

Viscosity and Viscoelastic Properties in Hydrophobically Modified Polymers for Enhanced Oil Recovery

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Preface

This dissertation is submitted as a part of the fulfillment for the degree of Philosophiae Doctor (PhD) at the University of Bergen (UiB), department of Chemistry. The research presented in this dissertation has been conducted at the Department of Chemistry at the University of Bergen and at the Centre for Integrated Petroleum Research (Uni Research CIPR) in the period 2012-2018.

The dissertation is divided in two parts, where the first part is divided into nine chapters. These consist of an introduction, thesis scope, methods and a summary of the work and main results in the research papers, an overall conclusion and ends with future outlook. The second part contains three research papers.

Acknowledgement

First and foremost, I would like to express my gratitude to my supervisors, Kristine Spildo and Tormod Skauge for excellent guidance and supervision during my Ph.D. study. I am very grateful for all the time you spent on countless meetings and discussions. Your remarks, suggestions and feedback have inspired me and have been of invaluable help.

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To friends and family, thank you for believing in me even when I did not. Thank you for all your support and patience. An extra thanks to Ingrid, Sarah and Henrik. Øyvind Andreas, it is hard to express how much your support, patience and love has meant and helped me through my PhD, I am forever grateful. Last but not least, little Magnus, thank you for being a ray of sunshine every day.

Abstract

Polymers have been studied and used for mobility control since the 1960s and found to improve the mobility ratio between the injected fluid and the displaced oil. However, small changes in polymer structure and/or relation between different physical aspects can change the polymers behavior and their viscosifying ability. The most used and studied polymer for EOR is hydrolysed polyacrylamide (HPAM). The viscosifying ability of HPAM is strongly dependent on temperature and brine salinity and is poor at HTHS (high temperature, high salinity) conditions. To address this problem, several modified polymers of HPAM, for instance hydrophobically modified HPAM have been introduced. Some have shown potential to withstand a loss of viscosity in high salinity brines and at high temperatures as the hydrophobic groups present are able to interact and create a network

A number of factors within the structure of a polymer; such as molecular weight, type of backbone, degree of hydrolysis, type of hydrophobic groups, length and amount of hydrophobic groups etc, can influence the polymer properties. External parameters as salinity, pH, temperature and shear forces applied will also affect how the polymer behaves.

In this thesis rheological behavior of two series of hydrophobically modified HPAM polymers, HMPAM, are studied and compared to their HPAM counterpart. The polymer series varies in degree of hydrophobicity, where the first series changes in amount of hydrophobic groups attached to the polymer backbone and the second changes in length of hydrophobic group. The study can be divided in three parts; influence of salinity, influence of temperature and differences in bulk viscosity and in-situ viscosity.

The first paper reports a salinity study on the first polymer series where the hydrophobicity changes with increasing amount of hydrophobic groups. The rheological measurements showed that in order to increase the viscosity in the HMPAM polymers above HPAM, a threshold value of amount of hydrophobic groups needed to be crossed. This threshold value was lowered with increasing salinity.

In the second paper, variation in both salinity and temperature was investigated for the polymer series with increasing length of the hydrophobic group. The main findings in this study showed that the polymer with the most viscosifying abilities at high salinity was outperformed by the less viscous polymer at high temperature, especially in both high salinity and high temperature.

Even though a polymer might have good properties in bulk rheology measurements, the behavior and interactions in a porous media might be very different. Paper III compared an HMPAM polymer with its HPAM counterpart in both bulk rheology and in-situ rheology measurements. The polymers showed similar behavior and shear viscosities in bulk measurements. However, HMPAM experienced higher in-situ viscosity, which most likely is a result of induced hydrophobic interactions in the porous media due to spatial restrictions.

List of publications

Paper I:

Viken, A. L., Skauge, T, Spildo, K, Rheological properties of a hydrophobically modified anionic polymer: Effect of varying salinity and amount of hydrophobic moieties. *Journal of Applied Polymer Science*, 2016. 133(23): p. 1-8.

Paper II:

Viken, A.L., Skauge, T., Svendsen, P., Time, P.A., Spildo, K., Thermo-thickening and Salinity Tolerant Hydrophobically Modified Polyacrylamides (HMPAMs) for Polymer Flooding, *Energy & Fuels*, 2018

Paper III:

Viken, A.L., Spildo, K., Reichenbach-Klinke, R., Djurhuus, K., Skauge, T., Influence of Weak Hydrophobic Interactions on in Situ Viscosity of a Hydrophobically Modified Water-Soluble Polymer, *Energy & Fuels*, 2018, 32, 89-98

Abbreviations

API	American Petroleum Institute
CIPR	Centre for Integrated Petroleum Research
CP	Cone plate
DLS	Dynamic light scattering
EOR	Enhanced oil recovery
HLB	Hydrophilic lipophilic balance
HMPAM	Hydrophobically modified hydrolysed polyacrylamide
HMWSP	Hydrophobically modified water-soluble polymers
HPAM	Hydrolysed polyacrylamide
IOR	Improved oil recovery
LCST	Lower critical solution temperature
LVE regime	Linear viscoelastic regime
PAA	Poly acrylic acid
PAM	Polyacrylamide
PPM	Parts per million, mass fraction (g/g)
RF	Resistance factor
rpm	Revolutions per minute
RRF	Residual resistance factor
SANS	Small-angle neutron scattering
SSW	Synthetic seawater

Symbols

A	Area [cm ²]
α	Shape parameter characteristic of pore structure, dimensionless
C	Polymer concentration [ppm]
c*	Critical overlap concentration [ppm]
γ	Shear rate [1/s]
$\dot{\gamma}_{eff}$	Effective shear rate [ml/min]
δ	Phase shift angle [°]
E _D	Microscopic displacement efficiency
E _A	Areal sweep efficiency
E _V	Vertical sweep efficiency
E _{vol}	Volumetric sweep efficiency
f	Fractional flow
f	Frequency [Hz]
G	Shear modulus (Pa)
G'	Storage modulus / Elastic modulus [Pa]
G''	Loss modulus / Viscous modulus [Pa]
η	Viscosity [Pa·s]
η_R	Reduced viscosity [cm ³ /g]
η_s	Shear Viscosity of solvent [Pa·s]
η_{sp}	Specific viscosity, dimensionless
η_0	Intrinsic viscosity [ppm ⁻¹]

I	Ionic strength [mol/kg]
K	Empirical constant to calculate Power Law curve
k	Permeability [m^3]
$k_{e,i}$	Effective permeability of component i
$k_{r,i}$	Relative permeability of component i
L	Length [cm]
λ	Mobility [$\text{m}^2/\text{mPa}\cdot\text{s}$]
λ_o	Mobility of oil [$\text{m}^2/\text{mPa}\cdot\text{s}$]
λ_w	Mobility of water [$\text{m}^2/\text{mPa}\cdot\text{s}$]
M	Mobility ratio, dimensionless
MDa	Mega Dalton
$\text{mPa}\cdot\text{s}$	Milli Pascal second
Mw	Molecular weight [g/mole or MDa]
μ	Viscosity [$\text{Pa}\cdot\text{s}$]
n	Empirical constant to calculate Power Law curve
P	Pressure [bar]
ΔP	Pressure difference in Darcy Law [bar]
q	Flow rate [ml/min]
Q	Volumetric flow rate [cm^3/s]
S_{or}	Residual oil saturation
S_{wi}	Irreducible water saturation
$\tan \delta$	Loss factor/ damping factor, dimensionless

T_{ass}	Association temperature [°C]
τ	Shear stress [N/m ²]
T_{max}	Maximum viscosity at given temperature
u	Darcy velocity [m/day]
V_{b}	Bulk volume [cm ³]
$V_{\text{n,eff}}$	Effective pore volume [cm ³]
φ	Porosity, dimensionless
φ_{eff}	Effective porosity, dimensionless
ω	Angular frequency [rad/s]
wt%	Mass weight percent [%]
z	Charge of ion

Contents

Preface.....	III
Acknowledgement.....	IV
Abstract	V
List of publications.....	VII
Abbreviations	VIII
Symbols.....	IX
1. INTRODUCTION.....	1
2. BASIC RESERVOIR ENGINEERING CONCEPTS.....	5
2.1 Oil recovery: primary, secondary and tertiary	5
2.2 Oil recovery efficiency: macroscopic and microscopic displacement efficiency	6
2.3 Porosity	8
2.4 Permeability and relative permeability	8
2.5 Relation Darcy velocity and shear rate	10
2.6 Mobility ratio and fractional flow theory.....	10
2.7 Resistance factor and residual resistance factor.....	12
3. ENHANCED OIL RECOVERY BY POLYMER FLOODING.....	13
3.1 Mechanisms of polymer EOR	13
3.1.1 Modification of mobility ratio.....	14
3.1.2 Microscopic diversion and viscoelastic effects.....	15
4. POLYMER RHEOLOGY.....	17
4.1 Bulk rheology.....	17
4.1.1 Shear viscosity	17
4.1.2 Viscoelasticity	19
4.1.3 Intrinsic viscosity	21
4.1.4 Power Law	22
4.2 In-situ rheology	23
4.3 Factors affecting polymer viscosity and viscoelasticity.....	25
5. EOR POLYMERS.....	29
5.1 Hydrolysed polyacrylamide, HPAM	30
5.1.1 Effect of salinity on viscosity.....	31
5.1.2 Effect of temperature on viscosity.....	33
5.1.3 Effect of shear on viscosity	33
5.2 Hydrophobically modified polyacrylamide, HMPAM.....	34
5.2.1 Associative polymers in aqueous solutions.....	35
5.2.2 Effect of salinity on viscosity.....	36

5.2.3 Effect of temperature on viscosity	38
6. MATERIALS AND METHODS	41
6.1 Polymers A series.....	42
6.2 Polymers P series	43
6.3 Brine composition	44
6.4 Rheological measurements.....	44
6.4.1 Shear and oscillatory measurement at ambient temperatures	44
6.4.2 Shear and oscillatory measurements at elevated temperatures	45
6.5 Core flooding	45
7. RESULTS AND DISCUSSION	47
7.1 Rheological properties of a HMPAM: Effect of salinity and mole% of hydrophobic units (Paper I).....	48
7.2 Thermo-thickening and Salinity Tolerant Hydrophobically Modified Polyacrylamides (HMPAMs) for Polymer Flooding (Paper II)	53
7.3 Influence of Weak Hydrophobic interaction on In-Situ Viscosity of HMPAM (Paper III)	63
8. CONCLUDING REMARKS	71
9. FURTHER WORK	75
REFERENCES.....	77

1. INTRODUCTION

Today oil and gas are the main energy sources in the world, and since traditional primary and secondary production methods (for instance waterflooding) typically recover one third of oil in place, new and improved methods are in demand (Sorbie, 1991). Enhanced oil recovery (EOR) methods have been important to develop a more efficient recovery process and hence increasing the oil production (Lake, 1989).

Methods to improve the oil recovery are continuously studied. One of the most known and used methods is waterflooding. Waterflooding is used to sweep the reservoir and thereby increase the oil production. However, in reservoirs with highly viscous oil, the significant difference in the mobility of the two phases creates some challenges. The water injected creates paths through the oil, thus creating an unstable displacement which leads to an early breakthrough of water and poor sweeping of the reservoir. (Lake, 1989, Sheng, 2011, Sorbie, 1991).

The aim of polymer flooding is to enhance the viscosity of the injected fluid to improve the mobility ratio between injected water and oil. Thus, creating a more stable front towards the displaced oil, which will increase the sweep efficiency in the reservoir (Lake, 1989, Sorbie, 1991). Reducing the mobility of the injected water can also improve the reservoir heterogeneity. In the reservoir, the permeability changes in different layers and areas. Injected fluids with a high mobility will tend to flow in the layers with a high permeability, therefore leaving the low permeability layers unswept. A better mobility ratio between the displaced and displacing fluid, can give an improvement of the sweep efficiency since the injected water can be diverted from areas that previously have been swept (Green and Willhite, 1998, Needham and Doe, 1987).

Partially hydrolysed polyacrylamide, HPAM, is the most used polymer in EOR and has been studied for mobility control since the 1960s, due to its viscosifying abilities and low cost (Sorbie, 1991, Wever et al., 2011). HPAM is shear thinning in rheometers, however often shows shear thickening in porous media. Even though HPAM have some great qualities for use in EOR, it also has shown limitation in high salinity, high

temperature and with high shear forces present (Lake, 1989, Sorbie, 1991, Wever et al., 2011). Being a polyelectrolyte, HPAM increases its viscosity due to repulsions between the charged sites along the backbone, giving a high hydrodynamic volume of the polymer and further a high viscosity. Therefore, with salt present these charges will be neutralized and reduce the repulsion between the polymer backbone, causing loss of hydrodynamic volume and loss of viscosity in the polymer solution (Dupuis et al., 1994, Dupuis et al., 2011, Ellwanger et al., 1980, Lake, 1989, Levitt and Pope, 2008). Also, mechanical degradation of HPAM has occurred in porous media, where high rates cause breakage in the polymer structure (Sorbie, 1991). As an alternative to HPAM, hydrophobically modified versions of HPAM have been presented to maintain viscosity in reservoir conditions.

Hydrophobically modified polymers, HMPAM, contains hydrophobic groups attached to the polymer backbone giving the polymer ability to create hydrophobic interactions. Therefore, the HMPAM polymer might be able to withstand loss of viscosity compared to HPAM under the same conditions. HMPAM is as HPAM also a polyelectrolyte and will experience screening of the anionic sites. However, increased polarity of the brine increases the hydrophobic interactions between the polymer chains, which further increase the viscosity of the solution (Reichenbach-Klinke et al., 2011).

Thesis objective:

Polymers used in enhanced oil recovery are added to improve the mobility ratio between oil and injected water. Therefore, knowing the polymers ability to generate high viscosity in reservoir conditions and maintain the viscosity at high salinities and temperatures are crucial. Hydrolysed polyacrylamide, HPAM, has been the most known EOR polymer due to its low cost and viscosifying ability (Sorbie, 1991, Wever et al., 2011). However, HPAM has shown large loss of viscosity in increasing salinity and at high temperatures. Although hydrophobically modified polymers are said to offer significant advantages over HPAM, the complex, polydisperse polymers fitted for polymer flooding are far less described in literature than HPAM and monodisperse HMPAM systems with low molecular weight.

The objective in this thesis is to evaluate how changes in the polymer structure such as degree of hydrophobicity, and changes in the surrounding environment, specifically salinity and temperature affect the rheological properties of the polymer.

The theory and research revolving low molecular weight, monodispersed polymer systems can be used to explain some of the behavior seen in the applied, polydisperse polymer. Knowledge about the behavior of the polydisperse polymer systems is important to get an impression if they are a good fit for EOR.

As mentioned previously, polymers used for mobility control need to have a high viscosity and be able to maintain most of their viscosity during flooding (Sorbie, 1991). One of the factors that contribute the most to increasing viscosity is the molecular weight of the polymers (Sorbie, 1991, Wever et al., 2011). This factor, as well as the industry's wish to apply cost efficient chemicals in the reservoir are contributing to choosing polydisperse, large polymers. The process of separation based on molecular weight is less precise in a large industrial scale and is cost-driving.

Both shear viscosity and elasticity of a polymer can be altered significantly with small changes in the structure (Kujawa et al., 2006, Wever et al., 2011). Hydrophobic groups creating intra- and intermolecular interactions are contributing to a characteristic behavior for the shear viscosity of HMPAM polymers with a steep increase in viscosity above the critical overlap concentration, c^* (Regalado et al., 1999). However, with low degree of hydrophobicity this behavior is typically not seen, and the HMPAM polymers are not behaving differently from HPAM (Kujawa et al., 2006, Wever et al., 2011). In this thesis I want to study this more closely. The shear viscosity and viscoelasticity were studied in two different series of HMPAM polymers. One of the series is with increasing number of hydrophobic groups attached to the backbone, and the other series with increasing length of the hydrophobic group. Looking at how the increasing hydrophobicity affected the shear viscosity, and if a certain degree of hydrophobicity is needed in order to build a network structure and enhance the viscosity beyond the viscosity of the HPAM counterpart, was one of the focuses.

External parameters as salinity; ionic strength and composition of the brine with divalent ions present, and temperature can also affect the interactions between the polymers and can both reduce and enhance the shear viscosity (Wever et al., 2011). Understanding the interplay between the external parameters (salt, temperature) and the inherent parameters (hydrophobicity) within the applied polymer can broaden our knowledge regarding which type of qualities needed to enhance the bulk and in-situ viscosity.

Viscosifying abilities of the hydrophobically modified polymers have been studied by using the shear viscosity measurements. However, spatial restrictions in the porous media can induce hydrophobic interactions, giving the HMPAM polymers a different behavior in-situ than seen in bulk rheology. Hydrophobic interactions in a porous media might not only create higher in-situ viscosity and better mobility control. One of the concerns is multilayer adsorption in the rock core, as the polymers adsorbed to the core are interacting with the flowing polymer. This can lead to a loss of polymer concentration and decreasing viscosity. Investigating the viscosifying abilities of the hydrophobically modified polymers in sandstone cores and comparing it towards the rheological shear viscosity measurement, provides us with more accurate information on how the polymer will behave in a reservoir and the potential uses of them.

2. BASIC RESERVOIR ENGINEERING CONCEPTS

In this chapter, oil recovery will be defined and the three recovery stages (primary, secondary and tertiary) will be explained. Further the oil efficiency with macroscopic and microscopic displacement efficiency will be presented.

2.1 Oil recovery: primary, secondary and tertiary

Primary recovery is defined as production by natural reservoir pressure, and there is no need for external heat or fluids to produce oil (Sheng, 2011). The natural pressure in the reservoirs can be caused by different driving forces as for instance gravity drainage and gas cap drive (Ahmed and McKinney, 2005).

Secondary recovery methods are generally used to maintain reservoir pressure by injecting either water or gas (Lake, 1989, Sheng, 2011). Injection of water is the most known and used secondary recovery method, with low cost and high efficiency. However, large amounts of oil are still left in the reservoir after secondary recovery as the oil is immobilized by capillary forces or left behind as unswept oil (Mai and Kantaz, 2009)

Tertiary recovery is the techniques used after secondary recovery and is injection of fluids, such as chemicals, gases and thermal energy (Lake, 1989). Improved oil recovery (IOR) is a broadly used term and implies improving oil recovery, enhanced oil recovery (EOR) however, is an IOR method and is more specific EOR methods often implies that other than plain water or brine is injected into the reservoir (Lake, 1989). The different recovery stages are illustrated in Figure 2.1.

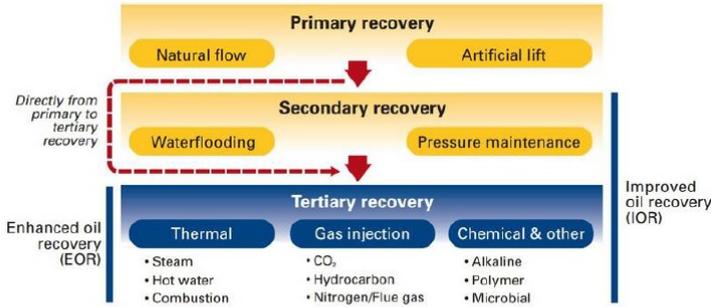


Figure 2.1: Oil recovery methods (Sevin, 2013)

2.2 Oil recovery efficiency: macroscopic and microscopic displacement efficiency

The displacement efficiency can be divided into macroscopic and microscopic displacement efficiency (Green and Willhite, 1998). Macroscopic displacement efficiency is also called the volumetric displacement, E_{Vol} , and is a measure of how well the displacing fluid is in contact with the parts of the reservoir containing oil (Green and Willhite, 1998). It is a measure of how effectively the displacing fluid sweeps the reservoir and moves the displaced fluid towards the production well, both vertical and areal sweeps. The frontal movement, the mobility and stability of the displacing fluid is controlled by the macroscopic displacement efficiency. The volumetric displacement is further divided into the vertical and areal sweep efficiency (Figure 2.2).

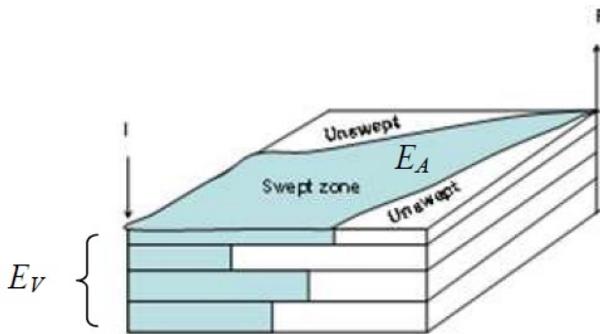


Figure 2.2: Schematic figure showing vertical and areal sweep efficiency in a reservoir (Skarestad and Skauge, 2009).

Geometry of the injection and productions wells pattern, heterogeneity in the reservoir and mobility ratio affects the areal sweep efficiency, while the vertical sweep efficiency is influenced by reservoir properties as permeability in the different layers and the mobility ratio between the displacing and displaced fluid (Green and Willhite, 1998)

Microscopic displacement efficiency, E_D is a measure of the displacement of oil at pore scale, and how effective the displacing fluid is at mobilizing oil where the displacing fluid contacts the oil (Green and Willhite, 1998). The microscopic displacement can affect the residual oil saturation, S_{or} and is mainly increased with EOR methods which reduces the interfacial tension, e.g. surfactant- and miscible gas flooding. The overall displacement can be expressed as:

$$E = E_D \cdot E_{Vol} = E_D \cdot E_V \cdot E_A \quad (2.1)$$

where E_D , E_A , E_V and E_{Vol} are respectively the microscopic, areal, vertical and volumetric displacement sweep efficiencies (Green and Willhite, 1998).

Polymer flooding improves the macroscopic sweep efficiency, and therefore mainly the volumetric (areal and vertical) sweep efficiency is of importance in a polymer flooding.

2.3 Porosity

Porosity is defined as the void in the total volume of the rock and is often referred to as the pore volume in the hydrocarbon reservoir (Skarestad and Skauge, 2009). Porosity can be divided into effective and ineffective porosity. The effective porosity is defined as the pore space which interconnects with other pores and allows fluid to flow, i.e. catenary pores which has more than one passage or cul-de-sac pores (dead-end pores) that only connects with other pores through one passage. Ineffective porosity is where the pores are closed for fluid flow (closed pores).

Effective porosity depends on several factors, i.e. rock type, grain size and grain packing, and can be described as the ratio between the effective pore volume, $V_{p,eff}$ and the bulk volume, V_b (Skarestad and Skauge, 2009, Sorbie, 1991):

$$\varphi_{eff} = \frac{V_{p,eff}}{V_b} \cdot 100\% \quad (2.2)$$

2.4 Permeability and relative permeability

The permeability of the porous media can describe the medium's ability to transmit fluids through a network in the pores and is directly linked to porosity (Lake, 1989, Sorbie, 1991). It is an important parameter and can influence the behaviour of the polymers within the porous media. Darcy's law is used to describe permeability in a linear, horizontal flow (Zolotuchin and Ursin, 2000):

$$Q = \frac{k \cdot A}{\mu} \cdot \frac{\Delta P}{L} \quad (2.3)$$

Q is the volumetric flow, k is the absolute permeability, A is the cross-sectional area, μ is the fluid viscosity, ΔP is the pressure difference over the porous media and L is the length of the core sample. The permeability is often expressed in Darcy (D) or millidarcy (mD) due to practical purposes, however the SI-unit for permeability is m^2 ($1D = 9.87 \times 10^{-13} m^2$) (Lake, 1989, Sorbie, 1991).

When two or more fluids are present in the flow, the individual phases will be dependent on the saturation of each fluid. An extension of Darcy's law to a multiphase flow will give the effective permeability ($k_{e,i}$) for each fluid (Zolotuchin and Ursin, 2000):

$$k_{e,i} = \mu_i \frac{L}{A} \frac{Q_i}{\Delta P_i} \quad (2.4)$$

The ratio between the effective permeability and absolute permeability is the relative permeability ($k_{r,i}$) and is defined:

$$k_{r,i} = \frac{k_{e,i}}{k} \quad (2.5)$$

Anderson (1987) stated that the relative permeability is “a direct measure of the ability of the porous system to conduct one fluid when one or more fluids are present”. Wettability and rock properties are affecting the relative permeability as these parameters can control the flow and spatial distribution of fluids in the core.

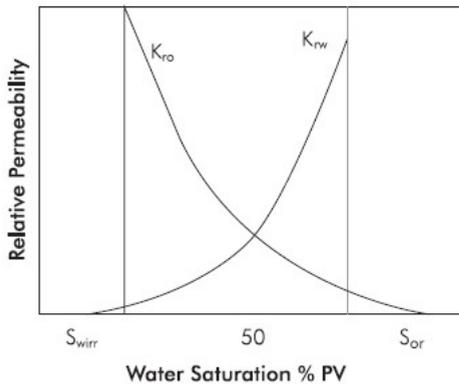


Figure 2.3: Relative permeability curve for oil and water in an oil wet reservoir (Anderson, 1986)

From Figure 2.3 the relative permeability for oil and water is presented were curve for k_{rw} shows the water phase and the curve for k_{ro} shows the oil phase. The relative permeability for each of the phases is reduced when the saturation of that phase decreases. When the relative permeability is zero, the phase is no longer able to flow. Therefore, the saturation of the phase is not possible to be further reduced. S_{or} in the

figure represents the residual oil saturation, and S_{wi} the irreducible water saturation. At saturations below S_{or} and S_{wi} , respectively oil and water are immobile, and these phases cannot be further reduced (Lake, 1989).

2.5 Relation Darcy velocity and shear rate

The Darcy velocity is a measure of the flow rate rate entering the porous media, per unit cross-sectional area of the sample (Equation 2.6)

$$u = \frac{Q}{A} \quad (2.6)$$

Effective shear rate (ml/min) can be calculated from the Darcy velocity by using Equation 2.7.

$$\dot{\gamma}_{eff} = \alpha \cdot \frac{4u}{\sqrt{8k\phi}} \quad (2.7)$$

k is the permeability and ϕ is the porosity of the rock. α is shape parameter characteristic of the pore structure. For sandstone cores, 2.5 is often used as a value of α . (Sorbie, 1991)

2.6 Mobility ratio and fractional flow theory

Mobility of a phase, i.e water, oil or gas is a measure of how easily this phase flows through a porous media in multiphase flow (Zolotuchin and Ursin, 2000).

Mobility ratio, M is defined as the ratio between the mobility of the displacing fluid, (water, polymer) and the mobility of the displaced fluid (oil):

$$M = \frac{\lambda_w}{\lambda_o} = \frac{(\mu_w/k_w)}{(\mu_o/k_o)} \quad (2.8)$$

λ , μ and k are respectively mobility, viscosity and effective permeability for oil (o) and water (w) (Sorbie, 1991). At $M > 1$ is the water more mobile than the oil, creating an unstable front, viscous fingering and might lead to an early breakthrough and an

inefficient displacement process (Figure 2.4) (Sorbie, 1991). When $M \leq 1$, the injected fluid is less mobile than the oil which creates a more stable front and a more piston manner displacement (Standnes and Skjevraak, 2014). Mobility control process is based on maintaining a favorable mobility ratio to improve sweep efficiency (Sheng, 2011) and is linked to every chemical process in the reservoir.

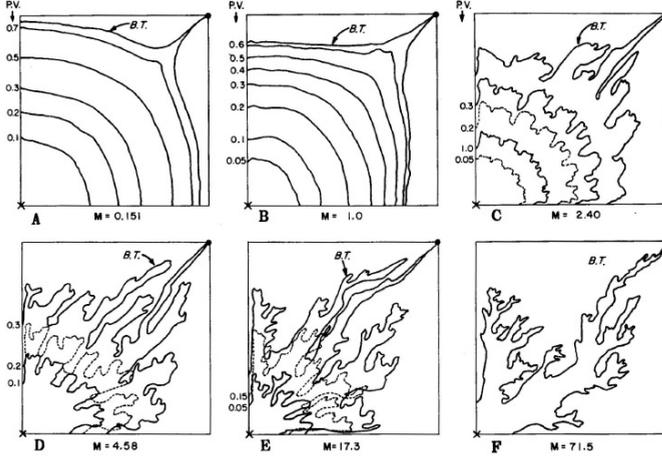


Figure 2.4: Displacement fronts at different mobility ratios and injected pore volumes until breakthrough. The model is a quarter five-spot (Habermann, 1960)

Oil and water will after breakthrough, flow simultaneously through the porous media until S_{or} is reached. Fractional flow theory can be used to simplify this two-phase flow of oil and water and can determine the fractional volumetric flow rate of the phases. Fractional flow equation presented by Buckley and Leverett (Buckeley and Leverett, 1942) and the relative permeability curves can be used to understand the displacement process between injected water and oil:

$$f_w = \frac{q_w}{q_w + q_o} = \frac{1}{1 + \frac{k_{ro}\mu_w}{k_{rw}\mu_o}} \quad (2.9)$$

$$f_o = 1 - f_w \quad (2.10)$$

where f_o and f_w are respectively the oil and water fractional flow, q_o and q_w are the oil and water flow rate, k_{ro} and k_{rw} are the relative permeabilities of oil and water, and μ_o and μ_w are the viscosity of respectively oil and water.

2.7 Resistance factor and residual resistance factor

As mentioned earlier, flooding polymer will increase the viscosity of the injected fluid and can reduce the permeability of the swept areas, which further will lead to a mobility reduction for the displacing fluid. The mobility reduction can be measured through the resistance factor, RF which is defined as the ratio of the mobility of the solvent of the polymer solution, λ_w , and the mobility of the polymer solution, λ_p (Sorbie, 1991):

$$RF = \frac{\lambda_w}{\lambda_p} \quad (2.11)$$

The residual resistance factor, RRF gives the polymer induced permeability reduction.

$$RRF = \frac{\lambda_1}{\lambda_{1a}} \quad (2.12)$$

where λ_1 is the mobility of a brine before and λ_{1a} is the mobility of the brine solution after polymer injection. RRF can also be expressed with the brine permeability before, ($k_{w,initial}$) and after ($k_{w,end}$) polymerflooding:

$$RRF = \frac{k_{w,initial}}{k_{w,end}} \quad (2.13)$$

3. ENHANCED OIL RECOVERY BY POLYMER FLOODING

This chapter will explain how polymers added in the injected water will affect the mobility ratio and fractional flow theory, and thereby the volumetric sweep efficiency. Further microscopic diversions and viscoelastic effects will be mentioned.

3.1 Mechanisms of polymer EOR

Polymer flooding is a chemical, tertiary method to enhance oil recovery, and is a further development of the secondary method, waterflooding. Polymers are normally preferred in reservoirs where the oil is highly viscous or where there is reservoir heterogeneity with oil bearing layers at different permeabilities (Skarestad and Skauge, 2009).

As mentioned previously, is the mobility ratio between the displacing fluid and the displaced oil crucial for the volumetric sweep efficiency of the reservoir. With a lower viscosity in the displacing fluid than the displaced fluid, there is a potential for an unstable front and possible fingering. This potential increases with increasing mobility ratio between the oil and water (Lake, 1989, Sorbie, 1991). Therefore, to improve the mobility ratio and thus the unstable front, polymers has been used to increase the viscosity of the injected fluid (Wever et al., 2011). This further enhances the performance of the displacing fluid with a better volumetric sweep efficiency. Polymer flooding cannot reduce the residual oil saturation (S_{or}) due to oil and water being immiscible fluids, and water is therefore not able to displace oil completely. However, the S_{or} can be reached earlier when polymers are present in the injected water which is beneficial economically (Needham and Doe 1987, Wang et al., 2000, Xia et al., 2004).

According to Needham and Doe (1987) there are three ways the polymers can increase the efficiency of the oil recovery process; polymers can affect the fractional flow,

improve the mobility ratio and as mentioned above divert injected water from areas that have been swept.

3.1.1 Modification of mobility ratio

Mobility ratio can be controlled by changing the viscosity of the displacing fluid (Green and Willhite, 1998). Polymers added to in the injected water will increase the viscosity and improve the mobility ratio between the highly viscous oil and the injected fluid. Thus, will due to a lower mobility ratio create a more stable displacement and decrease the viscous fingering effect (Figure 2.4). Therefore, creating a better sweep and a better volumetric sweep efficiency.

Sorbie (1991) stated that even in reservoir with a $M \approx 1$, there might be inefficient sweep. Due to heterogeneity in the reservoir, with different permeabilities in the layers, an early water breakthrough in the high permeability layers might occur. This causes low vertical sweep efficiency. Lowering the mobility ratio further ($M \sim 0.1-0.3$) by adding polymers to the injected fluid leads to crossflow of fluids between the different layers. The viscous cross-flow effects improve the vertical sweep efficiency. Polymers can also be used as diversion techniques in heterogeneous reservoirs. By injecting a polymer gel in high-permeable zones, the water will be diverted into low-permeable zones to improve the sweep efficiency in areas with lower permeability.

Another effect with increasing the viscosity of the displacing fluid, μ_w , is the change in fractional flow. As the viscosity of the displacing fluid increases, the ratio $k_{ro}\mu_w/k_{rw}\mu_o$ (Equation 2.7) increases. Therefore, a higher fractional flow of oil will occur, thus will accelerate the production of oil (Equation 2.7 and 2.8). After flooding, the polymers also reduce the relative permeability to water, k_{rw} (Figure 2.3) which will further improve the ratio between oil and water (Needham and Doe, 1987). Polymer flooding is proven to be more beneficial when polymer is added early in the waterflooding process and before waterflooding residual saturation is reached (Sorbie, 1991). A high saturation of water will cause a low relative permeability of oil, k_{ro} (Figure

2.3). Therefore, the fractional flow of oil, f_o will remain relatively low even with increasing viscosity of injected water.

To measure the mobility reduction and permeability reduction after water or polymer flooding, the resistance factor, RF and the residual resistance factor, RRF are found. The resistance factor, RF is the injectivity of brine to that of a single-phase polymer solution, while the residual resistance factor is mobility of a brine solution before and after polymer injection.

3.1.2 Microscopic diversion and viscoelastic effects

There have been some discussions regarding the effect of viscoelasticity and the polymers ability to reduce S_{or} by mobilizing inaccessible oil in dead-end pores (Delshad et al., 2008, Wang et al., 2001, Yin et al, 2006, Zhang et al., 2008, Zhang and Yue, 2008). Flexible coil polymers like HPAM and modified versions of HPAM can during flow in porous media be stretched due to contraction/expansion and give a higher elastic contribution during flooding. Some researchers claim that the elastic effect might enable the polymer to “pull” the oil out of the dead-end pores (Sheng, 2011).

4. POLYMER RHEOLOGY

4.1 Bulk rheology

4.1.1 Shear viscosity

Viscosity is defined as a material's resistance to flow when external forces are applied (Mezger, 2011), and will change based on the ambient temperature, amount of force applied and be influenced by the fluid's nature.

The dynamic or shear viscosity is defined as (Newton's law):

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (4.1)$$

where η is the shear viscosity, τ is the shear stress and the $\dot{\gamma}$ is the shear rate in laminar flow. Shear viscosity is often presented as Pascal seconds [Pa s], or as centipoise [cP]. Based on the response in viscosity when shear forces are applied, the fluids are categorized as Newtonian or Non-Newtonian fluids. Newtonian fluids do not change their viscosity with increasing shear stress applied, while non-Newtonian fluids are either increasing their viscosity with increasing shear forces (shear thickening) or decreasing in viscosity (shear thinning) (Mezger, 2011).

Most polymer solutions are non-Newtonian fluids, which implies that the viscosity of the solution is shear dependent. Viscosity in a non-Newtonian fluid is a property that is influenced by the external forces, for example, temperature, pressure and pH. The flow curve in Figure 4.1 shows the different stages a shear-thinning polymer solution experiences with increasing shear forces.

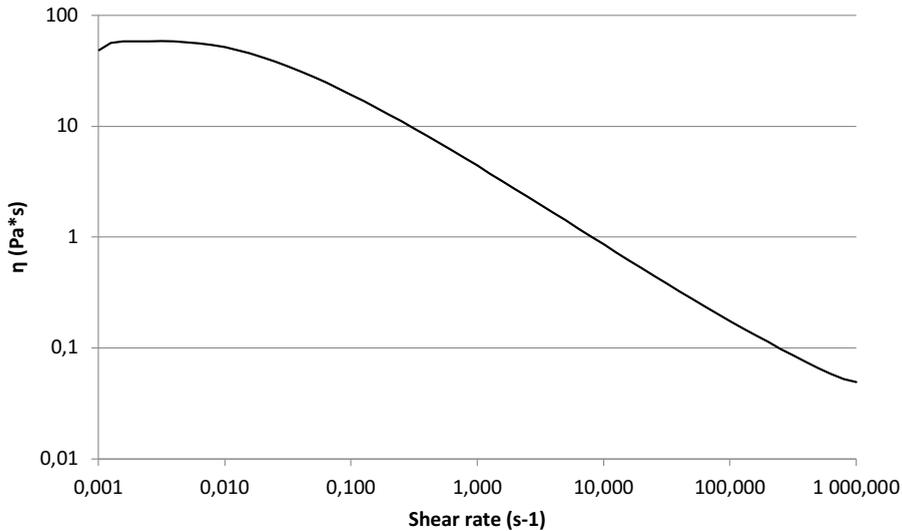


Figure 4.1: Shear viscosity curve. Viscosity as a function of shear rate for a typical shear-thinning polymer solution.

The Newtonian region: At low shear rate, and the polymer is experiencing Newtonian behaviour. Since the shear forces in this region are low, it is believed that they are too weak to affect the equilibrium state in the polymer solution. The result is a constant viscosity with increasing shear rate.

The shear thinning region: As the shear forces increases the polymer is entering the shear thinning region, and the viscosity is decreasing with increasing shear rate. The shear forces are higher and strong enough to affect the equilibrium state and un-coils the polymers. The viscosity decreases as more polymers is un-coiled and is aligned in flow direction.

Lower Newtonian Plateau: At high shear rate all the macromolecules are stretched out, and they are orienting in shear direction. The polymer solution is at its lowest value at this point.

Shear thickening region (dilatant): Some polymer solutions experiences a shear thickening region where the shear forces are high, and the polymer solutions is

experiencing turbulence that shows as increase in viscosity. This effect is often seen in porous media at high flow rates. This increase can also be explained by increased elasticity in the polymer solution, and extensional viscosity dominates over shear viscosity.

4.1.2 Viscoelasticity

An ideal elastic material is often referred to as a material that is able to restore to its original shape after pressure or stress that has been applied is removed. Ideally viscous materials on the other hand are not able to store the deformation energy and are deformed by the stress. Materials that shows both elastic and viscous characteristics when undergoing deformation, is referred to as viscoelastic materials. Polymer solutions above c^* often show strong viscoelastic characteristics, which can include shear-thinning, normal stresses and time-dependent rheology. However, even though there are several models and a lot of theory revolving rheology, there still is not a model that covers all of the viscoelastic phenomena seen in a polymer solution. (Sochi, 2010)

Sochi (2010) points out that the relaxation time is a common parameter in all of the viscoelastic models. It can be described from the fluid memory, which describes the stress at the present time upon the strain or rate of strain for all past times.

Viscoelasticity is divided in two regimes: linear and non-linear (Sochi, 2010). The linear viscoelastic (LVE range) is viscoelastic behaviour under a very low strain and where small deformation occurs. In this region the structure of the molecules is intact due to low strain, thus keeps a linear relationship between strain and viscoelasticity. Non-linear region is the study of large deformation at higher strain. In oscillatory measurements, sinusoidal strain or stress is applied to the solution and the amplitude is measured, which results in a phase shift angle δ (Mezger, 2011). The shear modulus is a combination of elastic modulus (G') and viscous modulus (G'') and each contribution is based on the phase shift angle.

The viscoelastic measurements combine Hook's law for elastic materials (Equ. 4.2) and Newton's law for viscous fluids (Equ.4.3).

$$\tau = G\gamma \quad (4.2)$$

$$\tau = \eta\dot{\gamma} \quad (4.3)$$

τ is shear stress, γ is shear strain, $\dot{\gamma}$ is strain rate or shear rate and G is shear modulus (Sheng, 2011). The elastic (storage) modulus, G' shows the ability of the materials to store energy, while the viscous (loss) modulus, G'' represent the loss of energy as heat due to internal friction. The relation between storage and loss modulus is expressed through the loss factor, $\tan \delta$.

$$\tan \delta = \frac{G''}{G'} \quad (4.4)$$

where δ is the phase angle. Equally viscous and elastic fluids have a $\tan \delta=1$. $\tan \delta < 1$ is elastically dominated, $\tan \delta > 1$ is viscously dominated (Mezger, 2011)

Amplitude sweep give an indication of the range of the LVE region within a polymer solution and can give insights to the rheological state and behaviour of the solution. The amplitude sweep is conducted at constant frequency, and with increasing amplitude. From an amplitude sweep a yield point can be determined, it represents the highest shear stress that can be applied without breaking the interactions holding the structure together

Frequency sweep is performed at constant amplitude, which is chosen within the LVE range from the amplitude sweep. From the frequency sweep, the complex viscosity and storage and loss modulus is found as a function of angular frequency.

4.1.3 Intrinsic viscosity

Polymers ability to enhance the viscosity based on its hydrodynamic volume is referred to as intrinsic viscosity, $[\eta_0]$ (Flory, 1953). The intrinsic viscosity of a polymer solution gives information about the interactions between the solvent and the polymer in the solution. However, the solution must be diluted to the degree where neighboring polymer molecules do not affect the interactions between the solvent and the polymer molecule, and the thermic movements of the molecule are more dominating than hydrodynamic and intermolecular interactions. The most important viscosifying parameter in a dilute polymer solution is the hydrodynamic volume of the molecules which depends on the molecular weight, the conformation of the polymer and hydrodynamic interactions within the molecule. The polymer is experiencing a higher hydrodynamic volume with a higher molecular weight. However, unfavorable polymer-solvent interactions can lead to lower hydrodynamic volume due to collapse of the polymer molecule. The critical overlap concentration, c^* , can be linked directly to the intrinsic viscosity.

The intrinsic viscosity is defined as the limit of the reduced viscosity, η_R , as the concentration goes towards zero:

$$[\eta_0] = \lim_{c \rightarrow 0} \frac{\eta - \eta_s}{c\eta_s} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \eta_R \quad (4.5)$$

$[\eta_0]$ is the intrinsic viscosity. $[\text{cm}^3/\text{g}]$ is the SI-unit for intrinsic viscosity; however, it is often preferred to use the unit $[1/\text{ppm}]$. η_R is the reduced viscosity $[\text{cm}^3/\text{g}]$, η_s is the solvent viscosity $[\text{Pa}\cdot\text{s}]$, η_{sp} is the specific viscosity (dimensionless), η is the solution's non-Newtonian shear viscosity platou $[\text{Pa}\cdot\text{s}]$ and c is the concentration of the solution $[\text{g}/\text{cm}^3]$ (Sorbie, 1991).

Intrinsic viscosity in associative polymers is regarded as being proportional to the reciprocal of a density in the solution. That meaning, the smaller intrinsic viscosity, the less swelled or denser the polymer solution (Dupuis, 2011). Kujawa et al (2004) studied intramolecular interactions in the dilute regime and concluded that intramolecular

hydrophobic interactions will dominate in this regime, which would lower the hydrodynamic volume. This supports the theory that an increase in hydrophobic groups will lower the intrinsic viscosity. However, Dupuis et al (2011) showed that this observation was not seen in with low hydrophobic content ($\leq 0.5\text{mol}\%$) attached to the backbone. It is clear that for some hydrophobic polymer solutions, the premise that there are no interactions between polymer molecules in the dilute regime, is not fulfilled.

4.1.4 Power Law

Power law or Ostwald and de Waele law describes the pseudoplastic region of a polymer solution, by the expression

$$\eta(\dot{\gamma}) = K'\dot{\gamma}^{n-1} \quad (4.6)$$

where η is the shear viscosity, $\dot{\gamma}$ is the shear rate and K' and n are empirical constants (Sochi, 2010). n is known as the Power Law index, and for a non-Newtonian fluid in the shear thinning region $n < 1$. The disadvantage with this model is that for most flow curves of polymer solutions the Power Law model is not applicable at high shear rates (infinite-shear viscosity) or low shear rates (zero shear viscosity). Since the Power law model is a simplified model which only describes the shear thinning part of the shear viscosity curve, other models can be used to describe the shear curve. The Carreau model for instance gives a more accurate fit and description of the shear curve, however more parameters are needed to find a good fit for a Carreau model.

4.2 In-situ rheology

HPAM and Xanthan is the most well-known and studied polymers for polymer flooding, however, new and improved polymers, for instance hydrophobically modified polymers, are showing promising results in both bulk and in-situ (Wever et al., 2011). Water-soluble hydrophobically modified polymers have shown shear thinning effects with injection into the porous media. Along the backbone of the charged water-soluble hydrophobically modified polymers, several hydrophobic groups are attached (Dupuis et al, 2012, Taylor and Nasr-El-Din, 1998). To minimize their exposure to water, these groups seek together and create intra- and intermolecular interactions, which contributes to a network structure between the polymer molecules. The strength and lifetime of the intra- and intermolecular interactions are dependent on the hydrophobicity of the polymer and external variables as salinity, temperature, pH and external forces applied to the polymer solution (Caputo et al., 2004, Tirtaatmadja et al., 1997). In a bulk rheology measurement, the polymer exhibits constant and gradually increasing/decreasing shear forces. While a porous media contains tight channels and pores in various sizes, which leads to contraction/expansion of the polymer molecules during the flow. During the in-situ flow, the shear forces and thermal fluctuations will constantly break and reform the hydrophobic interactions, giving a different viscosity and behaviour than seen in a rheometer (Reichenbach-Klinke et al., 2011). To use polymers in EOR, knowledge about the reservoir conditions and the polymers rheology both in dynamic rheology and in-situ is crucial to understand how the polymer might behave (Sorbie, 1991).

Molecular weight and chain distribution play an important role in the characteristics of the polymer flow in porous media. To decrease the cost of flooding, improvement in the molecular structure or high molecular weight polymer can lead to a better sweep (Reichenbach-Klinke et al., 2011). A higher molecular weight HPAM provides higher viscosity, thus a more stable displacement front. The downside to injecting a high molecular weight polymer is that the shear degradation increases with a larger polymer. In a porous media, the shear forces are highest at the injection well, which may cause an irreversible degradation of the HPAM polymer early in the process. The polymer backbone will break into smaller fractions, reducing the hydrodynamic volume and

further reduce the viscosity of the polymer (Reichenbach-Klinke et al., 2011). Compensating for the shear degradation, by increasing the concentration, will increase the cost of flooding. HMPAM has the potential to, due to the hydrophobic groups, create intermolecular interactions and enhance the viscosity in polymers in lower molecular weight polymers compared to HPAM. When shear forces are applied to a low molecular weight HMPAM, the weak intermolecular interactions created by the hydrophobic groups will break. Thus, not causing severe breakage in the polymer backbone. When the shear forces are reduced, for example when the polymer has been injected into the reservoir, the hydrophobic groups can reform the intermolecular interactions and increase the viscosity to its original level (Reichenbach-Klinke et al., 2011, Taylor and Nasr-El-Din, 1998)

Retention of the polymer in a porous media is an important factor to determine the economic viability of a polymer in a porous media (Sorbie, 1991). According to Sorbie (1991) the three mechanisms causing retention are adsorption of polymer, mechanical entrapment and hydrodynamic retention. Mechanical entrapment is mainly large polymers that are stopped by the smaller pores and can be avoided by filtration of the polymer solution. Hydrodynamic retention gives a small contribution to the retention and is reversible (Zhang and Seright, 2015). Therefore, both hydrodynamic retention and mechanical entrapment can be considered less important factors affecting the retention. Polymer adsorption is a common problem regarding loss of concentration during polymer flooding as the interaction between the rock surface and the polymer can cause the polymer to adsorb to the rock, by van der Waals forces and hydrogen bonding (Sheng, 2011). The adsorbed polymer can affect the flow of the polymer as the radii of the pore throats are reduced and thus reduce the water permeability (Hirasaki and Pope, 1974).

Adsorption of polymer on the rock surface is a known contribution to the loss of concentration and has previously shown to increase in HMPAM polymers due to the formation of multilayer adsorption. The ability to form network structures with hydrophobic interactions between the polymers becomes a drawback regarding adsorption. The adsorbed layer on the rock surface creates hydrophobic interactions to the flowing polymer, thus forms multilayers and further reduced radii of the pore throats.

The degree of retention will vary with type of polymer, hydrophobicity, salinity of the brine, flow rate, temperature and rock composition (Sheng, 2011).

4.3 Factors affecting polymer viscosity and viscoelasticity

Partially hydrolysed polyacrylamide and hydrophobically modified polyacrylamide are both polyelectrolytic polymers with negative anionic sites along their backbone, that dissolves in water (Wever et al., 2011). The negatively charged sites can also influence the viscosity of the polymer solution. Viscosity of a polymer is often reflected in the volume the polymer molecule occupies described as the hydrodynamic volume. Repulsions between the molecule forces the polymer to demand more volume in the solution, thus increasing the viscosity. Cations in the solution neutralizes the negative charges and weakens the repulsions (Sheng, 2011, Sorbie, 1991).

As mentioned, HMPAM polymers is known for their ability to enhance the viscosity due to interactions between the hydrophobic groups incorporated. Since the hydrophobic groups are not water-soluble, they will seek towards each other creating interactions, either intra- or intermolecular interactions depending on concentration, and length of the hydrophobic groups (Figure 4.2).

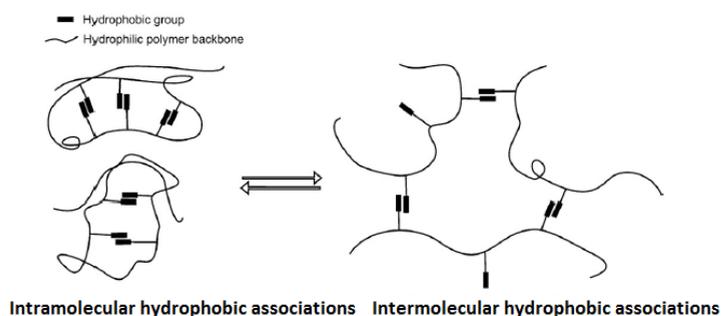


Figure 4.2: Illustration of intra- and intermolecular interactions between hydrophobic groups in an HMPAM polymer (Wever et al., 2011)

The rheological characteristics of a polymer solution is dependent on the polymer concentration and especially the concentration regimes. Three main regimes have been characterized for polymer solutions and is shown in Figure 4.3. The first regime is the diluted regime, here the polymers act as individual coils and are not interacting or affecting each other. Intramolecular interactions for hydrophobically modified polymers dominate in this regime and no significant increase in viscosity is seen with increasing concentration before the critical overlap concentration, c^* is reached. The critical overlap concentration is an important parameter that links the interactions between the polymer and the solvent (Heemskerk et al., 1984, Regalado et al., 1999) Above c^* the semi-diluted regime begins, and the hydrodynamic volume of the polymers starts to overlap which is shown in a sudden increase in viscosity. The degree of entanglements and intermolecular interactions in this regime depends on the degree of overlap between the polymer molecules. Since HPAM and HMPAM are polyelectrolytes will repulsions between the polymer molecules forces the polymer to stretch and the hydrodynamic volume increases, thus increasing the viscosity (Sorbie, 1991, Wever et al., 2011).

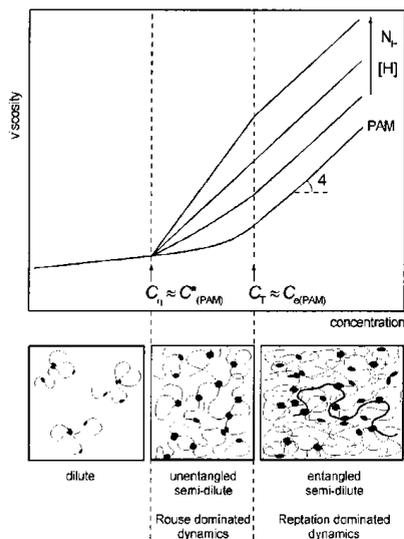


Figure 4.3: modified figure from Regalado, showing viscosity as a function of concentration which is further divided in three concentration regimes (Regalado, 1999).

Molecular weight can affect the concentration regime for the polymer solution, and at which concentration the critical overlap concentration, c^* occurs. A higher molecular weight gives an “earlier” c^* as the polymers overlap at a lower concentration (Wever et al., 2011). In the entangled semi-dilute regime, the molecules start to entangle in each other.

5. EOR POLYMERS

In this chapter, the EOR polymers partially hydrolysed polyacrylamide, HPAM and hydrophobically modified polyacrylamide, HMPAM will be further introduced. The rheological properties of these polymers are strongly affected by the structural variables, and external parameters as salinity, temperature and pH. These aspects will be described later in this chapter.

Polymers can either be synthetic or biological. For EOR, synthetic polymers like HPAM was first introduced as a viscosity enhancer due to having extensive applications in paper manufacturing, as flocculants and drag reducers (Sorbie 1991). Due to its low cost, viscosifying abilities and easy access HPAM has quickly become the most used polymer for EOR, however some limitations are seen in the form of a decrease in viscosity with increasing salinity and temperature (Lake, 1989, Sorbie, 1991).

Biopolymers like Xanthan have shown great viscosifying abilities in porous media (Sorbie, 1991). Xanthan is a polysaccharide produced by fermentation of glucose and fructose. Like HPAM, Xanthan is also a polyelectrolyte with charged side groups, however the polysaccharide is not as sensitive towards salt as HPAM. The viscosifying abilities in Xanthan depend on the molecular weight and the rigidity of the backbone (Wever et al., 2011). Biopolymers are a more environmentally friendly alternative to synthetic polymers as it is biodegradable, however this might also be the one of the drawbacks. Bacteria and microorganisms present in the reservoir degrades the polymer and reduces its viscosity. Therefore, biocides have been used to maintain the viscosity in biopolymers (Wever et al., 2011). Xanthan has proven to be cheaper than synthetic polymers per viscosifying unit, however the need for biocides generally increases the cost of Xanthan compared to HPAM.

5.1 Hydrolysed polyacrylamide, HPAM

HPAM is by far the most known and used polymer in EOR. HPAM is a water-soluble synthetic straight chain polyelectrolyte, consisting of repeating units of acrylamide and acrylic acid monomers (Morgan, 1990). Acrylic acid can be obtained by hydrolysis of polyacrylamide (PAM), where the amide groups will react to the surrounding water and substitute NH_2 with OH^- ions, or copolymerization of sodium acrylate with acrylamide (Morgan, 1990). The degree of hydrolysis in HPAM is usually in the range between 25-30% and is important to some of the polymer's inherent properties, such as adsorption, shear stability and thermal stability (Seright et al., 2010, Sorbie 1991, Wever et al., 2011). The viscosity enhancement within HPAM is mainly driven by repulsions. Coulomb repulsions between the electrostatic charges along the backbone causes chain extension and an increased hydrodynamic volume, which further increases the viscosity in the polymer solution. Therefore, a lower limit of 25% hydrolysis is preferable to increase the repulsions, thus increasing the hydrodynamic volume and viscosity of the polymer (Lake, 2010, Wever et al., 2011). However, above 40% hydrolysis the polymer might experience solubility issues, and be more sensitive towards salinity and hardness of the brine due to shielding of the electrolytic sites. An increase in solution temperature might increase the hydrolysis further (Choi et al., 2014, Moradi-Araghi and Doe, 1987, Ryles, 1988, Seright et al., 2010, Sorbie, 1991).

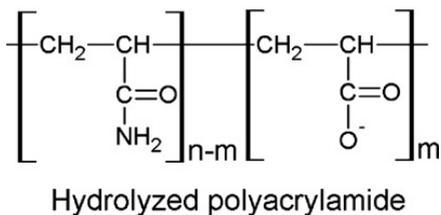


Figure 5.1: The structure of partially hydrolyzed polyacrylamide (Wever et al., 2011)

The thickening capability of HPAM is not only dependent on the degree of hydrolysis; the molecular weight of the polymer contributes to a high viscosity solution as the

hydrodynamic volume of the polymer chain is increased (Sorbie, 1991). HPAM polymers used in EOR normally have a molecular weight of $2\text{-}20 \times 10^6$ g/mole, although higher values might occur (Sorbie, 1991). Even though high molecular weight HPAM promotes high viscosity in bulk solution and lowers the critical overlap concentration, there are some drawbacks when used in porous media. Injections into formations with low permeability might not be possible due to the large hydrodynamic volume, and the polymer is more sensitive to shear degradation during flooding and injection (Reichenbach-Klinke et al., 2011). A polymer with high molecular weight contributes to a high viscosity for the injected fluid, however is also more shear sensitive. Shear forces in-situ can more easily tear apart long polymer chains, thus lowering the molecular weight and the viscosity of the solution. To compensate for the viscosity loss at the inlet of the porous media, higher concentration can be added in the polymer injection process. However, this further increases the cost of using the polymer in polymer flooding (Reichenbach-Klinke et al., 2011)

5.1.1 Effect of salinity on viscosity

Polyelectrolytes present some limitations in contact with counterions from seawater. Salt has a significant influence on the rheological behavior of the polymer solution, and the amount of salt in the solution can affect the viscosity of the polymer (Sukpisan et al., 1998). Without ions present is HPAM mainly experiencing viscosifying effects due to Coulomb repulsions between the anionic sites on the backbone, thus creating a high hydrodynamic volume. Addition of salt reduces the Coulomb repulsions between the anionic sites on HPAM, as the cations neutralize the negatively charged backbone (Dupuis et al., 1994, Dupuis et al., 2010, Ellwanger et al., 1980, Lake, 1989). By weakening the repulsion between the polymer backbones, the polymer molecules start to coil, and the relative hydrodynamic volume of the polymers is reduced (Figure 5.2). A reduction in the volume leads to a decrease in viscosity. When all the anionic sites are neutralized, further addition of salt does not affect the polymer solution or the viscosity of the solution. Divalent cations amplify this effect, due to higher screening capability

of multivalent cations (Sorbie, 1991). A more complex reaction mechanism is seen with divalent ions and multivalent ions, as they work as a cross binder and can both create intra- and intermolecular cross-bindings in HPAM. Intramolecular bindings will enhance the coiling of the polymer and reduce the viscosity, while intermolecular might create a larger hydrodynamic volume as two coils are linked together.

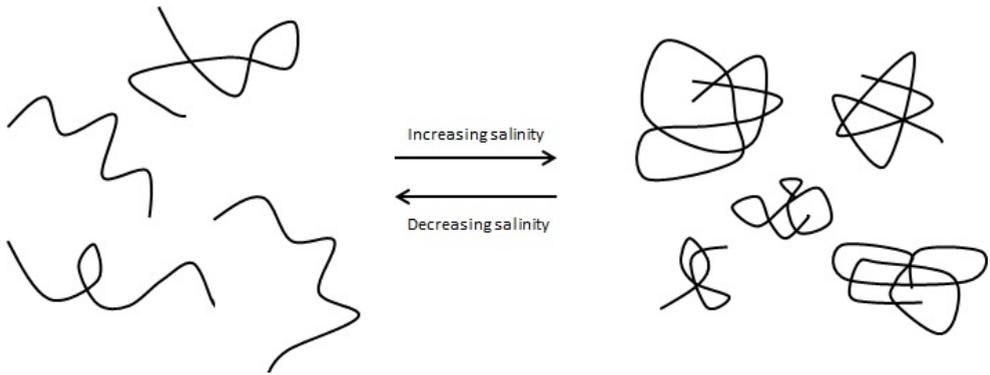


Figure 5.2: Effect of salinity on structural conformations of HPAM. Modified figure from Sorbie (1991)

Salts dissociate to ions when dissolved in distilled water. The concentration of the ions can be used to find the ionic strength of the solution and is a measure of screening potential in the absence of specific ion effects. Ionic strength is defined as:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (5.1)$$

where I is the ionic strength of the solution, n is number of components in the solution, c is the molar concentration of the composition (i) and z is the charge of the ion. Ionic strength is a measurement of the total concentration of ions in that solution. Multivalent ions contribute more to the ionic strength compared to monovalent ions.

5.1.2 Effect of temperature on viscosity

HPAM is also sensitive to increasing temperature. As mentioned previously, increased temperature (above 60°C) leads to further hydrolysis of the backbone where amide groups are hydrolysed to carboxylate groups (Choi et al., 2014, Moradi-Araghi and Doe, 1987, Ryles, 1988, Seright, 2010 et al., Sorbie, 1991). Increased degree of hydrolysis might cause shear thickening at low shear rates (Wever et al., 2011). However, above 40% hydrolysis the polymer starts to experience solubility issues and becomes more sensitive towards salt. Flocculation might occur at a degree of hydrolysis above 40% (Sheng, 2011). Several studies have shown that with increase in temperature, the viscosity is reduced (Jiang et al., 2015, Lai et al., 2013, Niu et al., 2001, Reichenbach-Klinke et al., 2011). A study from Zhong et al (2009) showed that with increasing temperature in the solution, faster movement of polymer chains and weaker hydrogen bonding will occur, thus could be a contributing factor for the loss of viscosity.

5.1.3 Effect of shear on viscosity

The sensitivity of shear degradation increases with increasing molecular weight of a polymer. When injecting the polymer solution into the reservoir, it is exposed to high shear forces at the inlet. This lowers the molecular weight of the polymers by tearing the polymer backbone apart, which lowers the viscosity. A higher dosage of the polymer needs to be used to compensate for the shear degradation, however, this leads to a higher cost when using high molecular weight polymers (Reichenbach-Klinke et al., 2011). Rapid viscosity build-up and mixing process are essential to performance and economy (Singhal, 2011)

5.2 Hydrophobically modified polyacrylamide, HMPAM

Hydrophobically modified water-soluble polymers, HMSWP, has been suggested as an alternative to the traditional HPAM polymers for use in polymer flooding. Limitations in HPAM regarding loss of viscosity in high salinity and high temperature have led to a search for more stable polymers for use under such conditions (Taylor and Nasr-El-Din, 1998). Hydrophobically modified polyacrylamide, HMPAM, have been used throughout this study and therefore HMPAM polymers will be referred to in this dissertation when talking about hydrophobically modified water-soluble polymers. HMPAM contain the same polyelectrolytic backbone as HPAM, however with hydrophobic chains incorporated along the water-soluble hydrophilic backbone. Thus, giving the polymer the ability to enhance its viscosity with interactions between the hydrophobic groups and further increase the hydrodynamic volume of the macromolecule due to network formation (Buchgraber et al., 2009, Reichenbach-Klinke et al., 2011, Seright et al., 2011a, b).

According to Taylor and Nasr-El-Din (1998) less than 1mol% incorporation of hydrophobic groups in the polymer can change its performance significantly. McCormick and Johnsen (1988) studied a hydrophobic modified polymer with a C-10 copolymer. Great viscosifying effects were seen in the 0.75 mole% copolymer compared to the unmodified HPAM in moderate concentrations.

The HMPAM polymers thickening ability can be adjusted by changing the type of the hydrophobic group, length and amounts of the hydrophobic group, how they are distributed along the backbone and the molecular weight and anionicity of the polymer (Kujawa et al., 2006). Due to the nature of the associating groups, the HMPAM polymer is less dependent on molecular weight and degree of hydrolysis than HPAM to increase viscosity. Enhanced viscosity is found in lower molecular weight polymers with hydrophobic groups present.

Several studies have reported that small changes in the length of the hydrophobic group can enhance the viscosity of the polymer significantly (Candau and Selb, 1999, Hill et al., 1993, Volpert et al., 1998). Short hydrophobic groups might not be able to contribute

to a strong network and too long hydrophobic chains can cause solubility issues as presence of hydrophobic associative groups will cause the polymer to be less water-soluble (Taylor and Nasr-El-Din, 1998, Wever et al., 2011). Amount and type of hydrophobe needs to be balanced to simultaneously achieve sufficient water solubility and high viscosity. A hydrophobically modified polymer with short hydrophobic groups, can have a higher percentage of hydrophobic substituent compared to long a polymer with longer hydrophobic groups. The hydrophobicity can be expressed as the hydrophilic-lipophilic balance (HLB) (Wever et al., 2011).

5.2.1 Associative polymers in aqueous solutions

While HPAM and Xanthan rely on chain extension and physical entanglement to enhance their viscosity, is HMPAM as mentioned previously also affected by hydrophobic associations between the different polymer chains (Kujawa et al., 2006; Taylor and Nasr-El-Din, 1998). Taylor and Nasr-El-Din (1998) compares the association to the formation of micelles in surfactant systems. HMPAM polymer dissolved in water expands and create inter- and intramolecular interactions to minimize their exposure to water (Wever et al., 2011). This gives rise to a three-dimensional network that strengthens the polymer solution. However, the amount of intermolecular interactions versus intramolecular interactions depends on the concentration of the solution and the concentration regimes presented in Chapter 4. Below the critical overlap concentration (c^*), the polymers are not in contact with each other, thus creating individual coils and intramolecular interactions (Argillier et al., 1996). In this concentration regime, intramolecular interaction dominates and is believed to make the coils tighter than in polymers without hydrophobic groups attached (Taylor and Nasr-El-Din, 1998). This can lower the viscosity of HMPAM below HPAM (Penott-Chang et al., 2007). As the concentration reaches c^* and transitions into the semi-dilute regime where the polymer coils start to overlap and make intermolecular interactions. In the semi-dilute regime, the viscosity increases with increasing concentration in both HPAM and associative polymers. However, the viscosity in associative polymers has a steeper and more obvious increase in viscosity as the intermolecular hydrophobic interactions

strengthens the network and enhances the viscosity (Figure 4.3) (Argillier et al., 1996, Volpert et al., 1996). Due to the formation of the hydrophobic interaction the HMPAM polymer is able to reach c^* at an earlier concentration than partially hydrolysed polyacrylamide (Wever et al., 2011). The transition from unentangled semi-dilute to entangled semi-dilute is not easily found for associative polymers. In the entangled semi-dilute regime, the molecules start to entangle in each other. For HPAM this will increase the viscosity further due to stronger interactions in the molecule network (Regalado et al., 1999)

The balance between ionic and hydrophobic groups creates a complex interplay. The viscosity within a hydrophobically modified polymer is affected by two opposing effects from electrostatic repulsion from the anionic backbone. Due to coil expansion, the hydrodynamic volume of the polymer increases, giving an increase in viscosity. However, the repulsions and the large volume lead to less intermolecular interactions which reduce the viscosity. When salt is present in the solution, the polymer becomes less extended and transitions into a coil as the charges along the backbone are screened. This transition reduces the viscosity; however, allows the hydrophobic interactions to create intermolecular interactions and further increase the viscosity. The salt can also affect the hydrophobic hydration and hydrophobe-hydrophobe interactions. The effect of salt on the thermo-responsive hydrophobe can also be linked to the hydrophobic hydration and hydrophobe-hydrophobe interactions (Akbari et al., 2017 a, b, Li et al., 2017, Wang and Dong, 2009). Therefore, the balance between electrostatic repulsion between the charged groups and the hydrophobic hydration and association is important to the viscosity of the polymer.

5.2.2 Effect of salinity on viscosity

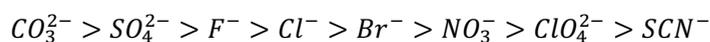
The salinity effect seen in HMPAM polymers is complex. An increase in the salinity will lower the solubility of the hydrophobic groups in the brine, and the amount of hydrophobe versus the salinity need to be balanced to solve the polymer and also achieve the desired viscosifying effect. Addition of salt in polyelectrolyte leads to screening of

the anionic sites, which weakens the repulsions between the polymers (Kujawa et al, 2006). This normally gives a lower hydrodynamic radius and a lower viscosity in the polymer solution. In HMPAM polymers, the charges along the backbone will be screened with addition of salt in the solution as for HPAM, however, this increases the ability for the hydrophobic groups to make interactions both due to lack of repulsion and that the groups will be less hindered from making intermolecular interactions (Figure 5.3) (Reichenbach-Klinke et al., 2011, Wever et al., 2011). Electrostatic repulsions will be weaker than the intermolecular interactions as the salinity increases (Zhuang et al., 2001). Thus, allowing a higher hydrodynamic volume and enhanced viscosity of the polymer solution (Wever et al., 2011).

Increase in viscosity is mainly seen in concentrations above the critical overlap concentration. In the dilute regime however, a highly polar solvent will cause tighter coils as more intramolecular interactions occur, which will lower the hydrodynamic volume and viscosity in this regime (Taylor and Nasr-El-Din, 1998)

The effect of divalent ions has shown to vary dependent on the polymer system. Akbari et al (2017a, b) studied a thermoassociative polymer in brines with pure NaCl and brines with Ca^{2+} present, with the same ionic strength. A decrease in viscosity was seen in the solution containing divalent ions. Feng et al (2005) on the other hand, found the pure $CaCl_2$ and NaCl polymer solutions to superimpose for a hydrophobically associating, un-hydrolysed polyacrylamide.

How an electrolyte affects the polymers interaction with the surrounding brine can be explained due to the Hofmeister series. The Hofmeister series classifies the ions based on whether they have salting-in (increasing solubility) or salting-out (decreasing solubility) effect on the polymers. Typical order of the Hofmeister anions is:



Anion to the right have a stronger salting-in effect where they stabilize the hydrophobic molecule and makes it more soluble, while the anions to the left have a stronger salting-out effect (Thormann, 2012).

The Hofmeister cations series is: $Na^+ > K^+ > Li^+ \approx Ca^{2+} \approx Mg^{2+} > NH_4^+$ However, the anions have a larger effect than the cations, due to the cations being more sensitive towards the nature of the solute (Long and McDevit, 1952, Hyde et al., 2017)

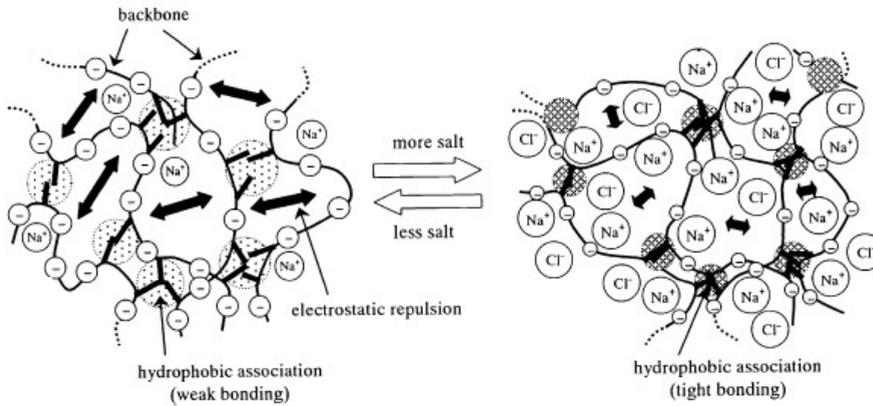


Figure 5.3: Effect of salt on the hydrophobic interactions in the polymer solution (modified from Kawakami et al. (2006))

5.2.3 Effect of temperature on viscosity

In petroleum reservoirs, the temperature changes throughout the reservoir matrix. The polymers must be able to maintain viscosity and viscoelastic properties with an increase in temperatures. While HPAM experiences hydrolysis at elevated temperature, is HMPAM due to its hydrophobic components less exposed, thus being able to further enhance its viscosity as temperatures increases (Reichenbach-Klinke et al, 2011). More intermolecular interactions will be created, forming microdomains. This presupposes that the concentration is above the critical overlap concentration (L'Allouet et al, 1995)

HMPAM polymers can both be thermo-thickening and thermo-thinning based on its structure, concentration and molecular weight, and the salinity of the brine. Several studies of HMPAM polymers have shown thermo-thickening abilities in the polymer solutions (Jiang et al, 2015, McCormick et al, 1988b, Niu et al, 2001, Reichenbach-Klinke et al, 2011, Zhong et al, 2009). Many thermo-responsive grafts show a sudden increase in viscosity with increasing temperature. This marks the lower critical solution temperature (LCST) or critical association temperature (T_{ass}) of the polymer where the thermo-sensitive groups start to segregate (Bokias et al, 1997, Hourdet et al, 1997, Hourdet et al, 2005). Hydrophobic interactions are also present below LCST; however, the thermo-sensitive grafts are able to create a more profound and stronger network when the temperature exceeds the LCST. As the temperature reaches LCST the components become less soluble, thus causing self-aggregation of the hydrophobic group (Winnik, 1989). With further increase in temperature, kinetic energy and thermal motion increases in the polymer solution, thus resulting in a competition between self-aggregation and dissociation of hydrophobic interaction. A viscosity maximum will be reached at a given temperature (T_{max}). Subsequently a decrease in viscosity will follow with further increase in temperature (Akbari et al., 2017a, b, L'Alloret et al., 1995, Li et al., 2017)

McCormick et al (1986) reported a decrease in viscosity with increasing temperature in a copolymer of acrylamide with AMPDAC (2-acrylamido-2-methylpropanedimethylammonium chloride). They proposed a theory, that decreasing viscosity with increasing temperature was caused due to changes in the conformation of the polymer and solvent associations giving a lower hydrodynamic volume.

Several factors can affect the thermo-response of the polymer solution i.e, salinity, molecular content and type of hydrophobe. L'Alloret et al (1995) found that the thermo-thickening effect can be influenced by the salinity of the solution. At a high salinity the thermo-thickening effect was reduced and a maximum viscosity was easier to achieve in a lower salinity.

6. MATERIALS AND METHODS

The polymers investigated in this thesis are two series of polymers. The first series (series A) has an increasing number of hydrophobic groups attached to the backbone. The polymer molecule is an anionic polyacrylamide with a charge density of 17%, and the hydrophobic monomer is an acrylamide derivative. Total amount of hydrophobic groups is varying from 0 to 0.3 mole%. Molecular weight is between 8 and 12 MDa.

Polymer series P, which is the second polymer series is changing also with increasing hydrophobicity, however the amount of hydrophobic group is constant, and the increasing hydrophobicity arrives from an increasing length of the hydrophobic group. Increase in hydrophobicity gives a lower hydrophilic-lipophilic balance (HLB). Average ionic content is around 30% and molecular weight is around 10-12 MDa. The intrinsic viscosity of the polymers in the series is found to be around 24 dL/g.

6.1 Polymers A series

Table 7.1: Relative hydrophobicity of polymer in series A. Polymers provided by SNF Floerger

Product	Relative Hydrophobicity based on A100
A0	0
A25	0.25
A33	0.33
A50	0.50
A75	0.75
A100	1

The polymer solutions were made after API procedure RP-63 as a stock solution of 5000 ppm. In a chosen solvent a vortex was established by stirring with a magnetic stirrer, and the polymer powder was poured in the shoulder of the vortex. After a few minutes the speed was reduced. The solution was further stirred for about 12 hours at about 150rpm. When the solution was prepared it rested un-agitated for 24 hours in an air tight container to make sure that the hydrophobic interactions were formed.

6.2 Polymers P series

Table 7.2: Hydrophilic-lypophilic balance (HLB) for the polymers in P series. Provided by BASF GmbH.

Polymers	HLB
P0	-
P1	13.9
P2	13.2
P3	13.1
P4	12.8
P5	12.5
P6	11.9

To obtain homogenic and reproducible solutions, the stock solutions for polymer series P were made in a round beaker with a rotating device. The rotating device was immersed in the solvent and stirred at 200rpm while the powder was poured into the solution. Once all of the powder was added, the speed was increased to 400 rpm and stirred for 30 minutes. Afterwards the speed was reduced to 200rpm and it was stirred for 17 hours.

All polymers in the series were experiencing heterogeneity, in both high and low salinities. Initially the polymers were dissolved in beakers with a metal rotatory blade. By changing the rotatory blades from metal to plastic and using a rounded flask for the solution, the polymers where able to better dissolve in brine, and the samples were reproducible. While mixing the powder in the flask, the speed was lowered to 200 rpm to avoid powder attaching to the glass flask instead of being stirred properly into the brine.

6.3 Brine composition

Brines for polymer series A were three NaCl brines with increasing ionic strength and a mixed brine similar to synthetic seawater. The mixed brine was included to add divalent ions to the brine, and to test the polymers in a brine more relevant to industry application. The NaCl brines were 0.5wt% NaCl, 5wt% NaCl and 10wt% NaCl with ionic strength of respectively 0.086M, 0.86M and 1.72M. The mixed brine contained the salts NaCl, KCl, CaCl₂, NaHCO₃ and NaSO₄, and had a similar ionic strength as 10wt% NaCl of 1.71M. More detailed information about the brines is explained in the first paper.

For polymer series P a different set of brines were used. A series of brines with a 9:1 weight/weight relationship between NaCl and CaCl₂ were used to investigate the effect of salinity on polymer series P. The brine are ranging from 0.1wt% to 20wt% salinity. For paper III with in-situ measurements a 1wt% brine with 9:1 mol/mol relation between NaCl and CaCl₂ was used.

6.4 Rheological measurements

6.4.1 Shear and oscillatory measurement at ambient temperatures

The shear viscosity and dynamic oscillatory measurements were performed on a Malvern Kinexus pro rheometer, with a cone plate (CP) geometry of either 4/40 (angle = 4°, diameter = 40 mm) or 2/50 (angle = 2°, diameter = 50 mm). The temperature for each measurement was obtained to 22±0.1°C. For the shear viscosity measurements, the range of shear rate was between 0.001 to 1000 s⁻¹ at concentrations above 2000ppm. For lower concentration the range was changed to 0.05 to 1000 s⁻¹ due to lower viscosity at lower shear rate.

Amplitude sweep was measured with a frequency of 1Hz and based on the linear viscoelastic regime a strain was chosen for the frequency sweep. A constant strain of 10% was chosen to compare between different measurements. 10% was found to be in the LVE range of all the polymer solutions where oscillatory measurements were

performed. Frequency sweeps were performed in the of 0.01-10 Hz frequency range. Dynamic oscillatory measurements were performed on samples that were viscous enough to provide sufficiently accurate data.

6.4.2 Shear and oscillatory measurements at elevated temperatures

A method for measuring temperature ramp was tested and verified within the group. One of the largest concerns with measuring temperature with the equipment used is evaporation of polymer sample. Silicon oil and 85% glycerol were tested using cone-plate geometry in a temperature ramp from 25°C to 70°C, and then back to 25°C. No significant sign of hysteresis was seen in silicon oil; however, 85% glycerol shows sign of significant changes in the viscosity ramps due to evaporation. A cone plate was found to be inadequate due to evaporation, and bob-cup geometry was used instead. In addition to larger volume of the sample, is it possible to add a thin layer of silicon oil on the top of the solution as an extra barrier against evaporation.

The temperature ramp of the polymer solutions in bob-cup was performed at a constant shear of 10s^{-1} . Since both the sample and the metal needed to reach the equilibrium temperature, the step rate was 5°C per 10 minutes for the range 25-75°C.

6.5 Core flooding

The dimensions and weight of the dry Bentheimer cores were measured, before saturated with brine. First the cores were placed in an excicator where vacuum was created, before introducing brine to the excicator. Since there might be some air bubbles left in the cores, they were mounted in Exxon core holders with overburden pressure of about 20 bars and flooded with brine to remove the remaining air. Weight was measured of the saturated cores to find the porosity of the cores. Before the polymer flooding, the absolute permeability, K_w , of the cores was measured.

The stock polymer solution at 3000ppm was filtered through a 60um filter, before either the polymer was flooded or diluted further before flooding. The cores were saturated

with the polymer solution at a flow rate for 1 ml/min. Setup of the core flooding is presented in Figure 6.5, where the first core work as filter to capture possible effects such as inlet plugging or filter cake formation. The second core represents polymer flooding in the reservoir.

Fuji FCX pressure transducers were used to measure the differential pressure over each core, and a Quizix SP 5200 pump injected the fluid at flow rates between 0.02-20 ml/min.

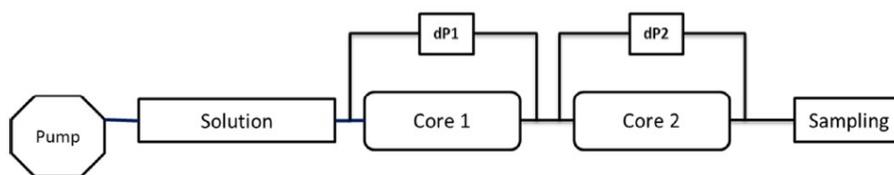


Figure 6.5: Core flood setup (Viken et al, 2018b)

During flooding, effluent samples from each of the polymer concentrations flooded were sampled and stored in a refrigerator before shear viscosity was measured in a rheometer. Shear viscosity was measured less than a day after flooding and again after one month. This could give information about the whether the intermolecular interactions in the polymer solution would reform at longer timescales. The effluent samples were collected from flooding at rates from 0.3- 32.3 m/day (0.2-25ml/min).

After the polymer was flooded, we performed a tapering process to replace the polymer with brine. The tapering was continuously flooding at low rate of polymer solutions with gradually lower concentration, before the rock cores were flooded with brine. Finally the permeability and RRF of the porous media after polymer flooding were measured.

7. RESULTS AND DISCUSSION

The experimental work can roughly be divided into three parts; salinity study, temperature study and in-situ flooding. In each of these parts the HMPAM polymers investigated have been compared to their HPAM counterpart. Two polymers series have been studied. One where the hydrophobicity is increased by incorporating an increasing mole% of the same hydrophobic group, and one where the mole% of hydrophobic groups are fixed but the hydrophobe chain length is increased.

Paper I is a salinity study of polymer series A. How the rheological properties as shear viscosity and viscoelasticity is affected with increasing hydrophobicity and salinity have been investigated. In the second paper (Paper II) we look further into the rheological behavior with change in hydrophobicity. Polymer series P changes its HLB value as the length of the hydrophobic groups increases. This study focuses both on increasing salinity and temperature to see what effects the HLB value has.

The last study is an in-situ study where the behavior of an HMPAM polymer is compared to its HPAM counterpart. Both polymers are flooded with various rates and the bulk viscosity is measure before and after flooding. While the HPAM polymer only was flooded in a 1000 ppm concentration, the HMPAM was studied in three different concentration regimes to get a deeper understanding on how the hydrophobic interactions acts in-situ.

7.1 Rheological properties of a HMPAM: Effect of salinity and mole% of hydrophobic units (Paper I)

This rheological study was performed to investigate how the shear viscosity and viscoelasticity is influenced with increasing hydrophobicity. The polymers used in this paper are a series of six polymers ranging from 0 to 0.3 mole% hydrophobic monomer content. Since hydrophobically modified polymers are known to show promising viscosifying effects in high salinities, the effect of increasing salinity was investigated by preparing polymers in four brines (0.5wt% NaCl, 5wt% NaCl, 10wt% NaCl and a high salinity mixed solution). The mixed solution brine is similar to synthetic seawater, SSW and consists of five different salts.

All six polymers in the series were measured in 0.5wt% NaCl and mixed high salinity solution. As shown in Figure 7.1, the polymers ranging from relative amount of hydrophobicity from 0.25 to 0.5 do not deviate much from the HPAM polymer in either of the salinities. This indicates that the hydrophobic monomer content is too low to provide sufficient intermolecular interactions. A100 on the other hand shows a steep increase in shear viscosity with increasing concentration as expected from a highly associative polymer. A75 is the most interesting polymer as it changes its behavior as the salinity increases. At low salinity, the shear viscosity of A75 is higher than the polymers with lower hydrophobic content, however; the behavior of the shear viscosity curve is a typical polyelectrolyte behavior. In the high salinity mixed brine, the viscosity of the A75 is experiencing an obvious change in viscosity after the critical overlap concentration, c^* , with a steep increase as the concentration increases further.

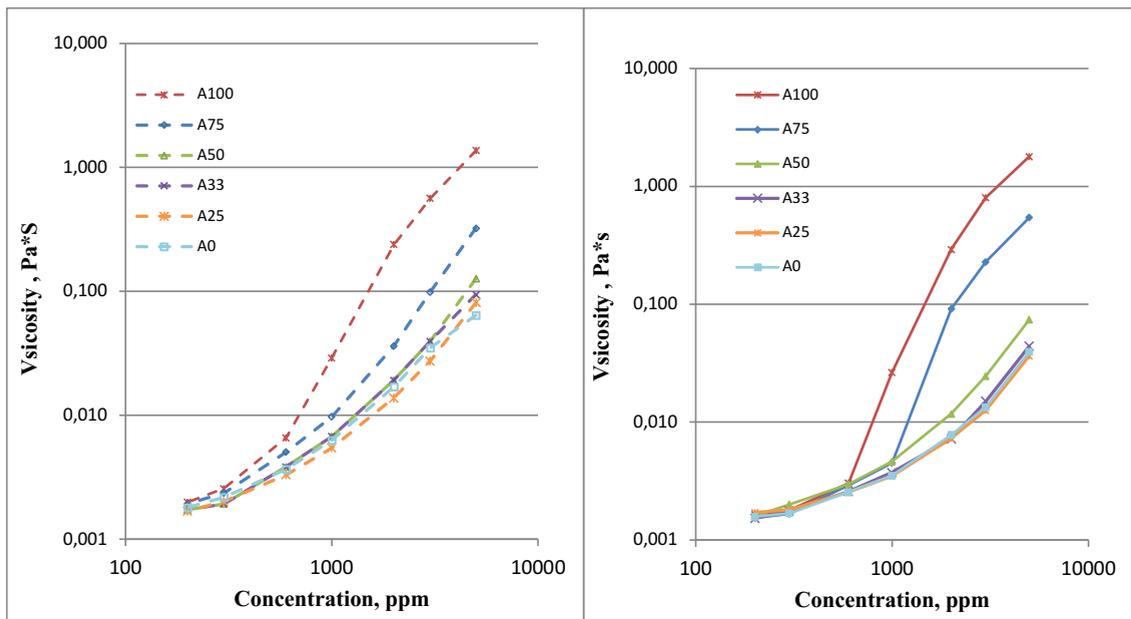


Figure 7.1: Shear viscosity as a function of concentration for A0 to A100 in 0.5wt% NaCl (left) and high salinity mixed solution (right). The high salinity brine has the same ionic strength as 10wt% NaCl (Viken et al, 2016)

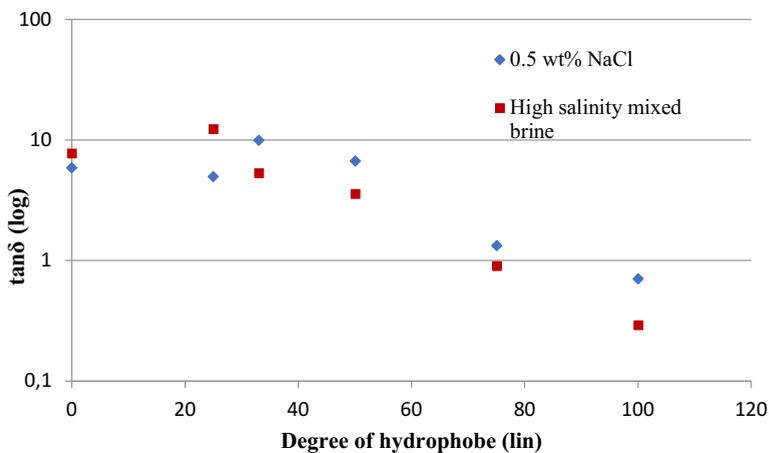


Figure 7.2: Loss factor against increasing degree of hydrophobicity in 0.5wt% NaCl and in the high salinity mixed brine for polymer series A (Viken et al, 2016)

With increasing hydrophobicity, the viscoelasticity in the polymer solutions change towards a more elastic dominated solution. From Figure 7.2, the loss tangent, $\tan \delta$ shows that the relative elasticity contribution increases as the degree of hydrophobicity increases, in both salinities. 3% error in each of the measured point, can contribute to the instability seen from A0 to A33, and therefore it is assumed that a threshold value in hydrophobicity is needed to also increase the elastic contribution of the polymer. The elastic contribution is increasing with further increase of hydrophobicity above the threshold value and is more profound in the high salinity brine.

A75 showed a significant change in behavior in the high salinity brine. To look further into this behavior, the polymer was prepared in two more salinities. 10wt% NaCl was chosen due to similar ionic strength as the mixed brine of 1.72 M. However, the 10wt% brine only consists of the monovalent NaCl, which could give an indication on whether divalent ions or ionic strength is the reason for the sudden change in behavior. 5wt% NaCl was chosen as an intermediate salinity brine and could give us an indication on the amount of salt needed to see this change in behavior. Figure 7.3 shows the viscosity at 10s^{-1} as a function of polymer concentration in all four salinities. Already at 5wt% NaCl the polymer solution has a more obvious c^* and shows more associative behavior. This behavior is further enhanced in the high salinity solution, 10wt% NaCl and the high salinity mixed solution. From the viscosity plot in Figure 7.3, the pure NaCl brine has a higher viscosity above the overlap concentration than the mixed brine. At this ionic strength, one can assume total screening of the anionic sites on the backbone. Therefore, one could expect similar viscosity for the A75 in brines with the same ionic strength. However, there might be competition between hydrophobic and electrostatic interactions that affects the viscosity between these two solutions.

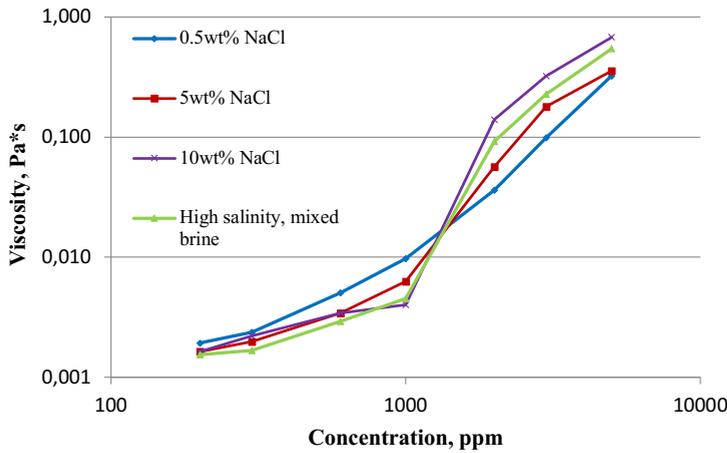


Figure 7.3: Viscosity of A75 solutions at constant shear rate of 10s^{-1} , as a function of concentration. Measured in 0.5wt% NaCl, 5wt% NaCl, 10wt% NaCl and high salinity mixed solution. (Viken et al., 2016)

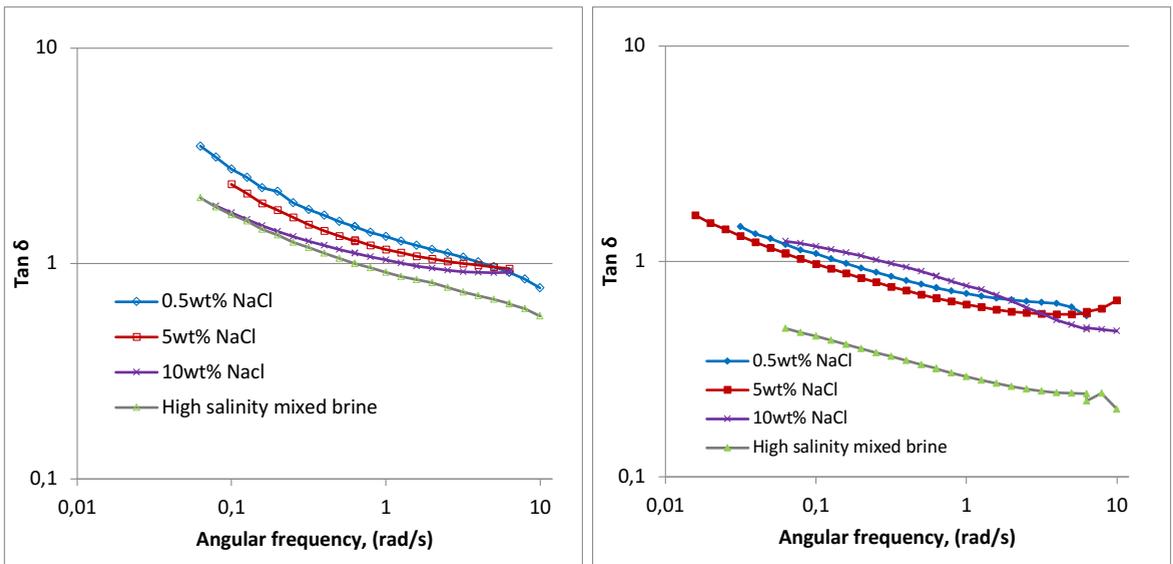


Figure 7.4: Loss factor, $\tan \delta$, as a function of angular frequency for A75 (left) and A100 (right) in four salinities. (Viken et al., 2016)

A0 and A100 were also measured in 5wt% NaCl and 10wt% NaCl to compare towards A75. Being an HPAM, A0 experienced decrease in viscosity with higher salinity. At 0.5wt% to 5wt% the viscosity dropped in all concentrations. With further decrease in salinity the polymer viscosity did not change significantly and the anionic sites on the polymer might be screened already at 5wt%. In the shear viscosity curve for A100, the associating behavior seen in the 0.5wt% NaCl is enhanced in 5wt% and 10wt% NaCl. The viscosity in the dilute regime is lower than seen in 0.5wt% NaCl due to more intramolecular coiling, thus giving a more profound viscosity increase above the critical overlap concentration.

Looking at the viscoelasticity for A75 and A100 in Figure 7.4, where the loss tangent is presented for all four salinities. The high salinity mixed brine affects the elastic contribution more than the shear viscosity. As the salinity increases the elasticity contribution increases. However, while the shear viscosity is higher in the 10wt% NaCl, the pure NaCl brines are not contributing significantly to the elasticity. The high salinity mixed brine on the other hand is contributing to a higher elastic contribution (Figure 7.4). This effect is more profound in the A100 polymer solution. In the shear viscosity measurements performed, the divalent ions in the mixed brine does not affect the viscosity significantly compared to the pure NaCl brines. However, the different ions seem to affect the viscoelasticity in the polymers with high hydrophobic content. The elasticity of both A75 and A100 is higher in the mixed brine than in the 10wt% NaCl which can indicate more a Hofmeister effect due to SO_4^{2-} being present in the brine. Anions on the left side of the Hofmeister series, e.g CO_3^{2-} and SO_4^{2-} have the ability to strengthen the hydrophobic interactions as they increase the polarity of the solvent (Thormann, 2012). Hofmeister cations as mentioned previously are more sensitive towards the nature of the solute and might not give the same contribution to the salting-in effect.

7.2 Thermo-thickening and Salinity Tolerant Hydrophobically Modified Polyacrylamides (HMPAMs) for Polymer Flooding (Paper II)

In the first paper we found that a threshold value in amount of hydrophobic groups needed to be crossed in get the desired associative behavior. To learn more about how the hydrophobicity affects the viscosifying abilities of the polymers, we looked closer into a polymer series (polymer series P) where the number of hydrophobic monomers in the polymer is the same. However, the length of the hydrophobic group is changing, giving different HLB (hydrophilic lipophilic balance) values for the hydrophobic groups. This polymer series have previously been studied in the group, and the polymers with high HLB shows little or no difference in behavior compared to HPAM. Thus, we wanted to study the two polymers with the lowest HLB further, as they seemed to be above a threshold value. The shear viscosity of the two polymers was studied further in increasing salinity and temperature. Performing a salinity study, with a broad range of salinities, can give an indication on how the structural differences in the polymer affects the shielding of the anionic sites. With salt present, the hydrophobic groups are shielding the anionic groups on the polymer backbone. Therefore, an increase in salinity is needed for charge screening in the HMPAM polymer. When the repulsion between the anionic sites decreases, the polymer becomes more flexible and are able to create hydrophobic interactions. This will further affect the steric hindrance.

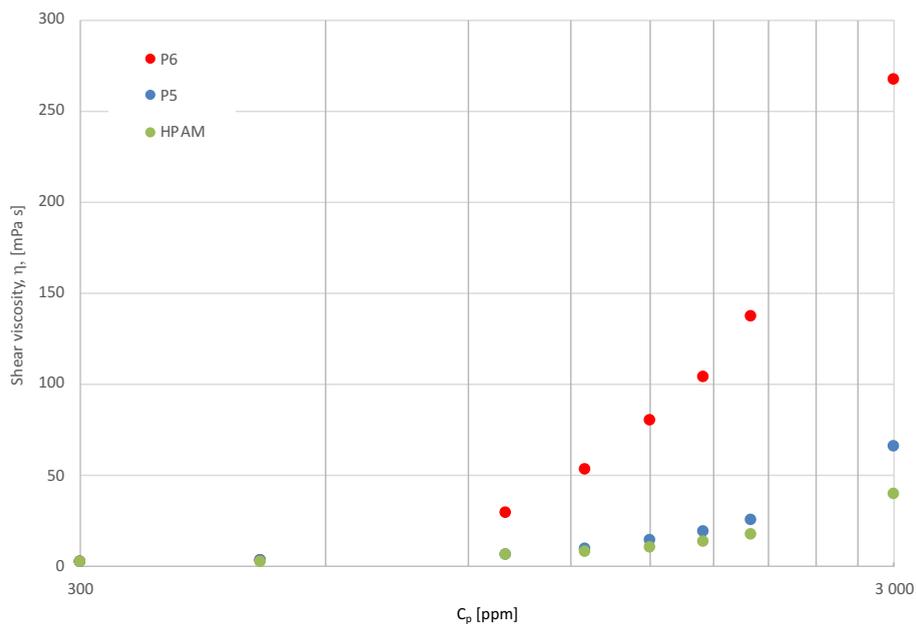


Figure 7.5: Viscosity as a function of concentration for P5 and P6 in 1wt% salinity brine. (Viken et al., 2018a)

Table 7.3: Power Law index for P5 and P6 at 5wt% brine and P0 in 4wt% brine.

CP (ppm)	P6	P5	P0
5000	0,29	0,55	0,52
3000	0,22	0,63	0,63
2000	0,11	0,71	0,72
1000	0,27	0,90	0,85
300	0,97	0,95	0,99

From Figure 7.5 where viscosity is presented as a function of concentration for P5 and P6 at 1wt% salinity brine, one can see that the viscosity of these polymers differs significantly. The longer hydrophobic groups in P6 can create network at lower concentrations, which can be seen by a more obvious critical overlap concentration and a steeper increase in viscosity in the semi-dilute regime for P6 compared to P5. Already at 1000 ppm, P6 has a much higher viscosity than P5. Also, in Table 7.3 where the power law index for HPAM, P5 and P6 in 5 wt% salinity at different concentrations is shown, P6 seems to differ from both HPAM and P5 above c^* . In the diluted regime at 300 ppm, all three polymers are close to Newtonian with a power law value close to 1. Above c^* , P5 and HPAM do not deviate significantly which can be seen in both the shear viscosity plot and based on similar power law values. Even though P6 only differs from P5 by approximately one $-CH_2$ group according to the Davies rule (Davies, 1957), their behavior deviates significantly. With higher concentration, P6 has a significant lower power law value, indicating a more shear thinning polymer solution, and higher viscosity in concentrations above c^* (Figure 7.5).

Viscosity at $10s^{-1}$ for 3000 ppm as a function of salinity is presented in Figure 7.6. As the salinity increases from 0.1wt% to 1wt%, HPAM experiences a decrease in viscosity. Screening of the anionic sites of the polyelectrolyte lead to coiling of the backbone and a decrease in the hydrodynamic volume of the polymer. Therefore, the viscosity of the HPAM polymer decreases and a further increase in salinity above 1wt% does not affect the viscosity of the HPAM polymer. P5 has a similar shear viscosity as HPAM in low and medium salinity. However, Figure 7.6 shows that with increase in salinity above 10wt% the viscosity of P5 increases. The same trend in P5 is also seen for P6. However, for P6 there is a more gradual decrease in viscosity from 0.1wt% to 10wt% salinity. Longer hydrophobic groups might cause more steric hindrance and shield the anionic sites on the backbone when salt is added to the solution. As the salinity increases to about 10wt%, the backbone of P6 is neutral. With further addition of salt, the viscosity of P6 increases. Due to less repulsion between the anionic sites causing a more flexible polymer, the hydrophobic groups are able to create intermolecular interactions. Thus, increasing the shear viscosity of P6.

As shown in Figure 7.7, where the loss factor is presented as a function of angular frequency for 3000 ppm solution of P5 and P6, a more viscous dominated behavior can be seen in P5. At 1wt% salinity P6 is for both 1 and 10wt% salinity, elastically dominated over the entire frequency range. With a further increase in salinity to 10wt%, the elasticity decreases and P6 becomes viscously dominated. The results in paper I showed an increase in elasticity with increasing salinity, and this effect became stronger with increasing hydrophobicity. This effect was also expected here.

Nair et al (Nair, 2011) indicated that the degree of connectivity might affect the viscoelasticity of the polymer. Increasing the salinity might therefore cause lower network connectivity, thus reducing the elasticity and the polymer solution becomes viscously dominated.

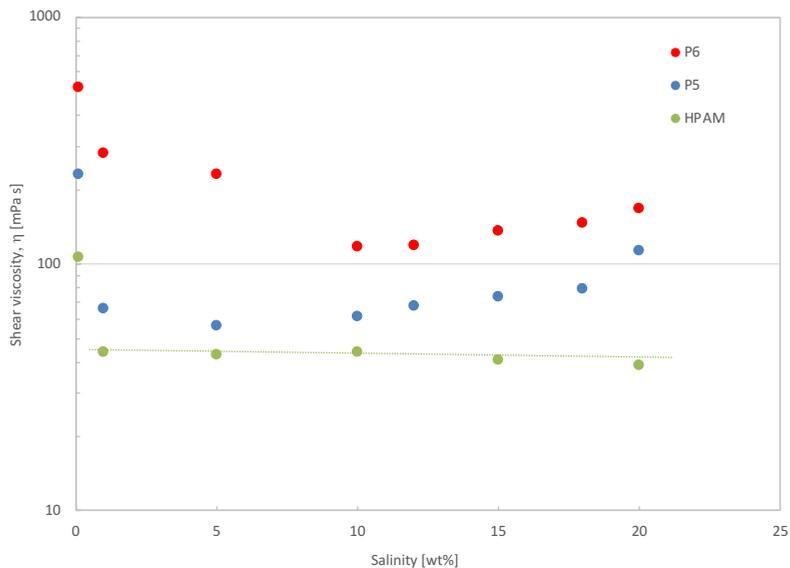


Figure 7.6: Viscosity at $10s^{-1}$ as a function of salinity for P0, P5 and P6 in 3000ppm (Viken et al, 2018a).

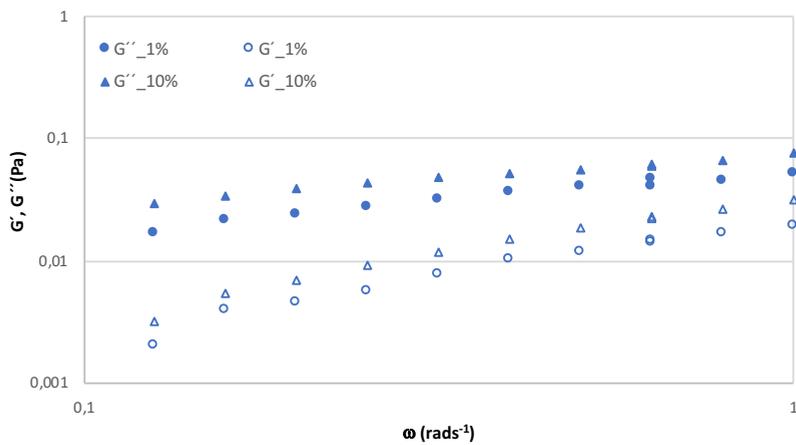


Figure 7.7: Loss factor as a function of angular frequency for 3000 ppm of P5 and P6 at 1wt% and 10wt% salinity (Viken et al, 2018a)

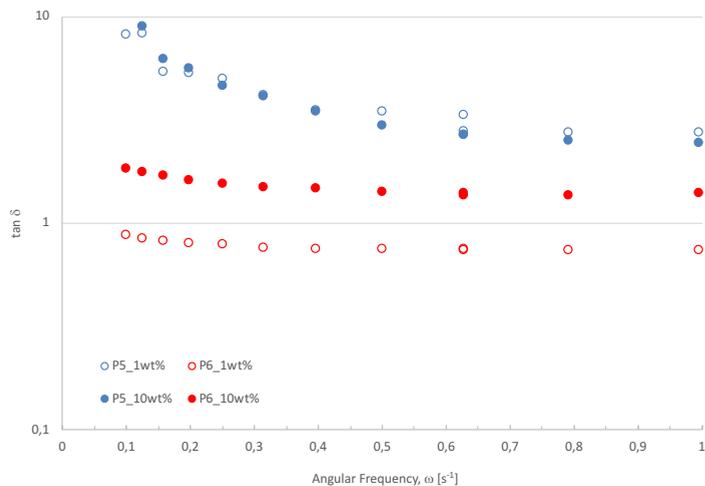


Figure 7.8: Elastic and viscous modulus as a function of angular frequency (rad/s) for 3000ppm solution of P5 at 1wt% and 10wt% salinity

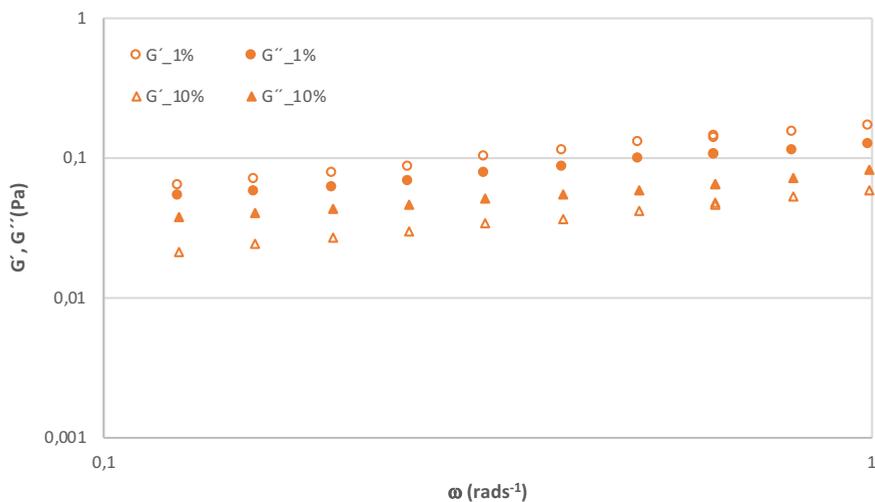


Figure 7.9: Elastic and viscous modulus as a function of angular frequency (rad/s) for 3000ppm solution of P6 at 1wt% and 10wt% salinity

Figure 7.8 and 7.9 shows the elastic and viscous modulus as a function of angular frequency in 1wt% and 10wt% salinity for P5 and P6 respectively. The G' is somewhat similar for the two polymers, however the G'' is significantly different.

For P5, the loss tangent in 1wt% and 10wt% is overlapping (Figure 7.7). This can be explained by the elastic and viscous modulus seen in Figure 7.8, where the G' and G'' for 10wt% are higher than for 1wt%. Thus, giving the same ratio between the elastic and viscous modulus for both salinities, and a similar loss factor. P6 has a decrease in both elastic and viscous modulus with increasing salinity (Figure 7.9), giving a lower $\tan \delta$ for 10wt%. This can be explained by charge screening of the anionic sites on the backbone with increasing salinity, thus giving a more coiled and less extended polymer, which will reduce the hydrodynamic volume. In 1wt% salinity, with partially extended polymer chains, a large amount of hydrophobic grafts is exposed to the water and available for creation of intermolecular interactions. With increasing salinity, and a more coiled conformational state, the hydrophobic groups are less exposed giving a reduced tendency for hydrophobic network formation. By increasing the salinity, one might also get a stronger network, however, with a lower degree of connectivity (Nair et al, 2011).

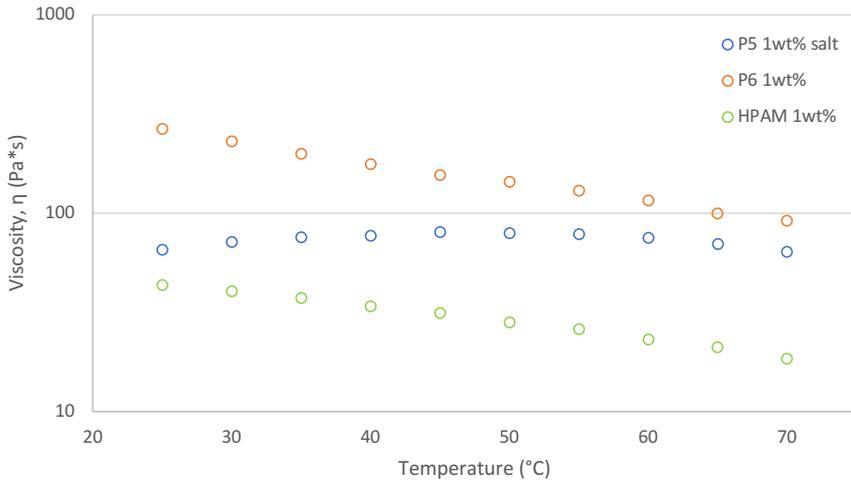


Figure 7.10: Viscosity at $10s^{-1}$ for 3000 ppm solution of P0, P5 and P6 as a function for temperature. Samples are at 1wt% salinity (Viken et al, 2018a)

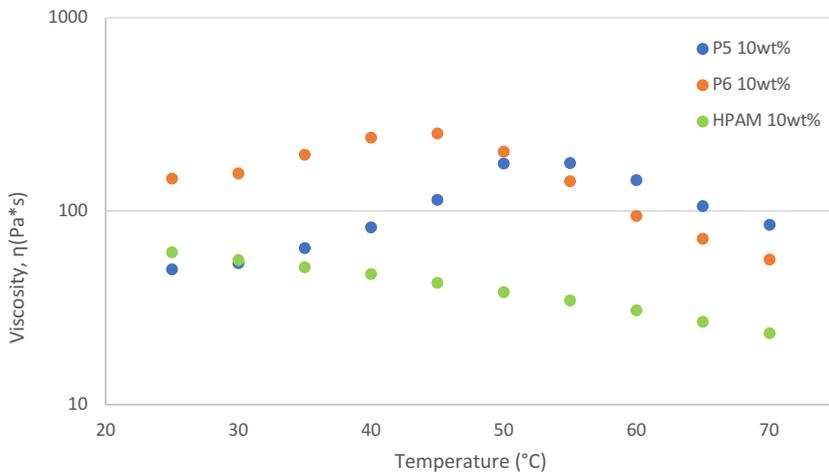


Figure 7.11: Viscosity at $10s^{-1}$ for 3000 ppm solution of P0, P5 and P6 as a function for temperature. Samples are at 10wt% salinity (Viken et al, 2018a)

Associative polymers are often thermo-responsive, and an earlier offset in viscosity increase can be seen in higher temperatures compared to HPAM. Therefore, the research group tested and developed a method for temperature studies in the rheometer (explained in Chapter 6). It became a priority to develop a method to use in the study for paper II to further investigate the viscosifying abilities within the HMPAM polymers.

Being an obvious more viscous and stable polymer with increasing salinity, P6 is weaker than expected as the temperature increases. Small differences in the structure of P5 and P6, results in significant differences in their behavior, both in increasing salinity and temperature. Figure 7.10 and 7.11 shows the viscosity for 3000 ppm of P0, P5 and P6 as a function of increasing temperature for respectively 1wt% and 10wt% brine. Each measuring point is at a constant shear rate of 10s^{-1} . P6 has a higher viscosity than P5 in the 1wt% salinity brine over the entire temperature range. The viscosity of P6 decreases with increasing temperature, while that of P5 does not change significantly as the temperature increases. At 10wt% salinity (Figure 7.11) the viscosity of both P5 and P6 increases with increasing temperature. A T_{max} is reached before both polymers lose their viscosity at further increase in temperature. P6 reaches its T_{max} (45°C) at a lower temperature than P5 (55°C) and has a steeper decrease in viscosity with increasing temperature. Hydrophobic interactions are known for their ability to enhance network formations and increase the polymer viscosity in high salinity and high temperatures. This ability is further enhanced when the hydrophobic content is increased. Therefore, one might expect P6 to perform better than P5 in 10wt% salinity at high temperatures. However, even though a high degree of hydrophobicity is important to increase the viscosity, the polymer might in high salinity and temperature experience poor solvent-polymer interactions which results in polymer coiling due to intermolecular interactions. HPAM is experiencing a slight decrease in viscosity with increasing temperature in both 1wt% and 10wt% salinity.

As seen in the salinity studies, P6 has a higher viscosity in the low salinity brines, while P5 already at 1wt% NaCl has lost significant parts of its network and has fewer intermolecular interactions. P6 has a higher aggregation number due to a larger network of intermolecular interactions and several active junctions in the within the polymer. Therefore, an increase in temperature weakens the network, and loss of aggregation number and viscosity of the polymer is seen. Due to a lower aggregation number and fewer active junctions present in the solution, an increase in temperature does not reduce P5 further, rather enhancing the network structure and improving the viscosity.

7.3 Influence of Weak Hydrophobic interaction on In-Situ Viscosity of HMPAM (Paper III)

From the rheological bulk measurements, we have seen how different degrees of hydrophobicity can influence the shear viscosity and viscoelastic properties of HMPAM compared to HPAM. To achieve associative behavior, a threshold value of hydrophobicity needs to be crossed. The behavior in bulk rheology has been thoroughly studied, and we can anticipate how the polymer might behave. However, the flow in porous media is more complex than the flow in a rheometer. In-situ in a rock core, the polymer will experience contraction-expansion due to the tight channels and larger pores. Thus, creating forced interactions between the polymer molecules. The in-situ viscosity and core flooding experiment can give an indication if the polymer is a good fit for polymer flooding. The resistance factor (RF) and residual resistance factor (RRF) provide information about the mobility reduction of the injected fluid, polymer retention, apparent viscosity and the irreversible resistance factor (Sorbie, 1991). One of the limitations by using HPAM, is the mechanical degradation, especially seen topside where shear forces might be higher (Sorbie, 1991; Reichenbach-Klinke et al., 2016, Seright et al., 1983). HPAM provides higher viscosity in bulk rheology with higher molecular weight, however, with increasing Mw increases the chances of breakage of the polymer backbone due to mechanical degradation (Sorbie, 1991). In Paper III, the P5 polymer studied in Paper II was investigated in-situ. Three concentrations of P5 from three different concentration regimes were measured and compared to a semi-dilute solution of the HPAM counterpart.

Shear viscosity of P5 and P0 was measured to establish the bulk rheology of the polymers. From Figure 7.12, the viscosity for P5 and P0 at 10s^{-1} is presented as a function of concentration. Three polymer concentrations of P5 were chosen, 3000 ppm (concentrated regime), 1000 ppm (semi-diluted regime) and 300 ppm (diluted regime), along with 1000ppm P0. Due to being in different concentration regimes, the polymer solutions were expected to behave differently in the porous media. From the shear viscosity in Figure 7.12, no significant difference between P5 and P0 is seen in either of the concentration regimes.

Adsorption and retention in the cores might cause loss of concentration. Therefore, before starting the flooding experiments, the cores were saturated with the respective polymer solution. For each of the polymer solutions the saturation lasted until stable values of pressure drop were obtained across both cores. For P5, stable dP values were obtained in the first core at similar injected polymer solution in the three concentration regimes. The second core had a delay before dP was stable. This delay increased with increasing concentration of the polymer solution. This might be due to in-situ gelling, which causes a rapid pressure build-up at the inlet and a leveling off due to channels opening in the gel. Thus, effectively forming a yield pressure (Dupuis et al., 2011, 2012). The pressure build-up in 1000 ppm P5 differs significantly from the pressure build up for HPAM (P0). Although the breakthrough is at the same amount of injected polymer, the pressure profile in P0 is at a significant lower value than P5, and both cores stabilize at a relatively low injected pore volume.

As large aggregates formed in the HMPAM solutions enter the porous media in first core, the structure in the polymer solution is disrupted. As a result, the polymer solution that enters the second core has a lower viscosity.

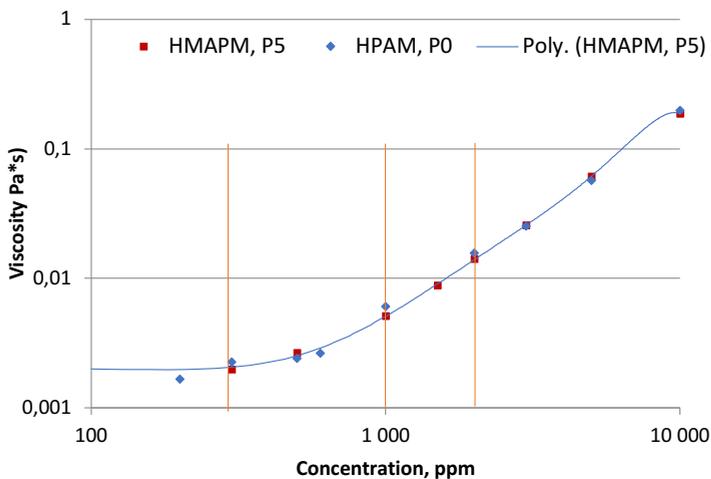


Figure 7.12: Shear viscosity at $10s^{-1}$ as a function of concentration for P0 and P5. (Viken et al., 2018b)

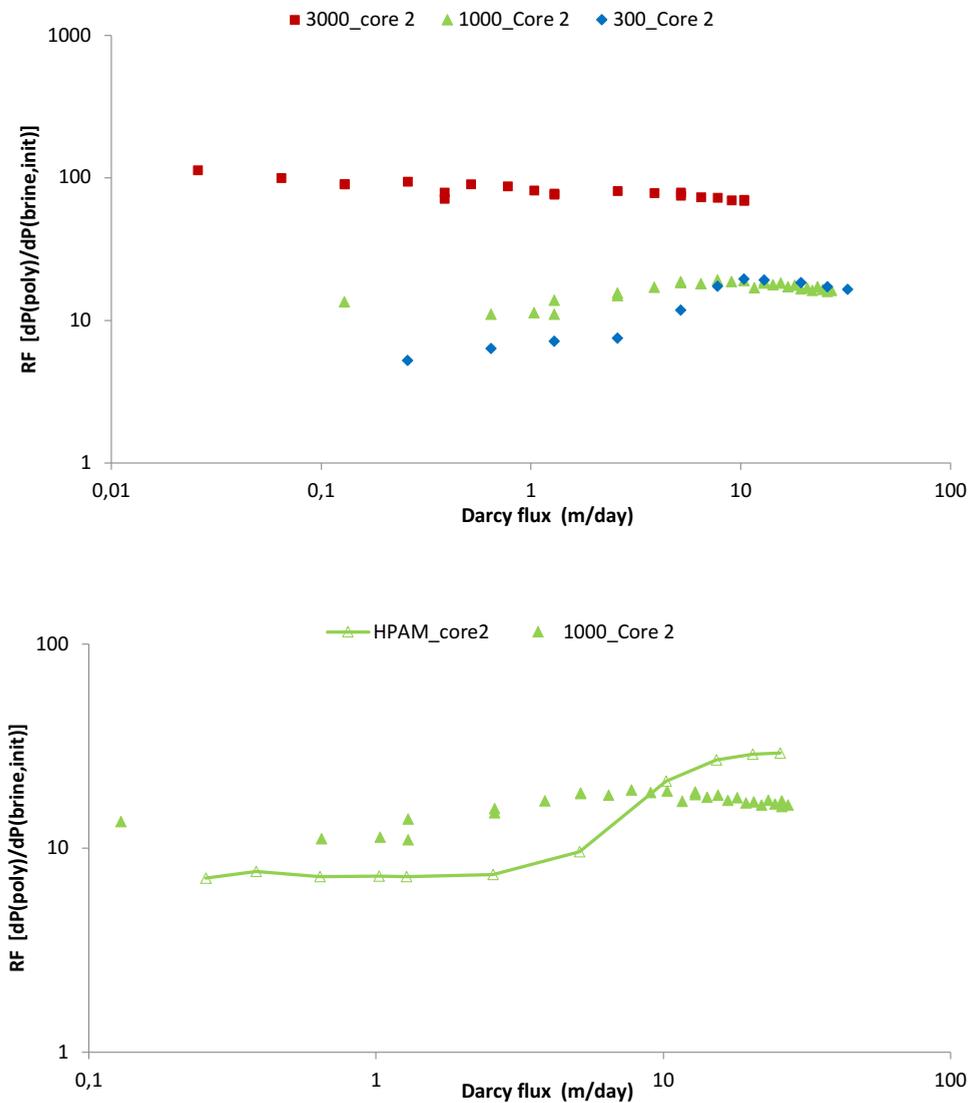


Figure 7.13: Resistance factor as a function of Darcy rate (m/day) for core 2, in 300 ppm, 1000 ppm and 3000 ppm P5 (upper figure) and 1000ppm for the HPAM, P0 (lower figure) (Viken et al, 2018b)

The resistance factor, RF, is often taken as a measure of in-situ viscosity, and thus on how the polymer affects the oil-water mobility ratio in the porous media. A high resistance factor shows high viscosity in the injected polymer solution and thereby reduction in the mobility of the injected fluid. Higher RF in the higher concentration regimes can also be expected, as more hydrophobic interactions dominate. The flow behavior in Figure 7.13 indicates that the behavior of P5 is dependent on concentration regime. Polymer solutions from the concentrated regime, 3000 ppm, show a weak rheo-thinning effect as the injection rate increases, and behave like a gel-like structure. Porous media induce more hydrophobic interactions compared to bulk, giving the polymer a higher in-situ viscosity. 1000 ppm and 300 ppm show a weak rheo-thickening behavior at moderate to high rates. 300ppm, do not experience intermolecular interactions in bulk. From the flow behavior, one can see that the 300ppm in-situ behaves similar to the 1000 ppm HPAM, which indicates absence of intermolecular interactions also in porous media. The rheo-thinning seen in the dilute and semi-dilute HMPAM polymers at high injection rates, is likely caused by fragmentation of the structure due to mechanical degradation.

For the 1000 ppm P5, the presence of intermolecular interaction provides a higher RF compared to P0 at low to moderate injection rates (Figure 7.13). The RF is 1.5 times higher in P5 in the semi-diluted regime at rates lower than 5 m/day. Also, the onset for rheo-thickening is significant earlier at low rates and has a significant earlier onset for rheo-thickening at 1m/day compared to P0 at 5 m/day. An early onset for RF is often seen in higher molecular weight polymers. P0 and P5 has the same Mw, which indicates that P5 has a higher effective molecular weight due to intermolecular interactions induced by the porous medium. 1000 ppm P5 and P0 have similar bulk viscosity, permeability reduction and molecular weight. Thus, difference in behavior in porous media is likely due to induced intermolecular interactions formed in the P5.

Furthermore, the residual resistance factor, RRF was investigated. RRF can give an indication on the irreversible retention of the polymer in the porous media, and therefore the permanent permeability reduction. HMPAM polymers often have a higher RRF than HPAM due to multilayer adsorption. Interestingly, there is no significant difference between the RRF values for HMPAM and HPAM, which indicates no multilayer

adsorption. As the polymer goes through the porous media the hydrophobic groups in the HMPAM are experiencing contraction and expansion, which may induce intermolecular interaction. This gives a high in situ viscosity seen as a high RF and a high RF/RRF ratio.

The concentration of the P5 seems to affect the retention in the porous media. 3000ppm has a higher RRF with an average of 4.9, compared to 1000 ppm and 300 ppm with an average of 3.4. Both this difference in RRF and the higher RRF for first core in 1000 ppm and 300 ppm, can be caused due to the tapering process (described in chapter 6). The first core might have experienced a more efficient cleaning compared to the second core, where there could have been accumulation. This is due to the first and the second core were still being connected in series during the tapering process.

After the polymer flooding, shear viscosity was further measured for at least five effluent samples for each polymer concentration. These samples were collected after core floods at different flow rates After passing through the core samples, the interaction created in the bulk are broken, giving the polymers lower viscosity. Figure 7.14 shows the relative viscosity for the three concentrations of P5 and the P0 at different rates. P5 experiences more loss of viscosity than P0 at all rates. This indicates that the viscosity loss is because the intra- and intermolecular interactions are altered during flow through the porous media, and not due to chemical alteration. The viscosity loss is more pronounced at higher concentrations and higher rates. Even though 1000 ppm HMPAM contributed to a higher in-situ viscosity compared to HPAM, the HMPAM polymer had a greater loss of viscosity in the effluent sample (Figure 7.15). The observed effect is irreversible. The effluent samples were stored in a refrigerator for a month and the shear viscosity was measured again, without significant change.

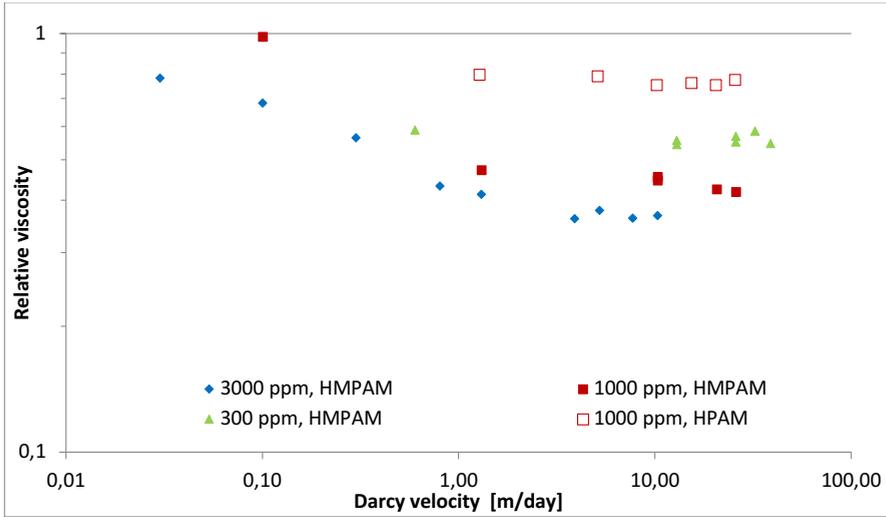


Figure 7.14: Relative viscosity for the effluent samples as a function of injection rate in m/day (Viken et al., 2018b)

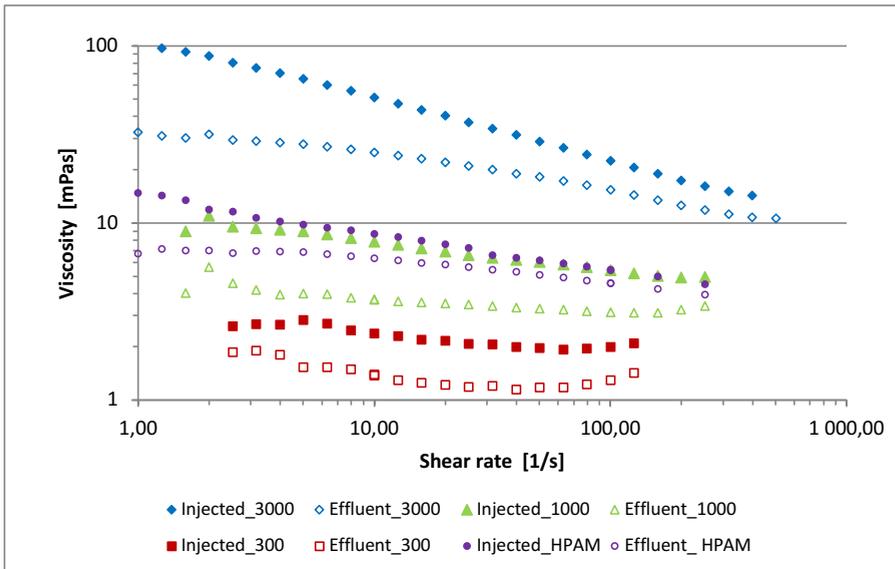


Figure 7.15: Shear viscosity for injected solutions and effluents at 1ml/min for HPAM and HMPAM

Even though P5 is an HMPAM polymer, the shear viscosity in the 1wt% brine does not differ from the HPAM, P0. The low viscosity builds up with increasing concentration and the low level of elasticity indicates weak hydrophobic interactions within P5. In bulk rheology, associative behavior is mainly seen in polymers with a high degree of hydrophobicity. In polymers with hydrophobicity below the threshold value, the hydrophobic groups do not contribute enough to increasing viscosity and strengthening of the polymer network. In-situ however, it seems to be beneficial to have a polymer with lower degree of hydrophobicity. P5 has shown great qualities in a porous media. Lack of multilayer adsorption, good injectivity and as intermolecular interactions are induced in the porous media, a high in-situ viscosity is seen.

8. CONCLUDING REMARKS

In the papers presented in this thesis, one polymer series changes with increasing number of hydrophobic groups attached to the polymer backbone, and in the other polymer series the length of the hydrophobic group varies. In both the polymer series the hydrophobicity needs to cross a threshold value in either number of hydrophobic groups or length of the groups to show associative behavior with steep increase in viscosity above c^* . It has been shown in the literature that several polymer systems need to cross a threshold value to obtain hydrophobic intermolecular interactions (Chang et al., 1993, Kujawa et al., 2006, McCormick et al., 1988a, Wever et al., 2011). With low amount of hydrophobic groups attached to the polymer backbone, or short hydrophobic groups, there is less possibility for the hydrophobic groups to create intermolecular interactions (Taylor and Nasr-El-Din, 1998, Wever et al., 2011). The polymers that have a low degree of hydrophobicity behaves more like a polyelectrolytic HPAM (Kujawa et al., 2006). Above a threshold value of hydrophobicity, it is easier for the polymers to connect and create a network formation as the distance between the hydrophobic groups are shorter (Wever et al., 2011).

Changes in salinity and composition of salt affect the polymers ability for intermolecular interactions (Akbari et al., 2017a,b, Kujawa et al, 2006, Wever et al., 2011) High polar brines have previously shown to increase the HMPAM polymers ability to enhance network formations and viscosity, as the hydrophobic groups seek closer together with increasing amount of ions in the brine (Reichenbach-Klinke et al, 2011). In polymer series A hydrophobic association occurs at a lower degree of hydrophobicity with higher ionic strength. At 0.75 relative amount of hydrophobic groups, the polymer behaves as an associating polymer at 5 and 10 wt% NaCl, but not at 0,5wt%. Polymer series P does not show the same effect with increasing ionic strength, rather a weaker network and lower viscosity, is observed at higher salinities. The viscosity decreases for the HMPAM polymers with increase in viscosity between 0.1wt% to 10wt%, and with a slight increase in viscosity with further increase above 10wt% brine. However, the viscosity of the polymers is not exclusively determined by its hydrophobicity. The balance and

interplay between all factors both inherent parameters and external variables affect the viscosity and viscoelasticity of the polymer solution (Wever et al., 2011).

The elastic contribution increases as the degree of hydrophobic interactions increases, which is further enhanced in higher salinity due to more hydrophobic interactions.

This is evident in polymer series A, where the elasticity of the polymers increases as the ionic strength increases. Though a higher ionic strength affects the elasticity, an even more profound effect on the elasticity comes from a brine composition with both divalent ions present and several anions. This trend is more evident in the polymer with the highest number of hydrophobic groups. By containing a constant ratio between NaCl and CaCl₂ and increasing the ionic strength in paper II, the polymer with the highest degree of hydrophobicity had a drop in both G' and G'' with increasing salinity. Thus, indicating a lower degree of connectivity within the polymer solution compared to P5 (Nair et al, 2011).

In-situ rheology and behavior in HMPAM compared to HPAM:

Although the HMPAM (P5) and HPAM (P0) had no significant difference in bulk rheology in the 1 wt% brine, significant differences are shown in the in-situ rheology. Due to spatial restriction within the porous media the HMPAM polymer experiences induced hydrophobic interactions during contraction-expansion flow (Lake, 1989, Sorbie, 1991). This results in a doubling of the RF of HMPAM relative to HPAM at low rates. The rate at which the resistance factor, RF starts to increase is 1m/day for HMPAM compared to 5 m/day in HPAM. Early onset is normally seen in high molecular weight polymers. Thus, indicating more hydrophobic interactions in the HMPAM polymer. Since hydrophobic interactions are induced in the porous media, multilayer adsorption might occur on the wall of the rock core. However, the residual resistance factor, RRF, for HMPAM and HPAM shows no significant difference, and is relatively low. This indicates no multilayer adsorption for the hydrophobically modified polymer. Therefore, there seems to be a molecular interaction between flowing polymer molecules and not between the flowing polymer molecules and the adsorbed polymer

molecules (Argillier et al., 1996). Based on a significant reduction in the effluent viscosity for the HMPAM polymer, it is likely that the intermolecular hydrophobic interactions in the polymer solution is irreversibly altered in the porous media and does no longer contribute to a high bulk viscosity. Another noteworthy observation is that even though P5 has a greater loss of effluent viscosity than P0, it has a higher in-situ viscosity.

The behavior of the HMPAM polymer, P5, depends on concentration regime. At low concentration, below c^* , there are no intermolecular interactions present, and the flow behavior of the 300ppm solution has the same trend as the HPAM solution. In the semi-diluted regime, there is a significant difference in flow behavior of the 1000ppm HMPAM and HPAM, with higher RF and onset for rheo-thickening in the hydrophobically modified polymer (Reichenbach-Klinke et al., 2016, Skauge et al., 2015, Zhang and Seright, 2015). When the concentration is increased to 3000ppm, the in-situ behavior transitions from a near-Newtonian behavior to a rheo-thinning behavior (Reichenbach-Klinke et al, 2011; Reichenbach-Klinke et al, 2016; Seright et al., 2011b).

Hydrophobically modified polymers has some advantages over HPAM in porous media. Bulk rheology of the polymers indicates weak hydrophobic interactions within P5. Based on the results from the flow behavior of P5 in porous media, weak interactions might be beneficial in-situ. This is due to induced interaction with contraction-expansion in the flow creating a higher in-situ viscosity and avoiding unwanted high RRF.

When this project started in 2012, some publications were performed on hydrophobically modified polymers as applied polymers in EOR. Through these years more articles have been published within this field, however many polymer studies are targeted towards the monodisperse polymers in more theoretical studies. Studies performed on monodisperse polymers with low molecular weight can contain SANS, DLS, fluorescence etc. can provide theoretical explanation for the changes seen in the polymer behavior. For large, polydisperse polymers these techniques do not yield data that are easily interpretable. Therefore, the theoretical studies of monodisperse polymers with low molecular weight can give information and understanding, which can be used

to explain some of the behavior seen in polydisperse polymers with high molecular weight. The behavior of the large polydisperse polymers is complex and might deviate from the behavior seen in the theory. To understand the interface between the theoretical studies and the applied use of the polymers, the high molecular, polydisperse polymers is important to study. Salinity and temperature can affect the polymers differently based on the structure and size of the molecule. The cost of using polymers for EOR is high and therefore the polymers injected must be selected based on thorough research. Comparing bulk rheology and in-situ rheology gives a broader understanding of how the hydrophobic groups affect the viscosity in theory, and how they will behave when forced into a porous media. This is especially important as some HMPAM polymers that seems to act as an HPAM in bulk rheology might inhibit favorable properties for polymer flooding.

9. FURTHER WORK

Polymer series A shows great viscosifying effect with increasing salinity. It would be interesting to investigate the salinity effect further on series A. The mixed high salinity brine could be investigated further with the same composition, however with a lower ionic strength similar to the pure NaCl brines. This could strengthen the comparison made between the mixed brines and the pure NaCl brines. Furthermore, a less complex brine containing divalent cations and only one type of anions might shed light on whether the Hofmeister anions has an effect on the elasticity or not. A further enhancement of the study in paper I would be to include a temperature study in different salinities.

From the second study, it would be interesting to look closer at the salinity effect. Some salinity studies have been performed where the ratio between NaCl and CaCl₂ changed. This effect was not significant, therefore expanding the matrix further would be more interesting. Expanding the matrix by introducing more salts, might give an effect in the viscoelastic properties, and thereby also here see if there are Hofmeister effects or not. It might also change the threshold value of wanted associating effect or give a more elastic contribution to the solution.

Increasing temperature did have a more significant effect on P5 in high salinity than first anticipated. A temperature effect might also be present in the polymers with higher HLB, (P1-P4) even though higher salinity did not. To expand the temperature study to involve more of the series could give an indication on whether the association would be present in a higher temperature, and how it would be affected by salinity.

The in-situ study was performed in low salinity and low temperature for P5 and compared to its HPAM counterpart. Some of the reasons to use P5 was its similarities to HPAM in shear viscosity measurement within these premises. The effects seen in-situ in P5 are most likely effects caused by hydrophobic interactions. Even though a loss of viscosity is seen at 10wt% salinity in shear viscosity in P5, forced interactions caused by contraction/extension in narrow pore throats and larger pores can induce higher viscosity in-situ. Therefore, a broader range of salinities would give a more thorough description of the EOR potential of the polymer.

As mentioned in paper II, P6 might be a good candidate for EOR applications. This due to the shear thinning behavior with increasing shear forces, which contributes to a relative low injection pressure. Also, P6 ability to increase its viscosity in low flow velocities compared to HPAM makes it a promising candidate for polymer flooding. A study of both P5 and P6 in porous media in low, intermediate and high salinity compared to HPAM would be of interest. Also including polymers with larger HLB can shed light on the induced hydrophobic interactions in porous media.

Increased temperature had a significant effect on the viscosifying ability of both P5 and P6 while the HPAM polymer had no significant change in viscosity. For shallow reservoirs, the temperature normally ranges between 40 to 50°C. An understanding on how the effects of increasing temperature would affect the polymer in-situ might be important for application offshore.

Furthermore, an in-situ study of polymer series A could give a better understanding of the rheological behavior versus the in-situ viscosity of HMPAM polymers. With a high degree of hydrophobicity, the polymers of series A showed great viscosifying abilities. Many aspects of the polymers could further be studied in a porous media; for example, if the threshold value seen in the salinity study would change to a lower degree of hydrophobicity when the intermolecular interactions are forced in narrow pores, or with a lower salinity.

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Rheological properties of a hydrophobically modified anionic polymer: Effect of varying salinity and amount of hydrophobic moieties

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ABSTRACT: Hydrophobically modified polyelectrolytes have been suggested as an alternative to the more commonly used polyelectrolytes in enhanced oil recovery (EOR) applications involving polymers. Compared to regular polyelectrolytes, the hydrophobically modified polyelectrolytes are known to be more stable at high salinities. In this study, we have investigated the influence of brine salinity and ionic composition for a series of six hydrophobically modified polyelectrolytes with the same polymer backbone, but with an increasing average number of hydrophobic groups per polymer molecule. Polymer characterization has been performed using a combination of steady-state shear viscosity and dynamic oscillatory measurements. Hydrophobic interactions leading to a change in rheological properties was only observed above a threshold value for the concentration of hydrophobe. At the threshold value, salt-induced hydrophobic interactions were observed. For higher concentrations of hydrophobe, high salinity solutions showed one order of magnitude increase in viscosity compared to the polymer without hydrophobic groups. This could partly be explained by an increase in elasticity. These findings have important implications for polymer selection for EOR. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43520.

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INTRODUCTION

In a chemical flooding process, a polymer solution with high viscosity is injected to improve the mobility ratio in the water flood and increase the recovery in the reservoir.¹ The polymers injected have to withstand high salinity, high temperature, and long injection times without decreasing in viscosity.^{1,2} High-molecular-weight polyelectrolytes, for instance partially hydrolyzed polyacrylamide (HPAM), are frequently used in oil field applications due to their relatively low cost and high viscosifying ability. However, at high salinities, particularly in the presence of divalent cations,³ their viscosity decreases significantly due to coiling of the polymer as a result of electrostatic shielding. As an alternative, the use of hydrophobically modified versions of these polyelectrolytes has been suggested as a mean of maintaining high viscosity at high salinity. Associative polymers differ from hydrolyzed polyacrylamide, mainly due to the hydrophobic groups attached to the backbone of the associative polymer. The polymers still experience shielding of the polyelectrolyte backbone; however their viscosity does not decrease in concentration above critical overlap concentration, c^* , due to interaction between the hydrophobic groups.^{4,5} In aqueous solutions, above c^* , the associative polymers form hydrophobic

intermolecular interactions between the side groups. This leads to the formation of a three-dimensional network,⁶ and enhances the viscosity and gives unique rheological properties. Petit-Agnley *et al.*⁷ has demonstrated that only a fraction of hydrophobic groups contributes to microdomain formation. Observations have shown that with increase in hydrophobic groups, one get better thickening capability. However, the presence of hydrophobic groups impairs the solubility of the polymer and can lead to solubility issues.⁸

BACKGROUND

Polymers in Solution

The behavior of associative polyelectrolytes is due to two effects, the repulsive interaction between the negatively charged ions in the backbone, and the attractive interactions of the hydrophobic groups. By adding salt in the polymer solution, the charged backbone will be shielded, and the repulsive electrostatic interaction is cancelled out.⁹ This results in a reduction in the hydrodynamic radius of the polymer, and a reduction in viscosity. An associative polymers response to salinity is different from that of polyelectrolytes like HPAM. Although a viscosity loss by charge screening is seen, the hydrophobic interactions will be even stronger in more polar, high salinity solutions;

both because of the lack of repulsion and the hydrophobic groups will be less hindered to make intermolecular interaction.¹⁰ According to Reichenbach-Klinke *et al.*,¹⁰ the viscosity increase due to the polar solvent is going to counteract the weakening repulsion between the anionic groups. The intermolecular interactions are dominant rather than the electrostatic repulsions.¹¹ The interaction due to polarity of the solvent can be explained by the Hofmeister series. The Hofmeister series is a classification of ions due to their ability to salt-in or salt-out proteins. For anions, the Hofmeister series the typical order is $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$. The anions on the right have a salting-in effect which increases the solubility and decreases the hydrophobic interaction while the anions on the left can lead to a decrease in solubility, that is, salting-out, and strengthens the hydrophobic interactions.¹² Although similar effect and ordering is found for cations, the effect for anions is more pronounced. The thickening ability of the associative polymer can be controlled by changing the content of the hydrophobic group¹³ and arrangement on the backbone,^{13,14} the molecular weight,¹⁵ and degree of hydrolysis.

The viscosity of hydrophobically modified polyelectrolytes depends strongly on the polymer concentration. With increasing concentration the viscosity increases as more interchain association takes place and a transient network is formed.¹⁶ For a non-associative polymer, the increment in viscosity due to increasing concentration is caused by an onset of overlapping polymer at the critical overlap concentration, c^* , and related to the molecular size.⁴ The concentration contains three different regimes: the dilute ($c < c^*$), the semidilute ($c > c^*$), and concentrated regime,¹⁷ the border lines between the regimes can be diffuse.⁴ For associative polymer, the chain overlap at the same molar mass cause formation of aggregates and form associating network at a concentration, CAC, which will be lower than c^* . As previously mentioned, formation of this network enhances the viscosity of the solution significantly.¹⁸

In the dilute region, below c^* , the polymers flow freely in the solution and are not in contact with each other. Here, the intramolecular association dominates¹⁹; which gives a low hydrodynamic volume, and a low viscosity. With an increase in the salinity for associative polymers in the dilute regime, the hydrophobic groups associate to minimize their exposure to water and more associations occur between hydrophobic groups of the same chain, which leads to tighter coil contraction and decrease in viscosity.²⁰ In the semidilute region, above c^* , the polymers start to overlap, and in the associating polymers the intermolecular interactions start to dominate, which leads to an increase in viscosity due to network formations.^{14,19} Penott-Chang *et al.*²¹ showed that hydrophobically modified HPAM (HMPAM) with concentration under c^* , had a lower viscosity than the original non-associating polymer. With higher polymer concentrations (>2000 ppm), the HMPAM had a steeper increase in viscosity which got more significant with an increase in hydrophobic groups.

Viscoelasticity

The materials viscoelastic properties are measured with an oscillatory test, where one apply sinusoidal strain, resulting in a shear stress response, which is shifted by the angle δ .²² The elas-

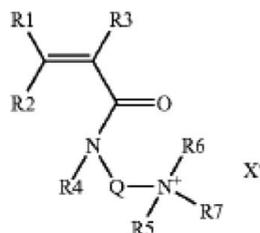


Figure 1. The backbone structure of polymer A.

tic (storage) modulus, G' , is a measure of the deformation energy stored by the sample during the shear process, while viscous (loss) modulus, G'' , is the deformation energy used up by the sample during the process and thereafter lost.²³ The loss factor, $\tan \delta$, is defined as the ratio between viscous and elastic modulus of the viscoelastic behavior.²³

$$\tan \delta = \frac{G''}{G'}$$

Ideal elastic or viscous behavior is characterized by frequency independent elastic and viscous moduli. G' completely dominates G'' , and thus $\delta = 0^\circ$ and $\tan \delta = 0$. On the other hand, for a fluid with ideal viscous behavior, G'' dominates G' , and thus $\delta = 90^\circ$ and $\tan \delta = \infty$.²³ For viscoelastic fluids, the storage modulus is higher than the loss modulus at high frequencies, and lower at low frequencies. At some intermediate frequency, referred to as the crossover frequency, ω^* , $G' = G''$, and thus $\tan \delta = 1$.

This article presents how the shear viscosity and the viscoelasticity of the polymers change due to increasing amount of hydrophobic groups in the structure in different salt solutions. The polymers contain the same backbone chain, the same degree of hydrolysis, the same type of hydrophobe, and they differ in the degree of hydrophobicity.

Previous studies by Kujawa *et al.*²⁴ have shown that the onset of the association in a polyelectrolytic associative polymer shifts toward lower concentration by increasing the length of the hydrophobic groups. The aim for this series was to give an indication at what the threshold value for the degree of hydrophobicity for the onset of association for this polymer is, and how the hydrophobicity affects the concentration of the onset.

As mentioned earlier, to enhance the recovery by polymer flooding, one needs a polymer which can tolerate high salinities and the presence of divalent cations. The salinity in this study has been varied from an ionic strength of 0.086 to 1.72 mol/L. The experimental study was conducted to examine the impact of salinity has on the threshold value towards the increment in viscosity and if it affects the concentration of the onset of association. In addition, the viscoelasticity has been a feature that still lack understanding concerning the behavior of the hydrophobic groups in solvents containing divalent cations.

EXPERIMENTAL

Materials and Preparation

In this study, we used an anionic polyacrylamide based polymer with different degree of hydrophobic monomer content

Table I. Relative Hydrophobicity of Polymer A

Product	Relative hydrophobicity based on A100
A0	0
A25	0.25
A33	0.33
A50	0.50
A75	0.75
A100	1

provided by SNF Floerger.²⁵ The polymer backbone is obtained by random polymerization with 83% acrylamide and 17% sodium acrylate, corresponding to a charge density of 17%. The molecular weight is between 8 and 12 MDa. The hydrophobic monomer is an acrylamide derivative (Figure 1), with 6–16 carbon atoms in the hydrocarbon chain (R7, Figure 1). As can be seen from the figure, the monomer is cationic, making the polymer amphoteric. The total hydrophobic monomer content varies from 0 to 0.3 mol % for the six polymers studied here. The polymer series differ only in the amount of hydrophobic groups distributed along the backbone. The relative amount of hydrophobe in the six polymers is presented in Table I.

The solvents used were four different salt aqueous solutions; composition of the different brines is provided in Table II. Three of the solvents were NaCl brines with different concentration, 0.5, 5, and 10 wt % NaCl with ionic strength of 0.086, 0.86, and 1.71M, respectively. The last brine is similar to synthetic seawater and is a mixture of five different salts (NaCl, CaCl₂, KCl, Na₂SO₄, NaHCO₃) with a total ionic strength of 1.72M. All of the brines were filtered through a 0.45- μ m filter before use. The stock solutions were made according to API stock solution procedure. All polymer solutions were prepared in stock solutions of 5000 ppm. A vortex was established with a magnetic stirrer in the relevant solvent; the polymer powder was poured slowly into the vortex. The solution was stirred at 150 rpm for 12 h. The stock solution was diluted to the desired concentrations. After each preparation and dilution, the polymer solution was left un-agitated in an air tight container for

24 h before starting any measurements. The pH of the solutions was measured to a constant value of 6.7 ± 0.5 .

Rheology

Rheological measurements were performed using Malvern Kinexus pro rheometer, equipped with a cone-plate geometry (angle = 4°, diameter = 40 mm). The temperature was maintained at 22 ± 0.1 °C. For the shear-dependent behavior, the viscosity measurements were carried out at shear rates ranging from 0.001 to 1000 s⁻¹. This range was changed to 0.05 to 1000 s⁻¹ for low concentrations (below 1000 ppm) because the sensitivity of the sensor did not allow getting accurate values at very low shear rates.

Linear viscoelasticity experiments were performed on stock solutions samples that provided significant viscosity to get accurate data. Frequency sweeps were performed in the of 0.01–10 Hz frequency range of, at a constant strain of 10%. The strain was picked to lie in the LVE range based on amplitude sweeps. The latter were performed at a frequency of 1 Hz.

RESULTS AND DISCUSSION

Degree of Hydrophobe

Steady Shear Flow Measurements. Figure 2 shows the shear viscosity as a function of concentration for polymer A in 0.085M NaCl at increasing relative hydrophobicity. At low polymer concentration, below 600 ppm, which can be assumed as the dilute concentration regime, the effect of relative hydrophobicity on solution viscosity is limited. However, above 600 ppm, behavior of A100 starts to deviate from the other polymer solutions with a steep increase in viscosity as a function of concentration. This gives rise to the assumption that the polymer solution has reached a critical overlap concentration (C^*), where the individual polymer molecules start to overlap in the semidilute regime. For associative polymers, this overlap of individual polymer molecules may give rise to intermolecular interactions between the hydrophobic groups, and thus to a steep increase in viscosity. By increasing the polymer concentration to a concentration in the semidiluted regime, the associative polymers exhibit a higher viscosity increase compared to the standard equivalent (A0),¹⁹ and the crossover becomes sharper as the relative hydrophobicity increases from A25 to A100. Earlier, it has

Table II. Composition of Brines

Component	Molecular weight (g/mol)	Composition at 1 kg solution							
		Low salinity (M)	Low salinity (ppm)	5 wt % (M)	5 wt % (ppm)	10 wt % (M)	10 wt % (ppm)	High salinity (M)	High salinity (ppm)
Na ⁺	22.99	0.086	1967	0.856	19,670	1.71	39,340	1.14	26,198
Ca ²⁺	40.08	-	-	-	-	-	-	0.10	4089
K ⁺	39.10	-	-	-	-	-	-	0.27	10,489
Cl ⁻	35.45	0.086	3033	0.856	30,330	1.71	60,660	1.58	56,174
HCO ₃ ⁻	61.02	-	-	-	-	-	-	0.024	1453
SO ₄ ²⁻	96.07	-	-	-	-	-	-	0.0035	338
TDS (ppm)	-	-	5000	-	50,000	-	100,000	-	98,742
Ionic strength (M)	-	0.086	-	0.856	-	1.71	-	1.72	-

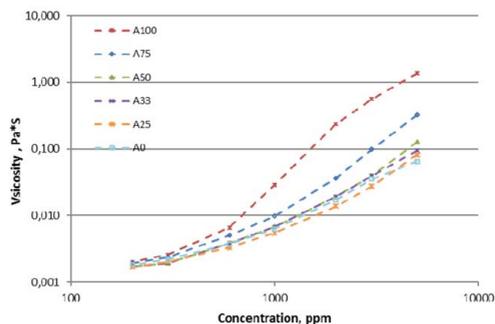


Figure 2. Shear viscosity as a function of concentration for polymer A series in 0.086M NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

been shown that the viscosity increase is sharper for polymers with longer hydrophobic groups.⁹ Martínez *et al.*²⁶ found that a chain length of minimum of six carbon atoms were necessary to see an associative effect of the hydrophobic groups. From Figure 2, one can draw the conclusion that to get a strong effect of the associative polymer with regard to viscosity enhancement, one need to cross a threshold value of the amount of hydrophobic groups present in the polymer.^{9,24} For A0 to A75, there is typical polyelectrolyte behavior in 0.086M NaCl, with a steady increase in viscosity with increase in concentration. For A100, however, there is a sharp increase in viscosity with concentration at polymer concentrations above 600 ppm, due to the formation of intermolecular hydrophobic interactions.

Viscoelasticity. We have shown that the viscosity increases in the polymer solutions with addition of hydrophobic groups in modified polyacrylamide. However, the viscoelasticity is also strongly influenced by the addition of hydrophobic groups.²⁷ From Figure 3, the loss modulus (G'') and the storage modulus (G') are plotted against angular frequency for 5000 ppm solution of A0, A33, A75, and A100 in 0.086M NaCl. The slopes of the G' curves change when increasing hydrophobicity. The solu-

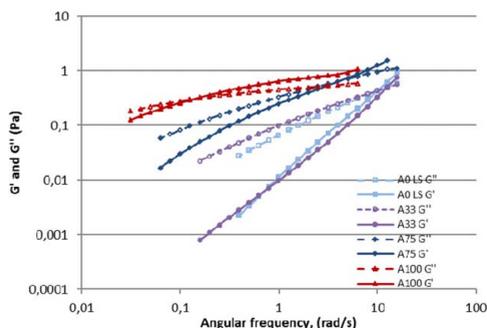


Figure 3. Frequency sweep of 5000 ppm solutions of A0, A33, A75, and A100 in 0.086M NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

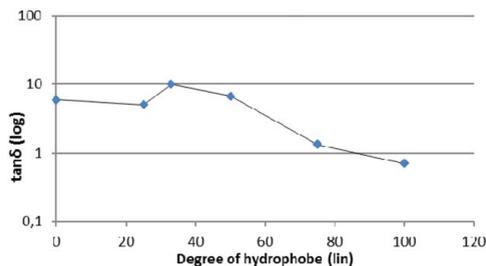


Figure 4. $\tan \delta$ as a function of degree of hydrophobe at 1 rad/s and 1% strain for 0.086M NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tions of A0 and A33 show a steep increment of G' when increasing the frequency with a ω^* around 10 rad/s. The slope for A75 solution is less steep, however the value of G' is higher and ω^* is shifted to lower values. For A100 solution, ω^* is much lower, and G' does not change much with frequency, which implies that A100 has a more gel like structure than the polymers with lower degree of hydrophobicity. A25 and A50, although not shown, have a similar behavior as A0 and A33.

The loss tangent ($\tan \delta$), obtained at a frequency of 1 Hz and 1% strain, is plotted against the degree of hydrophobe at 0.086M NaCl in Figure 4. With increasing the hydrophobicity, the loss tangent decreases towards a $\tan \delta$ close to 1. At this frequency, only the solution of A100 shows an elastic behavior with a $\tan \delta$ value below 1. The error in each of these points is about 3%.

Effect of Salt

Steady Shear Flow Measurements. Figure 5, viscosity as a function of concentration at different salinities, shows a significant change in behavior for A75 solution, with an increase in salinity. At 0.086M NaCl brine, is the slope of the viscosity versus concentration plot for A75 similar to the polymers with lower hydrophobicity, in the semidilute regime (>600 ppm). With addition of salt and increase in the ionic strength, there is a significant change in the slope of the viscosity versus concentration plot starting at a polymer concentration around 1000 ppm. This indicates the onset of significant intermolecular hydrophobic interactions due to the aqueous phase becoming a poorer solvent for the hydrophobic groups at increasing ionic strength.¹¹ In addition to having higher ionic strength, the high salinity aqueous phase also contains divalent cations (Ca^{2+} , Mg^{2+}) and anions different from Cl^- (HCO_3^- , SO_3^{2-}). Thus, whether the observed response is due to specific ion effects or ionic strength is not clear. To further investigate this, A0, A75, and A100 were used further in two NaCl brines, 0.86 and 1.71M NaCl (Figures 6 and 7). The 1.71M NaCl has the same ionic strength as the high salinity brine, and thus serves as a direct comparison of ionic strength versus specific ion effects.

The hydrophobe-free polymer, A0, behaves as can be expected from a polyelectrolyte in saline solution. In the dilute regime the polymer chains do not entangle, and the ionic units within the polymer backbone lead to repulsion and expansion of the

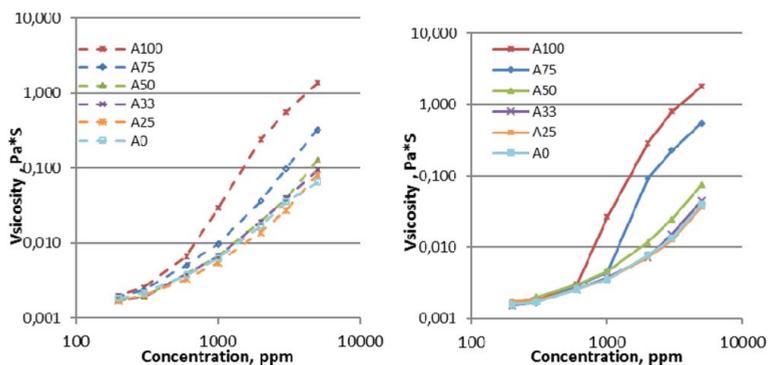


Figure 5. Concentration as a function of shear viscosity at 10 s^{-1} for polymer A in 0.086 M NaCl (left) and 1.72 M mixed solution (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer coils. This gives a high hydrodynamic radius for each coil, which leads to higher viscosity. Addition of salt to the polymer solution, leads to electrostatic screening of the charges within the polymer chain, and the Coulomb repulsion becomes less effective¹⁰ (Figure 6). This leads to contraction of the chains, a reduction in the hydrodynamic radius and thus a decrease in viscosity. In Figure 6, the viscosity of A0 in different solvents is plotted against the concentration at 10 s^{-1} . The 0.086 M NaCl has a higher viscosity all over compared to the other brine. From 0.086 M NaCl to 0.86 M NaCl, the viscosity of the polymer decreases. The viscosity measurement with 1.71 M NaCl and HS is almost the same as 0.86 M NaCl, and it seems to be little effect of adding salt beyond 0.86 M NaCl. All the charges within the solution are here already screened and there is little or no effect of adding more salt to the solvent. This result is in accordance with Levitt *et al.*'s³ viscosity study, which showed that above 3% NaCl in the solvent there is no significant difference in viscosity in HPAM solutions.

From Figure 7, the shear viscosity at 10 s^{-1} is plotted against the concentration of the polymer solutions. In the dilute area ($c < 600 \text{ ppm}$), the A75 behaves like a polyelectrolyte: the low

salinity solution has the highest viscosity, and viscosity is reduced with addition of salt.^{3,28} In the dilute regime the coils are not in contact with each other, and interaction between hydrophobic groups is mainly intramolecular. Addition of salt screens the electrostatic charges along the backbone chain of the polymer and gives tighter intramolecular interactions. The effect increases with higher ionic strength of the solvent. Above a polymer concentration of 1000 ppm , there is a change in viscosity response to salinity and, at polymer concentrations above 1000 ppm , the lowest viscosities are found for the 0.086 M solution. The viscosities increase in the order 0.086 M NaCl $<$ 0.86 M NaCl $<$ 1.72 M mixed $<$ 1.71 M NaCl. While the increase in viscosity with increasing NaCl concentration from 0.086 M NaCl to 1.71 M NaCl is in accordance with previous observations for associative polymers,¹¹ and can be attributed to enhanced intermolecular hydrophobic associations, the reason for the difference in viscosity between the 1.72 M mixed and 1.71 M NaCl brine is not clear. The brines have the same ionic strength but differ in ionic composition. The high salinity brine contains five different salt, and among them, CaCl_2 . The presence of the Ca^{2+} ion leads to lower viscosity in HPAM, and might be the

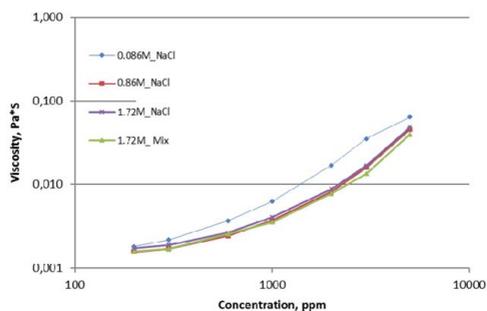


Figure 6. Viscosity A0 at constant shear rate of 10 s^{-1} , as a function of concentration. Measured in 0.086 M NaCl, 0.86 M NaCl, 1.71 M NaCl, and 1.72 M mixed solution solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

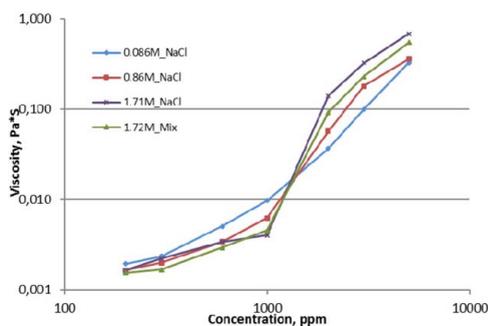


Figure 7. Viscosity of A75 solutions at constant shear rate of 10 s^{-1} , as a function of concentration. Measured in 0.086 M NaCl, 0.86 M NaCl, 1.71 M NaCl, and 1.72 M mixed solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

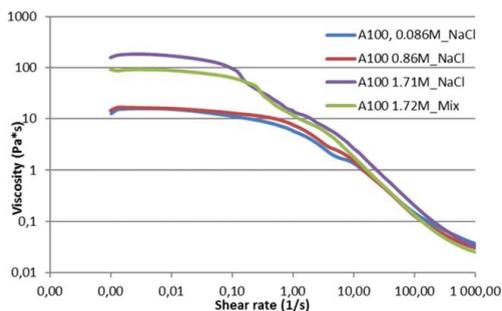


Figure 8. Shear viscosity of stock solutions (5000 ppm) of A100 in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reason that the high salinity brine also has lower viscosity in the associative polymer, although other effects cannot be excluded due to competition between hydrophobic and electrostatic interaction.

Variation in viscosity depends significantly on the polymer concentration.⁹ While viscosity curve of A75 solution showed a significant change of behavior from 0.086M to 0.86M NaCl in the impact of salinity on viscosity profile of A100 is only observed for salt concentration above 0.86M NaCl (Figure 8). The increase in viscosity is more evident in the low shear rate area, and shows a steep increase in viscosity above 0.86M NaCl, this effect is not as obvious at 10 s^{-1} . In 0.086M NaCl, the polymer behaves like an associative polymer; however, this trend is enhanced with an increase in salinity (Figure 9). The sudden change in slope at c^* (600 ppm) is more distinct and gives a higher increase in viscosity from 600 to 2000 ppm. In the dilute

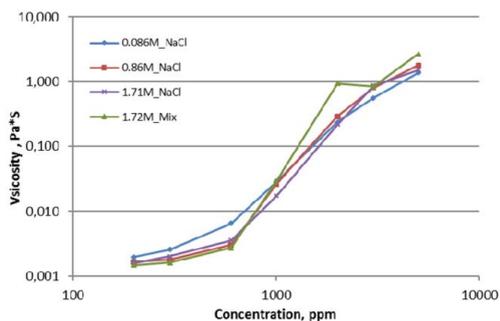


Figure 9. Shear viscosity at 10 s^{-1} against concentration for A100 in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

regime is the viscosity for the higher salinity solutions lower than for 0.086M NaCl, this is due to the intramolecular interactions within the coils, which are strengthened with the addition salt.

Linear viscoelasticity. Loss modulus (G'') and storage modulus (G') are plotted against angular frequency for A75 and A100 in the four brines (Figure 10). For the A75 solutions, the 0.086M and 0.86M NaCl has a small deviation in the elastic modulus at high frequencies, and viscous modulus is higher for 0.086M NaCl than for 0.86M NaCl. The ω^* shift is at the same angular frequency, however with a lower value of G' and G'' . The 1.72M mixed solution has a both higher storage modulus and loss modulus than the 1.71M NaCl solution, and a shift in ω^* toward the left.

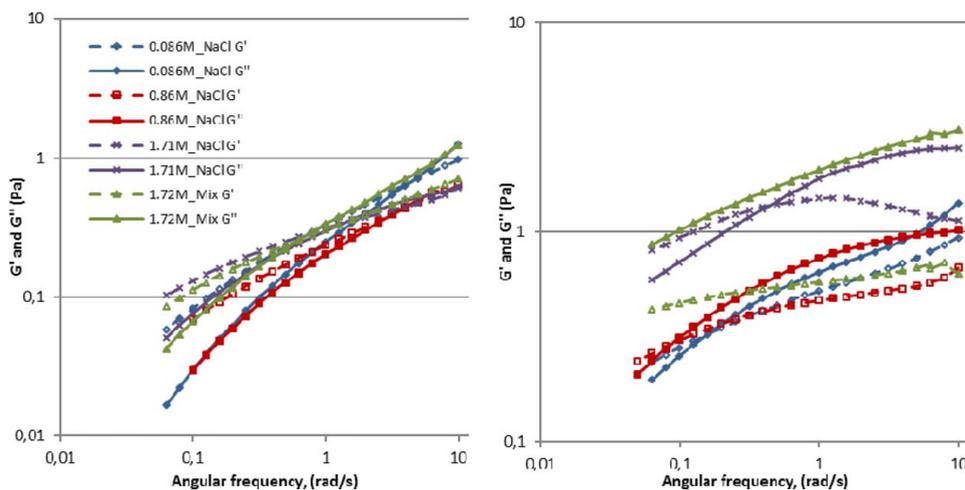


Figure 10. G' and G'' for stock solution (5000 ppm) of A75 (left) and A100 (right) in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

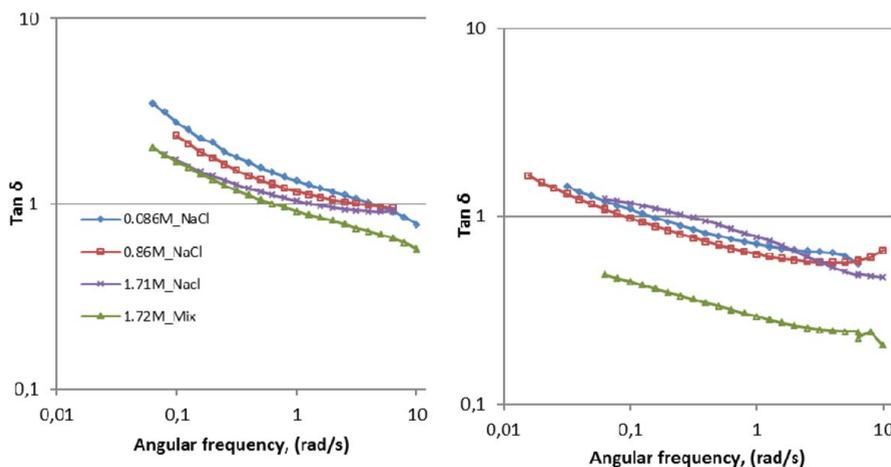


Figure 11. Loss tangent ($\tan \delta$) for stock solution (5000 ppm) of A75 (left) and A100 (right) in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For A100 solutions, G' and G'' are much lower for 0.086M NaCl and 0.86M NaCl brines than for the 1.71M NaCl and 1.72M mixed brines. The ω^* shift toward the left from 0.086M NaCl to 0.86M NaCl, and the storage modulus decreases. From 0.86M to 1.71M NaCl, the ω^* increases and shift toward the right. For the mixed high salinity solution, G' is above G'' for all the frequencies indicating that ω^* is shifted far to the low values.

1.71M NaCl and 1.72M mixed brines have the same ionic strength but the second ones contain divalent cations. The 1.72M mixed solution contributes to a higher elastic effect in the polymers with relative high hydrophobicity, "... which might be due to the presence of divalent cations or be a Hofmeister effect: in the mixed solutions SO_4^{2-} ions, which can strengthen the hydrophobic interactions, are present." This effect is more evident in A100 with a high elastic modulus within the whole frequency sweep. In Figure 11, the polymer solutions from Figure 10, is presented as loss tangent as a func-

tion of angular frequency. The difference in elasticity is more evident as regards to the loss tangent. 1.72M mixed solution is the brine that contributes most to the elasticity with the presence of divalent cations, and the effect is enhanced with an increase in hydrophobicity. Increasing salinity induces a shift towards more elastic behavior of the solutions of associative polymers. Divalent cations enhance this effect.

In Figure 12, the loss tangent is plotted as a function of the degree of hydrophobe in 0.086M NaCl and 1.72M mixed solution. The polymers with no or relative low hydrophobicity, A0 and A25, has a higher elasticity in the 0.086M NaCl than in the 1.72M mixed solution. However, this change as the hydrophobicity increases, and around 0.33 relative amount of hydrophobic groups (polymer A33), the highest elasticity in the two brines is found for the polymer solutions with the mixed brine. This is likely due to the onset of intermolecular hydrophobic associations as the polarity of the solvent is increased in the presence of a sufficient amount of hydrophobic groups. In the mixed high salinity brine, the polymer with more than 0.75 relative amount of hydrophobic groups present an elastic behavior, whereas for the 0.086M NaCl solution, the level of hydrophobic moieties has to be raised to at least 0.9.

CONCLUSIONS

The effect of degree of hydrophobicity on shear viscosity and viscoelasticity for an associative polymer was investigated and correlated with the presence of salt at different ionic strengths and ion compositions.

Regardless of ionic strength, there is significant increase in shear viscosity at polymer concentrations above 600 ppm with increasing degree of polymer hydrophobicity from 50 to 75% relative hydrophobicity. At lower relative hydrophobicity, the degree of hydrophobicity only has a limited effect on shear viscosity. Thus, one needs to cross a threshold value of

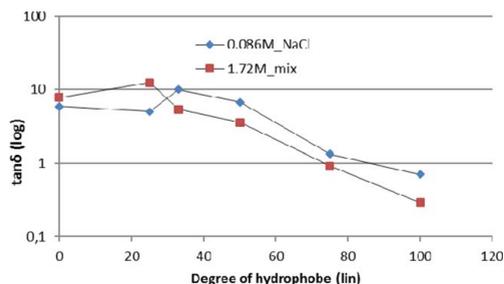


Figure 12. $\tan \delta$ as a function of the degree of hydrophobe at 1 rad/s and 1% strain for 0.086M NaCl and 1.72M mixed solution with polymer concentration of 5000 ppm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrophobicity in the polymer to get onset of sufficient associative behavior to significantly influence shear viscosity.

Below 75% relative hydrophobicity, the shapes of the shear viscosity versus polymer concentration plots are similar to those of non-associating polyelectrolytes for all investigated brine compositions. The same is true for the polymer with 75% hydrophobicity (A75) at 0.086M NaCl brine. However, with an increase of salinity to 0.86M NaCl, there is a distinct change in the shape of the shear viscosity against concentration plots for A75. Thus, increasing salinity promotes hydrophobic associations when the relative hydrophobicity is high enough for the onset of sufficient associative behavior.

The storage modulus also increases with an increase in ionic strength. However, the elasticity seems to be more affected by the divalent salts than the ionic strength. The effect of divalent ions is not this evident in the shear viscosity.

In both, 1.71M NaCl and 1.72M mixed solution at 1000 ppm, has A100 one order of magnitude higher viscosity than A0, which implies a much more suited polymer for high salinity reservoirs.

ACKNOWLEDGMENTS

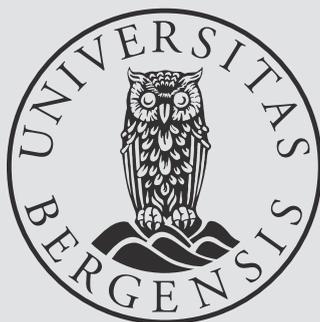
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