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Experimental Study: Investigating The Anions And Cations' Effects On The Elasticity Of The Anionic And Cationic High Viscosity Friction Reducers

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Experimental Study: Investigating the Anions and Cations' Effects on the Elasticity of the Anionic and Cationic High Viscosity Friction Reducers

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Abstract

High viscosity friction reducers (HVFRs) are widely used as friction-reducing agents and proppant carriers during hydraulic fracturing. The reuse of produced water has gained popularity due to environmental and economic benefits. Currently, the field's most commonly used friction reducers are anionic and cationic HVFRs. Anionic HVFRs are typically pumped with freshwater, while cationic HVFRs are used with high Total Dissolved Solids (TDS) produced water. Cationic friction reducers are believed to have better TDS tolerance, friction reduction performance, and proppant transport capabilities compared to anionic friction reducers under high TDS conditions due to their superior viscoelastic properties. In addition, the impact of different anions and cations on the viscosity of HVFRs has been thoroughly studied, and viscosity reduction mechanisms include charge shielding, increasing the degree of hydrolysis, and forming coordination complexes. However, anions and cations' effects on the elasticity of HVFRs still remain to be investigated. Besides, most previous experimental studies either do not specify experimental procedures or control the experimental variables well. Therefore, the ultimate objective of this experimental study is to analyze various cations and anions' effects on the elasticity of anionic and cationic HVFRs comparably and precisely with experimental variables well controlled. Two hypotheses based on anions and cations' effects on the viscosity of HVFRs are proposed and will be tested in this study. First, the elasticity reduction of anionic HVFRs is mainly due to cations, whereas the elasticity reduction of cationic HVFRs is mainly due to anions. Second, the salts' effects on the elasticity reduction of HVFRs should follow the same trend as the salts' effects on the viscosity reduction of HVFRs. For anionic HVFRs, monovalent Alkali metals should have a similar effect; divalent Alkaline earth metals should have a similar effect; transition metals should have the most severe effect. For cationic HVFRs, SO_4^{2-} should have more pronounced effects than Cl^-. To demonstrate both hypotheses, an anionic and a cationic HVFR at 4 gallons per thousand gallons (GPT) were selected and analyzed. The elasticity measurements of both anionic and cationic HVFRs were conducted with deionized (DI) water and various salts respectively. Fe^{3+} and H^+ (or pH) effects were specifically investigated. The results showed both hypotheses were accepted.

Introduction

The oil industry has been accelerating the adoption of HVFRs as proppant carriers in hydraulic fracturing due to their many operational and economic advantages over traditional fracturing fluids like slickwater, linear gels, and crosslinked gels (Hu et al. 2018; Johnson et al. 2018; Biheri and Imqam 2020, 2021a). These advantages include lower operational costs, higher retained conductivity in the fractured formation, and improved production (Johnson et al. 2018; Ba Geri et al. 2019, McIntyre et al. 2021; Biheri and Imqam 2021b, 2022). However, the limited use of freshwater due to environmental concerns has resulted in the use of produced water as the main source of fluid in many oil and gas production basins, such as the Marcellus Shale region (Paktinat et al. 2011). However, the high TDS of the produced water can significantly affect the performance of HVFRs (Mantell et al. 2011).

According to Galindo (2019), the proppant-carrying capabilities of HVFRs are dependent on both fluid viscosity and elasticity, which are affected by anions and cations in solution. Different anions and cations' effects on the viscosity of HVFRs and the mechanisms behind these effects have been studied extensively. For the monovalent Alkali metals (i.e., Na^+ and K^+), their effects on viscosity reduction of anionic HVFRs are described as the charge screening mechanism. They will react with anionic carboxylic groups within anionic HVFRs polymer, decrease the repulsions between the anionic carboxylic groups, and make polymer molecules not fully stretched (Tang and Allen 2009). For the divalent Alkaline earth metals (i.e., Ca^{2+} and Mg^{2+}), they can reduce the viscosity of anionic HVFRs by charge screening, increasing the degree of hydrolysis, and forming polyion-metal complexes (Wang et al. 2013). Therefore, they usually have more pronounced effects on the viscosity reduction of anionic HVFRs than the monovalent Alkali metals. For transition metals (i.e., Fe^{3+}), they can form coordination complexes with either amide groups or anionic carboxylic groups within anionic HVFRs polymer chain (Nakamoto 1978; Girma et al. 2005), which is also known as "Gummy bears" problem in fields (Hazra et al. 2020). Only a small amount of iron can make anionic HVFRs lose their viscous property. For H^+, it can increase the degree of hydrolysis of anionic HVFRs and curb the process of hydrogen ions dissociating from carboxylic acid groups within anionic HVFRs polymer chain, which make polymer molecules not fully stretched and extended (Ma et al. 2015).

In contrast, the published research works regarding ions' effects on the elasticity of HVFRs and the mechanisms behind these effects are still limited. The elastic properties of polymers are strongly dependent on the molecular structure of the polymer network (entanglements) and the polydispersity of its strands (Panyukov 2020). As mentioned above, anions and cations will change the structure of the HVFRs polymer network by charge screening, increasing the degree of hydrolysis, and forming polyion-metal complexes, which will definitely change the elasticity of HVFRs. Meanwhile, based on our previous experimental works, the elasticity of HVFRs has a strong positive correlation with their viscosity (Ge and Imqam 2022; Ge et al. 2022). In other words, the higher viscosity, the higher elasticity. Therefore, it is reasonable to propose that the effects of ions on the elasticity of HVFRs may follow a similar trend as their effects on viscosity for this study.

To address these concerns, the elasticity of a PAM-based anionic HVFR was compared with that of a cationic HVFR using DI water and various salts respectively at 25°C room temperature. Fe^{3+} and H^+ effects on the elasticity of both HVFRs were specifically investigated. To guarantee the accuracy and precision of this experimental study, experimental procedures were detailly stated in this paper with experimental variables well controlled.

Experimental Materials and Description

Experimental Materials

Preparing HVFR Fracturing Fluids. Two types of PAMs, FLOJET DRP 2340X (anionic) and FLOJET DRP 419X (cationic) from SNF Holding Company, were chosen to create HVFR solutions. The HVFRs were in dry powder form and had to be hydrated before testing. A concentration of 4 GPT (around 0.127% by weight) was used, which is a common concentration used in the fields (Ba Geri et al. 2019). The solutions were prepared using deionized water and mixed with American Chemical Society (ACS) grade salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, $MgSO_4$, Na_2SO_4, and $FeCl_3 \cdot 6H_2O$) as well as HCl respectively to create test solutions. The solutions were mixed for 12 hours at 300 rpm to eliminate any air bubbles. To ensure consistent test conditions, all rheology measurements were conducted immediately after mixing. The tests were repeated three times and the closest values were averaged and reported.

Rheometer. The dynamic oscillatory shear measurements were performed using a high-precision advanced rheometer (Anton Paar MCR 302) with a parallel-plate system. The rheometer had a minimum torque rotation of 1 nNm and a normal force range of 0.005 N to 50 N. The measurements were conducted using a parallel-plate measuring system (PP50) with a 0.50 mm gap, at a laboratory temperature of 25°C.

Rheological Characterization of HVFRs

Oscillatory Shear Profile Measurement. The dynamic oscillatory shear measurements were performed to determine the elasticity profiles, including storage modulus (G'), loss modulus (G''), and relaxation time. Before conducting the oscillatory shear tests, amplitude sweep tests were performed to identify the limit of the linear viscoelastic (LVE) region for each sample. A strain value of 1% (0.01) was then selected for the oscillatory shear tests, as it fell within the LVE region for all samples. The tests were performed at a range of angular frequencies from 0.1-10 rad/s at a temperature of 25°C.

Results and Discussion

Elasticity Measurement Tests

Elasticity measurements were conducted for both anionic and cationic HVFRs with a variety of salts. In this section, oscillatory shear test results are presented.

Effects of anions and cations. Based on the previous literature and our experiments, the mechanisms of salt effects on viscosity reduction of HVFRs included charge shielding, increasing degree of hydrolysis, and forming coordination complexes. We found that for the cationic HVFR, anions contributed the most effects on viscosity reduction and, SO_4^{2-} had a more pronounced effect on the viscosity than Cl^-. For the anionic HVFR, cations contributed the most effects on viscosity reduction. The monovalent Alkali metals (i.e., Na^+ and K^+ here) had similar effects on viscosity reduction while the divalent Alkaline earth metals (i.e., Ca^{2+} and Mg^{2+}) had similar effects on viscosity reduction. Moreover, the divalent Alkaline earth metals had a more pronounced effect on viscosity reduction than the monovalent Alkali metals. Fe^{3+} had more pronounced effects on the viscosity reduction of both anionic and cationic HVFRs compared to cations from the Alkali and the Alkaline earth metals (or S-block metals). Meanwhile, these effects were much more severe for the anionic HVFR than its cationic counterpart.

Following these findings, two hypotheses were proposed for this study in terms of anions and cations' effects on the elasticity of HVFRs. First, the elasticity reduction of anionic HVFRs is mainly due to cations, whereas the elasticity reduction of cationic HVFRs is mainly due to anions. Second, the salts' effects on the elasticity reduction of HVFRs should follow the same trend as the salts' effects on the viscosity reduction of HVFRs. For anionic HVFRs, monovalent Alkali metals (i.e., Na^+ and K^+ here) should have similar effects; divalent Alkaline earth metals (i.e., Ca^{2+} and Mg^{2+} here) should have similar and more pronounced effects; transition metals (i.e., Fe^{3+} here) should have the most severe effects. The cations' effects on the elasticity reduction of anionic HVFRs can be ranked as $Fe^{3+} > Ca^{2+} \approx Mg^{2+} > Na^+ \approx K^+$. Similarly, for the elasticity reduction of cationic HVFRs, the anions' effects can be ranked as $SO_4^{2-} > Cl^-$.

To demonstrate both hypotheses, precise experimental designs with experimental variables well-controlled were strictly required. For each salt's concentration, molarity (M) should be used instead of weight concentration (ppm). For this study, 200 ppm of NaCl salt was selected as the benchmark as shown in Table 1. Then, the molarity of cation (i.e., Na^+ here) and anion (i.e., Cl^- here) was calculated, which was 0.00342 mole/L. Note that the investigated salt concentration was carefully selected. Instead of focusing on the practical meaning, this study more focused on quantitatively investigating anions and cations' effects on the elasticity of HVFRs. In fields, the concentration of TDS is usually much higher than 200 ppm. High concentration of TDS would make the elasticity of HVFRs become negligible (Ge and Imqam 2022; Ge et al. 2022).

Table 1—Composition of salt contents.

Salt type	Weight concentration (ppm)	Molecular weight (g/mole)	Molarity, M (mole/L)	Molarity of cation (mole/L)	Molarity of anion (mole/L)	pH	
						Cationic HVFR	Anionic HVFR
NaCl	200	58.5	0.00342	0.00342	0.00342	4.2	7.4
KCl	255.043	74.6	0.00342	0.00342	0.00342	4.6	7.3
$CaCl_2$	189.915	111.1	0.00171	0.00171	0.00342	4.4	7.1
$MgCl_2$	162.906	95.3	0.00171	0.00171	0.00342	4.4	7.1
$MgSO_4$	411.521	120.37	0.00342	0.00342	0.00342	4.8	7.1
Na_2SO_4	485.709	142.07	0.00342	0.00684	0.00342	4.2	7.4
$FeCl_3.6H_2O$	308.188	270.435	0.00114	0.00114	0.00342	2.2	4.5

4 GPT cationic HVFR was first tested with different salt solutions while keeping the molarity of anions in each salt solution the same as shown in Table 1. The pH of each salt solution after mixing with the cationic HVFR was also recorded in Table 1. The elasticity of fluids is quantified by dynamic oscillatory shear measurements, which are made over a range of frequencies from 0.1 rad/s to 10 rad/s. Fig.1 shows the elastic modulus, G', and the viscous modulus, G'', as functions of the angular frequency, ω, for the cationic HVFR in DI water and various salt solutions at 25°C ambient temperature. When the G'' values are higher than the G' values, fluids are more viscous than they are elastic; when the G'' values are lower than the G' values, fluids are more elastic than they are viscous; when G''(ω) and G'(ω) are equal, the ω values of crossover points for each test fluid are presented in Table 2. Then, the relaxation time, T, can be calculated by inverting ω, which is also shown in Table 2. The relaxation time is a measure of the elasticity of a fluid. A fluid with zero relaxation time is referred to as an inelastic fluid, and the elasticity of the fluid is greater if it has a longer relaxation time.

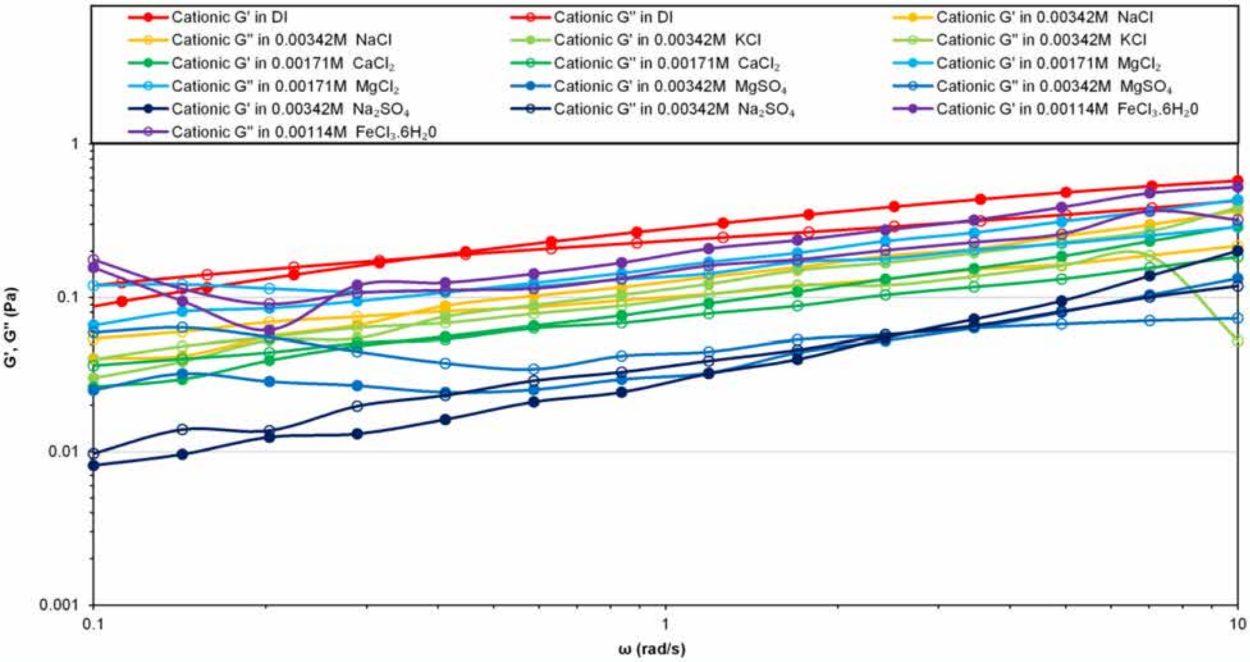

Figure 1—Oscillatory shear measurement of the 4 GPT cationic HVFR in DI water and various salt solutions at 25°C.

Table 2—Loss modulus and storage modulus crossover points and relaxation times of the 4 GPT cationic and anionic HVFRs in DI water and various salt solutions at 25°C.

Salt type	Cationic HVFR		Anionic HVFR	
	Crossover, ω (rad/s)	Relaxation time, T (s)	Crossover, ω (rad/s)	Relaxation time, T (s)
DI water	0.371	2.695	0.0828	12.077
NaCl	0.343	2.915	0.305	3.279
KCl	0.361	2.770	0.345	2.899
$CaCl_2$	0.348	2.874	1.55	0.645
$MgCl_2$	0.467	2.141	1.99	0.503
$MgSO_4$	3.51	0.285	1.7	0.588
Na_2SO_4	2.67	0.375	0.815	1.227
$FeCl_3.6H_2O$	0.267	3.745	10	0.100

To identify the elasticity reduction impact differences of different salts on the cationic HVFR more clearly, the relaxation time of the cationic HVFR with DI water and various salt solutions was plotted in Fig. 2. NaCl, KCl, $CaCl_2$, and $MgCl_2$, the salts with Cl^- as the anion, had close effects on the elasticity of the cationic HVFR. The elasticity did not change much compared to the cationic HVFR with DI water. The reason for this was that a small amount of these salts might increase the hydrolysis of the cationic HVFR polymer, which compensated for the side effects on elasticity (Seright et al. 2010). $MgSO_4$ and Na_2SO_4, the salts with SO_4^{2-} as the anion, also had similar effects on the elastic reduction of the cationic HVFRs. Besides, both salts had lower relaxation time than the previous four salts, which was around 0.3s. Finally, the cationic HVFR with $FeCl_3{\cdot}6H_2O$ had a similar relaxation time as the previous four salts with Cl^- as the anion, even though the solution was more acidic. These observations matched our predictions. Overall, monovalent and divalent cations from S-block had very limited effects (or even no effects) on the elasticity of the cationic HVFR. Instead, anions contributed the most effects on the elastic reduction of the cationic HVFR, and SO_4^{2-} had a more pronounced effect on the elasticity of the cationic HVFR than the Cl^-. Finally, Fe^{3+} and low pH (or H^+) showed limited effects on the elasticity reduction of the cationic HVFR.

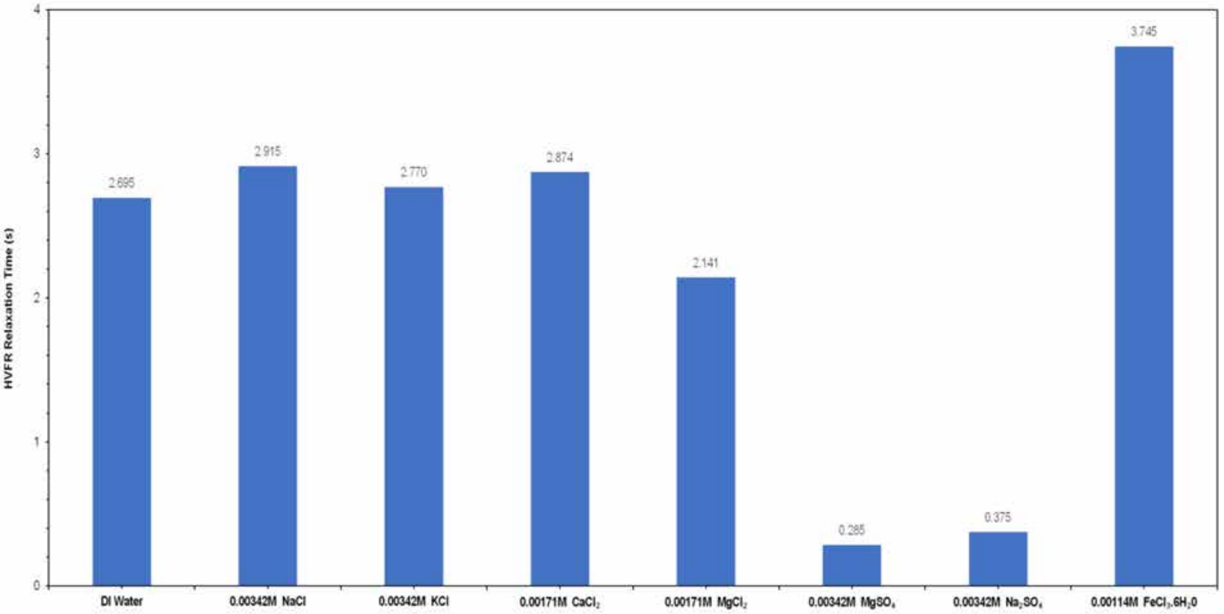

Figure 2—Relaxation time of the 4 GPT cationic HVFR in DI water and various salt solutions at 25°C.

Then, 4 GPT anionic HVFR was tested with the same salt solutions used for the cationic HVFR as shown in Table 1, and followed with the same procedures. The pH of each salt solution after mixing with the anionic HVFR was also recorded in Table 1. Fig. 3 showed the elasticity profiles of the anionic HVFR with DI water and various salt solutions at 25°C. The relaxation time was recorded in Table 2.

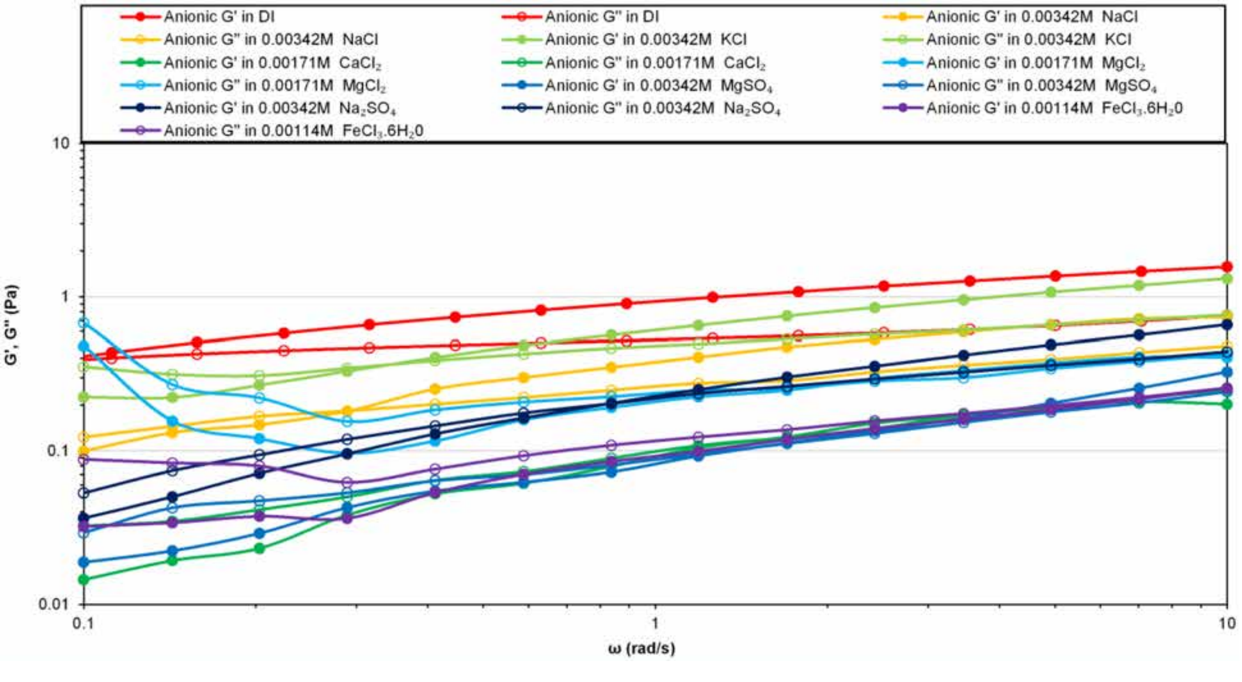

Figure 3—Oscillatory shear measurement of the 4 GPT anionic HVFR in DI water and various salt solutions at 25°C.

To identify different salts' effects on the elasticity reduction of the anionic HVFR more clearly, the relaxation time of the anionic HVFR with DI water and various salt solutions was plotted in Fig. 4. NaCl and KCl, the salts with monovalent cations, had close effects on elastic reduction of the anionic HVFR. For the anionic HVFRs in salts with divalent cations (i.e., $CaCl_2$, $MgCl_2$, and $MgSO_4$ here), they also had close relaxation time values. Besides, these values were decreased by a factor of 6 compared to the anionic HVFR with NaCl and KCl. For the anionic HVFR with Na_2SO_4, relaxation time was slightly lower than the anionic HVFR with NaCl and KCl, which was mainly due to the double concentrations of monovalent cation (i.e., Na^+ here). Finally, by looking at the anionic HVFR with $FeCl_3{\cdot}6H_2O$, the relaxation time was significantly small, which indicated the elasticity of fluid was negligible. Overall, it was reasonable to conclude that the monovalent Alkali metals (i.e., Na^+ and K^+ here) had similar effects on the elasticity reduction of the anionic HVFR while the divalent Alkaline earth metals (i.e., Ca^{2+} and Mg^{2+}) had the similar effects on the elasticity reduction of the anionic HVFR. Moreover, the divalent Alkaline earth metals had a more pronounced effect on the elasticity reduction than the monovalent Alkali metals. Anions (i.e., Cl^- and SO_4^{2-} here) had limited effects on the elasticity of the anionic HVFR. $FeCl_3{\cdot}6H_2O$ had significant effects on the elasticity reduction of the anionic HVFR. Meanwhile, the solution was more acidic. Whether pH or Fe^{3+} caused extremely low elasticity and which one had more pronounced effects would be specifically investigated in the next section.

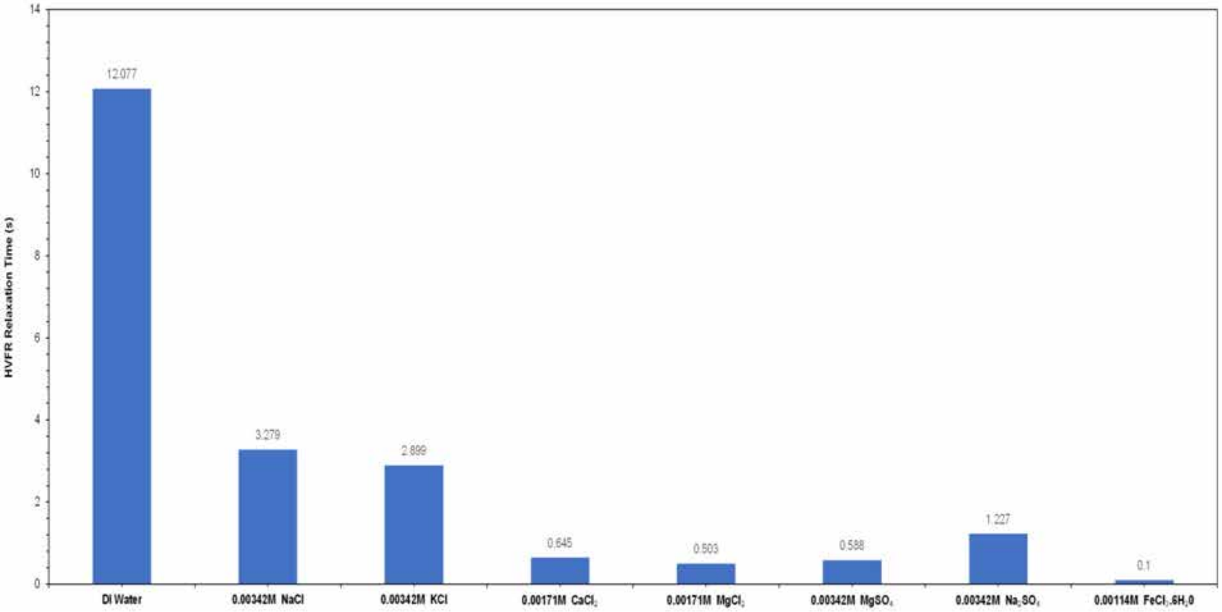

Figure 4—Relaxation time of the 4 GPT anionic HVFR in DI water and various salt solutions at 25°C.

In the end, the relaxation time of both anionic and cationic HVFRs with DI water and various salt solutions at 25°C were plotted in Fig. 5 to comparatively investigated the differences of anions and cations' effects on the elasticity of both HVFRs. Under DI water conditions, the anionic HVFR had a relaxation time almost five times as high as its cationic counterpart. For brine solutions with both monovalent cations and anions (i.e., NaCl and KCl here), the anionic HVFR had a similar relaxation time as its cationic counterpart. However, the relaxation time of the anionic HVFR decreased significantly compared to the DI water condition while the relaxation time of the cationic HVFR was almost kept the same. For brine solutions with divalent cations and monovalent anions (i.e., $CaCl_2$ and $MgCl_2$ here), the cationic HVFR had a higher relaxation time than its anionic counterpart. For brine solution with both divalent cations and anions (i.e., $MgSO_4$ here), the anionic HVFR had a similar relaxation time as the cationic HVFR. For brine solution with monovalent cations and divalent anions (i.e., Na_2SO_4 here), the anionic HVFR had a higher relaxation time than its cationic counterpart. Moreover, for produced water from fields, high concentrations of monovalent and divalent cations and anions are usually contained in the solution, which makes the elasticity of anionic and cationic HVFRs close to each other. High reservoir temperature will make this difference even smaller (Ge and Imqam 2022; Ge et al. 2022). However, cationic HVFRs are still preferred to be used when fracturing with high salinity produced water. We believe Fe^{3+} is one of the most important factors. With a low pH $FeCl_3$ brine solution, the elasticity of the anionic HVFR was negligible whereas the cationic HVFR still had certain elastic properties at 25°C. The effect of Fe^{3+} on the elasticity of both anionic and cationic HVFRs will be specifically investigated in the next section.

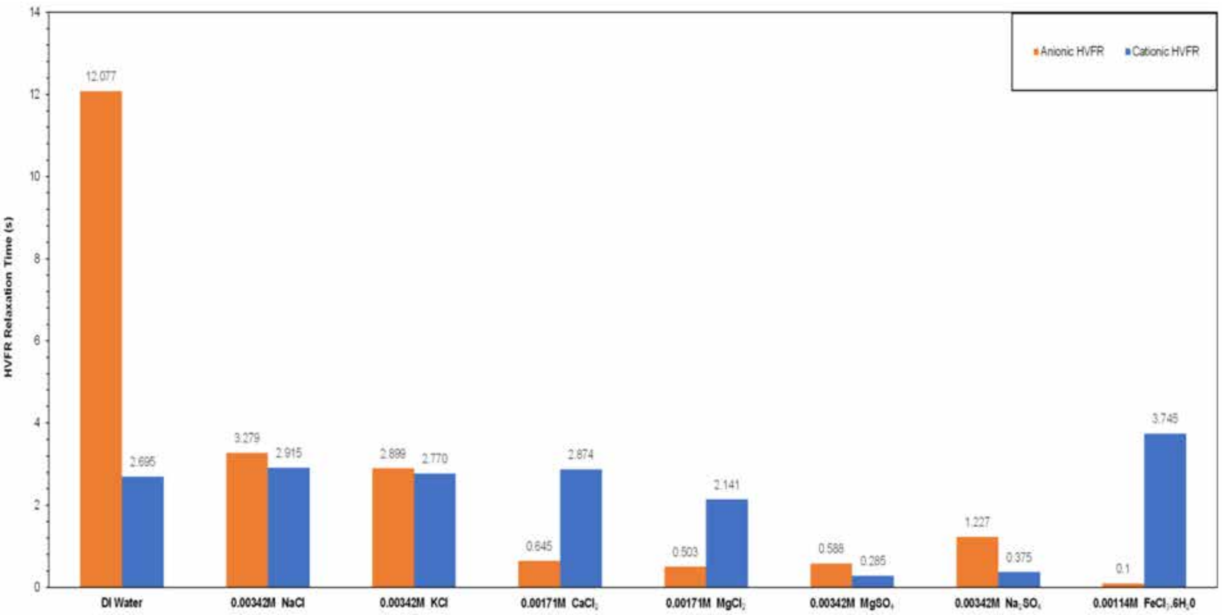

Figure 5—Relaxation time of the 4 GPT anionic and cationic HVFRs in DI water and various salt solutions at 25°C.

Effect of Ferric (Fe^{3+}) and pH. Ferric cation (Fe^{3+}) is also a commonly found cation in produced water from oil fields. It can originate from various sources such as reservoirs, corroded pipes, and corroded equipment (Shen et al. 2019; Hazra et al. 2020; Ge et al. 2022). In order to investigate the effects of pH and Fe^{3+} on the elasticity of the cationic HVFR, HCl solution with the same molarity of Cl^- as $FeCl_3 \cdot 6H_2O$ was needed as the benchmark. The molarity of cations and anions for HCl as well as $FeCl_3 \cdot 6H_2O$ and NaCl was listed in Table 3.

Table 3—Concentration and pH of NaCl, $FeCl_3 \cdot 6H_2O$, and HCl.

Solution type	Weight concentration (ppm)	Molecular weight (g/mole)	Molarity, M (mole/L)	Molarity of cation (mole/L)	Molarity of anion (mole/L)	pH
NaCl	200	58.5	0.00342	0.00342	0.00342	4.2
$FeCl_3.6H_2O$	308.188	270.435	0.00114	0.00114	0.00342	2.2
HCl	124.650	36.46	0.00342	0.00342	0.00342	2.2

Fig. 6 showed elasticity profiles of the cationic HVFR with DI water, NaCl, $FeCl_3 \cdot 6H_2O$, and HCl solutions at 25°C. The relaxation time was recorded in Table 4. To observe the differences more clearly, the relaxation time of each test fluid was also plotted in Fig. 7. The cationic HVFR with DI water, NaCl, $FeCl_3 \cdot 6H_2O$, and HCl had almost the same relaxation time. Therefore, it was reasonable to conclude Fe^{3+} and H^+ had very limited effects (or even no effects) on the elasticity of the cationic HVFR, which was similar to the effects of cations from the Alkali and the Alkaline earth metals (i.e., Na^+, K^+, Ca^{2+}, and Mg^{2+} here).

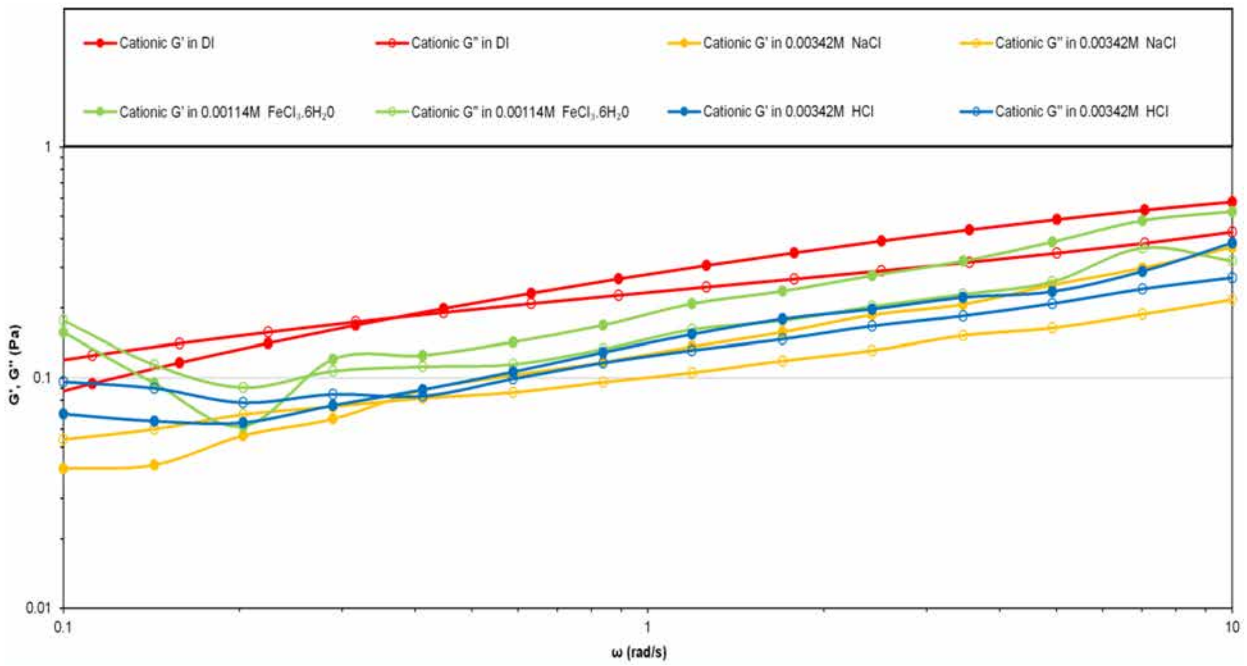

Figure 6—Oscillatory shear measurement of the 4 GPT cationic HVFR in 0.00342M NaCl, 0.00114M $FeCl_3·6H_2O$, and 0.00342M HCl as well as DI water at 25°C.

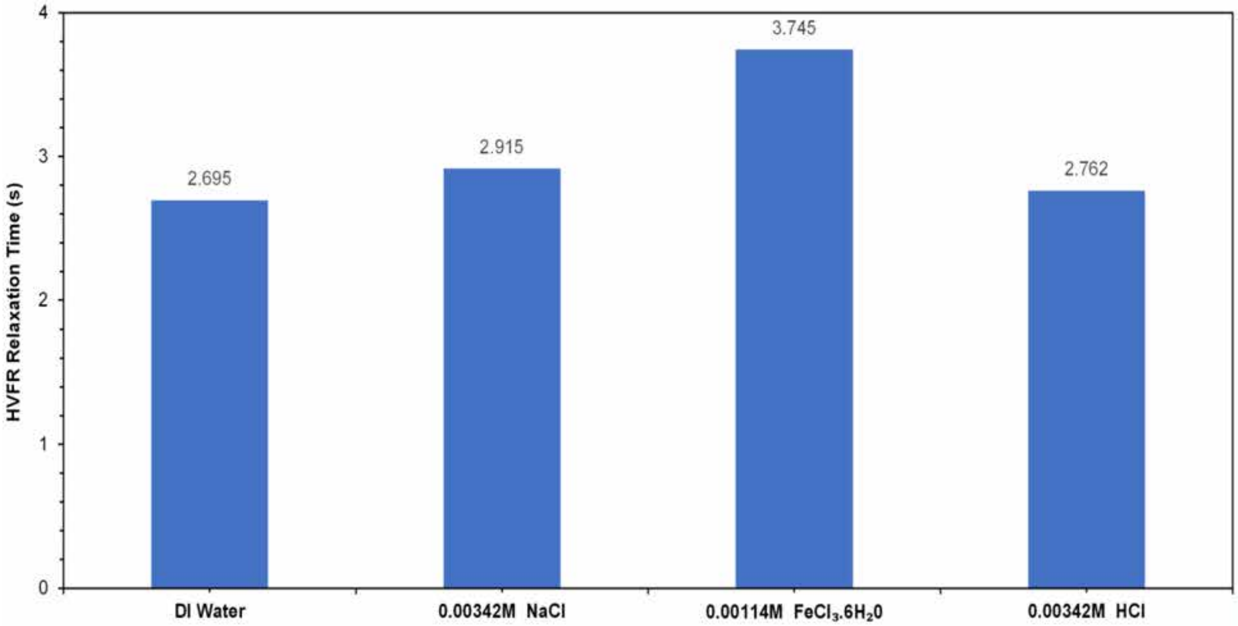

Figure 7—Relaxation time of the 4 GPT cationic HVFR in 0.00342M NaCl, 0.00114M $FeCl_3·6H_2O$, and 0.00342M HCl as well as DI water at 25°C.

Table 4—Loss modulus and storage modulus crossover points and relaxation times of the 4 GPT cationic HVFR in 0.00342M NaCl, 0.00114M $FeCl_3·6H_2O$, and 0.00342M HCl as well as DI water at 25°C.

Salt type	Cationic HVFR	
	Crossover, ω (rad/s)	Relaxation time, T (s)
DI water	0.371	2.695
0.00342M NaCl	0.343	2.915
0.00114M $FeCl_3.6H_2O$	0.267	3.745
0.00342M HCl	0.362	2.762

To investigate the Fe^{3+} and pH effects on the anionic HVFR, 0.00114 and 0.00342 mole/L HCl was selected and tested as benchmarks as shown in Table 5.

Table 5—Concentration and pH of NaCl, $CaCl_2$, $FeCl_3·6H_2O$, and HCl.

Solution type	Weight concentration (ppm)	Molecular weight (g/mole)	Molarity, M (mole/L)	Molarity of cation (mole/L)	Molarity of anion (mole/L)	pH
NaCl	200	58.5	0.00342	0.00342	0.00342	7.4
$CaCl_2$	189.915	111.1	0.00171	0.00171	0.00342	7.3
$FeCl_3.6H_2O$	308.188	270.435	0.00114	0.00114	0.00342	4.5
HCl	41.550	36.46	0.00114	0.00114	0.00114	6.7
	124.650		0.00342	0.00342	0.00342	4.2

Fig. 8 showed elasticity profiles of the anionic HVFR with DI water, NaCl, $CaCl_2$, $FeCl_3·6H_2O$, and HCl solutions at 25°C. The relaxation time was recorded in Table 6. To observe the differences more clearly, the relaxation time of each test fluid was also plotted in Fig. 9. By comparing with 0.00114 mole/L $FeCl_3·6H_2O$, the anionic HVFR with 0.00114 mole/L HCl had a much higher relaxation time. Therefore, Fe^{3+} had a more pronounced effect on the elasticity reduction of the anionic HVFR than H^+. Fig. 10 showed both anionic and cationic HVFRs with $FeCl_3·6H_2O$. The solution was turbid and brown flocculent precipitates were presented for the anionic HVFR. This was because Fe^{3+} can form coordination complexes with both amide groups and anionic carboxylic groups within the anionic HVFR polymer chain. (Nakamoto 1978; Girma et al. 2005). By comparing with 0.00342 mole/L NaCl, the anionic HVFR with 0.00342 mole/L HCl had no relaxation time, which indicated that the elasticity was negligible. Therefore, H^+ had a more pronounced effect on the elasticity reduction of the anionic HVFR than other cations from Alkali metals (i.e., Na^+ and K^+ here).

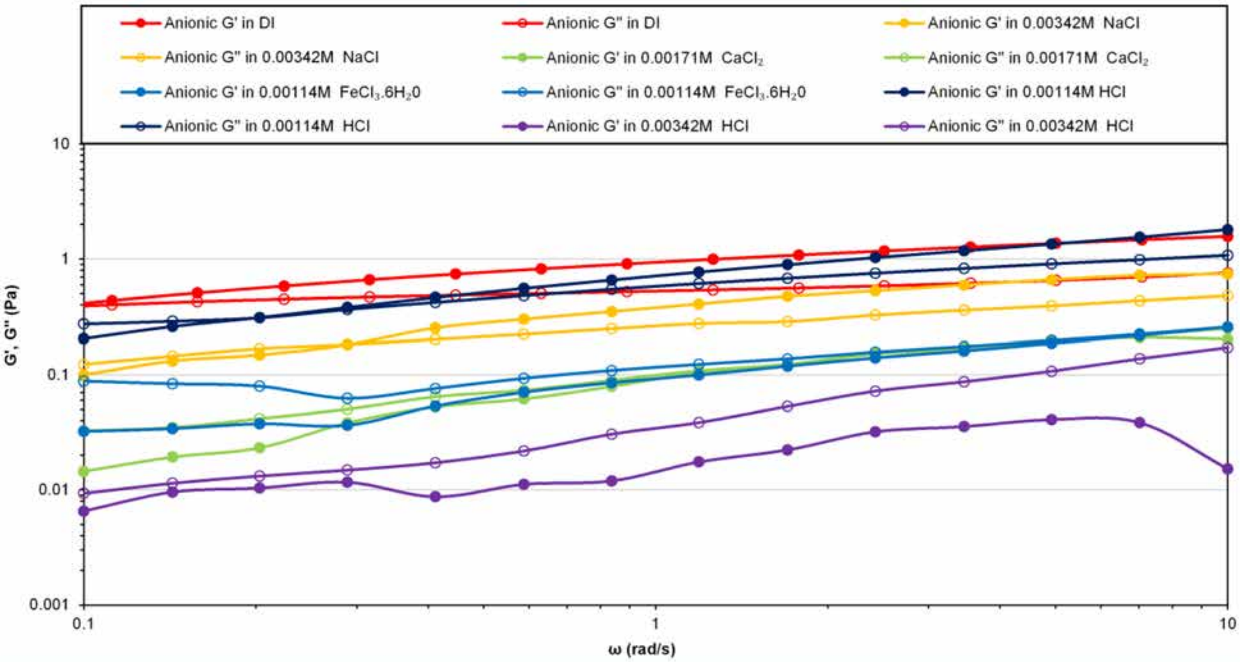

Figure 8—Oscillatory shear measurement of the 4 GPT anionic HVFR in 0.00342M NaCl, 0.00171M $CaCl_2$, 0.00114M $FeCl_3 \cdot 6H_2O$, 0.00114M HCl, and 0.00342M HCl as well as DI water at 25°C.

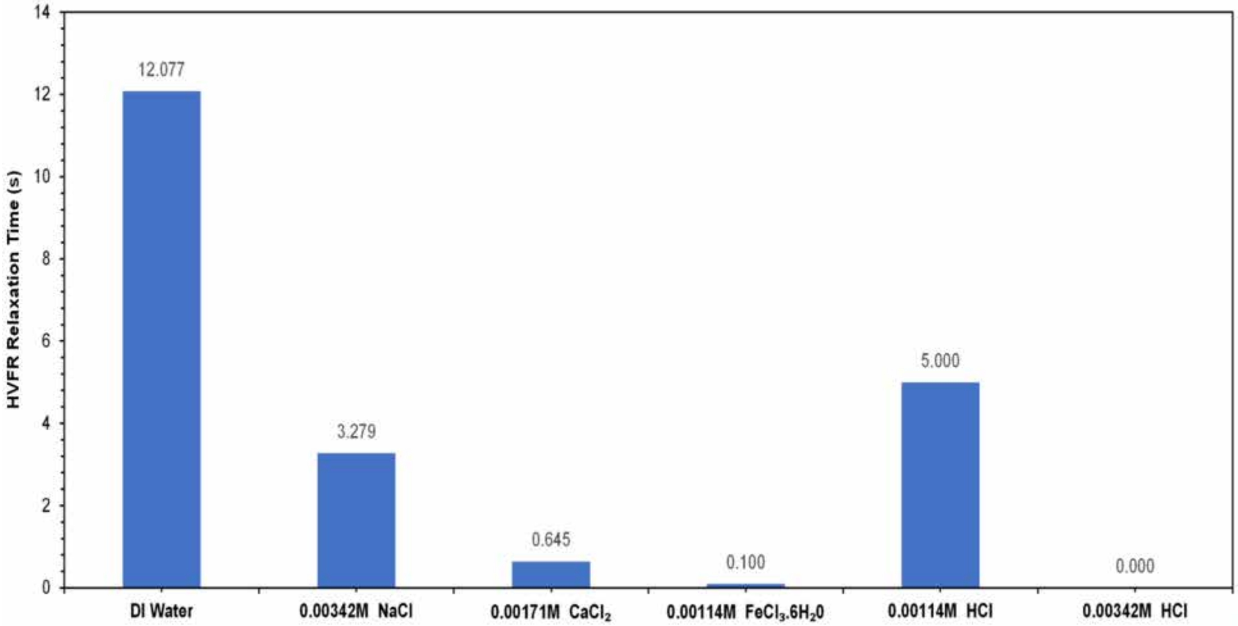

Figure 9—Relaxation time of the 4 GPT anionic HVFR in 0.00342M NaCl, 0.00171M $CaCl_2$, 0.00114M $FeCl_3 \cdot 6H_2O$, 0.00114M HCl, and 0.00342M HCl as well as DI water at 25°C.

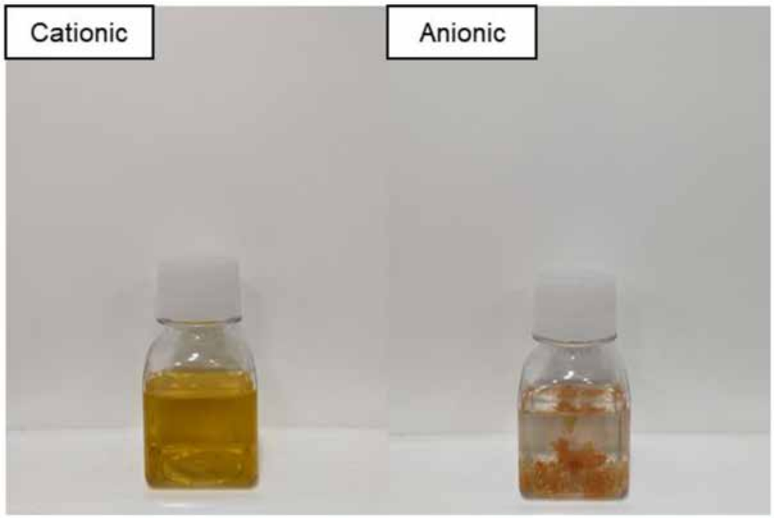

Figure 10—The 4 GPT anionic and cationic HVFRs in 0.00114M $FeCl_3 \cdot 6H_2O$ at 25°C.

Table 6—Loss modulus and storage modulus crossover points and relaxation times of the 4 GPT anionic HVFR 0.00342M NaCl, 0.00171M $CaCl_2$, 0.00114M $FeCl_3 \cdot 6H_2O$, 0.00114M HCl, and 0.00342M HCl as well as DI water at 25°C.

Salt type	Anionic HVFR	
	Crossover, ω (rad/s)	Relaxation time, T (s)
DI water	0.0828	12.077
0.00342M NaCl	0.305	3.279
0.00171M $CaCl_2$	1.55	0.645
0.00114M $FeCl_3.6H_2O$	10	0.100
0.00114M HCl	0.2	5.000
0.00342M HCl	N/A	N/A

To sum up, Fe^{3+} and H^+ had very limited effects on the elasticity reduction of the cationic HVFR. In contrast, they had much more pronounced effects on the anionic HVFR. Small concentrations of Fe^{3+} and H^+ significantly destroyed the elastic property of the anionic HVFR. Fe^{3+} had more severe effects than H^+.

Conclusions

An anionic and a cationic HVFR were tested with various salts while keeping experimental variables well controlled. Based on the results, the following conclusions can be drawn:

- For the cationic HVFR, anions contribute the most of effects on the elasticity reduction. A small concentration of Cl^- has limited effects while SO_4^{2-} has more pronounced effects.
- For the anionic HVFR, cations contribute the most of effects on the elasticity reduction. The monovalent Alkali metals have similar effects on elasticity reduction while the divalent Alkaline earth metals have similar effects on elasticity reduction. Moreover, the divalent Alkaline earth metals have more pronounced effects on elasticity reduction than the monovalent Alkali metals.
- Fe^{3+} and H^+ (or pH) have very limited effects on the elasticity of the cationic HVFR, which are similar to the effects of cations from the Alkali and the Alkaline earth metals. In contrast, they have much more pronounced effects on the elasticity reduction of the anionic HVFR. Fe^{3+} had more severe effects than H^+.
- Overall, the two hypotheses proposed for this research study are accepted. More cations from each selected group (i.e., Cs^+ from the Alkali metals, Sr^{2+} and Ba^{2+} from the Alkaline earth metals,

and Co^{2+} and Cu^{2+} from the transition metals) can be further investigated to demonstrate both hypotheses even though some cations are not commonly presented in produced water. More anionic and cationic HVFRs in the industrial market also remain to test in order to draw more general conclusions.

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