

Comparative Study on Enhancing Oil Recovery under High Temperature and High Salinity: Polysaccharides Versus Synthetic Polymer

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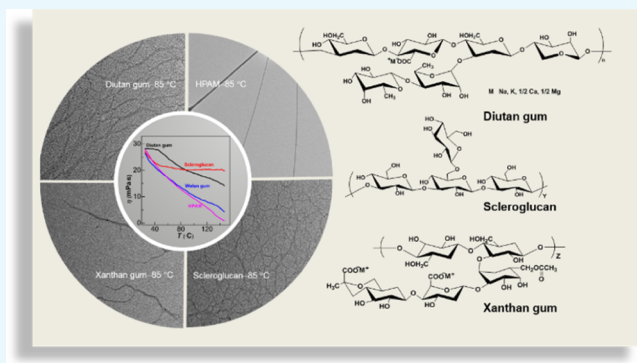
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Supporting Information

ABSTRACT: The synthetic water-soluble polymer, partially hydrolyzed polyacrylamide (HPAM), has been most widely used for enhanced oil recovery (EOR); however, its poor thermal stability and weak salt tolerance impede further application in high-temperature and high-salinity oil reservoirs. To address such deficiencies, three polysaccharides, xanthan gum, diutan gum, and scleroglucan, were examined in comparison with HPAM on rheological behaviors, shearing resistance, long-term thermal stability, and core flooding test. It was found that all of these three polysaccharides were less sensitive to salinity and shearing time, while HPAM showed a monotonous decrease in viscosity with increasing monovalent cations and shearing history. After 90 days of aging at 85 °C and $10.1 \times 10^4 \text{ mg}\cdot\text{L}^{-1}$ of total dissolved solids with $1.0 \times 10^3 \text{ mg}\cdot\text{L}^{-1}$ of Ca^{2+} , the viscosity of diutan gum and scleroglucan solutions nearly remained unchanged; on the contrary, the viscosity of xanthan gum and HPAM solutions drops massively. Core flooding tests at 85 °C with the same initial viscosity demonstrated that all polymers showed good transportation in porous media, and 16, 13, and 11% of oil recovery were obtained by diutan gum, scleroglucan, and xanthan gum, respectively, while only 10% was obtained from HPAM. These comparative results may underpin the potential of diutan gum and scleroglucan to be used in the EOR process in HTHS oil reservoirs.



1. INTRODUCTION

Water-soluble polymers, mainly partially hydrolyzed polyacrylamide (HPAM), have been widely used in the chemically enhanced oil recovery (EOR) process. Relative to the water flooding process, addition of HPAM in the displacing fluid can further recover 5–30% of original oil in place¹ by enlarging the sweep efficiency and increasing the oil/water mobility ratio.^{2,3} With HPAM being used in the chemical EOR process, around 14 million tons of incremental crudes is produced annually in Daqing Oilfield, China, owing to its mild reservoir conditions ($T = 45 \text{ }^\circ\text{C}$; the dissolved solids, $\text{TDS} = 4.5 \times 10^3 \text{ mg}\cdot\text{L}^{-1}$). However, the intrinsic salt sensitivity and poor thermal stability severely impede its use in harsh high-temperature, high-salinity (HTHS) oil-bearing strata underground, such as the class III reservoirs in Shengli Oilfield, China ($T = 80\text{--}95 \text{ }^\circ\text{C}$, $\text{TDS} > 3 \times 10^4 \text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] > 2.0 \times 10^2 \text{ mg}\cdot\text{L}^{-1}$). Therefore, water-soluble polymers with improved salt tolerance and better thermal stability are highly desirable. In the polymer flooding operation, a high molecular weight water-soluble polymer,

polyacrylamide or its derivatives, is added to thicken the displacing fluid, so as to reduce the mobility of the aqueous phase, enlarge the swept volume, and, consequently, to improve oil recovery efficiency.^{4,5} Additionally, polymer adsorption onto the rocks decreases the permeability to water, and the viscoelasticity of the polymer solution can increase the microscopic displacement efficiency.⁶

As a typical linear anionic polyelectrolyte, HPAM can make fresh water viscous in small dosages under a less hostile environment, nevertheless, its thickening power and oil recovery ability are strongly weakened under HTHS conditions. Monovalent cations such as Na^+ and K^+ present in brine can shield the electrostatic repulsion among the carboxylate charges ($-\text{COO}^-$) along the HPAM chains, causing polymer chain coils to collapse.² Divalent ions,

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particularly Ca^{2+} and Mg^{2+} , would complex with $-\text{COO}^-$, leading to the precipitation of HPAM in brine.^{4,5} Moreover, the elevated temperature can accelerate the hydrolysis of amide ($-\text{CONH}_2$) groups to $-\text{COO}^-$, aggravating the electrostatic shielding effect and complexation with divalent cations. When the divalent cations in brine exceed $200 \text{ mg}\cdot\text{L}^{-1}$, the ceiling temperature for HPAM used in the EOR process should be lower than $75 \text{ }^\circ\text{C}$.^{3,6}

To address these challenges, great efforts have been made to improve the thermal stability and salt tolerance of the synthetic polymers. Copolymerizing acrylamide with thermally stable sodium 2-acrylamido-2-methylpropane sulfonic acid, vinylpyrrolidone, or comonomers containing imide rings can effectively enhance the salt tolerance and thermal stability.^{7–9} However, the thermal stability and salt tolerance of the above copolymers are limited, depending on the content, cost, and reactivity of functional monomers. In addition, $-\text{CONH}_2$ groups, the majority part along the copolymer chains would inevitably be hydrolyzed at high temperatures. Other modified synthetic polymers, such as hydrophobic-associated polymers or thermoviscosifying polymers, are still altered on the backbone of HPAM.^{10–12} Thus, the long-term aging stability cannot be maintained at high temperatures, restricting their applications in HTHS reservoirs.

Alternatively, polysaccharides may be better candidates for EOR in the HTHS hostile environment. Xanthan gum (Scheme S1) has been widely applied during the EOR process.¹³ Negatively charged pyruvate molecules wrapped around the main chain of xanthan gum to impart to it a rigid rod-like structure, contributing to its excellent resistance to shearing degradation.¹⁴ Nevertheless, the unordered coil conformation conversion occurs under high temperature conditions,¹⁵ with the temperature tolerance limited below $90 \text{ }^\circ\text{C}$.³ Fortunately, the newly developed diutan gum and scleroglucan may overcome these defects and take the place of xanthan gum.

Diutan gum (Scheme S1), produced by the genus *Sphingomonas sp.*, is an anionic extracellular polysaccharide. Vicious aqueous solutions of diutan gum show a strong ability of water retention capacity, salt tolerance, suspending power, and thermal stability ranging from 5 to $150 \text{ }^\circ\text{C}$.^{16,17} As an effective thickening agent to maintain free water in cement-based materials and prevent the separation of concrete,¹⁸ it is widely used in concrete industries such as self-compact cement and plaster. While it was reported that diutan gum can also be used in drilling and spacer fluids in the petroleum industry,¹⁷ the study for EOR has been rarely reported. Xu et al. utilized diutan gum in enhanced heavy oil recovery at $75 \text{ }^\circ\text{C}$ and TDS of $9503 \text{ mg}\cdot\text{L}^{-1}$, with 25.1% heavy oil recovery efficiency compared with water flooding.¹⁹

Scleroglucan (Scheme S1) is a neutral polysaccharide produced by fermentation of a plant pathogen fungus genus *Sclerotium*, also with excellent insensitivity to salt and temperature. The semi-rigid structures of scleroglucan provide thermal stability to its aqueous solutions at high temperatures,^{20,21} and charge neutrality enables it to be insensitive to electrolytes. Owing to these unique properties, scleroglucan was used in food and cosmetic industries,²² and petroleum may be another potentially promising domain. Akstinat²³ found that scleroglucan remained stable at $80 \text{ }^\circ\text{C}$ for 3 months under highly saline conditions. Rivenq and coworkers^{24,25} observed high retention viscosity for scleroglucan in seawater at $90 \text{ }^\circ\text{C}$. Kalpakci et al.²⁶ showed that scleroglucan solutions displayed

improved thermal stability at 93 and $100 \text{ }^\circ\text{C}$ in seawater with a TDS of $3.0 \times 10^4 \text{ mg}\cdot\text{L}^{-1}$.

Because of these promising features, diutan gum and scleroglucan are expected to be used in HTHS reservoirs, however, there is still a lack of detailed research particularly comparison and core flooding results aiming at the HTHS environment. In this work, we examined the thickening ability, shearing stability, and long-term stability, as well as core flooding tests of diutan gum and scleroglucan under a typical HTHS oil reservoir environment ($\text{TDS} = 10.1 \times 10^4 \text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] = 1.0 \times 10^3 \text{ mg}\cdot\text{L}^{-1}$, $T = 85 \text{ }^\circ\text{C}$), in comparison with HPAM and xanthan gum. The main aim of this study is to explore the potential application of polysaccharides at HTHS conditions and illuminate why polysaccharides exhibit better performance over HPAM. Our work indicated that both diutan gum and scleroglucan possessed much better salt tolerance, long-term thermal stability, and higher oil recovery efficiency over HPAM and xanthan gum. These findings may widen the applications of these newly developed polysaccharides and pave the way for seeking potential EOR polymers used in the HTHS environment.

2. RESULTS AND DISCUSSION

2.1. Rheological Behaviors of Polymer Solutions.

2.1.1. Temperature Dependence of Polymer Solutions. A steady rheological test and transmission electron microscopy (TEM) observation were combined together to study the influence of temperature on the properties and microstructure of polysaccharides and HPAM solutions, and a high salt environment would cause a negative effect on the TEM observation, so polymer powders were dissolved in pure water during the study of temperature dependence of polymer solutions. To reach the same initial viscosity ($28.0 \text{ mPa}\cdot\text{s}$) with $0.1 \text{ wt } \%$ diutan gum in pure water at $25 \text{ }^\circ\text{C}$ ($\dot{\gamma} = 100 \text{ s}^{-1}$), the plot in Figure S1 was used to determine the concentration of polysaccharides and HPAM. Figure 1 compares the viscosity

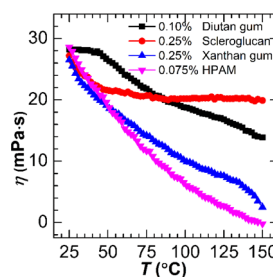


Figure 1. Apparent viscosity plotted as a function of temperature for polysaccharide and HPAM solutions (no salt, $\dot{\gamma} = 100 \text{ s}^{-1}$).

variation of HPAM and three polysaccharide solutions with increasing temperature. The above polymer solutions all exhibited thermo-thinning behavior: the viscosity of HPAM and xanthan gum solutions decreased dramatically with increased temperature, while the viscosity of diutan gum and scleroglucan solutions were less reduced. At $85 \text{ }^\circ\text{C}$, the viscosity retention (Φ) (Table S1) of diutan gum and scleroglucan solutions were 73.6 and 73.8%, respectively, while xanthan gum and HPAM solutions were only 49.8 and 42.9% separately. It is worth noting that scleroglucan solutions have a viscosity retention of 72.3% at $150 \text{ }^\circ\text{C}$, with potential to be applied to more hostile conditions.

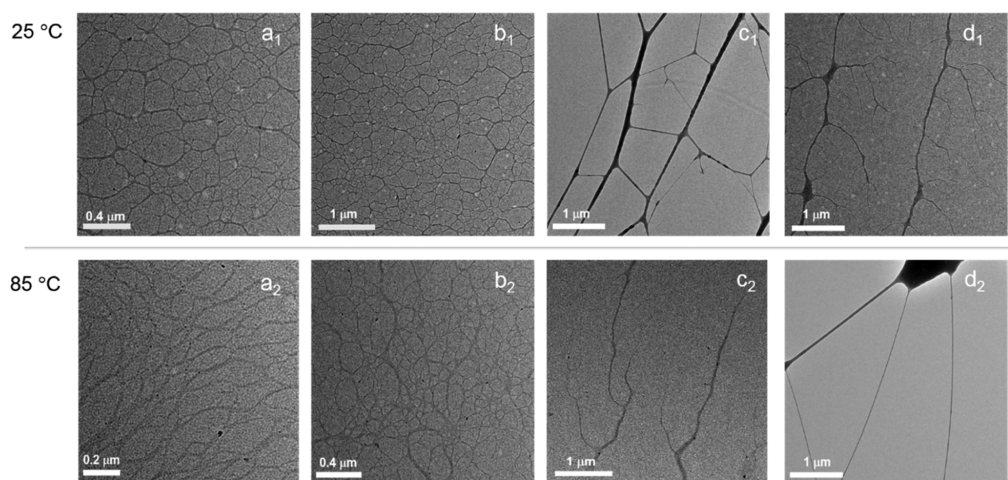


Figure 2. TEM micrographs for diutan gum ($a_{1,2}$), scleroglucan ($b_{1,2}$), xanthan gum ($c_{1,2}$), and HPAM ($d_{1,2}$) at 25 and 85 °C ($C_p = 0.05$ wt %, no salt).

Generally, the entanglements of macromolecules and the strength of the network for polymers are mainly formed by van der Waals forces and hydrogen bonds.²⁷ Nevertheless, the increasing temperature accelerates the motion of the molecules and then weakens these molecular forces. Obviously, both diutan gum and scleroglucan exhibited lower insensitivity to temperature compared to xanthan gum and HPAM, just as shown in Figure 2 $a_{1,2}$, $b_{1,2}$, the dense network structures were formed, no matter at 25 or 85 °C. For diutan gum, plentiful water molecules are still tightly trapped in double helix structures at high temperatures for the strong internal forces,²⁸ keeping the water retention constant and higher viscosity remained. The molecular chains of scleroglucan exist as rod-like structures in aqueous solutions, beneficial to its stabilities at higher temperatures.²⁹ Conversely, the network structure of xanthan gum was formed at 25 °C (Figure 2 c_1) and destroyed at 85 °C (Figure 2 c_2), it undergoes a conformational transition from an ordered structure to a random coil. Moreover, the water molecules clustered around the double helix chains would migrate away, which results in the decline of viscosity of xanthan gum with increasing temperature.¹⁵ For HPAM, it formed the coarse and branch-shaped structure at 25 °C (Figure 2 d_1), while the backbone of the branch structure was hairline and entangled to gobbets at 85 °C (Figure 2 d_2). Hence, diutan gum and scleroglucan solutions have better thermal stability.

2.1.2. Salt Tolerance of Polymer Solutions. The salt tolerance of polymer solutions with the same initial viscosity was first investigated at 85 °C, and the results were depicted in Figure 3. As the NaCl concentration increased from 0 to 1.0×10^4 mg·L⁻¹, the viscosity of HPAM solutions decreased sharply from 19.0 to 2.5 mPa·s, with the viscosity retention of only 13.1%. Increasing the NaCl concentration gradually to 20.0×10^4 mg·L⁻¹, the viscosity of HPAM (1.5 mPa·s) was approximate to that of brine (1.0 mPa·s). Comparatively, the viscosity changes of diutan gum, scleroglucan, and xanthan gum solutions were much lower as the concentration of NaCl increased from 0 to 20.0×10^4 mg·L⁻¹, with the viscosity retentions of 94.3, 99.5, and 87.2%, respectively.

Generally, cations in brine have two side effects on anionic polyelectrolytes, namely, the electrostatic shielding and the hydrated layer compression around polyelectrolyte molecules.^{30,31} Both the two adverse influences would cause the

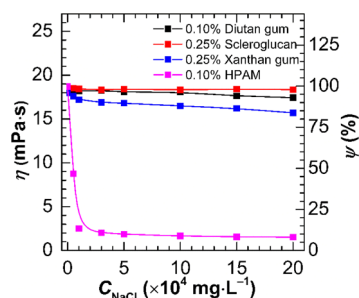


Figure 3. Apparent viscosity and viscosity retention (ψ) plotted as a function of NaCl concentrations for different polymers ($T = 85$ °C, $\dot{\gamma} = 100$ s⁻¹).

decrease in viscosity of polymer solutions. In HPAM solutions, the existence of Na⁺ could screen the negative charge repulsion along the HPAM chains, forcing the polymer chains to coil and reducing its hydrodynamic volume.³² Double electrical layers on HPAM molecular chains were compressed for the increase of ionic strength, resulting in a decrease in viscosity of HPAM solutions. For biopolyelectrolytes, xanthan gum, and diutan gum, their side chains wrap around the main chain to make the rod-like structure in the presence of salt.^{14,33} Negative charges along diutan gum chains locate on the backbone of the helix structure which can be protected by pendant chains, effectively restricting the electrostatic effect.³⁴ It is inevitable that Na⁺ would compact the peripheral hydrated layer around long-chain molecules, decreasing the viscosity of diutan gum and xanthan solutions. The nonionic polysaccharide structure explains its insensitivity to salt.³⁵ Consequently, polysaccharides were virtually independent of the ionic environment.

2.1.3. Concentration Dependence of Polymer Solutions. Figure 4 shows the variation of viscosity with different concentrations for polysaccharides and HPAM in brine ($TDS = 10.1 \times 10^4$ mg·L⁻¹, $[Ca^{2+}] = 1.0 \times 10^3$ mg·L⁻¹) at 85 °C. Apparently, the apparent viscosity of polysaccharide solutions increased more rapidly with the increased concentration, while that of HPAM solutions was only increased slightly. To achieve the same apparent viscosity (19.0 mPa·s) of 0.1 wt % of diutan gum, 0.25 wt % of scleroglucan and xanthan gum were needed. Meanwhile, for HPAM, it required a much higher concentration, reaching at about 0.5 wt % to attain the same apparent viscosity under identical conditions.

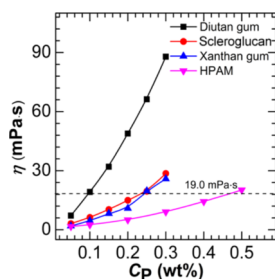


Figure 4. Apparent viscosity plotted as a function of concentration for different polymer solutions in brine ($T = 85\text{ }^{\circ}\text{C}$, $\text{TDS} = 10.1 \times 10^4\text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] = 1.0 \times 10^3\text{ mg}\cdot\text{L}^{-1}$, $\dot{\gamma} = 100\text{ s}^{-1}$).

Generally, in polymer aqueous solutions, the macromolecules greatly tend to intertwine with each other, and the size of the entanglements can effectively affect the viscosity of polymer solutions. Stronger hydrogen bonds would contribute to the greater aggregation and entanglements of molecular chains. Under the HTHS environment, the size of the polysaccharide aggregates was obviously greater than that of HPAM, and in turn polysaccharides showed better thickening ability than HPAM. To further explore the thickening mechanism of the above polymers at HTHS conditions, dynamic rheology was performed to study their viscoelastic behavior at different polymer concentrations.

Figure 5 shows the frequency dependence of the dynamic elastic modulus (G') and viscous modulus (G'') for polysaccharide and HPAM solutions at $85\text{ }^{\circ}\text{C}$. For diutan gum and scleroglucan solutions, the crossover was at the middle frequency between G' and G'' at the solution

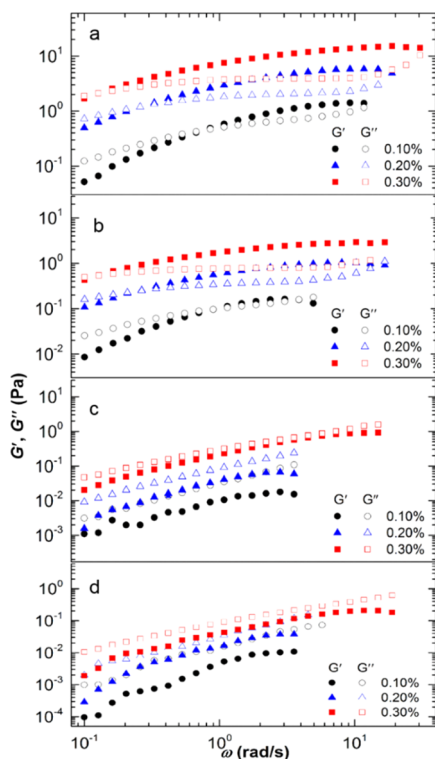


Figure 5. G' and G'' plotted as a function of frequency for different polymer solutions at different concentrations in brine at $85\text{ }^{\circ}\text{C}$ ($\text{TDS} = 10.1 \times 10^4\text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] = 1.0 \times 10^3\text{ mg}\cdot\text{L}^{-1}$); (a) diutan gum; (b) scleroglucan; (c) xanthan gum; (d) HPAM.

concentrations of 0.1–0.3 wt %, indicative of the existence of the viscoelastic fluids or entangled system. Correspondingly, as displayed in TEM images (Figure 2a₂,b₂), network structures were even well shaped at $85\text{ }^{\circ}\text{C}$. Accordingly, the crossover frequency decreased while the plateau elastic modulus, G_0 , increased, showing that the intensity of the temporary network greatly enhanced with the increasing number of junction points caused by the increasing concentration of diutan gum and scleroglucan solutions.³⁶ Nevertheless, for xanthan gum and HPAM, G' was consistently lower than G'' at solution concentrations of 0.1–0.3 wt %, showing the typical characteristic of viscous fluids. Consequently, the thickening mechanism of diutan gum and scleroglucan comes from the enhanced temporary three-dimensional network structures when increasing polymer concentration,³⁷ coinciding with the TEM imaging, while the intermolecular and intramolecular forces of xanthan gum and HPAM solutions are simply enhanced without network structures.

2.2. Long-Term Thermal Stability of Polymer Solutions. To examine whether polymer solutions can keep enough viscosity during a several month-long EOR process, the long-term thermal stability of polymer solutions should be tested under a simulated environment.³⁸ Figure 6 displays the

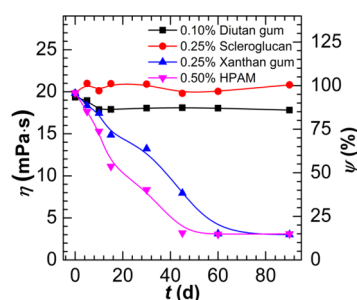


Figure 6. Apparent viscosity and viscosity retention (ψ) plotted as a function of aging time for different polymer brine solutions at $85\text{ }^{\circ}\text{C}$ ($\text{TDS} = 10.1 \times 10^4\text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] = 1.0 \times 10^3\text{ mg}\cdot\text{L}^{-1}$, $\dot{\gamma} = 100\text{ s}^{-1}$).

viscosity variation and viscosity retention of polysaccharide and HPAM solutions aging in brine ($\text{TDS} = 10.1 \times 10^4\text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] = 1.0 \times 10^3\text{ mg}\cdot\text{L}^{-1}$, $[\text{NaN}_3] = 2.0 \times 10^2\text{ mg}\cdot\text{L}^{-1}$) at $85\text{ }^{\circ}\text{C}$, which mimics the typical oil reservoir environment in Shengli Oilfield, China. Clearly, the viscosity of scleroglucan and diutan gum solutions nearly remained unchanged after aging for 90 days at $85\text{ }^{\circ}\text{C}$. Conversely, the apparent viscosity of xanthan gum and HPAM solutions decreased from 19.8 to 3.1 and 20.0 to 3.2 mPa·s, respectively. In conclusion, diutan gum and scleroglucan solutions had better long-term thermal stability than xanthan gum and HPAM.

The remarkable declining viscosity of HPAM at $85\text{ }^{\circ}\text{C}$ may be attributed to the thermal degradation during the aging time. The $-\text{CONH}_2$ groups along the HPAM chains were easily hydrolyzed at $85\text{ }^{\circ}\text{C}$, as was discussed in the “Introduction” part, the increased hydrolysis degree will aggravate the electrostatic shielding effect and make HPAM chains complex with Ca^{2+} , adverse to the long-term stability of HPAM solutions. For xanthan gum solutions, a severe decrease in viscosity was also observed. The disordered state at high temperatures caused xanthan molecules to be more easily attacked chemically.² On the contrary, diutan gum and scleroglucan showed much improved long-term stability,

indicating that their structures were not destroyed under this HTHS condition. These findings imply that diutan gum and scleroglucan are promising to be applied in hostile oil reservoirs.

2.3. Core Flooding. With regard to oil displacement in reservoirs, identifying the mobility of polymer solutions in the HTHS environment is of great significance, to ensure whether these polymer solutions can be smoothly propagated in the porous media. Therefore, we first evaluated the resistance factor (RF) and residual RF (RRF) of polysaccharides and HPAM solutions. The mechanical stability was also measured at higher shear rates for each polymer (Figure S2), which suggests that polysaccharides would keep relatively good viscosity when exposed to the high shear rates near the wellbore.

The core flooding tests of polysaccharides and HPAM were performed at the simulated condition of Shengli Oilfield (TDS = 10.1×10^4 mg·L⁻¹, [Ca²⁺] = 1.0×10^3 mg·L⁻¹, $T = 85$ °C), the concentration of polymer solutions was selected based on Figure S3. The curves of the flooding pressure with the injected pore volume (PV) for polymer solutions were compared in Figure 7, RF and RRF were presented in Table 1.

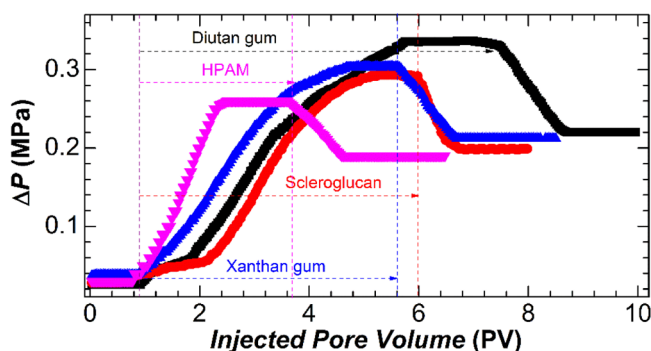


Figure 7. Pressure drop plotted as a function of injected PV for polysaccharide and HPAM solutions at 85 °C (TDS = 10.1×10^4 mg·L⁻¹, [Ca²⁺] = 1.0×10^3 mg·L⁻¹).

From Figure S5, one can see that the relative concentration of diutan gum, scleroglucan, xanthan gum, and HPAM solutions all can be stable after injecting the specified volume of 5.8 PV, 5.1 PV, 4.7 PV, and 2.8 PV, respectively, implying that the retention has been dynamically equilibrated and the longer time was needed for polysaccharides to reach equilibrium of adsorption retention on porous media. Meanwhile, polysaccharides are more sensitive to shear and exhibit shear-thin behavior, the viscosity of polysaccharide solutions entering to the core port is lower than HPAM. Therefore, the pressure increased slowly with the increased volume of polysaccharide solutions, along with the balanced pressure delayed (Figure 7). As can be seen in Table 1, the adsorption values of diutan gum, scleroglucan, xanthan gum, and HPAM solutions were 0.104, 0.127, 0.152, and 0.177 respectively. The

molecular weight of HPAM (1.5×10^7 g·mol⁻¹) is much higher than polysaccharides (2.0×10^6 to 5.0×10^6 g·mol⁻¹), which can cause more a significant mechanical entrapment than polysaccharides,³⁹ polysaccharide solutions can possess a higher effective viscosity in porous media.

It was evident that both RF and RRF of diutan gum and scleroglucan were greater than those of xanthan gum and HPAM, which was preferable for the ability of mobility control. We ascribed this difference to their viscoelasticity at HTHS conditions, the formed three-dimensional networks can bring a greater flow resistance and decreased permeability, along with a higher RF and RRF. As can be seen in Figure 5, diutan gum and scleroglucan solutions were all viscoelastic fluids, while xanthan gum and HPAM were only viscous fluids at the HTHS environment. The entanglements of diutan gum and scleroglucan molecular chains were minimally changed, intercepted, or recovered rapidly through the pore throat under the reservoir conditions. Thus, they can efficiently level down the permeability and keep higher effective viscosity of porous media.⁴⁰ The adsorption values of xanthan gum and HPAM are higher, which would be detrimental to the mobility control.

For the smooth flowing behavior of the above polymer solutions, the oil recovery was further performed. As depicted in Figure 8, 16, 13, 11, and 10% of the incremental oil efficiency could be recovered by diutan gum, scleroglucan, xanthan gum, and HPAM solutions, respectively. In addition, their mobility ratios were all lower than 1 (Table S2), favorable for the displacing fluids to push out crude oil from the core holes. All of these polymer solutions could achieve the oil recovery factor to some extent. Diutan gum and scleroglucan solutions have a relatively better ability to improve oil recovery efficiency for their higher effective viscosity during the flooding process. Xanthan gum and HPAM solutions exhibited a lower oil recovery factor for their poor performance at HTHS conditions. Consequently, diutan gum and scleroglucan would be prospective to be used in HTHS reservoirs.

One may doubt the tiny difference in the oil recovery factor among these polymers, but we must bear in mind that the 1 day laboratory core flooding test is just the simulated experiment, which cannot thoroughly reflect the process of polymer flooding in the real oil reservoirs. Generally, depending on the well spacing between the injector and producer, it would take a minimum of six months or years (depending on the injection rate) for polymer solutions to propagate from the producer to the injector. Compared to the long-term thermal stability of polysaccharides with HPAM after being aged for three months in Figure 6, we found that the viscosity retention of diutan gum and scleroglucan solutions still exceeded 85%, while xanthan gum and HPAM were less than 20%. This means that the remaining viscosity of xanthan gum and HPAM cannot keep them from playing the role of the displacing agent. On the contrary, the excellent long-term thermal stability of diutan gum and scleroglucan

Table 1. Mobility of Polysaccharide and HPAM Aqueous Solutions ($T = 85$ °C)

core number	samples	ϕ (%)	1 PV (mL)	K_w (mD)	η_p (mPa·s)	RF	RRF	adsorption value (mg·g ⁻¹)	η_{ef}
1	diutan gum	23.4	34.4	365	18.7	13.0	8.5	0.104	1.53
2	xanthan gum	20.6	30.3	271	19.2	7.9	5.6	0.152	1.41
3	HPAM	22.1	32.5	340	19.1	8.7	6.4	0.177	1.35
4	scleroglucan	21.1	31.1	303	19.2	10.6	7.1	0.127	1.49

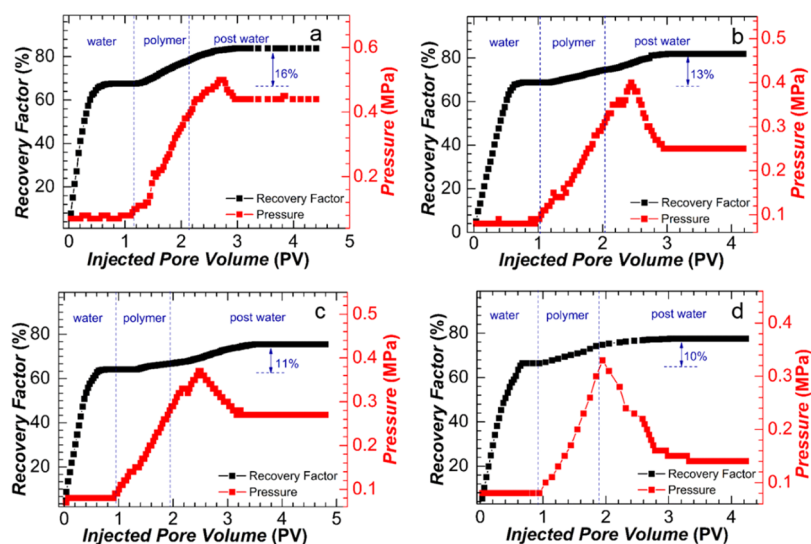


Figure 8. Recovery factor and pressure drop plotted as a function of injected PV for polysaccharide and HPAM solutions at 85 °C (TDS = 10.1×10^4 mg·L⁻¹, [Ca²⁺] = 1.0×10^3 mg·L⁻¹). (a) diutan gum; (b) scleroglucan; (c) xanthan gum; (d) HPAM.

under HTHS conditions make them good candidates for EOR under a hostile environment.

3. EXPERIMENTAL SECTION

3.1. Materials. Diutan gum was purchased from Azelis Co., Ltd. Scleroglucan and xanthan gum were kindly provided by Huanghelong Biological Engineering Co., Ltd. HPAM (weight-average molecular weight, $M_w = 1.5 \times 10^7$ g·mol⁻¹) was supplied by Daqing Oilfield Company, PetroChina. NaCl, CaCl₂, and NaN₃ were all of analytical grade and bought from Chengdu Kelong Chemical Reagents Co., Ltd. Dehydrated and degassed crude oil, offered from Daqing Oilfield Company, PetroChina, was diluted with kerosene to get a viscosity of 5.8 mPa·s at 85 °C. The artificial cores composed of sand consolidated by an epoxy resin, with a length (L) of 30 cm and diameter (d) of 2.5 cm, were offered by Beijing Shidarongzhi Technology Co., Ltd.

3.2. Sample Preparation. Two types of synthetic brine were prepared for the salts impacting on polymers and the tests in a simulative environment; the first one only contained NaCl and water with different salinity (TDS, 0–20.0 × 10⁴ mg·L⁻¹), and the second class of brine consisted of water, NaCl, NaN₃ (bacteriostat), and CaCl₂, with a final TDS of 10.1×10^4 mg·L⁻¹ ([Ca²⁺] = 1.0×10^3 mg·L⁻¹, [NaN₃] = 2.0×10^2 mg·L⁻¹). The polymer solutions were prepared by slowly, uniformly sprinkling a designated amount of dry polymer powders to the shoulder of the brine vortex to avoid the formation of “fish eyes”, then with gentle magnetic stirring at a speed of 60–80 rpm to keep the solid particles from settling to the bottom and avoid mechanical degradation of the polymer chains, and finally stirring hermetically for 1 day prior to the tests.

3.3. Characterization of Molecular Weight with Gel Permeation Chromatography. The weight- and number-averaged molecular weights, M_w and M_n , as well as molecular weight distribution, M_w/M_n , of polysaccharides were determined by gel permeation chromatography (GPC) with Malvern TDA and GPC max systems (Malvern Inc., United Kingdom) equipped with an A Guard and A6000m General Mixed Aq column (300 × 8.0 mm² i.d., P/N: CLM3021) coupled in line with VISCOTEK TDA detectors, and the results were shown in Table 2 and Figure S4. 100 μL of

Table 2. M_w , M_n , and M_w/M_n of Xanthan Gum, Diutan Gum, and Scleroglucan

sample	M_w (g·mol ⁻¹)	M_n (g·mol ⁻¹)	M_w/M_n
diutan gum	2.85×10^6	2.81×10^6	1.02
xanthan gum	3.32×10^6	1.05×10^6	3.27
scleroglucan	4.81×10^6	4.25×10^6	1.13

polysaccharide solutions (0.5 mg·mL⁻¹), filtered through 0.22 μm membrane filters (Millipore), was injected into the column. The eluent (0.1 mol·L⁻¹ NaNO₃) was used at a flow rate of 0.7 mL·min⁻¹. The temperature of the detector and column was fixed at 45 °C with a built-in thermostatic system and column oven.

3.4. Rheological Measurements. Temperature scanning was made on a Physica MCR 302 rotational rheometer (Anton Paar, Austria) equipped with a high-pressure and high-temperature cell, in which the concentric cylindrical geometry CC25 with a measuring bob (radius, 12.55 mm) and a measuring cup (radius, 13.56 mm) was employed. The steady apparent viscosity was recorded during temperature ramps going from 25 to 150 °C (heating rate = 2 °C·min⁻¹) at a fixed shear rate ($\dot{\gamma} = 100$ s⁻¹). The pressure in the measuring cup was set at 1 MPa to avoid forming too much vapor to affect the accuracy of the apparatus. The shear rate was fixed at 100 s⁻¹ to ensure enough torque and precision in our viscosity measurement at high temperatures. In addition, for the uniformity of this article, the shear rate in the viscosity measurement was always fixed at 100 s⁻¹, except for the polymer solutions used in core flooding. The flow rate of polymer solutions propagating in porous media is closer to 10 s⁻¹, so the apparent viscosity of the polymer solutions used in polymer flooding was measured at 10 s⁻¹.

The dynamic rheology of polymer solutions was also registered on the same rheometer but equipped with concentric cylinder geometry CC27 with a measuring bob (radius, 13.33 mm) and a measuring cup (radius, 14.46 mm). The strain amplitude of 2.5% was selected to ensure that polysaccharide solutions fell within the linear viscoelastic region, and the mechanical spectra was obtained within the frequency range of 1–100 rad·s⁻¹ in the oscillation mode.

3.5. TEM Observation. The polymer solutions used for TEM visualization were preheated at the desired temperatures (25 and 85 °C) and placed on a carbon-coated holey film supported by a copper grid. The grid was quenched quickly into liquid nitrogen. Then, the frozen specimens were transferred into a vacuum freezer drier (−20 °C) to swab off ice. Finally, the dehydrated specimens were transferred to a Tecnai G² F20 S-TWIN TEM with an acceleration voltage of 200 kV.

3.6. Long-Term Thermal Stability. To avoid the redox reaction detrimental to the viscosity of polymer solutions,^{41,42} the dissolved oxygen in polymer solutions should be eliminated. N₂ was first sparged into polymer solutions for 60 min to preliminarily remove oxygen, then these samples were transferred into a glovebox ([O₂] < 0.1 ppm), and stirred for 2 h to further degas oxygen. After the dissolved oxygen was absolutely removed, polymer solutions were put into steel containers and sealed inside the glovebox. Finally, these steel containers were taken out and aged in a thermostatic oil bath at 85 °C. At every consecutive time interval, polymer solutions were taken out for viscosity measurement.

3.7. Core Flooding Test. **3.7.1. Preparation of the Core Test.** The cylindrical artificial cores were dried at 85 °C in a vacuum oven until their weight was constant. The PV was calculated as the ratio of the weight difference between the water-saturated core and dry core to the brine density, and the porosity (ϕ) was the ratio of the PV to the core volume. The brine was injected at three different flow rates (4, 2, or 1 mL·min^{−1}) and the pressure drop was recorded to calculate the average value for brine permeability (K_w) of cores.

3.7.2. Injectivity Test. When the constant temperature was obtained, the water-saturated core was successively injected with brine, polymer solution, and brine at a rate of 1 mL·min^{−1}, and their stable pressure drop was recorded as (ΔP)_{wb}, (ΔP)_p, and (ΔP)_{wa}, respectively. The RF describes the mobility reduction, obtained by comparing the pressure drop during polymer displacement with water flooding before polymer injection. The RRF reflects the reduction in permeability of porous media induced by polymer adsorption,⁴³ determined by the ratio of pressure difference during water flooding after polymer injection and the corresponding pressure before polymer injection. Effective viscosity (η_{ef}) can provide accurate viscosity when a polymer solution flows in porous media. RF, RRF, and η_{ef} were defined as⁴⁴

$$RF = \frac{\Delta P_p}{\Delta P_{wb}} \quad (1)$$

$$RRF = \frac{\Delta P_{wa}}{\Delta P_{wb}} \quad (2)$$

$$\eta_{ef} = \frac{RF}{RRF} \quad (3)$$

Meanwhile, the material balance method⁴⁴ was used to measure the dynamic adsorption of polysaccharide and HPAM solutions. The flow rate was 1 mL·min^{−1} when the polymer solutions and brine were injected into the artificial core. Throughout the experiment, water flooding was performed to achieve a stable pressure, followed by the injected polymer solution until the concentration of the produced fluid determined by UV absorption analysis (UV-6100, MAPADA Instruments) was the same or similar to the initial

concentration of the polymer dope, then follow-up water flooding was conducted until the polymer concentration of the output fluid was close to zero. The standard curves of absorption plotted as the relative concentration were shown in Figure S6. The relative concentration is defined as the ratio of the concentration of the produced fluid to the initial concentration of polymers. The dynamic retention of the polymer solution was obtained by the followed equation⁴⁵

$$R = \frac{C_0 V_0 - \sum_{i=1}^n C_i V_i}{W} \quad (4)$$

where R is the density of polymer retention (mg·g^{−1}), C_0 is the initial concentration of polymer solution, V_0 is the volume of the polymer solution, C_i and V_i denote the concentration and volume of the output fluid, and W represents the dry weight of the artificial core.

3.7.3. Core Flooding. When the core flooding system was maintained at 85 °C, the crude oil was injected into the water-saturated cores to set the initial oil saturation. Primary water flooding was executed until no more oil was produced, then polymer flooding was conducted by injecting 1 PV of the polymer solution, and finally post water flooding was performed until oil production became negligible. The incremental oil recovery by polymer solutions and post water-flooding was used to evaluate the efficiency of these systems. The injection rate of displacing slug was controlled at 1 mL·min^{−1}.

4. CONCLUSIONS

The rheological behaviors, shearing stability, long-term stability, and core flooding feasibility of the polymer solutions were comparatively studied, and the solutions contained diutan gum, scleroglucan, xanthan gum, and HPAM, respectively.

In the rheological measurements, the apparent viscosity of diutan gum and scleroglucan showed a relatively lower dependence on temperature and salinity. Under HTHS conditions, diutan gum and scleroglucan solutions were viscoelastic fluids while xanthan gum and HPAM were viscous fluids within the range of the studied concentrations, and increasing concentration of their solutions enhanced the temporary three-dimensional network. For the long-term stability, the apparent viscosity of diutan gum and scleroglucan solutions almost remained constant after being monitored continuously for 90 days at 85 °C. Flow and flooding tests demonstrated that diutan gum and scleroglucan possessed excellent mobility control and effectively improved higher oil efficiency in porous media. Consequently, diutan gum and scleroglucan would be excellent candidates for EOR under HTHS conditions, potential to meet the urgent need of HTHS oil reservoirs for salt tolerance and thermally stable polymers.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00717.

Molecular weight measurement, temperature resistance, mechanical stability, and calculation of oil recovery efficiency (PDF)

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Notes

The authors declare no competing financial interest.

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