppm solution (pH=8.2) of FP3630 S in 0.4% NaCl measured at  $10 \text{ s}^{-1}$  and  $25 \text{ }^\circ\text{C}$**





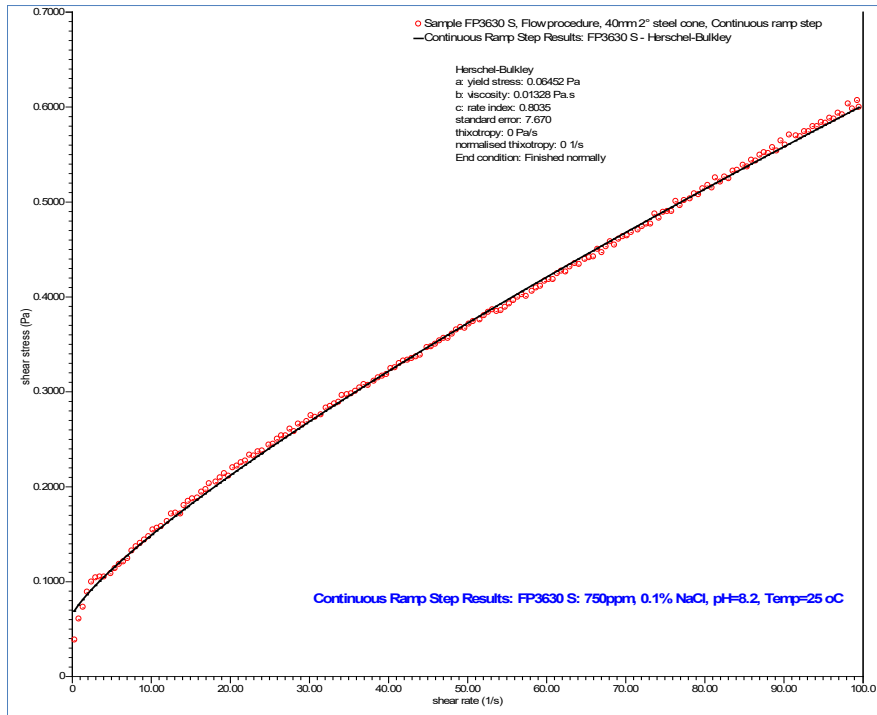
**Figure 24 - Peak hold testing of 750 ppm solution (pH=8.2) of FloComb C3525 solution in 0.4% NaCl measured at @ 10 s<sup>-1</sup> and 25 °C**



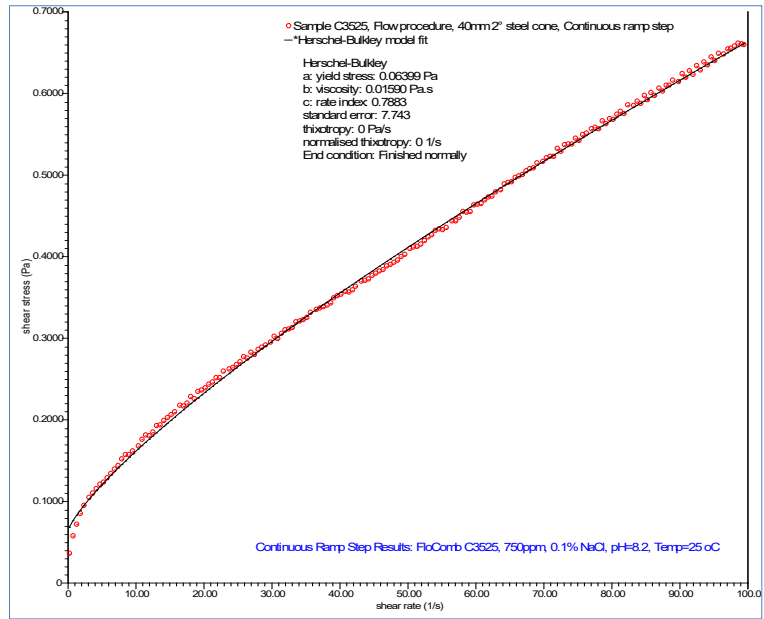
**Figure 25 - Peak hold comparison showing time-based viscosity stability for 750 ppm solutions (pH=8.2) of FP3630 S and FloComb C3525 @ 10 s<sup>-1</sup> in 0.4% NaCl**

#### 1.4.12 Continuous Ramp Test

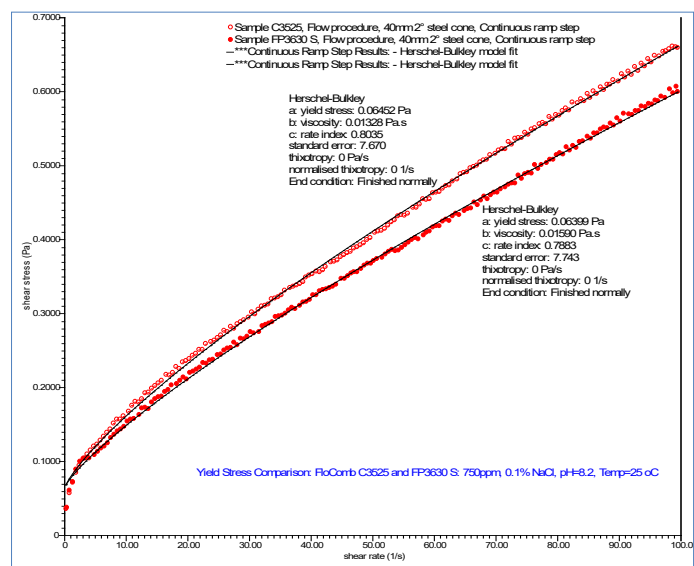
Continuous ramp test involves small incremental transition from a lower to a higher shear rate. The shear rate changes continuously in an incremental manner at a pre-defined rate to obtain a continuous curve. Figures 26 and 27 show the continuous ramp test results for 750 ppm solutions (pH=8.2) of FP3630 S and FloComb C3525 in 0.1% NaCl measured at 25 °C from 0.1-100 s<sup>-1</sup>. The ramp test was conducted to compare the yield property of the two samples. Data fit to Herschel-Bulkley model using TA Instruments advantage data analysis software shows that both samples (FP3630 S and FloComb C3525) have almost similar yield stresses (Figure 28).



**Figure 26 - Continuous ramp results for sample FP3630 S in 0.1% NaCl. The sample has a yield stress of about 0.06452 Pa**



**Figure 27 - Continuous ramp step results for sample FloComb C3525 in 0.1% NaCl. The sample has a yield stress of about 0.06399 Pa**

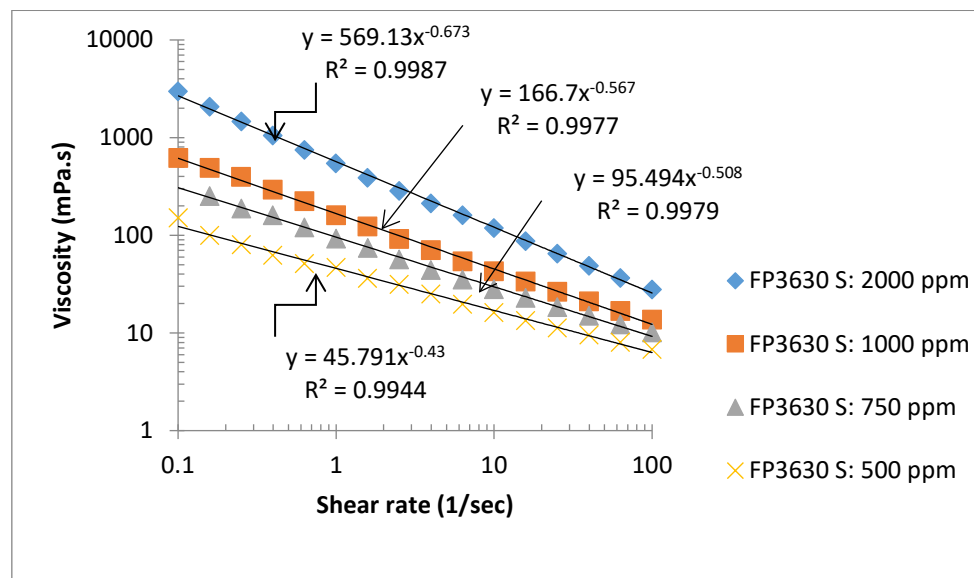


**Figure 28 - Data fit to Herschel-Bulkley model for samples FP3630 S and FloComb C3525: open cycles (o) is experimental data for FloComb C3525**

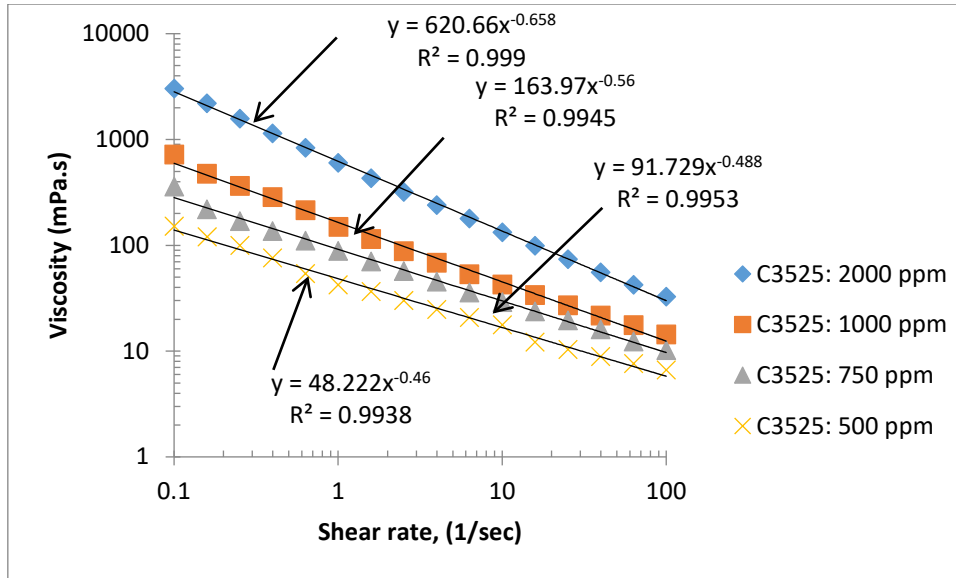
## 1.5 Modelling rheological behaviour of polymer solutions under shear and concentration

Polymer solutions are non-Newtonian fluids that conform to the power-law given by Eqn. (6) in Section 1.4.4.1. Greater loss of polymer viscosity has been attributed to the effect of shear rate. Factors such as salinity/hardness, shear rate, molecular weight, concentration, temperature, pore structure, etc. are known to affect polymer viscosity performance. For example, previous studies have shown that HPAM degradation is by physical breakdown resulting from shear (Jennings et al., 1970). Interestingly though, the results published by Seright et al. (2011) appears to suggest that shear has little effect on HPAM flow in actual reservoirs. Similarly, Ward and Martin (1981) showed that salinity/hardness adversely affects viscosity of HPAM solution. However, it appears models available for polymer risk assessments are being utilised for all scenarios with questionable results; with most of the models focussing on residual resistance factors (RRF) in modelling rheological behaviour of polymers in porous media.

In this section, data from viscosity measurements of two HPAM polymer products (SNF FP3630 S and FloComb C3525), each of different concentrations as described in Section 1.4 of this chapter. The rheological data were characterised using the power-law (Ostwald-de Waele) function given by Eqn. (6) (Bird et al., 1987, 1960). Viscosity and shear rate relationship for the two polymers are shown in Figures 29 and 30 respectively.



**Figure 29 - Data fit to Power-law of the rheological property of FP3630 S under different polymer concentrations. The polymer solutions were prepared in 0.1% NaCl brine, adjusted to pH of 8.2 and tested at 25 °C.**



**Figure 30 - Data fit to Power-law of the rheological property of C3525 under different polymer concentrations. The polymer solutions were prepared in 0.1% NaCl brine, adjusted to pH of 8.2 and tested at 25 °C.**

The experimental data and their power-law matching parameters for two polymer types are shown in Table 1. From the table, it is shown that polymer concentration affect the consistency index ( $K$ ), i.e., as polymer concentration increases,  $K$  increases. In contrast, the flow behaviour index ( $n$ ) reduces as polymer concentration ( $C_p$ ) increases.

**Table 1 - Power-law curve fitting parameters for FP3630 S and FloComb C3525.**

Polymer type	Concentration (mg/L)	Power-law parameters		
		$K$ (mPa.s $^{n-1}$ )	$n$	Variance
FP3630 S	500	45.79	-0.430	0.999
	750	95.50	-0.508	0.998
	1000	166.70	-0.567	0.998
	2000	569.13	-0.673	0.994
FloComb C3525	500	48.222	-0.460	0.999
	750	91.729	-0.488	0.995
	1000	163.97	-0.560	0.995
	2000	620.66	-0.658	0.994

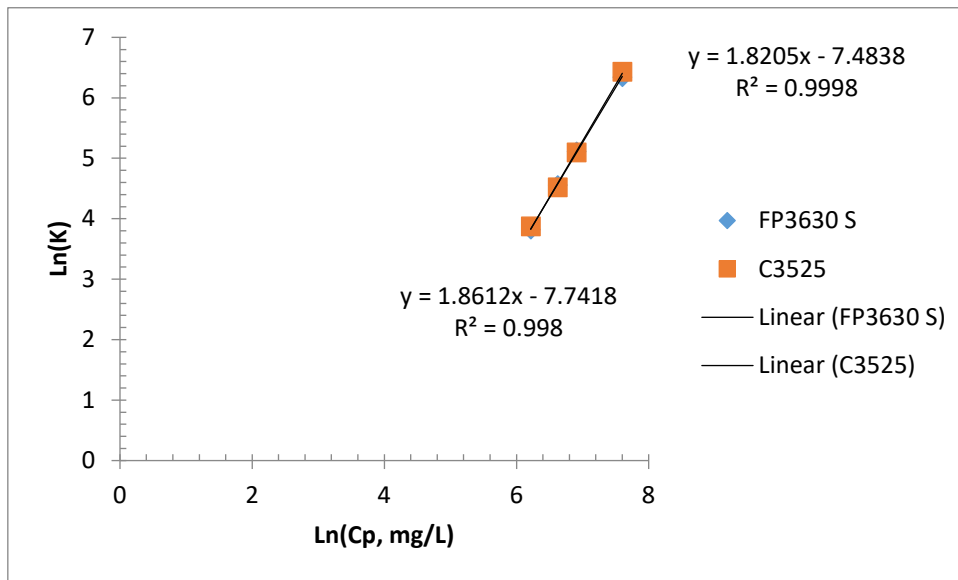
A generalised relationship between consistency coefficient ( $K$ ) and polymer concentration ( $C_p$ ) can be expressed as Eqn. (10 or 11); while the relationship between flow behaviour index ( $n$ ) and polymer concentration ( $C_p$ ) is written as Eqn. (12):

$$\ln(K) = a + b \ln(C_p) \tag{10}$$

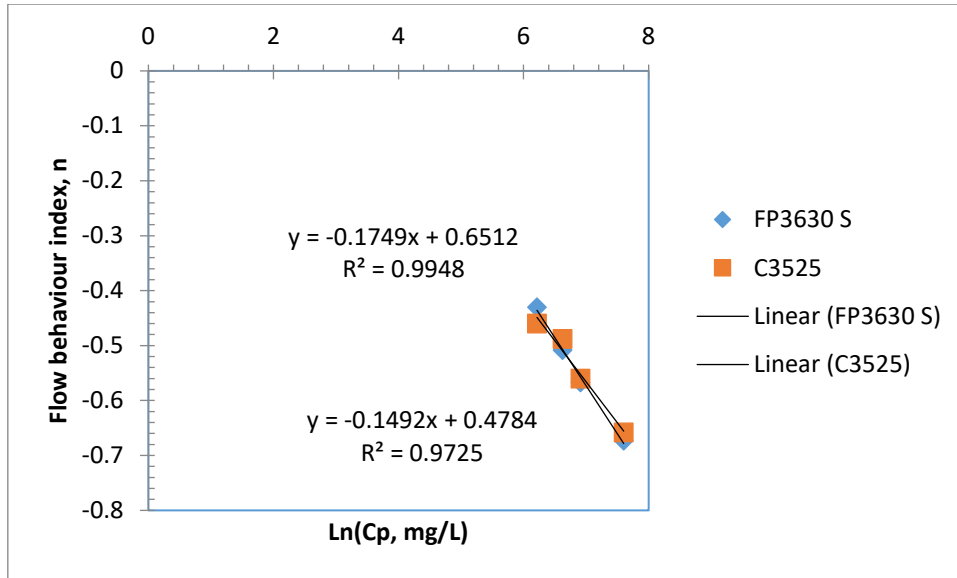
$$\text{Or } K = C_p^b e^a \tag{11}$$

$$n = c + d \ln(C_p) \tag{12}$$

where,  $a$ ,  $b$ ,  $c$ , and  $d$  are parameters measured in the laboratory. By use of equations 10 to 11, HPAM viscosity at 25 °C can be predicted under shear if the concentration of the polymer is known. Figure 31 shows the relationship between  $K$  and  $C_p$ ; while Figure 32 shows the relationship between  $n$  and  $C_p$ . The two figures clearly show that the two HPAM products have similar properties. Equations 10 to 12 are a useful tool for the prediction of HPAM rheological behaviour in field applications. The fitting parameters in equations 10 to 12 are tabulated in Table 2.



**Figure 31 - Fitted curve showing relationship between consistency coefficient and polymer concentration for FP3630 S and C3525. The figure shows that both polymers have identical properties.**



**Figure 32 - Fitted curve showing relationship between flow behaviour index and polymer concentration for FP3630 S and C3525. The figure shows similarity in flow behaviour for both polymers.**

**Table 2 - Fitting constants for polymer rheological models.**

Polymer type	Parameters and values					
	a	b	r <sup>2</sup>	c	d	r <sup>2</sup>
FP3630 S	-7.4838	1.8205	0.999	0.6512	-0.1749	0.995
FloComb C3525	-7.7418	1.8612	0.998	0.4784	-0.1492	0.973

## 1.6 Conclusion

Petroleum production operation encompasses all the technical and engineering activities or operations that take place during the production phase of an oilfield to maintain existing level of production or improve production with the aim being to ensure optimum production of hydrocarbon from the composite production systems based on the modelled inflow performance relationship and vertical lift performance. Production operation therefore includes, though not by means limited to, sand control, mineral scale control and treatment, wax, hydrate and asphaltene control and treatment, well production testing, production logging, well perforation, enhanced oil recovery, improved oil recovery, acidizing, hydraulic fracturing, acid fracturing, water shut off, reservoir pressure maintenance, gas lift etc. which can broadly be categorised into stimulation, chemical

treatment, water control, enhanced oil recovery and artificial lift operations. Polymers are widely used in most of these operations modify either the fluid properties or alter flow characteristics of the host reservoir rocks.

Many types of polymers are commonly used in the oil and gas industry including Xanthan gum, Polyacrylamide (PAM), Partially Hydrolysed Polyacrylamide (HPAM), Hydrogel and Hydroxyl Ethyl Cellulose (HEC). However, the most commonly used polymers in the oil and gas industry include Xanthan gum, Polyacrylamide (PAM), Partially Hydrolysed Polyacrylamide (HPAM), Hydrogel and Hydroxyl Ethyl Cellulose (HEC).

Polymer solutions are non-Newtonian fluids that conform to the power-law and Carreau rheological models. Viscosity is their most important property in petroleum production operation applications. However, a lot of factors can affect their viscosity including shear rate, salinity, active polymer concentration, pH, hardness and temperature. All polymers exhibit a shear-thinning behaviour; this behaviour is a result of intra-molecular effect that occurs due to the polymer extensional and orientational character while in solution.

A generalised model showing the relationship between consistency coefficient ( $K$ ) and polymer concentration ( $C_p$ ) of HPAM was developed.

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