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Research into the Impact of Seawater Ionic Composition on the Rheological Characteristics of a Cationic Guar Gum-Based Fracturing Fluid

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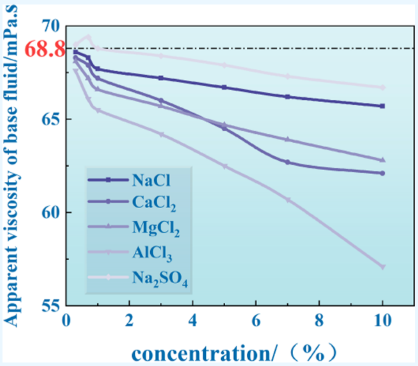
ABSTRACT: This study examined the effects of salt content and salt type on the properties of the hydroxypropyl guar gum fracturing fluid. In this study, we conducted a thorough analysis of the impact that various ions in seawater have on the performance of fracturing fluids. We identified the cross-linked polymer that performs optimally at a specific concentration of the binding agent. The experimental conditions, with a constant temperature of 90 °C and a shear rate of 100 s^{-1}, were designed to simulate harsh reservoir environments. The results indicated that high concentrations of inorganic salt impede the swelling of guava gum, consequently reducing the viscosity of the solution. Initially, the addition of sodium sulfate enhances the viscosity of the guar-based solution; however, as the concentration increases, the effect becomes less pronounced. Solution containing multivalence cations exhibited a more substantial adverse impact on viscosity. In addition, the presence of SO_4^{2-} and Ca^{2+} influenced the temperature resistance of the fracturing fluid. While a minimal concentration of SO_4^{2-} can boost the viscosity, excessive amounts lead to a reduction. The addition of tetrasodium ethylenediamine tetraacetate (EDTA-4Na) first chelates the calcium ions in the salt solution and then increases the viscosity of cationic guar gum by electrostatic action. SEM cryo-electron microscope revealed that the fracturing fluid network became denser after the addition of EDTA-4Na, although the viscosification effects varied among different ions.



1. INTRODUCTION

Hydraulic fracturing increases production by decontaminating near-wellbore areas and creating artificial fractures to increase the reservoir permeability. The effectiveness of the fracturing fluid has a direct bearing on the postfracturing outcome. The fracturing operation can be carried out by forming a fracture capable of withstanding the closure pressure with the assistance of proppants. When devising a fracturing plan, two aspects, namely, the formation type and the availability of freshwater, need to be taken into account. The selected additives, proppant, and injection rate will mirror these considerations.[1] In the design of fracturing fluid, the optimal viscosity is one that enables the formation of the deepest possible fractures while remaining practical for application. It should possess sufficient elasticity and viscosity to maintain the proppant in suspension at the lowest possible settling rate. Once the proppant is in place, this fluid ought to break and flow back out of the formation.[2,3]

The ideal fracturing fluid will contribute to the attainment of these objectives during the fracture design. Fracture design aims to determine the optimal dimensionless fracture conductivity by optimizing other parameters such as the fracture half-length, width, and permeabilities of the fracture and the reservoir. These parameters necessitate that the fluid be able to transport the proppant with minimal velocity settling, fluid loss, and formation damage. The fracturing fluid incorporates numerous additives to achieve these characteristics, and the crucial additives are the gelling agents. Guar gum can be chemically modified to yield a variety of derivatives. This is accomplished by substituting the reactive hydrogen of the free hydroxyl groups along the macromolecular backbone with diverse reactive functional groups. Such a modification serves multiple purposes. It addresses the inherent challenges of guar gum, including viscosity reduction caused by an uncontrolled hydration rate, pH-dependent solubility, turbidity in aqueous dispersion, and high vulnerability to microbial attack, which otherwise restrict its long-term application. Additionally, it enhances the solubility and overall properties of guar gum.[4] These residues impede the flow within the fractures and thereby limit the fracturing efficiency. In comparison to guar gum, the interaction between the polymer and

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polysaccharide intensifies with the increase in the hydroxypropyl degree of guar gum. The composite fabricated using guar gum and hydroxypropyl guar gum (HPG) as fillers exhibits superior mechanical properties, and its elongation and water absorption are also enhanced.[5] HPG is the most prevalent guar derivative in the oil industry. In contrast, Hydroxypropyl guano trimethylammonium chloride (HPGTAC) has excellent solubility and thickening properties, which is beneficial for reducing the impairment to the reservoir conductivity, and good temperature and shear resistance. The pad initiates the fracture and provides sufficient leak-off as the slurry (cross-linked fluid + proppant) is pumped into the formation, minimizing fluid loss.[6] Figure 1 depicts the structure of HPGTAC.

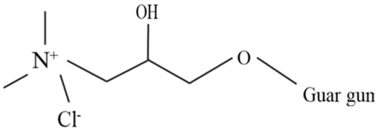


Figure 1. Generic structure of Hydroxypropyl guar gum trimethylammonium chloride.

A higher viscosity fluid is needed to propagate a fracture, which can be achieved by adding a cross-linker. At lower concentrations of guar derivatives, the cross-linker exhibits the capacity to elevate the viscosity to the range of several hundred centipoises. Nevertheless, fluids with excessive viscosity may inflict damage upon the formation. Additionally, the cross-linker augments the fluid's elasticity, thereby effecting a transformation in its rheological behavior from a predominantly viscous state to a viscoelastic one. Cross-linkers are constituted of phosphate esters, potassium hydroxide, isopropyl alcohol, and metals such as aluminum, antimony, and titanium. Among these constituents, borate and zirconium are the most commonly employed. Borates function as immediate cross-linkers and are deployed to maintain viscosity stability under elevated temperature conditions, giving rise to the formation of borate-cross-linked guar derivative salts. In fracturing operations, delayed zirconium cross-linkers are exploited to facilitate the efficient transportation of proppants.[7−11]

Saline water possesses a more robust cross-linking mechanism and exhibits lower hydration levels in contrast to freshwater. The divalent ions present in saline water contribute to the hardness of the water, subsequently leading to hydration insufficiencies and potential damage to the formation. The instability of produced water and fluids based on saline water at elevated temperatures is a significant concern. Chelating agents, including EDTA, ethanolic phosphotungstic acid, and GLDA, find extensive application in the oil industry for diverse objectives such as clay stabilization, pH modulation, ion regulation, reduction of surface tension, and thermal stabilization. These compounds sequester ions and mitigate water hardness during fracturing operations. EDTA has the ability to bind anions such as sulfates and carbonates, whereas GLDA can bind cations such as calcium and magnesium. GLDA is capable of withstanding temperatures up to 149 °C without undergoing degradation, and its ion reaction varies in response to pH fluctuations. Excessive concentrations of chelating agents can impede the cross-linking process; thus, their levels necessitate meticulous control.[12−15]

Physically cross-linked polymer thickeners produce reversible three-dimensional network structures through physical association, and their shear resistance and gum-breaking properties are outstanding. In this article, the physical cross-linking through the intermolecular electrostatic attraction is reversible cross-linking, which greatly reduces the friction resistance and improves the shear resistance of the system. The use of middle and low-molecular-weight cationic HPG polymer as thickener can reduce the residue after gumming, and the damage degree to the formation is not high, which can solve many problems existing in the current fracturing fluid system.[16−20]

Sedaghatzadeh et al.[21] examined the impact of various cation concentrations and types on the rheological properties and stability of cross-linked gels made from guar, xanthan, and partially hydrolyzed polyacrylamide (HPAM) through experimental analysis. Additionally, a novel approach was developed to mitigate the adverse effects of cations by utilizing multiwalled carbon nanotubes (MWCNTs). The presence of cations in the cross-linked gel system leads to a decrease in gel viscosity, with higher cation concentrations resulting in lower viscosity. Bivalent cations exhibit a more pronounced reduction in viscosity compared to monovalent cations. The stability of cross-linked gels is compromised in the presence of cations, particularly exacerbated under elevated salinity conditions.

This research explores the impact of cross-linkers on the specific ions associated with saline water and purified water. The study excludes other ions related to saline water and purified water as they have minimal influence on the behavior of saline water.[22] The experiments were conducted at specific concentrations of each ion. Separate studies have examined varying ion concentrations and the influence of the chelating agents. The first part studies the law of the influence of different ions on the viscosity of the cationic guar adhesive. The second part studies the law of viscosification of different valence anions on fracturing fluid and demonstrates more intuitively the viscosification effect of anions on fracturing fluid utilizing differential scanning calorimetric analysis and SEM cryo-electron microscopy. The third part gives an in-depth study of the influence of Ca^{2+} on the properties of cationic guar adhesive fracturing fluid.

2. METHODOLOGY

2.1. Materials.

In this work, we used an MCR102 rheometer to measure the viscosity value of different additives (calcium chloride, sodium chloride, sodium sulfate, sodium phosphate, potassium chloride, aluminum chloride, magnesium chloride, ethylenediamine tetraacetic acid tetrasodium), cationic gum mixture, and organic boron cross-linker mixture under constant temperature and constant shear condition.[23] The experimental reagents and their concentrations are listed in Table 1.

HPG is widely used as a thickener in oilfield fracturing fluids. HPG thickener has high viscosity and strength and can be used as a proppant and control fluid loss. At present, The main fracturing measures in the world use HPG water-based fracturing fluids.[24]

2.2. Experimental Design.

The first part is a basic fracturing fluid system. The second part is the influence of anion valence on the viscosity of the cationic guar gum fracturing fluid. The third part is the study of the methods and steps of viscidity increase. The third part is the anion viscidity

Table 1. Experimental Reagents

reagent names	reagent concentration
HPG (cation)	analytical purity
organic boron cross-linker RW-G30	50.1%
$CaCl_2$	analytical purity
NaCl	analytical purity
Na_2SO_4	analytical purity
Na_3PO_4	analytical purity
KCl	analytical purity
$AlCl_3$	Analytical purity
$MgCl_2$	analytical purity
EDTA-4Na	99%
distilled water	

increase effect test of cationic guar gum.1. Preparation of HPG fracturing fluid. (1) Distilled water was poured into a beaker with a mixer, the speed was set to 500 rpm, HPG was slowly added, and stirred for 10 min so that it becomes a uniform solution. (2) In the stirring state of a mixer of 400 rpm, the organoboron cross-linker (RW-G30) was added into the prepared HPG solution beaker and stirred for 3 min to prepare the fracturing fluid.2. Screening of viscosifying additives for hydroxypropyl guar gum fracturing liquid. The HPG base liquid was prepared according to the method in (1), and different selected additives were added to the base liquid, and then the cross-linking agent was added to form the HPG fracturing fluid. 70 mL of the prepared fracturing fluid was put into the cylinder of an Austrian Anton Paar MCR102 rheometer, and the shear rate was set at 100 s^{1-}. The viscosity of the fracturing fluid was measured at 90 °C for 10 min.

3. RESULTS AND DISCUSSION

3.1. Effect of Different Ions on the Viscosity of the Cationic Guar Gum Fracturing Fluid. To optimize the formula for seawater-based fracturing fluid, the effects of different ions on the base fluid's apparent viscosity, cross-linking time, temperature resistance, shear resistance, and residue content were analyzed. The experimental protocol involved two primary stages: (1) Preparation of the inorganic salt solution. Inorganic salt is added to distilled water in a beaker with a mixer set at 500 rpm, stirring continuously for 10 min, creating a homogeneous inorganic salt solution. (2) Preparation of HPG fracturing fluid. Initially, HPG was gradually added to the previously prepared inorganic salt solution while maintaining the mixer speed at 500 rpm, ensuring the mixer remained uniform after stirring for 10 min. Subsequently, the mixer's speed was reduced to 400 rpm, and an optimized cross-linking agent, RW-G30, was incorporated and stirred for 3 min to finalize the fracturing fluid. (3) Measurement of the apparent viscosity of the base solution. A 200 mL sample of the HPG solution was taken with the measuring cylinder, and the apparent viscosity of the base liquid was recorded with a ZNN-D6 rotary viscometer at a rotational speed of 100 rpm once the viscometer stabilized.

The apparent viscosity is calculated according to the following formula:

$$\mu = \frac{5.077\alpha}{1.704}$$

μ—the apparent viscosity of the test sample is measured in milliseconds (mPa·s).

5.077—the value of shear stress when α is 1, the unit is 10 negative primary square 1 Pa (10-square).

1.704—the number of revolutions of the viscometer is the shear rate of 1 rpm in negative first-order square seconds (s^{-1}).

Amani et al.[25] observed that adding salt to water reduces the overall viscosity of gels. Consequently, drawing from Einarson et al.,[26] the salt concentration in all experiments was capped at 10^{-1} to prevent a decline in polymer solubility at high salinity levels, which could adversely affect the performance of cross-linked gels. To study the influence of salt content and types on the characteristics of cationic HPG fracturing fluid, various concentrations of sodium chloride, calcium chloride, aluminum chloride, magnesium chloride, and sodium sulfate: 0.3, 0.7, 1, 3, 5, 7, and 10% were prepared, respectively. These inorganic salt solutions were mixed with the selected cationic HPG to create a 0.5% HPG solution. The apparent viscosity of this base solution was measured by using a ZNN-D6 rotational viscometer. The actual results are shown in Figure 2.

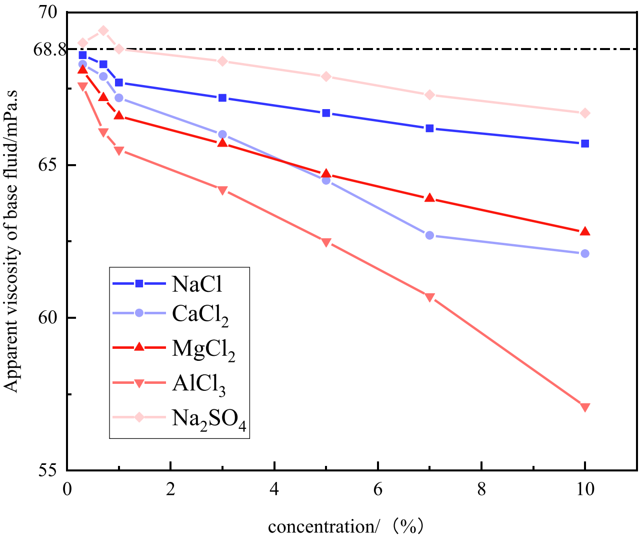


Figure 2. Effect of salt content and type on the viscosity of the base solution.

According to the experimental data presented in Figure 2, the apparent viscosity of the HPG solution prepared with pure distilled water is 68.8 mPa·s. Except for solutions containing sodium sulfate, the viscosities of all guar gum base solutions prepared with salt water are lower than the reference value under salt-free conditions. As the salt content increases, there is a consistent downward trend in the viscosity of the base solution. This trend suggests that high concentrations of inorganic salt inhibit the swelling of guar gum, leading to a decrease in the viscosity of the base solution. Conversely, the addition of sodium sulfate initially increases the viscosity of the guar gum base solution. However, as the concentration of sodium sulfate continues to rise, the viscosity begins to decrease, although the rate of decline is slower compared to other inorganic salts. Thus, sodium sulfate has a relatively minor effect on the viscosity of the base solution. In addition, the experiments show that in solutions with equivalent concentrations of inorganic salt, those containing higher valence cations lead to greater decreases in viscosity. The higher the valence of the cations, the more significant their negative effect on the viscosity of the guar gum base solution.

3.2. Effect of Salt Content and Type on Temperature Resistance and Shear Viscosity of the HPG Fracturing Fluid.

(1) The effects of Na$^+$ and Cl$^-$ ions on temperature resistance and shear viscosity of the fracturing fluid were studied using the same experimental method mentioned above. Sodium chloride solutions with mass fractions of 1, 3, and 5% were prepared. These solutions were then mixed with the cationic HPG, as selected in the previous chapter, to produce a 0.5% HPG solution. Then, 0.4% of the cross-linking agent RW-G30 was added to this base fluid for a cross-linking reaction, resulting in the formation of the HPG fracturing fluid. The prepared fracturing fluid was evaluated for its temperature-resistant and shear-resistant viscosity properties. The experimental results, depicted in Figure 3, aimed to provide insights into how the presence of Na$^+$ and Cl$^-$ affects these critical performance characteristics of the fracturing fluid under various conditions.

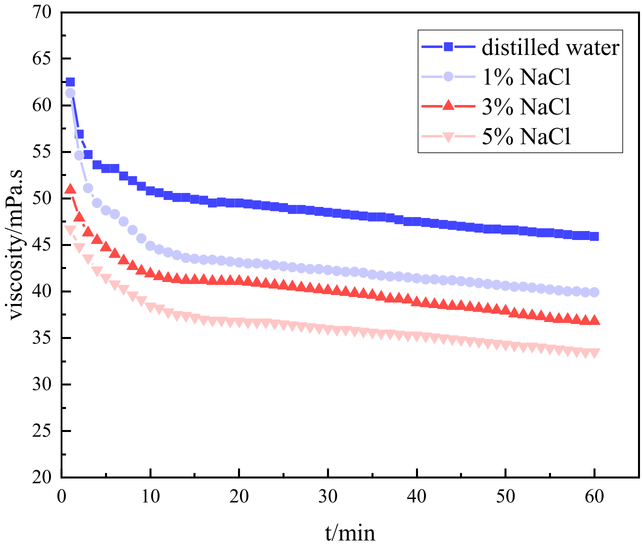


Figure 3. Effect of Na$^+$ and Cl$^-$ on the temperature and shear viscosity of the fracturing fluid.

Figure 3 illustrates that the viscosity of the fracturing fluid decreases gradually and stabilizes after continuous shearing for 60 min at 90 °C. The fracturing fluid containing high concentrations of NaCl exhibits lower viscosity compared to those prepared with distilled water. Furthermore, as the NaCl concentration increases, the viscosity, temperature resistance, and shear resistance of the high-pressure fracturing fluid deteriorate. Specifically, after shearing for 60 min, the average viscosity measurements are as follows: the fracturing fluid prepared by distilled water shows a viscosity of 45.9 mPa·s, with 1%NaCl, the viscosity is 39.9 mPa·s, with 3% NaCl, it is 36.8 mPa·s, and with 5% NaCl, it drops to 33.5 mPa·s. This data indicates that while high concentrations of NaCl negatively impact the temperature and shear resistance of fracturing fluid, the overall effect on the fracturing fluid's properties remains relatively minor.

(2) Using the experimental methods previously outlined, the effect of K$^+$ on temperature resistance and shear viscosity of fracturing fluid was investigated. Potassium chloride solutions with mass fractions of 1, 3, and 5% were prepared. These solutions were mixed with cationic HPG, as specified in the previous chapter, to form a 0.5% hydroxypropyl guar base solution. Subsequently, 0.4% cross-linking agent RW-G30 was added to this base solution to initiate the cross-linking reaction, resulting in the production of HPG fracturing fluid. The properties of the prepared fracturing fluid, specifically its temperature-resistant and shear-resistant viscosity, were evaluated. The results are presented in Figure 4, offering insights into how varying concentrations of K$^+$ impact the performance characteristics of the fracturing fluid under stress conditions typical of hydraulic fracturing operations.

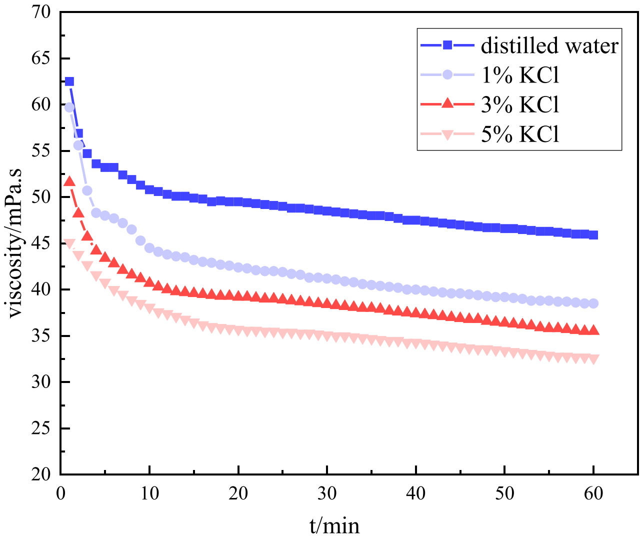


Figure 4. Effect of K$^+$ on the temperature and shear viscosity of the fracturing fluid.

Figure 4 reveals that the viscosity of fracturing fluid decreases gradually and stabilizes after continuous shearing for 60 min at 90 °C. The fracturing fluid with a high concentration of K+ exhibits lower viscosity compared to that prepared with distilled water, and the high temperature resistance and shear resistance are also inferior in fluids with distilled water. Specifically, after the shearing process, the average viscosity is as follows: 38.5 mPa·s for the fracturing fluid prepared with 1%KCl, 35.5 mPa·s for 3%KCl, and 32.6 mPa·s for 5%KCl. The temperature resistance and shear resistance of these solutions are comparable to that of fracturing fluids prepared with the equivalent concentration of NaCl. Research by Esmaeilirad et al.[27] and the results of experiment (1) have confirmed that Cl$^-$ has a minimal impact on the temperature and shear viscosity of fracturing fluids. The comprehensive experimental results indicate that K$^+$ similarly has little effect on the temperature resistance and shear viscosity of the fracturing fluid. This suggests that while the presence of K$^+$ influences the initial viscosity of the fluid, its overall impact on the key performance characteristics of temperature resistance and shear viscosity is relatively minor.

(3) Effects of Mg^{2+} on temperature resistance and shear viscosity of the fracturing fluid. Using the same experimental method as previously described, magnesium chloride solutions with mass fractions of 1, 3, and 5% were prepared. These solutions were then mixed

with the cationic HPG selected in the previous chapter to produce a 0.5% HPG base fluid. Next, 0.4% cross-linking agent RW-G30 was added to the base fluid for a cross-linking reaction, resulting in the formation of the HPG fracturing fluid. The temperature-resistant and shear-resistant viscosity of the prepared fracturing fluid was measured, and the experimental results are shown in Figure 5.

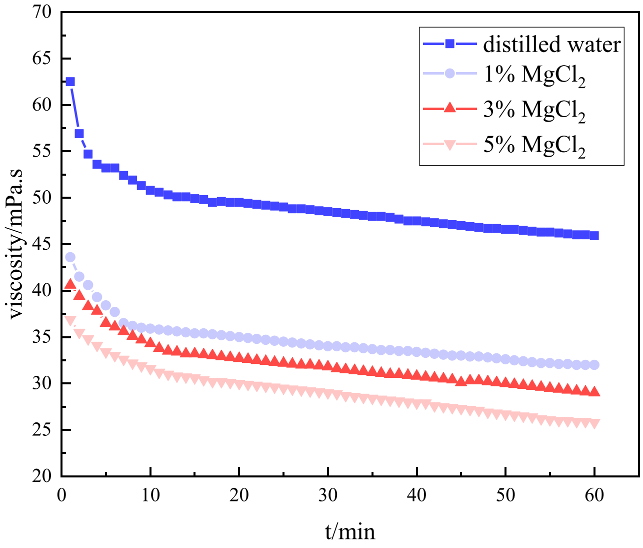


Figure 5. Effect of Mg^{2+} on the temperature and shear viscosity of the fracturing fluid.

Figure 5 indicates that after 60 min of continuous shearing at 90 °C, the viscosity of the fracturing fluid decreases gradually and stabilizes. The fracturing fluid containing high concentrations of Mg^{2+} shows significantly lower viscosity compared to that of the fracturing fluid prepared with distilled water. In addition, the viscosity, temperature, and shear resistance of the high-pressure fracturing fluid worsen as the concentration of Mg^{2+} increases. Specifically, at the end of the shearing process, the average viscosity measurements are as follows: 32 mPa·s for the fracturing fluid prepared with 1%$MgCl_2$, 29 mPa·s for the fluid with 3% $MgCl_2$, and 25.8 mPa·s for the one with 5% $MgCl_2$. These results suggest that the presence of Mg^{2+} leads to a more significant reduction in viscosity compared with similar concentrations of NaCl and KCl solutions. The experimental results show that high-valent cations, like Mg^{2+}, have a greater negative impact on the temperature resistance and shear resistance of fracturing fluids than lower valent cations.

(4) Effect of Ca^{2+} on temperature resistance and shear viscosity of the fracturing fluid. Calcium chloride solutions with mass fractions of 1, 3, and 5% were prepared by the same experimental method, respectively, and mixed with cationic HPG selected in the previous chapter to prepare 0.5% hydroxypropyl guar base solution, and then 0.4% cross-linking agent RW-G30 was added to the base fluid for a cross-linking reaction. HPG fracturing fluid was prepared. The temperature-resistant and shear-resistant viscosity of the prepared fracturing fluid is determined, and the experimental results are shown in Figure 6.

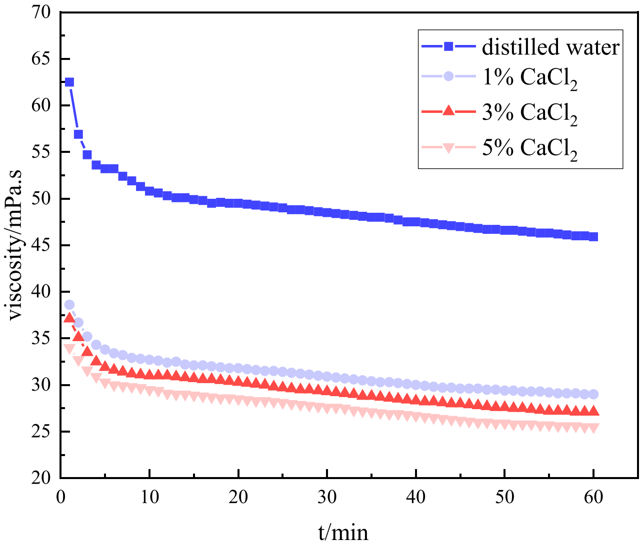


Figure 6. Effect of Ca^{2+} on the temperature and shear viscosity of the fracturing fluid.

Figure 6 indicates that the viscosity of the fracturing fluid decreases slowly and tends to be stable after continuous shearing for 60 min at 90 °C. The viscosity of the fracturing fluid containing a high concentration of Ca^{2+} is much lower than that of the fracturing fluid prepared by distilled water, and the viscosity, temperature, and shear resistance of the high-pressure fracturing fluid with the concentration of Ca^{2+} are worse. When shearing to the last minute, the average viscosity of fracturing fluid prepared with 1%$CaCl_2$ solution is 29 mPa·s, the fracturing fluid prepared with 3% $CaCl_2$ solution is 27.1 mPa·s, and the fracturing fluid prepared with 5% $CaCl_2$ solution is 25.5 mPa·s. The viscosity of fracturing fluid decreases greatly and is lower than that of fracturing fluid prepared with NaCl, KCl, and $MgCl_2$ solutions at the same concentration. Ca^{2+} has the greatest influence on the temperature and shear resistance of the fracturing fluid.

(5) Using the experimental method outlined previously, the effect of SO_4^{2-} on the temperature resistance and shear viscosity of fracturing fluid was assessed. Sodium sulfate solutions with mass fractions of 1, 3, and 5% were prepared. These solutions were mixed with cationic HPG selected in the previous chapter to create a 0.5% hydroxypropyl guar base solution. Subsequently, 0.4% cross-linking agent RW-G30 was added to the base fluid for a cross-linking reaction, producing the HPG fracturing fluid. The temperature-resistant and shear-resistant viscosity of the prepared fracturing fluid was then measured, and the experimental results are shown in Figure 7.

Figure 7 depicts that the viscosity of the fracturing fluid decreases gradually and stabilizes after 60 min of continuous shearing at 90 °C. In the experiment, the viscosity of the fracturing fluid prepared with 1% Na_2SO_4 solution consistently remains higher than that of the fracturing fluid prepared with distilled water over the 60 min period. This increase in viscosity can be attributed to the nature of the HPG used, which is cationic. When this gum is cross-linked with the cross-linking agent, it further interacts with SO_4^{2-}, enhancing the viscosity of the fracturing fluid. Conversely, the viscosity of the fracturing fluid prepared with 3% and 5% Na_2SO_4 solution is

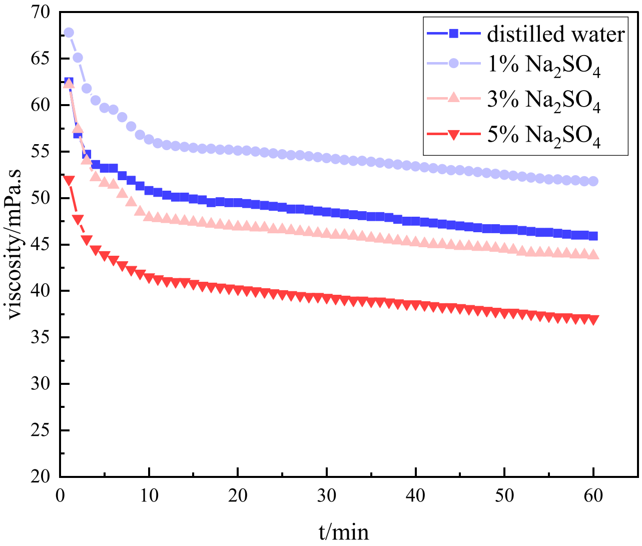


Figure 7. Effect of SO_4^{2-} on the temperature resistance and shear viscosity of the fracturing fluid.

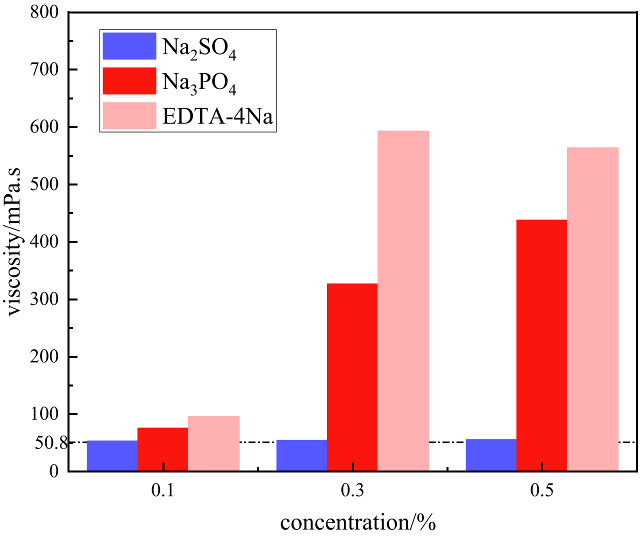


Figure 8. Effect of different additives on the viscosity of the HPG fracturing fluid.

consistently lower than that of the fracturing fluid prepared with distilled water within the same time frame. This observation indicates that while a small amount of SO_4^{2-} can increase the viscosity of cationic guar gum fracturing fluid, excessive SO_4^{2-} leads to a supersaturation that reduces the fluid's viscosity.

3.3. Effect of Different Valence Anions on the Viscosity of Cationic Guar Gum. In the first part of the experiment, it was observed that sodium sulfate had a less detrimental effect on the viscosity of cationic guar gum compared with sodium chloride, indicating that sulfate ions might positively affect the viscosity of cationic guar gum. In the second part, the tackifying effects of various anions with different valences were examined. Preparation of HPG fracturing fluid. (1) Distilled water was poured into a beaker with an agitator set at 500 rpm. HPG was gradually added and stirred for 10 min to ensure it dissolved completely. (2) The mixer's agitation speed was then reduced to 400 rpm, and an organic boron cross-linking agent, RW-G30, was added and stirred for an additional 3 min to complete the preparation of the fracturing fluid. (3) The HPG base fluid was prepared according to the method in (1). Then, different additives were added to this base, and the HPG fracturing fluid was formed by thoroughly stirring, and then the cross-linking agent was added. A 70 mL sample of the prepared fracturing fluid was then placed into the cylinder of an Austrian Anton Paar MCR102 rheometer, set to a shear rate of 100 s^{1-}, and heated to a constant temperature of 90 °C to measure its viscosity over 10 min. This experiment utilized a control variable method to prepare a 0.5% HPG solution with distilled water. The pH of this base solution was adjusted to 9 using a pH regulator before it was divided into equal parts. Subsequent additions of 0.1, 0.3, and 0.5% concentrations of sodium sulfate, sodium phosphate, and EDTA-4Na were made to the HPG base fluid. Finally, after thorough stirring and the addition of the cross-linking agent, the mixture's viscosity was measured under the defined conditions, and the results are shown in Figure 8.

The experimental results show that the baseline viscosity of the fracturing fluid without any additives stands at 50.8 mPa·s. When additives were introduced into the fluid, significant changes in viscosity were observed. These additives were categorized based on their anionic charge into negative bivalent, negative trivalent, and negative tetravalent groups. As the concentration of these additives increased, the tackifying effect on the HPG fracturing fluid intensified. Notably, additives with higher anionic charges produced a stronger tackifying effect compared with those with lower charges. This is similar to the Schulz−Hardy rule, which states that multivalent ions destabilize colloidal suspensions more efficiently than monovalent ones. Aggregation in colloidal suspensions proceeds through the growth of particle aggregates and their subsequent sedimentation.[28] Among the additives tested, EDTA-4Na exhibited the most potent tackifying ability at equivalent concentrations. Specifically, at a 0.3% concentration of EDTA-4Na, the viscosity reached 542 mPa·s, which is nearly 12 times higher than the initial viscosity without additives.

3.4. Differential Scanning Calorimetric Analysis. The solvation effect of polymer is pivotal to their dissolution in aqueous solutions, as the attraction between polymer and water molecules is greater than that between polymer molecules themselves.[29] For fully solvated polymers, polymer chain units are closely bound to several water molecules through intermolecular forces, such as van der Waals forces and hydrogen bonding. In solution, all polymers are highly solvated, surrounded by a layer of solvated solvent molecules that are integral to the polymer chain. The observed properties of polymer solutions are the sum of the properties of both the polymer and the solvated solvent.[30] Due to polymer solvation, water in the fracturing fluid can be categorized into two types: free water and bound water. Free water involves interactions between water molecules themselves and between polymer and water molecules.[31] Conversely, bound water exhibits only weak interactions with the polymer matrix, forming close associations with the polymer due to its higher degree of interaction. This bound water does not transition between solid and liquid states with temperature changes. The relative content of these water types is mainly affected by factors such as polymer concentration viscosity and polymer segment hydrophilicity. Higher polymer concentrations and greater hydrophilicity typically increase bound water content while decreasing free water levels in the solution.[32−34] To investigate the effect of EDTA-4Na on the properties of HPG fracturing fluid, we prepared HPG fracturing fluid containing 0.3% ethylenediamine tetraacetic acid tetrasodium and HPG fracturing fluid without ethylenediamine tetraacetic acid tetrasodium according to the same experimental method mentioned above. DSC analysis was performed on both formulations to assess their properties. The experimental results are listed in Figure 9.

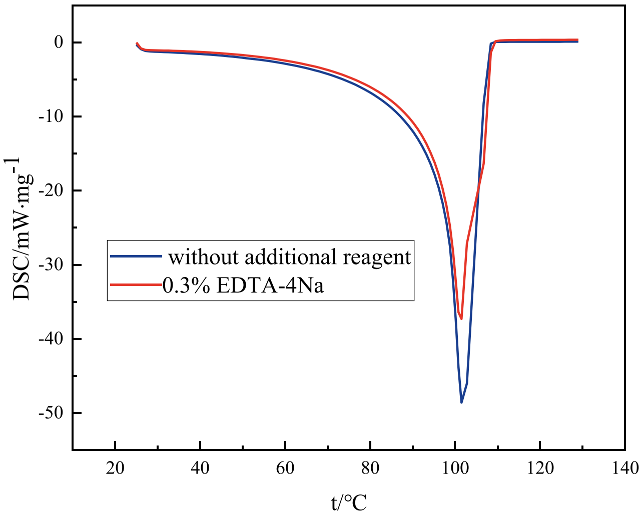


Figure 9. DSC curve of the HPG fracturing fluid at a heating rate of 5 °C/min.

Figure 9 illustrates the dehydration behavior of the HPG fracturing fluid, both with and without the addition of EDTA-4Na, as the temperature is raised from 25 to 150 °C. Both fluids exhibit only one dehydration peak, occurring at approximately 100 °C. However, the dehydration peak for the fracturing fluid without EDTA-4Na is higher, and the rate of dehydration is faster compared to the fluid containing EDTA-4Na, where the peak is lower and the dehydration rate is slower. This observation indicates that the addition of EATA-4Na affects the fluid's properties significantly. The presence of high-valent anions in EDTA-4Na interacts electrostatically with the cationic HPG, leading to secondary cross-linking. This increased cross-linking density enhances the intermolecular force within the fluid, making it more challenging for free water to escape. Essentially, EDTA-4Na modifies the structural integrity of the fracturing fluid, thus altering its thermal dehydration characteristics.

3.5. SEM Frozen Electron Microscope. Because the viscosity of the HPG fracturing fluid was significantly increased by the addition of EDTA-4Na, the HPG fracturing fluid was examined with an SEM equipped for cryogenic imaging; see Figure 10. The image comprises two samples: one without adding EDTA-4Na (a) and one with 0.3% EDTA-4Na (b). The SEM images reveal that both samples of the fracturing fluid exhibit a network-like microstructure, where the water is held within the voids of the grid. In Figure 10a, the voids within the fracturing fluid network appear larger, and the network structure has more space, facilitating the easy escape of water and thereby making the fluid more prone to dehydration. This structure sparsity results in lower viscosity and quicker water loss under thermal conditions. Conversely, Figure 10b shows that the addition of EDTA-4Na results in smaller voids and a denser network structure. This configuration traps water more effectively within the voids, making the fracturing fluid less susceptible to dehydration and resulting in higher viscosity.

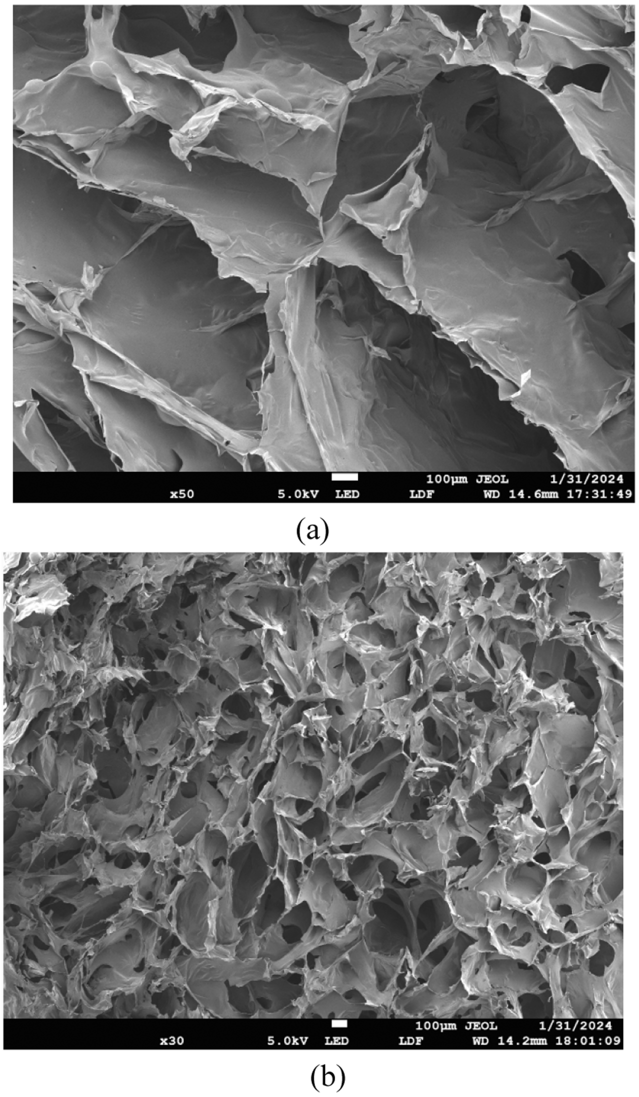
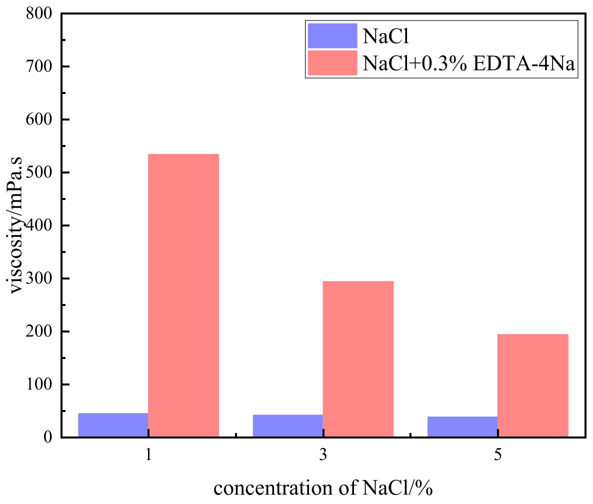


Figure 10. Micromorphology of the fracturing fluid blank control (a) and with addition of 0.3%EDTA (b).

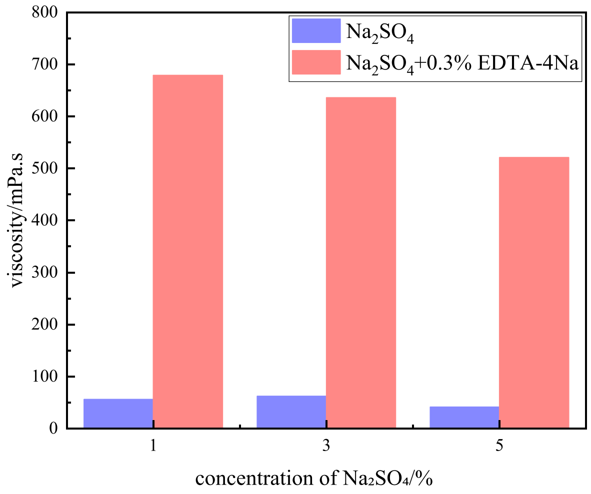
3.6. Effect of Different Ions on the Tackifying Effect of EDTA-4Na. Due to the high content of Na^+ and Cl^- in seawater and the impactful role of Ca^{2+} on fracturing fluid performance, this study aimed to investigate how different ions and their concentrations influence the tackifying effect of EDTA-4Na. We prepared 1, 3, and 5% concentrations for sodium chloride, calcium chloride, and sodium sulfate, respectively, using the prepared salt solution as the dispensing water for preparing the HPG base solution, following the method in experiment (1). The pH of the base solution was adjusted to 9. Each solution concentration was divided into two parts: one part remained unaltered, while the other part was enhanced with 0.3% EDTA-4Na. Both parts were then cross-linked with 0.4% of the selected cross-linking agent RW-G30 to produce the HPG fracturing. A 70 mL sample of each prepared fracturing fluid was put into the cylinder of an Austrian Anton Paar MCR102 rheometer. The shear rate was set to 100 s^{1-}, and the samples were maintained at a constant temperature of 90 °C for a 10 min measuring period. This process allowed for the determination of the viscosity of the fracturing fluid. The experimental results are shown in Figure 11.

The experimental data from Figure 11 highlight the impact of adding 0.3% EDTA-4Na on the viscosity of HPG fracturing fluids prepared with different saline solutions. Specifically, when using sodium chloride solution, the viscosity increases observed for 1, 3, and 5% sodium chloride solution were 489.1, 252.1, and 155.7 mPa·s, respectively. Similarly, when 0.3% EDTA-4Na was added to the HPG fracturing fluid prepared with 1, 3, and 5% sodium sulfate solution, the viscosity of the fracturing fluid increased by 623, 573.8, and 479.5 mPa·s, respectively. Conversely, when 0.3% EDTA-4Na was added to the HPG fracturing fluid prepared with 1, 3, and 5% calcium chloride solution, the viscosity of the fracturing fluid increased by 4.4, 3.3, and 1.2 mPa·s, respectively. This suggests a diminishing tackifying effect of EDTA-4Na with increasing salt concentrations. According to the analysis of experimental data, the tackifying effect of EDTA-4Na gradually decreased with the increase in salt concentration. EDTA-4Na, as a chelating agent, can effectively shield Ca^{2+} and other metal ions in water, reducing their detrimental impact on the fracturing fluid properties. However, the experimental results show that even in the absence of metal ions (as with distilled water), EDTA-4Na still enhanced the viscosity of the HPG fracturing fluid. This shows that EDTA-4Na plays a dual role both as a chelating agent to reduce the effect of metal and as a promoter of secondary cross-linking through electrostatic interaction with cationic guar gum. However, the data also indicates that as the concentration of the salt solution increases, more EDTA-4Na is needed to chelate metal ions, reducing the availability of anions for cross-linking with cationic guar gum and thus reducing the tackifying effect. Therefore, to ensure the tackifying effect in a salt solution, it is necessary to add a sufficient amount of EDTA-4Na.

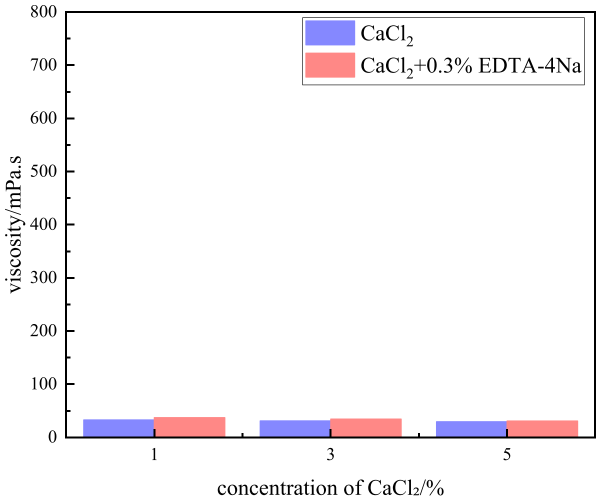
3.7. Main Effects of Ca^{2+}. Various metal ions affect the performance of fracturing fluid, among which Ca^{2+} has the greatest influence on the performance of fracturing fluid.[1,35] However, data from Figure 12 suggest that Ca^{2+} does not significantly alter the tackifying effect of EDTA-4Na in the HPG fracturing fluid prepared with calcium chloride solution. Combined with the above experiments, experiments were conducted by using the control variable method to explore the chelating and tackifying ranges of EDTA-4Na. For these experiments, solutions of calcium chloride were prepared at concentrations of 0.1, 0.2, and 0.3% to simulated seawater conditions, where the typical concentration was 0.1%. According to the experimental method (1), 0.5% HPG solution was prepared with the calcium chloride solutions, and the pH value of each base solution was adjusted to 9. Each solution was then divided into equal parts. For the solutions with 0.1 and 0.2% calcium chloride, increments of 0, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1, and 1.5% EDTA-4Na were added. Similarly, for the base solution with 0.3% calcium chloride, the same increments of EDTA-4Na were introduced. After fully stirring, 0.4% of the selected cross-linking agent RW-G30 was added to induce cross-linking, resulting in the formation of the HPG fracturing fluid. A 70 mL sample of each prepared fracturing fluid was then placed into the cylinder of an Austrian Anton Paar MCR102 rheometer. The shear rate was set to 100 s^{-1}, and the samples were sheared for 60 min at 90 °C to measure their temperature and shear resistance. The experimental results are listed in Figure 12.



(a) Effect of sodium chloride on the tackifying effect of EDTA-4Na



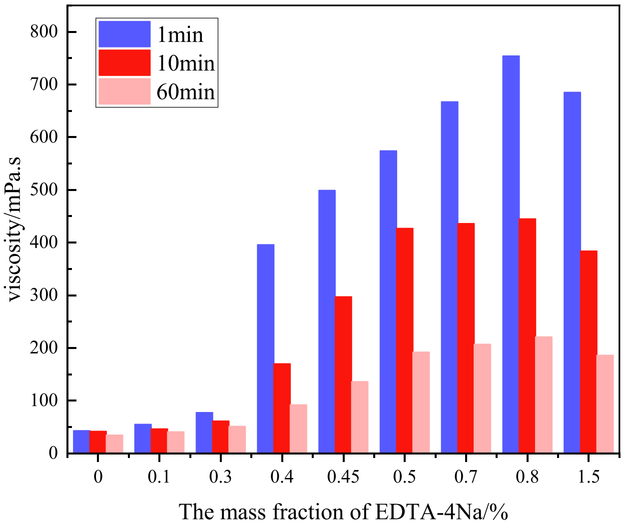
(b) Effect of Sodium Sulfate on the tackifying effect of EDTA-4Na



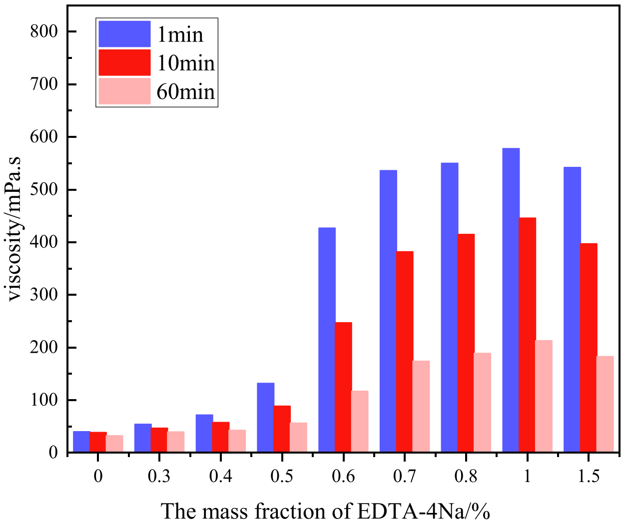
(c) Effect of calcium chloride on tackifying effect of EDTA-4Na viscosity

Figure 11. Effect of different Ions on the tackifying effect of EDTA-4Na.

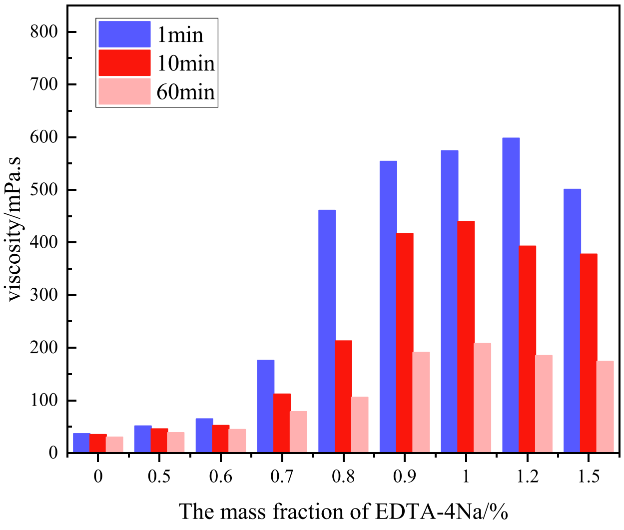
Figure 12a illustrates the relationship between the concentration of EDTA-4Na and its effects on the fracturing



(a) Including 0.1%$CaCl_2$



(b) Including 0.2%$CaCl_2$



(c) Including 0.3%$CaCl_2$

Figure 12. Effect of different concentrations of EDTA-4Na on the viscosity of the fracturing fluid prepared with 0.1% calcium chloride solution.

fluid in the presence of varying levels of Ca^{2+}. For a solution containing 0.1% calcium chloride, which corresponds to a Ca^{2+} concentration of 360 mg L^{-1}, the data delineate specific ranges for chelating and tackifying effects induced by EDTA-4Na. In this setup, the chelating range of EDTA-4Na, where its primary function is to sequester Ca^{2+} and mitigate its impact on the fracturing fluid, extends from 0 to 0.3%. Within this concentration range, EDTA-4Na effectively neutralizes the negative effects of Ca^{2+} on the fluid's performance. Progressing to a concentration of 0.4% to 0.8% EDTA-4Na marks the tackifying range. At this level, Ca^{2+} ions have already been sufficiently chelated, allowing the excess EDTA-4Na to engage in secondary cross-linking interactions with HPG. This secondary cross-linking significantly enhances the viscosity of the fracturing fluid. The optimal tackifying effect occurs at 0.8% EDTA-4Na, but it begins to weaken once the concentration exceeds 1.5%. When the concentration of Ca^{2+} is increased to 720 mg L^{-1}, the chelating range of EDTA-4Na adjusts to 0 to 0.5%, and the tackifying range shifts to 0.6 to 1%. When the concentration of Ca^{2+} is even higher at 1080 mg L^{-1}, the chelating range of EDTA-4Na extends to 0.7%, while the optimal tackifying range is between 0.8 and 1.2%. In summary, for a solution with 360 mg L^{-1} Ca^{2+}, the amount of EDTA-4Na should be at least 0.4% to achieve the tackifying effect. Compared with the more common vegetable gum fracturing fluid system,[36] it was found that EDTA-Na has a significant viscosity increasing effect on the cross-linked guanidine rubber fracturing fluid, and a low viscosity increasing effect is found, which has a high field application value.

4. CONCLUSIONS

This study investigated the rheological properties of HPG polymers at various ion concentrations and compared the effects in distilled water and seawater to determine the optimal "chelating" mixture and its concentration to enhance the performance of the fracturing fluid.

(1) The findings reveal that anions positively affect the viscosification of cationic guar gum by enhancing the polymer's ability to increase fluid viscosity. This can be explained by the Schulz−Hardy rule, which states that multivalent ions destabilize colloidal suspensions more efficiently than monovalent ones.

(2) The addition of EDTA-4Na reduces the dehydration rate of the fracturing fluid, indicating enhanced cross-linking and increased intermolecular forces. This leads to a denser network structure, making it more difficult for free water to escape.

(3) The effect of different salt ions on fracturing fluid viscosity can draw a conclusion that lower concentrations of Na_2SO_4 initially increase the viscosity before a subsequent decline with higher concentrations. In contrast, the addition of $CaCl_2$ consistently reduces the viscosity, with higher concentrations further amplifying this effect.

(4) It highlights the importance of considering the addition of EDTA-4Na and the presence of various ions in optimizing the performance of the fracturing fluid. These factors significantly influence the fluid's dehydration rate and viscosity, which are crucial for enhancing the effectiveness of hydraulic fracturing operations and achieving improved production outcomes.

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Notes

The authors declare no competing financial interest.

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