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# Effect of Salt Valency and Concentration on Shear and Extensional Rheology of Aqueous Polyelectrolyte Solutions For Enhanced Oil Recovery

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# Effect of salt valency and concentration on shear and extensional rheology of aqueous polyelectrolyte solutions for enhanced oil recovery

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**Abstract**

The injection of polymer solutions into an oil basin can lead to enhanced oil recovery (EOR) by increasing the microscopic sweep of the reservoir, improving the water-oil motility ratio and thus leading to greater yield from oil fields. In this contribution, we characterize both shear and extensional rheological response of aqueous solutions of partially hydrolyzed polyacrylamide (HPAM), the most commonly used polymer for EOR, for velocity gradients in both the flow direction (extensional) and perpendicular to flow (shear) arise in EOR applications. As HPAM is a charged polymer, to better emulate the environment in oil basins, the rheological response was investigated in presence of salt, sodium chloride and calcium chloride, with concentrations 3.7 x $10^{-4}$ - 1.5 M, as a function of polymer molecular weight (2 – 10 million g/mol) and concentration (0.005 – 0.3 wt%). The extensional relaxation times and extensional viscosity are measured using dripping-onto-substrate (DoS) rheometry protocols, and a commercial shear rheometer was utilized for characterizing the shear rheology response. The polyelectrolyte solutions formed by HPAM exhibit shear thinning in steady shear, but show strain hardening in response to extensional flow. Even though an increase monovalent salt concentration leads to a decrease in both shear viscosity and extensional relaxation times, an increase in divalent salt concentration leads to an increase in extensional viscosity and relaxation time, implying that ion coordination can play a role in the presence of multivalent ions

*Key Words:* *polyelectrolyte, rheology, extensional flow, salt condensation*

**Introduction**

Energy generated from fossil fuels makes up the majority of global energy production and consumption, with over 32% of the world's primary energy consumption derived from oil ("BP Statistical Review of World Energy June 2014," 2014). However, at the current rate of production and consumption, the world's current known oil will last only 54 years. Most oil reservoirs produce only 20-40% of the oil originally in place (OOIP) (Advanced Resources International 2006; Olajire 2014); accessing the remaining oil could greatly increase the time for which oil is available. Enhanced oil recovery (EOR) seeks to reach this oil and has shown to allow up to 65% of the OOIP to be recovered (Advanced Resources International 2006). Traditionally oil recovery starts by utilizing the pressure differential between the surface and the oil basin. During waterflood, also known as secondary recovery, water is injected into the basin to recreate this pressure differential. Enhanced oil recovery, or tertiary recovery, goes beyond the use of water. There are many methods of EOR, including water-alternating-gas, in which a waterflood and a gas flood are alternated, and chemical flooding in which chemicals are added to the waterflood. One type of chemical EOR, alkaline-surfactant-polymer (ASP) flooding, has enabled recovery of 83% of the OOIP (Shutang et al. 1995). In ASP EOR, alkali and surfactant are added to the waterflood; a separate waterflood containing polymer often follows (Muggeridge et al. 2014). This polymer in the waterflood causes the viscosity of the water phase to increase. This improves recovery of oil by increasing the capillary number and decreasing the mobility ratio between oil and water, improving the microscopic and macroscopic sweep efficiency, respectively (Muggeridge et al. 2014; Olajire 2014).

Partially hydrolyzed polyacrylamide (HPAM) is a polymer commonly used in EOR for its high viscosity in solution (Wever et al. 2011). The structure of HPAM is shown in Figure 1. In solutions with pH above the pKa of polyacrylic acid (between 6 - 7) (Katchalsky and Spitnik, 1947; Petrov et al 2003), the polyacrylic acid repeat units are deprotonated and adopt a negative charge. In the aqueous solutions of HPAM that incorporate sodium acrylate rather than acrylic acid in the repeat unit, the chain adopts a negative charge and the sodium ions form a diffuse layer close to the chain, approximately within a distance (Debye length) determined by ionic strength. The percent hydrolysis of HPAM represents the portion of repeat units that are hydrolyzed to form acrylic acid or sodium acrylate. Thus, percent hydrolysis acts as a measure of the charge fraction or the relative

number of charges on the polymer backbone. See Equation 1, where $m$ is the number of hydrolyzed monomers and $n + m$ is the total degree of polymerization (Lewandowska 2006).

$$\% \ hydrolysis = \frac{m}{n+m} * 100\% \quad (1)$$

In oil basins, HPAM is often in the deprotonated state (Muggeridge et al. 2014), and as the charged groups repel each other in solution, the polymers adopt an expanded conformation. Polymers like HPAM that have charge bearing monomers in their repeat unit are known as polyelectrolytes. Aqueous polyelectrolyte solutions are used in a variety of technical applications, including drinking water filtration (Weidman et al. 2016) and treatment (Metaxas et al. 2018), additives for cementitious materials (Murray and Erk 2014), and as rheology modifiers for formulations used in pharmaceutical, food, cosmetics and paints and coatings industries (Radeva 2001; Calvert 2001). In salt-free solutions, the electrostatic expansion caused by the charges along the polymer results in a relatively low overlap concentration ($c^*$) for polyelectrolytes in comparison with $c^*$ for neutral polymers (Colby 2010). Solutions with polymer concentration below the overlap concentration are considered to be in the dilute regime, and above the overlap concentration are said to be in the semi-dilute regime (Colby 2010). Experimentally, the overlap concentration can be identified as the concentration at which solution viscosity becomes twice the solvent viscosity (Colby 2010).

In dilute solutions without other ions present, polyelectrolytes adopt an extended conformation due to the electrostatics-induced charge repulsion, and show R ~ N, where R is the radius of gyration and N is the number of repeat units or ideal blobs. This is in contrast to R ~ $N^{1/2}$ (for theta solvents) observed for neutral polymers (Colby 2010; De Gennes et al. 1976). The larger coil sizes for polyelectrolytes in solution make accessing the dilute regime experimentally challenging as the overlap concentration is quite low (Rubenstein and Colby 2003). The coil size changes dramatically above overlap concentration in semi-dilute regime, where interchain interactions, together with the role played by long and short-range electrostatic interactions, impact the conformations and the rheological response (Colby 2010; Schweins and Huber 2001; Volk et al. 2004). However, at present, polymer entanglements in aqueous salt solutions are not well-understood, though unlike neutral solutions, the unentangled semi-dilute regime usually spans more than one decade in concentration. Scaling laws seem to capture the concentration-dependent variation in shear rheological response of charged polymers in low or no salt added limit (Colby

2010). The effect of added salt, especially multivalent salt, on the rheological properties of polyelectrolytes are less well-understood and focus of this study.

In particular, even though electrostatic interactions are known play critical role in determining polyelectrolyte conformation and rheological response for HPAM in oil fields of varying salinity, *a priori* determination of such effects can be quite challenging since the valence, type and concentration of counterions may vary geographically (Muggeridge et al. 2014; Rashidi et al. 2010). Water is generally present in an oil basin at formation and this connate water has a variety of salts present (Timm and Maricelli 1952). In the Illinois basin, USA, the most prevalent monovalent cation is $Na^+$ and the most prevalent divalent cation is $Ca^{2+}$, whereas chloride ($Cl^-$) is the most common anion (Stueber and Walter 1991; Stueber et al. 1993). Monovalent cations such as $Na^+$ often act in solution to screen charges on polyelectrolytes from one another, thus reducing the electrostatics induced stretching and consequently also the radius of the polymer coils in solution (Volk et al. 2004). This in turn alters the overlap concentration of the solution, and also influences both the intrachain and interchain interactions, which in turn influences the rheological behavior of the solutions.
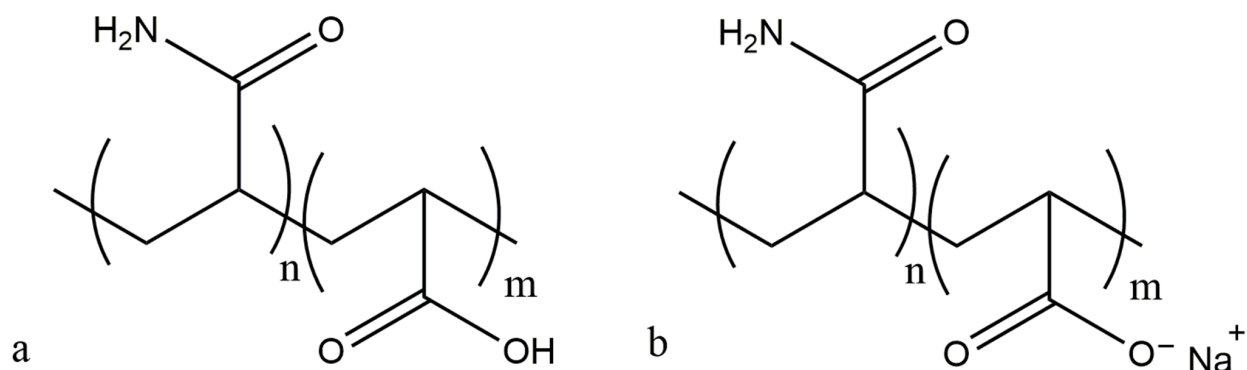


**Fig. 1** Chemical structure of HPAM. (a) the polyacrylic acid form and (b) the sodium salt, sodium acrylate. The degree of hydrolysis is given in equation 1. When dissolved in solutions with pH > ~7, the carboxylic acid groups shown in (a) deprotonate, creating a negative charge along the polymer backbone

While the presence of monovalent salts generally decreases the polymer coil size, divalent charges can interact with polyelectrolytes in a multitude of ways. The divalent cations can form specific ion pairs with the negative charges either along a polymer backbone (intrachain pairs) (Huh et al.

2009) or between charges on different polymer chains (interchain). The divalent cations can associate with the polyanion chains by undergoing "Manning condensation" in which the cations are closely associated with the chain so as to keep the local charge density electrically neutral (Schweins and Huber 2001). These effects can cause the polymer chain to collapse into a tight coil or even a "pearl necklace" conformation, consisting of collapsed chain segments connected together (Schweins and Huber 2001). Many studies have investigated the effect of sodium (Jung et al. 2013; Sedaghat et al. 2013; Ward and Martin 1981, Odell and Haward 2008) or calcium (Francois et al. 1997; Huh et al. 2009; Sheng 2011; Ward and Martin 1981, Odell and Haward 2008) cations on the conformation and behavior of HPAM and other water-soluble polymers in aqueous solutions. The literature however is inconclusive on the conformation of HPAM in the presence of aqueous divalent calcium. It is generally observed that when calcium and sodium cations are both present in solution with HPAM, the solution shear viscosity is lower than that with only sodium present (Huh et al. 2009; Ward and Martin 1981). The mechanism of interaction between divalent ions and polyelectrolytes in solution (both with or without additional monovalent ions) is still under debate. Some papers suggest intermolecular interactions, or two distinct polymer chains bridged by a calcium ion. Others suggest intramolecular interactions (Odell and Haward 2008) or a transition between inter- and intra-molecular interactions (Francois et al. 1997).

Here we investigate the nature and influence of interactions between commercial HPAM and salt ions in aqueous solutions via shear and extensional rheometry. Rheological response is exquisitely sensitive to polymer conformations and degree of overlap, i.e. to the influence of both intrachain and interchain interactions. In this study, type (valency) and concentration of salt in aqueous solutions are varied as well as a range of polymer molecular weights and concentrations. The range of shear rates tested mimic the range of shear rates experienced during both the pumping of solutions and the shear rates encountered in the oil basin. Though shear rheology of polyelectrolyte solutions (especially in presence of monovalent counterions) has been the focus of many studies (Boris and Colby 1998; Colby 2010; Jung et al. 2013; Sedaghat et al. 2013), there are only a few reported measurements of the extensional rheology response (Dunlap et al. 1987; Jimenez et al. 2018; Miles et al. 1983; Rodríguez-Rivero et al. 2014). In porous media, the flow field is extensional in nature as the fluid traverses through converging and diverging channels. In the current contribution, we characterize the extensional rheology response of polyelectrolyte solutions using dripping-onto-substrate extensional (DoS) rheology technique (Dinic et al. 2017a;

Dinic et al. 2017b; Dinic et al. 2015; Jimenez et al. 2018) The DoS rheometry relies on quantifying both extensional viscosity and extensional relaxation time by analysis of capillary-driven thinning and pinch-off dynamics of an unstable fluid neck formed by dripping a finite volume of fluid from a nozzle onto a substrate. Therefore, combined with shear rheometry, DoS rheometry allows us to model the complete rheological profile of polyelectrolyte solutions for EOR while investigating the effect of counterion type and concentration on rheological behavior.

**Materials and Methods**

Commercial polymers made by SNF (Andrézieux, France) in their FLOPAAM series were used in this study without further purification. The reported molecular weight and approximate degree of hydrolysis for three commercial polymers used are shown in Table I (Seright et al. 2011; SNF Floerger.; Veerabhadrappa et al. 2013). Solid sodium chloride, NaCl, and anhydrous calcium chloride, $CaCl_2$, were used as received to modify the salinity of solutions.

| Table I. Physical properties of FLOPAAM samples used in this study. | | |
|---|---|---|
| FLOPAAM species | Reported Molecular Weight | Approximate % hydrolysis |
| 3330 s | 8 – 10 million g/mol | 25-30 |
| 3230 s | 4 – 6 million g/ mol | 25-30 |
| 3130 s | 1 – 2 million g/ mol | 25-30 |

Solutions for shear and extensional rheology were prepared by mixing an appropriate amount of polymer and salt, followed by overnight stirring using a magnetic stir bar, and sonication for 1 hour in a bath sonicator. Solutions at very low polymer concentrations were prepared by serial dilution. For shear rheometry, solutions contained 0.30 wt% of FLOPAAM 3330; the concentration of NaCl ranged from $3.7 \times 10^{-4}$ M – 1.5 M and the concentration of $CaCl_2$ ranged from 0.0386 M – 1 M. These salt concentration ranges were chosen to approximate the range of monovalent and divalent ion concentrations found in oil basins (Pan 2005; Stoll et al. 2011; Timm and Maricelli 1952). Solutions that were used for extensional rheometry span a wide range of concentrations so that the semidilute and dilute regimes of polymer solutions may be accessed. Solutions of FLOPAAM 3130, 3230, and 3330 were used at 0.005, 0.025, 0.05, 0.1, and 0.3 wt% of polymer. Salt concentrations were either 0.0386 M or 1 M for each salt, chosen to model basins with relatively high and low salinity. There was no visual evidence of precipitation or coacervation, and the solutions remain colorless and transparent over the course of the

investigation. Solutions were investigated within a week of preparation, as preliminary data indicated that solution behavior over the shear rate range of interest was unchanged during this time.

<u>Shear Rheometry</u>

The Anton Paar MCR 702 was used in single drive mode for all shear rheometry experiments. All shear rheometry measurements were performed with the double gap fixture with diameter of 26.7 mm (DG26.7) at a constant temperature of 25 °C, maintained by a Peltier heating system with water as the heat transfer fluid.

The shear rheology experiments were carried out on a torsional rheometer using the experimental protocol outlined in Figure 2. A constant shear rate of 1 s$^{-1}$ was applied for 10 minutes, with measurements being recorded every 6 s for a total of 100 measurements. The shear rate was then ramped logarithmically from 1 s$^{-1}$ to 10 s$^{-1}$ with 5 points per decade and 30 s allowed per point. A shear rate of 10 s$^{-1}$ was then applied and maintained for 5 minutes, again with measurements taken every 6 s. This process was repeated for 100 s$^{-1}$ and 500 s$^{-1}$. After the measurement at a constant 500 s$^{-1}$, the shear rate again ramped 500 s$^{-1}$ to 1 s$^{-1}$. The focus of the measurements was assessment of steady shear viscosity values at the shear rates experienced by solutions during EOR applications. Solutions in EOR applications typically experience high shear rates (500 s$^{-1}$ or more) during pumping, but lower shear rates (1 s$^{-1}$ or less) in transit and in the oil basin. This procedure was repeated with 5 aliquots of the same solution.

Viscosity measurements reported here are the average of the measurements taken from the last 200 s during constant shear. The outlined procedure ensures that the viscosity values reported here are extracted from the steady shear, and in experiments reported here, the last 200 s of data is generally stable, as seen in Figure 2b. The measurements conducted by ramping the shear rate up were contrasted with measurements made using ramp down to assess both the possibility of aggregate formation and hysteresis.
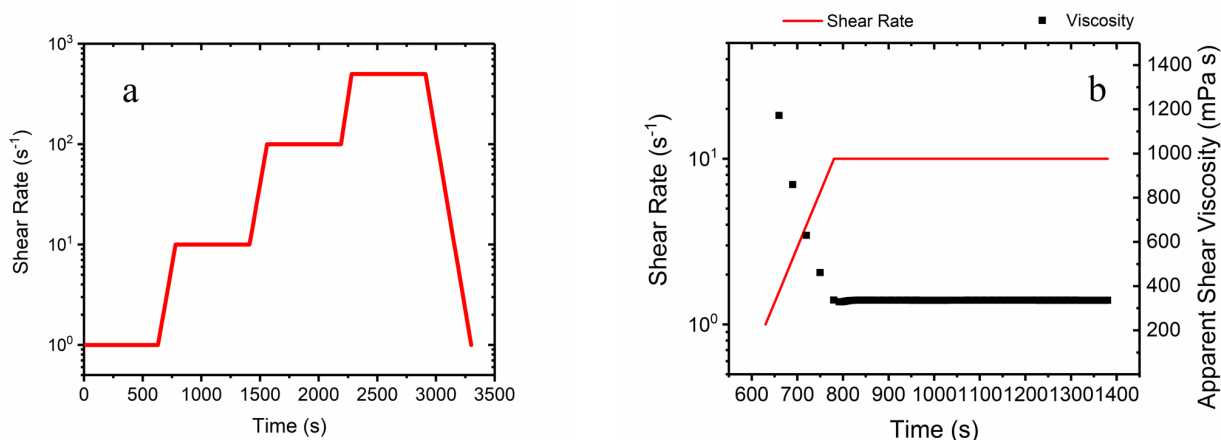
**Fig. 2** a: Shear rate applied during all shear rheometry tests. For each sample, this procedure was repeated for a total of 5 times, using a new aliquot each time. b: An example of applied shear rate (solid line) and measured viscosity (points) during one plateau. Viscosity data shown is from a solution of 0.3 wt% of 3330 in water with no salt

Extensional Rheometry

Extensional viscosity and extensional relaxation time were measured using the dripping-onto-substrate (DoS) rheometry (Dinic et al. 2017b; Dinic et al. 2015) set-up shown schematically in Figure 3. A finite volume of polyelectrolyte solution is released from the nozzle onto a substrate using a syringe pump at a relatively low flow rate of $Q$ = 0.02 ml/min (kept constant in all experiments). The syringe pump is switched off just as the drop touches the substrate, and even before the liquid neck emerges. The shape and shape evolution of the liquid neck formed between a sessile drop and the nozzle undergoes self-thinning that is completely determined by the local balance of forces, and retains no memory or influence of the flow history. (Dinic et al. 2015; Dinic et al.2017b) The distance between the nozzle and substrate $H$ is kept constant, and experiments described here were carried out for an aspect ratio $H/R_0 = 3$, where $R_0$ is the radius of the nozzle. The stretched capillary bridge formed between the nozzle and the sessile drop is visualized using the imaging system that consists of a light source with a diffuser and a high-speed camera (Fastcam SA3) with a train of lenses (Nikkor 3.1x zoom (18-25 mm) lens, plus a macro lens) attached for obtaining images with high magnification. The radius evolution of the thinning neck is tracked and analyzed with a specially written code in ImageJ and MATLAB to extract radius evolution datasets. For viscoelastic polymer solutions, the neck radius evolution data can be fit to obtain

extensional relaxation time and extensional viscosity. At least four measurements were carried out for each composition of the polyelectrolyte solutions.
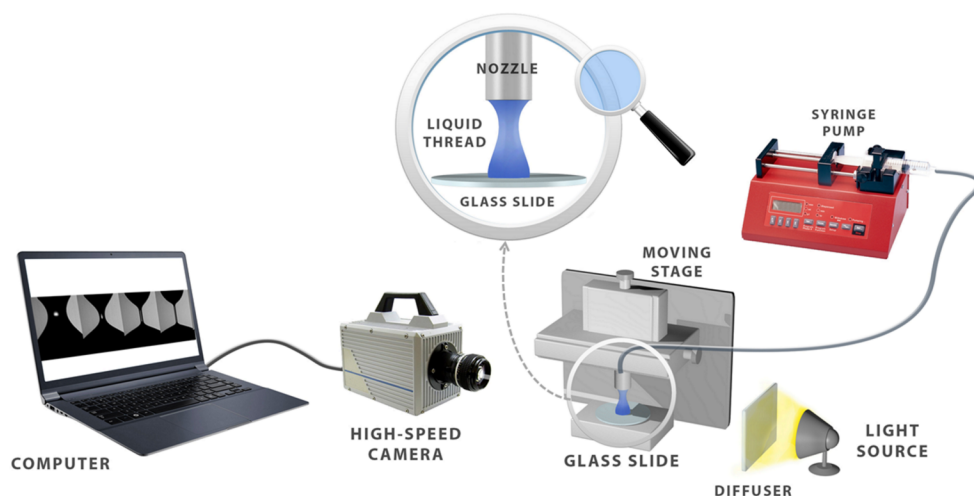


**Fig. 3** Schematic for Dripping-onto-Substrate (DoS) Rheometry technique (adapted from Dinic et al (J. Polym. Sci Polym. Phys). The dispensing system comprises of a syringe pump connected to a nozzle. A finite volume of a fluid is pumped through a nozzle on to a substrate. An imaging system consisting of a high-speed camera with attached magnification lenses, a light source, diffuser and computer is used for capturing the neck shape and neck shape evolution

The interplay of capillary, inertial, viscous and elastic stresses determine the shape and shape evolution of the fluid neck created in dripping-onto-substrate set-up as well as for necks formed by stretching liquid bridges or during dripping or jetting (McKinley 2005; Sharma et al. 2015). The characteristic behavior in DoS observed for Newtonian fluids (inviscid as well as viscous), power law fluids, and viscoelastic fluids are detailed elsewhere (Dinic, et al. 2017b; McKinley 2005). The inviscid Newtonian fluid response that is exhibited by low viscosity fluids, including water, which is used as the solvent in this study, is associated with formation of a conical neck. The thinning dynamics of inviscid fluids are described as an intertio-capillary response with a characteristic radius evolution $R \propto (t_p - t)^{2/3}$, where R is the thinnest radius of the neck, t is time and $t_p$ is the critical time for breakup. In contrast, the viscocapillary response shows a linear decrease in radius $R \propto (t_p - t)$ and is exhibited by the high viscosity Newtonian fluids. Radius evolution follows viscocapillary behavior for Newtonian fluids if the dimensionless viscosity, as characterized by Ohnesorge number, $Oh = \eta/(\rho \sigma R_0)^{1/2}$ ($\eta$ is the fluid viscosity, $\rho$ is the fluid density, and $\sigma$ is the interfacial or surface tension), is higher than unity (or $Oh > 1$). Addition of

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polymers dramatically changes the neck radius evolution, often leading to the emergence of the elastocapillary thinning dynamics that can be described using the following expression based on a theory developed by Entov and Hinch (1997):

$$\frac{R(t)}{R_0} \approx \left(\frac{G_E R_0}{2\sigma}\right)^{\frac{1}{3}} \exp\left[\frac{-t}{3\lambda_E}\right] \quad (2)$$

Here $G_E$ is an apparent extensional modulus, $\sigma$ is the surface tension, and $\lambda_E$ represents the extensional relaxation time. The extensional rate, $\dot{\varepsilon} = -2\dot{R}(t)/R(t)$, where R(t) represents the radius at time t, attains a nearly constant value during the elastocapillary regime, but the extensional strain progressively increases. In some cases, the radius evolution shows a third regime called the finite extensibility regime. The radius evolution in finite extensibility regime shows a viscocapillary thinning response; however, the effective viscosity is much higher than solution or solvent viscosity.

For the data analysis presented here, the interfacial tension of all solutions with air is assumed to be 62 mN/m. Several previous studies (Taylor et al. 2007; Okubo 1988) determined that highly charged polymer solutions do not display any dynamic adsorption. However, pendant drop tensiometry measurements carried out for aqueous solutions of lower molecular weight PAA (450 kg/mol) (that were utilized in a parallel rheometry study by Jimenez et al. 2018), interfacial tension decreases to values > 62 mN/m over the course of an hour or more. Thus, for all practical purposes, the dynamic adsorption effects are unlikely to influence both the neck thinning dynamics and the measured values of extensional relaxation time as filament thinning leading to pinch-off occur in less a second. The absolute value of surface tension affects the computed value of the transient extensional viscosity, but the effect is relatively marginal. The interfacial tension for salt solutions are assumed to be that of the salt solution with no polymer added, (Dutcher et al. 2010) as shown in Supplementary Information. The extensional viscosity $\eta_E$ value is extracted from the ratio of capillary stress $\sigma/R(t)$ and the extensional rate $\dot{\varepsilon} = -2\dot{R}(t)/R(t)$, which are both determined from the radius evolution data. Following the procedure outlined by Anna and McKinley, and others, (Anna et al. 2001; Miller et al. 2009) the elasto-capillary and finite extensibility regimes were both be fit using the following empirical equation:

$$\frac{R(t)}{R_0} = Ae^{-Bt} - Ct + D \quad (3)$$

Here A is related to the pre-factor in equation (2), $B = 1/3\lambda_E$ is inversely proportional to the longest extensional relaxation time, and C correlates with the steady, terminal extensional viscosity values measured in the finite extensibility regime.

**Results**

Shear Rheometry

Typical results comparing the shear ramps and steady shear measurements are shown in Figure 4. For polyelectrolyte solutions without salt, the shear rate ramps and steady shear data are similar, and show a rate-dependent response. However, upon the addition of salt, higher effective viscosity is observed for the steady shear measurements at relatively low shear rates ($< 10$ s$^{-1}$), and this is accompanied by increased standard deviations at these low shear rates which is also seen in Figures 5-7. Such hysteresis and relatively mild shear thinning response (power law index $< 0.3$) implies that HPAM may form aggregates in aqueous solution and that the deformation of aqueous salt solutions at high shear rates can disrupt these aggregates. (Arnolds et al. 2010; Tam et al. 1998).
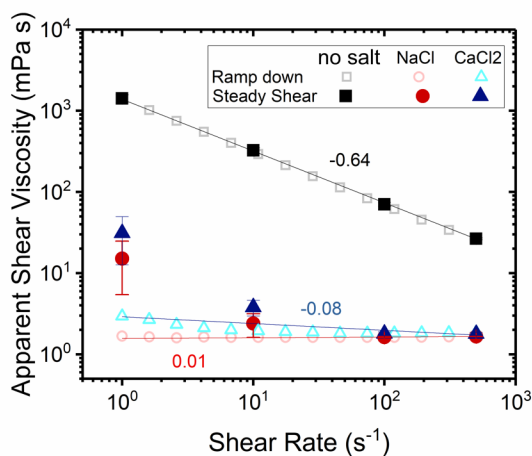


**Fig. 4** Comparison of steady shear data to shear ramps for polyelectrolyte solutions. Data shown from solutions of 0.3 wt% of 3330 in water with no added salt (squares), 0.435 M NaCl (circles), and 0.435 M CaCl$_2$ (triangles). All steady shear data (filled points) represent ensemble averages and the associated error bars represent one standard deviation of the combined viscosity values for all aliquots from the last 200 s of measurement. Ramp down data (open points) are from a representative single aliquot. Solid lines represent the lines of best fit of the steady shear data; nearby numbers indicate the corresponding slopes

Indeed, all the aqueous polyelectrolyte solutions investigated show a concentration-dependent increase in steady shear viscosity, as shown in Figures 5 and 6. The aqueous HPAM solutions display an apparent shear thinning behavior for the range of shear rates investigated, and the magnitude of the apparent shear viscosity agrees with the measurements reported elsewhere (Clarke et al. 2015; Huh et al. 2009; Jung et al. 2013; Sedaghat et al. 2013; Sheng 2011; Veerabhadrappa et al. 2013). For the lowest concentration included in Figure 5, a rate-independent response is measured at higher shear rates ($>100$ s$^{-1}$), which is again correlated with the disruption of aggregates at higher deformation rates.

The steady shear viscosity as a function of shear rate shows dramatic shear thinning in Figure 5 as well as Figure 6. The measured shear viscosity decreases with decrease in molecular weight. Polymers with lower reported molecular weight show a lower shear viscosity at all shear rates investigated here. The polymers 3330 and 3230 display similar power law behavior ($n = 0.362$ and $n = 0.391$, respectively). On the other hand, 3130 displays higher power law exponent ($n = 0.844$).
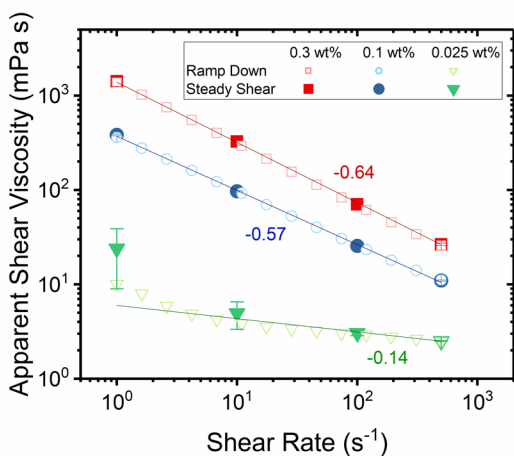


**Fig. 5** Effect of polymer concentration on the shear viscosity of aqueous polyelectrolyte solutions. All data is from aqueous solutions of 0.3 wt% (squares), 0.1 wt% (circles), and 0.025 wt% (triangles) of 3330 with no salt. All steady shear data (filled points) represent ensemble averages; error bars represent one standard deviation of the combined viscosity values for all aliquots from the last 200 s of measurement. Note that ramp down data (open points) are from a representative single aliquot. Solid lines indicate the lines of best fit for the steady shear data; nearby numbers indicate the corresponding slope
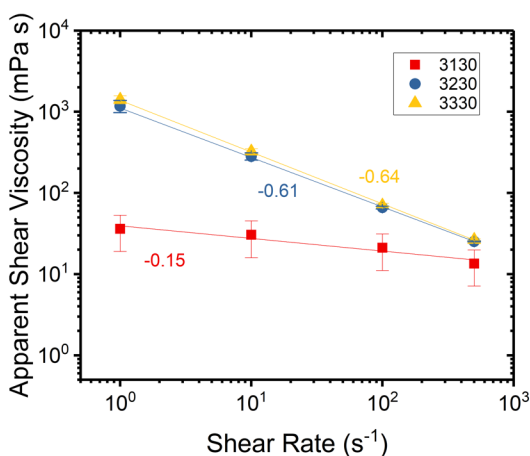
**Fig. 6** Effect of polymer molecular weight on the shear viscosity of polyelectrolyte solutions. All data is from aqueous solutions containing 0.3 wt% of polymer: squares (3130), circles (3230), triangle (3330); all solutions contain no added salt. All points represent ensemble averages; error bars represent one standard deviation of the combined viscosity values for all aliquots from the last 200 s of measurement. Solid lines represent lines of best fit; numbers indicate corresponding slopes

Upon the addition of monovalent salt to polymer solutions, the magnitude of steady shear viscosity decreases at the shear rates investigated as shown in Figure 7. The steady shear viscosity shows a pronounced shear thinning response for low salt concentrations ($c_s <$ 0.435 M NaCl) in the shear rate range shown in Figure 7. However, at $c_s >$ 0.435 M NaCl, the solutions show rate-independent viscosity at higher shear rates ($\geq$ 100 s$^{-1}$), while at lower shear rates ($\leq$ 10 s$^{-1}$) the solutions exhibit shear thinning response. Figure 7b also shows a comparison of the shear viscosity values obtained at a nominally high shear rate of 500 s$^{-1}$; the comparison illustrates the apparent non-monotonic concentration-dependent shear viscosity values for polyelectrolyte solutions at shear rates solutions may encounter in EOR applications. The high shear rate viscosity values decrease with added salt up to concentration of approximately 0.5M NaCl, beyond which the values increase again.
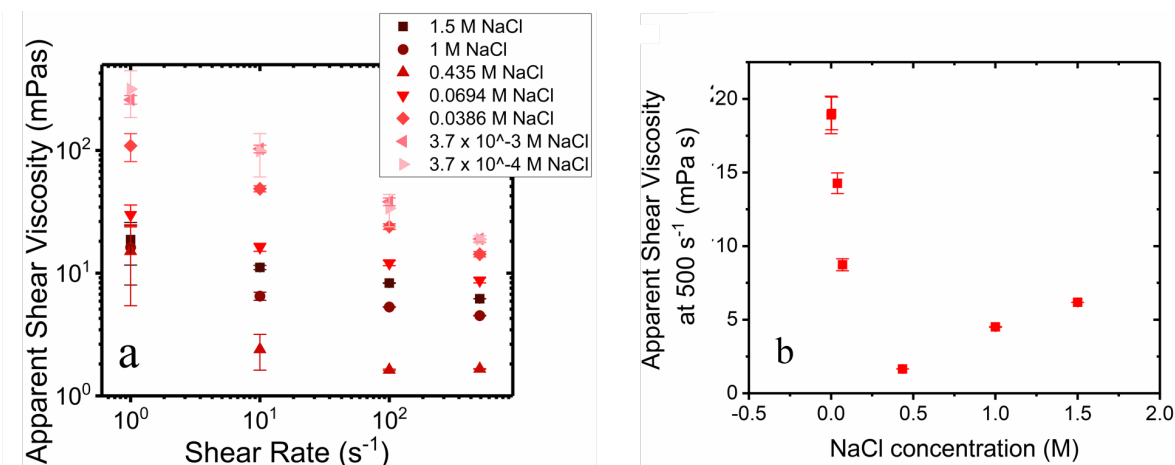
**Fig. 7** Effect of monovalent salt concentration on shear viscosity of aqueous polyelectrolyte solutions. (a) Data is from solutions containing 0.3 wt% of 3330 and $3.7 \times 10^{-4}$ (light) to 1.5 M NaCl (dark). (b) Shows the data from (a) at 500 s$^{-1}$ as a function of monovalent salt concentration. All points represent ensemble averages; error bars represent one standard deviation of the combined viscosity values for all aliquots from the last 200 s of measurement

The effect of divalent cations on the steady shear viscosity behavior as a function of shear rate is shown in Figure 8a, and the absolute value of shear viscosity is compared to that of monovalent salt in Figure 8b. The presence of $CaCl_2$ led to a significant decrease in the rate-dependent viscosity in comparison to both salt-free solutions and the solutions with the same molar concentration of NaCl. This can be attributed to more effective screening caused by the higher charge of calcium ions, as well as the possibility of a higher degree of intra- and inter-chain association. The steady shear viscosity behavior shows a rate-independent behavior at high shear rates even though shear thinning response is observed at low shear rate values for solutions with a $CaCl_2$ concentration above 0.0694 M. Similar behavior is observed for the NaCl solutions above a higher critical salt concentration (0.435 M). While other studies reported precipitation upon the addition of divalent salts (Huh et al. 2009; Rashidi et al. 2010), neither precipitation nor coacervation was observed for the solutions studied here, even after days without agitation. When considering the behavior of solutions as a function of salt concentration, an increase in effective viscosity at the highest divalent salt concentrations is observed. For both NaCl and $CaCl_2$, shear viscosity values measured at nominal high shear rate of 500 s$^{-1}$ show non-monotonic dependence on the ionic strength of the solutions, as shown in Figure 8b.
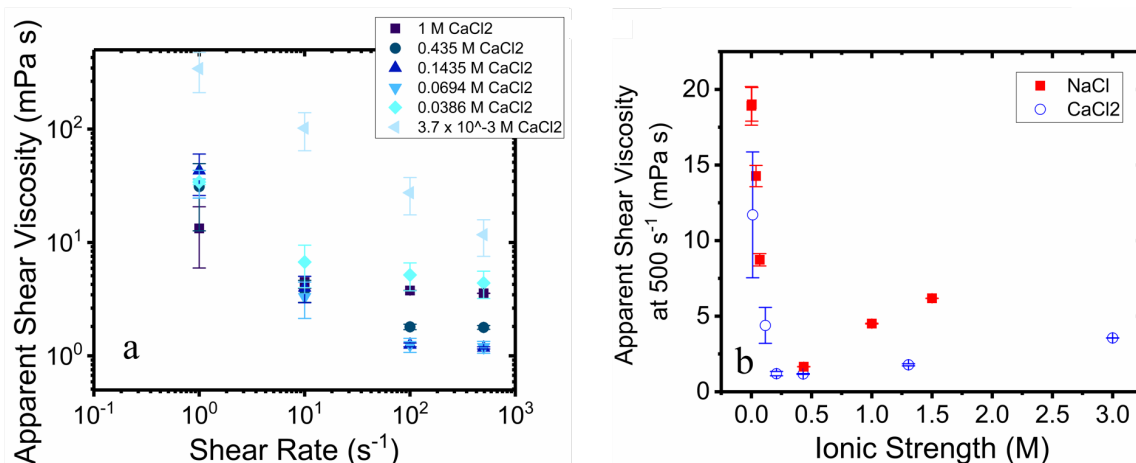
**Fig. 8** Effect of divalent salt concentration on shear viscosity of aqueous polyelectrolyte solutions. (a) Data are from solutions containing 0.3 wt% of 3330 and $3.7 \times 10^{-3}$ (light) to 1 M $CaCl_2$ (dark). (b) Comparison of shear viscosity as a function of concentration of NaCl (filled squares) and $CaCl_2$ (open circles). All points represent ensemble averages; error bars represent one standard deviation of the combined viscosity values for all aliquots from the last 200 s of measurement

Extensional Rheometry

DoS rheometry relies on visualization and analysis of neck thinning dynamics, and the sequence of images included Figure 9a-d show the typical neck shapes observed for the HPAM solutions. The radius evolution data is plotted in Figure 9e and shows three distinct regimes: a sharp transition point separates the inertio-capillary regime from the elastocapillary regime. On a semi-log plot the radius evolution in elastocapillary regime appears as linear, and an additional last regime, known as the finite extensibility regime, can be observed in several cases.
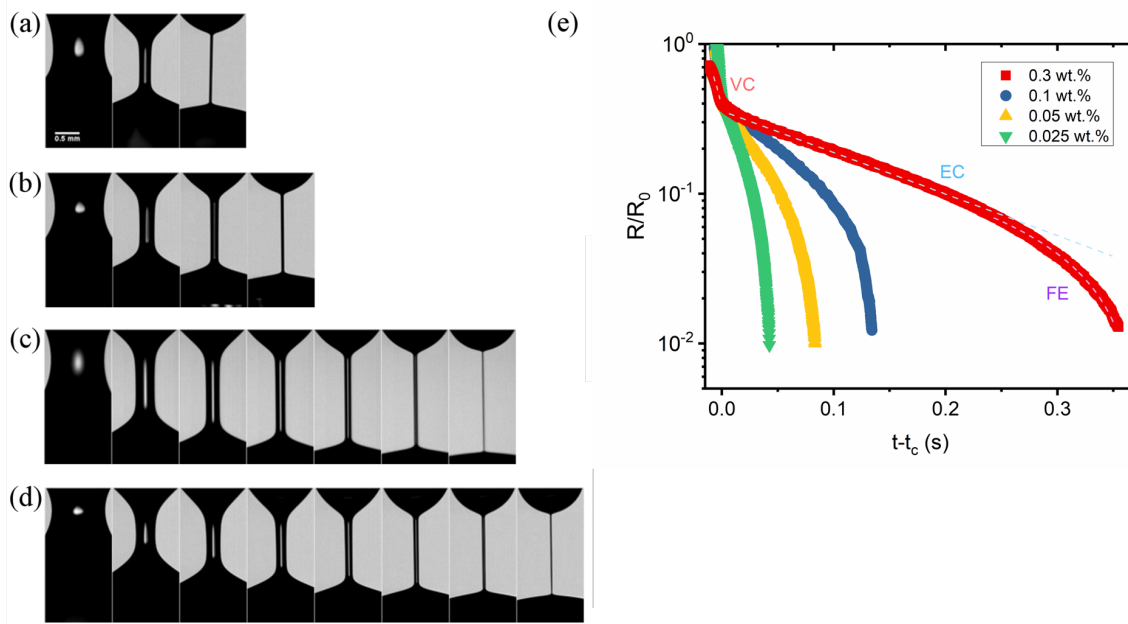
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**Fig. 9** Radius evolution over time for aqueous polyelectrolyte solutions obtained using DoS Rheometry. Image sequences (a) – (c) 25 ms apart show slender, cylindrical neck shapes for solutions of 0.025%, 0.05% and 0.1 wt% of 3330 in water with no salt, respectively, and the image sequence in (d) has time step of 50 ms for a solution of 0.3 wt% of 3330 in water. (e) Corresponding radius evolution plots show that concentration dependent variation in both shape of the curves and pinch-off time. As the solution viscosity is relatively high, the data shows an initial visco-capillary region, followed by an elastocapillary region (EC) and before pinch-off, the finite extensibility (FE) regime can be observed

The effect of polymer molecular weight and concentration on the extensional relaxation time extracted from the elastocapillary regime in radius evolution data shown in Figure 10. Increase in polymer concentration leads to longer relaxation times for the three polymer molecular weights considered, and the extensional relaxation time increases with molecular weight. The extensional relaxation times measured here are 1-30 ms, and as these values are quite short, such measurements are not possible on CaBER, the commercially-available extensional rheometer that requires more than 50 ms to set-up the liquid bridge (Dinic et al. 2015; Rodd et al. 2005).
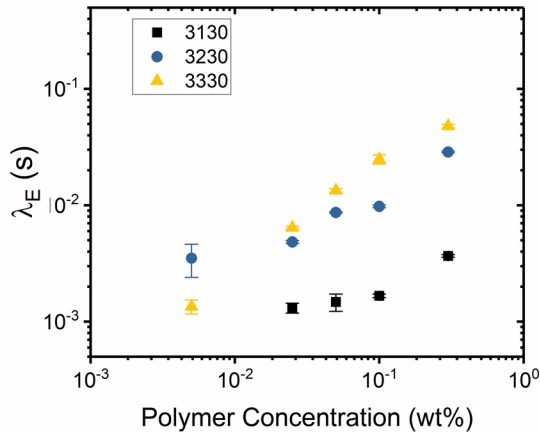
**Fig. 10** Extensional relaxation time as a function of polymer concentration for solutions of FLOPAAM with three different molecular weights water with no salt. Data are extracted from radius evolution data and represent averages; error bars represent one standard deviation. The extensional relaxation time increases with both concentration and molecular weight

As briefly discussed in the methods section, the value of extensional viscosity is calculated from the ratio of capillary stress to the extensional rate. Capillary stress is calculated as $\sigma/R(t)$ where $\sigma$ is the surface tension and R is the neck radius. The extensional rate, $\dot{\varepsilon}$, is computed using $\dot{\varepsilon} = -2\dot{R}(t)/R(t)$. Upon careful examination of this this method and Equation 2, it becomes clear that increasing extensional relaxation time leads to increasing extensional viscosity and therefore the results in Figure 10 indicate that the extensional viscosity increases with increasing polymer molecular weight. The concentration-dependent increase in extensional viscosity for polyelectrolyte solutions can be observed in Figure 11. The elastocapillary regime provides a measurement of the transient extensional viscosity as a function of Hencky strain, whereas the finite extensibility region provides a measure of rate-independent, strain-independent steady, terminal extensional viscosity. All polyelectrolyte solutions display strain-hardening, or increasing viscosity with increasing extensional strain. The extensional viscosity was found to be several orders of magnitude higher than the shear viscosity and increases with increasing polymer molecular weight. Both transient and steady, terminal extensional viscosity increase with molecular weight and concentration, and display values that are directly proportional to extensional relaxation time, in agreement with literature data (Dinic et al. 2017a; Jimenez et al. 2018).
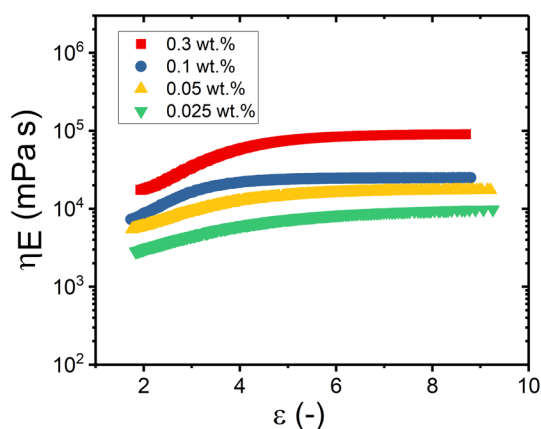
**Fig. 11** Extensional viscosity of polyelectrolyte solutions as a function of Hencky strain. Solutions show strain hardening with increasing polymer concentration. Solutions with higher polymer concentrations have higher extensional viscosities. All data shown is from solutions of 3330 in water with no salt. Curves are from one drop of each solution

The presence of either monovalent or divalent salt results in a decrease in both extensional relaxation time and transient extensional viscosity as shown in Figure 12, and the polyelectrolyte solutions with salt are also strain hardening like their counterparts without salt. Consistent with shear rheometry results, solutions containing higher concentrations of NaCl (1 M) have a lower transient extensional viscosity than solutions with a lower concentration of NaCl (0.0386 M). Further, the solutions containing 1 M of $CaCl_2$ have longer relaxation times than solutions containing 1 M of NaCl. Of special note are the extremely long strains to which the solution with 1 M $CaCl_2$ persists in the elasto-capillary regime. The polyelectrolyte solutions in presence of salt are also strain hardening, quite like the salt-free solutions; however, the terminal extensional viscosity values are lower. The data show that an increase in polymer concentration for a fixed concentration of salt leads to an increase in both extensional relaxation time and extensional viscosity. However, even though the presence of salt ions in the solution decreases the extent of electrostatic stretching leading to a decrease in extensional viscosity, the divalent salt data illustrates the importance of the role played by multivalent ions in promoting formation of stronger interchain interactions.
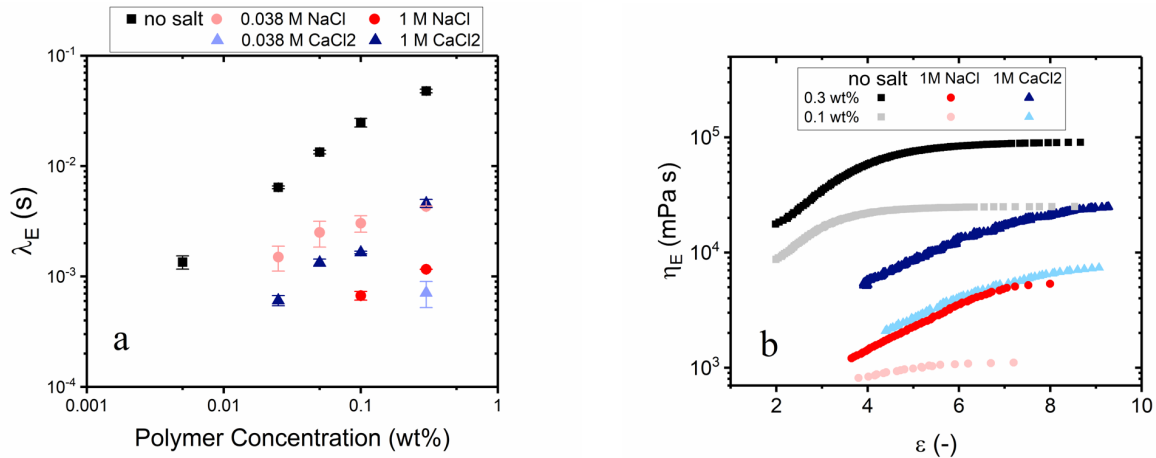
**Fig. 12** Effect of salt and polymer concentration on extensional relaxation time and viscosity. All data shown is from solutions of 3330. Some data not shown because solutions did not display elasto-capillary behavior. Points in (a) are averages of data from multiple drops; curves in (b) are data from a single representative drop

## Discussion

Shear Rheometry

The weak power law response ($n < 0.3$) displayed by steady shear viscosity as a function of shear rate suggests presence of aggregates. Though shear thinning response arises for high molecular weight polymer and polyelectrolyte solutions typically the power law index is higher ($n > 0.6$). The very different power law index observed for solutions of 3130 may indicate that there are other additives in the polymer that were not removed, as the polymer was not purified. The onset of shear thinning can be used for defining a shear relaxation time (Colby et al. 2007, Boris and Colby 1998; Colby 2010; Dobrynin et al. 1995; Jimenez et al. 2018), and for semi-dilute polyelectrolyte solutions, as the shear relaxation time decreases with concentration, the critical shear rate at the onset of shear thinning regime can increase with concentration. Based on the extensional relaxation time data that shows typical values around 1ms, the shear thinning regime is not observed for the shear rate range measured.

The change in solution behavior on the addition of salt, shown in Figure 7, shows trends expected for aqueous polyelectrolyte solutions. Effective shear viscosity is reduced from that in water without salt and shear thinning behavior is maintained, although at high salt concentrations, a

Newtonian plateau is observed at high shear rates (> 100 s$^{-1}$) The negative charges on the HPAM chains repel each other, causing the polymers to adopt an extended conformation. The increase in the concentration of ions due to the dissolved salt leads to progressive screening of charge. This lowers the repulsion between the charges, lowering the hydrodynamic volume of each polyelectrolyte chain, thus decreasing their degree of overlap and consequently decreasing the viscosity of the solution, consistent with what is observed here.

In this work, the apparent viscosity computed at 500 s$^{-1}$ first decreases, then increases with increase in concentration of added monovalent as well as divalent salt as shown in Figure 7 and 8. Such non-monotonic viscosity variation with monovalent salt concentration could be result of several factors, including the relatively high concentration of polyelectrolyte used (for in entangled regime, high salt leads to increase in solution viscosity), and the possibility of extra interchain interactions including hydrogen bonding promoted by the high degree of screening at high salt concentration (Rashidi et al. 2010; Wyatt et al. 2011; Wyatt and Liberatore 2010). At higher divalent salt concentrations, the divalent cations may complex to the negative charges on the polyelectrolyte chain (Chremos and Douglas 2016), potentially forming ionic bridges that can act as transient crosslinks between charges on two different polyelectrolyte chains (intermolecular complexation) or within the same chain (intramolecular complexation).

Whether the calcium ions complex intermolecularly or intramolecular may depend on the molecular weight and percent hydrolysis of the HPAM as well as the concentration of calcium in solution (Francois et al. 1997; Huber 1993; Peng and Wu 1999; Schweins and Huber 2001; Ward and Martin 1981). The non-monotonic behavior may be due to a transition between intramolecular bridges at low calcium concentration and intermolecular bridges at high calcium concentration. Additionally, the chloride ions also contribute to screening. Since calcium chloride has twice as much chloride on a molar basis than sodium chloride, the screening effect of the chlorides alone is much greater for solutions with CaCl$_2$ than NaCl. This higher amount of screening would promote closer polymer-polymer interactions, which may also lead to increased viscosity at high added salt concentration (as described above).

Additionally, the trends illuminated here may be generally applicable to other monovalent and divalent salts; however, variations are expected for different monovalent and divalent salts. Specifically, ion size and hydrated ion radius will have a large impact on the results. As detailed

in Wyatt and Liberatore 2010, in solutions of different salts, the replacement of counterions by a counterion of a different size may occur. In highly concentrated polymer solutions in which the polymer chains are close to one another due to the increased screening of the chains caused by the high salt concentration, this change in counterion size could have a noticeable effect. For example, should the introduced counterions from the salt solution be larger than the previous counterions (in the case of poly(acrylic acid) and not poly(sodium acrylate) this would be the case universally), the added volume may force the polymer coils to expand.

Extensional Rheometry

The increase in the value of extensional relaxation times with increase in polymer concentration in salt-free solutions, shown in Figure 10, is consistent with the shear data reported here and with similar extensional data reported recently by Jimenez et al. (2018) for polyelectrolyte solutions made with both poly(acrylic acid) and sodium poly(styrene sulfonate). The transient extensional viscosity plots as function of extensional strain show a pronounced strain-hardening. It is well established that polymer coils are only weakly perturbed in shear flow, whereas stretching and orientation in response to high extensional rate, can lead to coil –stretch transition, and even full unraveling of chains in the finite extensibility limit.

In the semi-dilute regime, the shear relaxation time decreases with concentration for unentangled polyelectrolytes, but increases with concentration in the entangled regime. The corresponding scaling law that describes the concentration-dependent shear relaxation time (extracted from shear rheology measurements) is correlated with the concentration-dependent behavior of the correlation blobs. In the case of neutral polymers, chains stretched by hydrodynamics in the semi-dilute regime show a stronger concentration dependent increase in extensional relaxation time, as stretching increases the degree of overlap, as well as screening of excluded volume and hydrodynamic interactions (Dinic et al. 2017a).

The extensional rates generated with the thinning necks are relatively high ($>10^3$ s$^{-1}$). Therefore, the polymers studied here may stretch during extension, disrupting the hydrogen bonds between polymer chains that cause the increase in shear viscosity shown in Figure 7. Additionally, this stretch would disrupt any inter- or intramolecular coordination by calcium ions. The increase in extensional relaxation time at higher calcium concentration, shown in Figure 12a, is approximately

one order of magnitude. Compared to the increase in shear viscosity at higher calcium concentrations shown in Figure 8b, which is within one order of magnitude, this increase during extension suggests that there is a mechanism opposing the stretch of the polymers that is not present (or weak) when shear forces are applied. Taking these differences into consideration, we suggest that the calcium ions in solution are replacing some of the sodium ions as counterions on the polyelectrolyte and that these calcium ions are coordinating negative charges along the polymer chain to each other, either within the same chain or between different chains.

Application to Enhanced Oil Recovery

The results support the widespread use of HPAM in EOR. The shear thinning nature of the solutions is beneficial during pumping and transportation of the solutions. Simultaneously, in the extensional flow fields encountered in porous media, the strain hardening behavior of the solutions would promote higher oil recovery by increasing the capillary number and dislodging more trapped oil droplets out of pores. In the past, it been an open question if the apparent benefits of utilizing HPAM in EOR are negated by the presence of salt or hard water (high calcium concentration). The results in this study show that the addition of salt, either monovalent or divalent, leads to a reduction in both shear and extensional viscosity. Despite this reduction, the shear thinning and strain hardening behavior remains in the presence of salt, even calcium, ions. Therefore, it is believed that even in high salinity and high hardness, solutions of HPAM would maintain the properties that are beneficial to EOR: shear thinning and strain hardening.

**Conclusions**

The behavior of polyelectrolytes in aqueous solutions with and without added salt has been investigated through shear and extensional rheology. It has been shown that while monovalent and divalent salts both decrease the shear and extensional viscosities of solutions from those without added salts, the effect of the concentration of salt differs between monovalent and divalent salts. The trend with monovalent salts is consistent with previously reported data; higher concentrations of monovalent salt screen negative charges on the polyelectrolyte backbone more effectively. Divalent cations may form transient complexes with the polyelectrolyte chain, causing higher extensional viscosity at high divalent salt concentrations. These features make these solutions attractive for enhanced oil recovery, both when considering fluid transport and behavior in the oil

basin. In addition to the application to EOR, this study furthers the understanding of polyelectrolyte-ion interactions that may can be applied to a wide variety of functions.

## Acknowledgements

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