Flow of polymer solutions through porous media - Prediction of mobility reduction from ex-situ measurements of elasticity

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When injected at high flow rates in porous medium, polymer solutions exhibit a resistance to flow which is a signature of chain conformation and size. For biopolymers, which exist in solution as rigid rods, mobility reduction follows the shear thinning behavior measured in shear flow on a rheometer. For flexible coils, such as hydrolyzed polyacrylamide, flow thickening is observed in porous medium whereas bulk viscosity presents a shear thinning behavior. These differences are the result of the complex flow experienced in the porous medium combined with the visco-elastic properties at large strains of the solutions.

In this study, we investigate the effect of physical chemistry parameters such as salinity, polymer concentration, molecular weight and degradation state on the mobility reduction in porous medium at high flow rates. We show that parameters describing the mobility reduction curve (flow rates corresponding to the onset and to the maximum of the mobility reduction curves, value of the maximum mobility reduction) are not correlated with bulk viscosity but rather with screen factor. This old and rough measurement, widely used in the EOR community to evaluate “solution elasticity”, is an indirect measurement of the extensional viscosity of polymer solutions. The pertinence and the physical meaning of this measurement is assessed through comparison with measurements performed on a newly developed extensional viscometer, which consists in measuring the pressure drop when the fluid is injected through a hyperbolic contraction (in which strain rate is constant at the centerline). A correlation “Screen factor” vs. “Extensional Viscosity” is obtained. Hence, from the knowledge of the mobility reduction curve in one porous medium in one set of conditions, it is possible to predict the mobility reduction in any other set of conditions from ex-situ measurements of screen factor or extensional viscosity. At last, the inadequacy of traditional small strain visco-elastic measurements to characterize the elastic behavior of polymer solutions at large strain is discussed.

These results give some insight on the behavior of polymer solutions in injectivity conditions along with the way to characterize their elastic properties from bulk measurements.

Key words: Polymer flooding – EOR – Injectivity – Shear thickening – Elasticity – Extensional rheology
Introduction

Polymer flooding has been considered for a long while has a mobility control process which improves the macroscopic sweep efficiency and speeds up the oil recovery. However, during the last fifteen years, lab and field observations revealed that polymer flood could also impact the microscopic oil recovery (Wang et al., 2000, Huh and Pope, 2008). All the experimental results come to the conclusion that elastic effects would be at the origin of this additional oil recovery (Wang et al., 2010, Levitt et al., 2010, Veerabhadrappa et al., 2013, Vermolen et al., 2014, Clarke et al., 2015, Koh et al., 2016, Qi et al., 2016). Several mechanisms have been proposed such as the recovery of the oil in dead end pores or enhanced pulling forces on oil blobs because of normal forces, stabilization of oil threads against snap off, local pressure/flow fluctuation at the pore level due to flow thickening... These mechanisms can be related to either linear or non-linear elastic effects.

Linear viscoelasticity measurements consist in deforming polymer chains around their equilibrium state at rest so that properties do not depend on the applied strain. In other words, a measurement at time t+dt is not dependent on the deformation state of the chain at time t. Classical measurements are performed through small amplitude oscillatory shear tests (SAOS) and give access to the elastic modulus G’ and the longest relaxation time τ of the polymer. In contrast, the measurement of the shear viscosity η or the normal forces Nf as a function of the shear rate in a rheometer is a non linear measurement since chains are highly deformed during the continuous shearing. However, there exist some links between linear and non linear properties (Graessley, 2008). For example, Cox-Merz rule states that complex dynamic viscosity |η*| can be compared with shear viscosity η at equal values of frequency ω and shear rate γ. Similarly, Laun’s rule enables to predict Nf versus γ in steady shear flow from measurements of G’ and G” versus ω (see Hincapie et al., 2015, for its application to EOR polymers).

When flowing in porous medium, HPAM exhibit an increased resistance to flow at a critical flow rate. The origin of this “flow thickening” is debated and could be the result of several mechanisms (cf. the bibliographic review below). This flow thickening could be responsible for a change of the macroscopic flow distribution in non uniform flows (Rodriguez et al., 1993) along with an increased oil mobilization at the microscopic level. For example, recently, Clarke et al. (2015) proposed a new mechanism based on the apparition of elastic turbulences which would generate local pressure fluctuations resulting in a fluctuating flow field at the pore level responsible for oil mobilization. The onset of elastic turbulence in porous medium would coincide with the onset of flow thickening (Howe et al., 2015). At last, this flow thickening could have a big impact on the pressure profile for injection wells in “true” matrix mode, even if this situation is unexpected in most of field injections (see Seright et al., 2009).

Objectives of this study

Although flow of EOR polymers in porous medium at high rates has been extensively studied, the effect of physical-chemistry parameters such as salinity, polymer concentration, molecular weight and degradation state, in the range encountered in EOR application, is not clear. Moreover, because of the complexity of the flow experienced in porous medium, strongly function of its topology, along with the highly stretchable character of HPAM, the question is raised about the possibility to model and to predict the flow thickening from ex-situ measurements of linear or non linear properties of the bulk solutions.

In this study, polymer solutions prepared in a variety of physical-chemistry conditions are characterized through viscosity, screen factor and extensional viscosity measurement (EVROC viscometer). Their behavior in porous medium is then evaluated through an injection on a short core (ceramic frit, kₜ=4D). We show that the complete mobility reduction curves can be modeled from the knowledge of 3 parameters: the onset rate of flow thickening, the maximum of mobility reduction and the flow rate at which this maximum occurs. After searching for the eventual scaling of these parameters with molecular weight and polymer concentration, we finally show how these parameters are correlated with ex-situ measurements of elasticity, assessed through screen factor or EVROC measurements.
Bibliographic review

Flexible coils: an unusual flow behavior in porous medium

When injected at high flow rates in porous medium, polymer solutions exhibit a resistance to flow which is a signature of chain conformation and size.

For biopolymers such as xanthan or scleroglucan, which exist in solution as rigid rods due to their conformation in double or triple helix, mobility reduction exhibits a shear thinning behavior close to that one measured in shear flow on a rheometer (Seright, 2011). In contrast, for flexible coils, such as hydrolyzed polyacrylamide (HPAM), flow thickening is observed at a critical flow rate in porous medium whereas bulk viscosity presents a shear thinning behavior. These differences are the result of the complex flow experienced in the porous medium combined with the visco-elastic properties at large strains of the solutions.

The nature of the flow in porous medium

Shear flow is the superposition of rotational and extensional flow. As a result, a coil will stretch in the flow direction, rotate because of the velocity gradient in the perpendicular direction and contract. This type of flow would occur in an ideal pore of constant diameter. In such a situation, flexible polymers would exhibit a shear thinning behavior.

In a real porous medium, the extensional component of the velocity gradient can dominate over the rotational component due to the acceleration in the successive contractions/expansions corresponding to pore throats/pore bodies. During these extensional events, chains are stretched in the flow direction. The behavior of polymer solutions in extensional flow has been investigated through first generation devices promoting ideal extensional flow with stagnation point: opposed jets, cross-slots, four roll mills (Keller and Odell, 1985). As predicted by De Gennes, it was found that for dilute solutions, coils experience a sudden coil-stretched transition if the strain rate (\(\dot{\varepsilon}\)) is higher than the inverse of the longest relaxation time of the unperturbed random coil. The critical strain rate at which the coil-stretch transition occurs was found to scale as \(\dot{\varepsilon}_c \propto 1/Mw^{1.5}\), which is consistent with Zimm relaxation time. This relaxation time is affected by the nature of the frictional contact between molecule and solvent which depends on molecular shape, solute-solvent interaction and solvent viscosity but does not depend on concentration. More recently, new devices were developed either based on filament stretching or specific microfluidic geometries (Galindo-Rosales et al., 2012). In contrast to the relaxation times obtained in small amplitude oscillatory shear, several authors (reviewed in Clasen et al., 2006) reported that relaxation time deduced from transient extensional experiments, continue to depend on concentration even well below the critical overlap concentration \(c^*\). In extensional flow, coils being highly extended, they would interact and overlap at far lower concentration than \(c^*\). A concentration of ultradilution \(c^\infty\) was defined in order to delimit the concentration at which extended chains do not interact and behave as really dilute. Above \(c^\infty\), the relaxation time exhibits a power law scaling with the reduced concentration \(c/c^*\) which can be predicted by considering the extended and overlapping polymer chains as a semi-dilute solution. Odell’s group (Chow et al., 1988) had already proposed a mechanism of transient network formation well below \(c^*\). The observation of these molecular interactions had been attributed to weak entanglements, active at only extremely short time scales, such as those encountered in strong extensional flows.

Flow thickening in porous medium

Different mechanisms have been proposed to explain the substantial increase in flow resistance in porous medium even for diluted solutions, beyond a critical flow rate.

James and McLaren (1975), Hass and Durst (1982) proposed an increase of the extensional viscosity following the coil-stretch transition of individual chains at a critical Deborah number defined as \(De = \dot{\varepsilon}_c \tau = 0.5\). In the extensional flow field, friction between elongated chains and solvent is enhanced and results in an extra dissipation. However, two experimental observations invalidate this mechanism, the critical character of the flow thickening and the concentration dependence of the onset rate. First of all, flow thickening is a very brutal phenomenon which occurs on a very narrow range of flow rates. The polydispersity of the polymer molecular weight and the spatial distribution of local strain rates encountered in porous medium would lead to a spread of the...
transition. Indeed, the width of the transition should reflect the range of relaxation times of the chains along with their complex history of deformation (Rodriguez et al., 1993). Secondly, the strong concentration dependence of the onset strain rate in the diluted regime is not compatible with the coil-stretch transition related to the stretching of isolated macromolecules.

Based on additional experimental evidences, Odell et al. (1988) proposed that extension thickening would be associated with the formation of transient network of weakly entangled chains. According to these proposed mechanisms which are based on the extensional character of the flow, we agree on the fact that “shear thickening” is maybe not the appropriated term and should be replaced by “extensional thickening”. However, two additional mechanisms were recently proposed, not necessarily associated with the existence of a strong extensional flow. For this reason, the term “flow thickening” is preferred. According to Howe et al. (2015), the onset of flow thickening would correspond to the onset of elastic turbulence in porous medium. This onset was found to be independent from the concentration even in the semi dilute regime. At last, James (2016), ardent partisan of the dramatic effect of extensional viscosity, advanced that in mixed flow (combination of shear and extension as for flow in porous medium), the normal stresses generated by shearing could be comparable with those generated by extension.

**Influence of physical-chemistry parameters on flow thickening**

Numerous authors investigated the effect of molecular weight, concentration, salinity and solvent type in porous medium. Based on the studies of Chauveteau (1981), Durst et al. (1981), Kulicke and Haas (1984), the onset rate for flow thickening decreases when concentration or molecular weight increase or salinity decreases. The magnitude of flow thickening increases with molecular weight and concentration. Salinity does not impact the magnitude excepted that the transition is sharper when salinity increases.

**Degradation in porous medium**

Coil stretching is at the origin of mechanical degradation of polymer chains. In diluted regime, in which chains does not interact, the hydrodynamic force exerted by the solvent over the length of the chain creates a tension that is able to break the chain at their center (Odell and Keller, 1986). In semi dilute regime, when chains are entangled, stress would be transmitted by junction points of the network. The relevant parameter that would determine degradation would be the stress per chain and the entanglement density c/c* (Nghe et al., 2010, Dupas et al., 2012). The scission rate was found to increase with concentration, as opposed to dilute solutions, where degradation is concentration independent. Moreover, the scission process would be randomized (Muller et al., 1992), contrary to the mid-chain scission characteristic of dilute solutions.

To summarize this review, the mechanism(s) at the origin of flow thickening are not clearly identified. The relaxation time related to the polymer solution along with the parameters that will trigger the startup of flow thickening are still debated (strain rate or shear rate or total accumulated strain which is the integral of the strain rate over time…). Trends have been established on the magnitude of the flow thickening with physical-chemistry parameters. However, a quantitative determination of this dependence is required in order to better understand the effect of each individual parameter on elastic effects.

**Experimental**

**Polymer solutions**

Partially-hydrolyzed polyacrylamide (HPAM) in powder form with 30% hydrolysis from the Flopaam series (SNF Floerger, Andrezieux, France) were used for all the experiments. Molecular weights were evaluated through viscosity measurements according to the following protocol. For each grade, intrinsic viscosity was measured. It was assumed that:

- the highest Mw grade (3630) has a molecular weight equal to $18.7 \times 10^6$ g/mol (18.7 MDa = value given by the supplier),

- all the grades follow a Mark Houwink relationship $[\eta] = KMw^a$ with an exponent $a$ equal to 0.8 (Mc Carthy et al., 1987, Klein and Conrad, 1980).
From these assumptions, the molecular weight $M_w$ of any grade of intrinsic viscosity $[\eta]$ can be expressed as:

$$M_w = ([\eta]/[\eta]_{1,630})^{1/\alpha} \times M_{w,3630}$$

The calculated $M_w$ (viscosimetric $M_w$) of each grade are summarized in Table 1.

<table>
<thead>
<tr>
<th>Polymer grade</th>
<th>$M_w$ ($10^6$ g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3130S</td>
<td>3.2</td>
</tr>
<tr>
<td>3230S</td>
<td>6.1</td>
</tr>
<tr>
<td>3330S</td>
<td>8.1</td>
</tr>
<tr>
<td>3530S</td>
<td>13.8</td>
</tr>
<tr>
<td>3630S</td>
<td>18.7</td>
</tr>
</tbody>
</table>

Table 1: Estimated molecular weights of the different grades of the HPAM Flopaam series.

Four brines were used whose compositions are summarized in Table 2. Most of the solutions were prepared in a brine at 6 g/L TDS.

<table>
<thead>
<tr>
<th>Salt</th>
<th>0.4 g/L</th>
<th>6 g/L</th>
<th>6 g/L + 50 g/L NaCl</th>
<th>6 g/L + 1 g/L CaCl2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.016</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>KCl</td>
<td>0.093</td>
<td>0.111</td>
<td>0.111</td>
<td>0.111</td>
</tr>
<tr>
<td>CaCl$_2$, 2 H$_2$O</td>
<td>0.034</td>
<td>0.745</td>
<td>0.745</td>
<td>2.069</td>
</tr>
<tr>
<td>MgCl$_2$, 6 H$_2$O</td>
<td>0.192</td>
<td>0.561</td>
<td>0.561</td>
<td>0.561</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.111</td>
<td>4.724</td>
<td>54.724</td>
<td>4.724</td>
</tr>
<tr>
<td>TDS (g/L)</td>
<td>0.446</td>
<td>6.147</td>
<td>56.147</td>
<td>7.471</td>
</tr>
</tbody>
</table>

Table 2: Compositions of the different brines used for preparing polymer solutions.

Physical properties of polymer solutions were varied by changing polymer concentration, brine salinity, and molecular weight of the polymer or degradation level as summarized in Table 3. One solution was prepared by mixing two polymer grades (3130 and 3530).

<table>
<thead>
<tr>
<th>Polymer grade</th>
<th>Concentration</th>
<th>Salinity</th>
<th>Degradation</th>
<th>Low shear Viscosity</th>
<th>$[\eta]$</th>
<th>$M_w$</th>
<th>C($[\eta]$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3630</td>
<td>100 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>1.6</td>
<td>5 400</td>
<td>18.7</td>
<td>0.5</td>
</tr>
<tr>
<td>3630</td>
<td>300 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>3.6</td>
<td>5 400</td>
<td>18.7</td>
<td>1.6</td>
</tr>
<tr>
<td>3630</td>
<td>500 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>7.2</td>
<td>5 400</td>
<td>18.7</td>
<td>2.7</td>
</tr>
<tr>
<td>3630</td>
<td>800 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>16.8</td>
<td>5 400</td>
<td>18.7</td>
<td>4.3</td>
</tr>
<tr>
<td>3630</td>
<td>1200 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>41.1</td>
<td>5 400</td>
<td>18.7</td>
<td>6.5</td>
</tr>
<tr>
<td>3630</td>
<td>800 ppm 6 + 50g/L NaCl</td>
<td>6 g/L</td>
<td>0%</td>
<td>9.5</td>
<td>4 008</td>
<td>18.7</td>
<td>3.2</td>
</tr>
<tr>
<td>3630</td>
<td>800 ppm 6 + 1g/L CaCl2</td>
<td>6 g/L</td>
<td>0%</td>
<td>9.5</td>
<td>4 000</td>
<td>18.7</td>
<td>3.2</td>
</tr>
<tr>
<td>3630</td>
<td>500 ppm 0.4</td>
<td>6 g/L</td>
<td>19%</td>
<td>80.3</td>
<td>15709</td>
<td>18.7</td>
<td>7.9</td>
</tr>
<tr>
<td>3630</td>
<td>800 ppm</td>
<td>6 g/L</td>
<td>40%</td>
<td>13.8</td>
<td>4 913</td>
<td>16.7</td>
<td>3.9</td>
</tr>
<tr>
<td>3630</td>
<td>800 ppm</td>
<td>6 g/L</td>
<td>58%</td>
<td>10.5</td>
<td>4 238</td>
<td>13.8</td>
<td>3.4</td>
</tr>
<tr>
<td>3630</td>
<td>800 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>7.7</td>
<td>3 525</td>
<td>11.0</td>
<td>2.8</td>
</tr>
<tr>
<td>3530</td>
<td>1200 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>24.6</td>
<td>4 232</td>
<td>13.8</td>
<td>5.1</td>
</tr>
<tr>
<td>3330</td>
<td>1200 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>10.4</td>
<td>2 761</td>
<td>8.1</td>
<td>3.3</td>
</tr>
<tr>
<td>3230</td>
<td>1200 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>7.2</td>
<td>2 195</td>
<td>6.1</td>
<td>2.6</td>
</tr>
<tr>
<td>3230</td>
<td>800 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>4.0</td>
<td>2 195</td>
<td>6.1</td>
<td>1.8</td>
</tr>
<tr>
<td>3230</td>
<td>1500 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>10.1</td>
<td>2 195</td>
<td>6.1</td>
<td>3.3</td>
</tr>
<tr>
<td>3230</td>
<td>1900 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>15.6</td>
<td>2 195</td>
<td>6.1</td>
<td>4.2</td>
</tr>
<tr>
<td>3530</td>
<td>1000 ppm</td>
<td>6 g/L</td>
<td>0%</td>
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<td>4 232</td>
<td>13.8</td>
<td>4.2</td>
</tr>
<tr>
<td>3330</td>
<td>1500 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>15.4</td>
<td>2 761</td>
<td>8.1</td>
<td>4.1</td>
</tr>
<tr>
<td>3130</td>
<td>3200 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>15.7</td>
<td>1 306</td>
<td>3.2</td>
<td>4.2</td>
</tr>
<tr>
<td>3130 / 3530</td>
<td>2050 / 360 ppm</td>
<td>6 g/L</td>
<td>0%</td>
<td>15.0</td>
<td>1 698</td>
<td>4.4</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 3: Conditions of preparation, viscosities and estimated $M_w$ of the different solutions tested.
Beyond the dilute regime in which polymer chains does not interact, there exist a regime in which polymer chains overlap but are not entangled. The transition occurs at a critical concentration $c^* \equiv 1/\left[\eta\right]$ (Colby, 2010). Looking at the product $c/\eta$ in Table 3, all the solutions are in the semidilute regime apart from the solution of 3630 at 100ppm.

**Preparation of polymer solutions**

A mother solution at 10000 ppm was first prepared by stirring the solution for two hours at 500rpm with a marine impeller. This solution was then diluted at the desired concentration in a beaker by gentle stirring with a magnetic stirrer. The solution was filtered at a constant flow rate of 50 mL/h through a ¼” tee-type Swagelok filter (TF series) with a 40 microns stainless steel strainer upstream of a short core (ceramic frit supplied by OFITE, $k_w=9D$, $L=2.54cm$, $D=6.35cm$). Pressure through the porous medium was recorded in order to stop the filtration in case of plugging.

Three solutions were pre-filtered and then re-injected at higher flow rate through the same core in order to degrade the solution.

**Characterization of solution properties**

**Viscosity:** Viscosity was measured at ambient temperature on a ProRheo low shear LS300 rheometer in the shear rate range $0.02-94s^{-1}$. With this very sensitive rheometer, it was possible to determine accurately the low shear Newtonian viscosity of all solutions.

**Screen factor:** As described in API RP63, this measurement consists in recording the times for a given volume of polymer solution ($t_P$) and water ($t_{H2O}$) to flow through five 100-mesh screens. The screen factor is defined as the ratio of times between polymer and water $SF = t_P / t_{H2O}$. Our screen factor apparatus has a bulb of approximately 40 mL, and 3 100-mesh screens. Measurements were performed at ambient temperature.

**Extensional viscosity:** Apparent extensional viscosity was measured with the EVROC® (Extensional Viscometer-Rheometer On a Chip) microfluidic device commercialized by Rheosense (San Ramon CA, USA). This extensional rheometer consists in forcing the solution at constant flow rate through a hyperbolically shaped contraction-expansion geometry. In this extensionally-dominated flow, the extensional pressure drop is evaluated by subtracting the predicted pressure drop due to viscous shearing in the geometry to the total measured pressure drop. This measurement enables to obtain qualitative extensional viscosity measurements as a function of the apparent extensional rate (Ober et al., 2013). The dimensions of our microfluidic contraction-expansion are: flow channel depth $= 195$ microns, flow channel width $= 3.3$ mm, throat width $= 400$ microns, throat length $= 800$ microns. Measurements were performed at ambient temperature.

**Behaviour in porous medium**

Polymer solutions were first characterized through screen factor, viscosity and extensional viscosity measurements. Then, they were injected through a short fritted ceramic core (supplied by OFITE, $k_w=4D$, porosity=44%, $L=2.54cm$, $D=4.7cm$). Injection was performed at constant flow rate using a syringe pump (1000D Teledyne ISCO). Flow rate was varied between 50 and 20000 mL/h which correspond to a flow rate per unit area $Q$ varying between 0.03 and 11.53 $m^3/m^2/h$. The flow rate per unit area is analogous to the Darcy velocity.

For each flow rate, pressure drop through the core and polymer viscosity at the exit of the core were measured. Rosemount 3051S differential pressure transducers were used.

The mobility reduction due to the polymer is expressed as $Rm = \Delta P_{polym} / \Delta P_{H2O}$ where $\Delta P_{polym}$ is the polymer solution pressure drop and $\Delta P_{H2O}$ is the water pressure drop before polymer injection.

The irreversible viscosity degradation is calculated according to: $Deg(\%) = \left(\frac{\eta_0 - \eta_{DEG}}{\eta_0 - \eta_S}\right) \times 100$ where $\eta_0$ is the low shear plateau viscosity of the non-degraded solution, $\eta_{DEG}$ is the low shear plateau viscosity of the degraded solution and $\eta_S$ is the water viscosity.
Results

Evaluation of the elastic properties of the polymer solutions

*EVROC measurements*

The measurements with the EVROC viscometer performed on a series of 3630 at varying concentration (100-1200ppm) are plotted on Figure 1, left. Below 500ppm, the EVROC viscosity increases with the extensional rate until a plateau whose value increases with concentration. Above 500ppm, the EVROC viscosity increases continuously and does not stabilize at a plateau value. Due to the limit of the pressure sensor, the maximal extensional rate, at which measurement can be performed, decreases with concentration. In order to compare the different solutions of this study, we will take the EVROC viscosity measured at 944s⁻¹ (maximum extensional rate for the 3630 solution at 1200ppm).

![Figure 1: EVROC viscosity vs apparent extensional rate in the hyperbolic contraction-expansion of the EVROC viscometer for 3630 (Mw=18.7MDa) solutions in 6g/L brine at various concentrations (100-1200ppm).](image)

As seen on Figure 2, left, the EVROC viscosity is a linear function of the polymer concentration for the two series: 3630, Mw = 18.7 MDa and 3230, Mw = 8.1 MDa. At constant concentration, EVROC viscosity scales as \( M_w^{2.3-3.3} \).

![Figure 2: Evolution of the EVROC viscosity measured at an apparent extensional rate of 944s⁻¹ for (Left) two series of polymer solutions (Mw=6.1 and 18.7 MDa) in 6g/L brine at various concentrations, (Right) two series of varying molecular weight (commercial grades at 1200ppm, and 3630 at varying degradation levels at 800ppm) in 6g/L brine.](image)

*Comparison of EVROC with Screen Factor measurements*

EVROC and screen factor measurements are similar insofar as they consist in flowing through a geometry in which the extensional component of the flow dominates. As a result, the elastic response of the solution at high deformation is promoted provided flow rate is sufficient to trigger the coil-
stretch transition (Lim et al., 1986). In contrast to EVROC for which flow rate is controlled, screen factor is measured at constant pressure drop. This pressure drop is the sum of the shear and the extensional viscosity contributions. We anticipate that screen factor is no more representative of polymer elasticity if the shear contribution is high compared to the extensional viscosity contribution. It could be the case of highly viscous solutions for which viscous contribution tends to decrease the flow rate which in turn decreases the extensional contribution (which is rate dependent). This trend is illustrated on Figure 3 by plotting the screen factor as a function of the polymer concentration for the two series Mw 3630 = 18.7 MDa and Mw 3230 = 8.1 MDa. The high curvature at high concentration for the 3630 would be the indication that flow is less and less dominated by the extensional viscosity. The origin of this curvature maybe the physical scaling of screen factor with concentration. We find $SF \propto c^{0.5-0.6}$. On the series of degraded 3630 at 800ppm, we find $SF \propto Mw^{1.7}$, on the series of commercial grades of varying Mw at 1200ppm, we find $SF \propto Mw^{1.1}$.

In the range of polymer concentrations, molecular weights and salinities investigated in this study, there is a very good correlation between screen factor and EVROC measurements as shown on Figure 3, right. Even though screen factor is an old, simplistic and rough measurement, its pertinence is confirmed. Moreover, looking at the slope of the correlation at low EVROC viscosity (Screen factor < 30), screen factor appears as more sensitive than the EVROC extensional viscometer.

Figure 3: (Left) Evolution of the screen factor for two series of polymer solutions (Mw=6.1 and 18.7 MDa) in 6g/L brine at various concentrations. (Right) Comparison of screen factor with EVROC viscosities at 944s⁻¹.

Mobility reduction in porous medium

Mobility reduction and degradation through the short core are plotted on Figure 4, left for the 3630 solution at 800ppm in the 6g/L brine. Mobility reduction is a bell-shaped curve. Because of the short length of the core, the shear thinning region at low flow rate is not accessible. It would require to measure extremely low pressure drops out of the pressure sensor range.

Flow-thickening (increase of the mobility reduction with flow rate) takes place between 0.03 and 1 m³/m²/h. At ~1 m³/m²/h, mobility reduction is maximal. For higher rates, shear thinning occurs. This behaviour results from the competition between the increase in flow resistance due to elasticity related effects and the polymer degradation which starts at the onset of flow-thickening.

Modelling of the mobility reduction curve

As seen on Figure 4, the mobility reduction curve can be described by 3 zones separated by the vertical lines (at $Q_c$ and $Q_{max}$): a shear thinning zone (Zone I) not accessible in our experiments, the flow thickening zone (zone II) and the terminal shear thinning zone (Zone III).

In order to compare the shape and the width of the mobility reduction curves for the different solutions injected, we normalize each curve as follow:

- $RM = Rm/Rm_{max}$ for the ordinates,
- $\beta \times Q$ for the abscissa where $\beta$ is a coefficient which enables to let coincide the flow rates $Q_{max}$ at which occurs the maximum of flow thickening ($Rm_{max}$) between a solution A and a
reference solution. If \( Q_{\text{max}}^A \) and \( Q_{\text{max}}^{\text{Ref}} \) are the flow rates at which these maxima occur, we have: \( \beta = Q_{\text{max}}^{\text{Ref}} / Q_{\text{max}}^A \). In analogy to the onset flow rate for flow thickening which is inversely proportional to a characteristic relaxation time \( \tau \) (which scale as Rouse time according to Howe and al., 2015), \( \beta \) can be considered as a ratio of relaxation times of both solutions: \( \beta = \tau_{\text{A}} / \tau_{\text{ref}} \).

The solution of 3630 at 800ppm in 6g/L brine is taken as the reference curve (\( \beta = 1 \)). Its mobility reduction curve (zones II and III) is fitted by the phenomenological viscosity function with continuous derivative proposed by Galindo-Rosales et al. (2011a, b):

\[
RM_{II}(Q) = RM_{\text{max}} + \frac{RM_{\text{max}} - RM_{\text{Ref}}}{1 + \lambda_{II}(Q - Q_{\text{Ref}})^{n_{II}}} \quad \text{for } Q < Q_{\text{Ref}} \leq Q_{\text{max}}
\]

\[
RM_{III}(Q) = \frac{RM_{\text{max}}}{1 + \lambda_{III}(Q - Q_{\text{Ref}})^{n_{III}}} \quad \text{for } Q_{\text{Ref}} < Q
\]

As seen on Figure 4, the fit is very good. The parameters used for the fit are:

\[
Q_{\text{C}} = 0.034 \text{m}^3/\text{m}^2/\text{h}, \ RM_{\text{C}} = 0.04, \ \lambda_{II} = 9, \ n_{II} = 1.1
\]
\[
Q_{\text{max}} = 1 \text{m}^3/\text{m}^2/\text{h}, \ RM_{\text{max}} = 1, \ \lambda_{III} = 0.16, \ n_{III} = 1.3
\]

**Figure 4:** (Left) Orange circles = mobility reduction curves of 3630 solution at 800ppm in 6g/L brine. Black squares = irreversible viscosity degradation measured on the solution after its passage through the core. The vertical line at \( Q_{\text{C}} \) indicates the transition from Zone I (shear thinning) to Zone II (flow thickening). That one at \( Q_{\text{max}} \) indicates the transition from Zone II to Zone III (shear thinning). (Right) Normalization of the mobility reduction curve \( (Rm/Rm_{\text{max}}=f(Q)) \) and modelling with the model proposed by Galindo-Rosales et al. (2011a, b).

**Influence of polymer concentration**

The mobility reduction curves of 3630 solutions (Mw=18.7MDa) in 6g/L brine in the concentration range 100-1200 ppm are presented in Figure 5. The onset of flow thickening \( (Q_{\text{C}}) \) and \( Q_{\text{max}} \) are shifted to higher flow rates when polymer concentration increases. \( RM_{\text{max}} \) increases with concentration. After normalization, the overlap of all the curves is very good. The shape and the width of the mobility reduction curve do not change in this concentration range.

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Influence of molecular weight and degradation level

The mobility reduction curves of the commercial series of Flopaam (Mw in the range 3.2-18.7 MDa) at a concentration of 1200ppm in the 6g/L brine are presented on Figure 6. \(Q_c\) and \(Q_{max}\) are shifted to higher flow rates when Mw decreases. As expected, \(Rm_{max}\) increases with Mw. When the curves are normalized, only shear thinning zones are superposed. The flow thickening region is less abrupt when Mw decreases. As a consequence, the pic is wider after normalization.

The trend for \(Q_c\), \(Q_{max}\) and \(Rm_{max}\) are similar for the degraded solutions of 3630 at 800ppm in the 6g/L brine (Figure 7). In comparison, the superposition of the normalized curves is very good. The main difference between degraded and commercial products is the molecular weight distribution. During degradation, chains of the high Mw tail are preferentially broken. Hence, a lower polydispersity is expected for the degraded solutions. The enlargement of the flow thickening region of commercial products seems to be related to their higher polydispersity. If flow thickening was
related to the coil-stretch transition only, polydispersity could be interpreted as a distribution of onset rates for flow thickening corresponding to a distribution of relaxation times. However, Rodriguez et al. (1993) calculated the width of the transition for a log-normal distribution with a polydispersity of 2 (commercial polymers have an higher polydispersity). They showed that the sharpness of the experimental transition of flow-thickening is not compatible with a coil-stretch transition mechanism taking into account the distribution of relaxation times.

Figure 7: (Left) Mobility reduction curves of 3630 solutions of varying pre-degradation levels (Deg = 0, 19, 40 and 58% corresponding to Mw = 18.7, 16.7, 13.8 and 11 MDa) at a concentration of 800ppm in 6g/L brine. (Right) Same curves after normalization. The red curve is the modelling of the reference solution of non degraded 3630 at 800ppm.

Influence of salt composition

The influence of salt was investigated through measurements on 4 solutions whose properties are summarized in Table 4. Flow curves are presented on Figure 8.

<table>
<thead>
<tr>
<th>Polymer grade</th>
<th>Concentration ppm</th>
<th>Salinity g/L</th>
<th>Low shear Viscosity cP</th>
<th>Rm max</th>
<th>β</th>
<th>Screen factor</th>
<th>EVROC viscosity Pa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>3630</td>
<td>800</td>
<td>6</td>
<td>16.8</td>
<td>220</td>
<td>1</td>
<td>56.6</td>
<td>16.5</td>
</tr>
<tr>
<td>3630</td>
<td>800</td>
<td>6 + 50g/L NaCl</td>
<td>9.5</td>
<td>220</td>
<td>0.85</td>
<td>56.3</td>
<td>16.7</td>
</tr>
<tr>
<td>3630</td>
<td>800</td>
<td>6 + 1g/L CaCl₂</td>
<td>9.46</td>
<td>187</td>
<td>1.1</td>
<td>52.2</td>
<td>12</td>
</tr>
<tr>
<td>3630</td>
<td>500</td>
<td>0.4</td>
<td>91</td>
<td>242</td>
<td>1.2</td>
<td>61.7</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table 4: Characterization of the solutions prepared in different brines through bulk measurements (low shear viscosity and elasticity through screen factor and EVROC viscosity at 944s⁻¹) and behaviour in porous medium (Rm max and β).

Salinity has a dramatic effect on viscosity (cf. Figure 8) whereas Screen factor and EVROC viscosity are dimly impacted (Table 4). The trend is similar in porous medium. As seen on Figure 9, \( R_{m_{max}} \) is nearly constant whatever the salinity in agreement with old measurements of Chauveteau and Durst et al. (1981). Hence, flow thickening at high rates (which is the manifestation of polymer elasticity at large strain) is neither correlated with shear viscosity nor with viscoelastic properties in the linear regime, in particular the elastic modulus G’. Indeed, viscoelastic properties are generally investigated through dynamic oscillatory measurements in the linear regime (Delshad et al., 2008, Spildo et al., 2015, Koh et al., 2016, Vermolen et al., 2014). In such experiments, the addition of salt results in a drop of the elastic modulus G’ and a decrease of the relaxation time. A solution with a lower G’ will be considered as less elastic. As a general rule, a variation of the chain conformation by salt addition will modify the “small strain elasticity”. Our results show that the extent of flow thickening (\( R_{m_{max}} \)) depends on the flow geometry (the topology of the porous medium) and not on
the initial conformation of polymer chains. Thus, it seems that the effect of elasticity at high rates is not correlated with measurements of $G'$ at small strains.

After normalization, it is clear that salt addition (from 0.4 to 6g/L and from 6 to 6g/L + 1g/L CaCl$_2$) results in a higher $Q_C$, a steeper transition (higher criticity) and little influence on $Q_{max}$ ($\beta$ is nearly constant). As a result, the pic is wider for the 0.4g/L solution and narrower for the solution with added CaCl$_2$. An interpretation can be given based on the mechanism of transient entanglement network formation proposed by Odell et al. (1988) and the flow induced degradation. As explained by Maerker (1975), the addition of Ca$^{2+}$ would make the entanglements more difficult to be removed by thermal Brownian motion, which would result in more probable mechanical degradation. As a consequence, $Rm_{max}$ should decrease because of degradation.

Concerning the brine at 0.4g/L, by decreasing the salt concentration, the electrostatic repulsion between charges decreases which tends to swell and rigidify the polymer coils (ultimately, polyelectrolyte in low salt environment adopt a highly extended conformation). Compared to the solution in 6g/L brine, swelled chains will be more sensitive to the friction exerted by the solvent and...
will deform and align in the flow direction more easily which explain the shift of the onset flow rate $Q_C$ to a lower value. At high enough strain rate, an entangled network is formed, composed of stretched chains, which completely forget their initial conformation state. Mechanical degradation will be the result of the global tension exerted on the stretched chains or chains pieces between entanglements. Hence, in the absence of constituent that promote interactions between chains (such as Ca$^{2+}$), degradation should occur at similar flow rate whatever the salinity. At last, $Rm_{max}$ should be similar since it will depend on the flow rate, the network structure and the degradation state of the chains. As a consequence, the flow thickening zone will be less abrupt for low salinity brines since chains start to uncoil at lower flow rates.

**Scaling of the parameters describing the mobility reduction curve with concentration and molecular weight**

*Dependence of $Q_C$ and $Q_{max}$ with concentration and molecular weight*

Howe and al. (2015) investigated the concentration and the Mw dependence of the onset rate for flow thickening. They attributed the apparent thickening to the development of elastic turbulence. They found that elastic turbulence is triggered by the Weissenberg number and appears at a critical shear rate corresponding to the inverse of a relaxation time that scales as the Rouse time, $\tau_R \propto \eta_s Mw^2 c^0$.

Our parameter $\beta = Q_{max}^{ref}/Q_{max}$, can be considered as a ratio of relaxation times $\beta = \tau_A/\tau_{ref}$. In the same way, we can define a ratio $\alpha$ comparing the onset rates for flow thickening as: $\alpha = Q_C^{ref}/Q_C$. Good superposition of the model curve with the experimental curves implies that $\alpha$ is equal to $\beta$ and that both ratio have the same scaling. In other words, the ratio $Q_{max}/Q_C$ is constant.

We plotted on Figure 10 the dependence of $\beta$ with the polymer concentration for two polymers (3630, Mw=18.7 Mda and 3230, Mw=6.1MDa).

![Figure 10: Dependence of $\beta$ with (Left) polymer concentration for two series at constant Mw (18.7 and 6.1MDa) in 6g/L, (Right) molecular weight Mw for two series (commercial grades of varying Mw at 1200ppm, degraded 3630 solutions at 800ppm).](image)

The dependence of $\beta$ can be fitted by a linear or a power law function. Using, the power law, we find a scaling $\beta \propto c^{0.8-0.9}$.

Concerning the dependency with molecular weight, from measurements on the two series (commercial grades of varying Mw at 1200ppm, degraded 3630 solutions at 800ppm), we find a scaling $\beta \propto Mw^{1.5-2.3}$. We don’t know if the difference between the exponents is due to the concentration variation or to the different Mw distributions of the two series of polymers.

These scalings are close to the Rouse scalings of terminal dynamics of neutral polymers in semidilute unentangled good solvent $\tau_R \propto Mw^{2}c^{0.31}$. For most of our experiments, we have $\beta = \alpha$. Thus, we clearly have a concentration dependence for the onset of flow thickening which is
contradictory with the results of Howe et al. (2015). Concentration dependence has been clearly observed by other workers, in the dilute (Haas and Kulicke, 1985, in the range 3-100ppm for a PAM, Mw = 18 MDa) and in semi-dilute regime (Rodriguez et al., 1993, in the range 25-1000ppm for a PEO with Mw = 5 MDa, Seright, 2011 in the range 25-1600ppm for a HPAM with Mw=18-20 MDa whose results seem to be concentration independent at first sight but reveal a dependence after deep analysis). We have no explanation about this discrepancy.

**Dependence of \( Rm_{\text{max}} \) with concentration and molecular weight**

As shown on Figure 11, from measurements on the series at variable concentrations and Mw, we find that \( Rm_{\text{max}} \) scales with concentration as \( Rm_{\text{max}} \propto c^{0.6-0.8} \) and with molecular weight as \( Rm_{\text{max}} \propto Mw^{1.3-1.7} \). These power law exponents are compared in Table 5 with those obtained with Screen factor and EVROC measurements. \( Rm_{\text{max}} \) and screen factor have concentration and Mw dependence that follow power laws with exponents very close to each other. As a consequence, a measurement of screen factor should enable to predict \( Rm_{\text{max}} \) in porous medium.

<table>
<thead>
<tr>
<th>Variable concentration</th>
<th>EVROC at 944s⁻¹</th>
<th>Screen Factor</th>
<th>( Rm_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mw=18.7 Mda</td>
<td>2.3</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Mw=6.1 Mda</td>
<td>3.3</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Commercial series 1200ppm</td>
<td>1</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Degraded series 800ppm</td>
<td>1</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

**Table 5:** Power law exponents for each series of polymer solutions at variable concentration and Mw.

The graphs of Figure 12 represent the dependence of \( Rm_{\text{max}} \) and \( \beta \) with low shear viscosity, EVROC viscosity at 944s⁻¹ and screen factor. The correlation of both parameters with EVROC viscosity and screen factor is remarkable, in contrast to the scatter plot with shear viscosity. The correlation with screen factor is linear. Hence, for any new porous medium, measuring the mobility reduction curves of two solutions of high and low screen factor will enable to establish the linear relation between \( Rm_{\text{max}}, \beta \) and screen factor. From then on, mobility reduction of any new polymer solution will be predicted from the ex-situ measurements of elasticity. To illustrate this, a solution containing 2050ppm of 3130 (Mw = 3.2 MDa) and 360 ppm of 3530 (Mw = 13.8 MDa) was...
prepared. Screen factor was measured before its injection through the porous medium. Then the mobility reduction curve was measured and the parameters $Rm_{max}$ and $\beta$ were determined. As seen on Figure 12, $Rm_{max}$ and $\beta$ are within the correlations with screen factor and EVROC. They could have been interpolated easily. It would have been possible to predict the whole mobility reduction curve without any injection in porous medium.

![Figure 12: Correlation of $Rm_{max}$ (Left) and $\beta$ (Right) with Screen factor, EVROC viscosity at 944s-1 and low shear plateau viscosity. Red symbols correspond to the polymer mix 3130/3630 at 2050/360 ppm.](image)

Degradation versus salinity and polymer concentration

As seen on Figure 13, a, when degradations are plotted as a function of the flow rate, it seems that the following trends appear:

- in 6g/L brine, degradation increases with polymer concentration,
- at 800ppm, degradation is slightly higher when 1g/L CaCl$_2$ is added to the 6g/L brine,
- at 800ppm, degradation is similar if 50g/L NaCl is added to the 6g/L brine,
- degradation is similar for the solution at 500ppm in 0.4g/L brine.

As a conclusion, salinity is found to have a minor effect on the degradation at high rates. This observation is in agreement with the fact that $Rm_{max}$ is also nearly constant. Indeed, at high rates, chains are highly stretched and forget their initial conformation state. Salinity does not influence their stretched state excepted if some salt species can enhanced interactions between chains (it would the case when Ca$^{2+}$ is added).

A fundamental question is still unresolved among the community of people trying to understand the mechanism of polymer degradation in porous medium: “which is the parameter controlling the degradation ? If we think in term of strain rate, we can propose the flow rate. If we think in term of energy dissipated, the Delta P or rather the product Delta P x Q can be proposed.

When degradations are plotted versus the product $\beta$ x Q, Delta P or Delta P x Q, the superposition of the curves is better, especially in the zone of high degradation. The best superposition is obtained with Delta P in abscissa. In the preceding section, we insisted on the fact that flow thickening is the result of the elasticity of the polymer chains combined with the extensional flow experienced in the succession of pore throats/pore bodies. On the other side, degradation results from a too high tension exerted on the stretched chain. It appears that degradation and flow thickening are concomitant. It seems that the right parameter controlling the degradation should be the “Delta P extensional” resulting from the extensional phenomena. It could be obtained by subtracting the Delta P due to viscous shearing to the total pressure drop (same principle as the EVROC extensional viscometer). For example, in case of long core, degradation will occur at the entrance. After a given length, the delta P will not contribute anymore to the degradation process. With our short core (L=2.54cm), most of the Delta P would be extensional and would contribute to the degradation process (as indicated by the good superposition on graph c).

A detail that could be at the origin of numerous apparent discrepancies in the literature: Degradation value depends on the shear rate at which viscosity is measured. Hence, the graph of...
Figure 13a, which corresponds to degradations calculated from viscosity measurements at the low shear plateau is compared in Figure 14 with degradations calculated from viscosity measurements at 7s^{-1}. The trend with concentration is conserved and the influence of salt composition is greatly intensified. Indeed, degradation at 7s^{-1} is extremely low in the brine at 0.4g/L. As a conclusion, it seems that degradation at the low shear plateau viscosity is the good measurement to understand the underlying physics since it gives for example, a minor effect of the salinity on the degradation. On the other hand, for applicative issue, it is better to calculate degradation at a shear rate as close as possible as on the field. In that case, a decrease of the salinity can “create” substantial economics.

Figure 13: Degradation of 3630 solutions (Mw=18.7 MDa) through the porous medium from viscosity measurements at the low shear plateau. Series at varying concentration (300-1200ppm) in 6g/L brine, 800ppm in 6 + 50g/L NaCl brine, 6 + 1g/L CaCl\(_2\) brine, 500ppm in 0.4g/L brine.

Figure 14: Degradation of 3630 solutions (Mw=18.7 MDa) through the porous medium from viscosity measurements at the low shear plateau (left graph); at 8s^{-1} (Right graph). Series at varying concentration (300-1200ppm) in 6g/L brine, 800ppm in 6 + 50g/L NaCl brine, 6 + 1g/L CaCl\(_2\) brine, 500ppm in 0.4g/L brine.
Conclusions

Polymer solutions prepared in a variety of physical-chemistry conditions were characterized through viscosity, screen factor and extensional viscosity measurement (EVROC viscometer). Their behavior in porous medium was then evaluated through an injection on a short core (ceramic frit, \(k_w=4D\)).

The following conclusions can be drawn:

Compared to the EVROC viscometer, which is a newly developed device based on the progress in microfluidics aiming at measuring the extensional viscosity, the screen factor is an old, simplistic and rough measurement. However, in the range of polymer concentrations (100-1200ppm), molecular weights (3-19 MDa) and salinities (0.4-56g/L) investigated in this study, there is a very good correlation between screen factor and EVROC measurements. The pertinence of screen factor to measure the elasticity of polymer solution is confirmed 40 years after its first use.

Mobility reduction curves at high rates have a bell shape. They can be modeled from the knowledge of 3 parameters: the onset rate of flow thickening \(Q_c\), the maximum of mobility reduction \(Rm_{max}\) and the flow rate at which this maximum occurs \(Q_{max}\). They were normalized by using only two parameters: \(Rm_{max}\) and a coefficient \(\beta\) which take into account the shift in \(Q_{max}\) when physical-chemistry conditions are varied. After normalization, at salinities of 6g/L or more, all the curves are well superposed whatever the concentration, the molecular weight or the degradation level. It means that the ratio \(Q_{max}/Q_c\) is constant. When salinity is decreased to 0.4g/L, \(Q_{max}\) stays constant whereas \(Q_c\) decreases to very small values.

It was found that \(Rm_{max}\) and \(\beta\) are linear or power law functions of the concentration and the molecular weight. They are quite insensitive to the salinity excepted if Ca\(^{2+}\) is added. This finding is for us a demonstration that \(Rm_{max}\) and \(\beta\) are not correlated with visco-elastic measurements in the linear regime.

Whatever the physical-chemistry conditions, \(Rm_{max}\) and \(\beta\) are strongly correlated with ex-situ measurements of screen factor or extensional viscosity on the bulk solutions. Hence, for any new porous medium, measuring the mobility reduction curves of two solutions of high and low screen factor will enable to establish the linear relation between \(Rm_{max}\cdot\beta\) and screen factor. From then on, the whole mobility reduction curve at high rates in any set of conditions can be predicted from the screen factor value.

Degradation (calculated from viscosity measurements at the low shear plateau) was found to decrease slightly for decreasing polymer concentration. The influence of salinity was found to be minor even when Ca\(^{2+}\) was added. In contrast, if degradation is calculated from viscosity measurements at 7s\(^{-1}\), the influence of the salinity is huge. This results stresses that the degradation value is highly dependent on the shear rate at which viscosity is measured. It could explain some discrepancies of the literature. Delta P was found to be the best parameter controlling the degradation in porous medium.

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Stavanger, Norway

19th European Symposium on Improved Oil Recovery

Sustainable IOR in a Low Oil Price World

19th European Symposium on Improved Oil Recovery
Stavanger, Norway | 24-27 April 2017
Flow of polymer solutions through porous media - Prediction of mobility reduction from ex-situ measurements of elasticity

Stephane JOUENNE
Guillaume HEURTEUX
Flow thickening and polymer flooding

HPAM = flexible coils

Xanthan ~ Rigid rod

Injectivity ?, conformance profile
Polymer flooding $\Rightarrow$ Improved macroscopic sweep efficiency
and
Microscopic sweep efficiency because of Elasticity

Stabilization of oil ganglia, dead end pores, local pressure/flow fluctuation at the pore level (elastic turbulence)....

- Huh and Pope, 2008
- Levitt et al., 2010
- Veerabhadrappa et al., 2013
- Vermolen et al. 2014
- Clarke et al., 2015,
- Howe et al., 2015
- Koh et al., 2016
- Qi et al., 2016
- Southwick, Manke, 1988
- Seright et al., 2009
- Wang et al., 2000
The manifestation of elasticity in porous medium

What is the physical origin of flow thickening?
Extensional Viscosity, elastic turbulence...

What is the relaxation time involved?
$\tau_S, \tau_E$...

Triggered by which adimensional number?
Wi, De, El...

What is the influence of physical-chemistry parameters?
Polymer concentration, Mw, high Mw tail, degradation, salinity...?

Can we predict flow thickening from bulk measurements?
Measurement of elasticity

Small deformation

Shear flow

\[ \dot{\gamma} = \frac{dV}{dy} \]

Extensional flow

\[ \dot{\varepsilon} = \frac{dV}{dx} \]

High deformation

Linear regime

\[ G'/G'' \]

Normal stress \( N_1 \)

Extensional viscosity

\( \tau_E \)

Screen factor

\[ SF = \frac{t_p}{t_{H_2O}} \]

EVROC® (Rheosense)

\[ \eta_{e,a} = \frac{1}{\varepsilon_H \dot{\varepsilon}_a} \quad \text{with} \quad \Delta P_E = \Delta P_C - \Delta P_V \]
## Polymer solutions

### Polymer grades

<table>
<thead>
<tr>
<th>Polymer grade</th>
<th>Mw (10^6 g/mol)</th>
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<tr>
<td>3130S</td>
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</tr>
<tr>
<td>3230S</td>
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</tr>
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<td>8.1</td>
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<tr>
<td>3630S</td>
<td>18.7</td>
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</table>

### Brines

<table>
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<tr>
<th>Salt</th>
<th>0.4 g/L</th>
<th>6 g/L</th>
<th>6 g/L + 50 g/L NaCl</th>
<th>6 g/L + 1 g/L CaCl2</th>
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<tbody>
<tr>
<td>Na₂SO₄</td>
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<td>0.007</td>
<td>0.007</td>
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<tr>
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<td>0.111</td>
</tr>
<tr>
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<td>0.745</td>
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<td>0.561</td>
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<td>54.724</td>
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</tr>
<tr>
<td>TDS (g/L)</td>
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### Polymer solutions

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<tr>
<th>Polymer grade</th>
<th>Concentration ppm</th>
<th>Salinity g/L</th>
<th>Degradation %</th>
<th>Viscosity η cP</th>
<th>Mw 10^6 g/mol</th>
<th>C[η] cm3/g</th>
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<td>0</td>
<td>15.0</td>
<td>1 698</td>
<td>4.4</td>
</tr>
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</table>

**Mw determination**

- $M_w^{3630} = 18.7 \text{ Mda}$
- $[\eta] = K M_w^a$ with $a=0.8$

$$M_w = ([\eta]/[\eta]_{3630})^{1/a} \times M_w^{3630}$$
Ex-situ measurements of elasticity

- Ex-situ measurements of elasticity show a range of values from 100ppm to 1200ppm.
- Apparent extensional rate is plotted against EVROC viscosity at 944 s\(^{-1}\).
- Data points indicate a significant increase in EVROC viscosity with increasing polymer concentration.
- Polynomial fits are used to model the relationship between EVROC viscosity and Mw (MDa): 
  - For 1200 ppm, Mw=18.7MDa: \( y = 0.02x^{2.27} \)
  - For 3630, 800ppm, Variable degradation: \( y = 0.00x^{2.29} \)
Comparison EVROC / Screen factor

EVROC = flow rate controlled
Screen factor = pressure controlled

Good correlation!
Behavior in porous medium

Core = Ceramic frit
Kw = 4D
$\phi = 44\%$

$$R_m = \frac{D_{P_{pol}}}{D_{P_{H2O}}}$$

$$\text{Deg} (%) = \frac{\eta_0 - \eta_{Deg}}{\eta_0 - \eta_{H2O}} \times 100$$
Modeling of in-situ rheology

Ref = 800ppm 3630 in 6g/L brine

\[ RM = Rm / Rm_{\text{max}} \]

\[ Q_{\text{norm}} = \beta \times Q \]

\[ \beta = Q_{\text{max}}^{\text{Ref}} / Q_{\text{max}}^{\text{A}} \]

\[ Q_C < Q \leq Q_{\text{max}} \]

\[ RM_{\text{C}} = 0.04 \quad Q_C = 0.034 \text{m}^3/\text{m}^2 \quad \lambda_{\text{II}} = 9 \quad n_{\text{II}} = 1.1 \]

\[ Q_{\text{max}} < Q \]

\[ RM_{\text{max}} = 1 \quad Q_{\text{max}} = 1 \text{m}^3/\text{m}^2 \quad \lambda_{\text{III}} = 0.16 \quad n_{\text{III}} = 1.3 \]

Galindo-Rosales et al., 2011 ≠ Lohne et al., 2016
Flow thickening and concentration

3630 (Mw = 18.7 MDa) in 6g/L brine
Flow thickening and Mw

1200ppm in 6g/L brine

**Mw**

<table>
<thead>
<tr>
<th>Mw</th>
<th>Deg</th>
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</thead>
<tbody>
<tr>
<td>3630</td>
<td>0%</td>
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<td>3530</td>
<td>19%</td>
</tr>
<tr>
<td>3330</td>
<td>40%</td>
</tr>
<tr>
<td>3230</td>
<td>58%</td>
</tr>
</tbody>
</table>

\[ R_m \rightarrow \beta \cdot Q \text{ (m}^3/\text{h/m}^2) \]

\[ R_m = \frac{R_m}{R_{m_{\text{max}}}} \]

\[ R_m \rightarrow \beta \cdot Q \text{ (m}^3/\text{h/m}^2) \]
Flow thickening and salinity

∀ salinity

\[ Rm_{\text{max}} = \beta \]

excepted for low salt water
Scaling of flow thickening parameters

Scaling laws should help to identify the mechanisms involved in flow thickening.
Prediction of flow thickening from ex-situ measurement of elasticity

<table>
<thead>
<tr>
<th>Polymer grade</th>
<th>Concentration</th>
<th>Salinity</th>
<th>Degradation</th>
<th>Low shear Viscosity</th>
<th>$[\eta]$</th>
<th>Mw</th>
<th>C$[\eta]$</th>
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<tr>
<td>3130 / 3530</td>
<td>2050 / 360</td>
<td>6</td>
<td>0</td>
<td>15.0</td>
<td>1698</td>
<td>4.4</td>
<td>4.1</td>
</tr>
</tbody>
</table>

$R_{m_{\text{max}}}$ and $\beta$ are correlated with EVROC or screen factor

$\Rightarrow$ Prediction at any physical-chemistry conditions from two measurements
Unique normalized flow thickening curve for all Mw, degradation levels and polymer concentration. A decrease of salinity affects the onset.

**New porous medium**
Measurement in two sets of physical chemistry conditions (high and low elasticity)

Knowledge of $Rm_{\text{max}}$ and $\beta$ vs Screen factor

Screen factor measurement enables to predict the whole curve in another set of conditions
Polymer degradation

Controlling parameter = Strain rate \( \Leftrightarrow Q \text{ vs.} \Delta P \text{ vs.} \Delta P \times Q \)
Degradation is not an intrinsic parameter

\[ \text{Deg}(\%) = \frac{\eta_0 - \eta_{\text{Deg}}}{\eta_0 - \eta_{\text{H}_2\text{O}}} \times 100 \]

Degradation depends on the shear rate at which viscosity is measured.

Higher influence of salinity and polymer concentration for viscosity measurements at 7s\(^{-1}\)
Conclusions

• Screen factor correlated with EVROC measurements ⇒ Screen factor = rough and simplistic but very pertinent measurement
• Mobility reduction at high rates = bell curve
• Normalization \[ RM = \frac{Rm}{Rm_{\text{max}}} \]
\[ Q_{\text{norm}} = \beta \times Q \]
• Modeling of flow thickening curve \[ Rm_{\text{max}}, Q_c, Q_{\text{max}} \]
• **Prediction from ex-situ measurements of elasticity**: RM and \( Q_{\text{norm}} \) are correlated with screen factor or EVROC (high strain measurements ≠ linear visco-elastic measurements)
• Degradation: pay attention to comparisons with viscosity measurements at different shear rates
Acknowledgements

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Why an hyperbolic contraction?

\[ \dot{\epsilon}(x) = \frac{dV(x)}{dx} = \text{cste} = \dot{\epsilon} \]

\[ V(x) = \dot{\epsilon} \times x + V_0 = \frac{Q}{hw(x)} \]

\[ V_u = V(x = 0) = \frac{Q}{hw_u} \]

\[ V_c = V(x = L_c) = \frac{Q}{hw_c} \]

\[ \dot{\epsilon} = \frac{Q}{L_c h} \left( \frac{1}{w_c} - \frac{1}{w_u} \right) \]

\[ w(x) = \frac{w_u x_0}{x_0 + x} \]

with \[ x_0 = w_c L_c / (w_u - w_c) \]
Relaxation time in transient extensional flow

Clasen et al., 2006

Oscillatory shear

McKinley., 2005

SAOS

capillary thinning

Clasen et al., 2006
Seright Data

\[ y = 0.3839x^{0.2139} \]

\[ y = 0.614x^{0.8333} \]