Investigation of Brine pH Effect on the Rheological and Viscoelastic Properties of HPAM Polymer for an Optimized Enhanced Oil Recovery Design

Mariam Shakeel, Peyman Pourafshary,* and Muhammad Rehan Hashmet

ABSTRACT: A novel approach to improve viscous and viscoelastic properties by exploiting the pH and salinity sensitivity of HPAM polymer is proposed in this paper. Polymer flooding is a well-developed and effective enhanced oil recovery technique. The design of the makeup brine is one of the most critical phases of a polymer flood project, since the brine composition, salinity, and pH directly influence the polymer viscosity and viscoelasticity. However, the viscoelastic properties of hydrolyzed polyacrylamide polymers have not been given much consideration during the design phase of polymer flood projects. Our experimental study focuses on the optimization of the makeup water design for polymer flooding by evaluating the optimum solution salinity and pH for better stability and improved viscoelastic behavior of the polymer. Initially, the brine salinity and ionic composition is adjusted and then hydrolyzed polyacrylamide (HPAM) polymer solutions of varying pH are prepared using the adjusted brine. Rheological experiments are conducted over a temperature range of 25–80 °C and at different aging times. Polymer thermal degradation as a function of pH is assessed by examining the solutions at 80 °C for 1 week. Amplitude sweep and frequency sweep tests are performed to determine the viscoelastic properties such as storage modulus, loss modulus, and relaxation time. A 15–40% increase in the polymer solution viscosity and a 20 times increase in relaxation time is observed in the pH range of 8–10 in comparison to the neutral solution. This can be attributed to the low-salinity ion-adjusted environment of the makeup brine and further hydrolysis and increased repulsion of polymer chains in an alkaline environment. These results indicate that the viscoelastic properties of a polymer are tunable and a basic pH is favorable for better synergy between the brine and the polymer. Alkaline low-salinity polymer solutions have exhibited 60% higher thermal stability in comparison to acidic solutions and thus can be successfully applied in high-temperature reservoirs. The results of this study show that polymer solutions with an optimum pH in the basic range exhibit a higher viscoelastic character and an increased resistance toward thermal degradation. Hence, the polymer solution salinity, ionic composition, and pH should be adjusted to obtain maximum oil recovery by the polymer flooding method. Finally, this study shows that more effective polymer solutions can be prepared by adjusting the pH and designing a low-salinity water/polymer recipe to get the additional benefit of polymer viscoelasticity. The optimized low-salinity alkaline conditions can reduce the residual oil saturation by stronger viscous and viscoelastic forces developed by more viscous polymers. The findings of this study can be employed to design an optimum polymer recipe by tuning the brine pH and salinity for maximum incremental oil recovery, particularly in high-temperature and high-salinity formations.

INTRODUCTION

Chemical-enhanced oil recovery (CEOR) techniques such as polymer flooding (PF), surfactant flooding (SF), and alkali—surfactant—polymer flooding (ASP) have been extensively utilized for decades to improve sweep and displacement efficiencies and recover residual oil. In a laboratory study, the oil recovery was improved by reducing the mobility ratio in both homogeneous and heterogeneous rock samples. Similarly, during an ASP project in the Daqing oil field, the addition of a polymer helped to achieve a viscosity ratio of above 2 between water and oil and resulted in 20% additional oil recovery. The basic principle in polymer flooding is the reduction of the mobility ratio by the addition of a polymer to the displacing phase, which is normally brine. Polymers are macromolecules comprised of long flexible chains that impart

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certain properties to these molecules such as elasticity, viscosity, and toughness. The two types of polymers used widely in the petroleum industry are biopolymers and synthetic polymers.

In addition to shear deformation, a complicated viscoelastic behavior is exhibited by synthetic hydrolyzed polyacrylamide (HPAM) polymers due to their flexible chain structure, resulting in an increased resistance during flow through porous media. The viscoelastic effect of synthetic polymers is characterized specifically by the shear-thickening regime, during which the extensional flow is dominant and the apparent polymer viscosity increases with shear rate. Polymer chain stretching and intermolecular interactions of the elongated coils lead to shear-thickening behavior. Extensional flow exists in porous media when a polymer solution passes through pore throats and constrictions, aligning the molecules and stresses in the direction of flow. Such viscoelastic effects can cause injectivity issues but can also reduce residual oil saturation.

Although there are different parameters and methods in the literature to quantify a polymer’s viscoelastic effect and resulting residual oil recovery, such as Deborah number, strain hardening index (SHI), relaxation time, screen factor, and continuum viscoelastic models, there exist contradictory studies in which no reduction in $S_{or}$ was observed by viscoelastic polymers from different Berea and Bentheimer cores.

Several studies have reported additional oil recovery and reduction in $S_{or}$ beyond waterflooding by viscoelastic polymers. A microfluidic study conducted by Xia et al. showed that more oil was displaced by a viscoelastic HPAM polymer in comparison to inelastic glycerin flooding. Coreflood experiments carried out by Wang et al. on Daqing oilfield cores showed that 5–8% more incremental recovery of residual oil was realized by injecting viscoelastic polyacrylamide polymer in comparison to an inelastic glycerin solution. Qi et al. performed coreflood experiments on Bentheimer sandstone cores and observed 5% reduction in $S_{or}$ by viscoelastic HPAM polymer flooding in comparison to a viscous glycerin flood at a constant pressure drop. In another study, a 6% reduction in $S_{or}$ was observed by low-salinity viscoelastic polymer flooding. The reduction in $S_{or}$ by viscoelastic polymers can be triggered by various mechanisms, including but not limited to shear-thickening behavior, oil-thread stabilization, and pulling and stripping of oil from pore walls. In contrast to Newtonian fluids, the velocity profile of a viscoelastic solution has a smooth front within the pore spaces and the velocity gradient increases closer to the pore walls. As a result, the viscoelastic fluid has a better capability to strip off the oil layer from the walls in comparison to a Newtonian fluid.

The sensitivity of HPAM polymers viscosity toward brine salinity and pH is a well-documented problem. Several studies have shown a detrimental effect of high salinity and divalent ion concentration on the polymer’s viscosity. However, the effect of pH on the viscous and viscoelastic properties of hydrolyzed polymers has not been studied in detail, despite pH being one of the critical design parameters for a polymer flooding project. This can be attributed to the fact that the contribution of the polymer’s viscoelastic character in reducing $S_{or}$ is still not universally accepted, and thus, the viscoelastic properties of the polymer have not been given much consideration during the design phase. The goal of the present study is to demonstrate how an optimum polymer solution can be designed by studying both the viscous and elastic behaviors of the polymer and adjusting the brine parameters to achieve the maximum viscous and elastic contributions simultaneously. The incremental oil recovery realized as a result of the improved design process proposed in this study can be considerably higher than that obtained by following a traditional design process. Figure 1 schematically illustrates the problem at hand: that is, a higher residual oil saturation by conventional polymer flooding in comparison to a considerably lower residual oil saturation by a viscoelastic polymer flood.

The design of the makeup brine has a strong influence on the viscosity and viscoelasticity of the resulting HPAM polymer solution. The brine salinity, ionic composition, hardness, and pH are among the major controlling factors for a successful polymer flooding design. Various studies have shown an increase in the viscous and viscoelastic behavior of HPAM polymers by lowering the salinity and tuning the ionic composition of the makeup brine. In the rheological study performed by Gao, 10 times increment in the viscosity of HPAM 3100 was observed by reducing the brine salinity from 2 wt % to 0.1 wt % at 50 °C. Similarly, Lee et al. showed around a 16% increase in HPAM Flopaam 3330S viscosity, when a low-salinity makeup brine containing 1000 ppm of SO$_4^{2-}$ ions was used in comparison to brine having 1000 ppm of Ca$^{2+}$ ions. Vermolen et al. performed oscillatory frequency sweep tests for a high-molecular-weight HPAM polymer over a wide range of concentrations and salinities. To quantify the effect of salinity on polymer viscoelasticity, the relaxation time was determined for each scenario. The results showed a 1 order of magnitude increase in relaxation time with a 10 times reduction in brine salinity, indicating a higher viscoelastic effect in low-salinity water.

In addition to brine salinity and composition, the pH of the makeup brine also has a strong influence on the viscous and viscoelastic properties of HPAM. In general, the viscosity of the HPAM polymer is lower in acidic brines and the viscosity increases as the brine pH increases toward neutral. A study performed by Huh et al. showed an increase in the viscosity of Flopaam 3330S polymer solution increased from 18 to 200 cP as the brine pH increased from 2 to 10 at a shear rate of 10 s$^{-1}$. Hence, both the salinity and pH of the makeup water must be critically designed in order to achieve the best performance from polymer flooding. However, the effect of pH on HPAM viscoelastic properties has not been studied in detail. There is no systematic study in the literature for the design of makeup brine salinity and pH for an optimum polymer flooding design.

A number of studies are available in the literature pertaining to the effect of salinity on the viscosity and viscoelasticity of...
HPAM polymer. However, there are only a few to no detailed studies discussing the combined effects of brine salinity, ionic composition, and pH on the viscoelastic and viscous properties of HPAM polymer. The experimental work presented in this paper has its novelty in being the first systematic and integrated study to evaluate and enhance the viscosity and viscoelasticity of HPAM polymer by sensitizing the critical makeup brine parameters (salinity, ionic composition, and pH). The findings of this study can be extremely helpful for the best design of a polymer flood project that will target both the volumetric and microscopic sweep efficiencies under extreme and challenging reservoir conditions.

In a previous work by our team, an optimum brine salinity and ionic composition was designed for HPAM FS115 on the basis of an extensive rheological study. Among four different HPAM polymers tested in the study, HPAM FS115 showed the maximum viscosity retention and highest resistance to thermal and mechanical degradation for a period of over 100 days. The same polymer was also used in an experimental study for polymer flooding design for the Hebron field located in Canada. FS115 provided the highest incremental oil recovery from sandstone core plugs of the Ben Nevis formation at a reservoir temperature of 62 °C. In view of the promising results of HPAM FS115, we decided to use it for this research. The objective of the current study is to assess the pH effect of the previously designed makeup brine on the rheological and viscoelastic properties of HPAM FS115 polymer and identify an optimum pH range to get the maximum benefit from the optimally designed polymer flooding technique.

The study follows a systematic theme. First, the methodology is presented for shear characterization and viscoelastic characterization of polymer solutions of varying pH. The results of both phases are presented, and important parameters such as thermal degradation, relaxation time, and loss factor for each case are calculated. The obtained results are discussed in light of the possible mechanisms for the observed trends, and the optimum brine recipe for the polymer under study is recommended. The main advantages and potential limitations of the study are presented next. Finally, the study is concluded with a summary and recommendations for future work.

### METHODOLOGY

The HPAM Flopaam S115 (FS115) polymer rheological and viscoelastic properties as a function of pH were estimated, and an optimum pH was studied. The materials used and the experimental procedure that was followed are presented in this section.

**Polymer Solution Preparation.** The rheology and viscoelasticity are greatly affected by the ionic composition and pH of the makeup brine. To study the effect of these parameters on HPAM FS115, a systematic rheological study was performed in two stages. In the first stage, the brine salinity and ionic content was adjusted to achieve the optimum viscofying behavior of the polymer. The results of the first stage have been reported elsewhere. In the final stage of the study, the pH of the brine was adjusted to determine an optimum pH range for the best viscous and viscoelastic behavior. To prepare polymer solutions, the ion-adjusted low-salinity brine from a previous study was used as the makeup brine. The ion-adjusted water was prepared by a 10 times dilution of South Caspian seawater (CSW) and spiking it with SO₄²⁻, Ca²⁺, and Mg²⁺ ions by 6 times, 3 times, and 1 time, respectively. The reason for selecting this makeup brine recipe is its compatibility with the polymer to be used in this work. The selected brine has also shown a better viscofying ability of the polymer under high-temperature conditions in a previous study. HPAM Flopaam S115 polymer was used in this study, which is a sulfonated hydrolyzed polyacrylamide polymer manufactured by SNF Floerger. The chemical structure of FS115 is depicted in Figure 2.

![Figure 2. Chemical structure of sulfonated polyacrylamide polymer.](https://pubs.acs.org/doi/10.1021/acsomega.2c00699)

**Table 1. Chemical and Physical Properties of FS115**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>acrylamide/ATBS/acrylic acid</td>
</tr>
<tr>
<td>Degree of hydrolysis</td>
<td>25%</td>
</tr>
<tr>
<td>Molecular wt</td>
<td>12 × 10⁶ g/mol</td>
</tr>
</tbody>
</table>

To prepare the ion-adjusted makeup brine, appropriate amounts of different salts were mixed in distilled water using a magnetic stirrer. Polymer solutions were prepared by weighing the required amounts of dry polymer to prepare solutions with known concentrations. The API standard procedure recommended for polymer solution preparation was followed. The aqueous solution was stirred at a constant speed of 600 rpm to obtain 70% vortex, and then the dry polymer was added at the vortex shoulder within 30 s. The solution was then stirred at a low speed of 100 rpm for 6–8 h and was left overnight to achieve complete hydration and dissolution of the polymer in the brine. These steps are necessary to avoid fish eyes formed by agglomeration of polymer molecules and to ensure the proper hydration of polymer in the solution. Polymer solutions of 1500, 3000, and 4500 ppm concentration were prepared using ion-adjusted water as the makeup brine. The study is subdivided in two sections which are discussed below.

**Polymer Shear Characterization.** The objective of the rheological experiments is to assess the effect of polymer concentration, temperature, aging time, and pH on FS115 viscosity. The pH of the solutions was adjusted to 2, 4, 6, 8, 10, and 12 using hydrochloric acid (HCl) as the acid and sodium hydroxide (NaOH) as the base to cover the acidic, basic, and neutral ranges. An Anton Paar MCR 301 rheometer with a plate–plate geometry was used for the measurement of different rheological and viscoelastic parameters, as shown...
The study was also performed on 1500 ppm concentration solutions of different pHs by placing them in the oven at 80 °C and measuring the viscosity at different aging times. To measure the viscosity, around 1 mL of the sample was placed on the rheometer plate by a pipet and the steady shear profiles were obtained over a shear rate range of 1−100 s⁻¹.

**Polymer Viscoelastic Characterization.** This stage of the study was designed to assess if F5115 had viscoelastic characteristics or not. To study the viscoelastic behavior, oscillatory rheological tests, namely amplitude sweep tests (ASTs) and frequency sweep tests (FSTs), were performed. An AST is performed by a stepwise increment in measuring system deflection while the angular frequency is kept constant. In contrast, the shear strain rate is kept constant during an FST while the angular frequency is varied in steps. The frequency sweeps are used to evaluate the time-dependent properties of a material such as elasticity within a linear viscoelastic region (LVER).

All oscillatory rheological experiments were performed at 25 °C. Amplitude sweep tests were conducted for pH 6 solutions with three different polymer concentrations (1500, 3000, and 4500 ppm) to determine the storage modulus (G’) representing the elastic component of the polymer structure and the loss modulus (G’’) indicating the viscous component. The angular frequency (ω) was set at 10 rad/s, and the shear strain rate (γ) was varied from 1% to 1000%. The main objective of this test was to obtain the limit of the LVER and select the value of constant shear strain within the LVER to perform subsequent FSTs for solutions under study. The LVER indicates the range in which the test can be conducted without damaging the polymer structure and is indicated as the region in an AST within which G’ and G’’ remain fairly stable. In the next step, frequency sweep tests were conducted for different pHs (2, 4, 6, 8, 10, and 12) and polymer concentrations (1500, 3000, and 4500 ppm) to determine the relaxation times. For FST, a constant shear strain rate of 5% within the LVER was used as identified from amplitude sweeps and the angular frequency range was set from 0.1 to 100 rad/s to cover both high and low frequencies. The relaxation time is a quantitative measure of a polymer’s viscoelastic character and is measured by taking the reciprocal of angular frequency values at the crossover point where the elastic modulus G’ and the viscous modulus G’’ intersect, as shown in Figure 4.

The formula used for calculation of relaxation time is given in eq 1.22 The relaxation time represents the elastic behavior of HPAM polymers. The longer the relaxation time, the higher the elastic nature of the polymer. The data were interpreted to quantify the effect of pH on the polymer rheology and its viscoelastic behavior.

\[
\text{relaxation time} = \frac{1}{\omega_{G', G''}}
\]

### RESULTS AND DISCUSSION

This section discusses the results of the HPAM F5115 polymer rheology and viscoelastic behavior as a function of pH. The objective of this rheological study is to design the best makeup water in terms of pH to achieve the most effective performance of the polymer to change both macroscopic and microscopic sweeps. The idea of this task was to assess the pH effect on the synthetic HPAM polymer being used in the study and select an optimum pH range for the best performance of the polymer in terms of both viscous and viscoelastic properties. The results are discussed herein.

**Shear Characterization.** To characterize the viscous behavior of F5115, the shear rate–viscosity profiles were obtained under different conditions of polymer concentration, pH, and temperature.

**Effect of pH on Viscosity.** The viscosity for 1500 ppm polymer solutions of pH 2, 4, 6, 8, 10, and 12 were measured at 25 °C for a shear rate range of 1−100 s⁻¹. The viscosity curves are presented in Figure 5. It can be seen from the graph that, as the pH of the solution went toward the acidic side, the viscosity decreased considerably (34% of the viscosity of the neutral pH solution, corresponding to a shear rate of 10 s⁻¹). This trend was due to the consumption of negatively charged carboxylic groups on the polymer backbones by hydrogen ions (H⁺), resulting in reduced stretching of the polymer chains. In contrast, the solution viscosity increased by 14% as the pH was increased from 6 to 8.

The solutions in the basic range showed higher viscosities in comparison to the solutions at neutral and acidic pHs mainly because of increased hydrolysis in the presence of alkali and higher repulsion among polymer chains. The presence of OH⁻...
ions in an alkaline solution increases the dissociation rate of amide groups on the HPAM backbone, generating more carboxylate ions (COO\(^-\)). The solution viscosity, in turn, increases due to higher repulsion between molecular chains.\(^{54}\) Conversely, in a low-pH environment, the charge screening effect is pronounced due to the presence of H\(^+\) ions, leading to increased coiling and degradation of polymer chains. The effect of pH on polymer viscosity is schematically shown in Figure 6. A similar behavior was also reported by Gu et al.\(^{60}\) for a HPAM/Cr\(^{3+}\) weak gel, where they observed the highest viscosity of the gel in the basic region.

Effect of Polymer Concentration and pH on Viscosity. The same steps were repeated for three different concentrations of polymer (1500, 3000, and 4500 ppm). Figure 7 shows the viscosity as a function of pH and polymer concentration at a shear rate of 10 s\(^{-1}\). This shear rate was chosen as it represents the typical shear rate observed in the field. The first observation was that, as the concentration increased, the solution viscosity also increased significantly. This effect can be attributed to a higher number of polymer molecules present in high-concentration solutions, leading to increased repulsion and higher viscosity.

The effect of pH has already been explained. It was observed that as the pH goes toward the highly basic region (>10), the viscosity starts to decrease again due to the precipitation of some polymer molecules in an excess quantity of NaOH, leading to some viscosity loss. Basically, there is an optimum range for the degree of hydrolysis, and as the hydrolysis increases beyond the optimum required degree, polymer molecules undergo precipitation. This is the reason for a decrease in polymer viscosity at a pH of above 10. These results indicate that the optimum pH range for this polymer is 8–10.

Effect of pH on Thermal Stability. To evaluate the pH effect on the thermal stability of F5115, the viscosities of 1500 ppm solutions at different pH values were measured at 25 °C. The solutions were then kept in the oven at 80 °C, and the viscosities were again determined at different aging times. The temperature setting in the rheometer was kept at 25 °C to compare the results with the viscosity of unaged solutions. Figure 8 presents the results for solutions with different pHs.

The viscosity of acidic solutions of pH 2 and 4 was drastically decreased from 15 and 18 cP to 10 and 4 cP, respectively, within 24 h of exposure to 80 °C. Hence, these solutions were not thermally stable.

An interesting observation here was that, for the first 2 days, the pH 12 solution showed a considerable increase in viscosity from 25 to 31 cP. This can be attributed to further hydrolysis and increased repulsion of polymer chains at high temperature. For the solutions in the pH range of 8–10, the thermal degradation in viscosity was the lowest and the viscosity for these solutions dropped only by 4–7 cP over a 1 week aging time. To understand the extent of thermal stability as a function of pH, the viscosity loss for each solution was calculated using eq 2

\[
\text{viscosity loss (\%)} = \left| \frac{\mu_0 - \mu_t}{\mu_0} \right| \times 100 \tag{2}
\]

where \(\mu_0\) is the fresh solution viscosity and \(\mu_t\) is the viscosity of the solution after 1 week aging time at 80 °C. Figure 9 shows the effect of pH on viscosity loss due to thermal degradation. The viscosity loss under acidic conditions was at a maximum (~60% higher than the viscosity of solutions in the basic range). The reason for the rapid decrease in viscosity was the increased reactivity of the acid with polymer molecules at high temperature. The H\(^+\) ions present in an acidic solution neutralize the HPAM carboxylate ions, leading to reduced repulsion among the polymer chains; the rate of this reaction becomes fast at high temperature. Fewer carboxylate ions on polymer backbones result in a reduction in repulsive forces among molecules, leading to increased entangling and coiling of polymer chains.

The solutions in the basic pH range exhibited the lowest viscosity loss (only 18% after 1 week) and maximum thermal stability due to higher repulsion among the molecules. The reason for the better thermal stability of F5115 in the pH range

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**Figure 6.** Mechanism for HPAM F5115 performance under acidic and basic conditions.

**Figure 7.** Effect of polymer concentration and pH on F5115 viscosity at 25 °C.

**Figure 8.** Effect of pH on the thermal stability of 1500 ppm F5115. The solutions were kept at 80 °C, while the viscosity was measured at 25 °C.

**Figure 9.** Effect of pH on viscosity loss due to thermal degradation.
Viscoelastic Characterization. The next section discusses the pH effect on the viscoelastic properties of HPAM F5115 polymer, as both viscous and elastic components play an important role in enhancing the oil recovery by HPAM-based polymers. Various parameters are available in the literature to quantify the viscoelastic effect of a polymer by conducting oscillatory rheology tests: i.e., AST and FST. Some of the factors analyzed in this study include the storage/elastic modulus ($G'$), viscous/loss modulus ($G''$), linear viscoelastic range (LVER), relaxation time, and loss factor ($\tan \delta$).

Analysis of Amplitude Sweep Test. Generally, the salinity has an inverse relationship with the polymer viscoelastic effect. As the brine salinity and divalent ion concentration increases, the relaxation time of the polymer decreases. The reason for this behavior is the protonation of carboxylic groups on polymer chains and the subsequent coiling of polymer molecules. In this context, the optimized ion-adjusted low-salinity brine was used to prepare polymer solutions for ASTs and FSTs. The primary objective of the AST was to determine the limit of the linear viscoelastic region for HPAM F5115 polymer, within which the polymer structure would not be destroyed. Some additional information was also derived from the magnitudes of $G'$ and $G''$. Figure 10 shows the results of ASTs for neutral pH solutions of 1500, 3000, and 4500 ppm polymer concentration at 25 °C.

The angular frequency for the AST was set at 10 rad/s. As expected, both viscous and loss moduli as well as LVER increased with polymer concentration. This can be attributed to increased intermolecular interactions, yielding a high viscosity and elasticity in the solution. At lower concentration, the LVER was relatively unstable, indicating lower elastic properties. Another observation was that, at high shear strain rates, the magnitudes of viscous and elastic moduli were almost the same, indicating that the polymer had equal contribution from viscous and elastic components. Furthermore, for a 4500 ppm concentration, the elastic modulus was higher than viscous modulus ($G' > G''$), making the solution more like a weak liquid gel. Hence, both $G'$ and $G''$ have a direct relation with polymer concentration; however, $G'$ is influenced more in comparison to $G''$. This could be because, when a large number of molecules are present, the number of elastic collisions increases. From this test, the limit of LVER was identified as a shear strain of below 50%, as the elastic modulus was relatively linear in this range. Consequently, the FSTs were performed at a constant strain rate of 5% within the LVER. It is critical to define a constant strain rate for the FST on the basis of the LVER identification from the AST, so that the polymer molecules do not undergo deformation at high angular frequencies. The elastic or storage modulus can be used to quantify the elastic character of the polymer. Figure 11 shows the elastic modulus values within the LVER as a function of pH for three concentrations.

Figure 9. 1500 ppm F5115 viscosity loss as a function of pH after 1 week aging time at 80 °C.

Figure 10. AST results for LVER detection for 1500, 3000, and 4500 ppm neutral pH solutions at 25 °C.
the elastic nature can be observed for the pH range of 8–10. A similar trend was observed for the viscous modulus, where it increased with increasing pH.

Analysis of Frequency Sweep Test. Once the LVER was determined, frequency sweep tests were performed at a constant shear strain rate of 5% while the angular frequency was varied from 1 to 100 rad/s. In the first stage, the FST was conducted for three concentrations of 1500, 3000, and 4500 ppm while the pH was kept neutral. The objective here was to check the effect of polymer concentration on \( G' \) and \( G'' \).

Effect of Polymer Concentration. Figure 12 presents the results of FSTs for three different concentrations of polymer at 25 °C. As the concentration increased, both \( G' \) and \( G'' \) also increased. An interesting observation was that, with an increase in polymer concentration, the difference between \( G' \) and \( G'' \) was significantly reduced, showing a pronounced effect of concentration on the storage properties of the polymer solution. An important result from the FST is usually the quantification of the viscoelastic properties of the polymer. The crossover point (where \( G' = G'' \)) can be used to compare the viscoelastic behavior of different solutions. Once the crossover point is reached, the solution then possesses a more elastic character afterward as the angular frequency increases. For the FS11S polymer being studied, the crossover point was reached earlier for higher concentration solutions. Additionally, the 4500 ppm solution exhibited higher elastic behavior over a wider range of frequencies.

Effect of pH. To analyze the effect of pH on the viscoelastic behavior of FS11S, frequency sweep tests were conducted for 4500 ppm solutions at pH 2, 6, and 8. Figure 13 shows the results of FSTs for this case. For the solution in the acidic range, both moduli showed a decrease, and under most of the test conditions, the solutions possessed only viscous properties. This was due to polymer chain coiling and degradation of the polymer viscosity and elasticity in acidic medium. However, in the basic pH range, the \( G' \) and \( G'' \) values considerably increased and there was also a region where the elastic component was dominant over the viscous component, making the solution more like a weak gel. The crossover point appeared earlier for the pH 8 solution, which could be due to increased repulsion and stretching of molecules in the presence of OH\(^-\) ions. The elastic properties of FS11S were dominant over the viscous properties in the basic pH range.

It is also evident from Figure 13 that the magnitude of both elastic and viscous moduli was highest for the polymer solution of pH 8 throughout the frequency range of interest. Hence, basic conditions can substantially improve the HPAM FS11S viscoelastic properties by promoting its elastic character. To adequately quantify the viscoelastic behavior of FS11S, the relaxation time was estimated using FST data acquired in the previous step. The relaxation time indicates the elastic behavior of polymers. The longer the relaxation time, the higher the elastic nature of the polymer.

The relaxation time as a function of pH is graphically presented in Figure 14. It was observed that a high pH significantly improved the relaxation time for all three concentrations, but the effect was more pronounced at higher polymer concentration. A longer relaxation time indicates that more time is required for polymer chains to adjust their alignment. The general trend was similar for all three concentrations, where the relaxation time increased with increasing pH up to a critical pH of 10. Beyond this pH, the polymer was degraded due to the high concentration of alkali and increased salinity, causing the polymer chains to deform and lose elasticity. The highest relaxation time was obtained for the 4500 ppm solution, as can also be observed from the crossover point of \( G' \) and \( G'' \) in Figure 12. Further useful information obtained from FST was the loss factor (\( \tan\delta \)).

Figure 11. pH effect on storage modulus for 1500, 3000, and 4500 ppm neutral pH solutions at 25 °C.

Figure 12. FST results for 1500, 3000, and 4500 ppm neutral pH solutions at 25 °C.

Figure 13. \( G' \) and \( G'' \) as a function of pH for 4500 ppm solutions at 25 °C.
which is the ratio of the loss and storage moduli of the viscoelastic materials (eq 3).

$$\text{loss factor (tan } \delta) = \frac{\text{loss modulus (} G'' \text{)}}{\text{elastic modulus (} G' \text{)}}$$ (3)

For ideal viscous fluids, the loss component totally dominates the storage component, making $\delta$ equal to 90°, and thus the loss factor becomes infinite. On the other hand, the storage component completely dominates the viscous component for a perfectly elastic fluid. $\delta$ in this case becomes zero and the loss factor is also zero.61

The elastic modulus of a viscoelastic polymer is higher than the viscous modulus at higher frequencies. However, at the crossover point where $G'$ and $G''$ are equal, the loss factor becomes 1. Hence, a loss factor value below 1 indicates a higher viscoelastic behavior of the material. Figure 15 shows the effect of pH on the loss factor for 4500 ppm polymer solutions. The loss factor for the solution in the acidic range stayed above 1, indicating a lower elastic behavior. For the solutions in the basic medium, the loss factor was less than 1 over a wider frequency range, showing a dominance of the elastic properties of the polymer under these conditions. The loss factors of pH 8 and 10 solutions became less than 1 quite quickly, suggesting it to be an optimum pH range for better viscoelastic behavior of HPAM F5115. It can be inferred from the results of this study that, under high-pH conditions, there is increased repulsion and stretching among polymer molecular chains due to the presence of negatively charged hydroxyl ions. Finally, polymer chains possess greater elasticity and have a tendency to stretch more when the flow through pore spaces under basic conditions. As a result, the polymer molecules are able to go deeper in the pore throats, enhancing the microscopic recovery efficiency by applying a stronger pulling force on the entrapped oil droplet.

Hence, the polymer viscosity and viscoelasticity increase by adding alkali, which can result in higher oil recovery by polymer flooding in an alkaline setting. Moreover, the adjustment of brine makeup ionic composition and salinity adds to the benefits of the polymer flooding technique by reducing the degree of polymer degradation under harsh reservoir conditions. This combination can also potentially lower the amount of polymer required, thereby improving the project economics. The improved viscoelastic behavior of the polymer with alkali can also reduce $S_{or}$ and increase microscopic efficiency.

Rheological parameters such as relaxation time, storage modulus, and loss factor are directly related to the recovery of residual oil. The polymers with a higher relaxation time, large storage modulus, and a loss factor below 1 tend to have a pronounced viscoelastic character and thus have a higher tendency to recover residual oil.42,62 In a laboratory study conducted by Vermolen et al., a higher incremental oil recovery was reported by using a polymer solution with higher relaxation time and consequently a higher viscoelasticity.63

The main advantage of this study lies in a novel approach toward designing a polymer solution that is capable of not only improving the macroscopic recovery efficiency but also targeting the microscopic sweep by taking advantage of the viscoelastic character of HPAM polymers. Furthermore, the design approach presented in this study has the potential to extend the application of polymer flooding to reservoirs with harsh conditions of salinity and temperature. A carefully designed polymer solution with salinity adjustment and alkaline pH will have a higher resistance toward thermal degradation. Additionally, preconditioning of the reservoir with a low-salinity water slug can also minimize the viscosity loss due to high-salinity water formation. Thus, the proposed
method of designing a polymer solution is equally or even more applicable in harsh environments.

A limitation of this study is the lack of an economic analysis proving the economic viability of the proposed design. However, an economic analysis is beyond the scope of current study. However, it can be assumed that the benefits obtained in terms of higher incremental oil recovery by using a chemically tuned and pH-adjusted makeup brine for HPAM polymer flood projects will offset the additional cost incurred in the pH-adjustment process. In most situations, a field-scale simulation study followed by an economic analysis will be instrumental in designing the optimum operating conditions such as brine salinity and pH for field-specific conditions.

**SUMMARY AND CONCLUSIONS**

In this rheological work, an optimum makeup brine for HPAM F5115 has been designed by tuning the brine ionic composition, salinity, and pH. The results and principal findings of the study are presented as follows.

- The viscous and elastic properties of HPAM polymer are pH-sensitive because of the negatively charged carboxyl groups attached to the polymer molecular chains. Under elevated pH conditions, these groups promote elongation of the polymer chains because of electrostatic repulsive forces among them. As a result, the viscosity and viscoelasticity of the polymer solution increase. In contrast, a low-pH environment induces polymer chain coiling by neutralizing the carboxy groups on the backbone, thereby decreasing the viscosity and viscoelasticity.

- A low-salinity ion-adjusted brine was selected for the F5115 polymer in our previous study. This experimental study has assessed the influence of pH on the viscous and viscoelastic properties of the HPAM F5115 polymer.

- HPAM F5115 has shown an improved viscous and viscoelastic behavior in the presence of alkali and an optimum pH range of 8−10, as observed by a 15−40% increase in viscosity and a 20 times increase in relaxation time for pHs between 7 and 10.

- The pronounced effect of pH on the polymer’s viscosity and viscoelasticity can also be attributed to the low-salinity ion-tuned brine particularly designed for F5115. The polymer maintained its viscous character in a low-salinity environment, and the addition of alkali provided more repulsion, stretching the polymer chains.

- The results of the rheological study show that the addition of alkali to a low-salinity ion-adjusted polymer solution causes increased repulsion between HPAM polymer chains, resulting in improved rheological and viscoelastic properties of the polymer.

- The HPAM F5115 polymer possesses viscous as well as elastic properties and exhibits pronounced viscoelastic behavior with increasing brine pH. The results of this study can be implemented for the best design of a polymer solution in order to gain the maximum benefit by increasing the viscoelastic effect of the polymer. For heterogeneous oil−water carbonates having high Sm values after waterflooding, the injection of viscoelastic polymers under reduced salinity and alkaline conditions can recover residual oil in addition to control of the mobility and improvement in the volumetric sweep efficiency.

Hence, a properly designed polymer solution can provide multiple benefits when it is combined with ion-adjusted low-salinity water and other chemicals such as alkali and a surfactant.

**AUTHOR INFORMATION**

**Corresponding Author**

Peyman Pourafshary — School of Mining and Geosciences, Nazarbayev University, Nur-Sultan 010000, Kazakhstan; orcid.org/0000-0003-4600-6670; Email: peyman.pourafshary@nu.edu.kz

**Authors**

Mariam Shakeel — School of Mining and Geosciences, Nazarbayev University, Nur-Sultan 010000, Kazakhstan; orcid.org/0000-0002-7946-913X

Muhammad Rehan Hashmet — Department of Chemical & Petroleum Engineering, United Arab Emirates University, Al Ain 00000, United Arab Emirates

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**NOMENCLATURE**

Cp, polymer concentration, ppm; G′, elastic or storage modulus, Pa; G″, viscous or loss modulus, Pa; γ, shear strain rate; μ0, fresh solution viscosity, cp; μv, viscosity after 1 week of aging at 80 °C, cp; ω, angular frequency, rad/s; Sres, residual oil saturation; tan δ, loss factor; ASP, alkaline surfactant polymer flooding; AST, amplitude sweep test; ATBS, acrylamide tert-butyl sulfonic acid; CEOR, chemical-enhanced oil recovery; CSW, Caspian seawater; F5115, Flopaam 5115; FST, frequency sweep test; HCl, hydrochloric acid; HPAM, hydrolyzed polyacrylamide; LVER, linear viscoelastic region; NaOH, sodium hydroxide; PF, polymer flooding; ppm, parts per million; SF, surfactant flooding; SHI, strain hardening index

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