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Effect of Seawater Ions on Polymer Hydration in the Presence of a Chelating Agent: Application to Hydraulic Fracturing

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ABSTRACT: Seawater (SW) and produced water (PW) could replace freshwater in hydraulic fracturing operations, but their high salinity impacts the fluid stability and results in formation damage. Few researchers investigated SW and PW individual ions' impact on polymer hydration and rheology. This research examines the rheology of carboxy methyl hydroxy propyl guar (CMHPG) polymer hydrated in salt ions in the presence of a chelating agent. The effect of various molar concentrations of SW and PW salt ions on the rheology of CMHPG polymer solution was examined. The tested salt ions included calcium chloride, magnesium chloride, sodium chloride, and sodium sulfate, which were compared to SW and deionized water (DI) solutions. The solutions were tested at 70 °C temperature, 500 psi pressure, and 100 1/s shear rate. A GLDA chelating agent was utilized at different concentrations to examine their impact on stabilizing the solution viscosity. We found that adding the GLDA to magnesium and calcium chloride solutions increased the viscosity. Results showed that sulfate ions control the rheology of seawater due to their similar rheological response to the addition of GLDA. The results help to understand how the SW and PW ions impact the rheology of fracturing fluids.
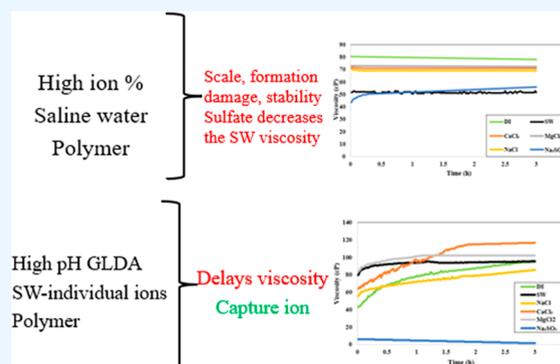
1. INTRODUCTION

The exploration of unconventional reservoirs has extensively increased with the increase in global energy demand. Productivity demands hydraulic fracturing in unconventional reservoirs. Hydraulic fracturing is used to stimulate a well by inducing fractures within the formation that boost reservoir productivity. This is accomplished by introducing fracturing fluid at a higher pressure than the formation fracture pressure. Proppant is utilized to keep the induced fractures open and prevent their closure after the hydraulic-surface pressure has been removed. The design of the fracturing fluid and its viscosity play a crucial role in determining the success or failure of hydraulic fracturing operations. Additionally, fracturing-fluid viscosity is essential for establishing the required width for proppant entrance into the fracture, allowing for proppant transport from the wellbore to the fracture tip, controlling fluid loss into the formation, and controlling pressure to ensure appropriate fracture height and growth.[1−3]

Water-based fluids are the most utilized type of fluids in hydraulic fracturing. Hydraulic fracturing of unconventional shale wells requires millions of gallons of fresh water. However, the availability of fresh water is one of the difficulties that face this operation, especially in water-deprived regions.[4] Also, transporting fresh water to offshore locations is costly, which adds to the difficulty of storing water storage on-site. The

scarcity of freshwater resources and the transportation and maintenance costs are both significant drawbacks. On the contrary, produced water from oil and gas operations and seawater are readily available. They could potentially replace fresh water in hydraulic fracturing if the associated challenges are addressed. Therefore, seawater and produced water can play a significant role in reducing fracturing operation costs.[5] The major challenges associated are the high total dissolved solids (TDS), pipes corrosion, scaling potential, and polymer hydration.[6]

A typical fracturing fluid contains water, viscosifiers, proppants, friction reducers, biocides, and other additives. Polymer-based viscosity-modifying agents such as poly (acrylic acid), poly(vinyl alcohol), guar gum and its derivatives, cellulose, and poly(acrylamide) are widely utilized. The number of functional groups, their location, and polymer molecular weight determine the characteristics of the polymer.[7] Among the guar gum derivatives, hydroxypropyl
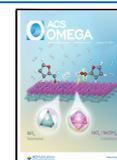
guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG) are extensively used in hydraulic fracturing due to the ease of hydration and minimum residue content.[8] The guar derivatives can be crosslinked to generate very high viscosity at a low concentration. A crosslinker is utilized to achieve high viscosity values that can range from hundreds to thousands of centipoises. The most popular metals for crosslinking guar-based fracturing fluids are boron, zirconium, and titanium.[9]

The challenge with utilizing produced water (PW) and seawater (SW) is the high concentration of ions such as Ca^{2+} and Mg^{2+}, which influence the thermal stability and the fracturing fluid viscosity. The presence of these ions could delay or prevent polymer hydration. Moreover, they may induce corrosion, cause scale, and reduce gel stability.[6] Both monovalent (Na^+ and K^+) and divalent (Ca^{2+} and Mg^{2+}) ions affect the viscosity and stability of fracturing fluids. The divalent ions are the source of viscosity reduction and precipitation, which is stronger with the presence of calcium ions. Monovalent ions reduced the viscosity only when no divalent ions existed in the prepared fluid.[10] In sandstone formations, the positive ions tend to be attracted to negatively charged rock. The anions such as SO_4^{2-} tend to disrupt the equilibrium of the fluid system, release the negatively charged oil compounds, and form compounds with the cations. The low salinity water can attract the cations in the formation brine, release the oil compounds, and improve productivity.[11] These ions may damage the formation or reduce the retained fracture conductivity. The precipitation of divalent ions (Ca^{2+} and Mg^{2+}) may occur at a pH higher than 10, and different scales can be formed. Therefore, the pH should be increased or scale inhibitors should be used if low pH is needed. High pH environments are needed to maintain stability at high temperatures.[12,13] The pH control improves the crosslinker durability with shearing, while the chelating agents capture the ions and reduce the PW and SW hardness.

Chelating agents are compatible with PW and SW and can improve thermal stability, reduce surface tension, adjust the pH, and as acids, breakers, biocides, and clay stabilizers. Different chelating agents used in the oil industry include ethylenediaminetetraacetic acid (EDTA), ethanolic phospho-tungstic acid (EPTA), and L-glutamic acid-N,N-diacetic acid (GLDA). The chelating agents are used to reduce the interfacial tension; the high pH chelating agents increase the negative value of zeta potential and change the rock toward water wet and enhance the productivity.[14] Chelating agents such as GLDA are stable at elevated temperatures up to 300 °F. It reacts differently with ions at different pH ranges.[15−19] The ions reduce the crosslinking capabilities of the guar due to their precipitation.[19] EDTA is used in the industry to capture anions such as sulfate and carbonate, while the GLDA is used to capture the cations such as calcium and magnesium.[18]

The literature showed that salt ions have an impact on the fracture fluid rheology and stability. However, little research has been done on the impact of each monovalent and divalent cation in the PW or SW on the viscosity, crosslinking, and breaking of fracturing fluids. In this study, we evaluated the impact of varied ions (Na^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-}) concentrations on the rheology of CMHPG polymer. We also investigated the effectiveness of GLDA as a chelating agent in various salt ions at 1 M concentration. Experiments on fresh water and seawater solutions were carried out as a

standard to determine which salt ion significantly influences the viscosity of the CMHPG polymer.

2. METHODOLOGY

2.1. Materials. In this study, we examined the hydration of the CMHPG polymer in DI, SW, and various concentrations of calcium chloride ($CaCl_2·2H_2O$), magnesium chloride ($MgCl_2·6H_2O$), sodium chloride (NaCl), and sodium sulfate (Na_2SO_4). We also looked at how well the polymer performed when SW, DI, and the other ions were combined with various concentrations of high pH GLDA. To attain rheological properties, we utilized an Anton Paar-MCR 302 rheometer. Table 1 shows the details of SW-associated salts in gram/liter.

Table 1. Ions Associated With 1 Liter of SW

ions	weight (g/L)	molar concentration (mol/L)
Mg^{2+}	2.1098	0.0104
Ca^{2+}	0.6496	0.0044
Na^+	18.3017	0.313
Cl^-	32.3278	0.2199
SO_4^{2-}	4.2864	0.0302
HCO_3^-	0.1198	0.0014

These ions affect the hydration of the polymer; however, in this work, we used the CMHPG polymer. The CMHPG is preferred by the industry because it has unique properties; it does not degrade as fast as the other polymers, it works fine at low pH, and it hydrates better than other polymers. Hydration is the process by which polymer chains absorb water to change their configuration from the compact state of coils into a more extended and relaxed state. The stable viscosity is recognized as the maximum hydrate state.[19−21]

To capture and remove the effect of the ions on the polymer, high pH GLDA chelating agent (N,N-dicarboxymethyl glutamic acid) was used. We received and used the GLDA product as it is having pH around 13.7. The GLDA raises the pH of solutions from 6 to more than 10, depending on the concentration of the GLDA. The fluid has 40% active content, and its chemical structure is detailed in Figure 1.
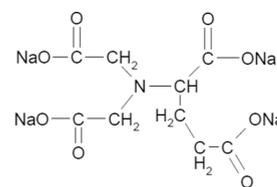
Figure 1. Dissolvine StimWell DGH GLDA structure—GLDA-Na$_4$.[22] Reprinted with permission from ref 22 Copyright 2022, American Chemical Society.

2.2. Procedures. The hydration period in each test was set at 45 min, and the GLDA was mixed for 5 min after hydration. All experiments were conducted under uniform conditions: 70 °C temperature, 500 psi pressure, and 100 1/s shear rate utilizing Anton Paar MCR-302 high-pressure cell geometry. We investigated SW, DI, $CaCl_2·2H_2O$, $MgCl_2·6H_2O$, NaCl, and Na_2SO_4 solutions in the first phase of the tests. Three different concentrations of each salt solution (1, 0.5, and 0.1 M) were examined. To explore the impact of GLDA concentrations at various salt ions, while comparing to SW and DI, a high pH (13.7) GLDA solution was used in the

Table 2. Summary of the Performed Experiments

water type	polymer (wt %)	ion concentration (M)	chelating agent (wt %)	chelating agent type	temperature (°C)	number of experiments
DI, SW	0.6				70	2
CaCl$_2$·2H$_2$O, MgCl$_2$·6H$_2$O, NaCl, Na$_2$SO$_4$	0.6	1, 0.5, 0.1			70	12
DI, SW	0.6		4, 10, 20	high pH GLDA (13.7)	70	6
CaCl$_2$·2H$_2$O, MgCl$_2$·6H$_2$O, NaCl, Na$_2$SO$_4$	0.6	1	4, 10, 20	high pH GLDA (13.7)	70	12

second phase. GLDA was used in three different concentrations (4, 10, and 20 wt %).

2.3. Experimental Design. The first phase's purpose was to assess the performance of CMHPG in various salts used at different concentrations. The CMHPG polymer was hydrated for 45 min in solutions of CaCl$_2$·2H$_2$O, MgCl$_2$·6H$_2$O, NaCl, and Na$_2$SO$_4$ at concentrations of 0.1, 0.5, and 1 M. The second phase's goal was to restore the polymer's viscosity by using GLDA, a chelating agent. There were three different concentrations of the GLDA utilized (4, 10, and 20 wt %). The polymer was hydrated for 45 min in DI, SW, and 1 M of above-mentioned salts separately followed by GLDA which was mixed for 5 min. Table 2 summarizes the concentrations and testing conditions applied in the study.

3. RESULTS AND DISCUSSION

3.1. Effect of Ions Concentration on the Viscosity. The baseline experiment of DI was repeated at 70 °C in 0.6 wt % CMHPG polymer hydrated in DI for 45 min to assess the deviation of the measured viscosity from the true values. The average percentage error was calculated, and the error bars were added to Figure 2; the same was applied to the

Figure 3. 0.6 wt % CMHPG in different concentrations of NaCl at 70 °C, 100 1/s, and 500 psi.

water to 75 cP after the addition of 0.1 M NaCl. Furthermore, as the concentration of NaCl increased, the viscosity dropped from 75 to 69 cP. This decrease in viscosity indicates that the addition of Na ions slightly hindered the polymer's hydration. This decrease is caused by the reduction of mutual repulsion between charges in the polymer backbone. The excess positive ions in the solution formed a shield that prevented repulsion.[23] Table 3 specifies the standard deviation (STDEV) in viscosity for each concentration of sodium chloride.

Table 3. Viscosity Average and STDEV for Sodium Chloride Solution

solution	average viscosity	STDEV
1 M	68.826	0.246
0.5 M	71.781	0.449
0.1 M	72.559	0.381
SW	51.717	0.526

Figure 2. Average percentage error of two DI-based solution experiments.

subsequent figures. The average percentage error in the DI experiment was 1.6%, which is within the acceptable range. For the rest of the figures, we illustrated the standard deviation from the average value for each data set.

The impact of several individual ions on the rheology of the polymer was examined in the first phase of the study. The various ions were investigated at three different concentrations (0.1, 0.5, and 1 M). Figure 3 depicts the effects of NaCl at three different concentrations, including 1 M NaCl, 0.5 M NaCl, and 0.1 M NaCl, on the viscosity of the polymer under investigation. The results showed that NaCl had an impact on CMHPG's viscosity. The viscosity decreased from 80 cP in DI

The viscosity profile of a CMHPG polymer that has been hydrated in MgCl$_2$ at concentrations of 1, 0.5, and 0.1 M is shown in Figure 4. It should be emphasized that MgCl$_2$ at any concentration has a negligible impact on the viscosity of the polymer. Additionally, all concentrations have a rather narrow range of viscosity values, between 72 and 75 cP. As the MgCl$_2$ concentration increased, the viscosity profile varied, dropping from 75 to 72 cP. Among all the salt ions, MgCl$_2$ was the most stable solution at 70 °C when the ion concentration changed. Table 4 specifies the viscosity STDEV for each concentration of magnesium chloride.

In CaCl$_2$ solutions, the performance of the CMHPG polymer was evaluated at three different concentrations: 1, 0.5, and 0.1 M. Figure 5 presents the viscosity profiles for all three concentrations. CaCl$_2$ was found to have no effect on the
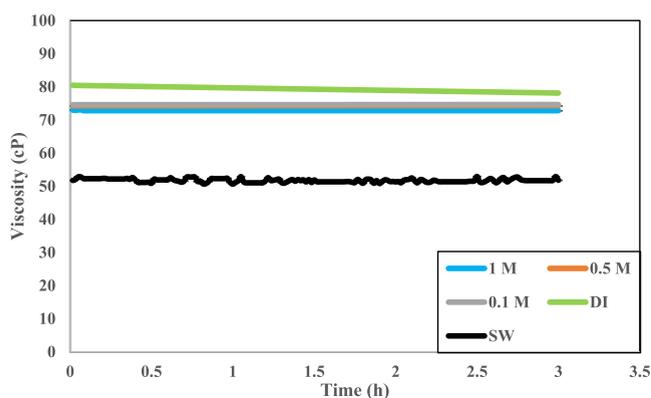
Figure 4. 0.6 wt % CMHPG in different concentrations of MgCl$_2$ at 70 °C, 100 1/s, and 500 psi.

Table 4. Viscosity Average and STDEV for Magnesium Chloride Solution

solution	average viscosity	STDEV
1 M	70.273	0.219
0.5 M	73.426	0.324
0.1 M	72.343	0.358
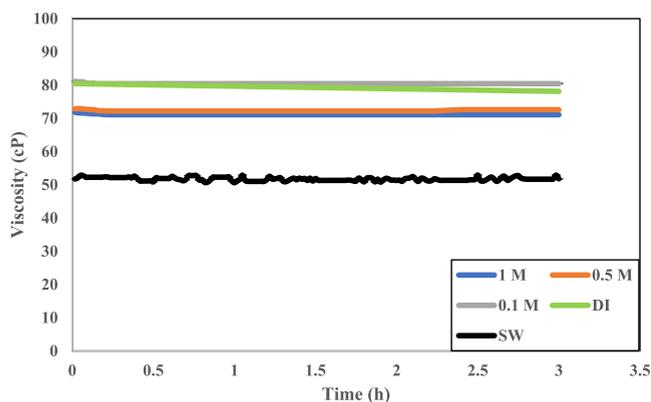
Figure 5. 0.6 wt % CMHPG in different concentrations of CaCl$_2$ at 70 °C, 100 1/s, and 500 psi.

polymer's stability. However, compared to sodium and magnesium ions, it resulted in a wider range of viscosity values. For instance, the viscosities of CaCl$_2$ solutions were 71, 73, and 81 cP for 1, 0.5, and 0.1 M, respectively. Furthermore, a small decrease in viscosity at the beginning of the test was observed in all three tested concentrations. A similar behavior was observed in the 1 M MgCl$_2$ solution. Table 5 specifies the viscosity STDEV for each concentration of calcium chloride.

Finally, the CMHPG polymer was tested in Na$_2$SO$_4$ solution to examine the effect of sulfate on the polymer performance. A 0.6 wt % of the polymer was hydrated for 45 min in 1, 0.5, and 0.1 M of the salt. Then the rheology tests were performed for the three solutions at 70 °C and 500 psi. Figure 6 shows the

Table 5. Viscosity Average and STDEV for Calcium Chloride Solution

solution	average viscosity	STDEV
1 M	70.607	0.285
0.5 M	72.268	1.262
0.1 M	79.554	0.483
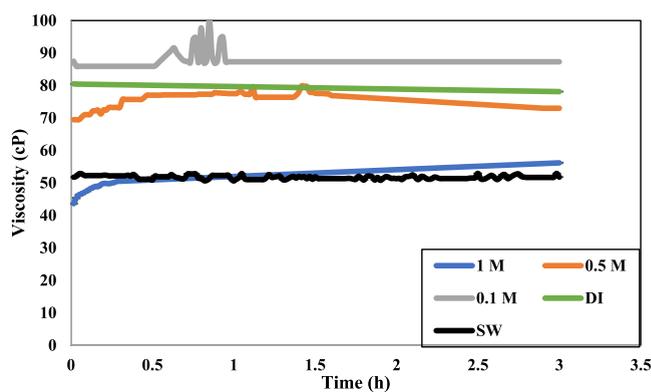
Figure 6. 0.6 wt % CMHPG in different concentrations of Na$_2$SO$_4$ at 70 °C, 100 1/s, and 500 psi.

results of these experiments. It can be noted that all concentrations of Na$_2$SO$_4$ affected the polymer hydration. The increase in the concentration had an important impact on viscosity. For the 1 M, the viscosity started low at 42 cP, and in less than 15 min, it reached 50 cP. However, it took 2 h and 45 min to nearly reach 60 cP. When the concentration was decreased to 0.5 M, a similar behavior was noted but in a narrower window between 70 and 77 cP. When the concentration decreased to 0.1 M better stability and higher viscosity were achieved reaching 87 cP. We noted that the sodium sulfate affects the system's stability and hence the fluctuations in the viscosity results. Table 6 specifies the viscosity STDEV for each concentration of sodium sulfate.

Table 6. Viscosity Average and STDEV for Sodium Sulfate Solution

solution	average viscosity	STDEV
1 M	52.831	2.185
0.5 M	74.823	2.519
0.1 M	87.436	2.165

3.2. Effect of Chelating Agent. From the experiment, it can be concluded that when the CMHPG polymer is dissolved in CaCl$_2$·2H$_2$O, MgCl$_2$·6H$_2$O, and NaCl solutions, the change in concentration has a small impact on the rheology. It was found that the concentration has a significant impact when the polymer is dissolved in Na$_2$SO$_4$; however, in all tested ions, decreasing the concentration increased the viscosity. This is because more positive ions of sulfur besides sodium are shielding the polymer ions and preventing the ion repulsion[23] As the water is a good solvent for the sodium sulfate, the sodium sulfate prevents the interaction between the gel and the water, it interacts strongly with water. As a result, the water easily can be released from the gel network, which ruins the polymer hydration and the gelation process.[24]

In the second part of the study, we tested the effect of the high pH GLDA chelating agent on the CMHPG polymer hydrated in CaCl$_2$·2H$_2$O, MgCl$_2$·6H$_2$O, NaCl, and Na$_2$SO$_4$ and compared it with GLDA in SW and DI. Figure 4 displays the viscosity of 0.6 wt % of polymer hydrated for 45 min in 1 M of CaCl$_2$, MgCl$_2$, NaCl, and Na$_2$SO$_4$ ions individually. The figure also shows the viscosity of the same polymer concentration hydrated in SW and DI water. From Figure 7, the viscosity of DI is the highest and most stable solution among the solutions. The viscosity in DI exceeded 80 cP, while
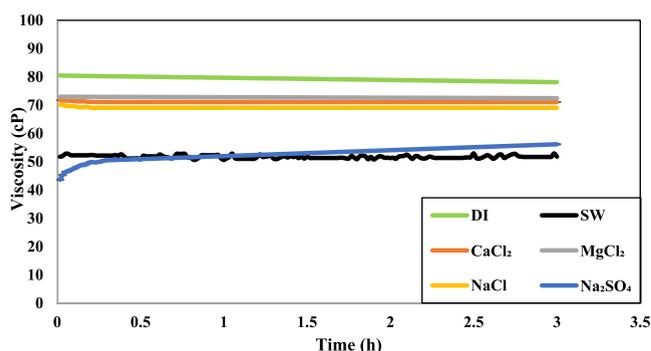
Figure 7. 0.6 wt % CMHPG in 1 M of individual ions compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

in $MgCl_2$, $CaCl_2$, and NaCl solutions, it showed very stable and similar viscosity values (72, 70, and 69 cP). SW and Na_2SO_4 were not stable and had much lower viscosity compared to the other solutions. Similar results of DI and SW were achieved in a similar study.[22] From the figure, it can be concluded that Na_2SO_4 is the source of viscosity reduction of the SW. Using the high pH increases the stability; however, the FTIR test performed by Kamal et al.[15] showed that at higher pH, a reaction happens between the GLDA and the base. This results in partial loss of a proton from the COOH group attached to the GLDA, which results in the presence of COO−. Th causes the viscosity to break which we noticed with the higher GLDA concentrations.

The effect of the chelating agent was investigated by adding 4% of high pH (13.7) GLDA. First, 0.6 wt % of the polymer was hydrated for 45 min in the desired salt solution. Figure 8
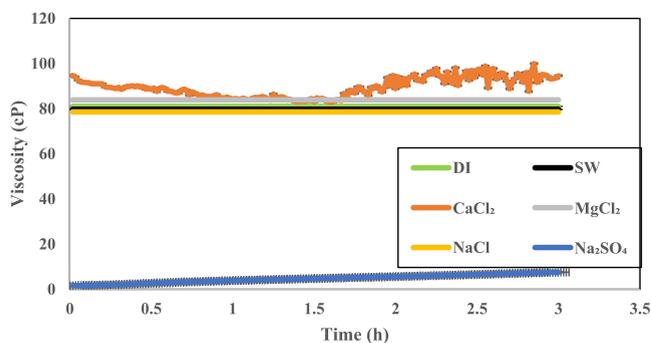
Figure 8. 0.6 wt % CMHPG in individual ions with 4% added GLDA compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

shows that adding 4% of high pH GLDA raised the viscosities to that of DI water without a chelating agent. However, it did not significantly affect the DI. On the contrary, Na_2SO_4 was negatively affected by the high pH GLDA, and the viscosity was less than 10 cP in all added GLDA concentrations. Similar conclusions and results were achieved in ref.[25] The figure also indicates that the GLDA positively impacted the Ca^{2+} solution as the viscosity reached 100 cP after 3 h. Although the SW contained Na_2SO_4, the GLDA could enhance its viscosity noticeably. The chelating agent did not only capture the ions, which make the solution behave like freshwater, but also increases the viscosity.[15] Table 7 specifies the viscosity STDEV for each solution when 4% GLDA was added.

Figure 9 shows the viscosity results when adding 10% of high pH GLDA to the polymer solution hydrated in DI, SW,

Table 7. Viscosity Average and STDEV for SW, DI and Individual Ions Solutions When 4% GLDA was Added

solution	average viscosity	STDEV
NaCl	78.531	0.633
$CaCl_2$	89.459	4.327
$MgCl_2$	82.134	1.008
Na_2SO_4	4.6711	1.713
DI	79.745	0.965
SW	79.214	0.577
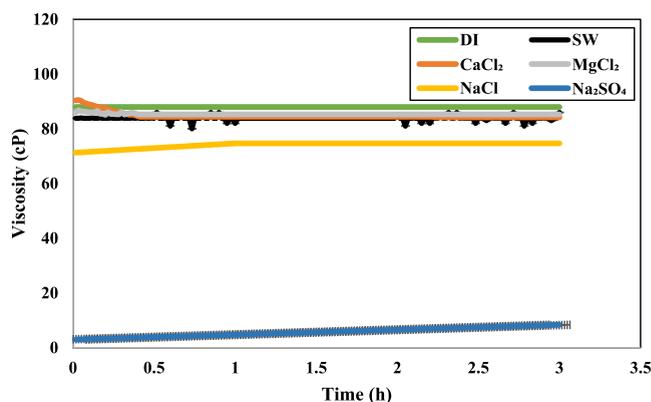
Figure 9. 0.6 wt % CMHPG in individual ions with 10% added GLDA compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

and 1 M of each of the ions individually. We can note that the viscosity of DI, SW, $MgCl_2$, and $CaCl_2$ slightly improved. Also, near the end of the test, the viscosity of $CaCl_2$ started increasing. Even with the 10 wt % GLDA, the Na_2SO_4 viscosity did not improve. The stability of SW was affected by the increase of GLDA, probably because of the negative behavior noted with sulfate ions. NaCl solution showed different behavior as the viscosity started at a lower value and increased with hydration. Although the behavior is not clear, similar behavior was noted with the lower GLDA volumes. Table 8 specifies viscosity STDEV of the solutions when 10% GLDA was used.

Table 8. Viscosity Average and STDEV for SW, DI and Individual Ions Solutions When 10% GLDA was Added

solution	average viscosity	STDEV
NaCL	73.751	1.136
$CaCl_2$	83.355	2.460
$MgCl_2$	86.148	0.671
Na_2SO_4	15.365	1.263
DI	86.067	0.427
SW	85.661	3.996

The addition of high pH GLDA in higher concentrations delays the polymer hydration.[26,27] In Figure 10, it can be noted that the addition of 20 wt % affected the solution behavior. It delayed the polymer hydration, but in different degrees, as was noted in all solutions except Na_2SO_4. $CaCl_2$ was the most affected as the hydration was delayed more; however, more viscosity gained after 1.5 h. All concentrations of GLDA could not raise the values of sodium sulfate viscosity as the chelating agent's mission is to chelate the cations. From our results and what has been highlighted in the literature,[11] the sulfate presence is good for after fracturing processes; however, while
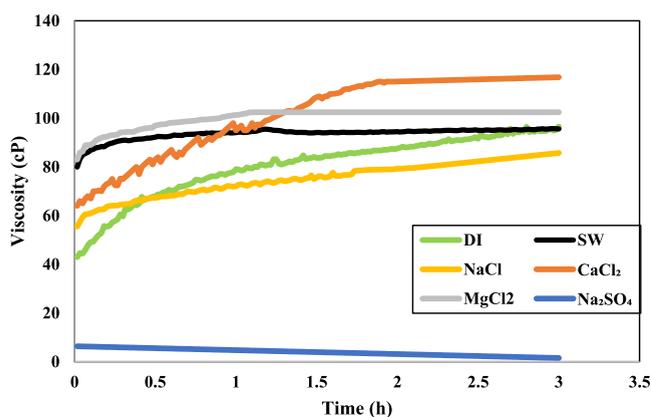
Figure 10. 0.6 wt % CMHPG in individual ions with 20% added GLDA compared to SW and DI at 70 °C, 100 1/s, and 500 psi.

fracturing, it decreases the viscosity and disturbs the fluid system equilibrium. Table 9 specifies each solution's STDEV when 20% GLDA is used.

Table 9. Viscosity Average and STDEV for SW, DI and Individual Ions Solutions When 20% GLDA Added

solution	average viscosity	STDEV
NaCL	74.866	6.924
$CaCl_2$	30.275	4.62
$MgCl_2$	99.825	4.178
Na_2SO_4	3.0260	1.678
DI	80.488	12.64
SW	93.573	2.406

Figure 11 shows a bar chart comparing the GLDA concentrations after 3 h of shearing. The light color represents
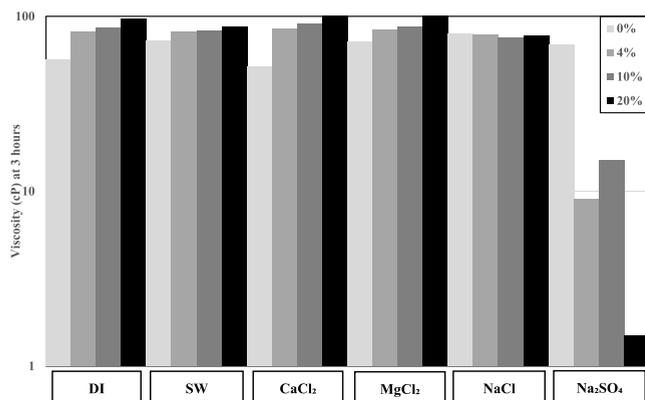
Figure 11. GLDA concentration effect on rheology, the columns shows 0, 4, 10, and 20% starting from the left.

the 0% GLDA, the dark colors represent the 20% GLDA, and the middle bars show the 4 and 10% GLDA. It can be noted that small volumes of GLDA can perform as well as big volumes. The differences in viscosity values between 4 and 20% are not great in the DI, $CaCl_2$, and $MgCl_2$. The increase in GLDA concentration did not improve individual ions' performance. However, in the cases of Na_2SO_4, the higher the GLDA, the lower the viscosity. A similar but small effect was also noted on NaCl; these ions reflected their impact on the SW behavior.

Table 10 is a summary for all remarkable results of the individual ion study on a hydrated polymer in the presence of a high pH GLDA chelating agent.

Table 10. Remarkable Results of Individual Ions Study

system without chelating agent	system with chelating agent
the concentration of NaCl, $CaCl_2$, and $MgCl_2$ did not affect the viscosity	high pH GLDA favors cations, it captures calcium first, and it has negative effect on sulfate
the concentration of Na_2SO_4 has a major impact on viscosity	GLDA at low concentration gave higher viscosities

4. CONCLUSIONS

The study evaluated the effect of SW and PW salt ions on the rheology of the CMHPG polymer. The research showed that the rheology of a system reacts differently to various ions, with divalent ions having the most significant effect. In addition, it was noticed that sulfate has an important impact on rheology. Nevertheless, GLDA improved the rheology and minimized the impact of salt ions in SW and PW-based fracturing fluid rheology.

1. The concentration of the salt has no significant effect on CMHPG rheology, except in the case of Na_2SO_4.
2. Na_2SO_4 is the source of viscosity reduction when the polymer is dissolved in seawater. Therefore, treated water with lower contents of sulfate can improve the rheological properties of seawater-based or produced water-based fracturing fluids.
3. High pH GLDA increases the viscosity of DI, SW, and individual salt solutions such as NaCl, $CaCl_2$, and $MgCl_2$.
4. The higher the concentration of Na_2SO_4 solution, the lower the repulsion in the polymer backbone, which reduces the viscosity.
5. If a limited high pH GLDA is added to SW or PW solutions, it will chelate Ca^{2+} ion first.
6. The high pH chelating agent has an adverse impact on Na_2SO_4; it breaks the viscosity of the solution.
7. Increasing the GLDA concentration up to 20% changes the behavior of the ions, DI and SW. In these solutions, the viscosity rises with time.

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Notes

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